A HÜCKEL MOLECULAR ORBITAL STUDY
OF SOME AROMATIC HYDROCARBONS

A thesis submitted to the University of Glasgow
for the degree of Doctor of Philosophy

by

David Antony Morton-Blake.

Chemistry Department, University of Glasgow - December 1963

Acknowledgments

It is a pleasure to thank Dr. T. H. Goodwin for the interest and unfailing helpfulness which he has extended throughout the three years during which I have worked under his supervision, and for the use of some of his programs for the DEUCE Computer, using which many of the calculations were carried out. I also gratefully acknowledge many interesting and helpful discussions with Dr. E. Clar and Professor D. W. J. Cruickshank.

I am particularly grateful to Professor J. Monteath Robertson for a maintenance grant during my first year of research (1960-1) and to H. M. Department of Scientific and Industrial Research for the award of a Studentship for the last two years (1961-3).

My thanks are also due to Mrs. J. Beresford, who undertook the task of typing the thesis.

CONTENTS

Page

§1 Introduction and Definitions 1

§2 Basic Theory 4

2.1 The LCAO-MO method 4

2.2 Matrix form of the Schrödinger equation....... 9

2.3 The Hückel theory 11

2.4 Variation in β' 14

2.5 Bond orders 16

2.6 Simplifications due to symmetry 20

§3 Application of the Hückel theory to the aromatic hydrocarbon 1-2, 6-7 dibenzpyrene, and the results obtained 24

3.1 Application of Group Theory 24

3.2 Results of the calculation:

(i) Electronic states 31

(ii) Electronic spectra 35

§4 The Clar theory of aromatic hydrocarbons 42

§5 Results of the computations on some aromatic hydrocarbons 47

5.1 The effect of iterating 47

5.2 Bond variations:

(a) Acenes 52

(b) Other hydrocarbons 55

(c) A comment on the relationship between the Clar and Hückel theories 60

Page

5.3 Molecular π electronic energies 60

(i) Aromaticity and stability 63

(ii) Calculated energies 69

(iii) A comparison of the stabilities of some isomers 74

§6 The construction of a new r(p) curve, and the calculation of more accurate bond orders and energies 79

6.1 A criticism of the r(p) and $\beta'(r)$ curves used for the calculations of the molecular constants listed in Appendix A 79

6.2 A more accurate order-length curve 80

Treatment of molecules containing long bonds. 90

6.3 Results obtained for aromatic hydrocarbons using the new order-length relationship.... 91

6.4 (a) The calculation of the positions of the electronic transition bands for aromatic hydrocarbons 97

(b) The calculation of spectral shifts due to annelation 103

§7 The calculation of aromatic character of the acene rings in terms of Clar's oscillating aromatic pair model 107

Page

§8 A simple treatment of inter-electronic repulsion in aromatic hydrocarbons 116

8.1 The ground state 116

Application to some hydrocarbons 122

8.2 The first excited singlet state 127

References 134

APPENDIX A: Molecular constants calculated using the Coulson-Goodwin p(r) curve and the Mulliken, Riecke and Brown $\beta'(r)$ curve.

APPENDIX B: Molecular constants calculated using the "improved" p(r) curve and the Longuet-Higgins and Salem $\beta'(r)$ curve.

APPENDIX C: Molecular constants calculated using the p(r) and $\beta'(r)$ curves used for Appendix B results, but with special provision made for extreme long and short bonds.

APPENDIX D: Papers with T. H. Goodwin submitted for publication:

(i) "L.C.A.O.-M.O. Calculations on Pyrene Benzologues": Tetrahedron Letters 14 901 (1963).

(ii) "The Configuration of Diphenyl in the Crystalline and in the Vapour States: A Simple Non-bonded H-H Potential Function": Theoretica Chemica Acta 1 458 (1963).

APPENDIX D (Cont'd):

(iii) "An Empirical Determination of the Huckel Parameter β, and of the C-C and C-H Bond Energies in Aromatic Hydrocarbons": To be published in Journal of the Chemical Society.

(iv) "A Simple Molecular-Orbital Study of the β, α and p-Bands in Triphenylenes": To be published in Theoretica Chemica Acta.

§1 INTRODUCTION AND DEFINITIONS

We shall discuss the application of the Hückel LCAO-MO method to some benzenoid alternant aromatic hydrocarbons and the results obtained, making comparisons where possible with the predictions of the theories developed by Clar concerning these molecules.

The term "benzenoid" will be defined as a description of those molecules composed only of six-membered rings of sp^2 hybridized atoms. An aromatic system is one containing ring atoms with each of which there is associated a 2p atomic orbital containing 0, 1 or 2 electrons, and which is directed perpendicular to the plane formed by the atom and its immediate neighbours. Alternant hydrocarbons are those in which the carbon atoms may be classified into two sets, "starred" and "unstarred", in such a way that each starred atom has only unstarred nearest neighbours, and vice versa. Alternant hydrocarbons therefore contain no odd-numbered rings. Some examples of molecules using these terms are naphthalene, which is a benzenoid alternant aromatic hydrocarbon, cyclobutadiene, which is an alternant aromatic hydrocarbon though not benzenoid, cyclooctatetraene, which is an alternant hydrocarbon but is neither benzenoid nor aromatic (since it is not planar), and azulene which is an aromatic hydrocarbon, but is neither benzenoid nor alternant. The molecules pyridine and borazole are in many ways similar to benzene, and by our definitions may be described as being both benzenoid and aromatic, but they are not hydrocarbons and so cannot be described as alternant or non-alternant.

In an aromatic molecule the 2_p atomic orbitals, which are usually directed at right-angles to a nuclear plane, interact, with the result that the electrons produce an electric field above and below this plane, in the regions where the atomic orbitals overlap. These electrons are therefore considered to be delocalised to a greater or less extent over the nuclear framework in discrete molecular orbitals. Since the wave functions of the basis set of 2_p atomic orbitals, and therefore of the molecular orbitals are antisymmetric with respect to the nuclear plane, both are termed π orbitals, and their associated electrons are called π electrons. This is principally to distinguish them from the σ electrons in the system, which are localised between two nuclei and are cylindrically symmetrical with respect to the internuclear line.

The principal results obtained from the Hückel LCAO theory calculations are the energies of the electron molecular orbitals as a linear combination of two parameters α and β_0. No attempt is made to calculate these quantities directly, but since the coefficient of the β_0 term varies from one orbital to another, it has been possible to estimate empirical values for β_0, which we have done on two different experimental bases, by comparing molecular orbital energies as derived from thermochemical measurements and also from the electronic transition energies in the U.V. absorption spectra. The calculations also furnish the π bond orders, which measure the degree of π bond formation between neighbouring pairs of carbon atoms.

Where it has been possible, we have attempted to compare our results with experimental data. This, however, has been difficult, both because of the uncertainties in the positions of the relevant U.V. spectral bands (which would make ideal comparisons for the calculated energies) and because sufficiently accurate bond lengths (which are useful measures of π bond orders) are available for only a very few aromatic hydrocarbons. From the comparison of our results for different molecules it has often been possible to observe some regularities in the behaviour of the π electrons, and in comparing these with the empirically-based rules of Clar, to effect indirect comparison with experiments.

The nomenclature of the aromatic hydrocarbons is that used in Clar's book "Aromatische Kohlenwasserstoffe", but the numbering of the carbon atoms in the Appendices and in the text to refer to bond orders etc., has been our own. The rather irregular form of the numbering is due to convenience in the computations, but because of the risk of errors in translation into Chemical numbering, has been used throughout.

§ 2 Basic Theory

2.1 The LCAO-MO Method, and σ- and π-separation

Because of the potential energy terms in the hamiltonian operator H, the solutions such as ϕ_i of the Schrödinger stationary -state equation

$$H \phi_i = E_i \phi_i$$

for an electron in the neighbourhood of an atom or ion are well-known to be discrete. The wave function Φ of the electon must then be written as a linear combination of the solutions:

$$\Phi = a_1 \phi_1 + a_2 \phi_2 + \ldots\ldots$$

Since the electron must be somewhere in space, we have the normality condition

$$\int \Phi^* \Phi \, d\tau = 1 \qquad (1)$$

where the integration is carried out over the whole range of the spacial coordinates of the wave functions Φ. It is convenient to use orthonormalised solutions (i.e. such that $\int_0^\infty \phi_i^* \phi_j \, d\tau = \delta_{ij}$) since then the normality condition (1) imposes the following simple restriction on the a's:

$$|a_1|^2 + |a_2|^2 + \ldots\ldots = 1$$

The quantity $|a_i|^2$ is therefore the probability that the electron is in the state described by the solution ϕ_i with energy E_i.

Because the discrete solutions ϕ_i are associated with particular energies E_i, it is convenient to speak of an atomic orbital (AO) with energy E_i which may be accommodated by either 0, 1 or 2 electrons, and which provides a real distribution function for the electron. In many cases the atomic orbitals can be just the solutions themselves or convenient approximations to them, but when more than one solution corresponds to the same energy E, it may be necessary to take linear combinations of these degenerate solutions to give functions which are real (i.e. not complex) and which may therefore be used to represent the distribution of the electron. We shall suppose that the atomic orbitals which we require are known, and shall denote them by the symbol ψ.

The electron is also in a bound state in a molecule, and analagous to the atomic case we can speak of molecular orbitals (MO's), in which the electron is associated with more than one atom. In principle a MO can be expressed as a linear combination of a complete set of wave functions. However except for very simple molecules (e.g. H_2 or H_2^+), this is unpracticable, and for many purposes satisfactory molecular orbital wave functions are obtained by taking a linear combination of appropriate atomic orbitals in the molecule (LCAO):

$$\Psi_{MO} = c_1\psi_1 + c_2\psi_2 + \dots + c_n\psi_n \qquad (2)$$

Even if we make use of the Born-Oppenheimer approximation, which allows us to neglect the effect of the nuclear motions on the electronic wave functions, Ψ_{MO} does not adequately cater for all the influences which the electron experiences in the molecule. However the "best" choice of coefficients c will reduce this uncetainty to the minimum possible for the particular set of ψ's used in (2).

The coefficients c may be determined by calculating the energy of the molecular orbital Ψ_{MO} according to the rules of quantum mechanics:

$$E = \int_0^\infty \Psi^* H \Psi \, d\tau \qquad (3)$$

where H is the hamiltonian operator for the system. The variation principle states that as long as we are using an accurate hamiltonian H, (which can usually be done quite readily) the energy given by (3) will be greater than or equal to the true lowest energy of the system. In other words the lower the value of E, the nearer is Ψ to the true MO wave function. The "best" Ψ of the form given in (2) can therefore be found by minimising (3) with respect to the various c's. In this way, although effects such as interelectronic repulsions have been neglected in forming the LCAO-MO (2), they may be included in the hamiltonian in (3) as "perturbation" energy-terms, and the LCAO-MO's evaluated will be such that the c's "allow for" these effects as far as is possible.

If Ψ_1, Ψ_2, etc. are the MO wave functions constructed in this way from the various AO's in the molecule, the ground state will be that in which the MO's with the lowest energies are occupied by electrons. We can write the wave function Γ for such a state of an n-electron molecule as a product of the n lowest-energy molecular orbitlas Ψ_1 to Ψ_n, in such a way that Γ is antisymmetrical to the interchange of any two electrons, in accordance with the Pauli principle. Γ is written

$$\Gamma = \mathcal{A}\left[\, \Psi_1(1)\ \ \Psi_2(2)\ \ldots\ldots\ \Psi_n(n)\, \right]. \qquad (4)$$

The general factor $\Psi_r(r)$ denotes the rth electron in the rth molecular orbital. The antisymmetrising operator $\mathcal{A}$ (which includes the normalising factor) permutes all the electrons and sums the antisymmetrised results, since there are equal probabilities of finding any one electron in any of the n MO's.

In forming the MO's Ψ it often happens that one or more of the component AO's do not combine with the others in the form (2) with any appreciable energy change. This may be because the centres of the AO's are too far apart, or because they belong to different symmetries. In either case the cross-terms in the expansion of (3), $\int_0^\infty \psi_a^* H \psi_b \, d\tau$ (the energy of the interaction of the AO's) and the overlap, $\int_0^\infty \psi_a^* \psi_b \, d\tau$ (which is often a useful simple measure of the former quantity) are very small or zero. The atomic orbitals ψ_a and ψ_b may therefore be treated as distinct by appearing in (4) in separate wave functions Ψ. For this reason the $2p_\pi$ AO's, which are directed at right angles to the molecular plane of the aromatic hydrocarbons, form distinct π Molecular orbitals, which may be distinguished from the σ MO's by their antisymmetry in the molecular plane, the σ MO's being symmetric.

These two kinds of MO are very different. The σ MO's may be manipulated (Coulson, "Valence" 2nd. edn., p.173) into the form of "bond orbitals" in which the electrons are localised in the internuclear regions and form what are known as σ bonds. The π MO electrons on the other hand are delocalised over large parts of the molecule. Since the localised σ bond orbitals are characteristic only of the two atoms forming the bond, the C-C σ bonds in an aromatic hydrocarbon are similar, and effectively provide a carbon atom framework over which the π electrons are delocalised. The π MO's are therefore highly dependent on the topology of the molecule, and in this thesis we shall suppose that many of the characteristics of the aromatic hydrocarbons (e.g. relative bond lengths and UV spectra) may be explained quite well by the π MO's alone.

The electronic energy E of a molecule in the state Γ,

$$E = \int_0^\infty \Gamma^* H \Gamma \, d\tau$$

contains kinetic energy and nuclear-attraction terms for each of the σ and π electrons. However there are in addition terms describing the mutual repulsions of the electrons;[7] some of these terms involve both σ and π functions, and express the interactions of the σ and π electrons. The existence of these σ-π "coulomb" and "exchange" integrals shows that the total energy of an aromatic molecule cannot be separated into parts which involve the σ and π electrons alone, since the two parts do not constitute independent systems.

Nevertheless it is convenient to suppose that the σ and π electron parts of the total energy can be separated, and that the description "π electron energy" applies to the sum of those energy terms which involve the π MO wave functions even if they also involve σ wave functions. Although π electron energy cannot be a strictly meaningful physical quantity, the σ-π separation procedure allows us to obtain results which are often surprisingly accurate for molecules whose complexities make them intractable to more rigorous treatments.

In the form of the σ-π separation procedure which we shall be using, our wave functions will be just those of the π MO's, and the π-electron hamiltonian will include a potential energy term which expresses the total coulombic interactions with the nuclei and the σ electrons. In the bulk of the thesis this term will also include the interelectronic repulsions of the π electrons, but in the final chapter an explicit account will be taken of these. The σ MO's will not be considered at all.

2.2 Matrix form of the Schrodinger equation.

We shall express the $\underline{i}$th MO according to (4) but in the convenient vector rotation

$$\Psi_i = \langle \psi | . | c_i \rangle$$

where $\langle \psi |$ is a row vector of the $\underline{N}$ $2p_\pi$ atomic orbitals in the system, and $|c_i\rangle$ is a column vector of the N coefficients relating to the $\underline{i}$th molecular orbital. The condition ensuring the normalisation and orthogonality of the MO's is that the vectors $|c_i\rangle$ (i = 1 to N) are orthonormal, i.e., the coefficients C_{ri} themselves, taken in columns, are normalised and orthogonal. If this is the case, then the N x N matrix $\mathbb{C}$ consisting of a row of the $\underline{N}$ $|c_i\rangle$ column vectors is a unitary matrix. The row vector of the $\underline{N}$ molecular orbitals may then be expressed as

$$\langle \Psi | = \langle \psi | \mathbb{C} \tag{2.5}$$

and the energy eigenvalues can be calculated by forming the square matrix

$$\mathbb{E} = \int \langle \Psi |^\dagger H \langle \Psi | \, d\tau \tag{2.6}$$

where $\langle \Psi |^\dagger$ is the adjoint of $\langle \Psi |$, and H is the hamiltonian operator relevant to the system. From (5) and (2) we have

$$\mathbb{E} = \int \mathbb{C}^{\dagger} |\Psi\rangle^{*} H \langle\Psi| \mathbb{C}\, d\tau = \mathbb{C}^{\dagger}\mathbb{H}\mathbb{C} = \mathbb{C}^{-1}\mathbb{H}\mathbb{C} \qquad (2.7)$$

where $\mathbb{H}$ is the matrix whose elements are $H_{rs} = \int \psi_r^{*} H \psi_s\, d\tau$. The replacement of $\mathbb{C}^{\dagger}$ by $\mathbb{C}^{-1}$ follows from the unitary property of $\mathbb{C}$. While in general the (r, s)th element in $\mathbb{H}$ is non-zero, the matrix $\mathbb{E}$ (formed by subjecting $\mathbb{H}$ to a unitary transformation using the $\mathbb{C}$ matrix) is diagonal and the diagonal elements E_{ii} are the energy eigenvalues.

Writing (7) as

$$\mathbb{H}\mathbb{C} = \mathbb{E}\mathbb{C} \qquad (2.8)$$

and using the fact that $\mathbb{E}$ contains only diagonal elements E_i, (8) may be separated into N vectoral equations

$$\mathbb{H}\, |c_i\rangle = E_i\, |c_i\rangle$$

which is the Schrödinger equation in matrix form. This can be rewritten

$$(\mathbb{H} - E_i . \mathbb{1})\ |c_i\rangle = \mathbb{O} \qquad \text{(null matrix)}$$

where $\mathbb{1}$ is the unit matrix equidimensional with $\mathbb{H}$, and for a non-trivial solution ($|c_i\rangle \neq 0$) it is necessary that

$$\det | H_{\lambda s} - E_i \delta_{\lambda s} | = 0$$

the N solutions of which are the eigenvalues E_i.

2.3 The Hückel Theory.

In the argument developed above, it has been implicitly assumed, following Hückel[1], that the atomic orbitals ψ, although not eigenfunctions of the Hamiltonian operator H, are orthogonal amongst themselves, so that the matrix $\int |\psi\rangle^* \langle\psi| \, d\tau$ is a unit matrix. This assumption as stated is not justifiable, but its adoption results in considerable simplifications of the computations, and may be "corrected for" afterwards, if desired.

A second simplification made by Hückel[1] is to suppose that the Hamiltonian has exactly the same form for each molecular orbital, so that each π electron moves in the same average electrostatic field provided by the nuclei and the other electrons. Moreover this field is the same at all $2p_\pi$ atomic orbitals in the molecule. For this reason another considerable simplification results if we do not explicitly consider the interactions between the atomic orbitals, but write the diagonal and non-diagonal elements of the H matrix respectively as

$$H_{rr} = \int \psi_r^* H \psi_r \, d\tau = \alpha_r$$

and $$H_{rs} = \int \psi_r^* H \psi_s \, d\tau = \beta_{rs}$$

From what we have just said, α_r is the same for all $2p_\pi$ atomic orbitals ψ_r in an aromatic hydrocarbon; it is theoretically the energy of a single electron in a 2p atomic orbital, and is written α. Making the next Hückel assumption[1] that only nearest-neighbour interactions need be considered, the interaction term β_{rs} becomes a bond parameter. Although a good first approximation is to assume that this is constant for all bonded atoms r, s, aromatic hydrobcarbons are characterised by some variation in their CC bond lengths. As a result, the value of β_{rs} is expected to depend somewhat upon the distance between the centres of the interacting atomic orbitals, i.e. upon the length of the bond r-s. We therefore write $\beta_{rs} = \beta'_{rs} \cdot \beta_0$ where β_0 is the interaction term for an arbitary standard bond, chosen in such a way that the numerical factor β'_{rs} is fairly close to unity. In our calculations β_0 is

the interempirical relations suggested by Mulliken, Rieke and

the the fBrown[2] or β_{rs} Longuet-Higgins and Salem[3].

the bond r-s with that of the benzene bond, using the empirical relations suggested by Mulliken, Rieke and Brown[2] or Longuet-Higgins and Salem[3].

Each element of ~~$\mathcal{H}$~~ $\mathbb{H} - E.\mathbf{1}$ (whose general element is $H_{rs} - E_i\delta_{rs}$) is now divided by β_o and the resulting elements are of two kinds, the non-diagonal elements which are independent of the energy E become simply β_{rs}, whereas all the diagonal elements are

$$\frac{\alpha - E_i}{\beta_o} = x_i \qquad \text{(say).} \tag{2.9}$$

x_i is the energy eigenvalue parameter (sometimes called the Hückel number) and becomes the general latent root of the matrix $\frac{1}{\beta_o}\mathbb{H}$.

The energy eigenvalues for the system are then given by (9) or

$$E_i = \alpha - x_i\beta_o \tag{2.10}$$

β_o is a negative quantity, so negative values of x_i lead to bonding MO's (molecular orbitals whose energies are less than the energy of the $2p_\pi$ atomic orbital), and positive values to antibonding ones. In certain cases, as for example a molecule containing an odd number of $2p_\pi$ atomic orbitals (which, because of the lack of complete spin pairing must be a free radical), x may be zero, resulting in an MO whose energy is seen by (10) to be just the same as that of a $2p_\pi$ atomic orbital. Such an MO is called a non-bonding molecular orbital.

In alternant aromatic hydrocarbons, the Hückel theory leads to x values which are paired in positive and negative values, so that for each bonding molecular orbital

$(-x_1)$ there is a corresponding antibonding one. A system of *N* interacting atomic orbitals must have *N* molecular orbitals, and so a neutral even alternant hydrocarbon possesses a ground state in which all *N* electrons are, by the Pauli Principle, accommodated in the N/2 bonding molecular orbitals. We may conveniently denote the number of occupied molecular orbitals by *n*. In the ground state, $N = 2n$.

2.4 Variation in β'

As was discussed in the last section, the β value for a CC bond in an aromatic hydrocarbon should be fairly constant, since the variations in bond lengths are seldom very marked. For this reason the *Simple Hückel Method* in which all the β' values are assumed to be unity, has often yielded very satisfactory results. We have sometimes used the results of the Simple Hückel Method in order to compare the results calculated for a series of hydrocarbons when we wish to avoid the difficulties of assigning uncertain bond β' values.

In cases where we *can* assign β' values, however, (when the bond orders or bond lengths are known with some degree of certainty) the results are probably better. Various relationships between the length of a bond and its β' value are to be found (these we shall call $\beta'(r)$), and we have used those due to Mulliken, Rieke and

Brown[2], and later to Longuet-Higgins and Salem[3]. Finally we have calculated a new $\beta'(r)$ relationship using some recently-determined force-constants and bond energies.

For a general hydrocarbon, however, the bond lengths are not known, so the required set of β' values cannot be assigned. Our procedure (following Goodwin) has been to compute the bond orders p_{rs} using the Simple Hückel Method first of all, infer from these the approximate set of bond lengths r_{rs} using an empirical bond order/bond length curve r(p) (such as that due to Coulson), and from these calculate a set of β' values by reference to a $\beta'(r)$ relationship. This set of β' values is then used in a second "iteration", and new sets p_{rs}, r_{rs} and β'_{rs} are computed. These latter values are expected to be more accurate than the first sets, and the bond orders and bond lengths obtained by a further iteration should be better still. Although at first sight successive iterations should yield progressively better results until self consistency is obtained, we have decided to stop after three iterations, since the desired self-consistency is generally not achieved. This is probably due to the uncertainties in the p(r) and $\beta'(r)$ curves used for the interpolations; later curves will be seen to improve the position somewhat.

2.5 Bond Orders.

The eigenvectors $|c_i\rangle$ consist of the coefficients C_{rs} of the atomic orbitals ψ_r in the i th MO as expressed by

$$\Psi_i = \sum_{r=1}^{N} c_{ri}\,\psi_r$$

In the following calculations all the coefficients will be assumed to be real, since this assumption considerably simplifies the computations which involve the products of the coefficients. Multiplication of $|c_i\rangle$ by its transpose $\langle c_i|$ yields an n x n matrix whose (r, s)th entry is $C_{ri} \cdot C_{si}$. Now the probability of finding an electron in the i th MO is $\int \Psi_i^* \Psi_i \, d\tau$ which for real vectors $|c_i\rangle$ is equal to

$$P = \int \Psi_i^2 \, d\tau = \int (c_{1i}^2 \psi_1^2 + c_{2i}^2 \psi_2^2 + \dots + C_{Ni}^2 \psi_N^2) \, d\tau = \sum_{r=1}^{N} C_{ri}^2$$

(assuming the orthogonality of all pairs of ψ's). The diagonal elements of a matrix $|c_i\rangle\langle c_i|$ therefore measure the probabilities of finding a π electron associated with the various atomic orbitals; C^2_{ri} thus is the π electronic charge q^i_r on atom r due to the i th MO. The non-diagonal terms in the same matrix might then reasonably be expected to measure the π electron density in the region between two atoms, i.e. C_rC_s is a measure of the amount of π bond character between atoms $\underline{r}$ and $\underline{s}$, and is called the <u>partial bond order</u>[4] p^i_{rs} of the bond r-s due to the $\underline{i}$ th MO. When a matrix of these quantities is multiplied by the occupation number ν_i of the $\underline{i}$ th MO (the number of π electrons in the orbital), and summed over all the MO's, it results in the total bond order matrix, whose elements are the total bond orders and charge densities:

$$\left.\begin{aligned} \mathbf{p} &= \sum_{i=1}^{n} \nu_i \mathbf{p}^i = \sum_{i=1}^{n} \nu_i |c_i\rangle\langle c_i| && \text{(a)} \\ p_{rs} &= \sum_{i=1}^{n} \nu_i p^i_{rs} = \sum_{i=1}^{n} \nu_i c_{ri} c_{si} && \text{(b)} \\ q_r &= \sum_{i=1}^{n} \nu_i q^i_r = \sum_{i=1}^{n} \nu_i c^2_{ri} && \text{(c)} \end{aligned}\right\} \qquad (2.11)$$

The total bond order p_{rs} of a bond or <u>Coulson bond order</u> accounts for the observed shortening of the bond due to π bond formation[5]. $p = 0$ implies an absence of π electrons (hence no π-bond), and $p = 1$ an ethylene-type π bond (which together with the σ bond, constitutes the classical "double bond"). The C-C bond orders in aromatic hydrocarbons are usually between 0.4 and 0.8.

The Coulson bond order is also a useful concept when calculating the π electron energy in a system or part of a system. This relationship is explained as follows.

The energy of the <u>i</u> th molecular orbital is

$$E_i = \int \Psi_i H \Psi_i \, d\tau = \int \langle \psi | . | c_i \rangle H \langle \psi | . | c_i \rangle \, d\tau$$

$$= \int \langle c_i || \psi_i \rangle H \langle \psi || c_i \rangle \, d\tau$$

$$= \langle c_i | \mathbb{H} | c_i \rangle \qquad (2.12)$$

$\mathbb{H}$ is now separated into two matrices which involve only α and the β terms respectively, as discussed in the last section:

$$\mathbb{H} = \alpha . \mathbb{1} + \mathbb{\beta}$$

(12) then becomes

$$E_i = \langle c_i | (\alpha \mathbb{1} + \mathbb{\beta}) | c_i \rangle$$

$$= \alpha \langle c_i || c_i \rangle + \langle c_i | \mathbb{\beta} | c_i \rangle$$

$$= \alpha \quad + \sum_{\substack{r=1 \\ r \neq s}}^{n} \sum_{s=1}^{n} c_{ri} c_{si} \beta_{rs} \; \text{(for real } C_r, C_s\text{)}$$

But the actual energy of the electrons in the <u>i</u> th molecular orbital is $\nu_i E_i$, where ν_i is the occupation number. The total π electron energy in the system is therefore:

$$\mathcal{E} = \sum_{i=1}^{n} \nu_i E_i = \alpha \sum_{i=1}^{n} \sum_{r=1}^{N} \nu_i c_{ri}^2 + \sum_{i=1}^{n} \sum_{\substack{r=1 \\ r \neq s}}^{N} \sum_{s=1}^{N} \nu_i c_{ri} c_{si} \beta_{rs}$$

$$= \alpha \sum_{r=1}^{N} q_r + \sum_{r \neq}^{N} \sum_{s}^{N} p_{rs} \beta_{rs}, \left[\text{by } 11(b, c) \right] \qquad (2.13)$$

The first term in (13) is $N\alpha$, which follows from the facts either that the C_{ri}'s are normalised over all r. and so the term is $\alpha n \sum_i \nu_i = 2n\alpha = N\alpha$ or simply that $\sum_{r=1}^{N} q_r$ must equal the total number of electrons, which is N.

So the ground state π electronic energy is

$$\mathcal{E} = N\alpha + \sum_{r \neq s}^{N} \sum^{N} p_{rs} \beta_{rs} \tag{2.14}$$

But from (10) $\mathcal{E} = \sum_i \nu_i E_i = N\alpha - \beta_0 \sum_{i=1}^{n} x_i \nu_i$ (2.15)

$\therefore$ from (14) and (15):

$$\sum_{i=1}^{n} x_i \nu_i = - \sum_{r \neq s}^{N} \sum^{N} p_{rs} \beta'_{rs}$$

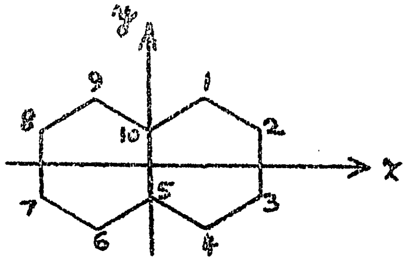
Since we are mostly concerned with the ground states, when $\nu_i = 2$ for $i = 1, \ldots, n$, the last equation becomes simply

$$\sum_{i=1}^{n} x_i = - \sum_{r > s}^{N} \sum^{N} p_{rs} \beta'_{rs} \tag{2.16}$$

That is, if we multiply each bond order by the corresponding β' value and sum the result over all the π bonds in the molecule, we shall obtain the sum of all the Hückel numbers.

We shall use this formula when we wish to know the π electron energy in a given part of a system, which could not be calculated using an energy formula such as (10).

2.6 Simplifications due to symmetry



The naphthalene molecule contains carbon atoms which are chemically equivalent because of the C_{2v} symmetry which may be assumed for the molecule. This means that the electron densities at certain positions in the molecule are equal. For the two equivalent carbon atoms r and s, we express this as

$$\int |c_{ri}|^2 |\psi_r|^2 d\tau = \int |c_{si}|^2 |\psi_s|^2 d\tau$$

Integrating over all the coordinates of ψ, we find that the coefficients of ψ_r and ψ_s must have the same modulus. The <u>i</u> th molecular orbital

$$\Psi_i = c_{1i}\psi_1 + c_{2i}\psi_2 + \cdots\cdots + c_{10i}\psi_{10}$$

may therefore be expressed in the form

$$\Psi_i = c_{1i}(\omega\psi_1 + \omega'\psi_4 + \omega''\psi_6 + \omega'''\psi_9) + c_{2i}(\omega\psi_2 + \\ + \omega'\psi_3 + \omega''\psi_7 + \omega'''\psi_8) + c_{5i}(\omega\psi_5 + \omega'\psi_6)$$

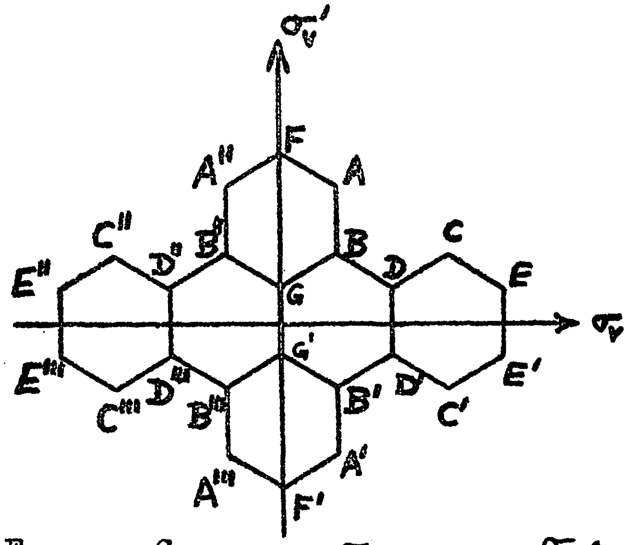
where the ω's are ±1. (For a molecule containing an n-fold symmetry axis, the ω's would in general be n th roots of unity). Writing the above equation for Ψ_i as

$$\Psi_i = d_1\phi_1 + d_2\phi_2 + d_5\phi_5 \qquad (2.17)$$

where $\phi_1 = \frac{1}{4}(\omega\psi_1 + \omega'\psi_4 + \omega''\psi_6 + \omega'''\psi_9)$ etc., the ϕ's may be called *symmetry orbitals*, and (17) expresses the molecular orbital Ψ_i as a linear combination of them. It is convenient, for computational purposes, to use normalised symmetry orbitals.

The correct ω's are given [6, 7, 33] in "character tables". These determine the forms of the symmetry orbitals in order that they shall be eigenfunctions of all the symmetry operators of the point-group of the molecule. Now since a symmetry operation leaves the hamiltonian invariant, the latter commutes with the symmetry operators, and so they possess the same eigenfunctions. The symmetry orbitals thus generated are those that are required in (17). There will in general be different sets of characters ω, and in the character tables these form the irreducible representations belonging to the various symmetry classes. Owing to the orthogonal properties of these characters, the symmetry orbitals belonging to the different symmetry classes are orthogonal, and so the $\mathbb{H}$ matrix element $\int \langle \phi_p | H | \phi_q \rangle \, d\tau$ is non-zero only if ϕ_p and ϕ_q belong to the same symmetry class. $\mathbb{H}$ therefore factorises into submatrices $\mathbb{H}_j$ corresponding to the various symmetry classes, showing that in constructing the molecular orbitals (17), only ϕ's belonging to the same symmetry class need be used.

The procedure obviously reduces the amount of calculation considerably: in the naphthalene problem, for example, instead of having to find the latent roots of a 10 x 10 matrix, we have instead two 3 x 3 and two 2 x 2 matrices. The generated matrices are necessarily symmetric matrices, and their latent roots and eigenvectors (i.e. energy eigenvalues and atomic orbital coefficients) may therefore be conveniently extracted using the Givens method[34], for which an electronic computer program is available.



	E	C_2	σ_v	σ_v'
	A	A'''	A'	A''
	B	B'''	B'	B''
	C	C'''	C'	C''
	D	D'''	D'	D''
	E	E'''	E'	E''
	F	F'	F'	F
	G	G'	G'	G
	A'	A''	A	A'''
	B'	B''	B	B'''
	C'	C''	C	C'''
	D'	D''	D	D'''
	E'	E''	E	E'''
	F'	F	F	F'
	G'	G	G	G'
	A''	A'	A'''	A
	B''	B'	B'''	B
	C''	C'	C'''	C
	D''	D'	D'''	D
	E''	E'	E'''	E
	A'''	A	A''	A
	B'''	B	B''	B
	C'''	C	C''	C
	D'''	D	D''	D
	E'''	E	E''	E
χ (R):	24	0	0	4

3. A description of the application of the Hückel LCAO-MO theory to an aromatic hydrocarbon 1-2, 6-7 dibenzpyrene, and of the results obtained.

dibenzpyrene, and of the results obtained

3.1 Application of Group Theory to form symmetric secular matrices.

The point-group of this molecule is D_{2h}, but we shall find it convenient to use the subgroup C_{2v}. The symmetry operations of this group consist of a two-fold axis of rotation, C_2, perpendicular to the plane of the molecule, and two mirror planes σ_v and σ_v' mutually at right-angles, and perpendicular to the molecular plane. In addition of course there is the identity operation E. The results of the operations on the 24 $2p_\pi$ atomic orbitals are shown in the table on the opposite page, in which each atomic orbital is denoted by its position in the molecular diagram. At the foot of each column is recorded the number of times that the symmetry operation R converts an atomic orbital into itself. This number, $\chi(R)$, must be the trace of the reducible representation matrix D(R) associated with R which acts on the basis set of atomic orbitals, and is therefore the sum of the traces $\chi_j(R)$ of the irreducible representations. We therefore have the relationship

$$\chi(R) = \sum_{j=1}^{h} a_j \chi_j(R)$$

where h is the order of the group (which is 4 for C_{2v}) and a_j is the number of times that the j th irreducible representation is used to form molecular orbitals belonging to the symmetry class j. It follows that

$$a_j = \frac{1}{h} \sum_R \chi(R) \chi_j(R) \qquad (5.1)$$

using the orthogonality properties of the characters $\chi_j(R)$. From the definition of a_j, this quantity is also equal to the number of non-zero symmetry orbitals in this class, and therefore to the order of the $\mathbb{H}_j$ submatrix. As usual the characters χ_j are given by a character table [6,7]:

C_{2v}	E	C_2	σ_v	σ_v'
A_1	1	1	1	1
B_2	1	-1	1	-1
A_2	1	1	-1	-1
B_1	1	-1	-1	1

From the characters of the irreducible representations given in this table, and those of the reducible representations $\chi(R)$, (1) gives

$$a_{A_1} = \frac{1}{4}\,(24.1 + 0.1 + 0.1 + 4.1) = 7$$

$$a_{B_2} = \frac{1}{4}\,(24.1 + 0.1 + 0.1 - 4.1) = 5$$

$$a_{A_2} = \frac{1}{4}\,(24.1 + 0.1 + 0.1 - 4.1) = 5$$

$$a_{B_1} = \frac{1}{4}\,(24.1 + 0.1 + 0.1 + 4.1) = 7$$

which predicts that the $\mathcal{H}_{A1}$, $\mathcal{H}_{B2}$, $\mathcal{H}_{A2}$ and $\mathcal{H}_{B1}$ matrices are respectively 7th, 5th, 5th and 7th order.

The symmetry orbitals are generated as described in the last section, using the characters given in the C_{2v} character table:

A_1 symmetry class

$$^{A_1}\phi_A = \frac{1}{2}\,(A + A''' + A' + A'')$$

$$^{A_1}\phi_B = \frac{1}{2}\,(B + B''' + B' + B'')$$

$$^{A_1}\phi_C = \frac{1}{2}\,(C + C''' + C' + C'')$$

$$^{A_1}\phi_D = \frac{1}{2}\,(D + D''' + D' + D'')$$

$$^{A_1}\phi_E = \frac{1}{2}\,(E + E''' + E' + E'')$$

$$^{A_1}\phi_F = \frac{1}{2}\,(F + F')$$

$$^{A_1}\phi_G = \frac{1}{2}\,(G + G')$$

B_2 symmetry class

$$^{B_2}\phi_A = \frac{1}{2}\,(A - A''' + A' - A'')$$

$$^{B_2}\phi_B = \frac{1}{2}\,(B - B''' + B' - B'')$$

$$^{B_2}\phi_C = \frac{1}{2}\,(C - C''' + C' - C'')$$

$$^{B_2}\phi_D = \frac{1}{2}\,(D - D''' + D' - D'')$$

$$^{B_2}\phi_E = \frac{1}{2}\,(E - E''' + E' - E'')$$

$$^{B_2}\phi_F = \frac{1}{2}\,(F - F' + F' - F) = 0$$

$$^{B_2}\phi_G = \frac{1}{2}\,(G - G' + G' - G) = 0$$

A_2 symmetry class

$$^{A_2}\phi_A = \tfrac{1}{2}(A + A''' - A' - A'')$$
$$^{A_2}\phi_B = \tfrac{1}{2}(B + B''' - B' - B'')$$
$$^{A_2}\phi_C = \tfrac{1}{2}(C + C''' - C' - C'')$$
$$^{A_2}\phi_D = \tfrac{1}{2}(D + D''' - D' - D'')$$
$$^{A_2}\phi_E = \tfrac{1}{2}(E + E''' - E' - E'')$$
$$^{A_2}\phi_F = \tfrac{1}{2}(F + F' - F' - F) = 0$$
$$^{A_2}\phi_G = \tfrac{1}{2}(G + F' - G' - G) = 0$$

B_1 symmetry class

$$^{B_1}\phi_A = \tfrac{1}{2}(A - A''' - A' + A'')$$
$$^{B_1}\phi_B = \tfrac{1}{2}(B - B''' - B' + B'')$$
$$^{B_1}\phi_C = \tfrac{1}{2}(C - C''' - C' + C'')$$
$$^{B_1}\phi_D = \tfrac{1}{2}(D - D''' - D' + D'')$$
$$^{B_1}\phi_E = \tfrac{1}{2}(E - E''' - E' + E'')$$
$$^{B_1}\phi_F = \tfrac{1}{2}(F - F' - F' + F)$$
$$^{B_1}\phi_G = \tfrac{1}{2}(G - G' - G' + G)$$

The symmetry operations have been applied only to the seven chemically distinct positions (the unprimed set); the other sets give symmetry orbitals which are identical with these. The number of non-zero symmetry orbitals in the four cases are 7, 5, 5 and 7, just as predicted by the application of (1).

The matrix elements of the $\mathcal{H}_j$ reduce to quite simple quantities involving the parameters α and β.

The element $\int \phi_A H \phi_B \, d\tau$ in $\mathbb{H}_{A_1}$ becomes

$$\int \phi_A H \phi_B \, d\tau = \frac{1}{4} \int (A H B + A''' H B''' + A' H B' + A'' H B'') \, d\tau$$

$$= \beta_{AB}$$

and the diagonal element $\int \phi_D H \phi_D \, d\tau$ in $\mathbb{H}_{B_1}$,

$$\int \phi_D H \phi_D \, d\tau = \frac{1}{4} \int (D H D + D''' H D''' + D' H D' + D'' H D'' - 2 D H D' - 2 D'' H D''') \, d\tau$$

$$= \alpha - \beta_{DD'} .$$

The matrices consequently become:

$$\left.\begin{matrix} A_1 \\ B_1 \end{matrix}\right\} = \begin{array}{c|ccccccc|} & A & B & C & D & E & F & G \\ \hline A & \alpha & \beta_{AB} & & & & \sqrt{2}\beta_{AF} & \\ B & \beta_{BA} & \alpha & & \beta_{BD} & & & \sqrt{2}\beta_{BG} \\ C & & & \alpha & \beta_{CD} & \beta_{CE} & & \\ D & & \beta_{DB} & \beta_{DC} & \alpha \pm \beta_{DD'} & & & \\ E & & & \beta_{EC} & & \alpha \pm \beta_{EE'} & & \\ F & \sqrt{2}\beta_{FA} & & & & & \alpha & \\ G & & \sqrt{2}\beta_{GB} & & & & & \alpha \pm \beta_{GG'} \\ \hline \end{array}$$

$$\left.\begin{matrix} B_2 \\ A_2 \end{matrix}\right\} = \begin{array}{c|ccccc|} & A & B & C & D & E \\ \hline A & \alpha & \beta_{AB} & & & \\ B & \beta_{BA} & \alpha & & \beta_{BD} & \\ C & & & \alpha & \beta_{CD} & \beta_{CE} \\ D & & \beta_{DB} & \beta_{DC} & \alpha \pm \beta_{DD'} & \\ E & & & \beta_{EC} & & \alpha \pm \beta_{EE'} \\ \hline \end{array}$$

where the upper and lower signs in the diagonal terms refer to the upper and lower symmetry classes on the left hand sides, respectively.

The factors of $\sqrt{2}$ in the F and G rows and columns occur with elements referring to bonds between atoms of different multiplicities (i.e. between those which are, and which are not, on a symmetry element). The fact that the coefficients of all the non-diagonal β's between atoms of the same multiplicities are ± 1 is explained as follows. The matrix element between symmetry orbitals ${}^{j}\phi_T$ and ${}^{j}\phi_S$ in $\mathcal{H}_j$ is

$$\int \phi_S^* \, H \, \phi_T \, d\tau = \int \left[\langle S | \cdot | \chi_j(R) \rangle \right]^{\dagger} H \langle T | \cdot | \chi_j(R) \rangle \, d\tau$$

where $\langle S|$ and $\langle T|$ are the row vectors of the basis set of atomic orbitals in ϕ_S and ϕ_T and $|\chi_j(R)\rangle$ is their column eigenvector, obtained by normalising the j th characters in the character table.

$$\int \phi_S^* H \phi_T \, d\tau = \int \langle \chi_j(R) | \cdot | S \rangle \, H \langle T | \cdot | \chi_j(R) \rangle \, d\tau$$

$$= \langle \chi_j(R) | \cdot \int |S\rangle H \langle T| \, d\tau \, \cdot \, |\chi_j(R)\rangle$$

Now $\int |S\rangle H \langle T| \, d\tau$ is a 4 x 4 diagonal matrix of β_{ST}'s; it is therefore a constant matrix and commutes with $\langle \chi_j(R)|$ The latter vector is unitary, and so the expression reduces to

$$\beta_{ST} \langle \chi_j(R) | \cdot | \chi_j(R) \rangle = \beta_{ST}$$

i.e. the matrix elements expressing the interactions between symmetry orbitals containing atoms of the same multiplicities are independent of the symmetry class.

3.2 Results of the calculation of energy eigenvalues and eigenvectors.

In the first approximation (the Simple Hückel Method) the β values for all the bonds were assumed to be equal, and the calculation was done in two ways. Firstly the determinental equation

$$\det \left| (H_j)_{RS} - E\,\delta_{RS} \right| = 0$$

was solved for the energies E, and these were then substituted in the secular equations

$$d_{Ri}(\alpha - E) + \beta \sum_{S} d_{Si} = 0$$

in order to determine the coefficients d_{Ri} of the symmetry orbitals. The second method was to use a computer program based on the Givens method[34] to find the latent roots of the symmetric $\mathbb{H}_j$ matrices and to determine the eigenvectors $|d_i\rangle$ of the symmetry orbitals. Consistent results were found by the two methods, and the eigenvalues and their associated eigenvectors are listed in their appropriate symmetry classes in Table I.

The discussion of the electronic states and of the spectra which follow is nominally of the results of the Simple Hückel Method (in which all the bond β values are assumed equal), but it is qualitatively also valid for the subsequent iterations, for which the energy eigenvalues and bond orders are summarised later (in Table IV).

(i) Electronic States.

In order to describe the lower excited electronic states, we shall need to know the symmetries of the singly-occupied molecular orbitals Ψ'_i with respect to the full symmetry point-group of the molecule, which is D_{2h}. The symmetry of an electronic state is that whose characters correspond to the direct product of the characters of the symmetry classes of the corresponding molecular orbitals. Consequently all doubly-filled levels are totally symmetric (all the characters are + 1), and therefore contribute nothing to the symmetry of the state.

The character table of the D_{2h} group is

D_{2h}	E	$C_2(x)$	$C_2(y)$	$C_2(z)$	i	σ_v	σ_v'	σ_h	
A_g	1	1	1	1	1	1	1	1	
A_u	1	1	1	1	-1	-1	-1	-1	
B_{1g}	1	1	-1	-1	1	-1	1	-1	
B_{1u}	1	1	-1	-1	-1	1	-1	1	x
B_{2g}	1	-1	1	-1	1	1	-1	-1	
B_{2u}	1	-1	1	-1	-1	-1	1	1	y
B_{3g}	1	-1	-1	1	1	-1	-1	1	
B_{3u}	1	-1	-1	1	-1	1	1	-1	z

Table II: Energy eigenvalues and eigenvectors for the π electron LCAO symmetry orbitals in 1-2, 6-7 dibenzpyrene calculated by the Simple Hückel Method.

A_1

x	-2.634328	-1.859943	-1.330675	-1.000000	+0.673293	+1.122809	+2.028844
d_A	.244660	.510057	.065306	0	.538161	.604513	.143759
d_B	.564029	-.204306	- .101876	0	- .470021	.231835	.595890
d_C	.300796	- .260382	.591197	0	- .204607	.352098	- .571289
d_D	.149701	.593129	.197493	.632455	- .321618	- .284770	- .047463
d_E	.494815	.355547	- .110592	- .632455	- .040722	- .393982	- .244202
d_F	.161479	- .197983	.628312	0	.429766	- .443479	.398219
d_G	.488065	- .335991	- .435697	.447214	.397246	- .154448	- .278230

B_2

x	-2.246980	-1.414214	-0.554958	+0.801938	+1.414214
d_A	.471314	.303891	- .168210	.681068	.439733
d_B	.377965	- .429766	.377965	- .377965	.621876
d_C	.168210	- .303891	.681068	.471314	- .439733
d_D	.377965	.733657	.377965	- .377965	- .182143
d_E	.681068	- .303891	- .471314	- .168210	- .439733

A_2

x	-1.414214	-0.801938	+0.554958	+1.414214	+2.246980
d_A	.439733	.681068	.168210	- .303891	- .471314
d_B	.621876	- .377965	- .377965	.429766	- .377965
d_C	.439733	- .471314	.681068	- .303891	.168210
d_D	.182143	.377965	.377965	.733657	.377965
d_E	.439733	.168210	- .471314	- .303891	.681068

B_1

x	-2.028844	-1.122809	-0.673293	+1.000000	+1.330675	+1.859943	+2.634328
d_A	.143759	.604513	.538161	0	.065306	- .510057	.244660
d_B	.595890	.231835	- .470021	0	- .101876	.204306	.564029
d_C	.571289	- .352098	.204607	0	- .591197	- .260383	- .300796
d_D	.047463	.284770	.321618	.632456	- .197493	.593129	- .149701
d_E	.244202	.393982	.040722	- .632456	.110592	.355547	- .494815
d_F	.398219	- .443479	.429766	0	.628312	.197983	.161479
d_G	.278230	.154448	- .397246	.447214	.435697	- .335991	- .488065

where the operations $C_2(x)$, $C_2(y)$ and $C_2(z)$ are rotations of 180° about the x, y and z axes; $\underline{i}$ is inversion through the centre of symmetry, and σ_h a reflection in the molecular plane. Applying these operations to the atomic orbital A in the symmetry orbital with the lowest possible energy (where the only node is in the molecular plane, a plane of antisymmetry) we have

E	$C_2(x)$	$C_2(y)$	$C_2(z)$	i	σ_v	σ_v'	σ_h
A	$-A'$	$-A''$	A'''	$-A'''$	A'	A''	$-A$

If we think of this sequence as a vector, its scalar product with the vector (1, -1, -1, 1, -1, 1, 1, -1) produces the atomic orbitals with the correct sign in the symmetry orbital $\phi_A(A_1)$ in Ψ_2 (see Table II).

Table II

Ψ_i	Huckel No. x_i	Symm. class j (C_{2v})	Symm. orbital ${}^{i}\phi_A$	Orbital vector $\langle x_j|$	Symm. class j (D_{2h})
Ψ_2	0.673293	A_1	$A+A'''+A'+A''$	1, -1, -1, 1, -1, 1, 1, -1	B_{3u}
Ψ_1	0.554958	A_2	$A+A'''-A'-A''$	1, 1, 1, 1, -1, -1, -1, -1	A_u
Ψ_{-1}	-0.554958	B_2	$A-A'''+A'-A''$	1, -1, 1, -1, 1, 1, -1, -1	B_{2g}
Ψ_{-2}	-0.673293	B_1	$A-A'''-A'+A''$	1, 1, -1, -1, 1, -1, 1, -1	B_{1g}

But this vector consists of the characters of the B_{3u} representation (see D_{2h} character table), hence Ψ_2 belongs to B_{3u}. Table II contains the symmetry orbitals ${}^{i}\phi_A$ for the two highest bonding molecular orbitals

Ψ_{-2} and Ψ_{-1} and the two lowest antibonding ones, Ψ_{1} and Ψ_{2}, together with their energies (in the form of the Hückel numbers x_i) and their symmetry classes in the full D_{2h} point-group.

The lowest excited state of the molecule is that in which one electron has been promoted from Ψ_{-1} to Ψ_{1} and as explained at the beginning of this sub-section, its symmetry is that of the direct product of the representations of Ψ_{-1} and Ψ_{1}. So the symmetry of the $\Psi_{-1}^{1}\Psi_{1}^{1}$ state is that whose characters are (1,1,1,1,-1,-1,-1,-1) x (1,-1,1,-1,1,1,-1,-1) = (1,-1,1,-1,-1,-1,1,1), i.e. B_{2u}. The second excited state is degenerate in the Hückel theory, since the states $\Psi_{-1}^{1}\Psi_{1}^{0}\Psi_{2}^{1}$ and $\Psi_{-2}^{1}\Psi_{-1}^{2}\Psi_{1}^{1}$ have the same energy. Their symmetries are both B_{1u}.

(ii) Electronic Spectra.

The probability of a transition between two electronic states Φ_a and Φ_b of the kind described above is proportional to the square of the electronic transition moment $\vec{\lambda}_{ab}$ which is defined as

$$\vec{\lambda}_{ab} = \int \Phi_a \sum_{v} \vec{r}_v \Phi_b \, d\tau$$

where $\vec{r}_v$ is the position vector of the vth electron. The integral may be resolved into components, and so the psobability of transition giving rise to radiation with a component in the x direction depends upon

$$\lambda_{x\,ab} = \int \Phi_a \sum_{v} x_v \, \Phi_b \, d\tau \qquad (3.2)$$

and there would be similar expressions for the y and z directions. One of the slection rules relating to such a transition states that it is allowed provided the product $\Phi_a \Phi_b$ transforms like the vector X, Y or Z. In other words, the representations of the electronic state must be the same as those of the radiation vector, in order that those of the product $\Phi_a \Phi_b$ shall be totally symmetric (Ag), and the integrand in (2) non-zero. Application of the D_{2h} operations to the radiation vectors X, Y and Z shows that those have symmetries B_{1u}, B_{2u} and B_{3u} respectively. The second selection rule is based on the fact that the spin operator commutes with the right hand side of (24), and so there can be no interaction

($\lambda_{a\ell} = 0$) between the states Φ_a and Φ_ℓ if they have different multiplicities. The allowed transitions are therefore singlet-singlet, triplet-triplet, etc.

Table III shows the 8 lowest electronic states, their energies and term symbols, and the polarisations of the allowed transitions between them. The symmetry terms are obtained by forming the direct product of the representations of the singly-occupied molecular orbitals Ψ_i (column 5 of Table II), and reference made to the D_{2h} character table. The multiplicity terms $s = 2S + 1$ (where S is the total spin quantum number) are written as superscripts.

Table III

The lower electronic states in 1-2, 6-7 dibenzpyrene.

El. state Φ	Occupation Nos. of Ψ_{-2}	Ψ_{-1}	Ψ_1	Ψ_2	Energy of Φ rel. to gd. st.$_{\Phi}$	Symm. & Mul. terms	Direction of polarisation of trans. to Φ_1	Φ_2	Φ_3	Φ_4	Φ_5	Φ_6	Φ_7
Φ_8	0	2	1	1	2.574837β	$^{1,3}B_{3g}$	(f)	x	y	~~(f)~~ y	(f)	(f)	(f)
Φ_7	1	1	1	1	2.456502β	$^{1,3,5}A_g$	"	y	x	x	"	"	
Φ_6	1	1	2	0	2.338167β	$^{1,3}B_{3g}$	"	x	y	y	"		
Φ_5	2	0	2	0	2.219832β	$^{1}A_g$	"	y	x	x			
Φ_4	1	2	1	0	1.228251β	$^{1,3}B_{1u}$	x	(f)	(f)				
Φ_3	2	1	0	1	1.228251β	$^{1,3}B_{1u}$	x	"					
Φ_2	2	1	1	0	1.109916β	$^{1,3}B_{2u}$	y						
Φ_1	2	2	0	0	0	$^{1}A_g$							

Recalling the symmetries of the radiation vectors X, Y and Z, the allowed transitions in which the ground state Φ_1 is the lower one are just those whose upper states belong to B_{1u}, B_{2u} or B_{3u}, whose associated radiations are polarised in the x, y or z directions respectively. Sub-column Φ_1 in column 5 shows that there are two distinct transitions, polarised in the x and the y directions. The polarisation directions of allowed transitions involving other states as lower states are also shown in column 5. (f) indicates a forbidden transition.

Some of the allowed transitions shown in column 5 are in fact many-fold degenerate. Each transition with Φ_2 as lower state for example is at least doubly degenerate, since it can be singlet-singlet or triplet-triplet, and similarly the transitions shown under $\Phi_{3,4}$ occur 8 times over. Moreover since the singlet, triplet and quintuplet states represented by Φ_7 are respectively two-fold and three-fold degenerate and non-degenerate (by the "branching diagram"), the degeneracies of the $\Phi_7 \rightarrow \Phi_2$ and of the $\Phi_7 \rightarrow \Phi_{3,4}$ transitions are increased by a factor of six.

The energy levels calculated from the subsequent iterations are summarised in Table IVa, where, however, the Hückel numbers of only the bonding MO's, together with their symmetry classes in the C_{2v} group, are given.

(iii) Bond Orders and Bond Lengths.

The second column of Table IV b contains the ~~Carbon~~ Coulson Bond Orders calculated from the data of Table I. Using Coulson's empirical bond orders/bond length curve[5] (amended by Goodwin[8] in the low-order region), a first-approximation set of bond lengths was interpolated. This set p^{I} was then used to infer the appropriate β'^{II} values for the next iteration, which yielded presumably more accurate energies and bond orders. Table IV b contains the $\underline{p}$, $\underline{r}$ and β' values for the eight distinct C-C bonds in the molecule for the four iterations which were carried out.

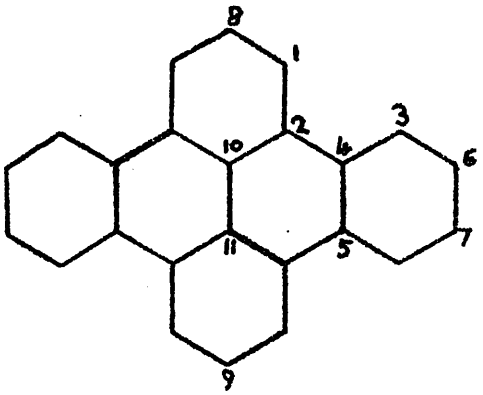
The bond orders show a certain tendency towards convergence, but do so at different rates. As a result the low-order bonds 2-4 and 10-11 which converge most slowly become excessively low-order (the third iteration length of the 2-4 bond is 1.606Å) which causes increasing aberrations in the orders of the other bonds. This behaviour is probably due to uncertainty in the order/length curve used: few of the lengths used to construct this curve are accurate to within 0.01Å, and in view of the paucity of experimental data in the low-order region, the abnormal values for these bonds is not unexpected.

It is clearly desirable to strike a balance between the two sources of error (insufficient and excessive iterations), and a possible way of doing this (following Goodwin[8]) is to stop iterating at a stage when the total π electron energy of the molecule becomes constant. The last row of Table IV a contains the sum of the Hückel numbers for the bonding orbitals, and the relative changes in these are small after the second iteration. Using Goodwin's criterion, then, we should accept p^{II} and r^{II} as the most reliable orders and lengths.

Even considering the iteration table as a whole, however, the general behaviour of the π bonds is preserved in the various iterations. This is that the pyrene part of the molecule tends towards two benzene rings connected by the low-order bond 10-11, and that the two annelated benzo-rings become more benzene-like and are joined to the rest of the system by means of the even lower-order bonds such as 2-4. The tendency of these benzo-rings towards benzene rings is shown by the bond orders, which approach the benzene bond order of $\frac{2}{3}$.

The calculation would suggest that 1-2, 6-7 dibenzpyrene should behave, if not like four loosely connected benzene rings, then to a certain extent, at least, like diphenyl in which benzene rings join the 2 and 2' and the 6 and 6' positions.

Table IV

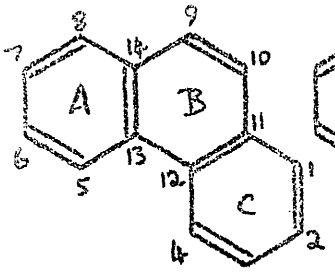


(a) Energy eigenvalues $-x_i$

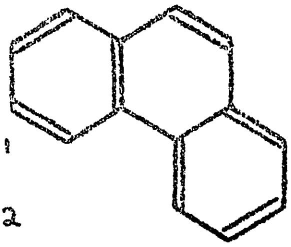
C_{2v} symm.	I	II	III	IV
A_1	2.634328	2.295189	2.259156	2.223204
	1.859943	1.830550	1.868839	1.911160
	1.330675	1.264078	1.235308	1.215826
	1.000000	0.906619	0.923630	0.950999
B_2	2.246980	2.047033	2.037332	2.027803
	1.414214	1.298507	1.253866	1.203296
	0.554958	0.600053	0.687294	0.770962
A_2	1.414214	1.246422	1.197235	1.146297
	0.801938	0.830170	0.870257	0.902765
B_1	2.028844	1.897162	1.910213	1.922399
	1.122809	1.072405	1.056662	1.040109
	0.673293	0.660868	0.705058	0.751680
$\sum_i (-x_i)$	17.082196	15.949056	16.004850	16.066500

(b) Bond orders, bond lengths and β^0-values

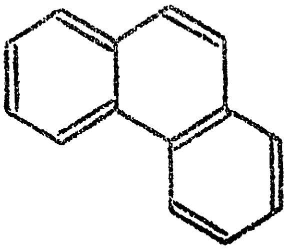
Bond		p^{I}	r^{I}	$\beta^{0\,I}$	p^{II}	r^{II}	$\beta^{0\,II}$	p^{III}	r^{III}	$\beta^{0\,III}$	p^{IV}	r^{IV}
1	2	.614	1.402	0.955	.639	1.394	0.982	.653	1.390	0.996	.662	1.388
1	8	.667	1.386	1.008	.665	1.387	1.006	.663	1.387	1.005	.663	1.387
2	4	.428	1.483	0.714	.342	1.538	0.571	.265	1.606	0.453	.194	1.684
2	10	.549	1.424	0.876	.579	1.413	0.914	.608	1.404	0.948	.628	1.397
3	4	.603	1.405	0.943	.617	1.401	0.958	.624	1.399	0.966	.630	1.397
3	6	.690	1.380	1.028	.699	1.378	1.036	.700	1.378	1.037	.698	1.379
4	5	.562	1.419	0.892	.605	1.404	0.945	.641	1.394	0.984	.666	1.387
6	7	.637	1.395	0.980	.626	1.398	0.968	.627	1.398	0.969	.631	1.397
10	11	.482	1.451	0.796	.421	1.487	0.703	.346	1.535	0.634	.286	1.583



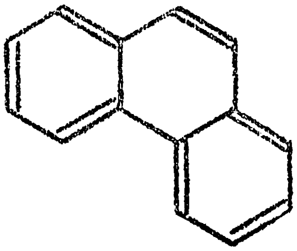
I



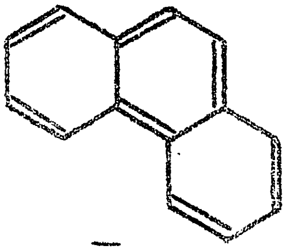
II



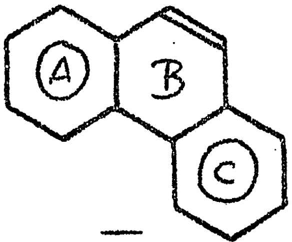
III



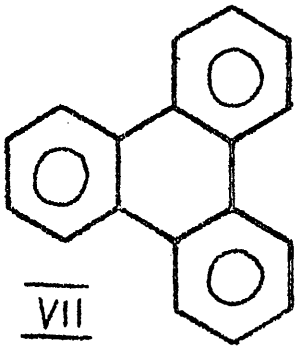
IV



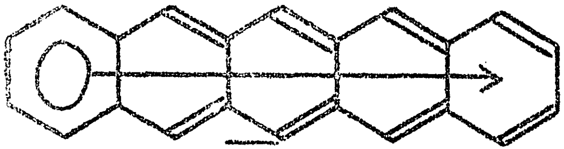
V



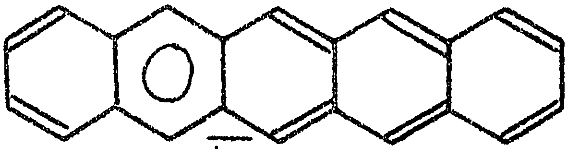
VI



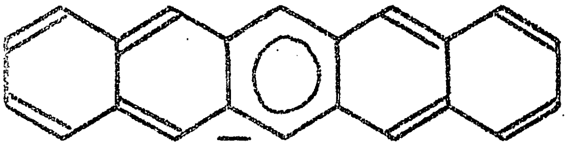
VII



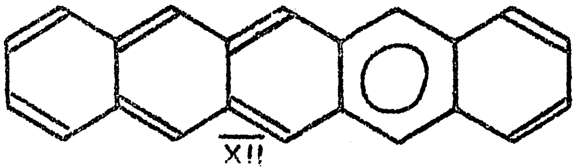
VIII



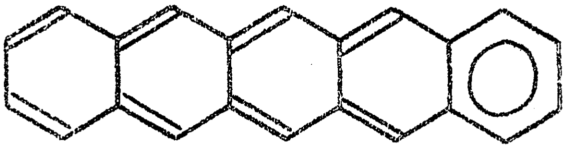
IX



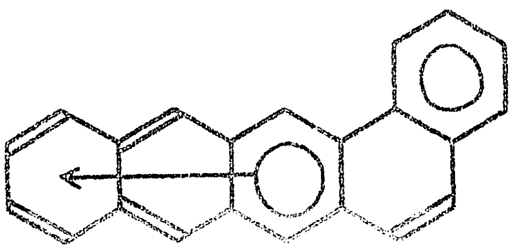
X



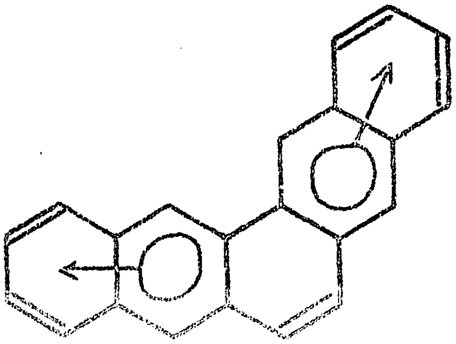
XII



XIII



XIV

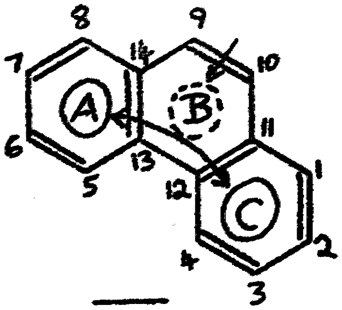


XV

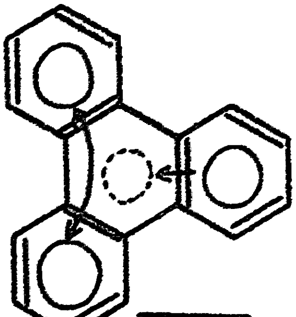
§ 4. The Clar theory of aromatic hydrocarbons.

According to the Fries[9] Rule, a benzenoid aromatic hydrocarbon tends to behave as if its π electron structure were that for which the greatest number of isolated aromatic sextets may be written. By the term "isolated aromatic sextet" we mean a benzenoid ring in which three formal alternating single and double bonds may be written, which are associated with this ring, but with no other. For example, of the Kekulé structures I to V which may be written for phenanthrene, I to IV contain aromatic sextets which are associated with rings A and C only, and V that in which only ring B contains an aromatic sextet. By the Fries Rule, phenanthrene would be predicted to behave as if its π structure corresponded to the former set (I to IV), and in Clar's system[10] etc. is written as VI, in which the circles represent the aromatic sextets, the precise nature of which is as yet undefined. The ring between the aromatic sextets, i.e. ring B, is considered non-aromatic, because it contains three single bonds, two "aromatic bonds" and an ethylenic double bond. Similarly triphenylene is written as VII, in which we have three aromatic sextets and one "empty ring". This accounts in a valence-bond way for the bond variations in these molecules. There is good chemical evidence[11] for the ethylenic 9,10 bond, which parallels also the Molecular Orbital results (previous section).

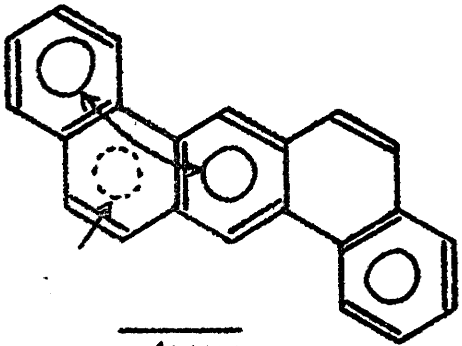
In an acene, only one benzenoid ring may contain an aromatic sextet at any one time, as is shown by the structures VIII to XII for pentacene. The other rings contain formal butadiene systems. Since one would expect these systems to have very nearly equal energies, Clar supposes[11,12,13] that the aromatic sextet can migrate from the extreme left hand ring throughout the system, thereby converting each ring in turn into an aromatic ring, in the sequence VIII to XIII. At structure XII the direction of the motion is reversed, and the sextet thus undergoes an oscillatory motion along the acene. We note that in order to account for the oscillation of the aromatic sextet, it is necessary to suppose the motion of only <u>two</u> electrons: since a non-aromatic acene ring already contains a butadiene system, it requires only two further electrons to complete its aromatic sextet. The motion of this "aromatic pair" is represented in Clar's system by means of the arrow in VIII. Clar's models of other aromatic hydrocarbons may be described similarly. For the phene isomers of pentacene, 1-2 benztetracene XIV and pentaphene XV, the Fries Rule stipulates the existence of



XVI



XVII

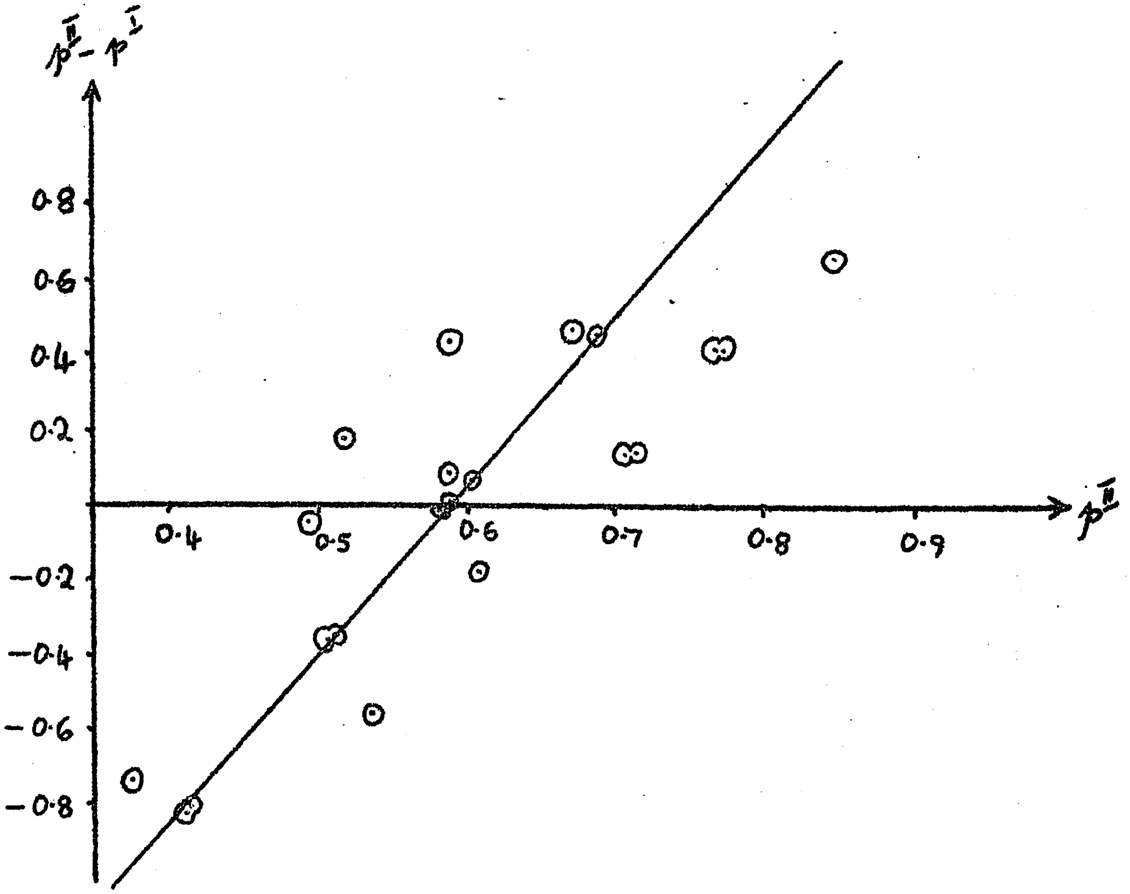


XVIII

two aromatic sextets. This accounts for the greater stability[11] and benzene-like character of these isomers over that of pentacene.

In order to complete the Clar theory, we shall give its picture of the aromatic benzenoid ring in its simplest form. Clar supposes that this ring which has hitherto been written  actually contains three double bonds[14] as does a Kekulé structure , two of which can interact[13,15] as in the valence-bond picture of 1,3 butadiene, but that the third bond may not because of opposed orbital directions, and is consequently different from the other two. When two aromatic rings are angularly annelated onto a third ring to give phenanthrene XVI, the electrons in the bonds 11-12 and 13-14 interact to give a system which, together with the electrons in the "different" bond 9-10 forms an induced aromatic sextet[14] in the ring B, which would be "empty" on the Fries picture. The interaction and the induction are indicated by arrows, and the induced sextet by a dotted circle. The effect is shown too for triphenylene XVII and 1-2, 5-6 dibenzanthracene XVIII. In the latter molecule we note that the induced aromatic sextet occurs on only one side of the molecule at any one time.

Fig.2. The relation between the bond orders in 1-2 benzanthracene and their increments between the first two iterations.



5. Results of the computations on some aromatic hydrocarbons.

5.1 The effect of iterating.

The negative Hückel numbers x_i defining the energy levels $E_i = \alpha - x_i \beta_0$ of the bonding MO's Ψ_i are given in parts (a) of the Tables in Appendix A, together with their sums, which define the total π electronic energies in the molecules. The columns labelled I, II and III refer to the three iteractions which were carried out on most of the molecules. Parts (b) contain the sets of bond orders p_{rs}, bond lengths r_{rs} and β'_{rs} values as calculated by the various iterations, the two latter quantities being interpolated using the Coulson-Goodwin[8] r(p) and the Mulliken, Rieke and Brown[2] $\beta'(r)$ curves. The first iteration energy eigenvalues and bond orders for some of the molecules have already been calculated by other workers[16], and we have usually accepted these bond orders for use in subsequent iterations. We have listed the values of x_i^{I} and $p_{\lambda s}^{I}$ for the sake of completeness and comparison, but have indicated with an asterisk when the values have been taken from elsewhere.

Although the total π electronic energies as measured by $\sum_i (-x_i)$ converge quite rapidly, the ideal self-consistency in the bond orders, and therefore in the individual energy levels, is not realised, particularly when the p^{I} values are less than 0.4; in this case serious divergence occurs, and leads to r values which may far exceed the length of the longest measured C-C bond! As we shall discuss later, this is probably due to defects in the r(p) and $\beta'(r)$ curves in the long-bond region. Since we are primarily interested in the tendencies in bond lengths, we shall not attach any particular significance to these abnormal results, and shall accept the second-iteration results as being probably the most reliable.

The tables in Appendix A show that the increment or decrement in the bond order p of a given bond between two successive iterations shows a rough dependence on p. On the average, the greater the bond order of a bond, the greater are the quantities $p^{II}-p^{I}$ and $p^{III} - p^{II}$. In Fig. 2 we have plotted the second-iteration bond order p^{II} for 1-2 benzanthracene against $p^{II} - p^{III}$. Although the resulting points are somewhat diffuse, many of them lie very close to a straight line which passes through the zero value of $p^{II} - p^{I}$ at $p^{II} = 0.585$. This value is near to the average bond order $\bar{p}^{II} = 0.596$, and hence we may infer an approximate proportionality between the iterational increment in bond order $p^{II} - p^{I}$ and the quantity $p^{II} - p^{II}$.

Since the average bond order is on inspection almost independent of the iteration, i.e. $\bar{p}^{II} \simeq \bar{p}^{I}$, the proportionality can be written

$$p^{II} - p^{I} = k\,(p^{II} - \bar{p})$$

i.e.

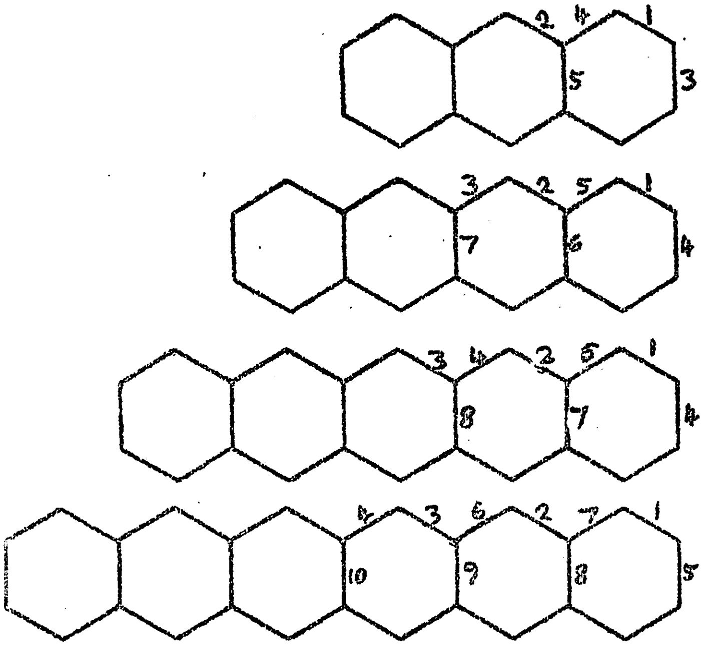
$$p^{II} = p^{I} + \frac{p^{I} - \bar{p}}{1 - k} \qquad (5.1)$$

For the acenes (Tables 1 to 4) where we have recorded the average bond orders $\bar{p}$, it is easy to verify the prediction of (1) that if $p^{I} > \bar{p}$, the effect of a further iteration is to increase the value of p, whereas if $p^{I} < \bar{p}$ the result is a decrease.

If the points had been a little more colinear, a relation such as (1) could have been used to estimate improved bond orders from the first-iteration set p^{I}. As it is, there would be too many uncertainties. However, our rule may be used as a rough guide to the reliability of a particular first-iteration bond order and to the probable effect of a second iteration.

Decreasing progression of bond orders in the acenes for iterations I and III

I



III

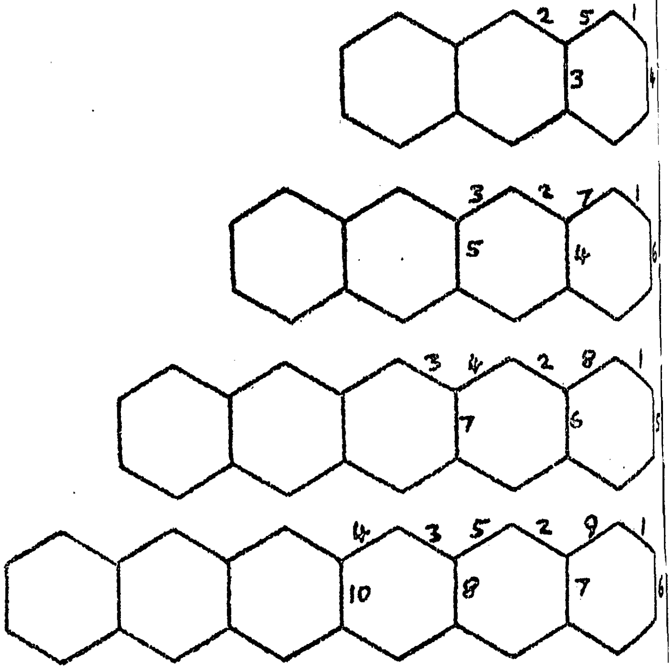


Table V

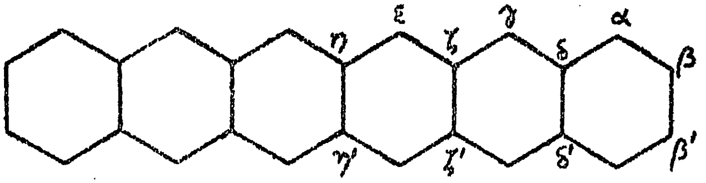
A comparison of the bond orders and (calculated) bond lengths of "corresponding bonds" in the acene series.

Acene / Bond	anthracene		tetracene		pentacene		hexacene	
	p^{II}	r^{II}	p^{II}	r^{II}	p^{II}	r^{II}	p^{II}	r^{II}
α β	.787	1.362	.795	1.361	.798	1.361	.799	1.361
γ δ	.630	1.397	.662	1.388	.673	1.385	.677	1.384
ε ζ	-	-	-	-	.615	1.401	.627	1.398
α δ	.490	1.447	.476	1.454	.471	1.456	.469	1.457
γ ζ	-	-	.584	1.412	.568	1.417	.561	1.420
ε η	-	-	-	-	-	-	.598	1.407
β β'	.520	1.421	.508	1.439	.503	1.441	.501	1.442
δ δ'	.486	1.449	.457	1.464	.446	1.471	.442	1.473
ζ ζ'	-	-	.438	1.476	.417	1.489	.408	1.494
η η'	-	-	-	-	-	-	.400	1.499

5.2 Bond variations

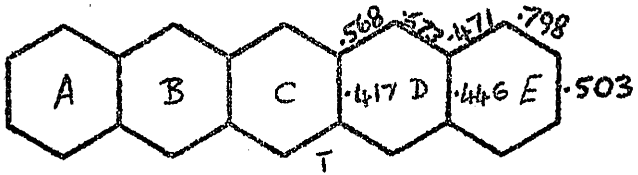
(a) Acenes.

Tables 1 to 4 in Appendix A show that the highest bond order in an acene is always that of the $\alpha\beta$ bond, the rest decreasing in the progression shown in the diagrams opposite, which were constructed from the results of the first and third iterations. The general pattern of the progressions is clearly very uniform for the four acenes illustrated. The bond orders of the bonds $\alpha\beta$, $\gamma\delta$ etc. (indicated here for hexacene, but extendable to all other acenes) and of the "peri" bonds $\beta\beta'$, $\delta\delta'$ etc., **decrease** with increasing distance from the ends of the acene, whereas the bond orders of the adjacent bonds $\alpha\delta$, $\gamma\zeta$ etc., increase.

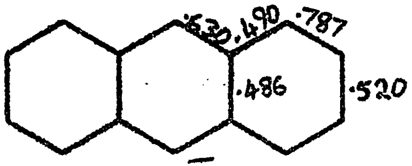


A comparison of I and III shows that iterating has no effect on this progression, but in each case, however, it has resulted in a relative lowering in the bond orders of the $\alpha\delta$ bonds.

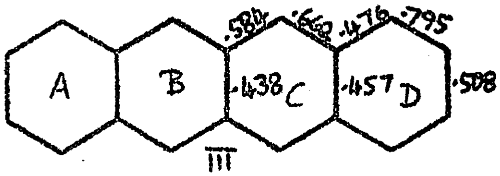
In Table V we compare the (second iteration) bond orders and bond lengths of the bonds which are in corresponding positions in the four acenes. While the bond orders of these bonds either increase or decrease as we pass from one member to the next, they show a clear tendency to reach limiting values. The bond lengths do so more rapidly (since experimental bond length is a fairly insensitive function of "three-figure" bond order), and it can be seen that the length of the $\alpha\beta$ bond has already reached a constant value at tetracene, i.e. that the $\alpha\beta$ bond lengths for tetracene and the higher acenes are equal.



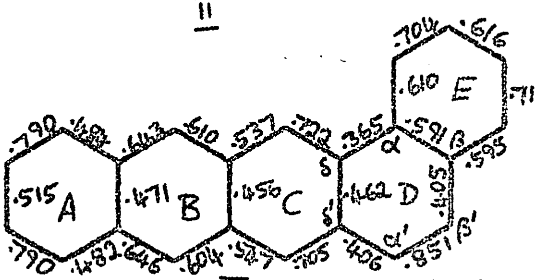
I



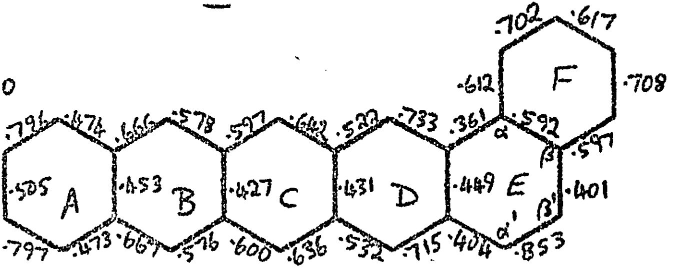
II



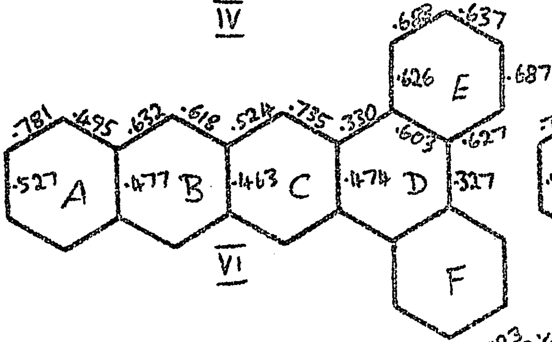
III



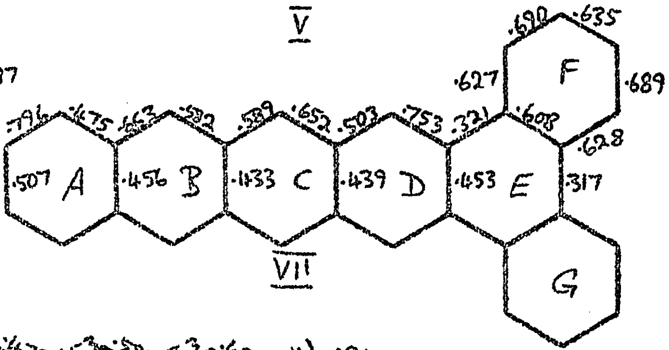
IV



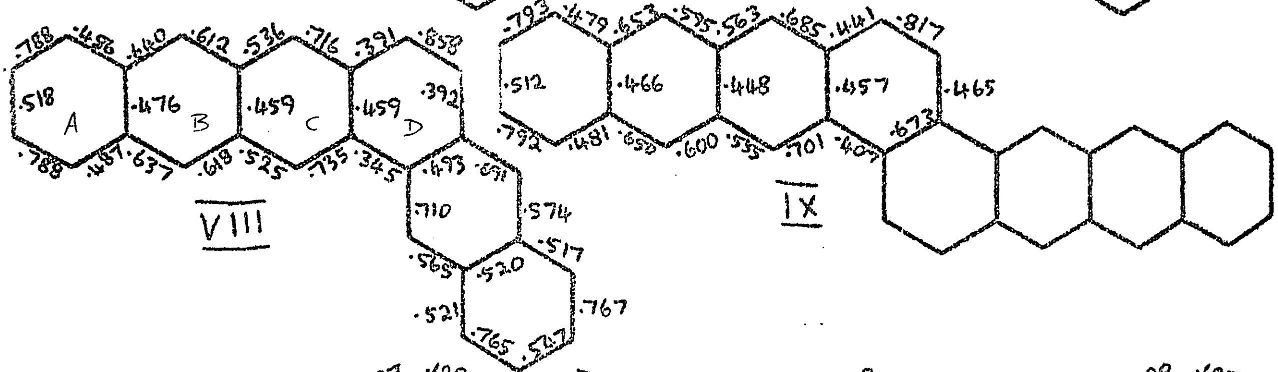
V



VI

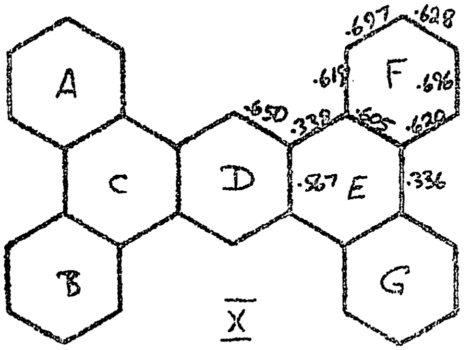


VII

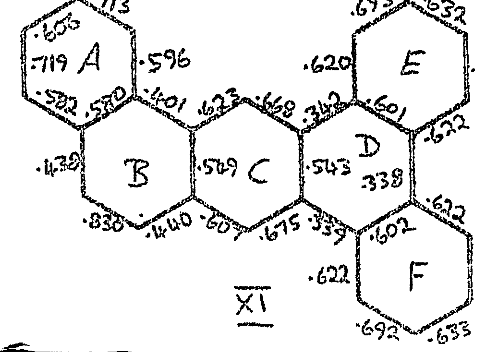


VIII

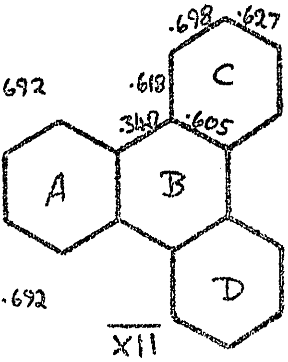
IX



X



XI



XII

(b) Other aromatic hydrocarbons. Comparison with Fries-Clar theory.

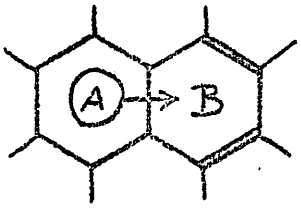
There are very few aromatic hydrocarbon series which are such that from a few "typical" members, a general picture of the whole series may be obtained, as was possible for the acenes. We shall therefore discuss briefly under this heading the results for the rest of the molecules studied. In order to reduce the complexity a little, it is useful to compare various kinds of aromatic hydrocrabons containing linearly annelated benzenoid rings with the corresponding acenes.

The diagrams opposite show the p^{II} values of some benzologues of tetracene and pentacene. Examination of the tetracene chains in IV, VI and VIII shows that the bond orders in the rings D, onto which the benzo rings are annelated, are much lower than those in the other rings, and that the acene residue resembles anthracene rather than tetracene. Similarly the molecules 1-2 benzpentacene and 1-2, 3-4 dibenzpentacene (V and VII) should be thought of as derivatives of tetracene, not pentacene. The bond orders in the annelated rings E and F in IV and VI, and F and G in VI and VII, depart fairly little from 0.667; these rings are therefore benzene-like, but with a small degree of bond alternation.

We may therefore make the general observation that a benzenoid ring at a branch point of otherwise linear annelated systems has little benzene-like character, and serves partially to isolate the systems which are annelated onto it. Such an isolated system may in fact be observed even when there is no annelated benzo system; in the phene series such as 1-2 benztetracene IV, 1-2 benzpentacene V and hexaphene VIII, the "un-annelated" bonds $\alpha\beta$ or $\alpha'\beta'$ become partially isolated ethylenic systems, as may be seen from their relatively high p^{II} values of 0.850 to 0.860.

The isolated benzene-like rings are in exactly the same positions as those of the aromatic sextets predicted by the Fries Rule. This is immediately clear in such simple cases as *s* tetrabenzanthracene X, and triphenylene XII, where the aromatic sextets are uniquely defined in rings A, B, D, F and G, and in A, C and D respectively. Although for a molecule containing a linearly annelated system it is not possible to define the position of the aromatic sextet uniquely, our calculations are still in agreement with the Fries Rule provided we assume with Clar that the aromatic sextet is shared between the various acene rings of the molecule. The molecule then contains a loosely-coupled acene system, which is the picture at which we arrived for the molecules IV to IX.

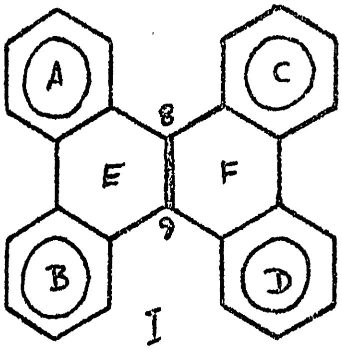
Using the concept of "isolated aromatic sextets" defined in § 4, we may amend the Fries Rule to deal more adequately with the general case as follows:

> The π electrons in a benzenoid aromatic hydrocarbon may be pictured in a valence-bond way as distributed so as to form the maximum number of isolated aromatic sextets. However, if as a result a ring A containing
>
> 
>
>
> an aromatic sextet is annelated onto a ring B containing an isolated butadiene system, the position of the aromatic sextet is not uniquely defined, and AB then resembles an <u>isolated naphthalene system</u> in bond lengths and chemical properties.

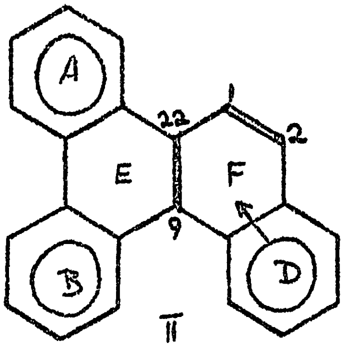
isolated naphthalene system in bond lengths

The rule may clearly be extended to account for the isolated anthracene and tetracene systems such as those discussed for the molecules IV to IX, and in fact to all the molecules whose molecular constants are listed in the appendices. Bisanthracene (Table 15) for example obviously tends to behave like two isolated anthracene molecules, and 1-12 benzperylene (Table 14) to a certain extent like two naphthalene molecules joined by the low-order bonds 11-12 and 13-14 and the ethylene-like bridge bond 9-10. Picene (Table 10) and 3-4, 9-10 dibenzpentacene (Table 22) show the isolation of terphenyl and quaterphenyl systems respectively, and also contain ethylene-like bridge linkages. The presence of these linkages, however, appears to distort the rings slightly, thus conferring more bond alternation than would be expected in the polyphenyls assuming the usual 6-fold symmetric model for the benzene-like ring.

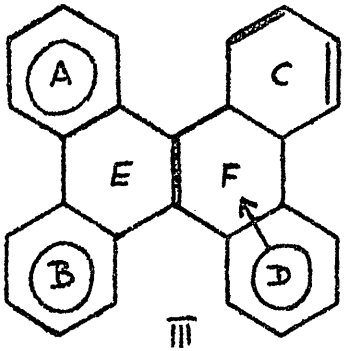
Earlier in this sub-section we observed that a ring containing a fixed or isolated aromatic sextet may be replaced by a fixed double bond without appreciably altering the rest of the bond orders in the molecule. An exception to this generality may be seen in the example 1-2, 3-4, 5-6 tribenznaphthalene (Table 31). Although this molecule might possibly be regarded as the symmetrical tetrabenznaphthalene I for which one of the isolated aromatic rings C has been amputated and replaced by an ethylenic bond 1-2 (see II), we now have one aromatic sextet D adjacent to a butadiene system in the ring F;



I



II



III

by the Fries Rule, therefore, the aromatic sextet will be shared between the rings D and F, creating a naphthalene-like system. This is confirmed by the comparison of the bond orders in rings D and F with those in the benzene-like rings A and B.

It is curious that in s tetrabenznaphthalene I, the bond order of the 8-9 bond, which the Fries Rule predicts to be nearly ethylenic, is almost benzene-like in the first two iterations, and only as a result of the third does it become the most pronounced π bond in the molecule. In the second iteration the value is almost identical with that of the 9-22 bond in tribenznaphthalene II (0.673 and 0.675 respectively), and it suggests that s-tetrabenznaphthalene tends to behave as if the aromatic sextet in one of the rings were shared, as shown in III, contrary to the Fries Rule.

(c) A comment on the relationship between the Clar models and the results of the Hückel Molecular Orbital calculations of bond orders.

Although the calculated bond orders are in some approximate agreement with the Clar models, a more quantitative relationship between the two theories should not be expected since the two theories are inherently contradictory. The Clar theory is based on the concept of the electron-pair bond; a C-C bond which is drawn as single in a Fries model has no π electron character, since the π electrons are required for coupling in another part of the system. Thus the 8-9 and the 1-6 bonds in phenanthrene (using the numbering system used in Table 5 of Appendix A) have zero π bond order, whereas the bond order of the 6-7 bond is unity. The Hückel MO theory on the other hand does not require electron-pairing for bond formation, and stipulates an approximately equal degree of interaction between the atomic orbitals of neighbouring carbon atoms. As a result all bonds between two sp^2 hybridized carbon atoms generally contain an appreciable amount of π bond character (p^{III} for the quoted bonds in phenanthrene are 0.351 and 0.381 respectively), unless the $2p_{\pi}$ atomic orbitals are directed at right-angles to each other.

The fact that approximate agreement is obtained is not altogether surprising, however. A Fries structure together with the Clar model of the oscillating aromatic pair (the "Fries-Clar model") constitutes a structure which is effectively a superposition of most of the Kekulé structures from the complete canonical set in the Valence Bond theory. Now if sufficient highly-weighted structures are selected, we should have a "truncated set", which from wave-mechanical experience is known frequently to furnish a good total state function. Pauling[17,18] shows that quite good bond lengths and qualitative pictures of benzene, naphthalene, anthracene, phenanthrene and even 1-14 benzbisanthrene, are obtained by considering the Kekulé structures alone. However, the importance of including the second- and higher-excited structures (i.e., the "Dewar structures") in the larger aromatic systems may be judged from the Valence Bond calculations that although the Kekulé structures in benzene contribute a combined weight of 78% to the total resonance structure, in naphthalene the figure is only 64%[34]. For the more complex hydrocarbons Pullman[19] has found increasing contributions from more excited structures, and that for molecules larger than anthracene the Kekulé structures are quite unimportant. In such cases we may expect no more than a rough agreement between the Fries-Clar model and the results of the Hückel calculations. An example of this is seen from the average bond orders $\bar{p}$ in various sizes of molecules; according to Hückel MO calculations $\bar{p}$ decreases from 0.667 in the smallest aromatic system (benzene) to 0.525 in the largest (graphite). While this is confirmed by the experimental bond lengths of 1.395 and 1.421Å respectively, the Fries-Clar theory predicts no change in bond order. Anticipating the calculations described in a later section (§ 6.2), we quote the result that the bond orders predicted by the Fries Rule to be benzene-like decrease towards the centre of the molecule. Thus, the decreasing bond orders in hexabenzcoronene (Table 11 in Appendix C) for the bonds 1-16, 1-2, 2-14 and 10-11 (.665, .629, .571 and .565) and the increasing values for bonds 2-3 and 7-10 (.373 and .438) indicate increasing graphite-like character towards the centre of the molecule. Again the Fries-Clar theory predicts only two different bond orders.

5.3 Molecular π electronic energies.

(i) Aromaticity and stability.

Chemical evidence suggests that aromatic molecules may be distinguished from other molecules by virtue of their π molecular orbitals, which confer on them a property called "aromatic character" or "aromaticity". We are now in a position to attempt to provide a more quantitative basis for this term. Let us firstly examine the empirical qualitative bases for aromaticity from chemical and physical aspects.

Chemically a molecule is said to be aromatic if its formula corresponds to a cyclic array of formal alternating single and double bonds on the Kekulé valence theory, but which nevertheless does not exhibit typical unsaturation properties. With electrophilic reagents it undergoes substitution rather than addition reactions, and shows a tendency to couple with diazonium compounds. Aromatic molecules are generally unreactive in comparison with olefinic unsaturated molecules, and since many of them may be heated to high temperatures without suffering decomposition, they are often described as "stable".

Physically an aromatic molecule may be diagnosed by the presence of prominent and intense bands in the UV absorption spectrum, characteristic diamagnetic susceptibility, and very low proton resonance frequencies for those hydrogen atoms outside (but σ-bonded to) the π-electron system. Aromaticity may also be detected by use of certain additive properties, since characteristic increments must be made for aromatic rings in Parachor, Molar Refractivity etc. studies. The most common criterion of aromaticity is that of Resonance Energy, which is a direct calorimetric measurement of the extra stability of an aromatic molecule over a hypothetical one which is structurally identical, but which contains "fixed" or Kekulé single and double bonds. This information is provided by Heats of Combustion and Heats of Hydrogenation. However, since Resonance Energy is by definition a Valence Bond concept, we shall prefer to work without it, and use instead the energy of a molecule which is provided by its π electrons; this is directly calculable from MO theory, is negative and tends to stabilise the molecule.

The most striking criterion of aromaticity which we have mentioned under the chemical and physical aspects is that of stability, and since this is easily the best measurable quantity, we shall use it as a basis for aromaticity. Now there are two quite different definitions of the term "stability", both of which have been implied above to contribute to aromaticity.

(a) Thermochemical stability: A molecule is thermochemically stable if its internal energy is low. If under certain conditions, A and B are in general equilibrium, the component said to be the more stable is the one with the lower internal energy, irrespective of the reaction path or of the activation energy barrier between A and B and thus of the ease of the reaction to the component with the lower energy. According to the definition we may, strictly speaking, compare the thermochemical stabilities only for isomeric molecules. However, since the atomisation states and the combustion products are each identical for all aromatic hydrocarbons, the heats of formation or heats of combustion *per repeating unit* may be compared for non-isomeric molecules.

(b) Thermodynamic stability: A molecule is *thermodynamically* stable if it possesses a large free energy of activation $\Delta F^{\ddagger}$ to the transition state. Although this quantity could in principle be evaluated from knowledge of the temperature, the enthalpy of activation $\Delta H^{\ddagger}$ (which could be computed if the transition state were known) and the entropy of activation $\Delta S^{\ddagger}$, the latter quantity is very difficult to calculate, and can certainly not be assumed constant over the very wide range of shapes and sizes of aromatic hydrocarbons considered!

Thus we have regretfully abandoned the attempt to calculate thermodynamic (i.e. chemical) stabilities, which would have been useful to correlate with kinetic data. We shall therefore use only definition (a) above, and claim that a molecule is stable if it possesses a high π stabilisation energy; this is the amount by which the energy of a structure is reduced due to the formation of π MO's. Since we shall be concerned with the stabilities of molecules only in their ground states, we shall define the π stabilisation energy as the modulus of equation (2.10) summed over all the n/2 bonding molecular orbitals, and the result doubled to take account of the occupation number 2 for each occupied molecular orbital:

$$\pi\,\text{s.e.} = n\alpha - 2\sum_{i=1}^{\frac{1}{2}n} x_i \beta_0 = E_\pi \qquad (5.2)$$

The molecular π stabilisation energy affords a basis of comparing the stabilities of aromatic hydrocarbons possessing the same number of atoms and electrons (i.e. isomers). To compare the aromaticities of non-isomeric molecules we shall have to coin a slightly different definition. For aromatic hydrocarbons we can use either

(i) π s.e per benzenoid ring.

(ii) π s.e per carbon atom.

or (iii) π s.e per electron.

(ii) and (iii) are of course identical for neutral aromatic molecules, but are different if we are dealing with their cations or anions.

Table VI: π stabilisation energies in the acene and 1-2 benzacene series.

	(i) N_R	(ii) N_C	(iii) E_π	(iv) ΔE_π	(v) E_π^c	(vi) ΔE_π^c	(vii) E_π^R	(viii) $-\Delta E_\pi^R$
Acenes	1	6	$6\alpha+8.000\beta_0$		$\alpha+1.3333\beta_0$		$6\alpha+8.000\beta_0$	
				$4\alpha+5.684\beta_0$		$.0351\beta_0$		$\alpha+1.1580\beta_0$
	2	10	$10\alpha+13.684\beta_0$		$\alpha+1.3684\beta_0$		$5\alpha+6.8420\beta_0$	
				$4\alpha+5.630\beta_0$		$.0112\beta_0$		$\frac{\alpha}{3}+0.4040\beta_0$
	3	14	$14\alpha+19.314\beta_0$		$\alpha+1.3796\beta_0$		$\frac{14}{3}\alpha+6.4380\beta_0$	
				$4\alpha+5.616\beta_0$		$.0054\beta_0$		$\frac{\alpha}{6}+0.2055\beta_0$
	4	18	$18\alpha+24.930\beta_0$		$\alpha+1.3850\beta_0$		$\frac{18}{4}\alpha+6.2325\beta_0$	
				$4\alpha+5.614\beta_0$		$.0034\beta_0$		$\frac{\alpha}{10}+0.1237\beta_0$
	5	22	$22\alpha+30.544\beta_0$		$\alpha+1.3884\beta_0$		$\frac{22}{5}\alpha+6.1088\beta_0$	
				$4\alpha+5.612\beta_0$		$.0022\beta_0$		$\frac{\alpha}{15}+0.0828\beta_0$
	6	26	$26\alpha+36.156\beta_0$		$\alpha+1.3906\beta_0$		$\frac{26}{6}\alpha+6.0260\beta_0$	
				$4\alpha+5.612\beta_0$		$.0017\beta_0$		$\frac{\alpha}{21}+0.0591\beta_0$
	7	30	$30\alpha+41.768\beta_0$		$\alpha+1.3923\beta_0$		$\frac{30}{7}\alpha+5.9669\beta_0$	
				$4\alpha+5.610\beta_0$		$.0012\beta_0$		$\frac{\alpha}{28}+0.0446\beta_0$
	8	34	$34\alpha+47.378\beta_0$		$\alpha+1.3935\beta_0$		$\frac{34}{8}\alpha+5.9223\beta_0$	
				$4\alpha+5.612\beta_0$		$.0010\beta_0$		$\frac{\alpha}{36}+0.0345\beta_0$
	9	38	$38\alpha+52.990\beta_0$		$\alpha+1.3945\beta_0$		$\frac{38}{9}\alpha+5.8878\beta_0$	
1-2 benz-acenes	3	14	$14\alpha+19.450\beta_0$		$\alpha+1.3893\beta_0$		$\frac{14}{3}\alpha+6.4833\beta_0$	
				$4\alpha+5.652\beta_0$		$.0053\beta_0$		$\frac{\alpha}{6}+0.2078\beta_0$
	4	18	$18\alpha+25.102\beta_0$		$\alpha+1.3946\beta_0$		$\frac{18}{4}\alpha+6.2755\beta_0$	
				$4\alpha+5.624\beta_0$		$.0020\beta_0$		$\frac{\alpha}{10}+0.1303\beta_0$
	5	22	$22\alpha+30.726\beta_0$		$\alpha+1.3966\beta_0$		$\frac{22}{5}\alpha+6.1452\beta_0$	
				$4\alpha+5.616\beta_0$		$.0012\beta_0$		$\frac{\alpha}{15}+0.0882\beta_0$
	6	26	$26\alpha+36.342\beta_0$		$\alpha+1.3978\beta_0$		$\frac{26}{6}\alpha+6.0570\beta_0$	
				$4\alpha+5.612\beta_0$		$.0007\beta_0$		$\frac{\alpha}{21}+0.0636\beta_0$
	7	30	$30\alpha+41.954\beta_0$		$\alpha+1.3985\beta_0$		$\frac{30}{7}\alpha+5.9934\beta_0$	
				$4\alpha+5.612\beta_0$		$.0005\beta_0$		$\frac{\alpha}{28}+0.0476\beta_0$
	8	34	$34\alpha+47.566\beta_0$		$\alpha+1.3990\beta_0$		$\frac{34}{8}\alpha+5.9458\beta_0$	

(ii) Calculated energies

As was discussed in the last section, molecules consisting of non-linearly condensed benzenoid rings contain some bonds which are of particularly low bond orders, and some of high bond order, both of which suffer distortion on iterating. When we were discussing the tendencies in bond variation, we did not regard this as being a very serious defect in the second iteration, but in the comparison of the stabilities of isomeric molecules where π electron energies differ very little, it raises some difficulty. We have therefore decided to use first-iteration energies for this purpose in order to avoid these iteration effects.

(a) Acenes and 1-2 benzacenes.

Table VI contains the results of energy calculations carried out on the acene and 1-2 benzacene series. The columns of the table refer respectively to:

(i) the number N_R of benzenoid rings in the molecule,

(ii) the number N_C of carbon atoms in the molecule,

(iii) the molecular π electron energy, E_π ,

(iv) the increment ΔE_π in (iii) between two successive members,

(v) the π electron energy per carbon atom E_π^c ,

(vi) the increment ΔE_π^c in (v) between two successive members,

(vii) the π electron energy per ring E_π^R

and (viii) the decrement $-\Delta E_\pi^R$ in (vii) between two successive members.

The results show that the increment in the molecular π stabilisation energy *(i.e. $-\Delta E_{\pi}$) between two successive members decreases slightly as we proceed along each of the two series illustrated, but that for $N_R > 4$ for the acenes and $N_R > 6$ for the benzacenes, the increment becomes constant at $4\alpha + 5.612\beta_0$. This means that the π s.e per carbon atom, $-E_{\pi}^{c}$, also increases slightly as the molecule gets larger, but tends to the limiting value of $\frac{1}{4}(4\alpha + 5.612\beta_0) = \alpha + 1.403\beta_0$.

Column (vii) shows that the π s.e per ring, $-E_{\pi}^{R}$ decreases as we ascend the two series. This indicates that the relative stability of an aromatic hydrocarbon is not necessarily ensured by the possession of a large number of rings. We know anyway that for a lea large acene $-E_{\pi}^{R}$ declines to $4\alpha + 5.612\beta_0$.

The decrease of the π s.e por ring, $-E_{\pi}^{R}$ as we move down the table indicates that the benzene-like character of the rings is lost as the length of the acene increases. The loss is initially very rapid, but soon decreases to a small quantity, as may be seen from

$$\Delta E_{\pi}^{R}$$

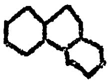
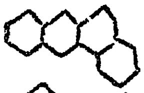
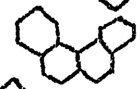
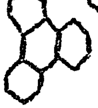
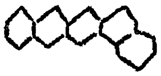
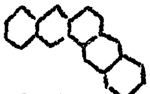
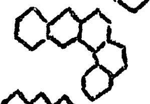
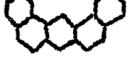
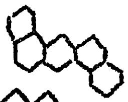
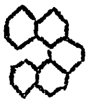
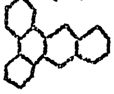
---

*In discussing the results of π electron energy computations, it is convenient to speak of π stabilisation energies (π s.e.) defined by (5.2) rather than the energies themselves.

the comparison of $-\Delta E_{\pi}^{R}$ for benzene-naphthalene and naphthalene-anthracene. The rapid loss of benzene character in an acene with increasing length corresponds with the constant increments of $\Delta E_{\pi} = 4\alpha + 5.612\beta_0$ for $N_R > 4$. That is, it would seem that for tetracene and the higher acenes, the only increase in π s.e. comes from the addition of discrete butadiene units, for which $E_{\pi} = 4\alpha + 4.472\beta_0$, together with a π stabilisation energy of $\frac{1}{2}(5.612 - 4.472)\beta_0 = 0.570\beta_0$ for each of the two connecting bonds. We recall that it was at tetracene too that the bond orders and lengths of the $\alpha\beta$, $\alpha\delta$ and $\beta\beta'$ bonds showed a tendency to converge (see Table V), when they assumed p and r values which tended towards those of a 1,3 butadiene system loosely coupled to the rest of the molecule. This result is in agreement with the Clar model of the acenes, and we shall examine the correlation later. For the 1-2 benzacenes the increment in π s.e. becomes constant at benzpentacene, suggesting that the benzacenes for which $N_R \geqslant 6$ resemble the acenes which contain one ring less than the number contained in the linear portion of the acene chain. (In other words 1-2 benz-(n)-acene resembles (n-1)-acene.) This observation is in qualitative agreement with the results of the bond order and bond length calculations for the benzacenes (see § 5.1 part (b)).

The Clar theory also accounts for the higher π s.e of each of the 1-2 benzacenes over those of the isomeric acenes. In the latter we have only one aromatic sextet, which, by means of the mobile aromatic pair, is shared between n rings, whereas in the latter there are two aromatic sextets: one is fixed forming a benzene-like ring, while the other is shared between n-2 rings. Therefore the 1-2 benzacenes contain more benzene-like character and less butadiene-like character than the acenes, and hence more π stabilisation energy. The π s.e. difference between n-acene and 1-2 benz(n-1)-acene increases as the sizes of the molecules increase, but becomes constant at hexacene- 1-2 benzpentacene reaching a value of 0.186β_0, suggesting an extra stabilising energy of ~ 3-4 kcal./mole due to the presence of an aromatic sextet.

Table VII π e.e's of some isomeric benzenoid aromatic hydrocarbons

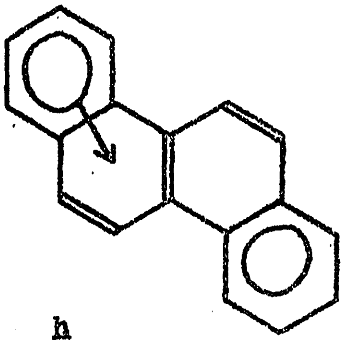
N_R	N_C	Ref.	Molecule	E_π	E_π^c	E_π^R
1	6	a		$6\alpha + 8.000\beta$.	$\alpha + 1.3333\beta$.	$6\alpha + 8.0000\beta$.
2	10	b		$10\alpha + 13.684\beta$.	$\alpha + 1.3684\beta$.	$5\alpha + 6.8420\beta$.
3	14	c		$14\alpha + 19.314\beta$.	$\alpha + 1.3796\beta$.	$\frac{14}{3}\alpha + 6.4380\beta$.
		d		$14\alpha + 19.450\beta$.	$\alpha + 1.3893\beta$.	$\frac{14}{3}\alpha + 6.4833\beta$.
4	18	e		$18\alpha + 24.930\beta$.	$\alpha + 1.3850\beta$.	$\frac{18}{4}\alpha + 6.2325\beta$.
		f		$18\alpha + 25.102\beta$.	$\alpha + 1.3946\beta$.	$\frac{18}{4}\alpha + 6.2755\beta$.
		g		$18\alpha + 25.187\beta$.	$\alpha + 1.3993\beta$.	$\frac{18}{4}\alpha + 6.2968\beta$.
		h		$18\alpha + 25.190\beta$.	$\alpha + 1.3994\beta$.	$\frac{18}{4}\alpha + 6.2975\beta$.
		i		$18\alpha + 25.275\beta$.	$\alpha + 1.4042\beta$.	$\frac{18}{4}\alpha + 6.3188\beta$.
5	22	j		$22\alpha + 30.544\beta$.	$\alpha + 1.3884\beta$.	$\frac{22}{5}\alpha + 6.1088\beta$.
		k		$22\alpha + 30.726\beta$.	$\alpha + 1.3966\beta$.	$\frac{22}{5}\alpha + 6.1452\beta$.
		l		$22\alpha + 30.763\beta$.	$\alpha + 1.3983\beta$.	$\frac{22}{5}\alpha + 6.1525\beta$.
		m		$22\alpha + 30.834\beta$.	$\alpha + 1.4015\beta$.	$\frac{22}{5}\alpha + 6.1668\beta$.
		n		$22\alpha + 30.838\beta$.	$\alpha + 1.4017\beta$.	$\frac{22}{5}\alpha + 6.1676\beta$.
		o		$22\alpha + 30.879\beta$.	$\alpha + 1.4036\beta$.	$\frac{22}{5}\alpha + 6.1758\beta$.
		p		$22\alpha + 30.880\beta$.	$\alpha + 1.4037\beta$.	$\frac{22}{5}\alpha + 6.1761\beta$.
		q		$22\alpha + 30.936\beta$.	$\alpha + 1.4062\beta$.	$\frac{22}{5}\alpha + 6.1872\beta$.
		r		$22\alpha + 30.942\beta$.	$\alpha + 1.4065\beta$.	$\frac{22}{5}\alpha + 6.1884\beta$.
		s		$22\alpha + 30.944\beta$.	$\alpha + 1.4065\beta$.	$\frac{22}{5}\alpha + 6.1888\beta$.

~~(b)~~ (iii) A comparison of the stabilities of some isomeric aromatic hydrocarbons.

Because of the difficulty of completely classifying aromatic hydrocarbons according to "families" as was possible for the acene and the 1-2 benzacene series the somewhat arbitrary method of classifying according to the number of benzenoid rings contained in the molecules will be used instead, i.e. we shall compare isomers.

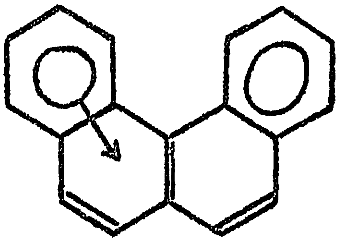
A glance at Table VII shows that roughly speaking the more branched or bent is the annelated benzenoid chain, the higher its π s.e. The Clar account of this observation is similar to that for the acenes and the benzacenes which was discussed under (a). The more branched or bent the chain, the greater the opportunity for "trapping" aromatic sextets in the short limbs, which serves to increase the benzene-like character of the aromatic hydrocarbon; the latter fact is interpreted by Clar as increased stability and therefore higher π s.e.

Writing the Fries or Fries-Clar structures for the molecules (a) to (s) in Table VII, it is easy to verify that the greater the number of aromatic sextets, and the smaller the number of rings over which they are shared, the higher is the π s.e. The similar stabilities for g and h for example would be accounted for by the diagrams



h

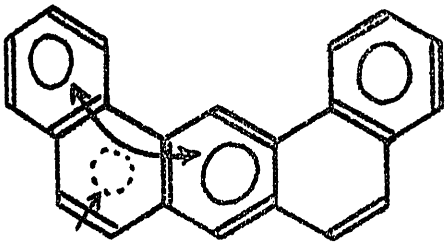
and



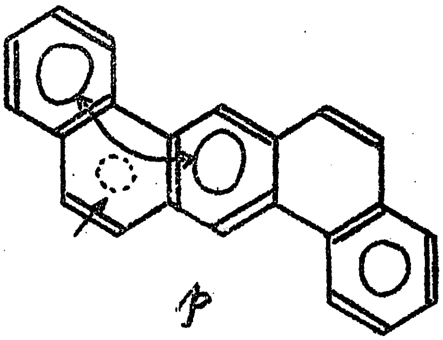
g

each of which shows "isolated" naphthalene and styrene systems. (Of course in reality h is appreciably more stable than g due to the serious overcrowding of hydrogen atoms and possibly other repulsions in the latter which distort the molecule from its planarity; we have not taken account of this fact here.) A comparison of the stabilities of k and l suggests that the loss in stability resulting from the extension of the aromatic sextet from one to two rings is more than compensated by the confinement of the aromatic sextet in the other limb from three rings to two. The similarity in π s.e's for m and n may be understood by drawing out the Fries-Clar structures, and identifying the similar isolated systems in each as we did for g and h.

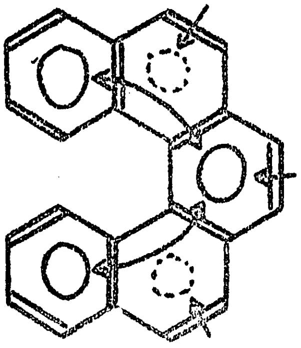
Finally we call attention to the effect of Clar's "induced sextet" concept (which was described in §4) in some of these molecules. Structures o and p each contain three aromatic sextets and two "fixed double bonds", and as expected have similar π s.e. values which are higher than those of the preceding molecules in the table, which contain no more than two sextets. But although three aromatic sextets and two "fixed double bonds" may similarly be written for q and s, the π s.e.'s of these two molecules is relatively much greater (the E_{π}^{c} values are $\alpha + 1.4062\beta_0$ and $\alpha + 1.4065\beta_0$ compared with $\alpha + 1.4036\beta_0$ and $\alpha + 1.4037\beta_0$ for o and p, respectively). The diagrams



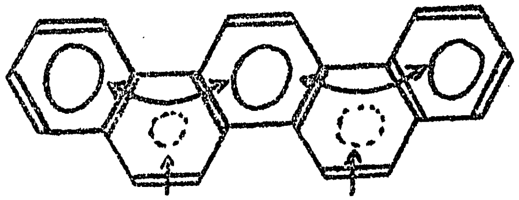
o



p



q



s

indicate the formation of the induced sextets. Assuming the $\mathcal{D}_{3h}$ nature of the aromatic sextet, it is clear that in o and p an induced sextet may be formed on one side of the molecule (indicated by a dotted circle) but not on the symmetrically equivalent opposite side. Since there is no reason to believe that the double bonds in Clar's aromatic sextet are permanently localised in the positions shown in the centre rings of o and p in the above diagrams, we must suppose that the structures in which the induced sextet appears in the right hand rings is equally probable. The energy barrier between the two forms is likely to be small, and so the result is a sharing of the ~~irpduced~~ induced sextet between the two sides of the molecule. The directions of the annelations in q and s, however, permit the induction of two permanent sextets as shown. The extra stabilisation energy contributed by the presence of a fixed induced aromatic sextet is small ($\simeq 0.05\,\beta_0$ $\sim$ 1 kcal./mole) in comparison with that for a normal ("inherent") aromatic sextet (3-4 kcal./mole; see (a) above).

An ideal way to confirm the predictions of both Hückel and Clar theories relating to the relative stabilities of the various molecules is to study their experimental molecular energies as revealed by thermochemical measurements. Unfortunately, few of these are available for the condensed benzenoid systems in which we are interested, but the heats of combustion of seven aromatic hydrocarbons are quoted in the paper submitted for publication "An Empirical Determination of the Hückel Parameter β and of C-C and C-H Bond Energies in Aromatic Hydrocarbons" in Appendix ~~C~~D. The order of the heats of combustion for the three isomeric hydrocarbons triphenylene, 1-2 benzanthracene and chrysene is exactly that predicted by the Hückel theory. The Clar theory also predicts the increased stability of triphenylene over 1-2 benzanthracene and chrysene, but fails to distinguish the stabilities of the two latter molecules.

§ 6. The construction of a new r(p) curve and the calculation of more accurate bond orders.

6.1 A criticism of the r(p) and $\beta'(r)$ curves used for the calculations of the molecular constants ~~tested~~ listed in Appendix A.

As was mentioned in § 5.1 the non-convergence with successive iterations of bond orders and lengths and of the π electron energy levels is probably due to erroneous bond order/bond length and bond length/ β' value relationships (i.e. r(p) and $\beta'(r)$) which were assumed in the region of low bond orders. Let us examine the forms of the curves in this region.

The empirical r(p) curve used was constructed by extrapolating[8] Coulson's 1951 r(p) curve[5], thereby implying a diverging bond length as p tends to zero. Using this curve the "long bond" lengths of 1.534 and 1.524Å measured[20] for quaterrylene were quite accurately calculated.

The $\beta'(p)$ curve was drawn from the calculations of Mulliken, Riecke and Brown[2], and it was further assumed that as p tends to zero, β' does the same; the curve therefore started at the origin. However, this is probably not correct: although the interaction quantity β_{rs} should increase with bond order p_{rs} the relationship between them is practically purely through the length of the bond r-s. Since the (ideal) pure bond between two sp^2-hybridized carbon atoms (i.e. p = o) has a finite length (probably somewhere between 1.48 and 1.54Å), it is unlikely that β actually decreases to zero at p = o, but should itself have a finite value.

6.2 A more accurate order/length curve.

In constructing[5] his original order/length curve Coulson calculated some 36 bond orders from 9 aromatic hydrocarbons using the Simple Hückel method, i.e. assuming that the β's of all the bonds were equal, and these were then plotted against the corresponding bond lengths as measured by X-ray analysis. Owing to the relatively large uncertainties in the latter, together with the error due to neglect of β-variation, the result was a rather scattered set of points, but which strongly suggested an r(p) curve, and it was this "best curve", together with Goodwin's extrapolation that was used for the molecules whose results are in Appendix A.

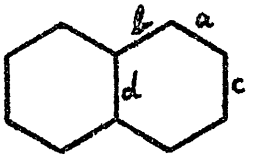
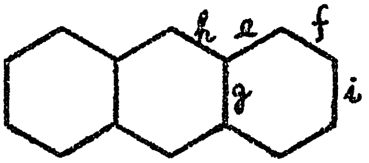
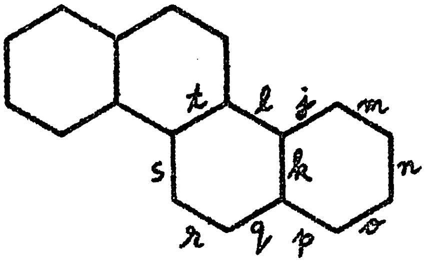
A more successful approach is to restrict the choice of data for the order/length curve to those bonds whose lengths are known accurately, and to use in the calculation β' values which are inferred from the experimental bond lengths. The compounds chosen were naphthalene and anthracene, which have recently been the subject of careful X-ray analysis[21], and also benzene[22] and graphite[23], whose bond lengths are reliable. The experimental bond lengths r_x, the inferred β' values and the calculated bond orders are given in columns 3, 4 and 5 of Table VIII. (We have used the $\beta(r)$ curve derived by Longuet-Higgins and Salem[3] for this and the subsequent calculations, since being based on more recent bond data, we believe it to be more reliable than the Mulliken, Rieke and Brown relationship[2]. According to this curve the β' value of a bond for which $p = o$ is 0.638 corresponding to a bond length of 1.532Å.) The Table also includes the Burns and Iball bond lengths[24] for chrysene, which although not as accurate as the naphthalene and anthracene values, serve as a comparison. The r(p) curve obtained by plotting column 3 against column 5 is shown in Fig.3. The ~~best~~ least-squares curve passing through the naphthalene, anthracene, benzene and graphite points is the straight line shown, and has the equation

$$r \simeq 1.532 - 0.209p \qquad (6.1)$$

For the 11 bonds in the molecules naphthalene, anthracene, benzene and graphite, the maximum vertical deviation from this line is 0.007Å for the bond *a* in naphthalene, which we calculate to be longer than the measured value. (The experimental "estimated standard deviation" for the 11 bonds is 0.005Å.) In column 6 of the Table, r_{calc} gives the "probable bond lengths" for the bonds in naphthalene, anthracene, chrysene, benzene and graphite obtained by substituting the calculated p values in the relationship (1), which probably corrects for slight inaccuracies in the X-ray bond length measurements.

The consistency between the order-length curve (1) and the chrysene bond data (denoted by X's in Fig.3) is a little less marked, but there are still only two deviations greater than 0.01Å. One of these refers to the bond ℓ whose length is well outside the range of the 11 bonds used to derive equation (1). The locus of the r(p) curve in this region is uncertain, but if the Burns and Iball length for the bond *l* is nearly correct it would indicate that the gradient of the r(p)

Table VIII   Measured bond lengths, inferred β^0 values and calculated bond orders for some aromatic molecules.

Molecule	Bond	r_x	β^0	p	r_{calc}
1) Naphthalene	a	1.364	1.095	.772	1.371
	b	1.421	0.910	.521	1.423
	c	1.415	0.929	.541	1.418
	d	1.418	0.919	.571	1.413
2) Anthracene	e	1.436	0.869	.475	1.433
	f	1.368	1.080	.796	1.365
	g	1.428	0.890	.506	1.426
	h	1.399	0.976	.628	1.401
	i	1.419	0.916	.510	1.425
3) Chrysene	j	1.409	0.945	.573	1.412
	k	1.409	0.945	.587	1.409
	l	1.468	0.780	.424	?
	m	1.381	1.035	.732	1.379
	n	1.394	0.995	.581	1.410
	o	1.363	1.095	.751	1.375
	p	1.428	0.890	.534	1.420
	q	1.421	0.910	.492	1.429
	r	1.368	1.080	.777	1.369
	s	1.428	0.890	.525	1.421
	t	1.401	0.970	.624	1.401
4) Benzene	u	1.395	1.000	.667	1.393
5) Graphite	v	1.421	1.000	.525*	1.422

---

* Ref.25

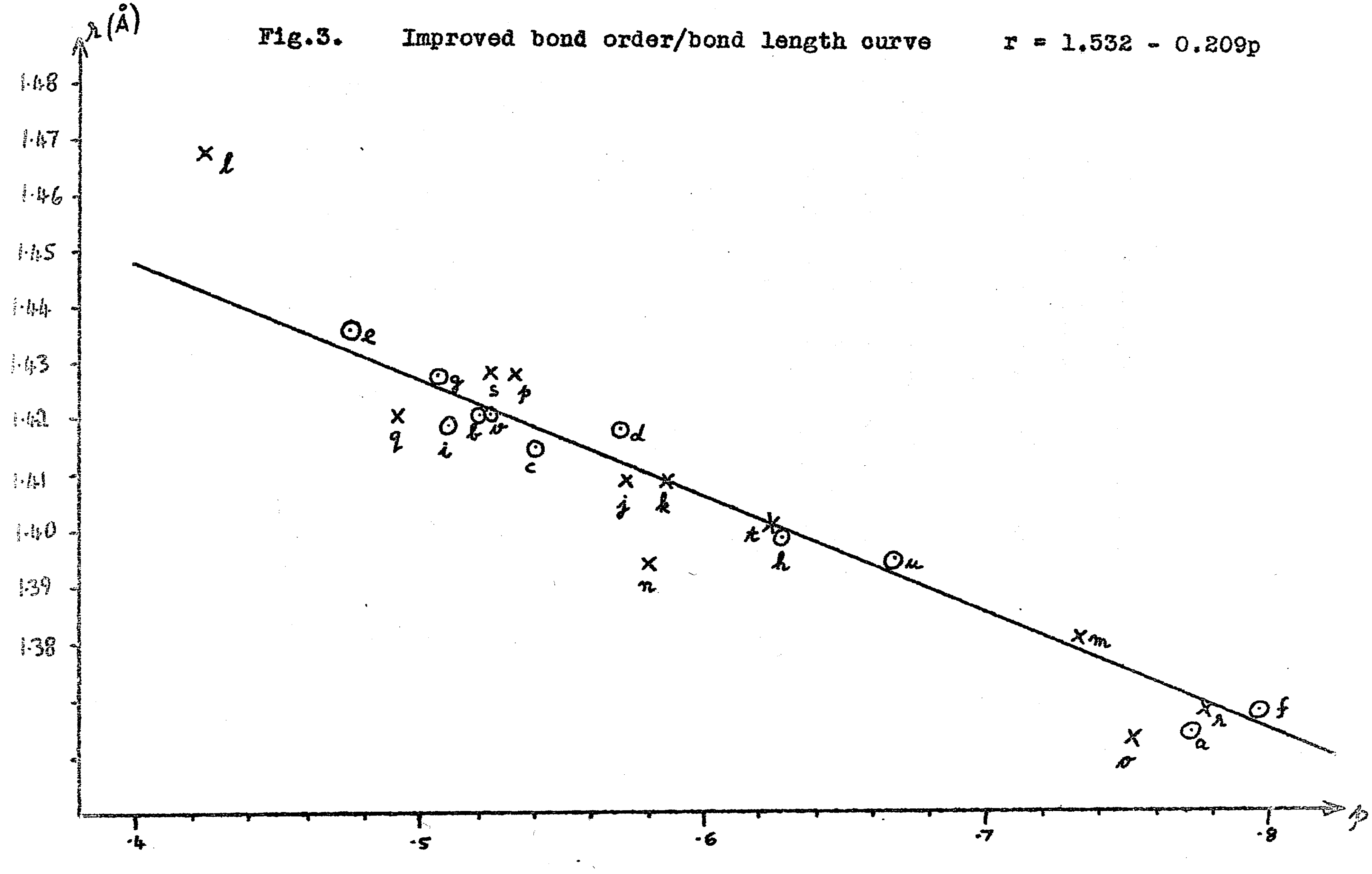


Fig.3. Improved bond order/bond length curve r = 1.532 - 0.209p

curve should increase negatively, i.e. depart from linearity, as p decreases from 0.5.

The length of the ethylene bond according to (1) is obtained by substituting $p = 1$, where we get $r = 1.323$Å, which is 0.01Å shorter than the now accepted value[26]. Putting $p = 0$ we get 1.532Å for the length of a bond between sp^2-hybridized carbon atoms for which there is no π bond character. This is exactly the value assumed by Longuet-Higgins and Salem[3] when deriving their $\beta(r)$ curve; they assumed that the length of such a pure σ bond was the C-C distance in ~~ethylene~~ ethane. It is now believed that such a bond is probably shorter[27, 28] than 1.532Å, but as yet there are no reliable estimates.

As a matter of interest, we observe that if the bonds a to i in Table VIII are disregarded, and a straight line joins the benzene and graphite points u and v (whose bond lengths are known ~~the~~ most accurately of all), the equation of such an order length relationship is

$$r = 1.517 - 0.183p \qquad (6.2)$$

The length 1.517Å for a pure sp^2 C-C σ bond which is implied by this equation is a reasonable value (Coulson[29] now uses 1.51Å). Moreover this equation predicts a length of 1.334Å for p = 1, which is very close to the measured length[26] of an ethylenic bond. However, because of the fact that equation (2) is that of a line drawn through only two points, we shall use (1) in preference to (2) in calculating bond lengths.

The effect of iterating using (1) is shown in Table IX. Here we have computed the bond orders etc. in naphthalene and anthracene by the usual method of starting with the Simple Hückel Method, and inferring bond lengths and improved β' values. The results of the six iterations show that almost complete convergence is now obtained for the bond lengths, and that the values converged to are very nearly the r_{calc} values in Table VIII, which we described as the probable bond lengths in naphthalene and anthracene. The results suggest that the use of the r(p) function (1) for bonds for which $0.45 < p < 0.8$ gives bond lengths which are free from the "iteration effects" described earlier.

Because of the non-validity of the order/length curve (1) in the region of low bond order ($p < 0.45$), it should clearly be used only for molecules which do not contain "long bonds". Such molecules can actually

Table IX (a): Energy eigenvalues for naphtahlene and anthracene calculated using the new order/length curve (equation 6.1) and Longuet-Higgins and Salem's $\beta(r)$ relationship. Six iterations, to test for convergence.

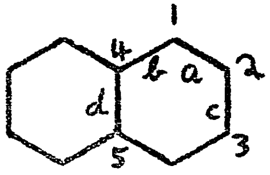
(i) naphthalene

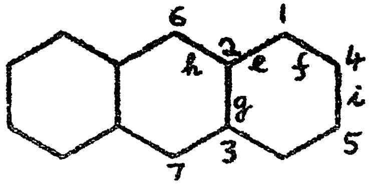
C_{2v} symm.	I	II	III	IV	V	VI
A_1	2.30278	2.191591	2.193508	2.193572	2.193911	2.193892
	1.00000	0.934187	0.928616	0.927788	0.927439	0.927079
B_2	1.61803	1.618048	1.620106	1.620892	1.621756	1.622193
A_2	0.61803	0.662048	0.683106	0.691892	0.696756	0.699193
B_1	1.30278	1.269778	1.269124	1.266360	1.265351	1.264971
$\sum_i (-x_i)$	6.84162	6.675652	6.694461	6.700503	6.705214	6.707327

(ii) anthracene

C_{2v} symm.	I	II	III	IV	V	VI
A_1	2.41421	2.271416	2.270316	2.270553	2.271944	2.272133
	1.41421	1.394118	1.399380	1.401730	1.403919	1.404047
B_2	1.33333	1.921526	1.917809	1.916810	1.917271	1.917233
	1.00000	0.908911	0.897882	0.894590	0.894184	0.893821
A_2	1.00000	1.003438	1.013691	1.019400	1.022455	1.024054
B_1	1.41421	1.377851	1.379864	1.378844	1.378358	1.377722
	0.41421	0.460683	0.487831	0.501439	0.508505	0.511457
$\sum_i (-x_i)$	9.65684	9.337944	9.366772	9.383366	9.396636	9.400467

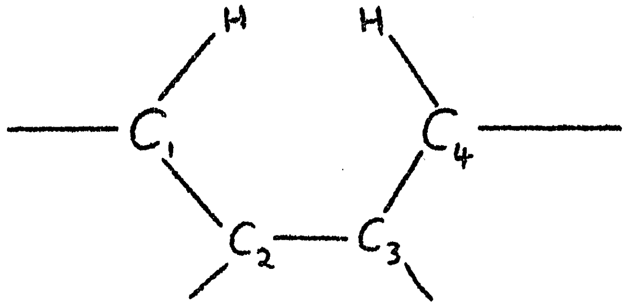
Table IX (b) **Bond orders, bond lengths and β^0 values for naphthalene and anthracene (six iterations)**





Bond	p^I	r^I	β'^I	p^{II}	r^{II}	β^{0II}	p^{III}	r^{III}	β^{0III}	p^{IV}	r^{IV}	β^{0IV}	p^V	r^V	β^{0V}	p^{VI}	r^{VI}	β^{0VI}	"$r_{calc.}$"
1) Naphthalene																			
1 2 (a)	.725	1.381	1.035	.748	1.375	1.052	.759	1.373	1.059	.764	1.372	1.063	.766	1.372	1.065	.768	1.372	1.066	1.371
1 4 (b)	.555	1.416	0.925	.540	1.419	0.916	.531	1.421	0.910	.526	1.422	0.907	.524	1.422	0.906	.523	1.422	0.905	1.423
2 3 (c)	.603	1.406	0.956	.573	1.412	0.937	.559	1.415	0.929	.553	1.416	0.925	.550	1.417	0.923	.549	1.417	0.922	1.418
4 5 (d)	.518	1.424	0.900	.540	1.419	0.916	.555	1.416	0.926	.563	1.414	0.931	.567	1.414	0.933	.569	1.413	0.934	1.413
2) Anthracene																			
1 2 (e)	.535	1.420	0.915	.507	1.426	0.893	.490	1.430	0.885	.481	1.432	0.880	.476	1.433	0.878	.474	1.433	0.877	1.433
1 4 (f)	.738	1.378	1.044	.770	1.371	1.069	.787	1.368	1.082	.795	1.366	1.089	.800	1.365	1.092	.802	1.364	1.093	1.365
2 3 (g)	.485	1.431	0.882	.488	1.430	0.884	.497	1.428	0.889	.503	1.427	0.893	.506	1.426	0.895	.508	1.426	0.971	26 1.4~~01~~
2 6 (h)	.606	1.405	0.960	.620	1.402	0.967	.624	1.401	0.970	.626	1.401	0.971	.626	1.401	0.971	.627	1.401	0.971	1.401
4 5 (i)	.586	1.410	0.945	.543	1.418	0.918	.520	1.423	0.903	.508	1.426	0.896	.502	1.427	0.892	.499	1.428	0.891	1.425

be easily recognised before making any calculations: in a molecule containing an arrangement of bonds:



it is invariably found that the bond order of the C_2-C_3 bond is low, as may be verified from the examples in Appendix A. Moreover, the hydrogen atoms which are bonded to C_1 and C_4 are situated at a mutual distance of 1.8 to 2.1Å, which is less than 2.4Å, twice the van der Waals radius for the hydrogen atom. Thus there is an additional uncertainty due to H-H repulsion, which may possibly cause some stretching of the C_2-C_3 bond[30].

The molecular constants (x_1, p, r and β') for

The molecular constants (x_1, p, r and β') for aromatic hydrocarbons not containing long bonds of the kind described in the last paragraph are listed in Appendix B. Again we get satisfactory convergence of the bond lengths: the third iteration in each case deals with an almost self-consistent model, and we may therefore claim that the bond lengths r^{III} are reliable to within about 0.003Å.

The self-consistency extends to the energy eigenvalues: the Hückel numbers of corresponding levels in the second and third iterations are usually consistent to within 0.01, which was not generally the case for computations on the same molecules recorded in Appendix A. These values may therefore be useful in the comparison of electronic energy levels with the observed UV spectra.

Treatment of aromatic hydrocarbons containing long bonds.

We should not expect the results of calculations of the molecular constants of molecules containing "long bonds" to be as accurate as those for the molecules listed in Appendix B if, for such calculations, the r(p) curve of Fig.3 is merely linearly extrapolated. However, for molecules which our earlier calculations show a resemblance to small aromatic systems which are loosely coupled by means of low-order bonds, some simplifications may be made which lead to improved accuracy.

1-2, 3-4, 5-6 tribenzanthracene is known somewhat to resemble four benzene rings and an ethylene bond which are coupled together by means of low-order bonds (see Table 21(b) of Appendix A). We therefore assign β' values of 0.7 to these low-order bonds, 1.0 to the bonds in the benzene-like rings and 1.1 to the ethylene-like bond 22-23, and perform the usual calculation. For the next iteration we use β' values corresponding to the p and r values obtained from the first iteration for the bonds in the benzene-like rings, but we keep the β' values for the low- and high-order bonds at 0.7 and 1.1 respectively. Successive iterations of this kind lead to satisfactory convergence, and the results are shown in Appendix C.

6.3 Results obtained for aromatic hydrocarbons using the new bond order-bond length relationship.

The energies listed in Tables X (a) and (b) are taken from the 4th iteration results in Appendices B and C respectively; they are obtained using the improved r(p) and the Longuet-Higgins and Salem β' (r) relationships, with the special provisions made for the extreme long and short bonds in the molecules in Table X(b), described in § 6.2. The 2nd, 3rd etc. columns refer respectively to the number of carbon atoms in the molecule, N_c, the number of aromatic sextets, N_B, the π stabilisation energy (which for conciseness has been expressed as $(E_\pi - N\alpha)/\beta_0$), the π s.e. per carbon atom, and the Hückel number of the highest bonding molecular orbital, x_n in units of β_0. The last two columns contain the wavelengths and wave numbers of Clar's p-bonds for these molecules, which will be used later.

From a comparison of the E_π^c values of various sizes and classes of aromatic hydrocarbons, we had hoped to reach some conclusion regarding the relative stabilities of the molecules, such as the confirmation of Hückel's 4n + 2 rule. However, the only regularity observed is a slightly increasing E_π^c value as the size of the molecule increases. In trying to compare this particular prediction with chemical experience, it must be remembered that there are as yet very few quantitative measurements of the stabilities of molecules according to our definition of E_π^c. Also the fact that some of the compounds listed in Tables X(a) and (b) contain "ethylenic" bonds introduces some chemical instability into these molecules; this requires a definition of thermodynamic stability (mentioned in § 5.3) for a proper description. However experiment essentially verifies the predictions for molecules which do not contain these "ethylenic" bonds.

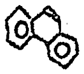
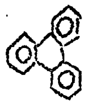
Calorimetric data reveals that diphenyl is indeed more stable than benzene; Clar[13] reports that triphenylene XVIII is certainly more stable than its isomers (we also deduced this from the results discussed in part (ii) of §5.3), since it does not dissolve in concentrated sulphuric acid. Dibenzpyrene XX is similarly very stable in comparison with pyrene, and may be heated without decomposition to 340° when sublimation takes place[11]. The molecules XXV and XXVI are also immune from attack by conc. sulphuric acid, and sublime at 400°. Hexabenzcoronene XXVII is the most stable hydrocarbon known, and melts only at 700°[13,31].

The progressive increase in the π s.e. of the isomers XXI, XXII and XXIII is accounted for by the Clar theory: all three molecules contain four inherent sextets, but whereas XXI contains only one induced sextet at any one time, there are reasons for believing that the double bond in XXII somehow participates in forming two sextets simultaneously[14]. The dibenzperylene XXIII, however, contains two normal permanent induced sextets and so has a correspondingly higher π s.e. The molecules XXI and XXII are exceptional in that their E^c_π values are less than those of the two preceding members XIX and XX which contain a smaller number of carbon atoms. Other examples of this behaviour are XXIV and XI. The reason for this is not understood.

Table X (a) Molecular constants for the molecules listed in Appendix B

Molecule	N_c	N_B	E_π	E_π^c	x_n	λ_p(Å)	$\tilde{\nu}_p \times 10^{-4}$ cm^{-1}
I naphthalene	10	1	13.4147	1.3415	0.6992	2865	3.490
II anthracene	14	2	18.8009	1.3429	0.5115	3781	2.645
III tetracene	18	3	23.5480	1.3082	0.3641	4728	2.115
IV pentacene	22	3	28.9243	1.3147	0.2797	5754	1.738
V hexacene	26	4	34.1058	1.3118	0.2204	6854	1.459
VI heptacene	30	5	39.8289	1.3276	0.1700	-	-
VII octacene	34	5	45.0928	1.3263	0.1381	-	-
VIII nonacene	38	6	50.3428	1.3248	0.1138	-	-
IX pyrene	16	2	21.3799	1.3362	0.5284	3372	2.966
X anthanthrene	22	3	29.8096	1.3550	0.3536	4331	2.309
XI coronene	24	4	32.3942	1.3498	0.4698	3415	2.928
XII 2-3,8-9 dibenzcoronene	30	5	40.7606	1.3587	0.2369	5236	1.910
XIII ovalene	32	5	43.9992	1.3750	0.3742	4560	2.193

Table X (b) Molecular constants for some "fully aromatic" molecules (Appendix C)

Molecule		N_c	N_B	E_π	E_π^c	x_n	λ_p(Å)	$\tilde{\nu}_p \times 10^{-4}$ (cm^{-1})
XIV	$CH_2=CH_2$	2	$\frac{1}{3}$	2.2000	1.1000	1.1000	—	—
XV		6	1	8.0000	1.3333	1.000	2068	4.835
XVI		12	2	16.0568	1.3381	0.765	2530	3.953
XVII		14	2	18.9256	1.3518	0.682	2.945	3.396
XVIII		18	3	24.4285	1.3571	0.701	2870	3.484

Cont'd....

Table X (b) cont'd.

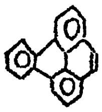
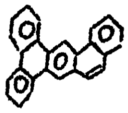
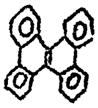
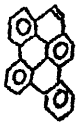
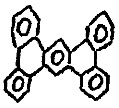
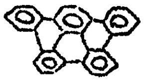
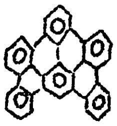
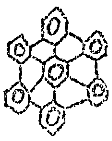
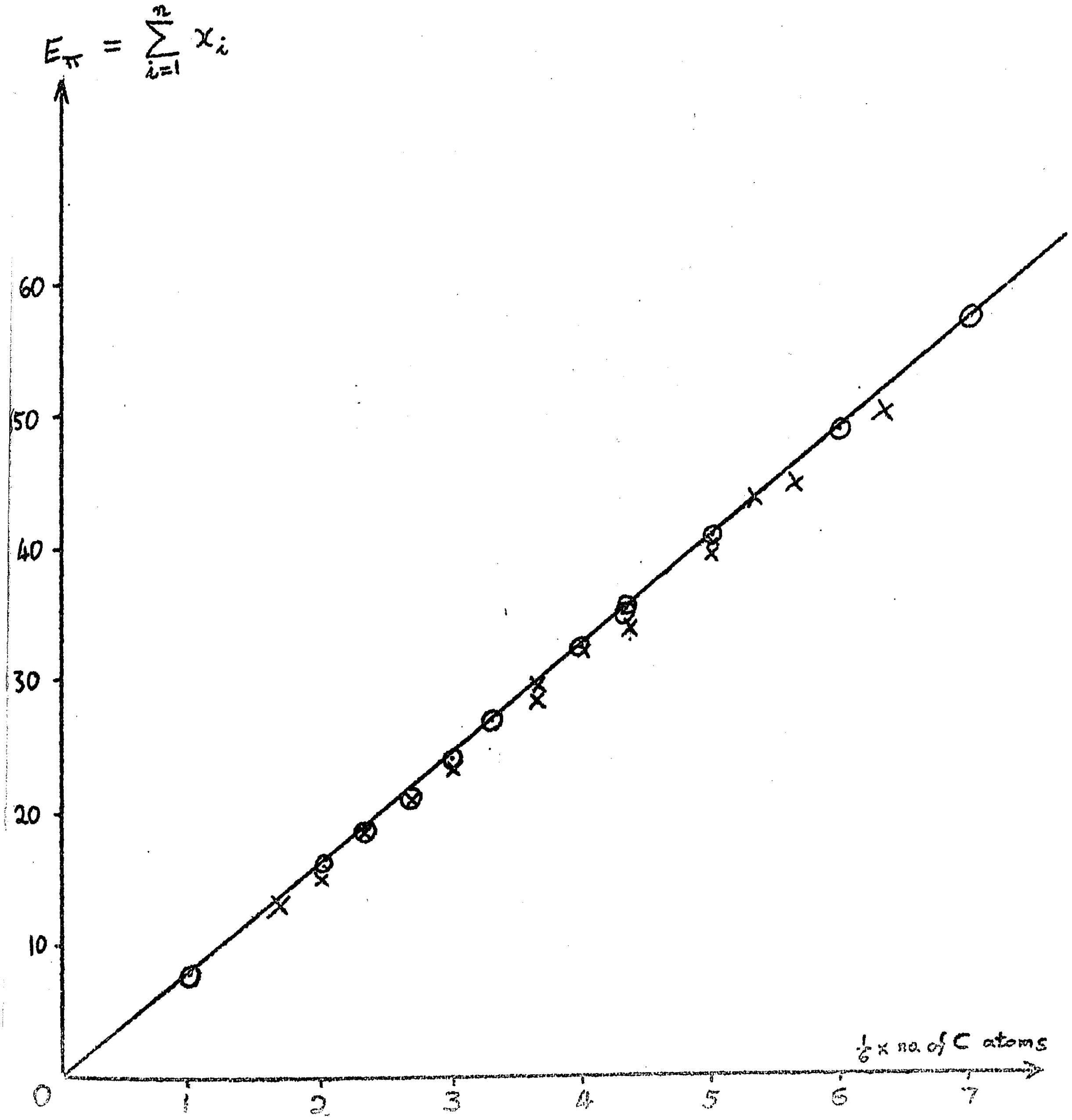
Molecule		N_c	N_B	E_π	E_π^c	x_n	λ_p(Å)	$\tilde{\nu}_p \times 10^4$ (cm^{-1})
XIX		20	3	27.2391	1.3620	0.564	3315	3.017
XX		24	4	32.7352	1.3640	0.587	3290	3.040
XXI		26	4	35.3800	1.3601	0.589	3450	2.899
XXII		26	4	35.3908	1.3612	0.555	?	?
XXIII		26	4	35.5733	1.3682	0.518	3775	2.649
XXIV		30	5	40.8620	1.3621	0.611	3310	3.026
XXV		30	5	41.0763	1.3692	0.534	3740	2.674
XXVI		36	6	49.4003	1.3722	0.531	3650	2.740
XXVII		42	7	57.9294	1.3793	0.490	3875	2.581

Fig.4. Molecular π s.e's plotted against the number of carbon atoms in the molecule.



The fact that a very small but fairly regular increase in E_{π}^{c} with N_c is obtained showing no departures for non-Hückel hydrocarbons (for which $N_c \neq 4n + 2$) indicates that we observe no validity of the Hückel rule for condensed benzenoid systems.

In Fig. 4 we have plotted the molecular π s.e. E_{π} against one-sixth of N_c, so that the abscissa measures the number of benzenoid rings in the molecule. Although we know that E_{π}^{c} increases slightly with N_c which must result in a corresponding increase in the gradient of the E_{π}/N_c curve, the curve is closely linear. This means that the π s.e. of any benzenoid aromatic hydrocarbon is nearly directly proportional to the number of carbon atoms in the molecule, and may be calculated approximately from the equation

$$E_{\pi} = N_c\,(\alpha + 1.373\beta_0).$$

6.4 (a) The calculation of the positions of the electronic transition bonds for aromatic hydrocarbons.

The energy of the electronic transition from the *i* th to the *j* th molecular orbital is calculated from equation (2.9) to be

$$\Delta E_{ij} = (\alpha - x_i\beta_0) - (\alpha - x_j\beta_0) = \Delta x_{ij}\beta_0$$

where Δx_{ij} is the difference $(x_j - x_i)$ between the "Hückel numbers" of the i th and j th MO's, where it is assumed that $E_i > E_j$ in order that the calculated transition energy ΔE_{ij} be positive. The frequency of the radiation ν_{ij} is therefore given by

$$\nu_{ij} = \frac{1}{h} \Delta x_{ij} \beta_o$$

and by comparing the observed values of ν_{ij} with the calculated Δx_{ij} an empirical value for β_o may be calculated.

It is generally supposed that Clar's p-bands in the UV absorption spectrum are caused by transitions from the highest occupied to the lowest unoccupied levels. This is evidenced by the fact that in naphthalene, anthracene and tetracene, the p bands are found experimentally[31] to be polarised in the direction parallel to the short axis of the acene, which indeed corresponds to the ${}^1B_{2u}$ symmetry expected for the transition $x_n \rightarrow x_{n+1}$. In alternant aromatic hydrocarbons $x_{n-i} = -x_{n+i+1}$, so the calculated frequency of the p-band is

$$\nu_p = \frac{2\beta_o}{h} x_n$$

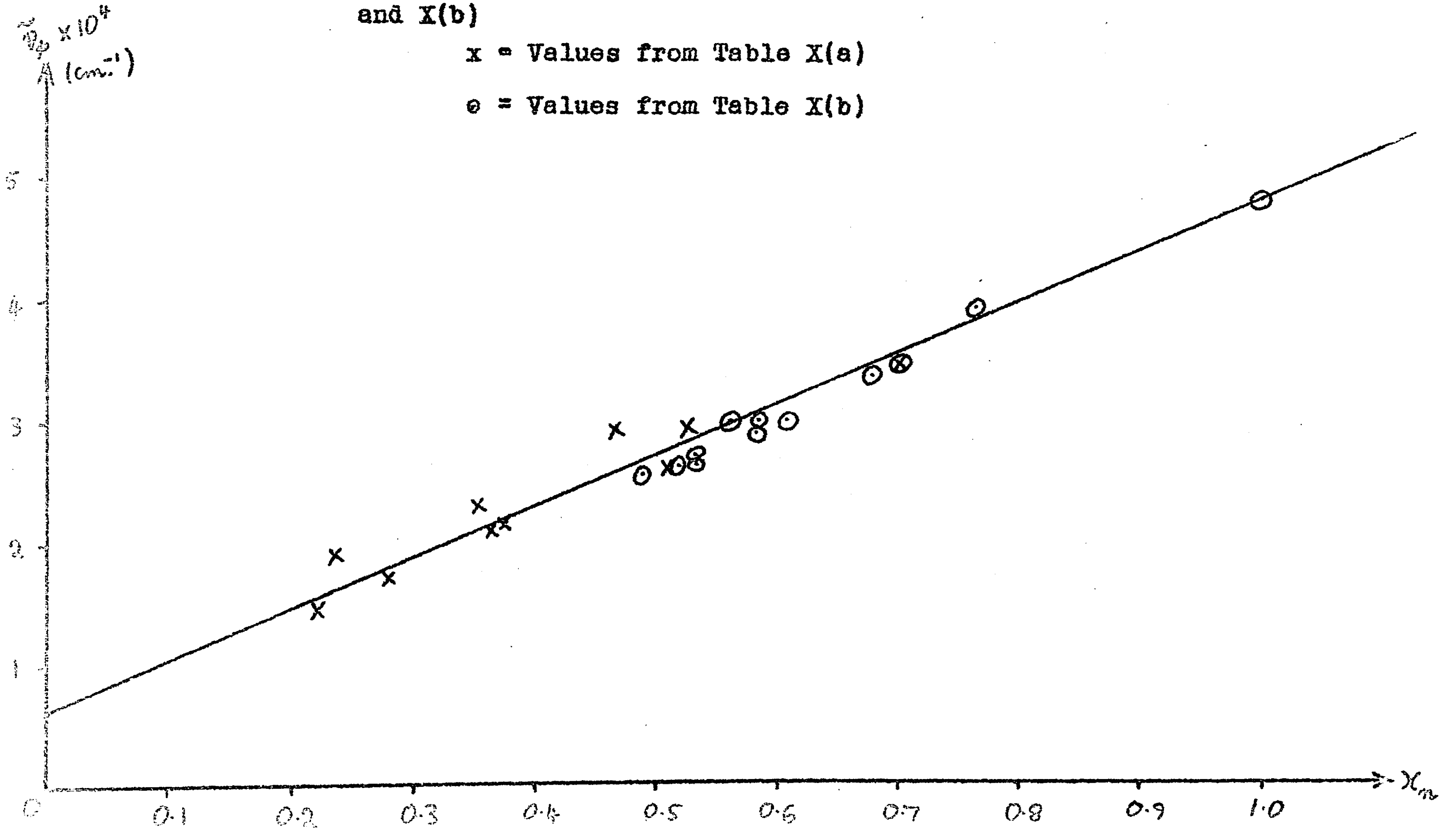
where x_n is the Hückel number of the highest occupied molecular orbital. Quite good linear correlations are obtained by plotting x_n against the experimental values of ν_p. Fig. 5(a) shows such an attempt; ν_p are taken from Clar[10-15], and x_n from the results of the calculations in Appendices B and C and summarised in Tables X (a) and (b). In Fig. 5 (b) we have plotted only the data for the acenes (benzene to hexacene) showing an almost perfect linear correlation. This shows the importance of taking account of bond length variations in assigning β' values: whereas the benzene point is colinear with the points for the other acenes in our treatment, it is not if Simple Hückel x_n values are used. Data for the other five molecules listed in Table X (a) do not give such a good correlation. It would appear that something has been neglected whose effect is revealed in comparing different classes of molecule.

The β_0 value calculated for the acenes is half the slope of the lower curve in Fig. 5(b), i.e. 2.12×10^4 cm^{-1} = 60 kcal/mole. This is more than twice the value obtained from a comparison of the calculated total π energies with thermochemical data (see for example Appendix D). The discrepancy is almost certainly due to neglect of configurational interaction, which occurs to different extents in the ground and excited states.

Fig.5a. Plot of the wave-numbers of the p-bands against the calculated highest occupied energy level for the molecules in Tables X(a) and X(b)

x = Values from Table X(a)

⊙ = Values from Table X(b)



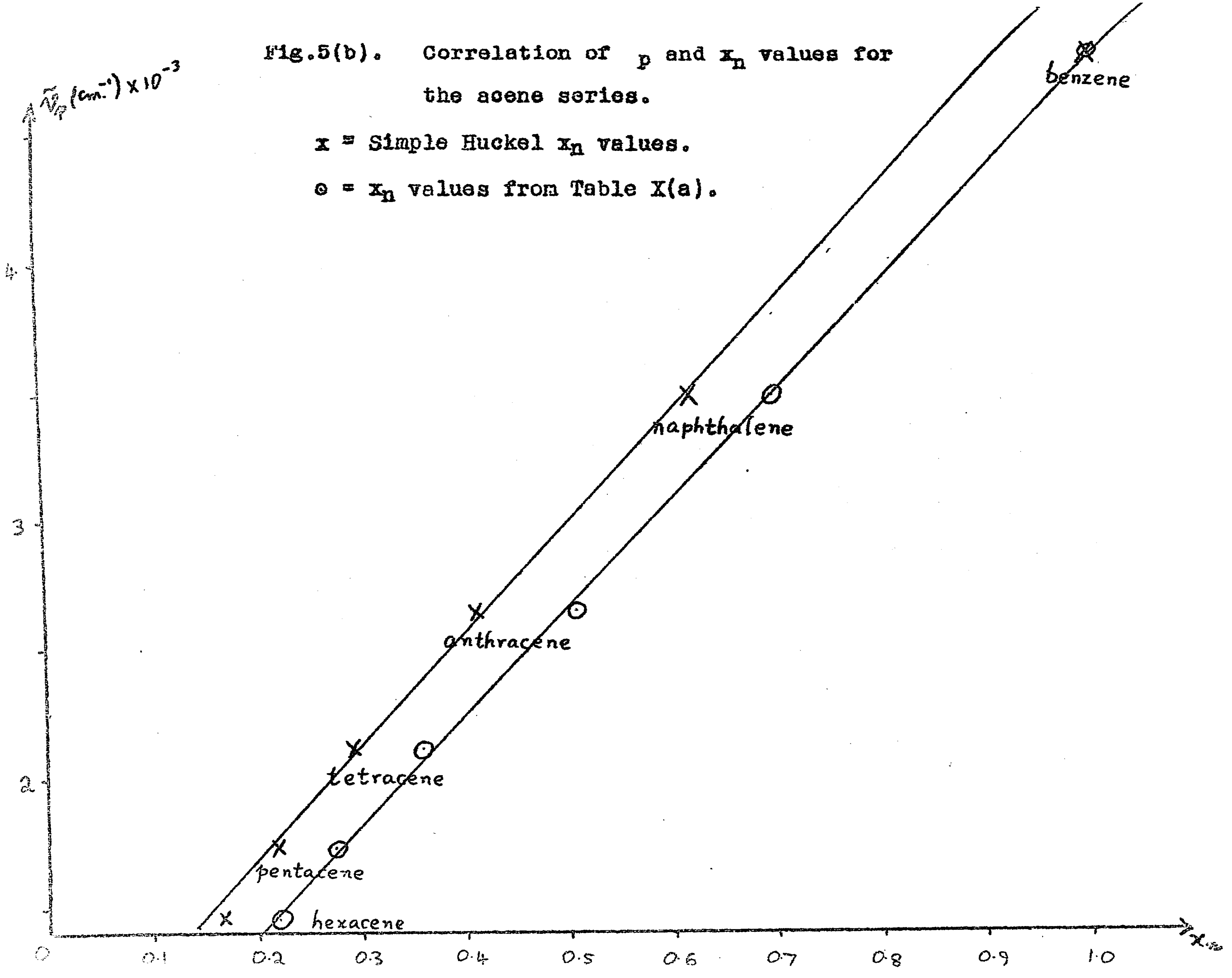


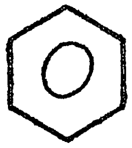
Fig.5(b). Correlation of p and x_n values for the acene series.

x = Simple Huckel x_n values.

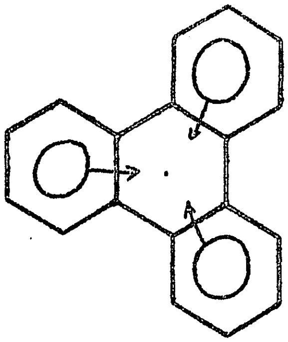
⊙ = x_n values from Table X(a).

The correlation line does not pass through the origin as might be expected; Fig. 5(a) shows that when $x_n = 0$, $\tilde{\nu}_p = 6$ x 10^4 cm^{-1}. Streitwieser (see p.213 of ref.7) explains that the calculated transition energy $2x_m\beta_0$ is for a transition from the "centre of gravity" of the singlet and triplet states to the ground state. Since the observed transition is the singlet to ground state (triplet to ground state is forbidden), the calculated transition energy $2x_m\beta_0$ will be too high by the factor E (singlet)-E(c. of g.). From the $\tilde{\nu}_p/x_n$ curve published by Streitwieser (p.220) in which Simple Hückel x_n values are used, E(singlet)-E(c. of g) is about 1.0 x 10^4 cm^{-1}. From our curve (Fig. 5 (b)) the quantity is 0.5 x 10^4 cm^{-1}. Since it has not been established that the Hückel energy levels are in fact the quantities suggested by Streitwieser, it is possible that with increasing refinements of the Hückel-type calculations, the quantity "E(singlet)-E(c. of g.)" may vanish altogether.

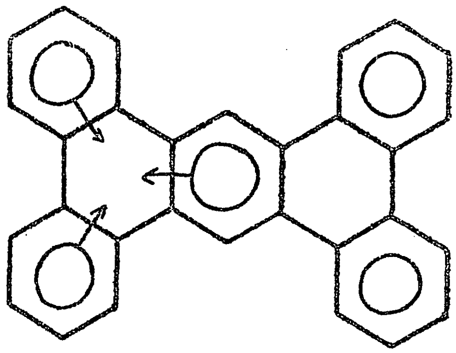
(b) The calculation of spectral shifts due to annelation



I



II



III

λp (Å) 2068 $\xrightarrow{802}$ 2870 $\xrightarrow{580}$ 3450

$\lambda\beta$ (Å) 1819 $\xrightarrow{751}$ 2570 $\xrightarrow{355}$ 2925

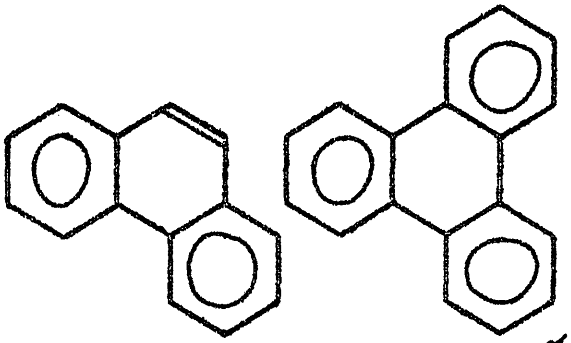
HOMO(β_o) (i) 1.000 $\xrightarrow{0.316}$ 0.684 $\xrightarrow{0.107}$ 0.577

(ii) 1.000 $\xrightarrow{0.299}$ 0.701 $\xrightarrow{0.080}$ 0.611

The above figures show the effect on the positions of the UV absorption bands, of the annelation of a diphenyl system, firstly onto benzene (I), and then onto the resulting triphenylene (II) to produce tetrabenzanthracene (III). The shifts in the wavelengths of the bands are much less in the second case than in the first, although the addendum is the same in both cases. This effect is called asymmetric annelation, and is interpreted by Clar as being due to the asymmetry of the fully aromatic rings. Whereas in the first annelation an induced sextet is formed in the central ring, it is not possible to produce a second induced sextet in III for the reason discussed in § 4, and the spectral shift is consequently much less.

Also shown above are the Hückel numbers x_n of the highest occupied molecular orbital (HOMO) in each case. These have been obtained (i) using the simple theory, in which β' values for all the bonds have been assumed to be unity, and (ii) assuming that there are two types of bonds: "single" and "aromatic" to which β' values of 0.7 and 1.0 were assigned, as described in § 6.2, and the calculation iterated until convergence was obtained. Since the lowest-energy transitions in each case are $(x_{n+1} - x_n)\beta_o = 2|x_n \beta_o|$, the HOMO Hückel numbers x_n may be used as a basis for the comparison of the spectral energy shifts. Both series of figures (i) and (ii) show that the "asymmetric annelation effect" is borne out in calculation.

An interesting annelation is that of a butadiene system onto a "fixed double bond" in fully aromatic hydrocarbons, which, as we observed in § 5.2, has little effect on bond orders. The simplest system which contains such a bond is phenanthrene, and the wavelengths of the β and p bands given below show that their positions are changed very little by the annelation of a benzo-ring onto the 9-10 position:



		% Energy shift	
$\lambda_p(\text{Å})$	$2945 \longrightarrow 2870$	~~-0.26%~~	-2.6%
$\lambda_\beta(\text{Å})$	$2547 \longrightarrow 2595$	~~0.18%~~	1.8%
HOMO (i)	$0.605 \longrightarrow 0.684$	~~1.31%~~	13.1%
" (ii)	$0.682 \longrightarrow 0.701$	~~0.28%~~	2.8%

This would appear to indicate two alternative explanations. The first is that the shift produced by the removal of the 9-10 "double" bond is approximately equal and opposite to that produced by the new aromatic sextet. The second is that the 9-10 "double" bond is present also in the corresponding position in triphenylene, indicating that in an aromatic sextet there are two electrons which are somehow different from the other four. Clar has adopted the second explanation to formulate his theory of aromaticity described in §4.

This annelation effect is also predicted by Molecular Orbital theory, as is shown by the figures in the last two rows. Clearly the improved Hückel treatment gives a better account of the percentage energy shift than the simple theory in which no account is taken of the variation in bond lengths.

Papers written on the calculation of spectral shifts in the pyrene and triphenylene homologues are given in Appendix D.

§ 7. The calculation of aromatic character of the acene rings in terms of Clar's oscillating aromatic pair model.

If the model of the oscillating electron pair in the acenes is a valid one, it is reasonable to suppose that the velocity of the quasi-particle (the electron pair) is a continuous function of position. This requires the magnitude of the velocity to be a maximum at the centre of the acene and zero at the ends. The function which gives the velocity of the particle at the distance x from the centre of the acene,

$$v_x = A(a^2 - x^2) \tag{7.1}$$

(where a is the amplitude of the oscillation and A is a constant related to the frequency), satisfies these conditions.

In order to calculate the aromatic character of, let us say, the x^{th} ring from the centre of an acene with an <u>even</u> number of rings, we need to know the time spent by the particle (the aromatic pair) in the x^{th} ring. Now the average speed of a particle between the points x-1 and x, and whose velocity is given by (1) is

$$\bar{v}_x = \frac{1}{2}A(2a^2 - 2x^2 + 2x - 1)$$

The time spent in the x^{th} ring is therefore given by

$$t_x = B(4a^2 - 4x^2 + 4x - 2)^{-1} \qquad (7.2)$$

We have introduced an extra factor of 2 into the denominator of (2) in order that the equation for t_x may resemble that appropriate to an acene with an odd number of rings. The equation in this case is

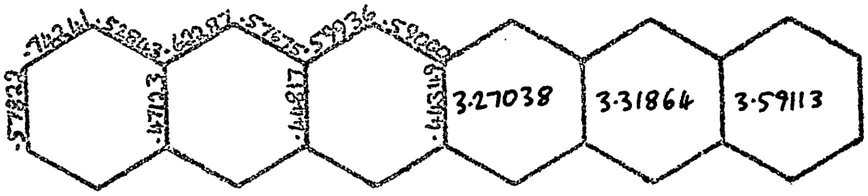
$$t_x = B(4a^2 - 4x^2 - 1)^{-1}$$

where the x^{th} ring is now defined as the x^{th} ring from the centre not including the centre ring.

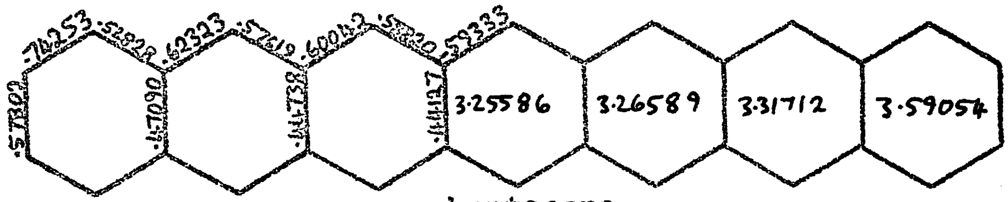
So assuming that the amount of aromatic character A_x in the x^{th} ring is proportional to the relative time spent by the oscillating aromatic pair in that ring, we get the equations

$$\left.\begin{aligned} A_x &= C(4a^2 - 4x^2 + 4x - 2)^{-1} \text{ for an even acene} \quad &(a)\\ \text{and} \quad A_x &= C(4a^2 - 4x^2 - 1)^{-1} \text{ for an odd acene} \quad &(b)\end{aligned}\right\} (7.3)$$

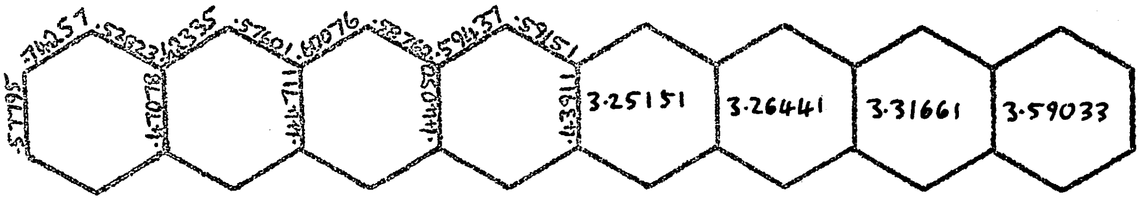
We can calculate a value for A_x also from the Hückel theory using the technique discussed in § 2.5. Equation (2.16) tells us that a measure of the energy in a given part of an aromatic hydrocarbon is provided by



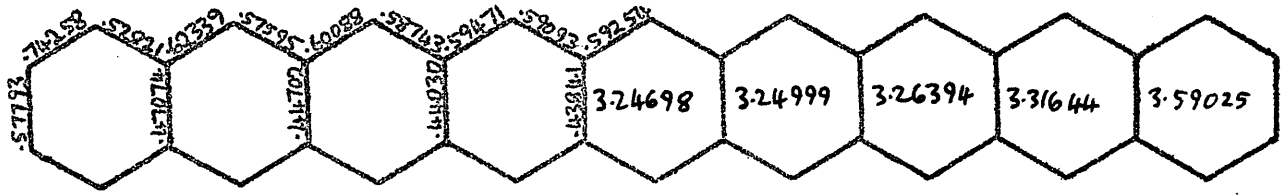
hexacene



heptacene



octacene



nonacene

Bond orders and individual ring energies

in some acenes as computed by the Simple Hückel Method.

summing the bond orders of the constituent bonds, each multiplied by its respective β' value. Since we are dealing with very approximate theories, we shall use the simplest Hückel method and assume that the values of all the bonds are equal (i.e. $\beta' = 1$ for each bond). The diagrams opposite indicate the required values: the quantities associated with the bonds are bond orders, p_b, and those written inside the rings x are the $\sum_{b=1}^{6} p_{xb}$ where the summation takes place over the π bonds b = 1 to 6 forming the benzenoid ring. The results of the calculations are summarised in Table X.

Figs. 6 - 9 show the result of plotting A_x calculated from equations (3) (a) and (b) against $\sum_{b=1}^{6} p_{xb}$ for the acenes hexacene to nonacene. The curves in each case are closely linear. While we do not claim that this result furnishes evidence for the electron oscillation theory, the latter may now be seen to lead to an acene model which is quantitatively similar to that obtained from Hückel theory calculations.

Table XI: A comparison of the π e.c's of the various rings in four acene molecules as calculated from the Clar theory and from the Simple Hückel Method.

Acene	x	A_x	$\sum_{b=1}^{6} p_{xb}$
Hexacene	1	.02941 C	3.27038
(a=3)	2	.03846 C	3.31864
	3	.10000 C	3.59113
Heptacene	0	.02083 C	3.25586
(a=3½)	1	.02273 C	3.26589
	2	.03125 C	3.31712
	3	.08333 C	3.59054
Octacene	1	.01613 C	3.25151
(a=4)	2	.01852 C	3.26441
	3	.02632 C	3.31661
	4	.07145 C	3.59033
Nonacene	0	.01250 C	3.24698
(a=4½)	1	.01316 C	3.24999
	2	.01563 C	3.26394
	3	.02273 C	3.31644
	4	.06250 C	3.59025

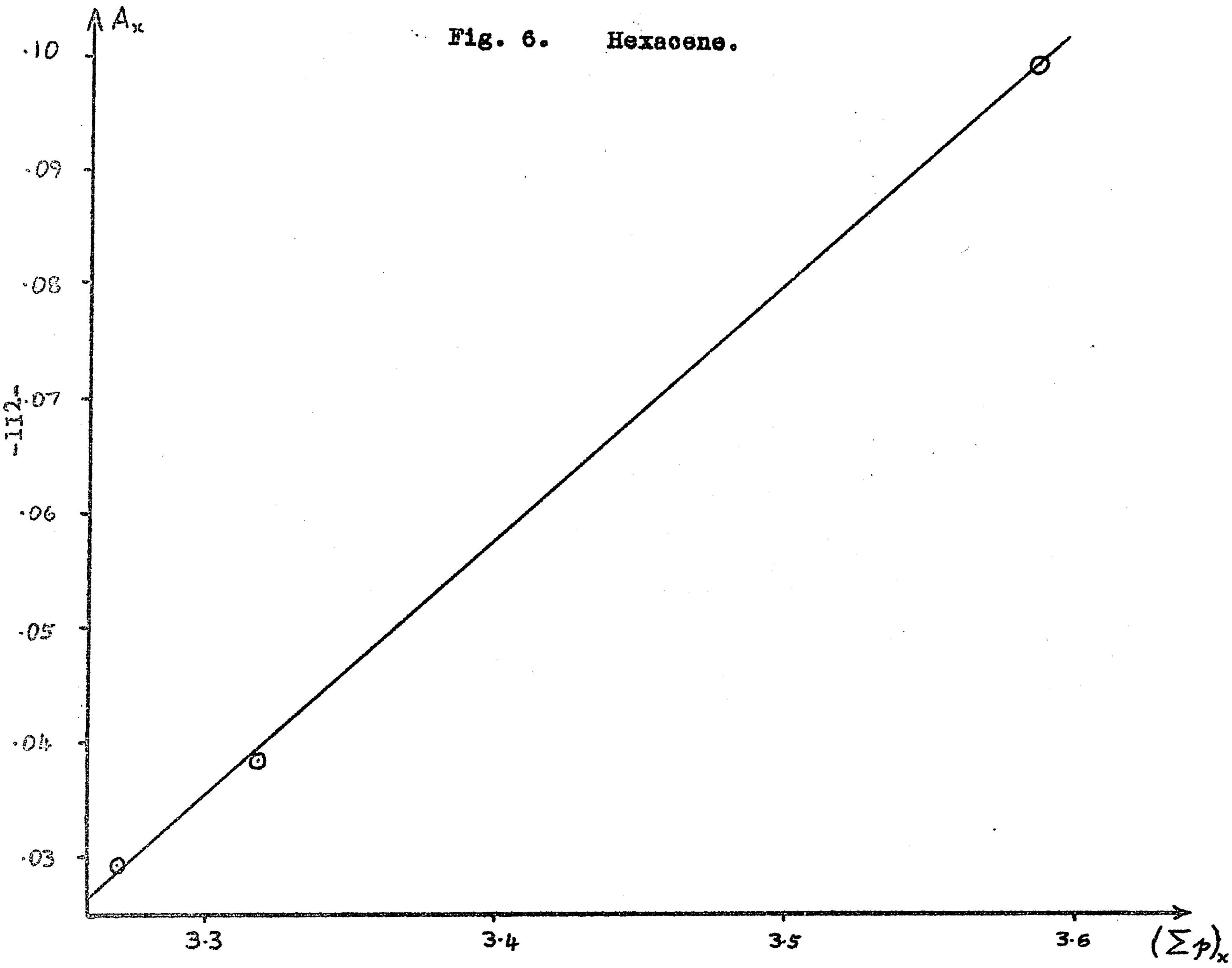


Fig. 6. Hexacene.

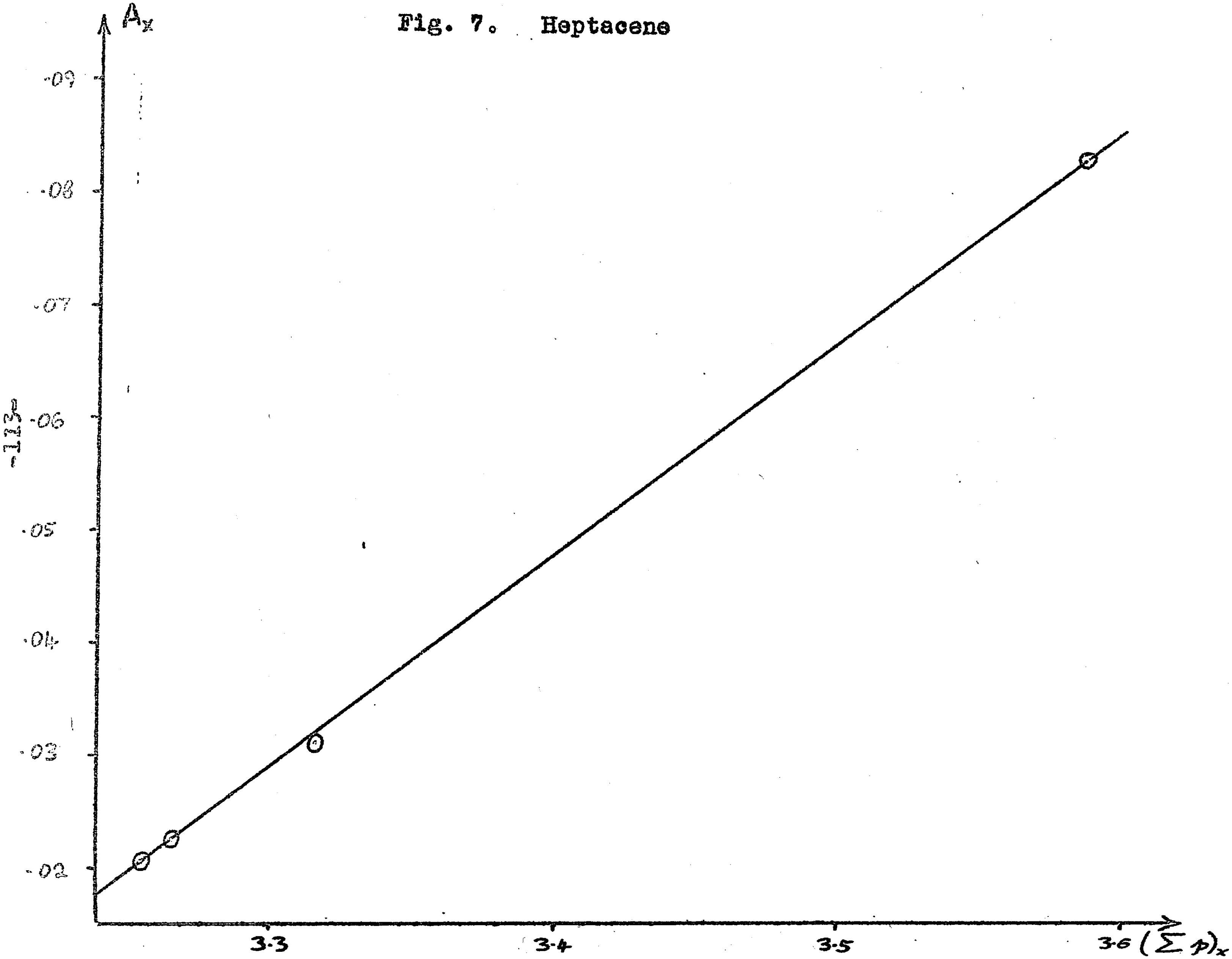


Fig. 7. Heptacene

Fig. 8. Octacene

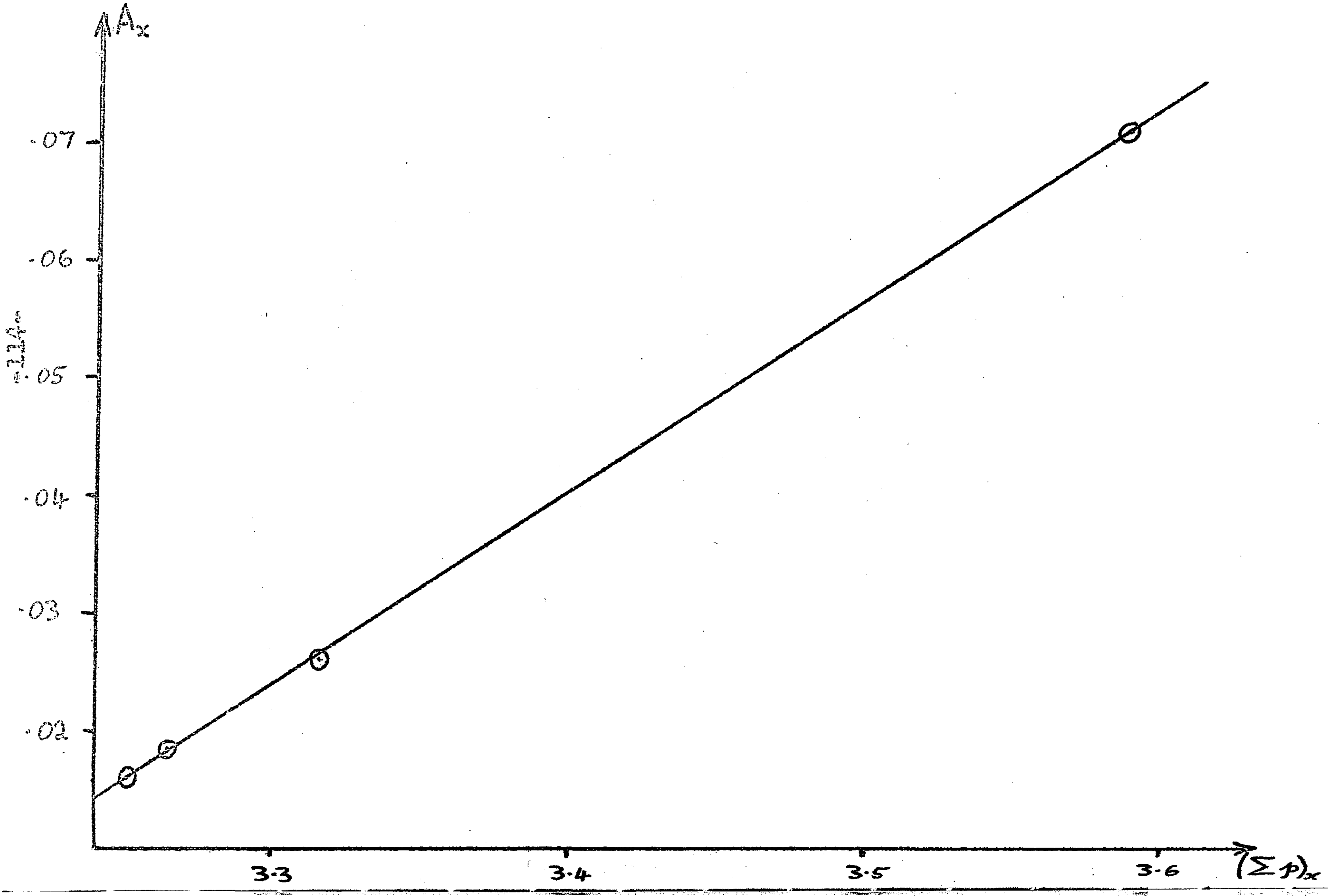
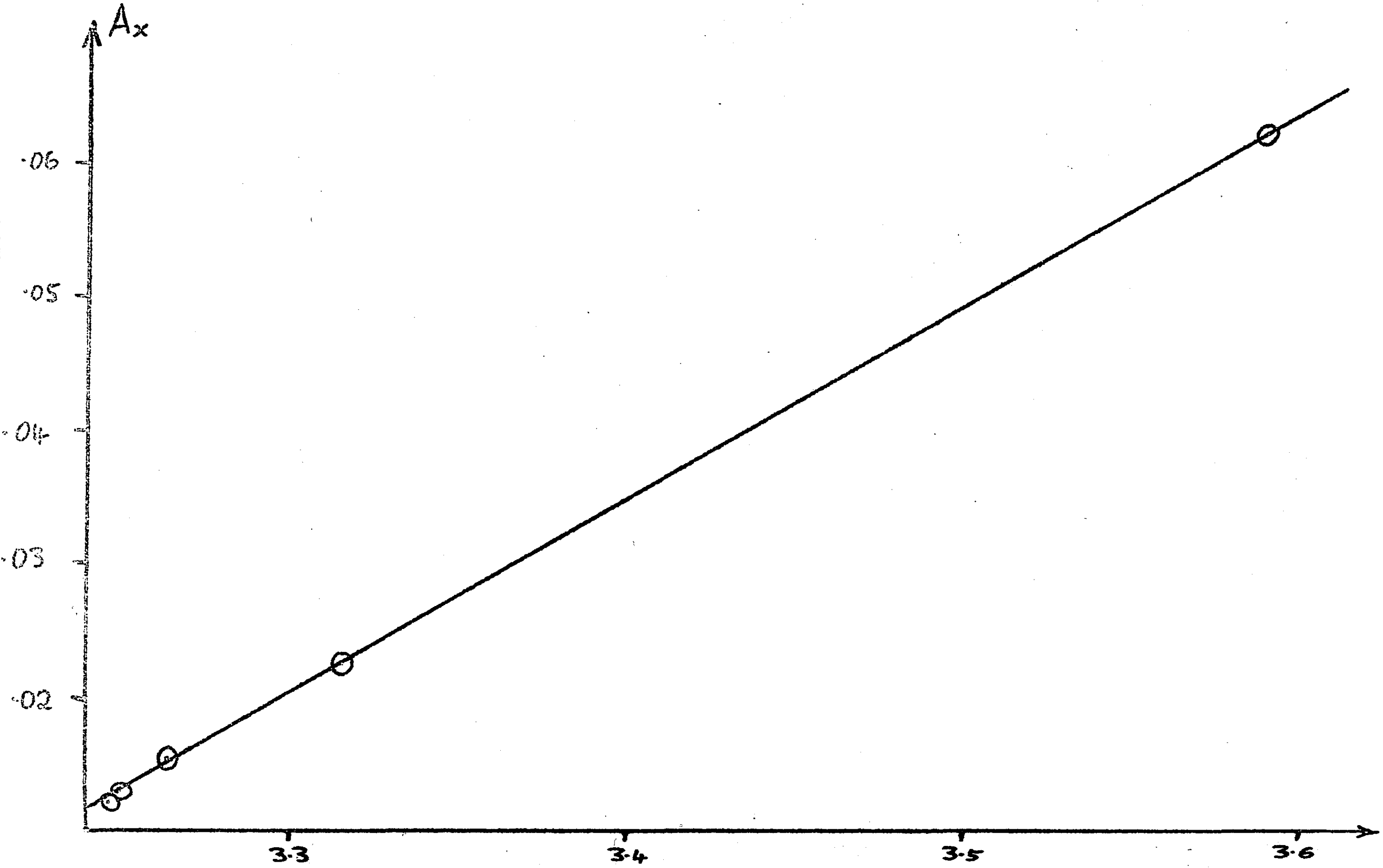


Fig. 9. Nonacene.



§ 8. A simple treatment of inter-electronic repulsion in aromatic hydrocarbons.

8.1 The ground state.

The state Ψ of an N-electron π system may be expressed as an antisymmetrical product of N one-electron spin-orbitals ψ_i. This is conveniently written as a determinant:

$$\Psi = (N!)^{-\frac{1}{2}} \det |\psi_1(1) \dots \psi_i(k) \dots \psi_m(N)|$$

where $\psi_1, \dots, \psi_i, \dots \psi_m$ are arranged in increasing energy order. The general element $\psi_i(k)$ refers to the ith one-electron orbital with which is associated the k^{th} electron. In the ground state $i = k$ for all i and k which indicates that all N electrons are accommodated in the N lowest energy orbitals

Applying this to aromatic hydrocarbons we can substitute for the ψ's the molecular orbitals obtained by the Hückel LCAO-MO method. For an even alternant hydrocarbon with N carbon atoms, N molecular orbitals are obtained, $\frac{1}{2}N = n$ of which are bonding and by the Pauli principle may accommodate all N π electrons in the ground state. The ground state wave function is therefore

$$\Psi_g = (N!)^{-\frac{1}{2}} \det |\psi_1(1)\,\bar{\psi}_1(2)\ldots\ldots\psi_n(N-1)\,\bar{\psi}_n(N)|$$

in which $\bar{\psi}_i$ differs from ψ_i only in the spin part of the orbital (ψ_i has α spin and $\bar{\psi}_i$ has β spin).

The Hamiltonian operator is

$$\mathcal{H} = \sum_{k=1}^{N} \left[-\frac{\hbar^2}{2m} \nabla_k^2 - \sum_{a=1}^{N} \frac{Ze^2}{r_{ai}} \right] + \frac{1}{2} \sum_{k \neq l}^{N} \sum^{N} \frac{e^2}{r_{kl}}$$

which is the sum of the one-electron Hamiltonian operators H(k) (sometimes called the "core" hamiltonian) plus the electronic repulsion terms $\frac{1}{2} \sum_{k \neq l}^{N} \sum^{N} \frac{e^2}{r_{kl}}$. (The internuclear repulsion terms $\frac{1}{2} \sum_{a \neq b} \sum \frac{Z^2 e^2}{r_{ab}}$ have been omitted from $\mathcal{H}$).

$$\therefore \quad \mathcal{H} = \sum_{k}^{N} H(k) + \frac{1}{2} \sum_{k \neq l}^{N} \sum^{N} \frac{e^2}{r_{kl}} \qquad (9.1)$$

The total π electronic energy of the ground state is therefore

$$E_g = \int \Psi_g^* \mathcal{H} \Psi_g \, d\tau = \int \Psi_g^* \sum_{k}^{N} H(k) \Psi_g \, d\tau + \frac{1}{2} \int \Psi_g \sum_{k \neq l}^{N} \sum^{N} \frac{e^2}{r_{kl}} \Psi_g \, d\tau$$

The general term in the complete expansion of the first integral is $\int \psi_i^*(l)\, H(k)\, \psi_j(m)\, d\tau$. In order that it shall be non-zero, k = l = m, and since the molecular orbitals ψ_i are orthogonal functions of the energy matrix $\mathbb{H}$ we have the condition that i = j. But the resulting general term $\int \psi_i^*(k)\, H(k)\, \psi_i^*(k)\, d\tau$ is just the Hückel energy eigenvalue (which we shall now write I_i) of the i^{th} molecular orbital, which we know already in terms of the parameters α and β_0. The second integral in the above equation describes the total π electron interaction and does not reduce to a sum of such simple terms. However it may be expressed (36) as the sums of two different kinds of integrals J_{ij} and K_{ij} known respectively as the Coulomb and Exchange integrals for the interactions between orbitals ψ_i and ψ_j :

$$\int \Psi_g^* \sum_{k \neq l}^{N} \sum^{N} \frac{e^2}{r_{kl}} \Psi_g \, d\tau = 2 \sum_{k \geqslant l}^{n} \sum^{n} (2\, J_{kl} - K_{kl})$$

where J_{ij} = Coulomb Integral for ψ_i and ψ_j, $= \int |\psi_i(1)|^2 \frac{e^2}{r_{12}} |\psi_j(2)|^2 d\tau$

K_{ij} = Exchange Integral for ψ_i and ψ_j $= \int \psi_i^*(1)\, \psi_j(1) \frac{e^2}{r_{12}}\, \psi_j^*(2)\, \psi_i(2)\, d\tau$

The ground-state energy is therefore

$$E_g = 2 \sum_{i=1}^{n} I_i + \sum_{i \geqslant j}^{n} \sum^{n} (2\, J_{ij} - K_{ij}) \qquad (8.2)$$

$$= 2 \sum_{i=1}^{n} I_i + 2 \sum_{i > j}^{n} \sum^{n} J_{ij} + \sum_i J_{ii} - \sum_{i > j} \sum K_{ij} \qquad (8.3)$$

(since $J_{ii} = K_{ii}$)

Substituting the molecular orbitals ψ_i by the LCAO expansions

$$\psi_i = \sum_{r=1}^{N} c_{ri} \chi_r$$

the molecular orbital integrals J_{ij} and K_{ij} may be expanded in terms of atomic orbital integrals, and we shall now proceed to consider this expansion.

Pople[36] assumed that the general term in the expansion of the J and K integrals in terms of atomic orbitals, namely $\int \chi_r^*(1)\chi_s(1)\frac{1}{r_{12}}\chi_t^*(2)\chi_u(2)\,d\tau$ is different from zero only if the following conditions hold simultaneously:

(1) $r = s$ and $t = u$

(2) Either $r = t$

or atoms r and t are "nearest neighbours", i.e., are σ bonded.

The ground state energy E_g of an aromatic hydrocarbon can therefore be expressed in terms of the Hückel parameters α and β_0 (coming from the I_1 terms), and in addition two new integrals A_r and B_{rs}:

$A_r = \int |\chi_r(1)|^2 \frac{e^2}{r_{12}} |\chi_r(1)|^2 d\tau$ the Atomic coulomb integral for carbon atom r

$B_{rs} = \int |\chi_r(1)|^2 \frac{e^2}{r_{12}} |\chi_s(2)|^2 d\tau$ the Bond coulomb integral for bond r-s.

(r and s are σ bonded atoms)

A_r is the repulsion energy of two electrons in the r^{th} $2p_z$ atomic orbital, and we shall suppose that this is the same for all atoms r in an alternant aromatic hydrocarbon, and denote the value by A. Strictly speaking B_{rs} is not an invariant parameter, since as the repulsion between the atomic orbitals on atoms r and s, it will vary with the length of the bond r-s. However, we shall assume that the variation is sufficiently small that we can use a mean bond coulomb integral B for all bonds r-s.

We shall now express the molecular integrals J and K in terms of the atomic integrals A and B.

$$J_{ij} = \int \psi_i^*(1)\,\psi_i(1)\,\frac{1}{r_{12}}\,\psi_j^*(2)\,\psi_j(2)\,d\tau \qquad \text{But } \psi_i = \sum_{r=1}^{N} c_{ri}\chi_r$$

$$= \int \left(c_{1i}^*\chi_1^*(1) + c_{2i}^*\chi_2^*(1) + \ldots + c_{Ni}^*\chi_N^*(1)\right)\left(c_{1i}\chi_1(1) + c_{2i}\chi_2(1) + \ldots + c_{Ni}\chi_N(1)\right)\frac{1}{r_{12}}\left(c_{1j}^*\chi_1^*(2) + c_{2j}^*\chi_2^*(2) + \ldots \ldots c_{Nj}^*\chi_N^*(2)\right)\left(c_{1j}\chi_1(2) + c_{2j}\chi_2(2) + \ldots + c_{Nj}\chi_N(2)\,d\tau\right.$$

$$= \int \chi_r^*(1)\,\chi_r(1)\,\frac{1}{r_{12}}\,\chi_r^*(2)\,\chi_r(2)\,d\tau \sum_{r=1}^{N} |c_{ri}|^2 |c_{rj}|^2$$

$$+ \int \chi_r^*(1)\,\chi_r(1)\,\frac{1}{r_{12}}\,\chi_s^*(2)\,\chi_s(2)\,d\tau \sum_{\underset{(\text{bonded})}{r \neq s}}^{N}\sum^{N} |c_{ri}|^2 |c_{sj}|^2$$

$$\text{i.e.}\quad J_{ij} = A\sum_{r=1}^{N} |c_{ri}|^2 |c_{rj}|^2 + B\sum_{\underset{(\text{bonded})}{r \neq s}}^{N}\sum^{N} |c_{ri}|^2 |c_{sj}|^2 \qquad (8.4)$$

$$K_{ij} = \int \psi_i^*(1)\,\psi_j(1)\,\frac{1}{r_{12}}\,\psi_j^*(2)\,\psi_i(2)\,d\tau$$

$$= \int \left(c_{1i}^*\,\chi_1^*(1) + c_{2i}^*\,\chi_2^*(1) + \dots + c_{Ni}^*\,\chi_N^*(1)\right)\left(c_{1i}\,\chi_1(1) + c_{2j}\,\chi_2(1) + \right.$$

$$\left.\dots + c_{Nj}\,\chi_N(1)\right)\frac{1}{r_{12}}\left(c_{1j}^*\,\chi_1^*(2) + c_{2j}^*\,\chi_2^*(2) + \dots + c_{Nj}^*\,\chi_N^*(2)\right) \times$$

$$\times \left(c_{1i}\,\chi_1(2) + c_{2i}\,\chi_2(2) + \dots + c_{Ni}\,\chi_N(2)\right)d\tau$$

$$= \int \chi_r^*(1)\,\chi_r(1)\,\frac{1}{r_{12}}\,\chi_r^*(2)\,\chi_r(2)\,d\tau \sum_{r=1}^{N} |c_{ri}|^2 |c_{rj}|^2$$

$$+ \int \chi_r^*(1)\,\chi_r(1)\,\frac{1}{r_{12}}\,\chi_s^*(2)\,\chi_s(2)\,d\tau \underset{\substack{r \neq s \\ (\text{bonded})}}{\sum^{N}\sum^{N}} c_{ri}^*\,c_{rj}\,c_{sj}^*\,c_{si}$$

i.e.
$$K_{ij} = A \sum_{r=1}^{N} |c_{ri}|^2 |c_{rj}|^2 + B \underset{r \neq s}{\sum^{N}\sum^{N}} c_{ri}^*\,c_{rj}\,c_{sj}^*\,c_{si} \qquad (8.5)$$

$$\therefore \quad E_g = \sum_{i=1}^{n} I_i + \underset{i \geqslant j}{\sum^{n}\sum^{n}} \left[2\left\{ A \sum_{r=1}^{N} |c_{ri}|^2 |c_{rj}|^2 + B \underset{r \neq s}{\sum^{N}\sum^{N}} |c_{ri}|^2 |c_{sj}|^2 \right\} \right.$$

$$\left. - \left\{ A \sum_{r=1}^{N} |c_{ri}|^2 |c_{rj}|^2 + B \underset{\substack{r \neq s \\ (\text{bonded})}}{\sum^{N}\sum^{N}} c_{ri}^*\,c_{rj}\,c_{sj}^*\,c_{si} \right\} \right]$$

$$= \sum_{i=1}^{n} I_i + \underset{i \geqslant j}{\sum^{n}\sum^{n}} \left[A \sum_{r=1}^{N} |c_{ri}|^2 |c_{rj}|^2 + B \left\{ \underset{\substack{r \neq s \\ (\text{bonded})}}{\sum^{N}\sum^{N}} |c_{ri}|^2 |c_{sj}|^2 - \right.\right.$$

$$\left.\left. \underset{r \neq s}{\sum^{N}\sum^{N}} c_{ri}^*\,c_{rj}\,c_{sj}^*\,c_{si} \right\} \right] \qquad (8.6)$$

Application to some hydrocarbons.

Benzene

The j^{th} molecular orbital ψ_j in benzene is given by

$$\psi_j = \frac{1}{\sqrt{6}} \sum_{r=1}^{6} e^{2\pi i r j/6} \chi_r$$

where (for the ground state molecular orbitals) $j = 0, \pm 1$.

Substituting these values in equations (4) and (5) we have

$$J_{00} = J_{-1-1} = J_{11} = J_{0-1} = J_{01} = J_{-11} = \frac{1}{6}A + \frac{1}{3}B;$$

$$K_{0-1} = \frac{1}{6}A + \frac{1}{6}B; \qquad K_{1,-1} = \frac{1}{6}A - \frac{1}{6}B; \qquad K_{01} = \frac{1}{6}A + \frac{1}{6}B$$

In the equation

$$E_g = 2\sum_{i=1}^{n} I_i + 2\sum_{i>j}^{n}\sum^{n} J_{ij} + \sum_{i=1}^{n} J_{ii} - \sum_{i>j}^{n}\sum^{n} K_{ij}$$

$$= 2\sum_{i=1}^{n} I_i + 2(J_{0-1} + J_{01} + J_{-11}) + (J_{00} + J_{-1-1} + J_{11}) - (K_{0-1} + K_{1-1} + K_c$$

we substitute the above J and K values, and the fact that $2\sum_{i=1}^{n} I_i = 6\alpha + 8\beta_0$

$$E_g = 6\alpha + 8\beta_0 + A + \frac{17}{6}B$$

Using real orthogonal molecular orbitals (for which the C_{rj} were obtained by applying C_{2v} symmetry to benzene), the resulting energy is slightly different, namely

$$E_g' = 6\alpha + 8\beta_0 + \frac{13}{12}A + \frac{11}{4}B$$

Other molecules

A computer program was written to calculate E_g from the eigenvalues and eigenvectors obtained from a Hückel-type computation, and the results obtained for some hydrocarbons are listed in Table XII. The last three summation terms in equation (3) have also been recorded, for purposes of checking. On examining these quantities it now appears that the first two summations, namely $\sum_{i>j}^{n}\sum^{n} J_{ij}$ and $\sum_{i} J_{ii}$ need not have been computed for the calculation of E_g since although not obvious from equation (6), column 5 of the table shows that the sum $2\sum_{i>j}^{n}\sum^{n} J_{ij} + \sum_{i=1}^{n} J_{ii}$ is in each case simply $\frac{1}{4}NA + \frac{1}{2}bB$ where N and b are respectively the number of C atoms and the number of C-C bonds in the molecule. This means that as far as the coulomb integrals J_{ij} are concerned, the coefficients of the atomic coulomb integral A and of the bond coulomb integral B in the energy expression are proportional respectively to the number of atoms and to the number of bonds in the molecule, a fact which might be expected from simple considerations. The only components of the repulsion energy which depend upon the π electron distribution (determined by the matrix $\mathbb{C}$), therefore, are the terms involving the

Table XII

Molecule	$\sum_{i=1}^{n} J_{ii}$	$\sum_{i>j}^{n} \sum^{n} J_{ij}$	$\sum_{i>j} \sum K_{ij}$
Ethylene	$\frac{1}{2}A + \frac{1}{2}B$	0	0
1,3 Butadiene	0.59996A + 0.699876B	0.199948A + 0.399954B	0.199948A + 0.099974B
Benzene {complex C	0.500000A + 1.000000B	0.500000A + 1.000000B	0.500000A + 0.166667B
{real C	1.000000A + 1.000000B	1.000000A + 1.000000B	1.000000A + 1.000000B
Napthalene	0.735897A + 1.035897B	0.882051A + 2.232051B	0.882051A + 0.563782B
Anthracene	0.777212A + 1.067171B	1.361394A + 3.466410B	1.361394A + 0.953292B
Tetracene	0.805091A + 1.141238B	1.847455A + 4.679381B	1.847455A + 1.317299B
Pentacene	0.825017A + 1.144214B	2.337491A + 5.927897B	2.337491A + 1.715237B
Hexacene	0.839821A + 1.185967B	2.830089A + 7.157016B	2.830089A + 2.093157B
Phenamthrene	0.798257A + 1.158434B	1.350871A + 3.420783B	1.350871A + 0.928081B
1-2 Benzanthracene	0.875253A + 1.198705B	1.812374A + 4.650648B	1.812374A + 1.317812B
1-2 Benztetracene	0.882750A + 1.208424B	2.308625A + 5.895788B	2.308625A + 1.716051B
1-2 Benzpentacene	0.941630A + 1.276064B	2.779185A + 7.111968B	2.779185A + 2.082541B
Chrysene	0.815300A + 1.210726B	1.842350A + 4.644637B	1.842350A + 1.323188B
Hexaphene	0.941072A + 1.271536B	2.779464A + 7.114232B	2.779464A + 2.096825B
Diphenyl	0.720477A + 1.025864B	1.139762A + 2.737066B	1.139762A + 0.797674B

Table XII (cont'd)

Molecule	$\sum_i J_{ii} + 2\sum_{i>j}\sum J_{ij}$	$E_g = 2\sum_{i=1}^{n} I_i + 2\sum_{i>j}^{n}\sum^{n} J_{ij} + \sum_{i=1}^{n} J_{ii} - \sum_{i>j}^{n}\sum^{n} K_{ij}$
Ethylene	$\frac{1}{2}$A + $\frac{1}{2}$B	2a + 2.0000β_0 + 0.5000A + 0.5000B
1,3 Butadiene	0.999856A + 1.499784B	4a + 4.4720β_0 + 0.7999A + 1.3998B
Benzene { complex c	1.500000A + 3.000000B	6a + 8.0000β_0 + 1.0000A + 2.8333B
real c	1.500000A + 3.000000B	6a + 8.0000β_0 + 1.0833A + 2.7500B
Naphthalene	2.499999A + 5.499999B	10a + 13.6832β_0 + 1.6179A + 4.9362B
Anthracene	3.500000A + 7.999991B	14a + 19.3137β_0 + 2.1386A + 7.0467B
Tetracene	4.500001A + 10.500000B	18a + 24.9294β_0 + 2.6525A + 9.1827B
Pentacene	5.499999A + 13.000008B	22a + 30.5440β_0 + 3.1625A + 11.2848B
Hexacene	6.499999A + 15.499999B	26a + 36.1560β_0 + 3.6599A + 13.4068B
Phenanthrene	3.499999A + 8.000000B	14a + 19.4492β_0 + 2.1491A + 7.0719B
1-2 Benzanthracene	4.500001A + 10.500001B	18a + 25.1012β_0 + 2.6876A + 9.1822B
1-2 Benztetracene	5.500000A + 13.000000B	22a + 30.7256β_0 + 3.1914A + 11.2839B
1-2 Benzpentacene	6.500000A + 15.500000B	26a + 36.3413β_0 + 3.7208A + 13.4175B
Chrysene	4.500000A + 10.500000B	18a + 25.1900β_0 + 2.6576A + 9.1768B
Hexaphene	6.500000A + 15.500000B	26a + 36.3905β_0 + 3.7205A + 13.4032B
Diphenyl	3.000001A + 6.499996B	12a + 16.3832β_0 + 1.8602A + 5.7023B

exchange integrals K_{ij}; (3) and (6) may consequently be written more simply as

$$E_g = 2\sum_{i=1}^{n} I_i + \frac{1}{4}NA + \frac{1}{2}\ell B - \sum_{i>j}\sum K_{ij}$$

$$E_g = 2\sum_{i=1}^{n} I_i + \sum_{i \gg j}^{n}\sum^{n} \Big[A\Big\{\frac{1}{4}N - \sum_{r=1}^{N} |c_{ri}|^2 |c_{rj}|^2\Big\} + B\Big\{\frac{1}{2}\ell - \sum_{\substack{r \neq s \\ (\text{bonded})}}^{N}\sum^{N} c_{ri}^{*} c_{rj} c_{sj}^{*} c_{si}\Big\}\Big]$$

If accurate values of the heats of combustion or of hydrogenation were known for these molecules, the values of the parameters α, β_0, A and B could be calculated empirically, in a similar way to the calculation described in the paper entitled "An Empirical Determination of the Huckel parameter β_0 and of the CC and CH Bond Energies in Aromatic Hydrocarbons", in Appendix D. However, the presence of the two extra parameters A and B introduces too much uncertainty into the set of simultaneous equations to enable even approximate values of the parameters to be calculated, using the currently available thermometric energy values.

8.2 The first excited singlet state Ψ_p

The first excited state results from the promotion of an electron in the highest occupied to the lowest unoccupied molecular orbital. The state wave function may be written as a linear combination of two wave functions Ψ_p' and Ψ_p'' :

$$\Psi_p = \frac{1}{\sqrt{2}}\left(\Psi_p' \pm \Psi_p''\right) \tag{8.7}$$

where $\Psi_p' = (N!)^{-\frac{1}{2}} \, det \, |\psi_1(1)\,\bar{\psi}_1(2) \ldots\ldots \psi_n(N-1)\,\bar{\psi}_{n+1}(N)|$

and $\Psi_p'' = (N!)^{-\frac{1}{2}} \, det \, |\psi_1(1)\,\bar{\psi}_1(2) \ldots\ldots \bar{\psi}_n(N-1)\,\psi_{n+1}(N)|$

(Ψ_p' and Ψ_p'' differ only in the spin part of the wave function and are therefore orbitally and energetically degenerate. They therefore appear with equal weight in (7)). The upper sign in (7) leads to one of the triplet state wave functions, and the lower one to the singlet state, which is of interest in the calculation of transitions to the ground state.

The energy $E_p = \int \Psi_p^* \mathcal{H} \Psi_p \, d\tau$ of the singlet first excited state, on substituting for Ψ_p and $\mathcal{H}$ from (7) and (1), becomes

$$E_p = \frac{1}{2}\left[E_p' + E_p'' - 2\int \Psi_p' \left\{ \sum_{i=1}^{n} H(i) + \frac{1}{2}\sum_{i \neq}^{n}\sum_{j}^{n} \frac{e^2}{r_{ij}} \right\} \Psi_p'' \, d\tau\right]$$

where E_p' and E_p'' are the energies of the states Ψ_p' and Ψ_p''. However, since these states are degenerate but orthogonal because of their spin functions, the term $\int \Psi_p' \sum_i H(i) \Psi_p'' d\tau$ is zero. The above equation therefore simplifies to

$$E_p = E_p' - \sum_{i \neq j}\sum \Psi_p'^{*} \frac{e^2}{r_{ij}} \Psi_p'' d\tau \qquad (8.8)$$

E_p' may be evaluated using (2), and the second term by multiplying the two determinants Ψ_p' and Ψ_p'' together with the factor e^2/r_{ij} expanding the molecular orbitals ψ in terms of atomic orbitals χ, and integrating over orbital- and spin-space. All the terms in (8) will then involve only the four parameters α, β_o, A and B.

The energy of the lowest-energy singlet-singlet transition (which is usually assumed to be responsible for Clar's p-bands) is then the difference between E_p and E_g. Since $N\alpha$ appears as a term common to both these energies, the p-band transition energy becomes a function of only the three parameters β_o, A and B.

Now the expression for E_p contains terms which are very tedious to evaluate, and we shall consider the ground and excited states of a molecule to be described purely by the highest bonding and lowest antibonding molecular orbital, treating the other π electrons as a "closed shell".

Making this approximation, the energy of the p-state is

$$E_p = I_{-1} + I_1 + \int |\psi_{-1}(1)|^2 \frac{1}{r_{12}} |\psi_1(2)|^2 d\tau + \int \psi_{-1}(1)\psi_1(1) \frac{1}{r_{12}} \psi_{-1}(2)\psi_1(2) d\tau(2) d\tau$$

where I_{-1} and I_1 are respectively the energies of the highest bonding and of the lowest antibonding Hückel molecular orbitals. Expending the two molecular integrals in terms of atomic integrals, and making use of the Pople approximations described in § 8.1, we have

$$\int |\psi_{-1}(1)|^2 \frac{1}{r_{12}} |\psi_1(2)|^2 d\tau = A \sum_{r}^{N} c_{r,-1}^2 c_{r,1}^2 + B \sum_{\substack{r \neq s \\ (\text{bonded})}}^{N} \sum^{N} c_{r,-1}^2 c_{s,1}^2$$

$$\int \psi_{-1}(1) \psi_1(1) \frac{1}{r_{12}} \psi_{-1}(2) \psi_1(2) d\tau = A \sum_{r}^{N} c_{r,-1}^2 c_{r,1}^2 + B \sum_{\substack{r \neq s \\ (\text{bonded})}}^{N} \sum^{N} c_{r,-1} c_{r,1} c_{s,-1} c_{s,1}$$

$$\therefore \quad E_p = I_{-1} + I_1 + 2A \sum_{r}^{N} c_{r,-1}^4 \qquad (8.9)$$

The explanation of the last step is as follows. In an alternant aromatic hydrocarbon, $C_{r,1} = \pm C_{r,-1}$, the sign depending upon whether the carbon atom r is a member of the arbitarily assigned "starred" or "unstarred" set. In an alternant aromatic hydrocarbon, any bond r-s must be formed between two atoms of different sets, and so $C_{r,1} C_{s,1} = -C_{r,-1} C_{s,-1}$. Hence $C_{r,-1} C_{r,1} C_{s,-1} C_{s,1} = -C_{r,-1}^2 C_{s,-1}^2$, and so the coefficient of B in E_p vanishes.

For comparison with the above treatment of the first excited state we require to calculate the energy of the ground state considering only the doubly-filled highest bonding molecular orbital ψ_{-1}. This energy is

$$E_g = 2\,I_{-1} + \int |\psi(1)|^2 \frac{1}{r_{12}} |\psi(2)|^2 \, d\tau$$

Expanded in terms of atomic orbitals this becomes

$$E_g = 2\,I_{-1} + A \sum_{r}^{N} c_{r,-1}^4 + B \sum\sum c_{r,-1}^2 c_{s,-1}^2 \qquad (8.10)$$

The energy of the p-band transition is therefore the difference of (9) and (10):

$$E_p - E_g = I_1 - I_{-1} + A \sum_{r}^{N} c_{r,-1}^4 - B \underset{\substack{r \neq s \\ (\text{bonded})}}{\sum^{N}\sum^{N}} c_{r,-1}^2 \, c_{s,-1}^2$$

and substituting $I_{\pm 1} = \alpha \mp |x_1|\beta_0$ where x_1 is the "Hückel number" of the highest bonding molecular orbital, we have

$$E_p - E_g = -2|x_1|\beta_0 + A \sum_{r}^{N} c_{r,-1}^4 - B \underset{\substack{r \neq s \\ (\text{bonded})}}{\sum^{N}\sum^{N}} c_{r,-1}^2 \, c_{s,-1}^2 \qquad (8.11)$$

Results.

Using the molecular orbitals calculated using Simple Hückel theory, the coefficients of A, B and β_0 are shown in Table XIII :

Table XIII

Molecule	$\lvert x_1 \rvert$	$\sum_{r}^{N} c_{r,-1}^{4}$	$\sum_{r \neq s}^{N} \sum^{N} c_{r,-1}^{2} c_{s,-1}^{2}$ (bonded)	$\nu_{exptl.}$ (cm.$^{-1}$)
benzene	$1.000000\beta_0$	0.166667	0.333333	48,356
naphthalene	$0.61803\beta_0$	0.150000	0.119098	34,900
anthracene	$0.37535\beta_0$	0.121792	0.066258	26,450
tetracene	$0.29496\beta_0$	0.104669	0.041155	21,150
pentacene	$0.21969\beta_0$	0.092667	0.027355	17,380
hexacene	$0.16938\beta_0$	0.083462	0.019066	14,590

Since three equations are sufficient to determine the unknown parameters β_0, A and B, the figures for naphthalene, tetracene and pentacene (benzene showed anomalous behaviour) were substituted into equation (11), and the parameters were thereby calculated to be as follows:

β_0 = -27,280 cm^{-1} = -77.99 kcal mole^{-1} = -3.38 eV
A = 88,050 cm^{-1} = 251.73 kcal mole^{-1} = 10.92 eV
B = 101,000 cm^{-1} = 288.76 kcal mole^{-1} = 12.52 eV

When these values are substituted into (11), the calculated transition energies of the p-bands for anthracene and hexacene are found to be 24,511 and 14,664cm^{-1} respectively. The values found by Clar are 26,450 and 14,590cm^{-1}.

The value of β_0 calculated here is somewhat greater in magnitude than that calculated (§6.4) neglecting electronic repulsions (-62·7 kcal.mole^{-1}). This is probably because in the latter case (the Hückel method) an implicit allowance was made for these repulsions and so the energy value of β_0 is increased.

It is interesting that the value of A, which is the repulsion energy between two electrons in the same atomic orbital, i.e. $\int |\chi_\lambda(1)|^2 \frac{e^2}{r_{12}} |\chi_\lambda(2)|^2 d\tau$ (called by Pariser and Parr[37] the $(11|11)$ integral) is so close to the value calculated by Parisor and Parr (11.08eV) from ionisation potentials and electron affinities. The quantity B is the repulsion between two π electrons at a bond length (~ 1.4Å) apart, and is sometimes called the $(11|22)$ integral. Its value should therefore be less than that of A, though from our calculation, the opposite is true. The cause of this anomaly is probably due to the fact that the calculation of B involves a very small difference between two large quantities, thus resulting in an inaccuracy in the calculated value of this quantity.

References

1. E. Hückel, *Z. Physik*, 70, 204 (1931).
2. R. S. Mulliken, C.A. Rieke and W. G. Brown, *J.Amer.Chem.Soc.*, 63, 41 (1941).
3. H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* A251,172 (1959).
4. C. A. Coulson, *Proc. Roy. Soc.*, A169, 413 (1939).
5. C. A. Coulson, *Proc. Roy. Soc.*, A207, 91 (1951); *J. Phys. Chem.*, 56, 311 (1952).
6. R. Daudel, R. Lefebvre and C. Moser, *Quantum Chemistry*, Interscience Publishers, New York (1959).
7. A. Streitwieser, *Molecular Orbital Theory for Organic Chemists*, John Wiley & Sons, Inc., New York (1961).
8. T. H. Goodwin, *J. Chem. Soc.*, 1960, 485.
9. K. Fries, R. Walter and K. Schilling, *Ann.*, 516, 248 (1935).
10. E. Clar, *Tetrahedron*, 5, 98 (1959).
11. E. Clar, *Aromatische Kohlenwasserstoffe*, Springer-Verlag, Berlin (1952).
12. E. Clar, *Tetrahedron*, 6, 355 (1959).
13. E. Clar, *Zeit. für Chemie.*, 2, 35 (1962).
14. E. Clar, *Tetrahedron*, 9, 202 (1960).
15. E. Clar, *Tetrahedron*, 18, 1471 (1962).
16. C. A. Coulson and R. Daudel, *Dictionary of Values of Molecular Constants, Volume II*, Céntre de Chimie Theorique de France, Paris (1955).
17. L. Pauling, L. O. Brockway and J. Y. Beach, *J.A.C.S.*, 57, 2705 (1935).
18. L. Pauling, *The Nature of the Chemical Bond*, pp.198-201, 232-239 Ithaca (1960).
19. A. Pullman, *Ann. Chim.*, 2, 5 (1947); see also C.A. Coulson, Ref.5.
20. H. N. Shrivastava and J.C. Speakman, *Proc. Roy. Soc.*, A257,477 (1960).
21. D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc.*, A258,270 (1960).
22. I. L. Karle, *J. Chem. Phys.* 20, 65 (1952); E. G. Cox, D. W. J. Cruickshank and J.A.S. Smith, *Proc. Roy. Soc.*, A247, 1 (1958); A. Almenningen, O. Bastiansen and L. Fernholt, *Kgl. Norske Vid. Selsk. Skr.* No.3 (1958); A. Langseth and B.P. Stoicheff, *Canad.J. Phys.*, 34, 350 (1956).
23. J. B. Nelson and D.P. Riley, *Proc. Phys. Soc.*, 57, 477, 486 (1945).
24. Originally D.M. Burns and J. Iball, *Proc. Roy. Soc.* A257, 491 (1960), corrected values in Ref. 21.
25. J. Barriol and J. Metzger, *J. chim. phys.*, 47, 432 (1950).
26. For further references see D. R. Lide, *Tetrahedron* 17, 125; B. P. Stoicheff, *ibid*, 135; O. Bastiansen and M. Traetteberg, *ibid*, 147 (1962).
27. C. A. Coulson, *Contribution à l'Étude de la Structure Moleculaire* (Victor Henri Memorial Volume) Desoer, Liège (1948).
28. M. J. S. Dewar and H.N. Schmeising, *Tetrahedron*, 5, 166 (1959).
29. C. A. Coulson and W. T. Dixon, *Tetrahedron*, 17, 215 (1962).
30. For example this repulsion may be the cause of the abnormal bond lengths in Ref.20.

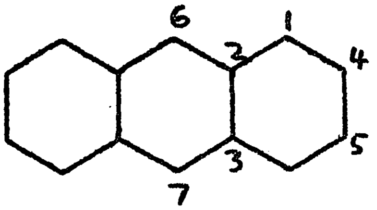
31. E. Clar, *J. Chem. Soc.* (1959) 142.
32. D. S. McClure, *J. Chem. Phys.* *22*, 1256, 1668 (1954);
    J. W. Sidman, *ibid.* 115, 122 (1956).
33. For a very comprehensive collection see S. L. Altmann, *Quantum Theory, Vol.II* (Edited by D. R. Bates), the Academic Press, New York (1962), pp.175-182.
34. See for example "*Modern Computing Methods*", National Physical Laboratory, H.M. Stationery Office, London (1961).
35. See also Clarkson, Coulson and Goodwin, *Tetrahedron* *19* (1963) (in press).
36. J. A. Pople, *Transactions of the Faraday Society*, *49*, 1375 (1953).
37. R. Pariser and R. G. Parr, *J. Chem. Phys.*, *21*, 466, 767 (1953).

APPENDIX A

Energy eigenvalues, bond orders, bond lengths and β^1 values of some benzenoid aromatic hydrocarbons as calculated using the Coulson and Goodwin bond order/bond length curve and the Mulliken, Riecke and Brown bond length/β^1 value curve.

An asterisk (*) denotes the energy eigenvalues and bond orders calculated by other workers, and found in Ref. 16.

Table 1: Anthracene



(a) Energy eigenvalues $-x_i$

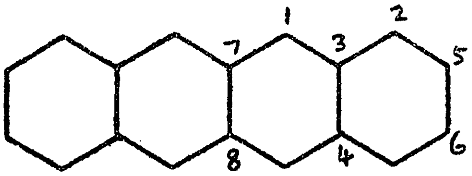
C_{2v} symm.	I*	II	III
A_1	2.41421	2.188035	2.116719
	1.41421	1.385490	1.387694
B_2	2.00000	1.875232	1.796839
	1.00000	0.845830	0.768595
A_2	1.00000	1.001062	0.988433
B_1	1.41421	1.363392	1.359914
	0.41421	0.490134	0.567499
$\sum_i (-x_i)$	9.65684	9.149176	8.985694

(b) Bond orders, bond lengths and β' values.

Bond	p^{I*}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}
1 2	.535	1.429	0.860	.490	1.447	0.758	.437	1.476	0.750
1 4	.738	1.370	1.065	.787	1.362	1.095	.827	1.357	1.111
2 3	.485	1.450	0.800	.486	1.449	0.735	.498	1.443	0.808
2 6	.606	1.403	0.945	.630	1.397	0.972	.647	1.392	0.990
4 5	.586	1.410	0.920	.520	1.421	0.842	.464	1.460	0.750

mean = .604

Table 2: Tetracene



(a) Energy eigenvalues $-x_i$

C_{2v} symm.	I *	II	III
A_1	2.46673	2.212575	2.171466
	1.77748	1.662737	1.624727
	1.00000	0.814609	0.764594
B_2	2.19353	2.005262	1.917537
	1.29426	1.229272	1.248572
A_2	1.19353	1.171060	1.129985
	0.29496	0.363474	0.449125
B_1	1.46673	1.422235	1.418260
	0.77748	0.807688	0.825527
$\sum_i (-x_i)$	12.46470	11.688911	11.549794

(b) Bond orders, bond lengths and β^1 values

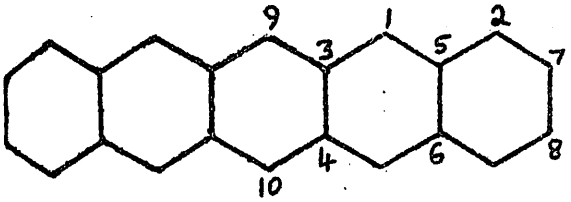
Bond	p^{I*}	r^I	β^{1I}	p^{II}	r^{II}	β^{1II}	p^{III}	r^{III}	β^{1III}
1 3	.618	1.400	0.960	.662	1.388	1.003	.703	1.377	1.039
1 7	.584	1.412	0.920	.584	1.412	0.920	.570	1.417	0.902
2 3	.530	1.432	0.855	.476	1.454	0.716	.395	1.502	0.662
2 5	.741	1.370	1.067	.795	1.361	1.099	.850	1.355	1.118
3 4	.475	1.454	0.785	.457	1.464	0.760	.467	1.458	0.742
5 6	.581	1.412	0.915	.508	1.439	0.827	.435	1.478	0.726
7 8	.458	1.463	0.760	.438	1.476	0.730	.460	1.462	0.765

mean =.594

Table 3: Pentacene

(a) Energy eigenvalues $-x_i$

C_{2v} symm.	I *	II	III
A_1	2.49551	2.225505	2.206876
	2.00000	1.828067	1.786598
	1.21969	1.122191	1.115375
B_2	2.30278	2.081386	2.039275
	1.61803	1.502393	1.475489
	1.00000	0.796976	0.735950
A_2	1.30278	1.271932	1.284300
	0.61803	0.661824	0.702414
B_1	1.49551	1.453092	1.486768
	1.00000	0.998938	1.019325
	0.21969	0.276733	0.338755
$\sum_{i=1} (-x_i)$	15.27202	14.219037	14.191125

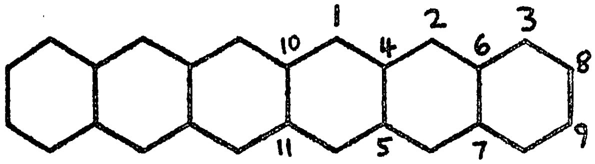


(b) Bond orders, bond lengths and β^{1} values

Bond	p^{I*}	r^{I}	β^{1I}	p^{II}	r^{II}	β^{1II}	p^{III}	r^{III}	β^{1III}
1 3	.579	1.413	0.915	.568	1.417	0.900	.543	1.420	0.870
1 5	.622	1.399	0.965	.673	1.385	1.013	.713	1.375	1.048
2 5	.529	1.432	0.853	.471	1.456	0.731	.417	1.489	0.698
2 7	.742	1.369	1.067	.798	1.361	1.100	.840	1.356	1.115
3 4	.451	1.466	0.750	.417	1.489	0.698	.418	1.488	0.699
3 9	.596	1.407	0.930	.615	1.401	0.956	.627	1.398	0.969
5 6	.472	1.455	0.782	.446	1.471	0.744	.433	1.479	0.723
7 8	.579	1.412	0.915	.503	1.441	0.822	.440	1.475	0.734

mean: .587

Table 4: Hexacene



(a) Energy eigenvalues $-x_i$

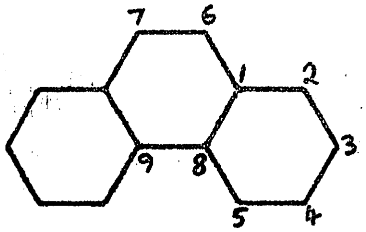
C_{2v} symm.	I	II	III
A_1	2.512943	2.232924	2.207674
	2.141658	1.936735	1.875294
	1.501509	1.375365	1.362615
	1.000000	0.783655	0.711801
B_2	2.370021	2.125681	2.072688
	1.843487	1.680765	1.640123
	1.169375	1.045237	1.036887
A_2	1.370021	1.334196	1.343294
	0.843487	0.861720	0.884835
	0.169375	0.216767	0.281569
B_1	1.512943	1.473341	1.514546
	1.141658	1.127141	1.127461
	0.501509	0.549197	0.606375
$\sum_i (-x_i)$	18.077986	16.742724	16.665162

(b) Bond orders, bond lengths and β^1 values

Bond	p^{I}	r^{I}	β^{1I}	p^{II}	r^{II}	β^{1II}	p^{III}	r^{III}	β^{1III}
1 4	.599	1.406	0.938	.627	1.398	0.970	.635	1.390	0.996
1 10	.590	1.409	0.926	.598	1.407	0.937	.596	1.408	0.934
2 4	.577	1.413	0.910	.561	1.420	0.891	.526	1.421	0.848
2 6	.623	1.398	0.963	.677	1.384	1.017	.731	1.371	1.061
3 6	.528	1.432	0.853	.469	1.457	0.736	.394	1.503	0.660
3 8	.742	1.369	1.068	.799	1.361	1.101	.852	1.355	1.118
4 5	.448	1.468	0.745	.408	1.494	0.683	.401	1.498	0.672
6 7	.471	1.455	0.781	.442	1.473	0.738	.427	1.483	0.713
8 9	.578	1.413	0.913	.501	1.442	0.819	.427	1.483	0.713
10 11	.443	1.470	0.740	.400	1.499	0.669	.393	1.503	0.659

mean = .583

Table 5: Phenanthrene



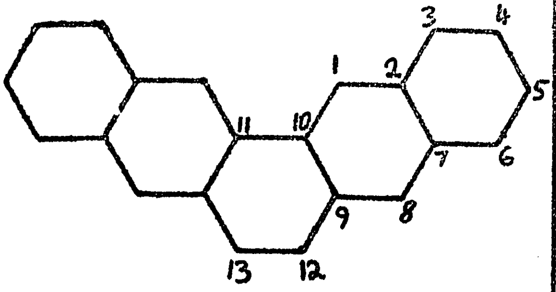
(a) Energy eigenvalues $-x_i$

C_s symm.	I *	II	III
A^{1}	2.43476	2.197145	2.176692
	1.51673	1.481947	1.449152
	1.30580	1.217168	1.190297
	0.60523	0.656614	0.703350
A^{II}	1.95063	1.882546	1.894248
	1.14238	1.059776	1.048613
	0.76905	0.756552	0.784630
$\sum_i (-x_i)$	9.72458	9.251750	9.246983

(b) Bond orders, bond lengths and β^{1} values

Bond	p^{I*}	r^{I}	β^{I}	p^{II}	r^{II}	β^{II}	p^{III}	r^{III}	β^{III}
1 2	.575	1.414	0.910	.577	1.414	0.911	.578	1.414	0.912
1 6	.506	1.441	0.825	.439	1.475	0.733	.381	1.511	0.641
1 8	.542	1.426	0.867	.583	1.412	0.919	.624	1.399	0.966
2 3	.707	1.377	1.042	.725	1.372	1.057	.733	1.371	1.062
3 4	.623	1.398	0.962	.598	1.406	0.938	.590	1.409	0.928
4 5	.702	1.378	1.037	.720	1.373	1.053	.728	1.372	1.059
5 8	.590	1.408	0.925	.590	1.409	0.927	.588	1.410	0.925
6 7	.775	1.364	1.088	.831	1.357	1.112	.872	1.353	1.124
8 9	.461	1.461	0.766	.406	1.495	0.680	.351	1.531	0.635

Table 6: Pentaphene



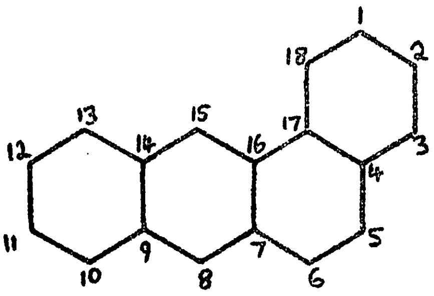
(a) Energy eigenvalues $-x_i$

C_S symm.	I *	II	III
A^I	2.51457	2.234765	2.201942
	2.00000	1.829125	1.772780
	1.50352	1.434988	1.414667
	1.23542	1.168758	1.160296
	1.00000	0.929244	0.919788
	0.43716	0.513814	0.587725
A^{II}	2.28379	2.087312	2.079424
	1.59703	1.520429	1.517902
	1.28899	1.244210	1.242861
	1.00000	0.855558	0.829863
	0.52086	0.583186	0.632148
$\sum_i (-x_i)$	15.38134	14.401389	14.359397

(b) Bond orders, Bond lengths and β^1 values

Bond	p^{I*}	r^I	β^{1I}	p^{II}	r^{II}	β^{1II}	p^{III}	r^{III}	β^{1III}
1 2	.578	1.413	0.912	.570	1.417	0.902	.551	1.420	0.879
1 10	.653	1.389	0.997	.706	1.377	1.042	.738	1.370	1.065
2 3	.548	1.424	0.875	.519	1.435	0.839	.494	1.445	0.784
2 7	.498	1.444	0.815	.519	1.435	0.839	.557	1.420	0.886
3 4	.728	1.372	1.058	.767	1.365	1.084	.793	1.361	1.098
4 5	.596	1.406	0.932	.544	1.420	0.870	.509	1.439	0.829
5 6	.729	1.372	1.059	.769	1.365	1.086	.795	1.361	1.099
6 7	.545	1.425	0.870	.514	1.437	0.834	.490	1.447	0.762
7 8	.584	1.411	0.919	.579	1.413	0.914	.559	1.420	0.888
8 9	.634	1.395	0.976	.688	1.381	1.027	.729	1.372	1.059
9 10	.501	1.443	0.820	.495	1.445	0.791	.490	1.447	0.762
9 12	.484	1.450	0.798	.394	1.503	0.661	.318	1.555	0.526
10 11	.435	1.475	0.725	.349	1.532	0.635	.296	1.572	0.483
12 13	.790	1.362	1.095	.858	1.354	1.120	.905	1.350	1.133

Table 7: 1-2 Benzanthracene (a) Energy Eigenvalues $-x_i$



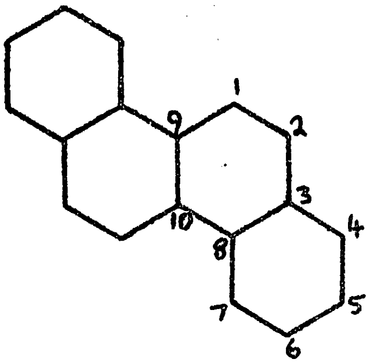
	I*	II	III
	2.48465	2.011990	2.196191
	2.17553	2.221993	2.005780
	1.75461	1.675881	1.654474
	1.47987	1.414973	1.387592
	1.32305	1.264846	1.255741
	1.16563	1.076482	1.063347
	1.00000	0.916023	0.914609
	0.71497	0.718802	0.740539
	0.45231	0.525520	0.595467
$\sum_i (-x_i)$	12.55062	11.826310	11.813739

(b) Bond orders, Bond lengths and β' values

Bond	p^{I*}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}
1 2	.628	1.396	0.970	.611	1.403	0.951	.608	1.404	0.948
1 18	.695	1.379	1.033	.709	1.376	1.044	.713	1.375	1.047
2 3	.700	1.378	1.036	.715	1.375	1.049	.717	1.374	1.051
3 4	.581	1.412	0.915	.590	1.410	0.927	.597	1.407	0.936
4 5	.494	1.446	0.810	.414	1.491	0.692	.341	1.538	0.570
4 17	.546	1.425	0.873	.590	1.409	0.927	.629	1.397	0.972
5 6	.783	1.363	1.092	.849	1.355	1.117	.893	1.351	1.130
6 7	.494	1.446	0.810	.413	1.491	0.691	.342	1.537	0.572
7 8	.628	1.397	0.970	.675	1.384	1.016	.708	1.376	1.043
7 16	.500	1.442	0.819	.496	1.445	0.813	.504	1.441	0.822
8 9	.590	1.409	0.925	.591	1.409	0.928	.578	1.414	0.913
9 10	.542	1.426	0.867	.507	1.440	0.826	.479	1.452	0.793
9 14	.495	1.445	0.814	.513	1.437	0.833	.547	1.425	0.874
10 11	.732	1.371	1.061	.774	1.364	1.089	.802	1.360	1.102
11 12	.593	1.407	0.928	.538	1.421	0.862	.499	1.443	0.817
12 13	.731	1.372	1.060	.773	1.364	1.088	.801	1.360	1.101
13 14	.545	1.425	0.871	.511	1.438	0.831	.483	1.450	0.798
14 15	.584	1.410	0.920	.583	1.412	0.918	.571	1.416	0.904
15 16	.646	1.391	0.990	.692	1.380	1.030	.719	1.373	1.052
16 17	.447	1.468	0.745	.374	1.515	0.639	.310	1.560	0.511
17 18	.597	1.406	0.932	.604	1.405	0.944	.608	1.404	0.948

Table 8: **Chrysene**

(a) Energy eigenvalues $-x_i$

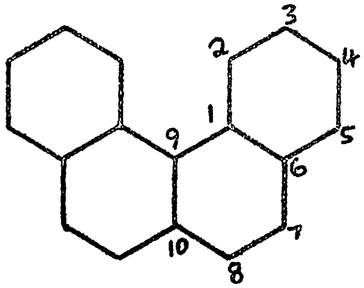


C_2 symm.	I*	II	III
A	2.4990	2.228365	2.211558
	1.7008	1.649414	1.646265
	1.2858	1.200426	1.185362
	0.7923	0.738649	0.758870
	0.5201	0.570916	0.620391
B	2.1655	2.012092	2.009877
	1.5398	1.482406	1.453109
	1.2164	1.096295	1.077060
	0.8753	0.891976	0.902400
$\sum_i(-x_i)$	12.5950	11.870540	11.864890

(b) Bond orders, bond lengths and β^1 values

Bond	p^{I*}	r^{I}	$\beta^{1\,I}$	p^{II}	r^{II}	$\beta^{1\,II}$	p^{III}	r^{III}	$\beta^{1\,III}$
1 2	.754	1.367	1.075	.802	1.360	1.102	.834	1.356	1.113
1 9	.538	1.428	0.863	.490	1.447	0.806	.449	1.469	0.747
2 3	.521	1.435	0.842	.471	1.456	0.781	.432	1.480	0.721
3 4	.568	1.416	0.900	.562	1.419	0.892	.554	1.422	0.883
3 8	.535	1.429	0.860	.572	1.416	0.905	.609	1.403	0.950
4 5	.712	1.376	1.046	.736	1.370	1.064	.750	1.368	1.074
5 6	.617	1.400	0.958	.586	1.411	0.923	.570	1.417	0.902
6 7	.707	1.377	1.042	.731	1.371	1.061	.746	1.368	1.071
7 8	.583	1.411	0.915	.574	1.415	0.908	.564	1.419	0.895
8 10	.476	1.454	0.786	.442	1.474	0.737	.409	1.494	0.684
9 10	.573	1.415	0.905	.637	1.395	0.980	.694	1.379	1.032

Table 9: 3-4 benzophenanthrene



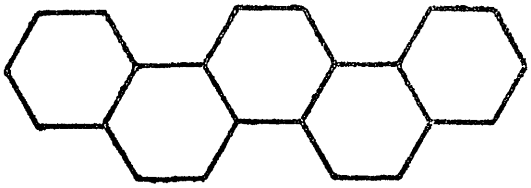
(a) Energy eigenvalues $-x_i$

C_s symm.	I*	II	III
A^1	2.5070	2.231960	2.332723
	1.7694	1.694779	1.757159
	1.4142	1.303874	1.297956
	1.1234	0.988157	0.954535
	0.5676	0.601381	0.738167
A^{II}	2.1358	1.998487	1.996029
	1.4142	1.385533	1.370725
	1.0000	0.984372	0.992630
	0.6621	0.682331	0.717212
$\sum_i (-x_i)$	12.5937	11.870874	12.157136

(b) Bond orders, Bond lengths and β^1 values

Bond	p^{I*}	r^{I}	β^{1I}	p^{II}	r^{II}	β^{1II}	p^{III}	r^{III}	β^{1III}
1 2	.578	1.413	0.913	.570	1.417	0.902	.570	1.416	0.903
1 6	.533	1.430	0.856	.570	1.417	0.902	.622	1.399	0.964
1 9	.489	1.447	0.805	.456	1.465	0.759	.371	1.517	0.625
2 3	.709	1.377	1.044	.733	1.371	1.062	.743	1.369	1.069
3 4	.616	1.400	0.956	.585	1.411	0.921	.574	1.415	0.907
4 5	.712	1.376	1.046	.736	1.370	1.064	.747	1.368	1.072
5 6	.570	1.416	0.902	.564	1.419	0.895	.560	1.420	0.890
6 7	.519	1.436	0.839	.469	1.458	0.778	.414	1.491	0.692
7 8	.762	1.366	1.080	.809	1.359	1.105	.861	1.354	1.121
8 10	.522	1.435	0.845	.475	1.454	0.785	.384	1.509	0.646
9 10	.574	1.414	0.906	.638	1.394	0.981	.769	1.365	1.086

Table 10: Picene



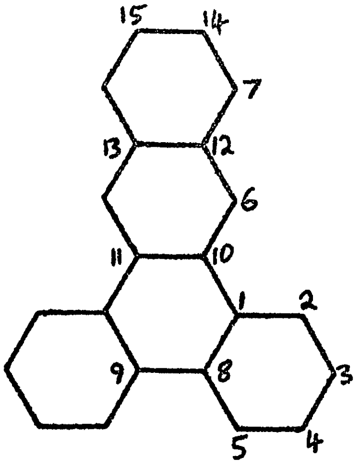
(a) Energy eigenvalues $-x_i$

C_s symm.	I*	II	III
A^{I}	2.53480	2.681167	2.224165
	1.93633	1.925163	1.845549
	1.56112	1.641610	1.470898
	1.20163	1.112136	1.046119
	1.00000	0.982602	0.992512
	0.50192	0.460636	0.578872
A^{II}	2.29599	2.196601	2.080795
	1.53446	1.703137	1.516044
	1.36559	1.328438	1.204040
	0.85948	0.895510	0.844055
	0.68030	0.808627	0.755182
$\sum_i (-x_i)$	15.47162	15.735627	14.498228

(b) Bond orders, Bond lengths and β^{1} values

Bond	p^{I*}	r^{I}	$\beta1^{I}$	p^{II}	r^{II}	$\beta1^{II}$	p^{III}	r^{III}	β^{IIII}
1 2	.471	1.456	0.781	.380	1.511	0.640	.359	1.525	0.603
1 10	.554	1.421	0.883	.598	1.407	0.937	.553	1.422	0.881
1 12	.563	1.418	0.892	.607	1.404	0.947	.650	1.391	0.992
2 3	.586	1.410	0.920	.591	1.409	0.928	.583	1.412	0.918
2 7	.537	1.428	0.861	.583	1.412	0.919	.618	1.400	0.960
3 4	.705	1.377	1.040	.724	1.373	1.056	.736	1.370	1.063
4 5	.619	1.399	0.960	.592	1.409	0.929	.578	1.414	0.913
5 6	.710	1.376	1.045	.735	1.370	1.064	.747	1.368	1.071
6 7	.570	1.416	0.902	.561	1.420	0.891	.555	1.422	0.885
7 8	.517	1.437	0.836	.477	1.453	0.786	.428	1.482	0.715
8 9	.758	1.367	1.077	.763	1.366	1.082	.821	1.358	1.110
9 12	.532	1.430	0.857	.554	1.420	0.882	.475	1.454	0.787
10 11	.732	1.371	1.061	.687	1.381	1.026	.744	1.369	1.070
12 13	.493	1.446	0.810	.401	1.498	0.672	.440	1.475	0.733

Table 11: 1-2,3-4 dibenzanthracene



(a) Energy eigenvalues $-x_i$

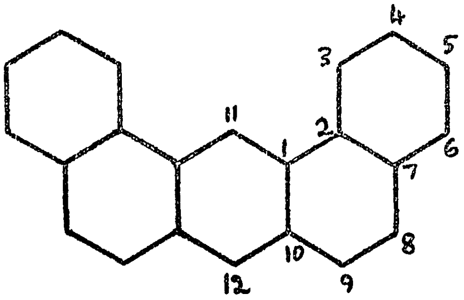
C_2 symm.	I*	II	III
A^1	2.5588	2.253620	2.205929
	2.2219	2.053335	2.042831
	1.7223	1.623528	1.607857
	1.3165	1.212531	1.167415
	1.2020	1.095837	1.064048
	0.7140	0.707760	0.750653
A^{II}	1.9711	1.908333	1.932182
	1.3797	1.302817	1.282524
	1.0949	1.039925	1.032103
	0.7908	0.807979	0.848123
	0.4991	0.589557	0.651802
$\sum_i (-x_i)$	15.4711	14.575221	14.585467

(b) Bond orders, bond lengths and β^1 values

Bond		p^{I*}	r^{I}	$\beta^{1\,I}$	p^{II}	r^{II}	$\beta^{1\,II}$	p^{III}	r^{III}	$\beta^{1\,III}$
1	2	.606	1.403	0.945	.624	1.399	0.967	.635	1.395	0.978
1	8	.565	1.418	0.895	.608	1.404	0.948	.642	1.393	0.985
1	10	.420	1.485	0.702	.324	1.550	0.538	.239	1.636	0.390
2	3	.686	1.382	1.024	.692	1.380	1.030	.690	1.380	1.029
3	4	.641	1.393	0.985	.633	1.396	0.976	.637	1.395	0.980
4	5	.687	1.381	1.025	.692	1.380	1.030	.690	1.380	1.028
5	8	.606	1.403	0.945	.624	1.399	0.967	.636	1.395	0.979
6	10	.658	1.388	1.000	.717	1.374	1.050	.754	1.367	1.076
6	12	.575	1.414	0.910	.559	1.420	0.888	.536	1.428	0.851
7	12	.548	1.424	0.875	.518	1.435	0.839	.497	1.444	0.814
7	14	.727	1.372	1.057	.767	1.365	1.084	.792	1.362	1.097
8	9	.420	1.485	0.702	.324	1.550	0.538	.237	1.638	0.386
10	11	.513	1.438	0.833	.503	1.441	0.822	.503	1.441	0.821
12	13	.503	1.442	0.848	.535	1.429	0.858	.572	1.416	0.905
14	15	.598	1.406	0.935	.547	1.424	0.874	.514	1.437	0.834

Table 12: 1-2,7-8 dibenzanthracene

(a) Energy Eigenvalues $-x_i$

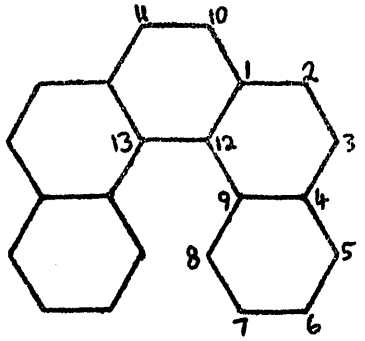


C_s symm.	I*	II	III
A^{I}	2.5219	2.243313	2.216372
	1.9402	1.842496	1.862516
	1.5123	1.437870	1.401240
	1.2584	1.168189	1.156546
	0.8735	0.910082	0.940114
	0.4917	0.557422	0.630528
A^{II}	2.3028	2.087509	2.068321
	1.6180	1.543774	1.501979
	1.3028	1.183846	1.151615
	1.0000	0.885010	0.880568
	0.6180	0.632802	0.668762
$\sum_i (-x_i)$	15.4396	14.492313	14.478559

(b) Bond orders, bond lengths and eigenvalues

Bond		p^{I*}	r^{I}	βl^{I}	p^{II}	r^{II}	βl^{II}	p^{III}	r^{III}	βl^{III}
1	2	.454	1.465	0.754	.390	1.505	0.656	.331	1.545	0.551
1	10	.513	1.438	0.833	.530	1.431	0.853	.561	1.420	0.891
1	11	.623	1.398	0.965	.646	1.392	0.989	.655	1.390	0.997
2	3	.594	1.407	0.930	.598	1.407	0.937	.599	1.406	0.938
2	7	.544	1.426	0.870	.586	1.411	0.922	.625	1.398	0.968
3	4	.697	1.379	1.035	.713	1.375	1.048	.720	1.373	1.053
4	5	.626	1.397	0.968	.606	1.404	0.946	.601	1.406	0.940
5	6	.703	1.378	1.039	.719	1.374	1.052	.724	1.373	1.056
6	7	.579	1.413	0.914	.585	1.411	0.921	.590	1.410	0.926
7	8	.498	1.444	0.815	.424	1.485	0.709	.359	1.525	0.604
8	9	.780	1.363	1.091	.840	1.356	1.115	.883	1.352	1.127
9	10	.498	1.444	0.815	.424	1.485	0.709	.360	1.524	0.605
10	12	.611	1.402	0.951	.638	1.395	0.981	.649	1.391	0.992

Table 13: 3-4,5-6 dibenzophenanthrene



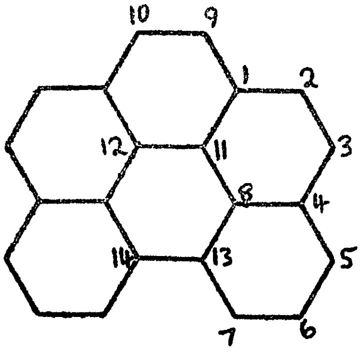
(a) Energy eigenvalues $-x_i$

C_s symm.	I	II	III
A^1	2.551076	2.252446	2.236240
	1.944188	1.838455	1.839960
	1.464192	1.367383	1.342954
	1.330644	1.265219	1.242587
	0.787244	0.825155	0.852071
	0.656705	0.655453	0.694478
A^{II}	2.257206	2.071294	2.061983
	1.655699	1.578302	1.555685
	1.218462	1.130658	1.120314
	1.067232	0.941470	0.927157
	0.535449	0.571388	0.618150
$\sum_i(-x_i)$	15.468098	14.497223	14.491579

(b) Bond orders, Bond lengths and β^1 values

Bond		p^{I*}	r^I	β^{1I}	p^{II}	r^{II}	β^{1II}	p^{III}	r^{III}	β^{1III}
1	2	.519	1.436	0.840	.465	1.459	0.773	0.419	1.488	0.701
1	10	.537	1.428	0.862	.508	1.439	0.828	0.490	1.447	0.806
1	12	.561	1.419	0.891	.615	1.401	0.957	0.664	1.387	1.006
2	3	.764	1.366	1.081	.815	1.359	1.107	0.850	1.355	1.118
3	4	.515	1.437	0.835	.459	1.463	0.763	0.412	1.492	0.689
4	5	.572	1.415	0.905	.569	1.417	0.901	0.564	1.418	0.895
4	9	.536	1.429	0.860	.574	1.415	0.908	0.613	1.402	0.954
5	6	.710	1.376	1.045	.732	1.371	1.061	0.743	1.369	1.069
6	7	.619	1.399	0.960	.591	1.409	0.928	0.577	1.414	0.911
7	8	.706	1.377	1.041	.728	1.372	1.059	0.740	1.369	1.067
8	9	.583	1.411	0.916	.578	1.414	0.912	0.571	1.416	0.904
9	12	.479	1.452	0.790	.438	1.476	0.731	0.394	1.502	0.661
10	11	.746	1.369	1.070	.782	1.363	1.093	0.801	1.360	1.102
12	13	.520	1.435	0.841	.511	1.430	0.831	0.496	1.444	0.814

Table 14: 1-12 Benzoperylene



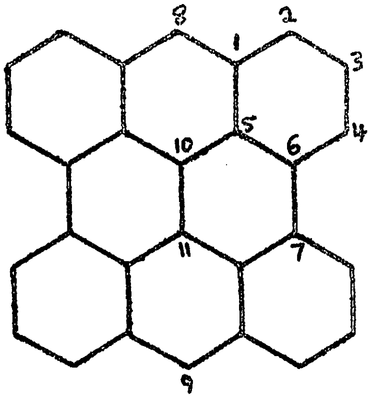
(a) Energy eigenvalues $-x_i$

C_s symm.	I*	II	III
A^I	2.63859	2.306786	2.290028
	2.08009	1.897950	1.887439
	1.59991	1.451827	1.417544
	1.35341	1.282734	1.267798
	1.00000	0.955273	0.952946
	0.68429	0.664678	0.682662
A^{II}	2.19906	2.004267	2.007787
	1.61296	1.539949	1.530808
	1.10504	0.978018	0.992861
	1.00000	0.936343	0.934650
	0.43922	0.486667	0.548312
$\sum_i(-x_i)$	15.71257	14.504494	14.512835

(b) Bond orders, Bond Lengths and β^1 values

Bond		p^{I*}	r^I	β^{1I}	p^{II}	r^{II}	β^{1II}	p^{III}	r^{III}	β^{1III}
1	2	.519	1.436	0.840	.467	1.458	0.775	.425	1.484	0.710
1	9	.550	1.423	0.878	.531	1.430	0.854	.516	1.436	0.837
1	11	.545	1.425	0.870	.588	1.410	0.924	.632	1.396	0.975
2	3	.765	1.365	1.082	.815	1.359	1.107	.847	1.355	1.117
3	4	.513	1.438	0.833	.458	1.464	0.761	.414	1.491	0.692
4	5	.579	1.412	0.911	.586	1.411	0.922	.588	1.410	0.925
4	8	.530	1.431	0.854	.558	1.421	0.887	.588	1.410	0.925
5	6	.688	1.381	1.025	.701	1.378	1.038	.712	1.375	1.047
6	7	.649	1.391	0.992	.631	1.396	0.974	.615	1.401	0.957
7	13	.627	1.397	0.970	.665	1.387	1.007	.693	1.380	1.031
8	11	.516	1.437	0.836	.486	1.449	0.801	.444	1.472	0.741
8	13	.537	1.428	0.862	.548	1.424	0.875	.557	1.421	0.886
9	10	.734	1.371	1.062	.763	1.366	1.082	.779	1.363	1.091
11	12	.519	1.436	0.839	.510	1.439	0.829	.499	1.443	0.817
13	14	.427	1.480	0.713	.342	1.538	0.571	.271	1.600	0.442

Table 15: Bisanthracene



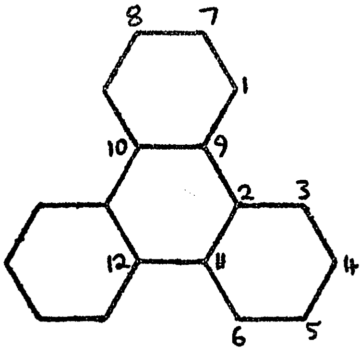
(a) Energy eigenvalues $-x_i$

C_{2v} symm.	I	II	III
A_1	2.701727	2.336394	2.309927
	1.697860	1.550060	1.531703
	1.657582	1.498860	1.483246
	0.866451	0.778193	0.754149
B_2	2.278414	2.023288	1.976314
	1.317431	1.193701	1.157412
	1.000000	0.876874	0.850116
A_2	1.891220	1.783562	1.781435
	1.000000	0.877145	0.850747
	0.704624	0.725136	0.796659
B_1	2.289795	2.064026	2.076249
	1.346607	1.320229	1.329014
	1.109792	1.055653	1.117063
	0.177427	0.226599	0.295698
$\sum_i (-x_i)$	20.038930	18.310740	18.309732

(b) Bond Orders, Bond Lengths and β^1 values

Bond		p^{I}	r^{I}	$\beta 1^{I}$	p^{II}	r^{II}	$\beta 1^{II}$	p^{III}	r^{III}	$\beta 1^{III}$
1	2	.541	1.427	0.866	.508	1.439	0.827	.477	1.453	0.790
1	5	.500	1.443	0.818	.496	1.444	0.814	.505	1.441	0.823
1	8	.561	1.409	0.928	.612	1.402	0.953	.625	1.398	0.967
2	3	.710	1.376	1.045	.749	1.368	1.073	.738	1.363	1.094
3	4	.625	1.398	0.968	.581	1.413	0.916	.532	1.430	0.856
4	6	.637	1.395	0.980	.697	1.379	1.035	.750	1.368	1.074
5	6	.528	1.431	0.851	.515	1.437	0.835	.490	1.447	0.806
5	10	.547	1.425	0.873	.568	1.417	0.900	.588	1.410	0.925
6	7	.423	1.485	0.707	.334	1.544	0.556	.258	1.614	0.422
10	11	.477	1.453	0.790	.423	1.486	0.706	.362	1.523	0.609

Table 16: Triphenylene



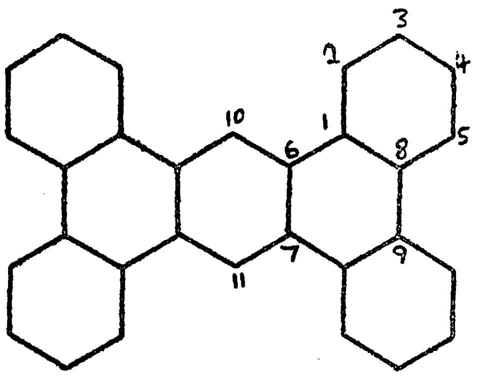
(a) Energy eigenvalues $-x_i$

C_s symm. (D_{3h})	I*	II	III
A^{I} (A_2)	2.53209	2.241482	2.202798
(E)	1.96962	1.905555	1.926641
(A_2)	1.34730	1.258122	1.216782
(E)	1.28558	1.183776	1.145069
(E)	0.68404	0.700129	0.764814
A^{II}(E)	1.96962	1.905555	1.926641
(E)	1.28558	1.183776	1.145069
(A_1)	0.87939	0.911603	0.938581
(E)	0.68404	0.700129	0.764814
$\sum_i (-x_i)$	12.63726	11.990127	12.031209

(b) Bond orders, Bond lengths and β^1 values

Bond	p^{I*}	r^{I}	$\beta 1^{I}$	p^{II}	r^{II}	$\beta 1^{II}$	p^{III}	r^{III}	$\beta 1^{III}$
1 7	.690	1.381	1.028	.698	1.379	1.036	.697	1.379	1.035
1 9	.603	1.404	0.943	.618	1.401	0.960	.627	1.398	0.970
2 9	.428	1.480	0.715	.340	1.539	0.567	.258	1.614	0.421
2 11	.562	1.419	0.893	.605	1.404	0.944	.641	1.394	0.984
4 5	.637	1.394	0.980	.627	1.398	0.970	.629	1.397	0.972

Table 17: 1-2,3-4,5-6,7-8 Tetrabenzanthracene



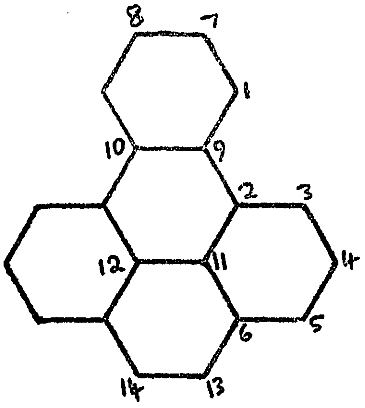
(a) Energy eigenvalues $-x_i$

C_{2v} symm.	I	II	III
A_1	2.605549	2.280060	2.236234
	1.955551	1.842823	1.873071
	1.314176	1.209359	1.167965
	0.899191	0.914792	0.952894
B_2	2.434764	2.158765	2.128793
	1.516274	1.336026	1.277140
	1.305800	1.193717	1.151230
	0.605225	0.608625	0.678059
A_2	1.950627	1.897721	1.921582
	1.142384	1.056279	1.039666
	0.769052	0.770133	0.815974
B_1	1.989161	1.913451	1.931603
	1.352714	1.248791	1.205150
	0.855187	0.890130	0.922361
	0.577404	0.621662	0.713050
$\sum_i (-x_i)$	21.273058	19.942334	20.014772

(b) Bond Orders, Bond Lengths and β^1 values

Bond		p^I	r^I	β^{1I}	p^{II}	r^{II}	β^{1II}	p^{III}	r^{III}	β^{1III}
1	2	.604	1.405	0.943	.619	1.400	0.960	.628	1.397	0.984
1	6	.426	1.483	0.712	.338	1.540	0.564	.257	1.615	0.488
1	8	.562	1.419	0.892	.605	1.405	0.944	.641	1.394	0.996
2	3	.689	1.381	1.028	.697	1.379	1.034	.696	1.379	1.040
3	4	.638	1.395	0.981	.628	1.397	0.970	.631	1.397	0.987
4	5	.689	1.381	1.027	.696	1.379	1.034	.696	1.379	1.039
5	8	.604	1.405	0.944	.620	1.400	0.961	.629	1.397	0.985
6	7	.538	1.426	0.863	.567	1.418	0.898	.603	1.405	0.960
6	10	.625	1.398	0.967	.650	1.391	0.992	.659	1.388	1.011
8	9	.425	1.484	0.710	.336	1.542	0.560	.254	1.619	0.482

Table 18: 1-2 benzpyrene



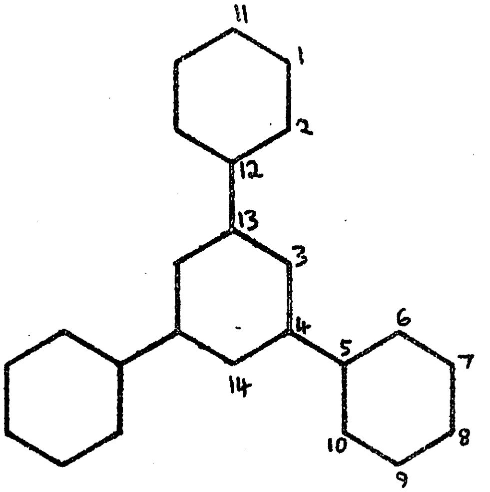
(a) Energy eigenvalues $-x_i$

C_s symm.	I	II	III
A^{I}	2.593539	2.278510	2.308632
	2.103636	1.965829	2.001557
	1.555940	1.497120	1.491530
	1.333928	1.276314	1.277119
	1.000000	0.942716	0.972772
	0.496971	0.559009	0.628243
A^{II}	2.015075	1.884231	1.924175
	1.350858	1.201713	1.193571
	1.000000	0.942127	0.960528
	0.718080	0.698426	0.732580
$\sum_i (-x_i)$	14.168027	13.245995	13.490707

(b) Bond Orders, Bond Lengths and β^{1} values

Bond		p^{I}	r^{I}	$\beta1^{I}$	p^{II}	r^{II}	$\beta1^{II}$	p^{III}	r^{III}	$\beta1^{III}$
1	7	.687	1.381	1.028	.697	1.379	1.041	.696	1.379	1.039
1	9	.604	1.405	0.944	.618	1.400	0.975	.625	1.398	0.982
2	3	.624	1.399	0.967	.660	1.388	1.012	.677	1.384	1.021
2	9	.427	1.483	0.712	.340	1.539	0.624	.283	1.586	0.538
2	11	.539	1.427	0.863	.555	1.422	0.908	.570	1.417	0.925
3	4	.653	1.390	0.995	.638	1.394	0.994	.631	1.397	0.987
4	5	.683	1.382	1.023	.694	1.379	1.038	.698	1.379	1.042
5	6	.585	1.411	0.921	.596	1.407	0.953	.604	1.405	0.961
6	11	.532	1.430	0.856	.562	1.419	0.915	.589	1.410	0.946
6	13	.505	1.441	0.824	.440	1.475	0.762	.393	1.503	0.698
7	8	.638	1.395	0.981	.628	1.398	0.984	.631	1.397	0.987
9	10	.562	1.419	0.892	.604	1.405	0.961	.631	1.397	0.987
11	12	.511	1.438	0.830	.471	1.456	0.806	.423	1.486	0.740
13	14	.777	1.364	1.090	.832	1.357	1.118	.864	1.353	1.125

Table 19: 1,3,5 triphenylbenzene



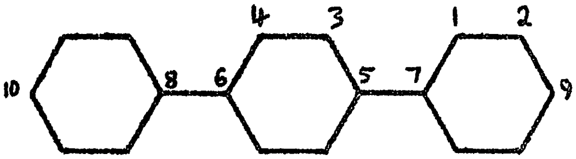
(a) Energy eigenvalues $-x_i$

C_s symm.	I*	II	III
A^{I}	2.41987	2.175970	2.129168
	2.13578	2.026832	2.021900
	1.82254	1.838582	1.898803
	1.41421	1.240774	1.164998
	1.00000	1.015000	1.017000
	0.90697	0.925243	0.967705
	0.66215	0.735955	0.830459
A^{II}	2.13578	2.026832	2.021899
	1.41421	1.240774	1.164998
	1.00000	1.015000	1.017000
	0.90697	1.015000	1.017000
	0.66215	0.735955	0.830458
$\sum_i (-x_i)$	16.48063	15.991916	16.081387

(b) Bond orders, bond lengths and β^1 values

Bond		p^{I*}	r^{I}	$\beta1^{I}$	p^{II}	r^{II}	$\beta1^{II}$	p^{III}	r^{III}	$\beta1^{III}$
1	2	.676	1.384	1.015	.676	1.384	1.017	.672	1.385	1.013
1	11	.660	1.388	1.001	.661	1.388	1.003	.664	1.387	1.005
2	12	.619	1.399	0.960	.643	1.393	0.896	.656	1.389	0.998
3	4	.622	1.398	0.963	.647	1.392	0.990	.658	1.389	1.000
4	5	.368	1.520	0.620	.249	1.624	0.406	.163	-	-

Table 20: p diphenylbenzene



(a) Energy eigenvalues $-x_i$

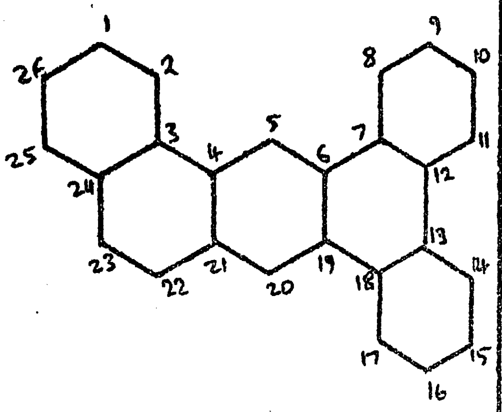
C_{2v} symm.	I*	II	III
A_1	2.34794	2.150563	2.151560
	1.84514	1.867565	1.923230
	1.00000	0.973133	0.999692
B_2	1.00000	1.028000	1.032000
	1.00000	1.015000	1.021000
A_2	1.00000	1.015000	1.021000
B_1	2.15365	2.033538	2.049487
	1.44679	1.261752	1.227041
	0.59264	0.667971	0.765954
$(-x_i)$	12.38616	12.012522	12.190964

(b) Bond orders, bond lengths and β^1 values

Bond		p^{I*}	r^{I}	$\beta 1^{I}$	p^{II}	r^{II}	β^{1II}	p^{III}	r^{III}	$\beta 1^{III}$
1	2	.677	1.384	1.015	.677	1.384	1.021	.672	1.385	1.019
1	7	.617	1.400	0.960	.641	1.394	0.996	.652	1.390	1.005
2	9	.660	1.388	1.001	.661	1.388	1.012	.664	1.387	1.014
3	4	.689	1.381	1.028	.689	1.381	1.032	.679	1.383	1.023
3	5	.611	1.402	0.951	.634	1.396	0.990	.649	1.391	1.002
5	7	.375	1.516	0.630	.259	1.613	0.492	.196	1.683	0.371

Table 21: 1-2, 3-4, 5-6 tribenzanthracene

(a) Energy eigenvalues



I	II	III
2.575530	2.320005	2.288920
2.359275	2.168169	2.149240
1.973033	1.931914	1.949581
1.941084	1.871279	1.888810
1.593673	1.527316	1.491491
1.414214	1.316527	1.282760
1.312436	1.231490	1.201311
1.271627	1.186023	1.158650
1.090294	1.023169	1.019050
0.877374	0.915455	0.942161
0.789409	0.804785	0.832900
0.637066	0.649420	0.695430
0.522346	0.582527	0.642140
18.357361	17.528079	17.542444

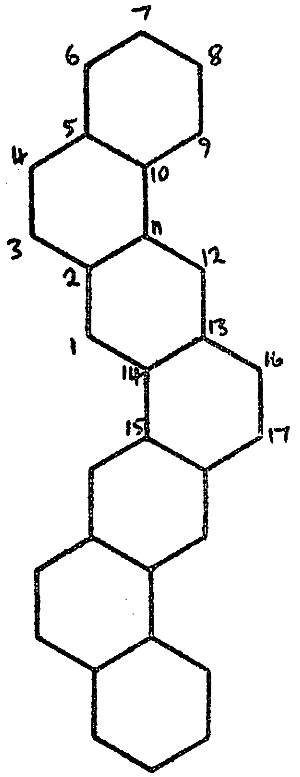
Table 21 (cont'd)

(b) Bond orders, bond lengths and β^{1} values

Bond		p^{I}	r^{I}	$\beta1^{I}$	p^{II}	r^{II}	$\beta1^{II}$	p^{III}	r^{III}	$\beta1^{III}$
1	2	.699	1.378	1.043	.713	1.375	1.055	.719	1.374	1.052
1	26	.625	1.398	0.981	.606	1.404	0.963	.602	1.405	0.941
2	3	.592	1.409	0.949	.596	1.407	0.953	.597	1.407	0.935
3	4	.456	1.465	0.786	.401	1.498	0.709	.354	1.529	0.595
3	24	.543	1.426	0.896	.580	1.413	0.937	.613	1.402	0.954
4	5	.612	1.402	0.969	.623	1.399	0.980	.624	1.399	0.967
4	21	.522	1.434	0.872	.549	1.424	0.902	.582	1.412	0.918
5	6	.635	1.395	0.991	.668	1.386	1.016	.681	1.383	1.021
6	7	.425	1.484	0.743	.342	1.537	0.627	.280	1.589	0.458
6	19	.528	1.431	0.879	.543	1.426	0.896	.566	1.418	0.897
7	8	.604	1.405	0.961	.620	1.400	0.977	.629	1.397	0.972
7	12	.562	1.419	0.916	.601	1.406	0.958	.629	1.397	0.971
8	9	.688	1.381	1.032	.693	1.380	1.037	.691	1.380	1.030
9	10	.638	1.394	0.994	.632	1.396	0.988	.636	1.395	0.979
10	11	.688	1.381	1.031	.692	1.380	1.036	.690	1.380	1.029
11	12	.605	1.404	0.962	.622	1.399	0.979	.631	1.397	0.974
12	13	.423	1.485	0.740	.338	1.540	0.622	.275	1.595	0.449
13	14	.605	1.404	0.962	.622	11399	0.979	.631	1.397	0.973
13	18	.563	1.419	0.917	.602	1.405	0.959	.629	1.397	0.972
14	15	.688	1.381	1.031	.692	1.380	1.036	.690	1.380	1.029
15	16	.639	1.394	0.994	.633	1.396	0.989	.636	1.395	0.979
16	17	.688	1.381	1.031	.692	1.380	1.036	.691	1.380	1.029
17	18	.605	1.404	0.962	.622	1.399	0.978	.630	1.397	0.973
18	19	.423	1.486	0.740	.339	1.540	0.622	.277	1.593	0.452
19	20	.641	1.394	0.996	.675	1.384	1.020	.687	1.381	1.026
20	21	.596	1.408	0.953	.607	1.404	0.964	.612	1.402	0.953
21	22	.503	1.441	0.850	.440	1.475	0.763	.388	1.506	0.652
22	23	.776	1.364	1.098	.830	1.357	1.117	.866	1.353	1.122
23	24	.502	1.442	0.849	.438	1.476	0.760	.385	1.508	0.648
24	25	.578	1.414	0.934	.582	1.412	0.939	.586	1.411	0.923
25	26	.704	1.377	1.047	.719	1.374	1.059	.723	1.373	1.055

Table 22: 3-4, 9-10 dibenzpentaphene

(a) Energy Eigenvalues



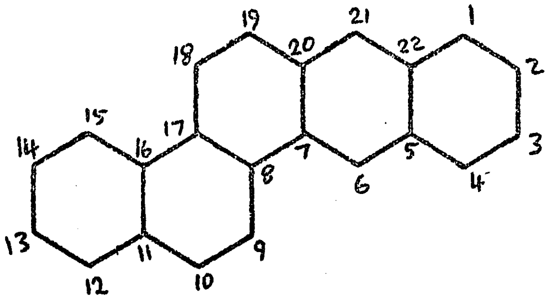
C_s symm.	I	II	III
A^{I}	2.553125	2.316903	2.289234
	2.227646	2.058982	2.041862
	1.724539	1.650034	1.607941
	1.459847	1.363755	1.335319
	1.365020	1.324841	1.295757
	1.000000	0.920807	0.924340
	0.816829	0.859885	0.878692
	0.432088	0.498399	0.561269
A^{II}	2.427048	2.222142	2.200268
	1.916930	1.543648	1.864409
	1.543829	1.490411	1.459631
	1.229280	1.142565	1.134894
	1.196109	1.107341	1.090137
	0.683570	0.699047	0.726269
	0.582329	0.621470	0.665805
$\sum_i(-x_i)$	21.158189	20.120250	20.075827

Table 22 (cont'd)

(b) Bond orders, bond lengths and β^1 values

Bond	p^{I}	r^{I}	$\beta^{1\,I}$	p^{II}	r^{II}	$\beta^{1\,II}$	p^{III}	r^{III}	$\beta^{1\,III}$
1 2	.601	1.406	0.958	.619	1.400	0.976	.629	1.397	0.971
1 14	.634	1.396	0.990	.661	1.388	1.012	.668	1.386	1.009
2 3	.502	1.442	0.850	.438	1.476	0.761	.385	1.508	0.647
2 11	.515	1.436	0.864	.534	1.429	0.887	.564	1.419	0.895
3 4	.777	1.364	1.098	.831	1.357	1.118	.869	1.353	1.123
4 5	.500	1.443	0.847	.434	1.479	0.755	.379	1.511	0.639
5 6	.578	1.414	0.935	.584	1.412	0.941	.589	1.410	0.926
5 10	.544	1.426	0.897	.582	1.412	0.939	.615	1.401	0.956
6 7	.703	1.377	1.045	.717	1.374	1.058	.721	1.373	1.053
7 8	.626	1.398	0.982	.608	1.403	0.965	.605	1.405	0.944
8 9	.698	1.379	1.402	.711	1.375	1.053	.716	1.374	1.050
9 10	.594	1.408	0.951	.599	1.406	0.956	.601	1.406	0.940
10 11	.452	1.467	0.780	.394	1.503	0.698	.345	1.535	0.578
11 12	.625	1.398	0.981	.645	1.392	0.999	.649	1.391	0.992
12 13	.609	1.403	0.966	.635	1.396	0.990	.648	1.392	0.991
13 14	.514	1.437	0.863	.530	1.431	0.881	.555	1.422	0.884
13 16	.495	1.445	0.840	.424	1.485	0.741	.367	1.520	0.616
14 15	.443	1.473	0.767	.376	1.514	0.674	.325	1.550	0.539
16 17	.780	1.363	1.100	.838	1.356	1.119	.877	1.352	1.125

Table 23: 3-4 benztetraphene



(a) Energy eigenvalues $-x_i$

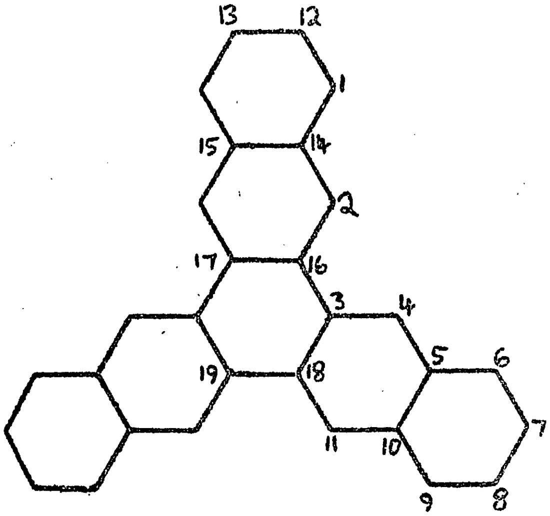
I	II	III
2.525067	2.298729	2.275391
2.289955	2.135487	2.128735
1.968607	1.862506	1.837479
1.592402	1.563450	1.554613
1.495587	1.441988	1.425457
1.357875	1.321543	1.314619
1.162639	1.100756	1.097662
1.095007	1.022034	0.998745
0.823052	0.784565	0.793605
0.704514	0.730773	0.750948
0.404791	0.470036	0.522736
15.419496	14.731867	14.699990

Table 23 (cont'd)

(b) Bond orders, bond lengths and β^1 values

Bond		p^{I}	r^{I}	$\beta^{1\,I}$	p^{II}	r^{II}	$\beta^{1\,II}$	p^{III}	r^{III}	$\beta^{1\,III}$
1	2	.733	1.371	1.070	.772	1.364	1.091	.797	1.361	1.100
1	22	.540	1.427	0.893	.507	1.440	0.856	.482	1.451	0.796
2	3	.591	1.409	0.948	.540	1.427	0.893	.506	1.440	0.825
3	4	.732	1.371	1.069	.771	1.364	1.095	.796	1.361	1.099
4	5	.543	1.426	0.896	.511	1.438	0.860	.485	1.449	0.800
5	6	.589	1.410	0.946	.595	1.408	0.952	.593	1.409	0.930
5	22	.492	1.446	0.836	.501	1.442	0.848	.525	1.433	0.847
6	7	.638	1.394	0.993	.672	1.385	1.019	.689	1.381	1.028
7	8	.460	1.462	0.791	.409	1.494	0.720	.368	1.519	0.618
7	20	.496	1.444	0.841	.493	1.446	0.837	.504	1.441	0.822
8	9	.544	1.425	0.897	.508	1.439	0.856	.479	1.452	0.793
8	17	.579	1.413	0.935	.643	1.395	0.998	.695	1.379	1.033
9	10	.748	1.368	1.081	.788	1.362	1.103	.813	1.359	1.106
10	11	.525	1.432	0.876	.486	1.449	0.827	.457	1.464	0.761
11	12	.567	1.418	0.921	.559	1.420	0.912	.552	1.423	0.880
11	16	.533	1.430	0.885	.564	1.419	0.918	.593	1.408	0.931
12	13	.714	1.375	1.055	.737	1.370	1.072	.749	1.368	1.073
13	14	.615	1.401	0.972	.587	1.411	0.944	.572	1.416	0.905
14	15	.709	1.376	1.051	.731	1.371	1.068	.744	1.369	1.070
15	16	.581	1.413	0.938	.573	1.416	0.928	.562	1.419	0.893
16	17	.481	1.451	.820	.455	1.466	0.784	.434	1.479	0.725
17	18	.524	1.433	.875	.467	1.458	0.801	.417	1.489	0.698
18	19	.764	1.365	1.092	.816	1.359	1.114	.852	1.355	1.118
19	20	.507	1.440	0.855	.447	1.471	0.772	.398	1.500	0.666
20	21	.620	1.400	0.977	.656	1.389	1.009	.677	1.383	1.018
21	22	.595	1.408	0.952	.603	1.405	0.960	.599	1.405	0.938

Table 24: Naphtho - (2'-3',6-7) - pentaphene



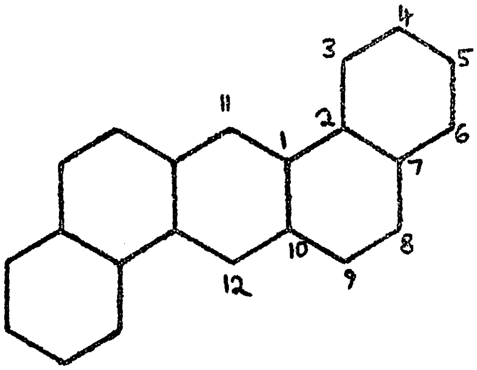
(a) Energy Eigenvalues $-x_i$

C_s symm.	I	II	III
A'	2.596155	2.321803	2.287053
	2.287050	2.140138	2.140540
	2.000000	1.848289	1.810337
	1.653864	1.583893	1.582493
	1.324922	1.295334	1.293583
	1.182644	1.056526	1.022570
	1.000000	0.913584	0.901852
	0.527938	0.588817	0.647570
A''	2.287050	2.140138	2.140540
	1.653864	1.583893	1.582493
	1.324922	1.295334	1.293583
	1.263077	1.242175	1.241505
	1.000000	0.913584	0.901852
	0.527938	0.590442	0.647570
	0.515722	0.588817	0.641455
$\sum_i (-x_i)$	21.145146	20.102767	20.134996

(b) Bond orders, bond lengths and β^0 values

Bond	p^{I}	r^{I}	$\beta^{0\,I}$	p^{II}	r^{II}	$\beta^{\prime\,II}$	p^{III}	r^{III}	$\beta^{0\,III}$
1 12	.725	1.372	1.063	.757	1.367	1.088	.777	1.364	1.091
1 14	.552	1.423	0.905	.531	1.430	0.882	.514	1.437	0.834
2 14	.568	1.417	0.923	.553	1.442	0.906	.533	1.429	0.857
2 16	.665	1.387	1.015	.720	1.373	1.060	.750	1.368	1.073
3 16	.410	1.493	0.721	.315	1.557	0.591	.252	1.621	0.412
12 13	.600	1.406	0.957	.559	1.420	0.912	.533	1.429	0.857
14 15	.505	1.441	0.853	.528	1.431	0.880	.562	1.419	0.892
16 17	.514	1.437	0.863	.506	1.440	0.854	.503	1.441	0.821

Table 25: 1-2, 5-6 dibenzanthracene



(a) Energy eigenvalues $-x_i$

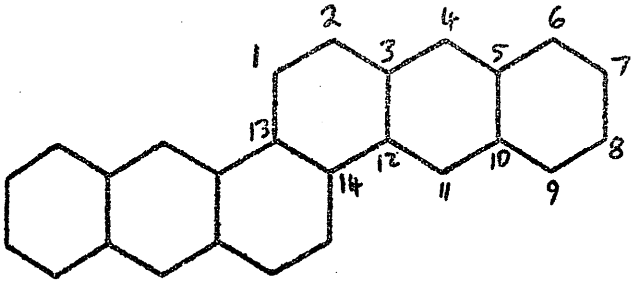
C_2 symm.	I*	II	III
A	2.5212	2.297931	2.272092
	1.9285	1.868925	1.885739
	1.4142	1.383560	1.354457
	1.0696	1.007036	1.009194
	0.7866	0.829201	0.849073
B	2.3059	2.135407	2.116235
	1.6588	1.607519	1.567686
	1.4142	1.319802	1.291535
	1.1834	1.098973	1.083250
	0.6843	0.684260	0.711983
	0.4735	0.540692	0.599867
$\sum_i(-x_i)$	15.4402	14.773306	14.741111

(b) Bond orders, bond lengths and β^0 values

Bond		p^{I*}	r^{I}	$\beta^{0\,I}$	p^{II}	r^{II}	$\beta^{0\,II}$	p^{III}	r^{III}	$\beta^{0\,III}$
1	2	.451	1.466	0.779	.391	1.504	0.695	.342	1.537	0.572
1	10	.513	1.438	0.862	.529	1.431	0.881	.557	1.421	0.886
1	11	.629	1.396	0.985	.652	1.391	1.005	.658	1.389	1.000
2	3	.594	1.407	0.951	.600	1.406	0.957	.602	1.405	0.942
2	7	.544	1.426	0.897	.583	1.412	0.940	.615	1.401	0.957
3	4	.697	1.379	1.042	.710	1.378	1.052	.715	1.375	1.049
4	5	.626	1.397	0.983	.609	1.403	0.966	.606	1.404	0.946
5	6	.703	1.378	1.047	.716	1.374	1.057	.719	1.373	1.053
6	7	.579	1.412	0.936	.585	1.411	0.942	.591	1.409	0.928
7	8	.499	1.444	0.845	.432	1.480	0.752	.376	1.513	0.633
8	9	.778	1.363	1.099	.853	1.357	1.118	.871	1.353	1.124
9	10	.501	1.443	0.848	.435	1.478	0.756	.381	1.511	0.641
10	12	.605	1.404	0.963	.627	1.398	0.984	.638	1.394	0.981

Table 26: Anthracene (2'-1', 1-2)-anthracene

(a) Energy eigenvalues $-x_i$



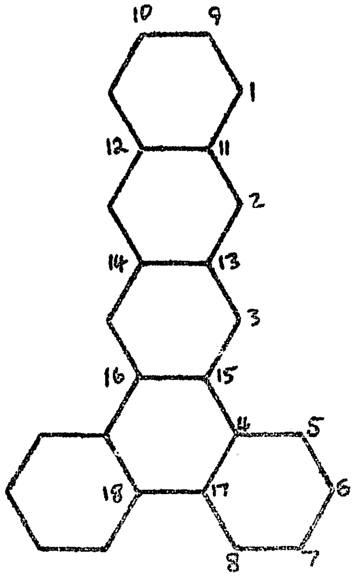
C_2 symm.	I	II	III
A	2.542614	2.306891	2.281989
	2.124721	1.977339	1.947379
	1.472215	1.409889	1.415119
	1.346698	1.336567	1.339953
	1.000000	0.956684	0.957879
	0.786504	0.742691	0.748813
	0.348233	0.414353	0.469712
B	2.358475	2.182259	2.175677
	1.826184	1.726634	1.703734
	1.533591	1.479795	1.455302
	1.216572	1.210015	1.209315
	1.115969	0.973528	0.939426
	0.570193	0.630183	0.668390
$\sum(-x_i)$	18.241968	17.346826	17.312689

(b) Bond orders, bond lengths and β' values

Bond		p^{I}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}
1	2	.758	1.366	1.039	.808	1.350	1.111	.842	1.356	1.116
1	13	.531	1.430	0.882	.479	1.452	0.818	.434	1.478	0.725
2	3	.510	1.438	0.859	.455	1.466	0.783	.410	1.493	0.686
3	4	.618	1.400	0.975	.652	1.390	1.005	.671	1.385	1.012
3	12	.494	1.445	0.839	.490	1.447	0.833	.501	1.442	0.819
4	5	.596	1.407	0.953	.606	1.404	0.963	.604	1.405	0.944
5	6	0.539	1.427	0.892	.506	1.440	0.854	.479	1.452	0.793
5	10	0.491	1.447	0.835	.499	1.443	0.845	.521	1.434	0.842
6	7	0.734	1.371	1.070	.773	1.364	1.097	.799	1.361	1.101
7	8	0.590	1.409	0.947	.538	1.428	0.891	.504	1.441	0.822
8	9	0.733	1.371	1.070	.772	1.364	1.096	.798	1.361	1.100
9	10	0.542	1.426	0.895	.509	1.439	0.858	.482	1.450	0.797
10	11	0.591	1.409	0.948	.599	1.406	0.956	.599	1.406	0.937
11	12	0.636	1.395	0.991	.668	1.386	1.016	.682	1.382	1.022
12	14	0.464	1.460	0.797	.419	1.488	0.735	.383	1.509	0.645
13	14	0.585	1.411	0.942	.656	1.389	1.009	.714	1.375	1.048

Table 27: 1-2, 3-4 dibenztetracene

(a) Energy eigenvalues $-x_i$

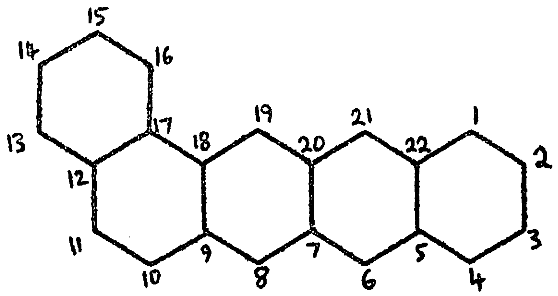


C_s symm	I	II	III
A'	2.568771	2.309339	2.278055
	2.349856	2.165173	2.150507
	1.981455	1.869387	1.854908
	1.567392	1.461518	1.441742
	1.312043	1.227891	1.194291
	1.136554	1.032799	1.019439
	0.726541	0.715493	0.736880
A''	1.971116	1.933319	1.952454
	1.441307	1.410405	1.416562
	1.213829	1.158838	1.145034
	0.914512	0.938548	0.956053
	0.746151	0.763419	0.804433
	0.355697	0.430070	0.495287
$\sum_i (-x_i)$	18.285223	17.416200	17.445644

(b) Bond orders, bond lengths and β^0 values

Bond		p^{I}	r^{I}	$\beta^{0\,I}$	p^{II}	r^{II}	$\beta^{0\,II}$	p^{III}	r^{III}	$\beta^{0\,III}$
1	9	.738	1.370	1.073	.781	1.363	1.100	.810	1.359	1.112
1	11	.535	1.429	0.887	.495	1.445	0.840	.462	1.461	0.794
2	11	.608	1.403	0.965	.632	1.396	0.988	.642	1.393	0.997
2	13	.600	1.406	0.957	.618	1.400	0.975	.627	1.398	0.984
3	13	.555	1.422	0.908	.524	1.433	0.075	.491	1.447	0.834
3	15	.671	1.385	1.018	.735	1.370	1.071	.776	1.364	1.098
4	5	.607	1.404	0.964	.626	1.398	0.982	.636	1.395	0.992
4	15	.419	1.488	0.375	.330	1.546	0.611	.266	1.605	0.506
4	17	.564	1.419	0.918	.603	1.405	0.960	.629	1.397	0.985
5	6	.685	1.381	1.029	.688	1.381	1.031	.685	1.382	1.028
6	7	.641	1.394	0.996	.637	1.395	0.993	.642	1.393	0.997
7	8	.685	1.382	1.028	.687	1.381	1.031	.684	1.382	1.028
8	17	.608	1.403	0.965	.627	1.398	0.983	.638	1.395	0.993
9	10	.585	1.411	0.942	.527	1.432	0.878	.486	1.449	0.828
11	12	.482	1.451	0.821	.477	1.453	0.815	.491	1.447	0.834
13	14	.471	1.456	0.806	.463	1.461	0.795	.481	1.451	0.820
15	16	.498	1.443	0.845	.474	1.455	0.811	.435	1.466	0.784
17	18	.418	1.489	0.733	.327	1.548	0.607	.261	1.611	0.496

Table 28: 1-2 benztetracene



(a) **Energy eigenvalues $-x_i$**

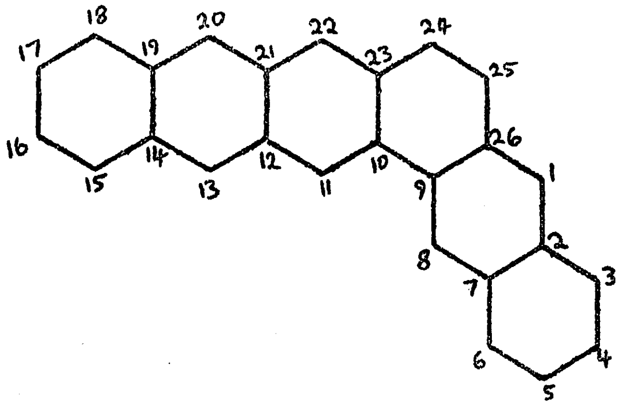
I	II	III
2.509115	2.234811	2.207084
2.303438	2.086652	2.063815
1.967577	1.836871	1.822231
1.633451	1.544939	1.506144
1.473261	1.400986	1.403309
1.349669	1.284117	1.266882
1.179718	1.100182	1.093923
1.086685	0.986837	0.985200
0.845431	0.801479	0.817049
0.687423	0.702903	0.717774
0.327052	0.401739	0.478451
15.362821	14.381521	14.361864

Table 28 cont'd:

(b) Bond orders, bond lengths, and β' values

Bond		p^{I}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}
1	2	.739	1.370	1.066	.790	1.362	1.096	.826	1.357	1.111
1	22	.533	1.429	0.851	.484	1.450	0.799	.442	1.474	0.737
2	3	.503	1.412	0.919	.515	1.437	0.835	.462	1.461	0.768
3	4	.739	1.370	1.066	.790	1.362	1.097	.827	1.357	1.111
4	5	.533	1.430	0.856	.482	1.450	0.797	.440	1.475	0.734
5	6	.613	1.402	0.954	.646	1.392	0.989	.663	1.387	1.005
5	22	.479	1.452	0.793	.471	1.456	0.782	.483	1.450	0.798
6	7	.592	1.409	0.929	.604	1.405	0.944	.610	1.403	0.950
7	8	.569	1.417	0.902	.547	1.425	0.874	.512	1.438	0.832
7	20	.466	1.459	0.773	.456	1.465	0.758	.478	1.452	0.792
8	9	.640	1.394	0.983	.705	1.377	1.041	.755	1.367	1.077
9	10	.492	1.446	0.808	.406	1.495	0.680	.330	1.546	0.549
9	18	.488	1.448	0.803	.462	1.461	0.768	.447	1.471	0.745
10	11	.785	1.363	1.094	.851	1.355	1.118	.900	1.350	1.132
11	12	.490	1.447	0.806	.405	1.496	0.677	.326	1.549	0.541
12	13	.584	1.412	0.919	.595	1.408	0.934	.606	1.404	0.946
12	17	.547	1.425	0.874	.591	1.409	0.928	.630	1.397	0.973
13	14	.698	1.378	1.035	.710	1.376	1.045	.710	1.376	1.045
14	15	.630	1.397	0.973	.616	1.401	0.957	.616	1.401	0.957
15	16	.693	1.380	1.031	.704	1.377	1.040	.706	1.377	1.042
16	17	.599	1.406	0.938	.610	1.403	0.951	.617	1.401	0.958
17	18	.443	1.473	0.739	.365	1.521	0.613	.291	1.577	0.476
18	19	.659	1.389	1.001	.722	1.373	1.055	.768	1.365	1.085
19	20	.563	1.419	0.894	.537	1.428	0.862	.503	1.441	0.821
20	21	.596	1.408	0.934	.610	1.403	0.950	.615	1.401	0.956
21	22	.611	1.402	0.952	.643	1.393	0.986	.660	1.388	1.002

Table 29: Hexaphene



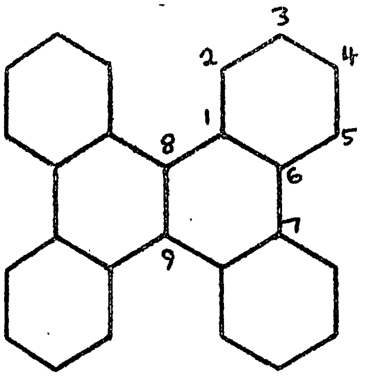
(a) Energy eigenvalues $-x_i$

I	II	III
2.529616	2.242956	2.209721
2.361777	2.133125	2.123053
2.133284	1.936795	1.888552
1.834132	1.690873	1.657985
1.534476	1.466607	1.453244
1.479086	1.381253	1.376889
1.361588	1.319562	1.318965
1.189726	1.141481	1.143207
1.127101	1.033246	1.024456
1.000000	0.856316	0.835975
0.823132	0.787079	0.784596
0.485598	0.553708	0.617625
0.335750	0.411825	0.490295
18.195264	16.954825	16.924563

Table 29 cont'd:

Bond	p^{I}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}
1 2	.581	1.412	0.917	.574	1.415	0.908	.553	1.422	0.882
1 26	.637	1.395	0.979	.691	1.380	1.030	.731	1.371	1.061
2 3	.546	1.425	0.873	.517	1.436	0.838	.494	1.445	0.810
2 7	.499	1.443	0.817	.520	1.434	0.842	.559	1.420	0.889
3 4	.728	1.372	1.059	.767	1.365	1.084	.792	1.362	1.098
4 5	.597	1.407	0.935	.547	1.425	0.874	.513	1.437	0.833
5 6	.727	1.372	1.058	.765	1.365	1.083	.791	1.362	1.097
6 7	.549	1.424	0.877	.521	1.434	0.843	.498	1.444	0.816
7 8	.575	1.415	0.909	.565	1.418	0.896	.545	1.425	0.871
8 9	.655	1.390	0.998	.710	1.376	1.045	.745	1.368	1.070
9 10	.433	1.479	0.723	.345	1.536	0.576	.266	1.605	0.434
9 26	.501	1.442	0.819	.493	1.446	0.810	.497	1.444	0.814
10 11	.666	1.386	1.008	.735	1.370	1.064	.784	1.363	1.094
10 23	.488	1.448	0.803	.459	1.463	0.764	.440	1.475	0.734
11 12	.557	1.421	0.887	.525	1.433	0.847	.485	1.449	0.801
12 13	.599	1.406	0.938	.618	1.400	0.960	.627	1.398	0.969
12 21	.468	1.458	0.776	.459	1.463	0.763	.482	1.451	0.796
13 14	.609	1.403	0.949	.637	1.395	0.980	.650	1.391	0.993
14 15	.535	1.429	0.859	.487	1.448	0.803	.447	1.471	0.744
14 19	.481	1.451	0.795	.476	1.454	0.788	.491	1.447	0.807
15 16	.738	1.370	1.065	.788	1.362	1.095	.823	1.358	1.110
16 17	.594	1.411	0.920	.518	1.435	0.838	.467	1.459	0.775
17 18	.738	1.370	1.066	.788	1.362	1.096	.824	1.358	1.110
18 19	.534	1.429	0.858	.486	1.449	0.801	.445	1.472	0.741
19 20	.610	1.403	0.951	.640	1.394	0.983	.653	1.390	0.996
20 21	.595	1.408	0.933	.612	1.402	0.953	.621	1.399	0.963
21 22	.564	1.419	0.895	.536	1.429	0.860	.495	1.445	0.812
22 23	.646	1.392	0.989	.716	1.374	1.050	.770	1.365	1.086
23 24	.483	1.450	0.798	.391	1.504	0.657	.310	1.560	0.510
24 25	.790	1.362	1.097	.858	1.354	1.120	.909	1.349	1.134
25 26	.481	1.451	0.793	.392	1.504	0.659	.309	1.561	0.508

Table 30: 1-2, 3-4, 5-6, 7-8 tetrabenznaphthalene



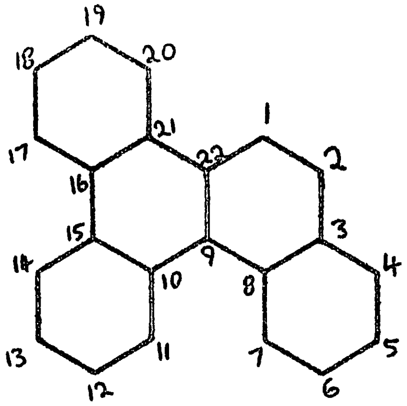
(a) Energy eigenvalues $-x_i$

C_{2v} symm.	I	II	III
A_1	2.621824	2.414229	2.269443
	1.661575	1.586302	1.528660
	1.308129	1.250619	1.195549
	0.511458	0.525395	0.575416
B_2	2.278414	2.150453	2.083562
	1.317431	1.262543	1.207767
	1.000000	0.981260	0.982092
A_2	1.891220	1.860851	1.871580
	1.000000	0.984451	0.991800
	0.704624	0.688954	0.716041
B_1	2.032624	1.951151	1.924959
	1.277730	1.199052	1.125157
	0.792632	0.792341	0.810953
$\sum_i(-x_i)$	18.397659	17.647599	17.282978

(b) Bond orders, bond lengths and β^0 values

Bond		p^{I}	r^{I}	$\beta^{0\,I}$	p^{II}	r^{II}	$\beta^{0\,II}$	p^{III}	r^{III}	$\beta^{0\,III}$
1	2	.590	1.409	0.948	.588	1.410	0.925	.593	1.409	0.930
1	6	.551	1.417	0.923	.572	1.416	0.905	.612	1.402	0.953
1	8	.459	1.436	0.869	.433	1.480	0.722	.371	1.517	0.624
2	3	.699	1.386	1.018	.711	1.375	1.046	.720	1.373	1.053
3	4	.629	1.400	0.973	.614	1.402	0.955	.604	1.405	0.944
4	5	.696	1.387	1.016	.708	1.376	1.043	.716	1.374	1.050
5	6	.597	1.407	0.953	.596	1.407	0.934	.600	1.406	0.940
6	7	.444	1.439	0.860	.415	1.490	0.694	.349	1.532	0.585
8	9	.631	1.400	0.974	.673	1.385	1.014	.758	1.366	1.079

Table 31: 1-2. 3-4. 5-6 tribenznaphthalene



(a) Energy eigenvalues $-x_i$

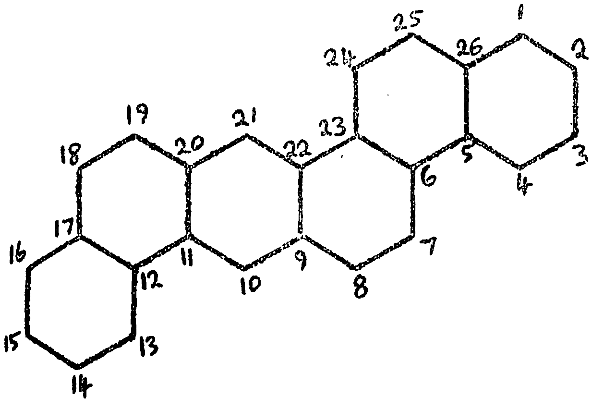
I	II	III
2.573324	2.262204	2.231741
2.204962	2.041310	2.039170
1.971009	1.900215	1.915986
1.698870	1.628259	1.617256
1.414214	1.326103	1.298772
1.311719	1.211216	1.176413
1.225088	1.104967	1.075929
1.000000	0.982515	0.991851
0.857702	0.855906	0.871293
0.710684	0.701129	0.749953
0.531921	0.570977	0.628817
15.499493	14.584783	14.597181

Table 31 cont'd:

(b) Bond orders, bond lengths and β' values

Bond	p^{I}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}
1 2	.746	1.368	1.071	.788	1.362	1.096	.813	1.359	1.106
1 22	.547	1.424	0.874	.510	1.438	0.830	.481	1.451	0.795
2 3	.531	1.430	0.854	.492	1.446	0.808	.464	1.460	0.771
3 4	.565	1.418	0.896	.553	1.422	0.881	.539	1.427	0.864
3 8	.528	1.431	0.851	.562	1.419	0.892	.597	1.407	0.935
4 5	.716	1.374	1.050	.744	1.369	1.069	.762	1.366	1.081
5 6	.612	1.402	0.953	.577	1.414	0.911	.554	1.422	0.882
6 7	.713	1.375	1.047	.741	1.369	1.068	.760	1.366	1.080
7 8	.574	1.415	0.907	.560	1.420	0.890	.543	1.426	0.868
8 9	.499	1.443	0.817	.478	1.453	0.791	.457	1.464	0.760
9 10	.452	1.467	0.753	.382	1.510	0.643	.311	1.559	0.513
9 22	.599	1.406	0.938	.675	1.384	1.016	.737	1.370	1.065
10 11	.593	1.408	0.931	.603	1.405	0.942	.609	1.403	0.950
10 15	.554	1.422	0.882	.595	1.408	0.933	.633	1.396	0.975
11 12	.696	1.379	1.033	.707	1.376	1.043	.709	1.376	1.044
12 13	.632	1.396	0.974	.617	1.401	0.959	.617	1.401	0.958
13 14	.693	1.380	1.031	.704	1.377	1.040	.706	1.377	1.042
14 15	.600	1.406	0.939	.611	1.403	0.951	.617	1.401	0.958
15 16	.437	1.477	0.729	.360	1.524	0.605	.289	1.580	0.472
16 17	.599	1.406	0.938	.610	1.403	0.950	.616	1.401	0.957
16 21	.557	1.421	0.886	.598	1.407	0.937	.635	1.395	0.978
17 18	.694	1.379	1.032	.704	1.377	1.040	.706	1.377	1.042
18 19	.633	1.396	0.976	.619	1.400	0.961	.618	1.400	0.960
19 20	.694	1.379	1.032	.705	1.377	1.041	.707	1.376	1.043
20 21	.598	1.407	0.936	.607	1.404	0.947	.613	1.402	0.955
21 22	.439	1.475	0.733	.366	1.520	0.616	.297	1.571	0.485

Table 52: 3-4, 8-9 dibenztetraphene



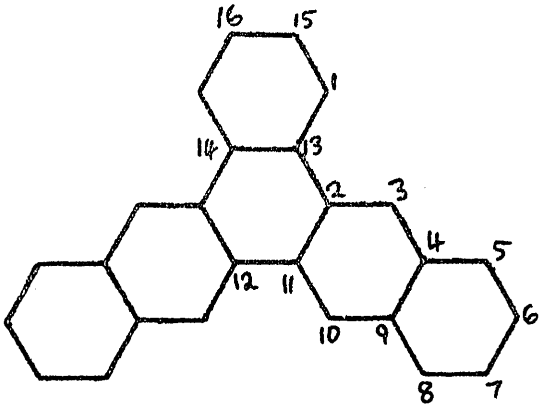
(a) Energy eigenvalues $-x_i$

I	II
2.545488	2.257034
2.381081	2.139071
2.100478	1.942875
1.772176	1.676881
1.595206	1.530009
1.462827	1.386244
1.344899	1.240654
1.270274	1.163249
1.085394	0.971138
0.911743	0.914740
0.729756	0.736810
0.682544	0.666276
0.428567	0.492448
18.310433	17.117430

(b) Bond orders, bond lengths and β' valu

Bond	p^{I}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}
1 2	.713	1.375	1.047	.738	1.370	1.065
1 26	.567	1.417	0.899	.560	1.420	0.890
2 3	.616	1.401	0.957	.585	1.411	0.920
3 4	.708	1.376	1.043	.733	1.371	1.062
4 5	.582	1.412	0.917	.573	1.416	0.906
5 6	.479	1.452	0.792	.449	1.469	0.748
5 26	.534	1.429	0.857	.569	1.417	0.901
6 7	.530	1.431	0.853	.474	1.455	0.785
6 23	.576	1.414	0.910	.643	1.393	0.986
7 8	.758	1.366	1.079	.811	1.359	1.105
8 9	.515	1.437	0.835	.458	1.464	0.761
9 10	.598	1.407	0.937	.614	1.402	0.956
9 22	.508	1.439	0.827	.522	1.434	0.844
10 11	.634	1.396	0.977	.666	1.387	1.007
11 12	.450	1.469	0.749	.383	1.509	0.644
11 20	.509	1.439	0.829	.519	1.435	0.840
12 13	.596	1.408	0.934	.602	1.405	0.941
12 17	.545	1.425	0.871	.587	1.411	0.923
13 14	.696	1.379	1.034	.711	1.375	1.046
14 15	.627	1.398	0.969	.608	1.404	0.948
15 16	.702	1.378	1.039	.717	1.374	1.051
16 17	.580	1.413	0.915	.587	1.411	0.923
17 18	.497	1.444	0.815	.422	1.486	0.705
18 19	.779	1.363	1.092	.840	1.356	1.115
19 20	.499	1.443	0.817	.425	1.484	0.709
20 21	.611	1.403	0.951	.642	1.393	0.985
21 22	.621	1.399	0.963	.638	1.394	0.981
22 23	.465	1.459	0.773	.421	1.487	0.703
23 24	.542	1.426	0.868	.498	1.443	0.816
24 25	.750	1.368	1.073	.796	1.361	1.099
25 26	.524	1.417	0.845	.477	1.453	0.790

Table 33: 6-7 benzpentaphene



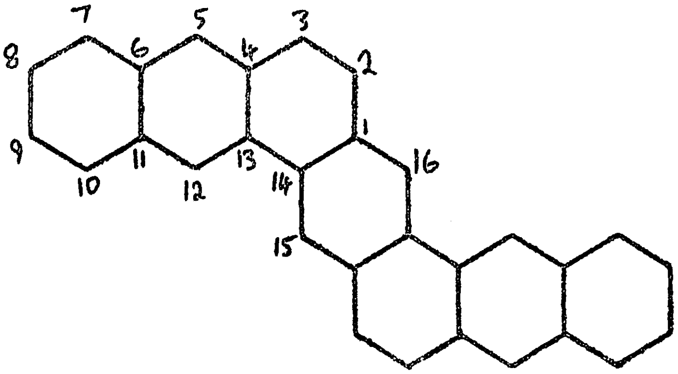
(a) Energy eigenvalues $-x_i$

C_s symm.	I	II
A'	2.579260	2.258597
	2.149134	1.997743
	1.812687	1.705029
	1.394159	1.322159
	1.212551	1.089387
	1.000000	0.914205
	0.505758	0.573546
A''	2.286939	2.093624
	1.644286	1.548461
	1.298063	1.247750
	1.140752	1.060924
	0.762824	0.746704
	0.520684	0.588203
$\sum_i(-x_i)$	18.307096	17.146331

(b) Bond orders, bond lengths and β' values.

Bond		p^I	r^I	β'^I	p^{II}	r^{II}	β'^{II}
1	13	.610	1.403	0.950	.629	1.397	0.972
1	15	.683	1.382	1.023	.688	1.381	1.027
2	3	.662	1.388	1.004	.722	1.373	1.054
2	11	.513	1.437	0.833	.503	1.441	0.821
2	13	.414	1.491	0.693	.313	1.558	0.516
3	4	.571	1.416	0.904	.555	1.422	0.883
4	5	.550	1.423	0.878	.525	1.432	0.847
4	9	.504	1.441	0.822	.530	1.431	0.853
5	6	.726	1.372	1.057	.762	1.366	1.081
6	7	.599	1.406	0.938	.552	1.423	0.880
7	8	.726	1.372	1.057	.762	1.366	1.081
8	9	.550	1.423	0.878	.525	1.432	0.847
9	10	.571	1.416	0.904	.555	1.422	0.884
10	11	.662	1.388	1.004	.722	1.373	1.054
11	12	.414	1.491	0.693	.314	1.558	0.517
13	14	.566	1.418	0.897	.609	1.403	0.949
15	16	.642	1.393	0.985	.637	1.395	0.980

Table 34: Naphtho (2'-3', 3-4) pentaphene



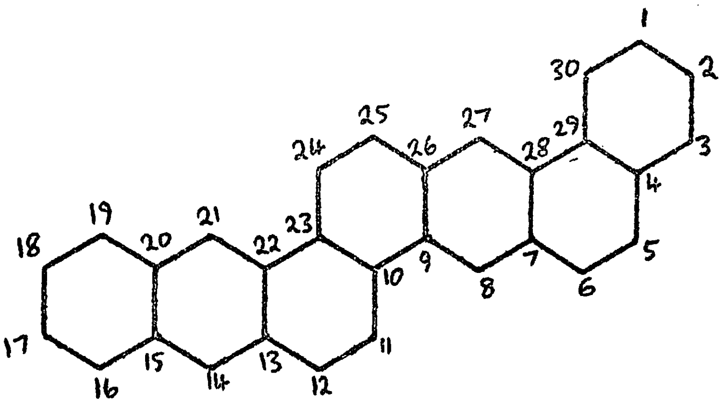
(a) Energy eigenvalues $-x_i$

C_2 symm.	I	II
A	2.550263	2.257236
	2.208499	2.015300
	1.678602	1.578989
	1.414214	1.365441
	1.161241	1.132605
	1.000000	0.864441
	0.536288	0.608269
B	2.416497	2.166232
	2.000000	1.806677
	1.550624	1.470954
	1.414214	1.304612
	1.197253	1.107040
	1.000000	0.890322
	0.576481	0.613605
	0.394037	0.462842
$\sum_i(-x_i)$	21.098212	19.644565

(b) Bond orders, bond lengths and β' values

Bond		p^I	r^I	β'^I	p^{II}	r^{II}	β'^{II}
1	2	.492	1.446	0.809	.411	1.493	0.688
1	14	.519	1.435	0.840	.541	1.427	0.866
1	16	.605	1.404	0.945	.630	1.397	0.972
2	3	.783	1.363	1.094	.848	1.355	1.117
3	4	.490	1.447	0.806	.406	1.495	0.680
4	5	.631	1.397	0.873	.681	1.383	1.021
4	13	.500	1.443	0.818	.494	1.445	0.811
5	6	.587	1.411	0.923	.585	1.411	0.922
6	7	.544	1.426	0.870	.511	1.438	0.831
6	11	.496	1.444	0.814	.515	1.437	0.835
7	8	.730	1.371	1.060	.771	1.364	1.087
8	9	.594	1.408	0.932	.541	1.427	0.867
9	10	.729	1.371	1.059	.770	1.365	1.086
10	11	.547	1.425	0.873	.515	1.436	0.835
11	12	.581	1.413	0.916	.577	1.414	0.911
12	13	.650	1.391	0.992	.698	1.378	1.035
13	14	.441	1.475	0.735	.364	1.522	0.611
14	15	.630	1.397	0.973	.657	1.389	0.999

Table 35: Anthraceno (2'-1', 8-9) tetraphene



(a) Energy eigenvalues $-x_i$

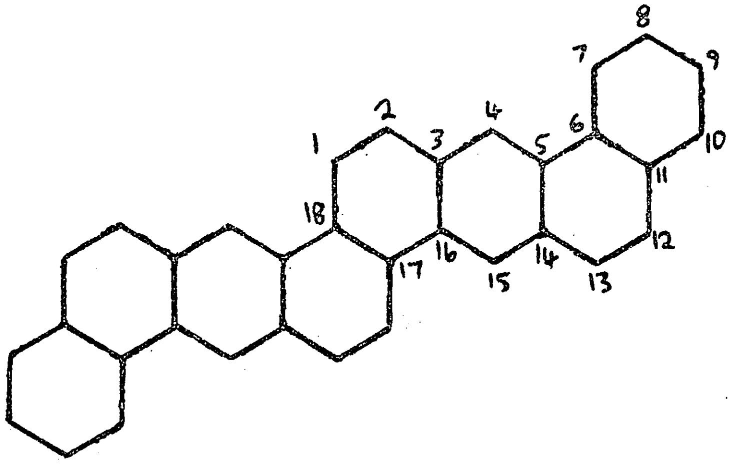
I	II
2.556939	2.262515
2.420842	2.168875
2.221184	2.015011
1.948637	1.804990
1.705199	1.605513
1.518789	1.426312
1.489155	1.406693
1.325618	1.270945
1.272037	1.183368
1.137608	1.051806
1.046266	0.913834
0.834681	0.837645
0.719463	0.687653
0.571777	0.615646
0.365130	0.433937
21.133329	19.684743

Table [illegible] contd.

(b) Bond orders, bond lengths and β' values

Bond	p^{I}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}
1 2	.627	1.398	0.970	.609	1.403	0.949
1 30	.696	1.379	1.034	.710	1.376	1.045
2 3	.702	1.378	1.038	.716	1.374	1.050
3 4	.580	1.413	0.915	.587	1.410	0.924
4 5	.497	1.444	0.814	.421	1.487	0.703
4 29	.545	1.425	0.871	.587	1.410	0.924
5 6	.780	1.363	1.092	.841	1.356	1.115
6 7	.499	1.443	0.817	.424	1.485	0.708
7 8	.612	1.402	0.953	.646	1.392	0.989
7 28	.508	1.439	0.827	.516	1.436	0.836
8 9	.619	1.400	0.961	.633	1.396	0.976
9 10	.470	1.457	0.780	.432	1.480	0.722
9 26	.506	1.440	0.824	.519	1.435	0.839
10 11	.529	1.431	0.851	.468	1.458	0.776
10 23	.582	1.412	0.917	.656	1.389	0.998
11 12	.760	1.366	1.080	.817	1.358	1.108
12 13	.509	1.439	0.828	.444	1.472	0.740
13 14	.619	1.400	0.961	.658	1.389	1.000
13 22	.495	1.445	0.812	.490	1.447	0.806
14 15	.596	1.408	0.934	.605	1.404	0.945
15 16	.540	1.427	0.865	.501	1.442	0.819
15 20	.492	1.446	0.808	.502	1.442	0.821
16 17	.734	1.371	1.063	.778	1.363	1.091
17 18	.591	1.409	0.928	.532	1.430	0.856
18 19	.733	1.371	1.062	.777	1.364	1.090
19 20	.542	1.426	0.868	.505	1.441	0.824
20 21	.590	1.409	0.927	.598	1.407	0.936
21 22	.637	1.395	0.980	.673	1.385	1.014
22 23	.462	1.461	0.769	.411	1.492	0.688
23 24	.537	1.428	0.861	.487	1.448	0.803
24 25	.752	1.367	1.075	.802	1.360	1.102
25 26	.519	1.435	0.840	.467	1.459	0.775
26 27	.596	1.407	0.935	.610	1.403	0.751
27 28	.636	1.395	0.978	.670	1.386	1.011
28 29	.449	1.469	0.748	.381	1.510	0.642
29 30	.596	1.407	0.934	.602	1.405	0.942

Table 36: Tetrapheno (9'-8', 8-9) tetraphene



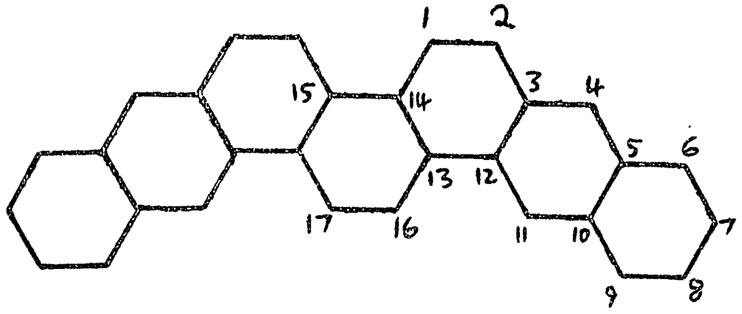
(a) Energy eigenvalues $-x_i$

C_2 symm.	I	II
A	2.566716	2.269742
	2.306855	2.069161
	1.798743	1.689594
	1.514793	1.422198
	1.271000	1.203547
	1.148803	1.049660
	0.855071	0.840854
	0.667535	0.639026
	0.382738	0.451170
B	2.459500	2.193953
	2.056634	1.901342
	1.671608	1.579231
	1.459899	1.373569
	1.372484	1.244709
	1.114314	1.001720
	0.795752	0.801933
	0.852062	0.624494
$\sum_i(-x_i)$	24.024508	22.355901

(b) Bond orders, bond lengths and β' values

Bond		p^{I}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}
1	2	.754	1.367	1.076	.805	1.360	1.103
1	18	.535	1.429	0.859	.483	1.450	0.797
2	3	.517	1.436	0.838	.463	1.460	0.770
3	4	.597	1.407	0.935	.612	1.402	0.952
3	16	.506	1.440	0.825	.520	1.434	0.841
4	5	.635	1.395	0.978	.668	1.386	1.009
5	6	.449	1.469	0.749	.382	1.510	0.643
5	14	.508	1.439	0.828	.517	1.436	0.838
6	7	.596	1.407	0.934	.602	1.405	0.941
6	11	.545	1.425	0.871	.587	1.410	0.924
7	8	.696	1.379	1.034	.711	1.375	1.046
8	9	.627	1.398	0.969	.608	1.403	0.948
9	10	.702	1.378	1.039	.717	1.374	1.051
10	11	.580	1.413	0.915	.587	1.411	0.923
11	12	.497	1.444	0.814	.421	1.487	0.704
12	13	.779	1.363	1.092	.841	1.356	1.115
13	14	.499	1.443	0.817	.424	1.485	0.709
14	15	.611	1.402	0.952	.644	1.393	0.987
15	16	.620	1.400	0.962	.635	1.395	0.978
16	17	.468	1.458	0.777	.427	1.483	0.713
17	18	.579	1.413	0.914	.649	1.391	0.991

Table 37: 2-3, 8-9 dibenzpicene



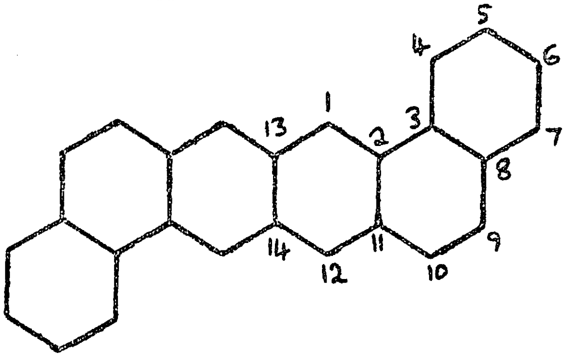
(a) Energy eigenvalues $-x_i$

C_s symm.	I	II
A'	2.561095	2.262631
	2.216503	2.014344
	1.679221	1.587760
	1.550440	1.459069
	1.272626	1.239038
	1.114141	0.954108
	0.770283	0.777764
	0.396334	0.471143
A''	2.412674	2.167020
	1.977103	1.798199
	1.446328	1.369844
	1.327251	1.271372
	1.072789	1.012224
	0.864166	0.755625
	0.460333	0.515571
$\sum_i (-x_i)$	21.121285	19.655712

(b) Bond orders, bond lengths and β' values

Bond		p^I	r^I	β'^I	p^{II}	r^{II}	β'^{II}
1	2	.769	1.365	1.085	.830	1.357	1.112
1	14	.518	1.435	0.838	.446	1.471	0.744
2	3	.502	1.442	0.820	.429	1.482	0.716
3	4	.623	1.399	0.966	.667	1.386	1.008
3	12	.497	1.444	0.815	.493	1.446	0.809
4	5	.592	1.409	0.930	.597	1.407	0.936
5	6	.541	1.427	0.866	.505	1.441	0.824
5	10	.494	1.445	0.810	.508	1.440	0.827
6	7	.732	1.371	1.062	.775	1.364	1.089
7	8	.592	1.409	0.930	.536	1.428	0.860
8	9	.731	1.371	1.061	.774	1.364	1.088
9	10	.544	1.426	0.870	.509	1.439	0.828
10	11	.587	1.411	0.923	.589	1.410	0.926
11	12	.642	1.393	0.985	.684	1.382	1.023
12	13	.454	1.466	0.756	.392	1.504	0.657
13	14	.564	1.419	0.895	.618	1.401	0.959
13	16	.567	1.418	0.899	.554	1.422	0.882
14	15	.504	1.441	0.823	.510	1.438	0.830
16	17	.719	1.373	1.053	.745	1.368	1.071

Table 38: 1-2, 6-7 dibenztetracene



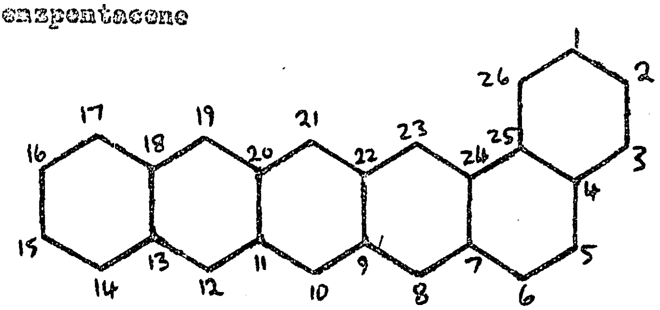
(a) Energy eigenvalues $-x_i$

C_2 symm.	I	II
A	2.531827	2.248847
	2.101845	1.948442
	1.556946	1.478853
	1.306423	1.168866
	1.093862	0.977481
	0.680018	0.666843
	0.358381	0.435522
B	2.387201	2.135995
	1.802675	1.700422
	1.802194	1.419896
	1.294106	1.223830
	0.931761	0.912545
	0.711366	0.746294
$\sum_i(-x_i)$	18.258605	17.063836

(b) Bond orders, bond lengths and β' values

Bond		p^I	r^I	β'^I	p^{II}	r^{II}	β'^{II}
1	2	.653	1.390	0.995	.708	1.376	1.043
1	13	.571	1.416	0.903	.557	1.421	0.887
2	3	.445	1.472	0.741	.369	1.518	0.621
2	11	.493	1.446	0.809	.478	1.453	0.791
3	4	.598	1.407	0.937	.608	1.403	0.948
3	8	.547	1.425	0.873	.590	1.410	0.927
4	5	.693	1.380	1.031	.705	1.377	1.041
5	6	.630	1.397	0.972	.614	1.402	0.955
6	7	.699	1.378	1.036	.712	1.375	1.046
7	8	.583	1.412	0.918	.593	1.408	0.931
8	9	.492	1.446	0.808	.409	1.494	0.685
9	10	.784	1.363	1.094	.848	1.355	1.117
10	11	.493	1.446	0.810	.411	1.493	0.688
11	12	.633	1.396	0.976	.688	1.381	1.027
12	14	.580	1.413	0.915	.572	1.416	0.905
13	14	.474	1.455	0.786	.478	1.453	0.790

Table 39: 1-2 benzpentacene



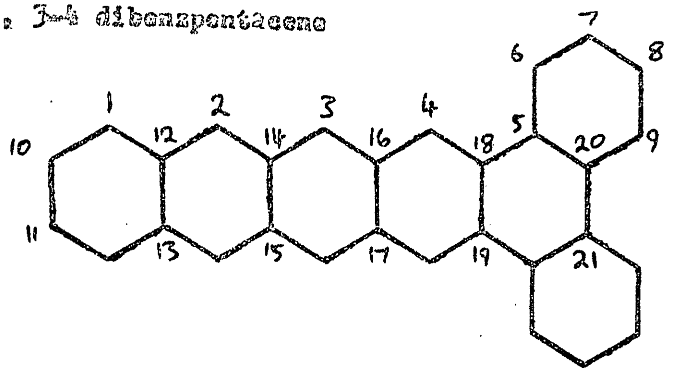
(a) Energy eigenvalues $-x_i$

I	II
2.523122	2.241214
2.377673	2.131665
2.123763	1.943341
1.819440	1.690782
1.558519	1.478011
1.472887	1.408024
1.361068	1.263762
1.230420	1.163712
1.089640	0.991453
1.000000	0.909692
0.752878	0.730016
0.617630	0.655549
0.243616	0.309677
18.170664	16.916902

Table 39 cont'd: (b) Bond orders, bond lengths and β' values

Bond	p^{I}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}
1 2	.631	1.397	0.974	.617	1.401	0.959
1 26	.692	1.380	1.030	.702	1.378	1.039
2 3	.697	1.379	1.035	.708	1.376	1.043
3 4	.584	1.411	0.920	.597	1.407	0.936
4 5	.489	1.448	0.804	.401	1.498	0.672
4 25	.547	1.424	0.874	.592	1.409	0.929
5 6	.786	1.362	1.094	.853	1.354	1.119
6 7	.491	1.447	0.807	.404	1.497	0.676
7 8	.643	1.393	0.986	.715	1.375	1.049
7 24	.483	1.450	0.798	.449	1.469	0.748
8 9	.564	1.418	0.895	.532	1.430	0.855
9 10	.604	1.405	0.943	.636	1.395	0.979
9 22	.457	1.464	0.761	.431	1.480	0.720
10 11	.591	1.409	0.928	.600	1.406	0.939
11 12	.581	1.413	0.916	.576	1.415	0.909
11 20	.454	1.466	0.755	.427	1.483	0.714
12 13	.620	1.400	0.962	.667	1.386	1.008
13 14	.530	1.431	0.853	.473	1.455	0.784
13 18	.474	1.455	0.785	.453	1.467	0.754
14 15	.741	1.369	1.068	.797	1.361	1.099
15 16	.580	1.413	0.915	.505	1.440	0.824
16 17	.741	1.369	1.068	.796	1.361	1.099
17 18	.530	1.431	0.853	.474	1.455	0.785
18 19	.619	1.400	0.961	.666	1.387	1.007
19 20	.582	1.412	0.918	.578	1.414	0.912
20 21	.589	1.410	0.926	.597	1.407	0.935
21 22	.608	1.404	0.948	.642	1.393	0.985
22 23	.558	1.421	0.887	.522	1.434	0.843
23 24	.663	1.388	1.004	.733	1.371	1.062
24 25	.442	1.474	0.737	.361	1.524	0.607
25 26	.600	1.406	0.938	.612	1.402	0.953

Table 40: 1-2, 3-4 dibenzpentacene



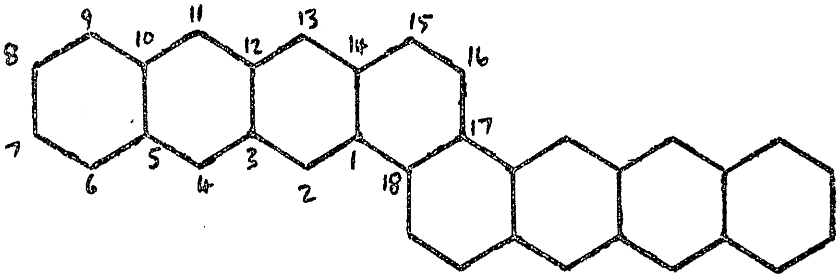
(a) Energy eigenvalues $-x_i$

C_s symm.	I	II
A'	2.573150	2.259404
	2.419469	2.160073
	2.150465	1.957846
	1.809396	1.657652
	1.457721	1.304200
	1.309285	1.199135
	1.095484	0.954826
	0.731905	0.703470
A''	1.971125	1.910516
	1.478700	1.432310
	1.292270	1.229525
	1.070259	1.034928
	0.812712	0.838360
	0.659703	0.684268
	0.262107	0.332698
$\sum_i(-x_i)$	21.093749	19.659211

(b) Bond orders, bond lengths and β' values

Bond		p^{I}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}
1	10	.741	1.369	1.068	.796	1.361	1.099
1	12	.530	1.431	0.853	.475	1.454	0.786
2	12	.618	1.400	0.960	.663	1.387	1.004
2	14	.584	1.412	0.919	.582	1.412	0.917
3	14	.587	1.411	0.923	.589	1.410	0.926
3	16	.612	1.402	0.953	.652	1.390	0.995
4	16	.550	1.424	0.877	.503	1.441	0.822
4	18	.674	1.384	1.015	.753	1.367	1.076
5	6	.608	1.404	0.948	.627	1.398	0.969
5	18	.419	1.488	0.701	.321	1.553	0.531
5	20	.564	1.419	0.895	.608	1.404	0.948
6	7	.685	1.382	1.024	.690	1.380	1.028
7	8	.641	1.394	0.984	.635	1.395	0.978
8	9	.684	1.382	1.024	.689	1.381	1.028
9	20	.609	1.403	0.949	.628	1.397	0.971
10	11	.580	1.413	0.915	.507	1.440	0.825
12	13	.475	1.454	0.786	.456	1.465	0.759
14	15	.456	1.465	0.758	.433	1.479	0.723
16	17	.462	1.461	0.768	.439	1.475	0.733
18	19	.494	1.445	0.810	.453	1.467	0.754
20	21	.417	1.489	0.697	.317	1.556	0.523

Table 41: Tetracene (1'-2', 1-2) tetracene



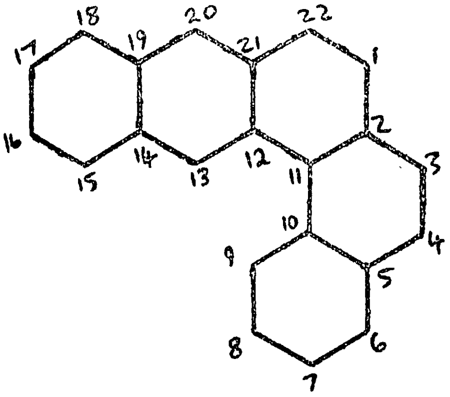
(a) Energy eigenvalues $-x_i$

C_2 symm	I	II
A	2.557882	2.259348
	2.303617	2.062669
	1.846024	1.684737
	1.472010	1.409634
	1.278652	1.196735
	1.158244	1.117944
	0.864472	0.761608
	0.703919	0.706392
	0.246964	0.313922
B	2.439063	2.185137
	2.095118	1.896835
	1.642044	1.542788
	1.506263	1.395907
	1.336351	1.281910
	1.087476	0.959818
	0.932112	0.870125
	0.393357	0.455468
$\sum_i(-x_i)$	23.863568	22.110977

(b) Bond orders, bond lengths and β' values

Bond		p^I	r^I	β'^I	p^{II}	r^{II}	β'^{II}
1	2	.648	1.392	0.991	.701	1.378	1.037
1	14	.482	1.451	0.796	.457	1.464	0.761
1	18	.461	1.462	0.767	.407	1.495	0.681
2	3	.570	1.417	0.902	.555	1.422	0.883
3	4	.592	1.409	0.929	.600	1.406	0.939
3	12	.463	1.461	0.769	.448	1.470	0.747
4	5	.614	1.402	0.955	.650	1.391	0.993
5	6	.532	1.430	0.856	.481	1.451	0.795
5	10	.478	1.453	0.791	.466	1.459	0.774
6	7	.740	1.369	1.067	.792	1.362	1.097
7	8	.582	1.412	0.918	.572	1.438	0.831
8	9	.740	1.369	1.067	.793	1.362	1.098
9	10	.532	1.430	0.855	.479	1.452	0.793
10	11	.615	1.401	0.956	.653	1.390	0.995
11	12	.588	1.410	0.925	.595	1.408	0.933
12	13	.576	1.414	0.910	.563	1.419	0.894
13	14	.630	1.397	0.972	.685	1.382	1.024
14	15	.508	1.439	0.828	.441	1.475	0.735
15	16	.759	1.366	1.079	.817	1.358	1.108
16	17	.528	1.431	0.851	.465	1.459	0.773
17	18	.589	1.410	0.925	.673	1.385	1.014

Table 42: 1-2 benztetraphene



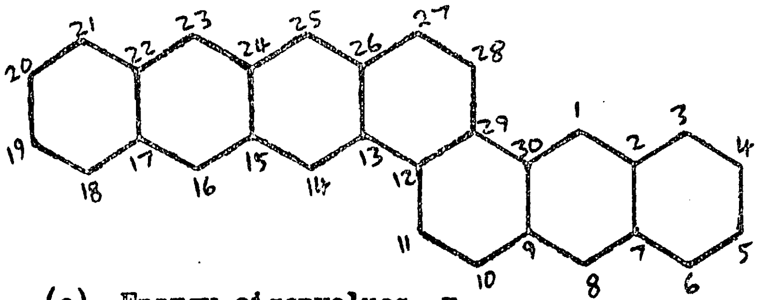
(a) Energy eigenvalues $-x_i$

I
2.533047
2.273711
1.965356
1.641058
1.464570
1.332738
1.198236
1.084844
0.844650
0.660116
0.418589
15.416915

(b) Bond orders, bond lengths and β' values

Bond		p^I	r^I	β'^I
1	2	.508	1.439	0.827
1	22	.772	1.364	1.087
2	3	.528	1.431	0.851
2	11	.580	1.413	0.915
3	4	.756	1.367	1.077
4	5	.524	1.433	0.845
5	6	.568	1.417	0.800
5	10	.530	1.431	0.852
6	7	.713	1.375	1.048
7	8	.614	1.402	0.955
8	9	.711	1.375	1.046
9	10	.576	1.415	0.910
10	11	.495	1.445	0.812
11	12	.473	1.455	0.784
12	13	.632	1.396	0.975
12	21	.494	1.445	0.810
13	14	.591	1.409	0.928
14	15	.542	1.426	0.867
14	19	.492	1.446	0.808
15	16	.733	1.371	1.062
16	17	.591	1.409	0.928
17	18	.733	1.371	1.062
18	19	.541	1.427	0.866
19	20	.594	1.408	0.932
20	21	.623	1.408	0.932
21	22	.505	1.441	0.823

Table 43. Anthracene (1'-2', 1-2) tetracene



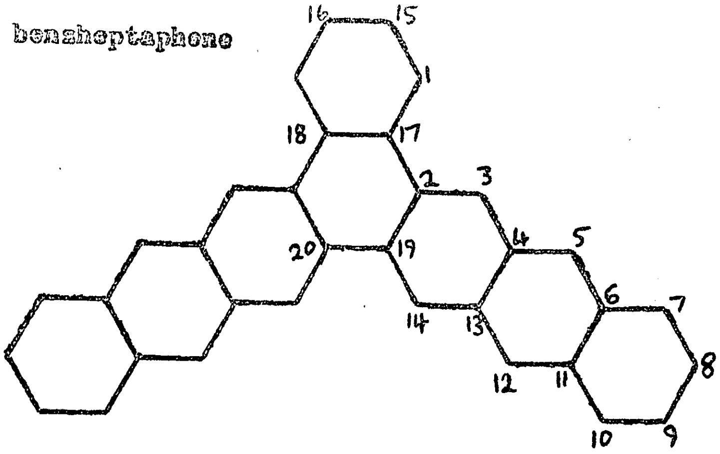
(a) **Energy eigenvalues $-x_i$**

I
2.551195
2.409129
2.227686
1.976496
1.704607
1.535281
1.450963
1.345303
1.257323
1.117555
1.069436
0.875695
0.763481
0.488799
0.279873
21.052819

(b) **Bond orders, bond lengths and β' values.**

Bond		p^{I}	r^{I}	β'^{I}
1	2	.591	1.409	0.929
1	30	.635	1.395	0.977
2	3	.542	1.426	0.867
2	7	.491	1.447	0.807
3	4	.733	1.371	1.062
4	5	.590	1.409	0.927
5	6	.734	1.370	1.063
6	7	.539	1.427	0.864
7	8	.597	1.407	0.935
8	9	.618	1.401	0.959
9	10	.512	1.438	0.831
9	30	.493	1.446	0.810
10	11	.756	1.367	1.078
11	12	.532	1.430	0.856
12	13	.460	1.462	0.765
12	29	.587	1.411	0.923
13	14	.649	1.391	0.991
13	26	.483	1.450	0.797
14	15	.569	1.417	0.902
15	16	.592	1.409	0.930
15	24	.463	1.461	0.769
16	17	.614	1.402	0.965
17	18	.532	1.430	0.856
17	22	.478	1.453	0.791
18	19	.739	1.369	1.067
19	20	.582	1.412	0.918
20	21	.740	1.369	1.067
21	22	.532	1.430	0.855
22	23	.615	1.401	0.956
23	24	.589	1.410	0.925
24	25	.575	1.415	0.909
25	26	.630	1.397	0.973
26	27	.507	1.440	0.826
27	28	.761	1.373	1.080
28	29	.526	1.432	0.849
29	30	.466	1.459	0.773

Table 44: 7-8 benzheptaphene



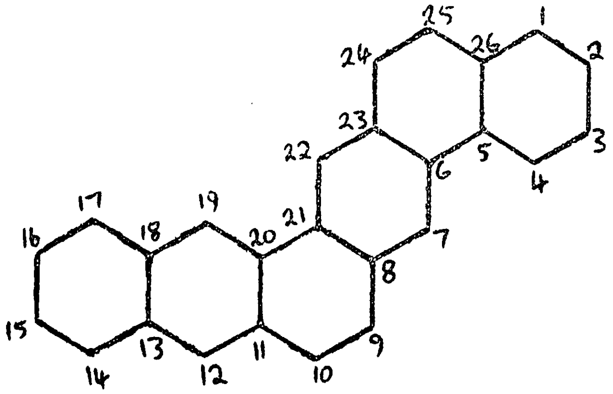
(a) Energy eigenvalues $-x_i$

C_s symm.	I
A'	2.592565
	2.303672
	1.978607
	1.638066
	1.447394
	1.208682
	1.116139
	0.810991
	0.372999
A''	2.406781
	1.984822
	1.509046
	1.371466
	1.140933
	0.932209
	0.765116
	0.358745
$\sum_i (-x_i)$	23.938233

(b) Bond orders, bond lengths and β' values.

Bond	p^I	r^I	β'^I
1 15	.682	1.382	1.022
1 17	.611	1.403	0.952
2 3	.676	1.384	1.017
2 17	.413	1.492	0.690
2 19	.498	1.444	0.815
3 4	.550	1.423	0.878
4 5	.603	1.405	0.942
4 13	.472	1.456	0.783
5 6	.606	1.404	0.946
6 7	.536	1.429	0.860
6 11	.483	1.450	0.797
7 8	.737	1.370	1.065
8 9	.586	1.411	0.922
9 10	.737	1.370	1.065
10 11	.536	1.429	0.860
11 12	.606	1.404	0.946
12 13	.602	1.405	0.942
13 14	.551	1.423	0.878
14 19	.675	1.384	1.015
15 16	.644	1.393	0.986
17 18	.565	1.418	0.897
19 20	.414	1.491	0.693

Table 45: 3-4, 8-9 dibenzotetraphene



(a) Energy eigenvalue $-x_i$

I
2.538366
2.371029
2.115733
1.805521
1.573142
1.463090
1.351267
1.234758
1.091378
1.000000
0.741522
0.554934
0.428737
18.269479

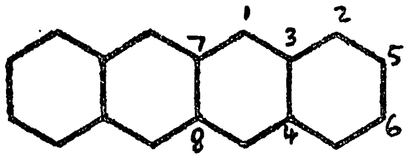
(b) Bond orders, bond lengths and β' values.

Bond		p^I	r^I	β'^I
1	2	.704	1.377	1.040
1	26	.578	1.414	0.913
2	3	.625	1.398	0.968
3	4	.698	1.378	1.035
4	5	.594	1.408	0.932
5	6	.453	1.467	0.755
5	26	.543	1.426	0.869
6	7	.623	1.399	0.965
6	23	.517	1.436	0.837
7	8	.612	1.402	0.953
8	9	.490	1.447	0.806
8	21	.515	1.436	0.835
9	10	.785	1.363	1.094
10	11	.488	1.448	0.804
11	12	.632	1.396	0.974
11	20	.500	1.442	0.818
12	13	.586	1.411	0.922
13	14	.544	1.426	0.870
13	18	.497	1.444	0.814
14	15	.730	1.371	1.060
15	16	.595	1.408	0.933
16	17	.729	1.372	1.059
17	18	.547	1.425	0.874
18	19	.580	1.413	0.915
19	20	.651	1.391	0.993
20	21	.439	1.476	0.732
21	22	.637	1.395	0.979
22	23	.599	1.406	0.938
23	24	.503	1.441	0.822
24	25	.776	1.364	1.090
25	26	.500	1.442	0.819

APPENDIX B

Energies, bond orders etc. calculated using the improved r(p) curve of Fig.3, and the Longuet-Higgins and Salem β'(r) curve.

Table 1: Tetracene



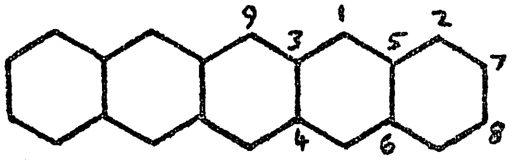
(a) Energy eigenvalues $-x_i$

C_{2v} symm.	I*	II	III
A_1	2.46673	2.278130	2.248053
	1.77748	1.686035	1.660570
	1.00000	0.875439	0.855706
B_2	2.19353	2.050627	2.036424
	1.29426	1.243099	1.243191
A_2	1.19353	1.169672	1.173807
	0.29496	0.336508	0.364052
B_1	1.46673	1.422300	1.403269
	0.77748	0.790870	0.788936
$\sum_i(-x_i)$	12.46470	11.852699	11.774006

(b) Bond orders, bond lengths and β' values

Bond		p^{I*}	r^I	β^I	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}
1	3	.618	1.400	0.964	.647	1.395	0.981	.666	1.390	1.008
1	7	.584	1.408	0.937	.534	1.420	0.900	.572	1.411	0.940
2	3	.530	1.420	0.898	.495	1.429	0.869	.471	1.435	0.870
2	5	.741	1.377	1.039	.778	1.370	1.060	.799	1.368	1.080
3	4	.475	1.434	0.853	.465	1.437	0.843	.463	1.438	0.861
5	6	.581	1.409	0.935	.531	1.420	0.899	.503	1.427	0.891
7	8	.458	1.439	0.839	.447	1.441	0.830	.471	1.435	0.870

Table 2: Pentacene



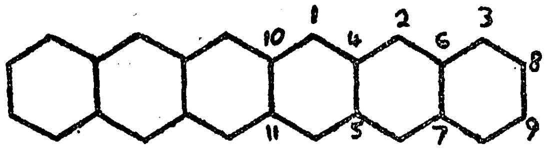
(a) Energy eigenvalues $-x_i$

C_{2v} symm.	I*	II	III
A_1	2.49551	2.295671	2.292528
	2.00000	1.869688	1.856761
	1.21969	1.146707	1.146349
B_2	2.30278	2.134603	2.123645
	1.61803	1.527553	1.520835
	1.00000	0.863527	0.843151
A_2	1.30278	1.270904	1.276311
	0.61703	0.640543	0.659125
B_1	1.49551	1.451297	1.462897
	1.00000	0.992417	1.000829
	0.21969	0.254116	0.279716
$\sum_i(-x_i)$	15.27202	14.447025	14.462145

(b) Bond orders, bond lengths and β' values

Bond	p^{I*}	r^I	β'^I	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	βI^{III}
1 3	.579	1.409	0.933	.571	1.411	0.929	.560	1.414	0.930
1 5	.622	1.400	0.965	.655	1.393	0.987	.674	1.389	0.980
2 5	.529	1.421	0.897	.491	1.431	0.865	.466	1.437	0.867
2 7	.742	1.377	1.040	.781	1.370	1.062	.802	1.367	1.081
3 4	.451	1.440	0.834	.432	1.445	0.819	.434	1.444	0.890
3 9	.596	1.406	0.945	.608	1.403	0.954	.613	1.402	0.967
5 6	.472	1.436	0.847	.457	1.439	0.837	.455	1.439	0.860
7 8	.579	1.409	0.933	.527	1.421	0.896	.497	1.429	0.886

Table 3: Hexacene



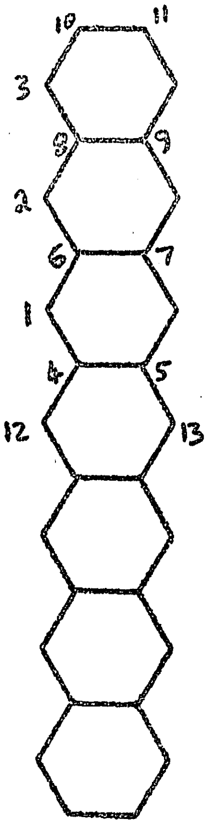
(a) Energy eigenvalues $-x_i$

C_{2v} symm.	I	II	III
A_1	2.512943	2.306494	2.299449
	2.141658	1.986675	1.971598
	1.501509	1.406481	1.398417
	1.000000	0.855924	0.827824
B_2	2.370021	2.187453	2.177512
	1.843487	1.719316	1.706633
	1.169375	1.080717	1.076209
A_2	1.370021	1.333529	1.344643
	0.843487	0.846437	0.861534
	0.169375	0.197673	0.220368
B_1	1.512943	1.468874	1.487777
	1.141658	1.121692	1.131485
	0.501509	0.527166	0.549437
$\sum_i(-x_i)$	18.077986	17.038431	17.052886

(b) Bond orders, bond lengths and β' values

Bond	p^{I}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}
1 4	.599	1.405	0.948	.617	1.401	0.955	.627	1.399	0.978
1 10	.590	1.407	0.941	.595	1.406	0.939	.594	1.406	0.953
2 4	.577	1.410	0.931	.566	1.412	0.920	.553	1.412	0.937
2 6	.623	1.399	0.967	.659	1.392	0.985	.679	1.388	1.011
3 6	.528	1.421	0.896	.490	1.431	0.858	.463	1.437	0.865
3 8	.742	1.377	1.039	.782	1.370	1.055	.803	1.367	1.081
4 5	.448	1.441	0.830	.425	1.445	0.800	.421	1.446	0.840
6 7	.471	1.436	0.847	.454	1.440	0.829	.449	1.441	0.851
8 9	.578	1.410	0.932	.525	1.421	0.890	.494	1.430	0.885
10 11	.443	1.443	0.827	.418	1.447	0.790	.413	1.448	0.833

Table 4: Heptacene



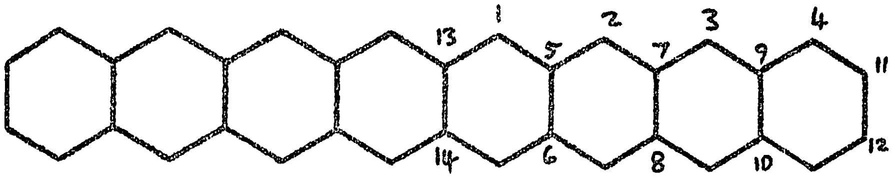
(a) Energy eigenvalues $-x_i$

C_{2v} symm.	I	II	III
A_1	2.524292	2.346230	2.346517
	2.236481	2.094551	2.092616
	1.718455	1.621209	1.619104
	1.134225	1.052033	1.048810
B_2	2.414214	2.252298	2.251570
	2.000000	1.880543	1.877563
	1.414214	1.333648	1.332421
	1.000000	0.878479	0.864625
A_2	1.414214	1.377057	1.386892
	1.000000	0.993098	1.006245
	0.414214	0.438813	0.457042
B_1	1.524292	1.481408	1.492602
	1.236481	1.212104	1.223317
	0.718455	0.729842	0.746163
	0.134225	0.154669	0.169964
$\sum_i (-x_i)$	20.883761	19.845989	19.914456

(b) Bond orders, bond lengths and β' values

Bond		p^{I}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}
1	4	.588	1.409	0.947	.589	1.409	0.947	.584	1.410	0.943
1	6	.600	1.407	0.955	.617	1.403	0.965	.627	1.401	0.971
2	6	.576	1.412	0.939	.565	1.414	0.932	.552	1.417	0.924
2	8	.623	1.402	0.969	.655	1.395	0.988	.673	1.391	1.000
3	8	.528	1.421	0.908	.490	1.430	0.886	.467	1.435	0.873
3	10	.743	1.377	1.048	.782	1.369	1.078	.803	1.364	1.094
4	5	.441	1.440	0.859	.420	1.444	0.847	.419	1.444	0.846
4	12	.593	1.408	0.950	.601	1.406	0.956	.604	1.406	0.958
6	7	.447	1.439	0.862	.430	1.442	0.852	.430	1.442	0.852
8	9	.471	1.434	0.875	.460	1.436	0.869	.457	1.437	0.867
10	11	.578	1.411	0.940	.526	1.422	0.907	.496	1.428	0.889

Table 5: Octacene



(a) Energy eigenvalues $-x_i$

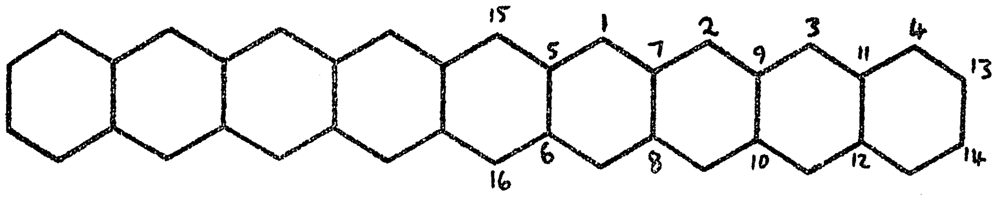
C_{2v} symm.	I	II	III
A_1	2.532089	2.351540	2.352318
	2.302776	2.150952	2.149354
	1.879385	1.764801	1.761894
	1.347296	1.261520	1.260032
	1.000000	0.875488	0.860597
B_2	2.444759	2.277110	2.277210
	2.111613	1.977607	1.975180
	1.618034	1.521024	1.519298
	1.108781	1.018150	1.013327
A_2	1.444759	1.405640	1.416335
	1.111613	1.095504	1.107647
	0.618034	0.632519	0.648952
	0.108781	0.125229	0.138081
B_1	1.532089	1.488875	1.501286
	1.302776	1.273146	1.284090
	0.879385	0.878948	0.893072
	0.347296	0.370331	0.387746
$\sum_i (-x_i)$	23.689468	22.468389	22.546423

Table 5: Octacene (cont'd)

(b) Bond orders, bond lengths and β' values

Bond	p^{I}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}
1 5	.594	1.408	0.951	.604	1.406	0.958	.609	1.405	0.961
1 13	.592	1.409	0.949	.597	1.407	0.953	.597	1.407	0.953
2 5	.588	1.409	0.946	.587	1.409	0.946	.582	1.411	0.942
2 7	.601	1.407	0.955	.618	1.403	0.966	.629	1.400	0.973
3 7	.576	1.412	0.939	.564	1.414	0.932	.551	1.417	0.923
3 9	.623	1.402	0.969	.656	1.395	0.989	.674	1.391	1.001
4 9	.528	1.421	0.908	.490	1.430	0.885	.466	1.435	0.872
4 11	.743	1.377	1.048	.782	1.369	1.078	.803	1.364	1.094
5 6	.441	1.440	0.858	.418	1.444	0.846	.416	1.445	0.845
7 8	.447	1.439	0.862	.429	1.442	0.852	.428	1.442	0.852
9 10	.471	1.434	0.875	.459	1.436	0.869	.456	1.437	0.867
11 12	.578	1.411	0.940	.525	1.422	0.907	.495	1.428	0.888
13 14	.439	1.440	0.858	.415	1.445	0.844	.413	1.445	0.843

Table 6: Nonacene



(a) Energy eigenvalues $-x_i$

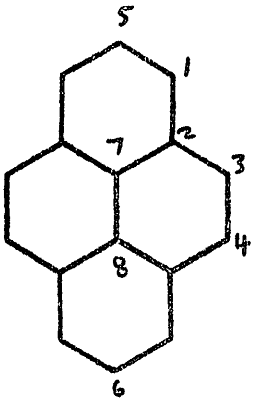
C_{2v} symm.	I	II	III
A_1	2.537673	2.356228	2.355961
	2.350830	2.192359	2.190361
	2.000000	1.872429	1.868745
	1.536547	1.438612	1.435907
	1.089819	0.992558	0.985322
B_2	2.466732	2.295466	2.294714
	2.193527	2.049381	2.046676
	1.777484	1.666032	1.662596
	1.294963	1.204546	1.201780
	1.000000	0.873142	0.857743
A_2	1.466732	1.426839	1.437431
	1.193527	1.171201	1.183084
	0.777484	0.782108	0.796305
	0.294963	0.316418	0.332690
B_1	1.537673	1.495117	1.507434
	1.350830	1.318202	1.328803
	1.000000	0.991042	1.003663
	0.536547	0.552523	0.568517
	0.089819	0.103303	0.113778
$\sum_i (-x_i)$	26.495151	25.097512	25.171417

Table 6: Nonacene (Cont'd)

(b) Bond orders, bond lengths and β° values

Bond	p^{I}	r^{I}	$\beta^{\circ\,I}$	p^{II}	r^{II}	$\beta^{\circ\,II}$	p^{III}	r^{III}	$\beta^{\circ\,III}$
1 5	.591	1.409	0.949	.595	1.408	0.952	.594	1.408	0.951
1 7	.595	1.408	0.951	.605	1.406	0.958	.611	1.404	0.961
2 7	.587	1.409	0.946	.587	1.410	0.945	.581	1.411	0.942
2 9	.601	1.407	0.956	.619	1.403	0.966	.629	1.400	0.973
3 9	.576	1.412	0.939	.564	1.414	0.931	.550	1.417	0.923
3 11	.623	1.402	0.969	.656	1.395	0.989	.675	1.391	1.002
4 11	.528	1.421	0.908	.490	1.430	0.885	.466	1.435	0.872
4 13	.743	1.377	1.048	.782	1.369	1.078	.803	1.364	1.094
5 6	.438	1.440	0.857	.413	1.445	0.843	.410	1.446	0.841
5 15	.593	1.408	0.950	.600	1.407	0.955	.602	1.406	0.956
7 8	.440	1.440	0.858	.417	1.445	0.845	.415	1.445	0.844
9 10	.447	1.439	0.862	.428	1.442	0.852	.428	1.442	0.851
11 12	.471	1.434	0.875	.459	1.436	0.868	.456	1.437	0.867
13 14	.578	1.411	0.940	.525	1.422	0.906	.495	1.429	0.888

Table 7: Pyrene



(a) Energy eigenvalues - x_i

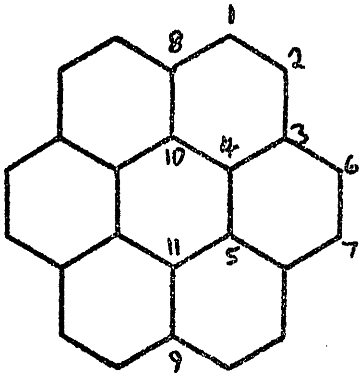
C_{2v} symm.	I*	II	III	IV
A_1	2.53209	2.327011	2.321134	2.319328
	1.34730	1.327295	1.324600	1.322599
	1.00000	1.003853	1.012262	1.013462
B_2	1.80194	1.706558	1.687924	1.680328
	0.44504	0.487658	0.514881	0.528408
A_2	1.24698	1.134904	1.127597	1.126055
B_1	2.00000	1.890524	1.895504	1.900703
	0.87939	0.805494	0.798672	0.799050
$(-x_i)$	11.25275	10.683397	10.682574	10.689934

(b) Bond orders, bond lengths and β' values

Bond	p^{I*}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}	p^{IV}	r^{IV}
1 2	.594	1.406	0.944	.610	1.403	0.955	.617	1.401	0.961	.620	1.400
1 5	.670	1.390	0.996	.669	1.390	0.996	.668	1.390	0.996	.667	1.390
2 3	.504	1.427	0.875	.459	1.439	0.839	.436	1.444	0.822	.424	1.447
2 7	.524	1.422	0.892	.535	1.419	0.902	.545	1.417	0.909	.551	1.415
3 4	.777	1.361	1.059	.815	1.366	1.075	.833	1.364	1.083	.841	1.362
7 8	.536	1.419	0.903	.521	1.423	0.888	.501	1.428	0.873	.489	1.431

Table 8: Coronene

(a) Energy eigenvalues

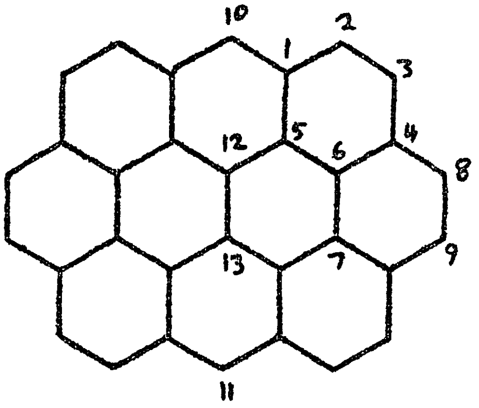


(C_{2v})	I*	II	III	IV
A_1	2.67513	2.435168	2.428158	2.424069
	1.67513	1.573301	1.566910	1.564005
	1.53919	1.456050	1.442156	1.431972
	0.53919	0.537891	0.549751	0.557263
B_2	2.21432	2.053330	2.047172	2.044518
	1.00000	1.041519	0.952065	1.061447
	1.00000	0.949914	0.952064	0.952176
A_2	1.67513	1.573301	1.566920	1.318438
	0.53919	0.537891	0.549754	0.469775
B_1	2.21432	2.053331	2.047169	2.044544
	1.21432	1.065595	1.050000	1.043692
	1.00000	0.949914	0.952082	0.802688
$\sum_i x_i$	17.28592	16.227205	16.207292	16.187113

(b) Bond orders, bond lengths and β' values

Bond	p^{I*}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}	p^{IV}	r^{IV}
1 2	.745	1.376	1.044	.769	1.372	1.055	.779	1.370	1.061	.785	1.369
1 8	.538	1.418	0.907	.518	1.423	0.888	.508	1.426	0.878	.502	1.427
3 4	.538	1.418	0.907	.562	1.413	0.921	.578	1.410	0.933	.589	1.407
4 5	.522	1.422	0.896	.512	1.425	2.883	.504	1.427	0.875	.498	1.429

Table 9: Ovalene



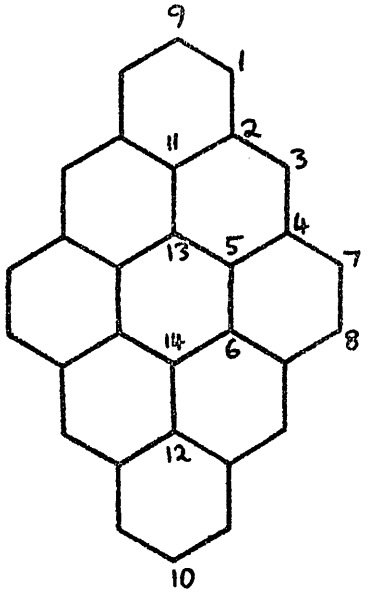
(a) Energy eigenvalues $-x_i$

C_{2v} symm.	I	II	III
A_1	2.741020	2.505390	2.516719
	2.000000	1.865987	1.875449
	1.697124	1.603302	1.611745
	1.000000	0.958520	0.968476
	0.824152	0.843389	0.861882
A_2	1.950627	1.826058	1.832752
	1.142384	1.004370	0.997019
	0.769052	0.759788	0.776765
B_2	2.434764	2.246374	2.257539
	1.516274	1.429085	1.431987
	1.305800	1.264749	1.276071
	0.605225	0.585008	0.591939
B_1	2.303555	2.137880	2.148662
	1.496453	1.392316	1.399443
	1.126413	1.068442	1.078937
	0.335875	0.355949	0.374229
$\sum_i (-x_i)$	23.248718	21.846608	21.999613

(b) Bond orders, bond lengths and β' values

Bond	p^{I*}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}
1 2	.511	1.426	0.895	.475	1.432	0.880	.461	1.438	0.861
1 5	.508	1.426	0.894	.513	1.424	0.900	.520	1.423	0.905
1 10	.604	1.40	0.955	.617	1.402	0.967	.622	1.399	0.978
2 3	.763	1.373	1.060	.796	1.365	1.090	.809	1.365	1.090
3 4	.519	1.42	0.900	.486	1.430	0.885	.471	1.436	0.869
4 6	.535	1.4	0.910	.555	1.415	0.929	.568	1.412	0.937
4 8	.557	1.41	0.925	.550	1.416	0.925	.550	1.416	0.923
5 6	.526	1.42	0.904	.514	1.424	0.900	.504	1.428	0.890
5 12	.541	1.41	0.915	.549	1.417	0.923	.554	1.415	0.928
6 7	.521	1.47	0.900	.516	1.423	0.904	.515	1.424	0.90^{0}
8 9	.726	1.38	1.035	.740	1.377	1.047	.742	1.374	1.060
12 13	.497	1.429	0.887	.479	1.431	0.882	.471	1.436	0.869

Table 10: 2-3, 8-9 dibenzcoronene



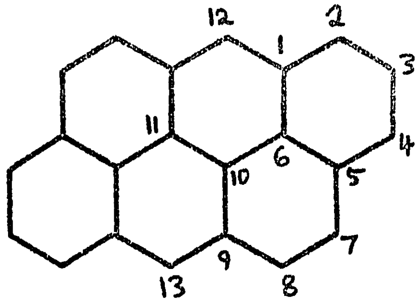
(a) Energy eigenvalues $-x_i$

C_{2v} symm.	I	II	III
A_1	2.716258	2.483119	2.491155
	2.037634	1.904079	1.907505
	1.596663	1.538727	1.551964
	1.115875	1.069640	1.069786
	0.538884	0.584518	0.616263
B_2	2.228328	2.073581	2.079108
	1.360409	1.269352	1.269263
	1.000000	1.001309	1.023172
	0.185885	0.216507	0.236935
A_2	1.774623	1.652786	1.660502
	1.000000	0.896963	0.892973
B_1	2.404039	2.217971	2.225061
	1.593990	1.505564	1.508991
	1.162195	1.078796	1.088492
	0.845089	0.766752	0.759128
$\sum_i (-x_i)$	21.559874	20.259662	20.380295

(b) Bond orders, bond lengths and β' values

Bond		p^{I}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}
1	2	.571	1.416	0.926	.580	1.411	0.941	.586	1.410	0.945
1	9	.670	1.386	1.017	.670	1.392	0.998	.670	1.392	0.998
2	3	.549	1.424	0.902	.530	1.421	0.909	.515	1.424	0.900
2	11	.510	1.438	0.859	.512	1.425	0.898	.517	1.424	0.901
3	4	.646	1.392	1.000	.688	1.388	1.011	.707	1.384	1.024
4	5	.487	1.449	0.828	.472	1.433	0.876	.465	1.435	0.872
4	7	.487	1.448	0.829	.434	1.441	0.855	.412	1.446	0.842
5	6	.567	1.418	0.921	.579	1.411	0.940	.581	1.411	0.942
5	13	.518	1.435	0.868	.519	1.423	0.903	.523	1.423	0.905
7	8	.788	1.362	1.103	.831	1.358	1.115	.847	1.355	1.127
11	13	.548	1.424	0.901	.549	1.417	0.922	.543	1.418	0.918

Table 11: Anthanthrene



(a) Energy eigenvalues $-x_i$

C_2 symm.	I	II	III
A	2.625997	2.416783	2.424732
	1.777259	1.682913	1.689656
	1.534285	1.469204	1.475342
	1.209901	1.169401	1.181641
	0.874820	0.796329	0.790454
	0.290959	0.329211	0.353582
B	2.261340	2.108319	2.114741
	1.965927	1.859047	1.865164
	1.232394	1.183119	1.185156
	1.103514	1.014571	1.015419
	0.750047	0.783785	0.808926
$\sum_i (-x_i)$	15.626442	14.812682	14.904812

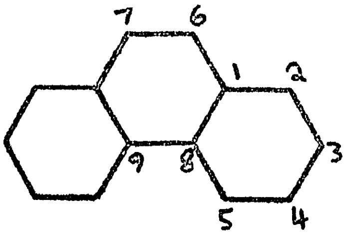
(b) Bond orders, bond lengths and β' values

Bond		p^I	r^I	β'^I	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}
1	2	.563	1.415	0.929	.561	1.415	0.929	.559	1.415	0.928
1	6	.507	1.428	0.891	.512	1.425	0.898	.521	1.423	0.903
1	12	.561	1.415	0.927	.549	1.417	0.922	.540	1.419	0.916
2	3	.689	1.389	1.008	.701	1.386	1.020	.708	1.384	1.024
3	4	.650	1.397	0.983	.637	1.399	0.978	.628	1.401	0.972
4	5	.606	1.406	0.956	.631	1.400	0.974	.644	1.397	0.982
5	6	.520	1.424	0.900	.523	1.422	0.905	.524	1.422	0.906
5	7	.494	1.430	0.885	.446	1.439	0.861	.425	1.443	0.850
6	10	.550	1.418	0.920	.547	1.418	0.921	.540	1.419	0.916
7	8	.784	1.369	1.078	.824	1.360	1.110	.840	1.357	1.121
8	9	.493	1.430	0.885	.444	1.439	0.860	.423	1.443	0.849
9	10	.487	1.432	0.880	.477	1.432	0.878	.474	1.433	0.877
9	13	.640	1.399	0.976	.676	1.391	1.002	.691	1.388	1.013
10	11	.541	1.420	0.915	.555	1.416	0.926	.565	1.414	0.932

APPENDIX C

Energies, bond orders etc. calculated as for molecules in Appendix B, but with special provision made for extreme short and long bonds, as described in § 6.3.

Table 1: Phenanthrene



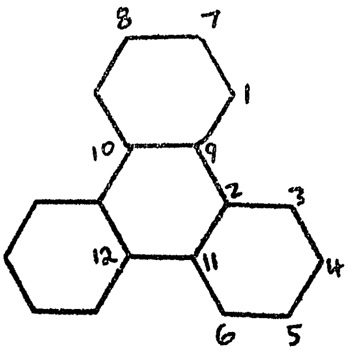
(a) Energy eigenvalues $-x_i$

C_2 symm.	I	II	III	IV
A'	2.255841	2.281178	2.284230	2.284601
	1.429019	1.503049	1.502608	1.502689
	1.209599	1.232885	1.240754	1.242503
	0.724083	0.703251	0.687811	0.681615
A''	1.940954	1.913817	1.908630	1.905832
	1.064673	1.070064	1.074528	1.076752
	0.812916	0.779482	0.771244	0.768825
$\sum_i (-x_i)$	9.437084	9.483726	9.469805	9.462817

(b) Bond orders, bond lengths and β' values

Bond	p^{I}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}	p^{IV}	r^{IV}	β'^{IV}
1 2	.628	1.401	0.972	.608	1.405	0.960	.595	1.408	0.951	.586	1.410	0.945
1 6	.339	1.460	0.804	.392	1.410	0.831	.415	1.445	0.844	.427	1.443	0.851
1 8	.607	1.405	0.959	.591	1.409	0.948	.586	1.410	0.945	.586	1.410	0.945
2 3	.682	1.389	1.006	.696	1.396	1.017	.708	1.384	1.024	.716	1.382	1.030
3 4	.649	1.396	0.985	.631	1.400	0.975	.619	1.402	0.967	.610	1.404	0.961
4 5	.680	1.390	1.005	.694	1.387	1.015	.705	1.385	1.023	.713	1.383	1.028
5 8	.632	1.400	0.975	.613	1.404	0.963	.601	1.407	0.955	.592	1.408	0.949
6 7	.895	1.345	1.166	.863	1.352	1.140	.848	1.355	1.128	.840	1.356	1.121
8 9	.317	1.465	0.791	.373	1.454	0.821	.395	1.449	0.832	.405	1.447	0.838

Table 2: Triphenylene



(a) Energy Eigenvalues $-x_i$

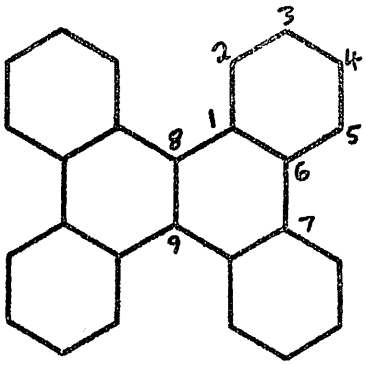
C_v symm ($\mathcal{D}_{3h}$)		I	II	III	IV
A'	(A_2)	2.332253	2.320636	2.345921	2.348122
	(E)	1.950012	1.925866	1.942828	1.922509
	(A_2)	1.275427	1.277255	1.289376	1.292069
	(E)	1.188240	1.195939	1.211062	1.214734
	(E)	0.758644	0.723369	0.707638	0.701191
A''	(E)	1.950012	1.925866	1.924828	1.922509
	(E)	1.188240	1.195939	1.211062	1.214734
	(A_1)	0.907680	0.898892	0.896297	0.897191
	(E)	0.758644	0.723369	0.707638	0.701191
$\sum_i(-x_i)$		12.309150	12.187131	12.218648	12.214250

(b) Bond orders, bond lengths and β^0 values

Bond	p^{I}	r^{I}	$\beta^{0\,I}$	p^{II}	r^{II}	$\beta^{0\,II}$	p^{III}	r^{III}	$\beta^{0\,III}$	p^{IV}	r^{IV}	$\beta^{0\,IV}$
1 7	.676	1.390	1.002	.684	1.389	1.008	.692	1.387	1.013	.697	1.386	1.017
1 9	.637	1.399	0.978	.626	1.401	0.971	.617	1.403	0.965	.611	1.404	0.961
2 9	.300	1.469	0.780	.334	1.462	0.800	.359	1.456	0.814	.369	1.455	0.818
2 11	.613	1.404	0.963	.603	1.406	0.957	.596	1.408	0.952	.595	1.408	0.951
4 5	.653	1.395	0.987	.643	1.397	0.982	.635	1.399	0.977	.629	1.400	0.973

Table 3: 1-2, 3-4, 5-6, 7-8 tetrabenznaphthalene

(a) Energy eigenvalues $-x_i$

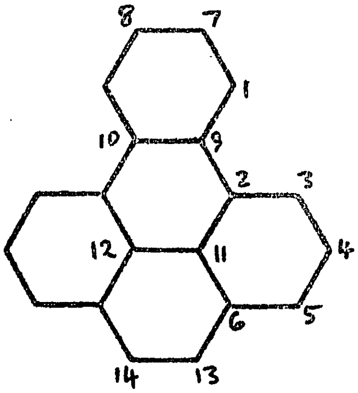


C_{2v} symm.	I	II	III	IV
A_1	2.341739	2.400140	2.409464	2.410867
	1.506626	1.579248	1.587492	1.587253
	1.209775	1.232438	1.239705	1.241681
	0.587146	0.565640	0.557610	0.554460
B_2	2.167050	2.157296	2.155108	2.154827
	1.230802	1.246968	1.253027	1.254749
	1.000000	0.988218	0.986695	0.987372
A_2	1.914530	1.881255	1.873645	1.871344
	1.000000	0.989173	0.988694	0.989967
	0.783322	0.732055	0.714489	0.707637
B_1	1.974111	1.957573	1.954064	1.953273
	1.141091	1.168372	1.177048	1.181041
	0.830084	0.805520	0.801160	0.800947
$\sum(-x_i)$	17.686278	17.703896	17.698198	17.695419

(b) Bond orders, bond lengths and β' values.

Bond	p^{I}	r^{I}	β^{I}	p^{II}	r^{II}	β^{II}	p^{III}	r^{III}	β^{III}	p^{IV}	r^{IV}	β^{IV}
1 2	.628	1.401	0.972	.609	1.405	0.960	.598	1.407	0.954	.592	1.408	0.949
1 6	.605	1.406	0.958	.588	1.409	0.947	.586	1.410	0.945	.586	1.410	0.946
1 8	.340	1.460	0.804	.387	1.451	0.828	.402	1.448	0.836	.409	1.446	0.840
2 3	.682	1.390	1.006	.695	1.387	1.016	.705	1.385	1.022	.711	1.383	1.027
3 4	.648	1.396	0.985	.633	1.400	0.975	.621	1.402	0.968	.614	1.404	0.964
4 5	.680	1.390	1.005	.693	1.387	1.014	.702	1.385	1.021	.708	1.384	1.025
5 6	.634	1.399	0.976	.616	1.403	0.964	.604	1.406	0.958	.598	1.407	0.954
6 7	.315	1.466	0.790	.369	1.455	0.818	.387	1.451	0.828	.394	1.449	0.832
8 9	.793	1.366	1.086	.737	1.378	1.044	.717	1.382	1.031	.707	1.384	1.024

Table 4: 1-2 benzpyrene



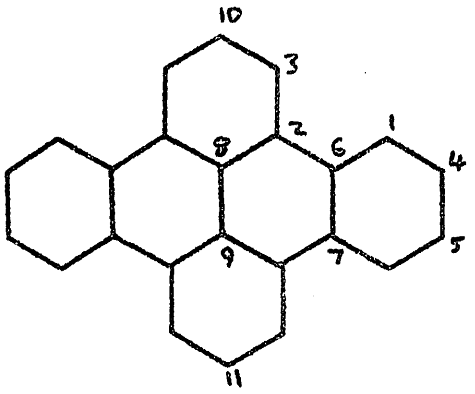
(a) Energy eigenvalues $-x_i$

C_2 symm.	I	II	III	IV
A'	2.373018	2.392873	2.395815	2.397330
	2.006793	2.010938	2.010629	2.010832
	1.463106	1.523436	1.523831	1.524240
	1.266656	1.282303	1.288296	1.290666
	0.873028	0.986286	0.982585	0.980349
	0.642699	0.594362	0.572950	0.564358
A''	1.973509	1.942598	1.933855	1.931314
	1.214079	1.234951	1.243835	1.247376
	0.963924	0.954760	0.953541	0.953830
	0.773788	0.733890	0.721874	0.719255
$\sum_i(-x_i)$	13.650601	13.656397	13.627210	13.619549

(b) Bond orders, bond lengths and β' values

Bond	p^{I}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}	p^{IV}	r^{IV}	β'^{IV}
1 7	.676	1.391	1.002	.685	1.389	1.009	.692	1.387	1.014	.697	1.386	1.017
1 9	.637	1.399	0.978	.624	1.402	0.969	.615	1.403	0.964	.610	1.404	0.961
2 3	.645	1.397	0.982	.642	1.398	0.981	.643	1.397	0.982	.645	1.397	0.983
2 9	.300	1.469	0.780	.346	1.459	0.807	.363	1.456	0.815	.368	1.455	0.818
2 11	.605	1.406	0.958	.577	1.412	0.939	.564	1.414	0.932	.559	1.415	0.928
3 4	.661	1.394	0.992	.656	1.395	0.989	.652	1.396	0.986	.648	1.396	0.985
4 5	.672	1.392	1.000	.678	1.390	1.003	.682	1.390	1.006	.685	1.389	1.008
5 6	.631	1.400	0.974	.617	1.403	0.965	.609	1.405	0.961	.605	1.406	0.958
6 11	.603	1.406	0.957	.580	1.411	0.941	.571	1.413	0.936	.568	1.413	0.934
6 13	.339	1.460	0.804	.392	1.450	0.831	.415	1.445	0.844	.425	1.443	0.850
7 8	.654	1.395	0.987	.642	1.398	0.981	.634	1.399	0.976	.629	1.400	0.973
9 10	.613	1.404	0.963	.598	1.407	0.954	.595	1.408	0.951	.596	1.408	0.952
11 12	.347	1.459	0.808	.419	1.444	0.846	.446	1.439	0.861	.457	1.437	0.867
13 14	.895	1.345	1.166	.864	1.352	1.140	.849	1.355	1.128	.841	1.356	1.122

Table 5: 1-2, 6-7 dibenzpyrene



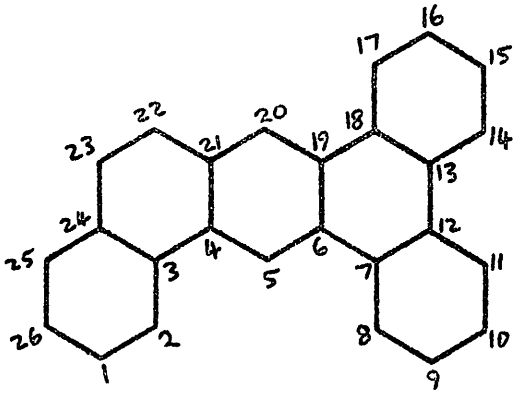
(a) Energy eigenvalues $-x_i$

C_{2v} symm.	I	III	III	IV
A_1	2.453521	2.422130	2.423471	2.424225
	1.879222	1.843399	1.837668	1.837014
	1.282965	1.277637	1.280943	1.282541
	0.970925	0.945419	0.942266	0.941556
B_2	2.134998	2.115472	2.115503	2.115886
	1.337631	1.339870	1.343870	1.345714
	0.650486	0.604997	0.591831	0.587355
A_2	1.285821	1.295061	1.300753	1.302482
	0.837294	0.821278	0.819451	0.820474
B_1	1.982360	1.950640	1.945853	1.944010
	1.082691	1.083037	1.085155	1.086209
	0.721582	0.689907	0.682340	0.680115
$\sum_i(-x_i)$	16.619494	16.388846	16.369102	16.367579

(b) Bond orders, bond lengths and β' values.

Bond	p^{I}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}	p^{IV}	r^{IV}	β'^{IV}
1 4	.678	1.390	1.004	.687	1.388	1.010	.694	1.387	1.015	.698	1.386	1.013
1 6	.632	1.400	0.975	.621	1.402	0.967	.613	1.404	0.963	.609	1.405	0.961
2 3	.638	1.398	0.979	.633	1.400	0.975	.631	1.400	0.974	.630	1.400	0.974
2 6	.324	1.464	0.795	.355	1.457	0.812	.367	1.455	0.817	.370	1.454	0.819
2 8	.596	1.408	0.952	.582	1.411	0.942	.576	1.412	0.938	.573	1.412	0.937
3 10	.666	1.393	0.995	.666	1.393	0.995	.666	1.393	0.995	.666	1.393	0.995
4 5	.651	1.396	0.986	.639	1.398	0.979	.632	1.400	0.975	.627	1.401	0.972
6 7	.606	1.406	0.958	.595	1.408	0.952	.594	1.408	0.951	.595	1.408	0.952
8 9	.374	1.454	0.821	.408	1.446	0.840	.424	1.443	0.849	.430	1.442	0.852

Table 6: 1-2, 3-4, 5-6 tribenzanthracene



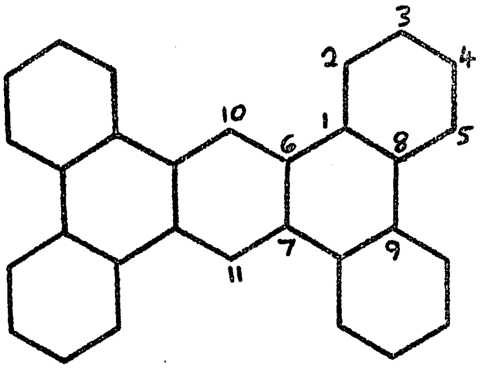
(a) Energy eigenvalues $-x_i$

I	II	III	IV
2.367521	2.380136	2.383953	2.384104
2.188349	2.204913	2.207058	2.207504
1.950650	1.929108	1.925715	1.924405
1.920537	1.868114	1.880587	1.877545
1.479890	1.539359	1.540036	1.539722
1.291391	1.324966	1.332452	1.334107
1.220772	1.236359	1.243024	1.245058
1.170802	1.190104	1.196875	1.198896
1.027811	1.026691	1.027573	1.027714
0.921024	0.905598	0.901975	0.901543
0.831685	0.810828	0.804055	0.802683
0.710626	0.664399	0.651908	0.648304
0.665045	0.619526	0.598278	0.589393
17.746101	17.720101	17.693486	17.680976

Table 6 cont'd.

Bond	p^{I}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}	p^{IV}	r^{IV}	β'^{IV}
1 2	.680	1.390	1.005	.694	1.387	1.015	.704	1.385	1.022	.711	1.383	1.027
1 26	.649	1.396	0.925	.633	1.400	0.975	.621	1.402	0.967	.613	1.404	0.963
2 3	.633	1.400	0.975	.613	1.404	0.963	.602	1.406	0.956	.595	1.408	0.951
3 4	.317	1.465	0.791	.372	1.454	0.820	.392	1.450	0.830	.400	1.448	0.835
3 24	.607	1.405	0.959	.590	1.409	0.948	.587	1.410	0.986	.587	1.410	0.946
4 5	.641	1.398	0.981	.632	1.400	0.975	.626	1.401	0.971	.623	1.402	0.969
4 21	.595	1.408	0.952	.569	1.413	0.935	.559	1.415	0.929	.556	1.416	0.926
5 6	.651	1.396	0.986	.651	1.396	0.986	.652	1.396	0.987	.654	1.395	0.988
6 7	.300	1.469	0.780	.345	1.459	0.807	.361	1.456	0.815	.366	1.455	0.817
6 19	.597	1.407	0.953	.567	1.414	0.934	.554	1.416	0.925	.548	1.417	0.921
7 8	.637	1.399	0.978	.625	1.401	0.970	.617	1.403	0.965	.612	1.404	0.962
7 12	.613	1.404	0.963	.598	1.407	0.953	.594	1.408	0.951	.595	1.408	0.951
8 9	.676	1.391	1.002	.684	1.389	1.008	.691	1.388	1.013	.695	1.387	1.016
9 10	.654	1.395	0.988	.643	1.397	0.982	.636	1.399	0.977	.631	1.400	0.974
10 11	.676	1.391	1.002	.684	1.389	1.008	.690	1.388	1.012	.695	1.387	1.015
11 12	.638	1.398	1.25	.626	1.401	0.970	.618	1.403	0.966	.613	1.404	0.963
12 13	.298	1.469	0.779	.344	1.460	0.806	.359	1.456	0.814	.365	1.455	0.816
13 14	.638	1.398	0.979	.625	1.401	0.970	.617	1.403	0.965	.613	1.404	0.953
13 18	.613	1.404	0.963	.598	1.407	0.954	.595	1.408	0.951	.595	1.408	0.952
14 15	.676	1.391	1.002	.685	1.389	1.008	.691	1.388	1.012	.695	1.387	1.016
15 16	.654	1.395	0.988	.642	1.397	0.982	.636	1.399	0.977	.631	1.400	0.974
16 17	.676	1.391	1.002	.684	1.389	1.008	.691	1.388	1.013	.695	1.387	1.016
17 18	.638	1.399	0.978	.624	1.401	0.970	.617	1.403	0.965	.613	1.404	0.963
18 19	.299	1.469	0.780	.345	1.459	0.807	.360	1.456	0.814	.365	1.455	0.817
19 20	.652	1.396	0.987	.653	1.395	0.987	.655	1.395	0.988	.657	1.395	0.990
20 21	.636	1.399	0.978	.625	1.401	0.971	.620	1.402	0.967	.616	1.403	0.965
21 22	.339	1.460	0.804	.391	1.450	0.830	.412	1.446	0.842	.422	1.444	0.848
22 23	.895	1.345	1.166	.865	1.351	1.141	.850	1.354	1.129	.843	1.356	1.123
23 24	.338	1.461	0.803	.389	1.450	0.829	.411	1.446	0.841	.421	1.444	0.847
24 25	.628	1.401	0.972	.608	1.405	0.960	.597	1.407	0.953	.589	1.409	0.947
25 26	.682	1.390	1.006	.696	1.387	1.016	.706	1.384	1.023	.713	1.383	1.028

Table 7: 1-2, 3-4, 5-6, 7-8 tetrabenzanthracene



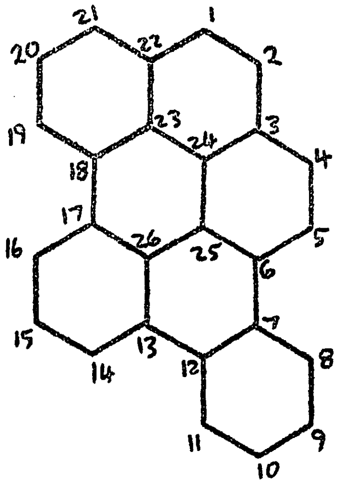
(a) Energy eigenvalues $-x_i$

C_{2v} symm.	I	II	III	IV
A_1	2.391968	2.399990	2.404763	2.405244
	1.923432	1.893354	1.886803	1.884131
	1.225414	1.239227	1.245473	1.246628
	0.944263	0.919206	0.912564	0.911260
B_2	2.248291	2.253785	2.257879	2.258323
	1.385184	1.399692	1.404797	1.405723
	1.205384	1.222948	1.230424	1.231692
	0.685264	0.636753	0.622378	0.618501
A_2	1.941927	1.917460	1.912915	1.911099
	1.068015	1.075543	1.079983	1.081652
	0.814065	0.784175	0.777580	0.775489
B_1	1.958255	1.938182	1.935331	1.934059
	1.244513	1.267452	1.278073	1.281802
	0.888609	0.874020	0.873759	0.874805
	0.693700	0.636314	0.617439	0.610596
$\sum_i(-x_i)$	20.618282	20.458290	20.440159	20.431003

(b) Bond orders, bond lengths and β' values.

Bond		p^{I}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}	p^{IV}	r^{IV}	β'^{IV}
1	2	.637	1.399	0.978	.623	1.401	0.969	.616	1.403	0.964	.611	1.404	0.962
1	6	.300	1.470	0.780	.347	1.459	0.807	.363	1.456	0.815	.368	1.455	0.818
1	8	.613	1.404	0.963	.598	1.407	0.955	.594	1.408	0.951	.595	1.408	0.951
2	3	.676	1.391	1.002	.685	1.389	1.009	.692	1.387	1.013	.696	1.386	1.016
3	4	.654	1.395	0.988	.642	1.398	0.981	.634	1.399	0.976	.629	1.400	0.973
4	5	.676	1.391	1.002	.684	1.389	1.008	.691	1.388	1.013	.696	1.387	1.016
5	8	.638	1.399	0.978	.624	1.401	0.970	.617	1.403	0.965	.612	1.404	0.962
6	7	.601	1.406	0.956	.576	1.412	0.939	.566	1.414	0.932	.562	1.415	0.930
6	10	.646	1.397	0.984	.641	1.398	0.981	.640	1.398	0.980	.640	1.398	0.980
8	9	.299	1.469	0.779	.345	1.459	0.806	.361	1.456	0.814	.366	1.455	0.817

Table 8: 1-12, 2-3 dibenzperylene



(a) Energy eigenvalues $-x_i$

I	II	III	IV
2.430480	2.448547	2.452237	2.453011
2.153936	2.163320	2.164851	2.165387
2.018463	2.002741	1.997322	1.995066
1.896101	1.861576	1.851943	1.848653
1.495398	1.557778	1.559443	1.560127
1.328533	1.347940	1.355849	1.358894
1.265475	1.288092	1.297511	1.300957
1.130766	1.141567	1.144708	1.145788
0.987265	0.995647	0.989680	0.986252
0.952573	0.945150	0.943301	0.942937
0.880546	0.862350	0.858513	0.888515
0.717348	0.670970	0.657195	0.653378
0.608789	0.551582	0.527768	0.517686
17.865672	17.837261	17.800320	17.786650

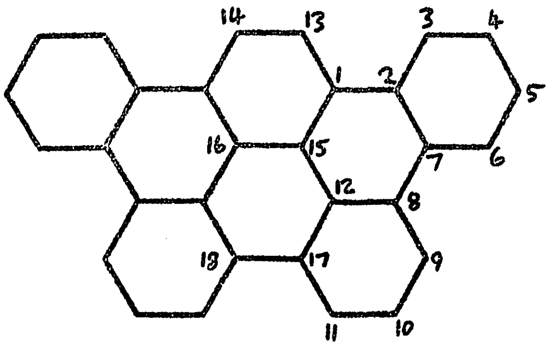
Table 8 cont'd.

(b) Bond orders, bond lengths and β' values.

Bond	p^{I}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}	p^{IV}	r^{IV}	β'^{IV}
1 2	.894	1.345	1.165	.860	1.352	1.138	.843	1.356	1.124	.834	1.358	1.117
1 22	.341	1.460	0.804	.395	1.449	0.832	.420	1.444	0.847	.433	1.441	0.854
2 3	.342	1.460	0.805	.399	1.448	0.834	.424	1.443	0.849	.438	1.440	0.857
3 4	.621	1.402	0.968	.597	1.407	0.953	.582	1.411	0.942	.571	1.413	0.936
3 24	.606	1.405	0.959	.587	1.409	0.946	.581	1.411	0.942	.581	1.411	0.941
4 5	.686	1.389	1.009	.703	1.385	1.021	.715	1.383	1.030	.724	1.381	1.035
5 6	.626	1.401	0.971	.604	1.406	0.957	.589	1.409	0.948	.580	1.411	0.941
6 7	.303	1.468	0.782	.354	1.457	0.811	.374	1.453	0.821	.382	1.412	0.825
6 25	.616	1.403	0.965	.602	1.406	0.956	.600	1.407	0.955	.601	1.406	0.956
7 8	.636	1.399	0.978	.621	1.402	0.968	.611	1.404	0.962	.605	1.406	0.958
7 12	.612	1.404	0.962	.596	1.408	0.952	.591	1.409	0.949	.591	1.409	0.949
8 9	.676	1.391	1.003	.687	1.388	1.010	.695	1.387	1.015	.700	1.386	1.019
9 10	.653	1.395	0.987	.640	1.398	0.980	.631	1.400	0.974	.625	1.401	0.970
10 11	.676	1.391	1.002	.686	1.389	1.009	.694	1.387	1.015	.699	1.386	1.019
11 12	.637	1.399	0.978	.623	1.402	0.969	.614	1.404	0.963	.608	1.405	0.960
12 13	.301	1.469	0.781	.350	1.458	0.809	.368	1.455	0.818	.376	1.453	0.822
13 14	.640	1.398	0.980	.632	1.400	0.974	.628	1.401	0.972	.625	1.401	0.971
13 26	.609	1.405	0.960	.586	1.410	0.945	.577	1.412	0.939	.574	1.412	0.937
14 15	.667	1.393	0.996	.668	1.392	0.996	.669	1.392	0.997	.670	1.392	0.998
15 16	.666	1.393	0.995	.665	1.393	0.994	.663	1.393	0.993	.662	1.394	0.992
16 17	.641	1.398	0.981	.635	1.399	0.976	.633	1.400	0.975	.633	1.399	0.976
17 18	.300	1.469	0.780	.347	1.459	0.807	.363	1.456	0.816	.368	1.455	0.818
17 26	.609	1.405	0.960	.586	1.410	0.945	.576	1.412	0.939	.572	1.413	0.936
18 19	.645	1.397	0.983	.643	1.397	0.981	.644	1.397	0.982	.647	1.397	0.984
18 23	.605	1.406	0.958	.577	1.412	0.939	.563	1.414	0.931	.557	1.416	0.927
19 20	.661	1.394	0.992	.655	1.395	0.988	.650	1.396	0.985	.645	1.397	0.983
20 21	.673	1.391	1.000	.679	1.390	1.004	.684	1.389	1.008	.688	1.388	1.011
21 22	.630	1.400	0.974	.615	1.403	0.964	.606	1.405	0.959	.600	1.407	0.955
22 23	.603	1.406	0.957	.579	1.411	0.941	.570	1.413	0.935	.566	1.414	0.933
23 24	.348	1.462	0.799	.397	1.449	0.834	.422	1.444	0.848	.432	1.442	0.853
24 25	.601	1.406	0.956	.568	1.413	0.934	.550	1.417	0.922	.540	1.419	0.916
25 26	.331	1.462	0.799	.397	1.449	0.834	.422	1.444	0.848	.432	1.442	0.853

Table 9: 1-12, 2-3, 10-11 tribenzperylene

(a) Energy eigenvalues $-x_i$



(a) Energy eigenvalues $-x_i$

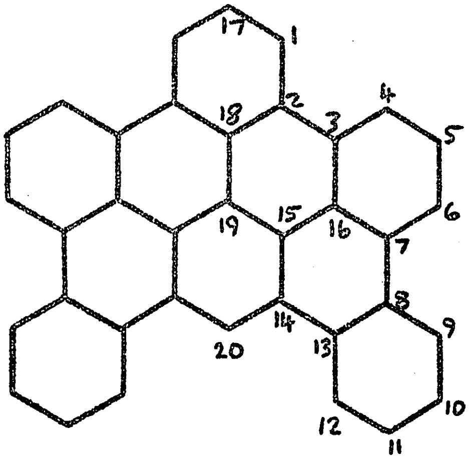
C_2 symm.	I	II	III	IV
A'	2.449316	2.461744	2.466843	2.468354
	2.063061	2.048616	2.046921	2.045548
	1.926334	1.895198	1.887807	1.885009
	1.334771	1.357595	1.367886	1.370785
	1.271637	1.293631	1.302465	1.305871
	1.000000	0.993214	0.994618	0.996062
	0.969123	0.954568	0.949916	0.947550
	0.704437	0.652605	0.637795	0.632904
A''	2.213538	2.216373	2.220206	2.221023
	1.883460	1.848679	1.840284	1.836833
	1.361340	1.379330	1.387786	1.390299
	1.175594	1.187417	1.193488	1.194732
	0.949310	0.940404	0.939075	0.939226
	0.806859	0.777892	0.771560	0.770258
	0.628579	0.564074	0.541853	0.533710
$\sum_i(-x_i)$	20.737358	20.571339	20.548503	20.538163

Table 9 cont'd.

(b) Bond orders, bond lengths and β' values

Bond	p^{I}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}	p^{IV}	r^{IV}	β'^{IV}
1 2	.302	1.469	0.781	.352	1.458	0.810	.371	1.454	0.820	.379	1.452	0.823
1 13	.631	1.400	0.974	.613	1.404	0.963	.603	1.406	0.957	.597	1.407	0.953
1 15	.612	1.404	0.962	.595	1.408	0.951	.590	1.409	0.948	.589	1.409	0.947
2 3	.637	1.399	0.978	.622	1.402	0.968	.612	1.404	0.962	.607	1.405	0.959
2 7	.613	1.404	0.963	.596	1.407	0.952	.592	1.408	0.950	.593	1.408	0.950
3 4	.676	1.391	1.002	.686	1.389	1.010	.694	1.387	1.015	.699	1.386	1.019
4 5	.653	1.395	0.987	.641	1.398	0.981	.632	1.400	0.975	.626	1.401	0.971
5 6	.676	1.391	1.002	.686	1.389	1.009	.693	1.387	1.014	.698	1.386	1.018
6 7	.637	1.399	0.978	.623	1.402	0.969	.614	1.404	0.964	.609	1.405	0.960
7 8	.300	1.469	0.780	.348	1.459	0.808	.366	1.455	0.817	.373	1.454	0.821
8 9	.641	1.398	0.980	.632	1.400	0.975	.629	1.400	0.973	.627	1.401	0.972
8 12	.609	1.405	0.960	.587	1.410	0.946	.578	1.411	0.940	.574	1.412	0.937
9 10	.666	1.393	0.996	.667	1.393	0.996	.668	1.392	0.996	.668	1.392	0.997
10 11	.666	1.393	0.995	.665	1.393	0.995	.664	1.393	0.994	.664	1.393	0.993
11 17	.641	1.398	0.981	.586	1.410	0.945	.632	1.400	0.975	.631	1.400	0.975
12 15	.331	1.462	0.799	.396	1.449	0.833	.421	1.444	0.847	.430	1.442	0.853
12 17	.609	1.405	0.961	.586	1.410	0.945	.577	1.412	0.939	.573	1.412	0.937
13 14	.680	1.390	1.005	.692	1.387	1.013	.700	1.386	1.019	.705	1.385	1.022
15 16	.606	1.405	0.958	.577	1.412	0.939	.563	1.414	0.931	.556	1.416	0.926
17 18	.300	1.469	0.780	.347	1.459	0.808	.364	1.456	0.816	.369	1.454	0.819

Table 10: 1-2, 3-4, 5-6, 10-11 tetrabenzanthanthrene



(a) Energy eigenvalues $-x_i$

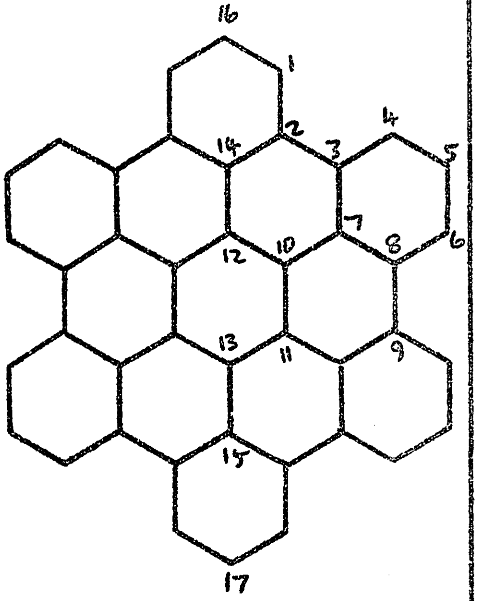
C_2 symm.	I	II	III	IV
A'	2.480455	2.493082	2.497368	2.498990
	2.151806	2.147803	2.149336	2.149895
	1.945161	1.910030	1.900673	1.896730
	1.863076	1.825775	1.816195	1.813196
	1.329778	1.352443	1.362409	1.366475
	1.235368	1.250317	1.257278	1.259288
	0.991032	0.966441	0.958534	0.954938
	0.949807	0.940805	0.939393	0.939558
	0.908025	0.892350	0.890530	0.890990
	0.639634	0.574895	0.553274	0.545177
A''	2.266721	2.272431	2.276283	2.277103
	1.979162	1.958907	1.955980	1.954646
	1.385193	1.404437	1.412253	1.414810
	1.354335	1.380294	1.391191	1.394933
	1.122834	1.131793	1.136947	1.138187
	0.947052	0.939669	0.939608	0.940351
	0.777817	0.743917	0.735501	0.733410
	0.623887	0.560103	0.539170	0.531458
$\sum_i (-x_i)$	24.95115	24.745490	24.711924	24.700135

Table 10 cont'd.

(b) Bond orders, bond lengths and β' values.

Bond	p^{I}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}	p^{IV}	r^{IV}	β'^{IV}
1 2	.641	1.398	0.980	.633	1.400	0.975	.630	1.400	0.974	.629	1.400	0.973
1 17	.666	1.393	0.996	.666	1.393	0.995	.666	1.393	0.995	.666	1.393	0.995
2 3	.301	1.469	0.781	.349	1.459	0.808	.366	1.455	0.817	.373	1.454	0.820
2 18	.609	1.405	0.960	.586	1.410	0.945	.576	1.412	0.939	.572	1.413	0.936
3 4	.641	1.398	0.980	.633	1.400	0.975	.630	1.400	0.973	.628	1.400	0.973
3 16	.609	1.405	0.960	.586	1.410	0.945	.576	1.412	0.939	.572	1.413	0.937
4 5	.666	1.393	0.995	.666	1.393	0.996	.667	1.393	0.996	.667	1.393	0.996
5 6	.666	1.393	0.995	.665	1.393	0.995	.665	1.393	0.994	.664	1.393	0.994
6 7	.641	1.398	0.981	.634	1.399	0.976	.632	1.400	0.975	.632	1.400	0.975
7 8	.300	1.469	0.780	.347	1.459	0.807	.364	1.456	0.816	.370	1.454	0.819
7 16	.609	1.405	0.961	.585	1.410	0.945	.575	1.412	0.938	.571	1.413	0.935
8 9	.637	1.399	0.978	.624	1.402	0.969	.615	1.403	0.964	.610	1.404	0.961
8 13	.613	1.404	0.953	.597	1.407	0.953	.594	1.408	0.951	.594	1.408	0.951
9 10	.676	1.391	1.002	.685	1.389	1.009	.692	1.387	1.014	.697	1.386	1.017
10 11	.653	1.395	0.987	.642	1.398	0.981	.634	1.399	0.976	.628	1.401	0.972
11 12	.676	1.391	1.002	.686	1.389	1.009	.693	1.387	1.014	.697	1.386	1.017
12 13	.637	1.399	0.978	.623	1.402	0.969	.615	1.403	0.964	.610	1.405	0.961
13 14	.300	1.469	0.780	.348	1.459	0.808	.365	1.455	0.817	.372	1.454	0.820
14 15	.604	1.406	0.957	.578	1.411	0.940	.567	1.414	0.933	.562	1.415	0.930
14 20	.644	1.397	0.982	.638	1.398	0.979	.636	1.399	0.978	.636	1.399	0.977
15 16	.332	1.462	0.800	.400	1.448	0.835	.425	1.443	0.850	.435	1.441	0.855
15 19	.609	1.405	0.961	.585	1.410	0.944	.575	1.412	0.938	.570	1.413	0.935
18 19	.332	1.462	0.799	.398	1.448	0.834	.423	1.443	0.849	.434	1.441	0.854

Table 11: Hexabenzcoronene



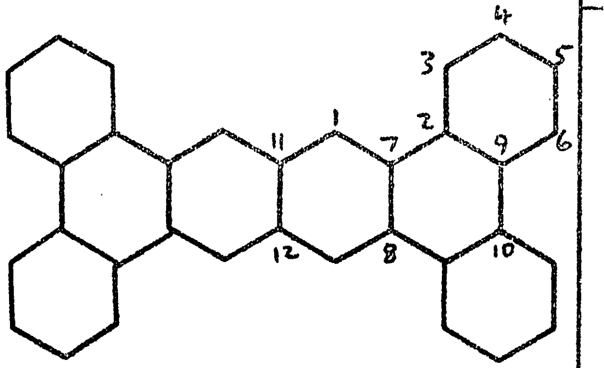
(a) Energy eigenvalues $-x_i$

C_{2v} symm.	I	II	III	IV
A_1	2.527381	2.541485	2.544998	2.546477
	2.017115	1.999535	1.996524	1.995389
	1.950362	1.908510	1.894704	1.890363
	1.266259	1.277876	1.283917	1.285988
	1.007843	0.977061	0.965699	0.959946
	0.940158	0.935345	0.936453	0.937802
B_2	2.281889	2.287809	2.291876	2.292586
	1.409481	1.444751	1.460078	1.465389
	1.385161	1.409759	1.418759	1.423173
	0.961180	0.950374	0.948605	0.948409
	0.595300	0.523692	0.498994	0.489826
A_2	2.017115	1.999465	1.996687	1.995287
	1.266259	1.277904	1.283968	1.286016
	0.940158	0.935265	0.936579	0.937691
	0.709481	0.664751	0.651078	0.647389
B_1	2.81889	2.287910	2.291702	2.292725
	1.830367	1.784929	1.772133	1.767918
	1.385161	1.409627	1.418798	1.423018
	0.961180	0.950319	0.948631	0.948344
	0.955219	0.944344	0.942054	0.941141
	0.595300	0.523682	0.498977	0.489819
$\sum_i(-x_i)$	29.284258	29.03440	28.981214	28.964696

(b) Bond orders, bond lengths and β' values.

Bond		p^{I}	r^{I}	β'^{I}	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}	p^{IV}	r^{IV}	β'^{IV}
1	2	.641	1.398	0.980	.633	1.400	0.975	.630	1.400	0.974	.629	1.400	0.973
1	16	.666	1.393	0.995	.666	1.393	0.995	.666	1.393	0.995	.665	1.393	0.995
2	3	.301	1.489	0.780	.349	1.458	0.809	.367	1.455	0.818	.373	1.454	0.821
2	14	.609	1.405	0.960	.585	1.410	0.945	.575	1.412	0.938	.571	1.413	0.935
7	10	.333	1.462	0.800	.401	1.448	0.836	.427	1.443	0.851	.438	1.440	0.857
10	11	.606	1.405	0.959	.581	1.411	0.941	.569	1.413	0.935	.565	1.414	0.932

Table 12: 1-2, 3-4, 5-6, 7-8 tetrabenztetracene (a) Energy eigenvalues $-x_i$

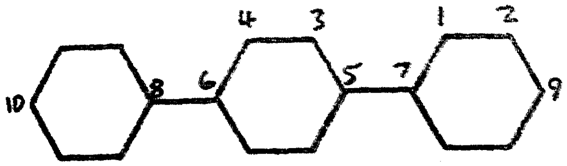


C_{2v} symm.	I	II	III	IV
A_1	2.402864	2.394380	2.399253	2.400027
	2.083483	2.051148	2.049112	2.048026
	1.285540	1.293314	1.297401	1.298159
	1.187358	1.204507	1.211528	1.212718
	0.703997	0.666931	0.657142	0.655167
B_2	2.294399	2.301825	2.307214	2.307987
	1.698915	1.683633	1.683668	1.683569
	1.221743	1.235327	1.242080	1.243086
	0.901426	01869903	0.862934	0.861761
A_2	1.948293	1.926426	1.923872	1.922695
	1.121115	1.145860	1.158617	1.163031
	0.838065	0.821672	0.822001	0.822874
	0.509010	0.489730	0.487407	0.486803
B_1	1.953589	1.932408	1.930344	1.929316
	1.400012	1.362442	1.364624	1.365214
	1.010011	0.986347	0.980755	0.979123
	0.799632	0.759083	0.747714	0.743443
$\sum_i(-x_i)$	23.35945	23.124933	23.125664	23.122997

(b) Bond orders, bond lengths and β' values.

Bond		p^I	r^I	β'^I	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}	p^{IV}	r^{IV}	β'^{IV}
1	7	.682	1.390	1.006	.698	1.386	1.018	.705	1.385	1.023	.708	1.384	1.025
1	11	.582	1.411	0.942	.561	1.415	0.930	.553	1.416	0.924	.549	1.417	0.922
2	3	.638	1.398	0.979	.627	1.401	0.971	.620	1.402	0.967	.617	1.403	0.965
2	7	.298	1.469	0.779	.340	1.460	0.804	.354	1.458	0.811	.357	1.457	0.813
2	9	.613	1.404	0.963	.599	1.407	0.954	.596	1.408	0.952	.596	1.408	0.952
3	4	.675	1.391	1.001	.682	1.389	1.007	.688	1.388	1.010	.691	1.388	1.013
4	5	.655	1.395	0.988	.645	1.397	0.983	.639	1.398	0.979	.635	1.399	0.977
5	6	.674	1.391	1.001	.682	1.389	1.006	.687	1.388	1.010	.691	1.388	1.012
6	9	.639	1.398	0.979	.627	1.401	0.972	.621	1.402	0.968	.618	1.403	0.966
7	8	.561	1.415	0.930	.518	1.424	0.902	.500	1.427	0.891	.494	1.429	0.888
9	10	.295	1.470	0.778	.338	1.461	0.803	.352	1.458	0.810	.356	1.457	0.812
11	12	.448	1.438	0.863	.493	1.429	0.887	.508	1.426	0.896	.515	1.424	0.900

Table 13: *p*-diphenylbenzene



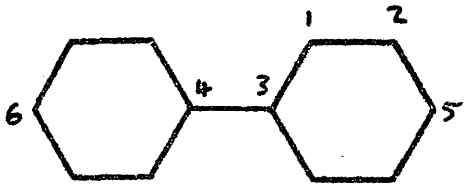
(a) Energy eigenvalues $-x_i$

C_{2v} symm.	I	II	III
A_1	2.218475	2.193541	2.192581
	1.877200	1.859483	1.859426
	0.999813	0.984235	0.982559
B_2	1.000000	1.003000	1.006000
	1.000000	0.999000	1.001000
A_2	1.000000	0.999000	1.001000
B_1	2.068386	2.048386	2.047976
	1.328540	1.311278	1.309100
	0.698562	0.674596	0.671490
$\sum_i(-x_i)$	12.190979	12.072518	12.071134

(b) Bond orders, bond lengths and β' values.

Bond		p^I	r^I	β'^I	p^{II}	r^{II}	β'^{II}	p^{III}	r^{III}	β'^{III}
1	2	.672	1.392	0.999	.674	1.391	1.001	.675	1.391	1.001
1	7	.641	1.398	0.981	.639	1.398	0.979	.639	1.398	0.979
2	9	.663	1.393	0.993	.662	1.394	0.992	.662	1.394	0.992
3	4	.678	1.390	1.003	.682	1.390	1.006	.683	1.389	1.007
3	5	.638	1.398	0.979	.635	1.399	0.977	.634	1.399	0.976
5	7	.270	1.475	0.766	.277	1.474	0.769	.277	1.474	0.769

Table 14: Diphenyl



(a) Energy eigenvalues $-x_i$

C_{2v} symm.	I	II
A_1	2.167050	2.145424
	1.230802	1.218781
B_2	1.000000	1.000000
A_2	1.000000	1.000000
B_1	1.914335	1.899696
	0.783122	0.764509
$\sum_i (-x_i)$	8.095310	8.028410

(b) Bond orders, bond lengths and β' values

Bond		p^I	r^I	β'^I	p^{II}	r^{II}	β'^{II}
1	2	.672	1.392	0.999	.674	1.391	1.001
1	3	.642	1.398	0.981	.640	1.398	0.980
2	5	.663	1.393	0.993	.662	1.394	0.993
3	4	.268	1.476	0.765	.274	1.475	0.768

APPENDIX D

Papers written with Dr T.H.Goodwin.

Reprinted from

TETRAHEDRON LETTERS

The International Organ for the Rapid Publication
of Preliminary Communications in Organic Chemistry

PERGAMON PRESS

OXFORD · LONDON · NEW YORK · PARIS

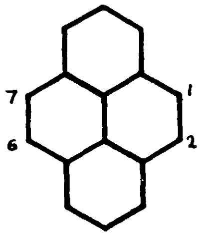
Tetrahedron Letters No. 14, pp. 901-904, 1963. Pergamon Press Ltd.
Printed in Great Britain.

L.C.A.O. - M.O. CALCULATIONS ON PYRENE BENZOLOGUES

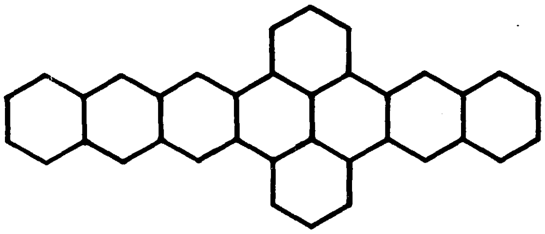
T. H. Goodwin and D. A. Morton-Blake
Chemistry Department, The University, Glasgow, W.2.

(Received 13 March 1963)

AT the suggestion of Dr. E. Clar, we have carried out some calculations on a number of benzologues of pyrene (I)



I



II

in which benzenoid rings are annelated linearly in the 1:2 and 6:7 positions. These have all been found by Clar and his co-workers[1] to have ultra-violet absorption spectrum bands, the positions of which are remarkably independent of the number of rings on the shorter side. If these molecules were thought of as dibenzoacenes this result would not be anticipated, as the absorption spectra would be expected to exhibit a resemblance to those of the corresponding parent acenes and to show marked and progressive displacement towards longer wave-lengths with increasing length of the acene chains. Moreover, the

---

[1] E. Clar, J.-F. Guye-Vuillème, A. McCallum, and I. A. Macpherson (private communication).

positions of the absorption bands of the pyrene benzologues are very different from those of acenes having the same number of collinear rings, thus showing that the former are not just simple derivatives of the latter.

For convenience we shall adopt the following system to describe the pyrene benzologues: if the molecule can be regarded as pyrene with n annelated benzene rings on one side and m on the other (m not greater than n) we shall denote it as nPm. Naphtho-[2'.3':1.2]anthraceno-[2".3":6.7]pyrene (II) will therefore be written 3P2.

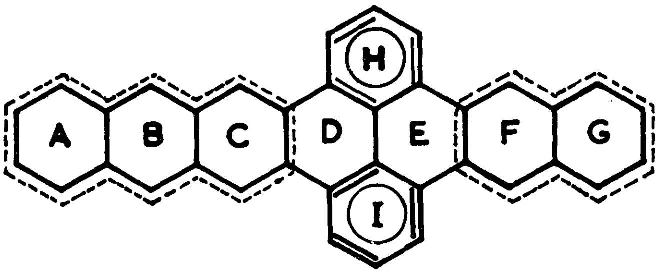
Calculations by the simplest Hückel method, *i.e.* with all overlap integrals neglected and all interaction integrals between orbitals on neighbouring atoms assumed equal to β_o, show moderate consistency in the energies of the highest occupied molecular orbitals, and hence in the transition energies of Clar's p-bands (highest occupied level to lowest unoccupied). If, however, we recognise a fundamental asymmetry[2] in the fully-aromatic benzenoid rings by allotting β-values in accordance with tendency towards the development of single-bond and double-bond character, then much more consistent results obtain.

The molecule 3P2, for example, was supposed to have an electronic structure indicated diagrammatically at (III). The bonds shown as single in rings D, E, H, I are, rather arbitrarily, assigned the value $0.8\beta_o$, those shown as double $1.1\beta_o$ (for pure single and double bonds the assignments would be $0\beta_o$ and $1.20\beta_o$ respectively)

---

[2] E. Clar, Tetrahedron, 5, 98 (1959); 18, 1471 (1962) etc.

while those forming part of a delocalised acene system[3] and enclosed by broken lines are taken to have values β_o. The "double" bonds in rings H and I have been assumed to



III

have such positions as to provide an induced aromatic sextet[2] in ring D, thus leaving ring E formally empty in accordance with Clar's picture of these molecules.

The π-bond energies ($E - \alpha$) of the highest occupied molecular orbitals calculated for the pyrene series 3Pm, 2Pm are given in the table together with the measured wavelengths of the p-bands. The consistency of the calculated energies in column 3 is seen to parallel that of the observed wavelengths in column 4. This appears to give strong support to Clar's picture of the aromatic hydrocarbons and, in particular to his conclusion regarding the asymmetry of the benzene ring.

---

3. E. Clar, Aromatische Kohlenwasserstoffe, p. 79, Springer-Verlag (1952).

MOLECULE	α - E(units of β_o) Simplest Hückel	α - E(units of β_o) Improved Hückel	Longest p-wavelength measured (Å)
3P3	0.3391	0.3629	4420
3P2	0.3549	0.3656	4390
3P1	0.3570	0.3658	4390
3P0	0.3587	0.3663	4420
2P2	0.4762	0.5117	3420
2P1	0.5009	0.5147	3410
2P0	0.5053	0.5168	3450

The method is being extended to other aromatic hydrocarbon systems.

One of us (D. A. M.-B.) thanks the D.S.I.R. for a maintenance grant.

Theoret. chim. Acta (Berl.) 1, 458—462 (1963)

Chemistry Department, The University, Glasgow, W. 2

The Configuration of Diphenyl in the Crystalline and in the Vapour States: A Simple Non-bonded H-H Potential Function

By

T. H. Goodwin and D. A. Morton-Blake

Electron diffraction shows that in the vapour the phenyl rings of diphenyl are inclined at about 42°. This is a compromise between the $2p_z$-orbital overlap, which tends to keep the whole molecule planar, and overcrowding of the 2:2′ and 6:6′ hydrogen atoms which causes twisting of the rings to reduce the steric repulsion. A potential function, having an exponential form, has been derived, which gives a minimum at the observed angle.

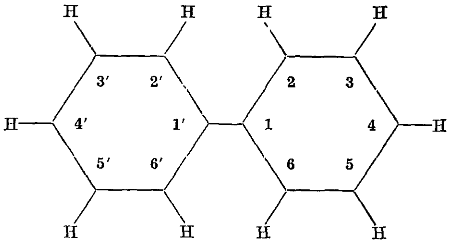
La diffraction électronique indique qu'en vapeur les anneaux phényles du diphényle s'inclinent à 42° approximativement. Cet angle est un compromis entre le recouvrement des orbitales $2p_z$ qui tend à maintenir plan la molécule entière, et l'encombrance des atomes d'hydrogène 2:2′ et 6:6′ qui font tordre les anneaux pour réduire la répulsion stérique. On a dérivé une fonction potentielle, d'une forme exponentielle, qui a un minimum à l'angle observé.

Die Elektronenbeugung zeigt, daß die beiden Ringe des Diphenyls im Gaszustand um einen Winkel von etwa 42° gegeneinander verdreht sind. Dieser Zustand stellt einen Kompromiß dar zwischen der Überlappung der p_z-Orbitale einerseits, die das ganze Molekül planar zu halten sucht, und der Pressung der van der Waals-Radien der 2,2′ und 6,6′-Wasserstoffatome andererseits, die die Ringe aus der gemeinsamen Ebene herausdreht, um die sterische Hinderung abzumindern. Für die potentielle Energie wurde eine e-Funktion mit einem Minimum am beobachteten Winkel hergeleitet.

X-ray diffraction studies show that in the crystalline state diphenyl is planar [*9*] or very nearly so [*12*], but electron diffraction results [*1*] indicate that in the vapour phase there is an angle of about 42° between the planes of the phenyl rings. Since in the vapour the molecules may be regarded as free from mutual interaction the configuration in this state may be regarded as an equilibrium compromise between the tendency towards planarity, which is promoted by p_z-orbital overlap across the bond between the rings and which favours a lowering of π-electron energy, and that towards non-planarity which favours reduction of steric repulsion energy between the overcrowded hydrogen atoms 2 and 2′, 6 and 6′.

1. Calculation of π-electron delocalisation energy across the interphenyl bond

For the planar diphenyl molecule it is a simple matter to calculate the total energy of the π-molecular orbitals by the usual Hückel approximation, particularly if group theoretical methods are used to factorise the 12th-order secular determinant of C_{2v} symmetry into the two quartics of the A_1 and B_1 symmetry classes and the two quadratics of the A_2 and B_2 classes. When the rings are not coplanar the interactions β_{rs} between neighbouring atomic orbitals on carbon atoms r, s remain unaltered except for that, $\beta_{1:1'}$, between the orbitals on atoms 1 and 1′, which becomes $\beta_{1:1'}\cos\theta$, θ being the angle by which one ring has been rotated about the axis 4:1:1′:4′ with respect to the other. It follows that, within the limits of the Hückel approximation ($\beta_{rs} = 0$ if r and s are not neighbours) the A_2 and B_2 determinants remain exactly as for the completely planar molecule since they do not involve the orbitals on the two-fold axis of the twisted structure, and the A_1 and B_1 determinants require only the multiplication of $\beta_{1:1'}$ by $\cos\theta$. Thus pseudo-C_{2v} symmetry remains.



Now the interphenyl bond, as measured by X-ray crystal analysis, is 1.50 Å long [*9*, *12*] whereas the electron diffraction spectrum [*1*] is interpreted as showing its length to be 1.48 Å. Dewar and Schmeising [*7*] believe that the length of apure σ-bond between sp^2 hybridised carbon atoms is 1.48 Å and this is supported by various other pieces of evidence [*10*, *13*]. We have assumed, therefore, that the small difference of 0.02 Å is significant, that the bond 1:1′ is stretched a little in the crystalline state to relieve the overcrowding of the hydrogen atoms at 2 and 2′ and at 6 and 6′, and that this extension persists for values of θ not greater than 20°, i.e. $\approx$ half of the observed 42° twist [*1*].

To calculate the π-electron energy levels for the molecule when $C_1 - C_{1'} = 1.48$ and 1.50 Å the corresponding β-values were inferred from the Longuet-Higgins and Salem [*11*] relationship as $0.750\,\beta_0$ and $0.710\,\beta_0$ respectively, β_0 being the interaction integral appropriate to the bond length in benzene, to which the ring bonds of diphenyl approximate fairly closely.

The total π-electron energy is then given, for the ground state, by

$$\mathscr{E}(\theta) = 2\sum_{i=1}^{6} \varepsilon_1(\theta) = 12\,\alpha - 2\beta_0 \sum_{i=1}^{6} x_i(\theta),$$

where $x_i(\theta)$ is the "Hückel number" (negative for binding orbitals) of the i-th molecular orbital, summation being over the six doubly occupied levels. The π-electron energy of two isolated benzene molecules in their ground states is $12\,\alpha + 16\,\beta_0$ and hence the "energy of delocalisation" across the bond 1:1′, i.e., the π-electron stabilisation gained by untwisting the molecule, is

$$\varepsilon_\pi(\theta) = -\left[2\sum_{i=1}^{6} x_i(\theta) + 16\right]\beta_0.$$

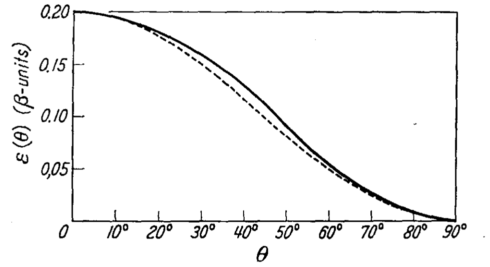


Fig. 1. $\varepsilon_\pi(\theta)$ against θ

Fig. 1 gives the plot of $\varepsilon_\pi(\theta)$ against θ for $0 \leqslant \theta \leqslant \pi/2$; that the curve is closely sinusoidal is shown by the degree of coincidence with the fitted curve (broken line)

$$\varepsilon_\pi(\theta) = 0.196\,\beta_0\cos^2\theta = -6.375\cos^2\theta \text{ kcal/mol} \tag{1}$$

when β_0 is given [*8*] the value —32.5 kcal/mol.

2. The Potential Function for Repulsion between the Hydrogen Atoms

The form of the repulsive potentials between the hydrogen atoms at carbons 2 and 2′ and at carbons 6 and 6′ is not known with certainty. It is discussed for some similar situations by Coulson and Haigh [4]. Most authors use a Buckingham "6-exponential" function [5]

$$V(r) = -Ar^{-6} + Be^{-cr} \tag{2}$$

in which r is the distance between the unbound hydrogens. We have worked, however, in terms of the variable θ and since $V(\theta)$ clearly decreases with increasing θ for $|\theta| < \pi/2$, we shall assume that it may be expressed by an exponential function

$$V(\theta) = V_0 \exp(-n\theta^{2m}) \tag{3}$$

the shape of which may be adjusted by means of the parameters n and m, m being integral. We have chosen this type of function for its simplicity and because it is symmetrical about a maximum at $\theta = 0$ as the problem requires. V_0 is the empirical barrier height for internal rotation due to the overcrowded hydrogen atoms *alone*, though this cannot be measured in the normal way for diphenyl because of the attractive contribution by the π-electrons to the observed barrier. We may, however, estimate it as follows. The energy difference between *cis* and *trans* butadiene is found [2] from thermodynamic considerations to be 2.30 kcal/mol. Since the π-electron energy in the two isomers is the same within the approximations of the Hückel theory, this difference must be accounted for by steric repulsions between the hydrogen atoms at the 1 and 4 positions of *cis* butadiene since in the *trans* compound no two hydrogen atoms approach within twice their van der Waals radius. Now the distance between the 2 and 2′ and the 6 and 6′ hydrogen atoms in diphenyl is very close to that in *cis*-butadiene. Hence we take V_0 in the former to be just twice the steric hindrance barrier height in the latter. (3) therefore becomes

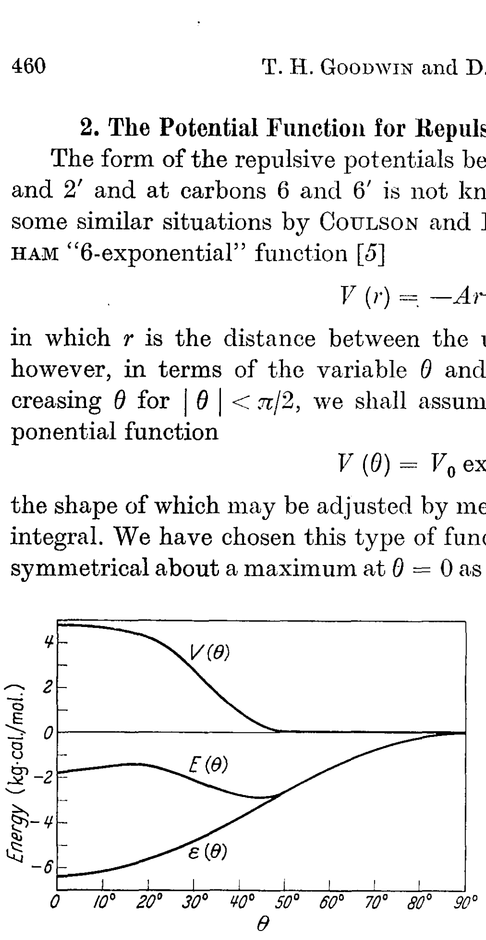


Fig. 2. $V(\theta)$, $\varepsilon_\pi(\theta)$, $E(\theta)$ against θ

$$V(\theta) = 4.60 \exp(-n\theta^{2m}) \text{ in kcal/mol.} \tag{4}$$

3. Minimisation of the Total Energy

That portion of the total energy of diphenyl which is dependent on θ is then given as the sum of (1) and (4)

$$E(\theta) = 4.60 \exp(-n\theta^{2m}) - 6.375 \cos^2 \theta. \tag{5}$$

Differentiating and using the fact that there is a minimum at $\theta = 42°$ we have

$$-9.20\, mn \times 0.7330^{2m-1} \exp(-0.7330^{2m} n) + 6.375 \sin 84° = 0. \tag{6}$$

For $m = 1$ no value of n makes $E(\theta)$ a minimum at $\theta = 42°$ but to each greater integral m there corresponds a value of n satisfying (6). With $m = 2, 3, 4, 5$

$V(\theta)$ has a flat portion with $|\theta|$ less than 20° and decreases almost to zero at $|\theta| = 45$ or 50°. We have selected (7), with $m = 2$,

$$V(\theta) = 4.60 \exp(-7.393\,\theta^4) \tag{7}$$

as the most likely of this family of curves since it has the shortest flat portion ($|\theta| < 10°$). With $m = 3, 4, 5$ $n \approx 18, 40, 80$ respectively. Curve (7) is shown in Fig. 2 along with $\varepsilon_\pi(\theta)$, the π-electron energy across the bond 1:1′, and the resultant energy $E(\theta)$. We note that besides the minimum in $E(\theta)$ at 42° a shallower minimum is found at 0°. This may account for the planarity in the crystalline state since only 1 kcal/mol need be supplied by the crystal forces to convert the twisted to the planar configuration.

4. Root Mean Square Amplitude of Twisting

Taking the potential well in $E(\theta)$ at $\theta \approx 42°$ as shown in Fig. 2, we may attempt to estimate the root mean square amplitude of the twisting of the phenyl rings with respect to each other by assuming the motion to be simple harmonic and calculating the force constant $\varkappa$

$$V(\theta) = \frac{1}{2}\varkappa\,\theta^2. \tag{8}$$

The best fit of (8) to $E(42°)$ is with $\varkappa = 0.003$ from which, using CRUICKSHANK's relationship [6]

$$\overline{\Phi}^2 = \frac{2\,kT}{\varkappa}$$

where k and T are the Boltzmann constant and the temperature, the mean square amplitude $\overline{\Phi}^2$ is found. Because of uncertainty in fitting (8) to (5) there is an appreciable uncertainty in $\varkappa$ and hence in $\overline{\Phi}^2$ but a smaller uncertainty in $(\overline{\Phi}^2)^{\frac{1}{2}}$, for which the value 28° is found, corresponding to a root mean square twist of each ring of 14° in opposite directions. The only experimental evidence which can be set alongside this calculation seems to be the inferences of ALMENNINGEN and BASTIANSEN [1] that the probability of finding the phenyl rings at any angle θ in the neighbourhood of 42° is quite large and that to reduce this probability to one half of the equilibrium probability the phenyl rings would need to be rotated through 17° in opposite directions.

5. Non-Bonded Repulsion as a Function of r

It is of interest to express the repulsive potential (7) in terms of the distance r between a pair of overcrowded hydrogen atoms. Using the bond lengths $C_1C_{1'} = 1.490$, $C_1C_2 = 1.398$, $C_2H_2 = 1.084$ Å and the angle $C_1C_2H_2 = 120°$

$$r = (12.4949 - 9.2397\cos\theta)^{\frac{1}{2}}. \tag{9}$$

When (9) is substituted into (7) we have

$$V(r) = 4.60 \exp\left\{-7.393\,[\cos^{-1}(1.3523 - 0.1082\,r^2)]^4\right\}. \tag{10}$$

The curve $V(r)$ is shown in Fig. 3. As for most repulsive potential functions it rapidly approaches zero, doing so, in fact, rather abruptly at approximately 2.6 Å, i.e., at just over twice the van der Waals radius of hydrogen (1.2 Å).

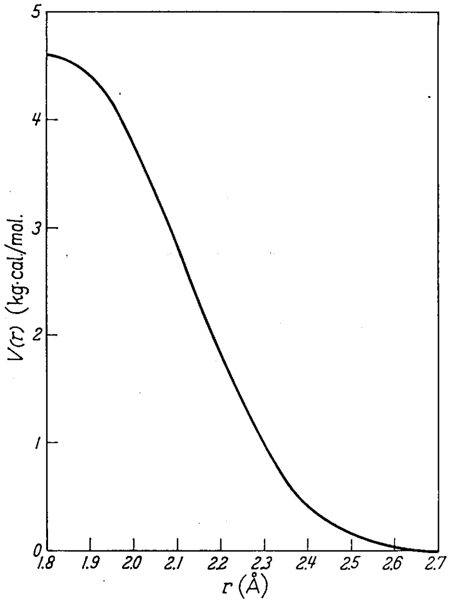


Fig. 3. $V(r)$ against r

6. C-H bending

The shoulder in $V(\theta)$ arises, of course, from the selection of a potential of the form (3). In planar and nearly planar molecules some relief of steric repulsion can be achieved by the bending of the $C—H$ bonds (in conjunction with the stretching of the $C—C$ bond) and would also have the effect of lowering (flattening) $V(\theta)$ at low θ. That such bending does occur is revealed by the accurately determined crystal structures of certain overcrowded molecules, e.g., chrysene [3].

The authors acknowledge the award of a maintenance grant to one of us (D.A.M.-B.) by H.M. Department of Scientific and Industria Research.

References

[1] Almenningen, A., and O. Bastiansen: Klg. Norske Videns Selsk. Skrifter 4 (1958).
[2] Aston, J. G., G. Szasz, H. W. Wolley and F. G. Brickwedde: J. chem. Physics **14**, 67 (1946).
[3] Burns, D. M., and J. Iball: Proc. Roy. Soc. **A 257**, 491 (1960).
[4] Coulson, C. A., and C. W. Haigh: Tetrahedron **19**, 527 (1963).
[5] See e.g. Ref. [4] for further references.
[6] Cruickshank, D. W. J.: private communication.
[7] Dewar, M. J. S., and H. N. Schmeising: Tetrahedron **5**, 166 (1959); **11**, 96 (1960).
[8] Goodwin, T. H., and D. A. Morton-Blake: to be published.
[9] Hargreaves, A., and S. Hasan Rizvi: Acta Cryst. **15**, 365 (1962).
[10] Lide, D. R.: Tetrahedron **17**, 125 (1962).
[11] Longuet-Higgins, H. C., and L. Salem: Proc. Roy. Soc. **A 251**, 172 (1959).
[12] Robertson, G. B.: Nature **191**, 593 (1961).
[13] Stoicheff, B. P.: Tetrahedron, **17**, 135 (1962).

(Received September 6, 1963)

To be published in "Journal of the Chemical Society" in February-March, 1964.

An Empirical Determination of the Hückel Parameter β and of the C-C and C-H Bond Energies in Aromatic Hydrocarbons.

by T. H. Goodwin and D. A. Morton-Blake

The atomic orbital interaction integral β is calculated from appropriate Morse functions and the Hückel theory of π-molecular orbitals, consistent results being obtained from data for benzene and ethylene. A third value, lying between these, has been derived from the heats of combustion of some aromatic hydrocarbons and estimates of the σ-bond energies of the C-C and C-H bonds in such compounds have been made.

1. Calculation of $\beta(r)$

The energy of the *i*th π-electron molecular orbital as calculated using the simple Hückel theory is of the form

$$\varepsilon_i = \alpha - x_i \beta \qquad (1.1)$$

where x_i is the "Hückel number" of the *i*th molecular orbital and has a negative value for the levels contributing to the ground state, α is the energy of a $2p_\pi$ atomic orbital χ i.e. $\alpha = \int \chi^* H \chi \, d\tau$ (in which H is the non-explicit Hamiltonian operator), and β is the matrix element $\int \chi_s^* H \chi_t \, d\tau$ expressing the interaction between the two atomic orbitals χ_s and χ_t. β is a function of the distance r between the atoms s and t but in the simple Hückel approximation it is considered negligible unless s and t are neighbours, in which case all β's are taken as equal within the compound under discussion although it is frequently proposed to derive bond orders and hence to infer differing bond lengths.

The total π-electron energy of the ground state of a molecule containing a system of n neighbouring $2p_\pi$ atomic orbitals is obtained by summing (1.1) over the $\frac{1}{2}n$ doubly occupied levels.

$$2\sum_{i=1}^{\frac{1}{2}n} \varepsilon_i = n\alpha - 2\beta\sum_{i=1}^{\frac{1}{2}n} x_i$$

from which it may be inferred that the total binding energy of the π-component of the bonds is given by

$$\varepsilon_\pi = -2\beta\sum_{i=1}^{\frac{1}{2}n} x_i \qquad (1.2)$$

For a system in which the π-molecular orbitals are spread over m equivalent bonds the total energy of the π-component of each of these is $E_\pi = \varepsilon_\pi / m$. In ethylene $m = 1$ and $\sum x_i = -1$, while for benzene these are 6 and -4 respectively. Hence

$$E_\pi^{\text{ethylene}} = 2\beta \qquad (1.3)$$

and

$$E_\pi^{\text{benzene}} = \frac{4}{3}\beta \qquad (1.4)$$

The terms on the left of (1.3) and (1.4) are, however, not directly measurable, since a π-bond is known only in association with a σ-bond. Nevertheless, from the energies of a "$\sigma + \pi$" bond and of a σ-bond of the same length we can calculate the energy of the corresponding pure π-bond if we neglect interaction of σ- and π-electrons. Thus

$$E_{\pi}(r) = E_{\sigma+\pi}(r) - E_{\sigma}(r) \qquad (1.5)$$

In general $E_{\sigma+\pi}$ and E_{σ} are known only at particular, unequal values of r, *viz.*, the equilibrium distance r_e. To calculate them at other bond lengths we require to take into account the energies of compression or expansion of the bonds. This may be done conveniently by use of the Morse function

$$E(r) = E(r_e) \left\{ e^{-2a(r-r_e)} - 2e^{-a(r-r_e)} \right\}.$$

The quantity a is characteristic of the particular bond and can be calculated from the stretching force constant.

However, the further difficulty arises that there is ample evidence[1,2,3] that $E_{\sigma}(r)$ depends on the hybridisation of the atoms involved and that C-C in ethylene should be compared not with that in ethane but with that in a hypothetical C-C σ-bond between sp^2-hybridised atoms. The length of such a bond is not unequivocally established nor, in the nature of things, can its stretching force constant and energy be directly known. We have taken[2] $r_e = 1.48$ with $E_{\sigma}(r_e)$ and a as in ethane. Otherwise our data are those selected by Coulson and Dixon and shown below.

C-C bond	$\underline{r}_e$	$\underline{E}(\underline{r}_e)$	$\underline{a}$
Ethylene	1.33Å	151 kg.-cal./mol.	2.189Å^{-1}
Benzene	1.39	124	2.093
Ethane	1.54	84	2.028
$\underline{sp}^2$-$\underline{sp}^2$	1.48		

From equations (1.3) to (1.5) we then have

$$\beta^{\text{ethylene}}(\underline{r}) = \tfrac{1}{2}\left\{E^{\text{ethylene}}(\underline{r}) - \underline{E}_{\sigma}(\underline{r})\right\} \qquad (1.6)$$

$$\beta^{\text{benzene}}(\underline{r}) = \tfrac{3}{4}\left\{E^{\text{benzene}}(\underline{r}) - E_{\sigma}(\underline{r})\right\} \qquad (1.7)$$

and within the limits of our approximations these should be equal, i.e., $\beta(\underline{r})$ is obtained from two independent sets of data. The results of these calculations are shown in Table 1. The last line gives a ratio which is frequently used in attempting to improve the simple Hückel approximation by allowing for the dependence of β or $\underline{r}$ and assuming that the β of the simple Hückel (β_0 of the next section) method is the same for all aromatic compounds.

The difference between the two values of $\beta(1.39)$, 1.39 Å being the benzene C-C bond length, is only 1.5 Kg.-cal./mol., i.e., 2.2%. Greater reliance should be placed on the benzene curve since $\underline{r}_e$ is nearer the middle of the range of $\underline{r}$-values used; this results in a more favourable application of the Morse function.

The "least-squares" quadratic expression

$$\beta(r) = 31.83\,\underline{r}^2 - 149.52\,\underline{r} + 178.85$$

fits the calculated curve almost exactly.

Table 1.

$\underline{r}$ (Å)	1.33	1.36	1.39	1.42	1.45	1.48	1.51	1.54
$\beta^{\text{ethylene}}(\underline{r})$(kg.-cal./mol.)	38.81	36.38	34.04	31.79	29.64	27.59	25.64	23.80
$\beta^{\text{benzene}}(\underline{r})$ (kg.-cal./mol.)	36.30	34.39	32.53	30.71	28.95	27.26	25.63	24.08
$\beta^{\text{benzene}}(\underline{r})/\beta^{\text{benzene}}(1.39)$	1.116	1.057	1.000	0.944	0.890	0.838	0.788	0.740

2. β and Bond Energies from Heats of Combustion.

For molecules containing only σ -bonds, heat of combustion is a simple additive property of the individual bond energies. For molecules containing, in addition, π -molecular orbitals it is necessary to include a further term even if σ-π interaction is neglected. This term is the total π -electron energy calculated usually by the simple Hückel approximation and given earlier as equation (1.2).

If we consider the heat of combustion as determined in two steps, first atomisation and secondly the conversion of the atomic fragments into the products of combustion, we have, neglecting energy terms due to changes in hybridisation

$$C_xH_y + (x+\tfrac{1}{4}y)O_2 \rightarrow xC + yH + (2x+\tfrac{1}{2}y)O$$

$$+ n_{CC}E_{CC} + n_{CH}E_{CH} + (x+\tfrac{1}{4}y)E_{OO} + \varepsilon_\pi \qquad (2.1)$$

$$xC + yH + (2x+\tfrac{1}{2}y)O \rightarrow xCO_2 + \tfrac{1}{2}yH_2O - xQ_{CO_2} - \tfrac{1}{2}yQ_{H_2O} \qquad (2.2)$$

where n_{CC} = number of C-C bonds in the Hydrocarbon C_xH_y,

n_{CH} = " " C-H " " " ",

E_{CC} = energy of C_{sp^2}-C_{sp^2} bond = E_σ of the previous section.

E_{CH} = " " C_{sp^2}-H " ,

E_{OO} = dissociation energy of oxygen molecule,

Q_{CO_2} = heat of atomisation of CO_2

Q_{H_2O} = " " " " H_2O.

Adding (2.1) and (2.2) we have

$$C_xH_y - (x+\tfrac{1}{4}y)O_2 \rightarrow xCO_2 + \tfrac{1}{2}yH_2O + C \qquad (2.3)$$

where $C = n_{CC}E_{CC} + n_{CH}E_{CH} + (x+\frac{1}{4}y)E_{OO} + \varepsilon_{\pi} - xQ_{CO_2} - \frac{1}{2}yQ_{H_2O}$ (2.4)

C being the heat of combustion of C_xH_y. The available experimental quantities on the right of (2.4) are Q_{H_2O}, Q_{CO_2} and E_{OO} for which we have taken the following values

$$Q_{CO_2} = 2 \times 192 = 384 \text{ kg.-cal./mol.},$$

$$Q_{H_2O} = 2 \times 110.6 = 221.2 \text{ kg.-cal./mol.},$$

$$E_{OO} = 119.1 \text{ kg.-cal./mol.}$$

Using the known heats of combustion of the three aromatic hydrocarbons benzene, naphthalene and anthracene (789.1, 1249.7, 1712.1 kg.-cal./mol.) we obtain three equations in the unknowns E_{CC}, E_{CH} and β_o where β_o represents a standard β supposed applicable to all these compounds. Then

$$C^{\text{benzene}} = 789.1 = 6\text{x}384 + 3\text{x}221.2 - 6E_{CC} - 6E_{CH} - (6+1\tfrac{1}{2})E_{OO} - 8.000\beta_o$$

or $\quad 1285.27 = 8\beta_o + 6E_{CC} + 6E_{CH}$,

and $\quad 2045.9 = 13.683\beta_o + 11E_{CC} + 8E_{CH}$,

$\quad 2904.75 = 19.314\beta_o + 16E_{CC} + 10E_{CH}$

Hence $\quad \beta_o = 32.96$ kg.-cal./mol.

$\quad E_{CC} = 77.58$ kg.-cal./mol.,

$\quad E_{CH} = 92.68$ kg.-cal./mol.

This β_o value compares very favourably with $\beta(1.39) = 32.53$ kg.-cal./mol. determined in the previous section. This is particularly interesting since (a) β_o may vary somewhat from compound to compound and (b) $\beta(r)$ varies with interatomic distance r even within the same molecule. It seems however to encourage confidence in the $\beta(r)$ values of the previous section.

E_{CC}, which we have noted as the E_σ of the first part of this paper has a numerically smaller value than the 84 kg.-cal./mol. which we supposed to be applicable to the pure *sp*^{2}-*sp*^{2} σ-bond. However we know that all the C-C bonds in the reference compounds are substantially shorter than 1.48Å. In fact the average of the 33 bonds[5] is 1.401Å with a spread from 1.361Å to 1.436Å. Applying the Morse equation for the *sp*^{2}-*sp*^{2} σ-bond to this average gives E_σ (1.40) = 81.4 kg.-cal./mol., which is in reasonable agreement with our 77.58 kg.-cal./mol. when the approximations are borne in mind.

Substituting the values for β_0, E_{CC}, E_{CH}, Q_{CO_2}, Q_{H_2O} and E_{OO} in (2.4) the general equation for the heat of combustion of a hydrocarbon becomes (within the limits of our approximation)

$$C = 264.9\underline{x} - 80.8\underline{y} - 77.58\,\underline{n}_{CC} - 92.68\underline{n}_{CH} + 65.92 \sum_{\underline{i}=1}^{\frac{1}{2}\underline{n}} \underline{x}_{\underline{i}} \qquad (2.5)$$

the (negative) Hückel numbers being summed over all the (doubly) occupied levels, *i.e.*, the occupation number (2) has been included in the term 65.92.

Using (2.5) we calculate the following heats of combustion

	$C_{calc.}$	$C_{obs.}$
Phenanthrene	1708.4 kg.-cal./mol.	1705.0 kg.-cal./mol.
Triphenylene	2163.6	2164.4
1:2-Benzanthracene	2169.3	2169.8
Chrysene	2166.4	2165.0

It is interesting to note that the quite small differences between the heats of combustion of the last three compounds are so accurately mirrored by the Hückel energies.

The authors thank H.M. Department of Scientific and Industrial Research for a maintenance grant to D.A.M-B., Chemistry Department, University of Glasgow.

References

1 Coulson and Dixon, Tetrahedron, 1962, 17, 215.

2 Dewar and Schmeising, ibid., 1959, 5, 166; 1960, 11, 96.

3 Coulson, Victor Henri Memorial Volume, "Contribution à l'Etude de la Structure Moléculaire", Desoer, Liège, 1948; Lide, Tetrahedron, 1962, 17, 125; Bastiansen and Traetteberg, ibid., p.147, etc.

4 Cottrell, "The Strengths of Chemical Bonds", Butterworths, London, 1958.

5 Stoicheff, Canad. J. Phys., 1954, 32, 339; Cruickshank, Acta Cryst., 1956, 9, 915; 1958, 11, 507.

To be published in "Theoretica Chemica Acta" in March, 1964.

A Simple Molecular-Orbital Study of the β, α, and p-Bands in Triphenylenes

by T. H. Goodwin and D. A. Morton-Blake

- - -

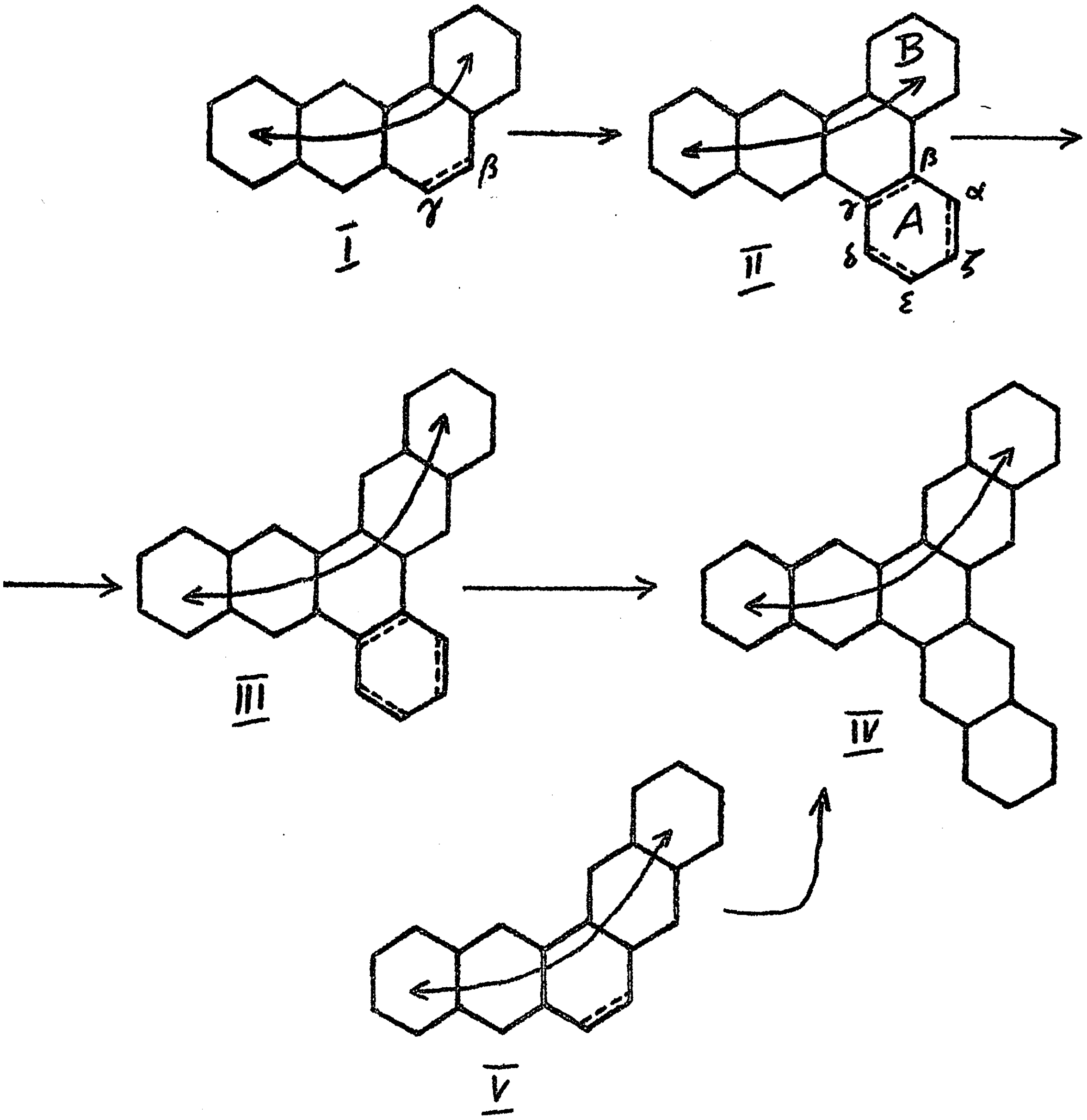
Clar has observed that the spectra of annelated derivatives of triphenylene such as I, II, III, IV below show remarkable resemblance to those of the phenes defined by the central ring of the triphenylene and its two longest acene chains, I and II resembling tetraphene and III and IV pentaphene V. We show that this observation can be explained in terms of a simple modification of the Hückel molecular-orbital method.

1. Energy levels in Triphenylenes.

In this paper we discuss the positions of the absorption bands in a large number of annelated derivatives of triphenylene, but since the systemmatic names of these compounds are often decidedly cumbrous we have used the following simple scheme for referring to them. The molecules consist of benzenoid rings annelated at three alternate bonds in benzene; we therefore describe them as sBml where s, m, l are the numbers of rings in the three limbs. s is separated from the other two indices and refers to the shortest limb; $\underline{l}$ is the longest; $\underline{s} \ngtr \underline{m} \ngtr \underline{l}$. Triphenylenes with the same $\underline{m}$ and $\underline{l}$ are said to form a class. Thus I to V (below) are described as OB1, 2; 1B1,2; 1B2,2; 2B2,2; OB2,2 and the first two and the last three belong to different classes.

Now Clar and his colleagues$^{(2)}$ have observed only very small shifts in the positions of the β ultra-violet absorption bands when an aromatic system is annelated to a bond of high π-electron density. In tetraphene, I, (OB1,2), mlecular-orbital calculations, show that the bond $\beta\gamma$ has a high double bond character corresponding to the chemical properties; for these reasons, and in accordance with Clar's ideas concerning these molecules we represent this bond as a formal double bond. The addition of a butadiene system at $\beta\gamma$ of I to give the triphenylene II, (1B1,2) is accompanied by a zero spectral shift of the β-band and this leads Clar to conclude that the phene system I is present in II and is unaffected by the presence of the newly formed benzenoid ring A.

The high order of the bond $\beta\gamma$ in I is apparently maintained in II with the consequence that the bonds are also of higher order and $\alpha\beta$, $\gamma\delta$, $\varepsilon\zeta$ of lower order than the average.



However, if a further ring is annellated to II at B (or A) to give III, it is found that the β -band of longest wavelength now occurs 240Å away at 3140Å. This is almost exactly the position of the corresponding band, 3170Å, in pentaphene V, and further extension of the shortest limb of III by a second ring to give IV is accompanied only by a very small (violet) shift to 3120Å. Thus, III, IV and V all give rise to the same β-band and presumably have, at the moment of producing the spectrum, the same aromatic conjugation, that of pentaphene. Clar therefore concludes that, as far as the origin of the first β-band is concerned, the aromatic conjugation of any triphenylene extends only over the two longest limbs and is unaffected by the benzenoid rings of the shortest limb. This is clearly demonstrated in Table I where all the absorption spectra recorded for phenes and triphenylenes are summarised. Fourteen spectra are noted including pairs of spectra for the five classes *s*B1,1, *s*B1,2, *s*B1,3, *s*B1,4, *s*B3,3 and three spectra for the class *s*B2,2. In no class is the spread of p-band heads greater than 60Å. Similar though less close agreement is observed in the α- and *p*-bands.

We must emphasise here that this paper is not concerned with the β′-bands which, according to Clar, originate from one of the two aromatic conjugation schemes which involve the shortest limb.

We have applied the method of molecular-orbitals to a large number of triphenylenes not strictly to calculate the positions of the β-, α- and p-bands, but to determine in units of β_0^*, the energy levels of the molecular orbitals transitions between which are responsible for those bands.

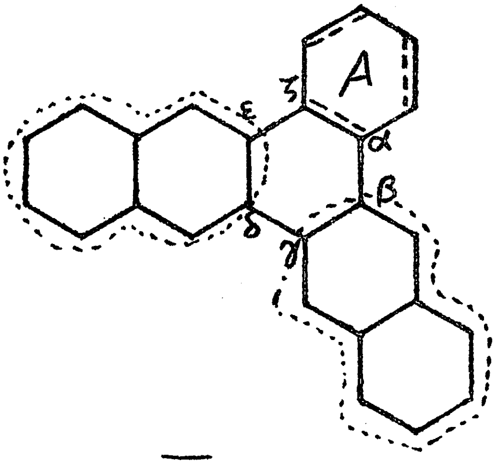
With alternant hydrocarbons having 2n carbon atoms in the π-electron system it is well recognised that the p-bands (of intermediate intensity, log $\varepsilon \approx 4$) arise from transitions between the nth and $(n + 1)$th electronic levels (counting the lowest as the first level) while the α- and β-bands (of low and high intensity log $\varepsilon \approx$ 2.5 and 5 resp.) both arise from transitions between the nth and $(n + 2)$th and between the $(n - 1)$th and $(n + 1)$th levels these being degenerate in the simple forms of the molecular-orbital theory in which overlap is neglected. We have not here attempted to break this degeneracy (see e.g. ref.[4] for one method of doing this) being more interested to see whether Clar's observations are explicable in terms of a simple molecular-orbital approach to the electronic structures of molecules. Thus we have required the

---

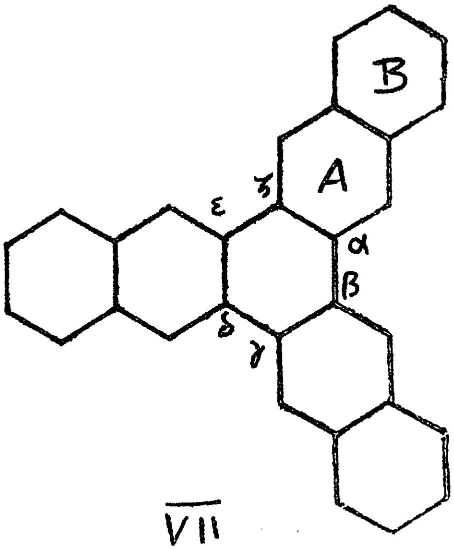
[*] Confusion is unlikely to arise between this β and that labelling the most intense absorption band.

energies of the highest and penultimate levels of the ground states of the molecules since $2k_n$ should be related to the p-band wavelengths and $k_n + k_{n+1}$ to those of the α and β -bands, where k is the (positive) Hückel number i.e. the coefficient of β in the energy expression $\varepsilon_i = \alpha + k_i \beta$ and $k_{2n+1-i} = -k_i$.

Two series of calculations have been carried out. In the first the β -values of the bonds were assumed equal except for the extreme single and double bonds. In VI, for example, the β's within the dotted islands were put equal to β_0 the interaction integral between atomic $2p_z$-orbitals on neighbouring carbon atoms separated by the standard C-C distance in benzene, and since the



VI



VII

formulae written by Clar (2) for these triphenylenes show the bonds $\alpha\beta$, $\gamma\delta$, $\epsilon\zeta$ as of low order, we have allotted them the β-values of $0.8\beta_0$. In the benzo-ring A we have supposed the β's to be alternately $0.8\beta_0$ and $1.1\beta_0$, $\alpha\zeta$ having, of course, the higher value.

In VII and in molecules having a shortest limb of two or more rings ($\underline{s} \geqslant 2$) we have, however, put all β's equal to β_0. Again the β's for $\alpha\beta$, $\gamma\delta$, $\epsilon\zeta$ have been taken to be $0.8\beta_0$.

We have felt justified in this approach by the results of Ahmed and Trotter$^{(1)}$ who have made a three-dimensional examination of the crystal structure of triphenylene and report a mean bond length of 1.446Å for the interphenylene bonds corresponding to $\alpha\beta$ etc. of VI and mean lengths of 1.415 (for the bond corresponding to $\alpha\zeta$), 1.416, 1.377, 1.402, 1.377 and 1.416Å round the peripheral rings. $\beta_{\underline{ij}}$ must depend on the distance between atoms $\underline{i}$ and $\underline{j}$ and these lengths imply (5, 6) β-values of $0.81\beta_0$ for $\alpha\beta$, $0.91\beta_0$ (for $\alpha\zeta$), $0.91\beta_0$, $1.04\beta_0$, $0.95\beta_0$, $1.04\beta_0$, $0.91\beta_0$. Our calculations were complete before the work of Ahmed and Trotter became available and in any case the X-ray results given above are not only the average values over all similar bonds in the crystal, but represent averages over many minutes or hours whereas spectroscopy presents the situation over an enormously shorter interval of time. It is therefore of considerable significance that the length reported for the interphenylene bonds corresponds with the β-value we have allocated to them and that the pattern of lengths in the peripheral rings corresponds (apart from $\alpha\zeta$) with the β's we have assumed for bonds in rings such as A of VI. We do not compare our selected β for the bonds between the rings with values appropriate to lengths such as the 1.50Å found by Hargreaves and Hasan Rizvi(5) for the central bond in diphenyl because we believe this bond to be elongated by repulsions between the 2:2' and 6:6' pairs of hydrogen atoms(4).

In the second series of calculations Clar's scheme was not invoked. The triphenylene *sBm.l* was regarded as formed from *s*-, *m*- and *l*-ring acenes joined by low order bonds $\alpha\beta$, $\gamma\delta$, $\varepsilon\zeta$. The β-values for the bonds of the various limbs were derived from the bond orders calculated for these acenes. In VI, for example, the β's for ring A were β_0, as in benzene, and those for the naphthalene systems were inferred from the calculated bond orders in naphthalene; those for $\alpha\beta$, $\gamma\delta$ and $\varepsilon\zeta$

Table 1.

		Absorption Bands				Hückel				Series I				Series II			
sBnℓ	n	p	α	β	Δ	k_n	k_{n-1}	k_n+k_{n-1}	Δ	k_n	k_{n-1}	k_n+k_{n-1}	Δ	k_n	k_{n-1}	k_n+k_{n-1}	Δ
011	7	2925A	3450A	25[illegible]	60A	0.605	0.769	1.374		0.741	0.816	1.556		0.741	0.816	1.556	0.058
111	9	2840	3400	2570		0.684d		1.368	0.006	0.749d		1.498	0.058	0.749d		1.498	
012	9	3590	3850	2900	0	0.453	0.715	1.168		0.502	0.814	1.316		0.569	0.719	1.288	0.042
112	11	3490	3750	2900		0.499	0.714	1.213	0.005	0.516	0.794	1.310	0.006	0.604	0.726	1.330	
013	11	4525		3190	10	0.327	0.688	1.015		0.357	0.782	1.139		0.460	0.728	1.188	0.020
113	13	4415		3180						0.366	0.777	1.143	0.004	0.481	0.727	1.208	
014	13	5510	~~[illegible]~~	3480	50					0.262	0.668	0.930		0.419	0.678	1.097	0.002
114	15	5385		3430						0.268	0.674	0.942	0.012	0.397	0.702	1.099	
022	11	3590	4230	3170	30	0.437	0.521	0.958		0.510	0.545	1.056		0.560	0.620	1.180	0.050
122	13	3390	3940	3140						0.531	0.545	1.076		0.605	0.620	1.225	
222	15	3400	3890	3150						0.531	0.566d	1.097	0.041	0.615d		1.230	
023	13	4400	4670	3580						0.371	0.531	0.902		0.468	0.597	1.065	0.046
123	15									0.378	0.541	0.918	0.028	0.488	0.617	1.105	
223	17									0.384	0.546	0.930		0.491	0.620	1.111	
033	15	4230	5190	35[illegible]	60												
133	17	4380	4850														

d - doubly degenerate level

Table II

		Series I				Series II			
smℓ	n	k_n	k_{n-1}	k_n+k_{n-1}	Δ	k_n	k_{n-1}	k_n+k_{n-1}	Δ
024	15	0.271	0.531	0.801		0.390	0.592	0.981	
124	17	0.275	0.542	0.817	0.022	0.402	0.617	1.019	0.043
224	19	0.279	0.545	0.824		0.404	0.620	1.024	
034	17	0.273	0.374	0.647		0.394	0.478	0.872	
134	19	0.276	0.381	0.657	0.021	0.403	0.494	0.897	0.048
234	21	0.278	0.390	0.668		0.392	0.498	0.890	
334	23	0.277	0.377	0.654		0.401	0.520	0.921	
044	19	0.271	0.276	0.547		0.394	0.398	0.792	
144	21	0.269	0.285	0.554		0.394	0.417	0.811	
244	23	0.266	0.297	0.563	0.016	0.390	0.425	0.815	0.023
344	25	0.262	0.299	0.561		0.385	0.429	0.814	
444	27	0.251	0.300d	0.551		0.372	0.431d	0.803	
055	23	0.205	0.210	0.415		0.321	0.324	0.645	
155	25	0.203	0.217	0.420		0.318	0.338	0.656	
255	27				0.009	0.315	0.343	0.658	0.013
355	29	0.198	0.226	0.424		0.313	0.346	0.658	
455	31	0.196	0.226	0.422					
555	33								

were again $0.8\beta_0$. In this way it was hoped that the two series of calculations would provide some evidence for or against the Clar theory of aromaticity. The results are shown in Tables 1 and 2. These differ only in that Table 1 includes all the spectra of triphenylenes known to us and such Hückel molecular-orbital levels as have been published, either in Coulson and Daudel's "Dictionary of Values of Molecular Constants"[3] or Streitwieser's "Molecular Orbital Theory for Organic Chemists"[9]. These Hückel molecular orbitals are based, as is well known, on the assumption of an interaction integral $\beta = \beta_0$ between all neighbouring orbitals. We have not ourselves made such calculations for all the many compounds which have been the subjects of our study here because they seemed less likely to yield the desired explanation of Clar's observations.

Inspection of Tables 1 and 2 shows that our Series I calculations do lead to fairly constant values of $\underline{k}_{\underline{n}} + \underline{k}_{\underline{n}-1}$ in any class of triphenylenes. The series II calculations are not generally quite so constant though the superiority of the series I results over those of series II and of the Hückel method is not so great as to compel out-of-hand rejection of the others or to constitute unequivocal

Fig. 1 β-band frequencies plotted against $k_n + k_{n-1}$

⊙ Series I

⊡ Series II

△ Hückel

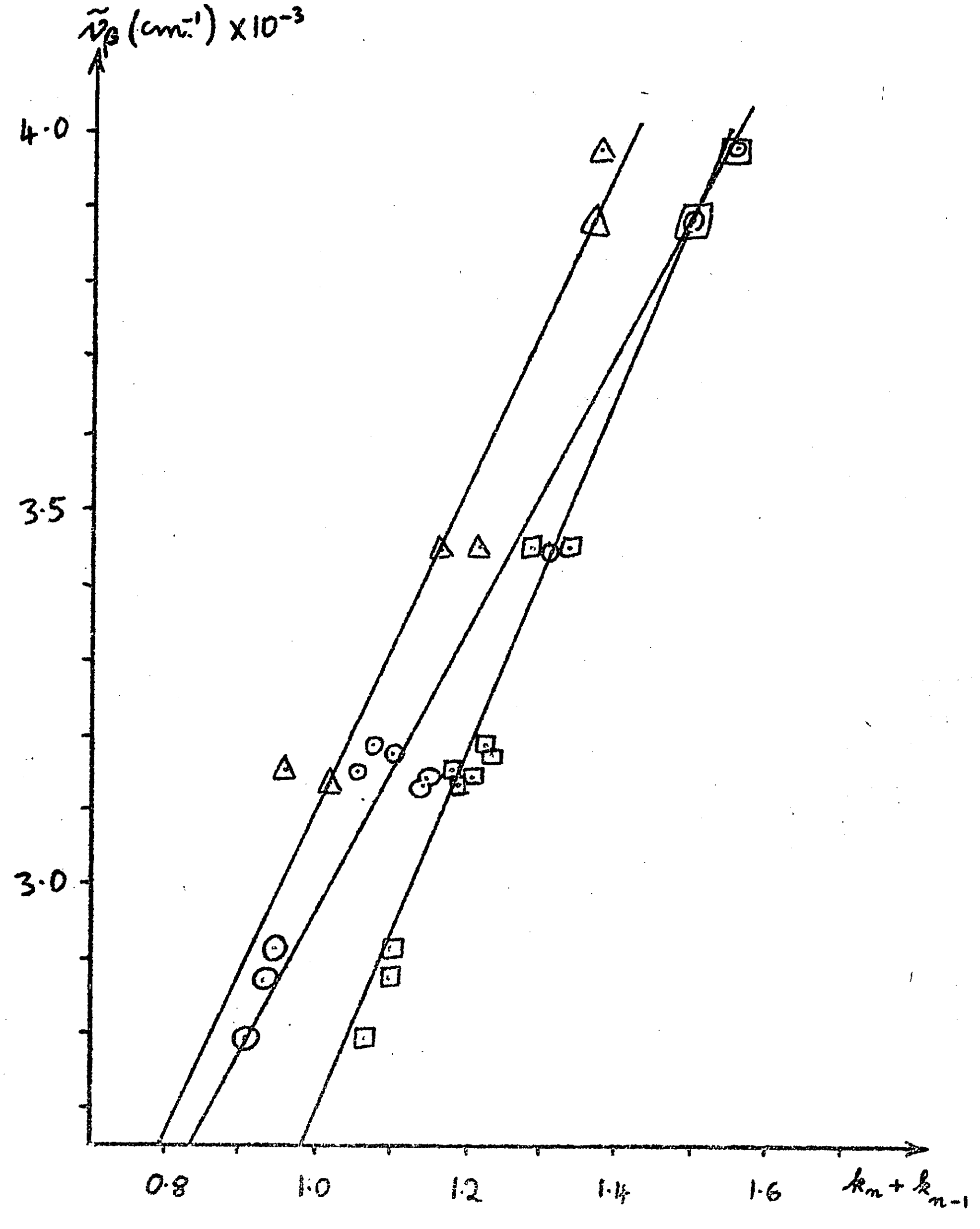


Fig. 2: p-band frequencies plotted against 2 k_n

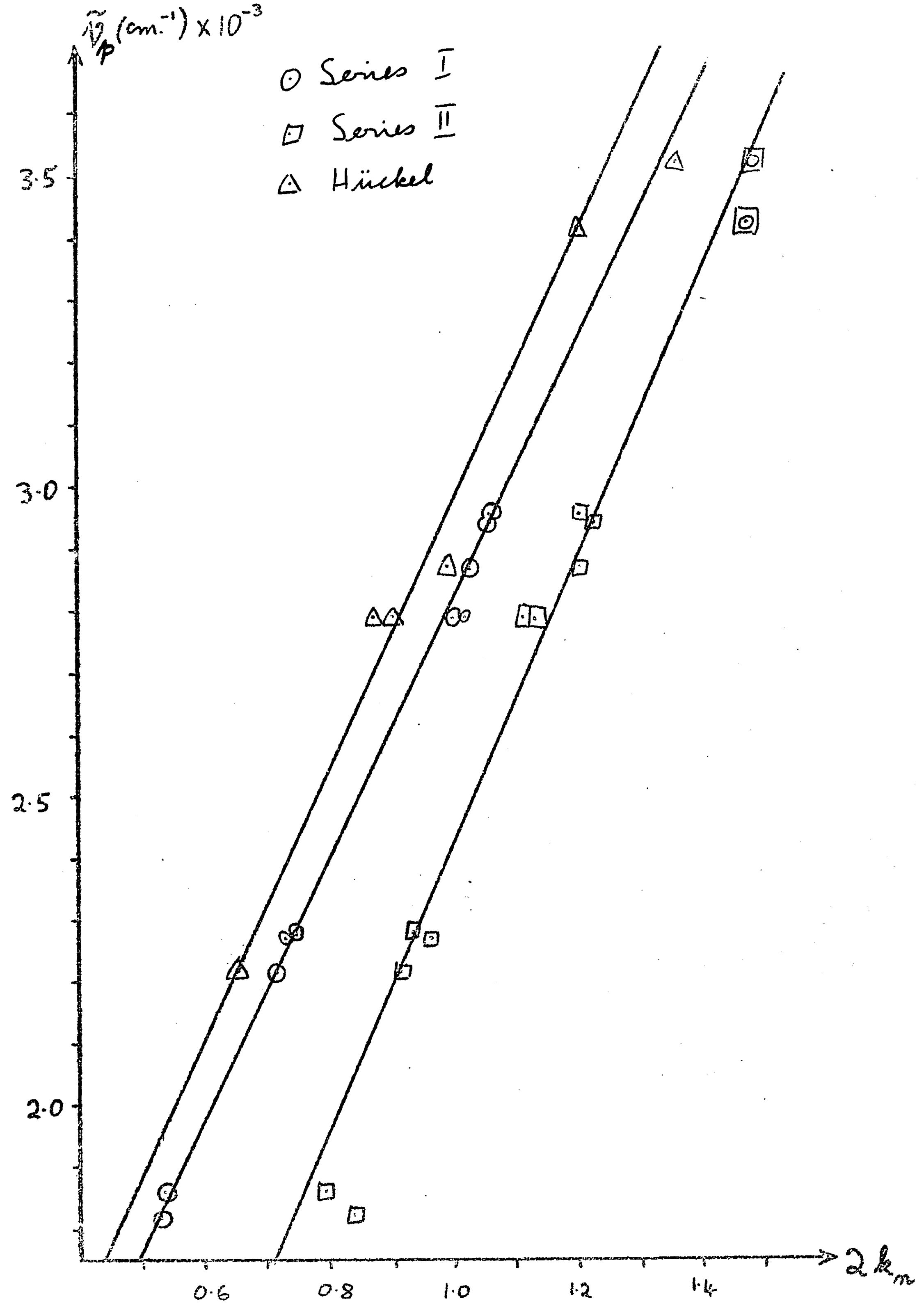
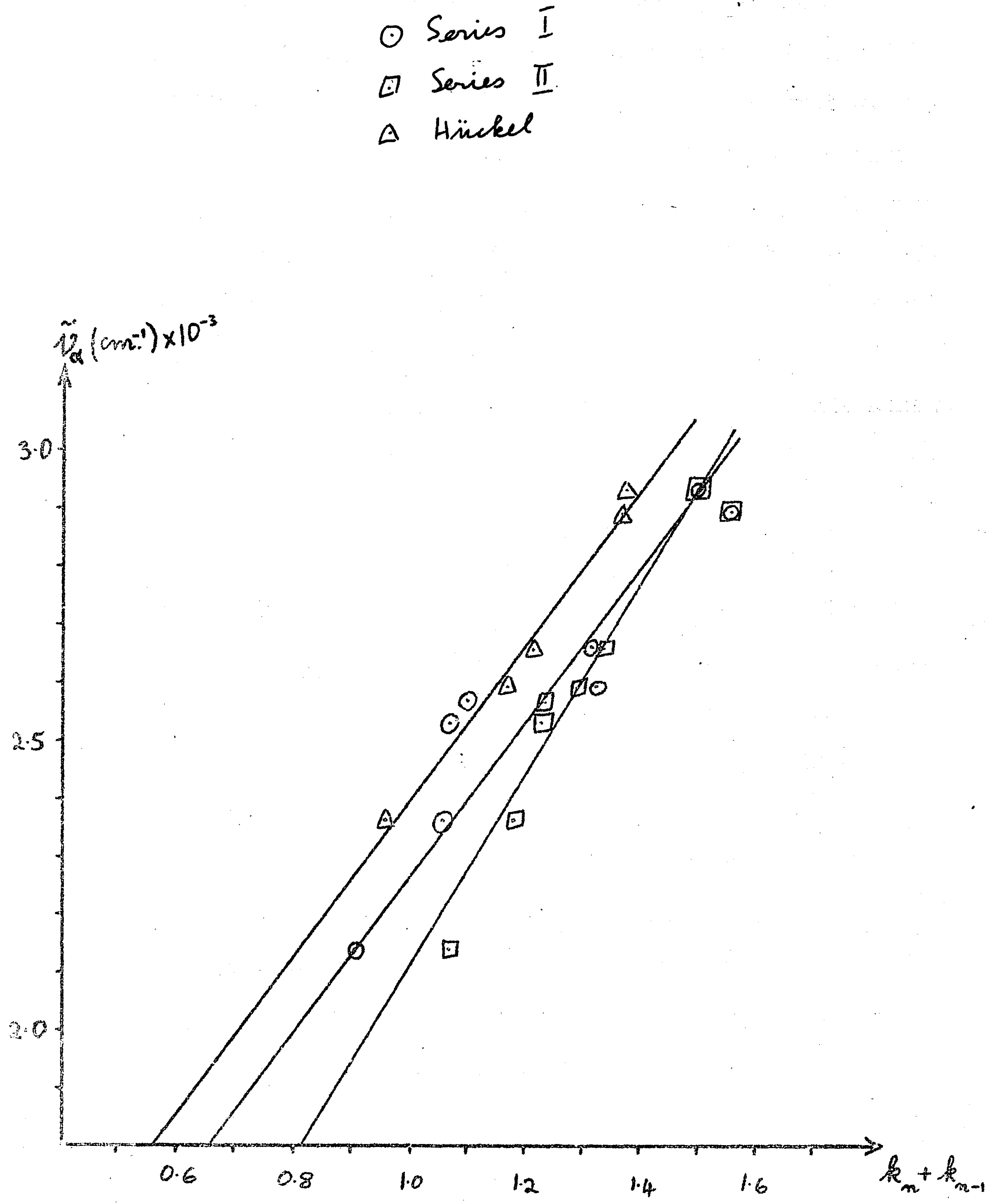


Fig. 3: α-band frequencies plotted against $k_n + k_{n-1}$



theoretical justification of Clar's conclusions. A more satisfactory comparison is to plot the frequencies of the β-bands against $k_n + k_{n-1}$, because Clar's conclusion is not accurate to an Å unit and the slight variations in β-band wavelengths correspond to the variations in $k_n + k_{n-1}$. Graphical representation of these results is shown in Fig.1 when it is seen that there is little to choose between our series I and series II results but that both are better than the Hückel values which show a much greater spread although, there being fewer of them, the comparison is not so extensive as one could desire.

Generally similar conclusions result from inspection of the values of k_n and Fig.2 (p-band frequencies against k_n) and of Fig.3 (α-band frequencies against $k_n + k_{n-1}$).

A particularly important point is however that just as the spectra (p, α- and β-bands as a whole) of pentaphene (OB2,2) and *iso*-pentaphene (1,2-benztetracene) (O B 1,3) are distinctly different so do the values of $2k_n$ and $k_n + k_{n-1}$ while agreeing within the classes sB2,2 and sB1,3 differ between the classes. So far this is in accordance with observation, but pentaphene and *iso*-pentaphene (1,2-benztetracene) have their β-bands at almost exactly the same wavelength. Our series I calculations suggest ($\underline{k}_n + \underline{k}_{n-1}$ different) that the β-bands should differ appreciably, but the series II calculations do make them almost equal. This suggests that the series II results are superior. Unfortunately, no other similar comparison can be made for lack of experimental data on triphenylenes with $\underline{m}_1 + \underline{l}_1 = \underline{m}_2 + \underline{l}_2$ but with $\underline{m}_1 \neq \underline{m}_2$.

2. Bond Length Alternation in a Benzenoid ring.

Consider a benzene molecule consisting of two kinds of C-C bonds alternating round the ring, with β-values

equal to β_1 and β_2.

equal to β_1 and β_2. The molecule would, therefore, have $\underline{D_{3h}}$ symmetry and the one-electron molecular orbitals $\underline{C_{3v}}$. This leads to the following linearly independent molecular orbitals of the A_1, the A_2 and the doubly degenerate E classes:

$$\Phi(A_1) = \frac{1}{\sqrt{6}}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$

$$\Phi(A_2) = \frac{1}{\sqrt{6}}(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)$$

$$\Phi'(E) = \frac{1}{2\sqrt{3}}(2\phi_1 + 2\phi_2 - \phi_3 - \phi_4 - \phi_5 - \phi_6)$$

$$\Phi''(E) = \frac{1}{2}(\phi_3 - \phi_4 - \phi_5 + \phi_6)$$

Expressing the energies $\mathcal{E}$ of these in terms of the interaction integrals $\int \phi_{i-1}^{*} \mathcal{H} \phi_i \, d\tau = \beta_1$,

$\int \phi_i^{*} \mathcal{H} \phi_{i+1} \, d\tau = \beta_2$ and the coulomb integrals

$\int \phi_i^{*} \mathcal{H} \phi_i \, d\tau = \alpha$ (the subscripts to ϕ being expressed in modulus 6) we have

$$\mathcal{E}(A_1) = \alpha + \beta_1 + \beta_2$$

$$\mathcal{E}(A_2) = \alpha - \beta_1 - \beta_2$$

$$\mathcal{E}^{\pm}(E) = \alpha \pm \left\{\beta_1^2 + \beta_2^2 - \beta_1\beta_2\right\}^{\frac{1}{2}}$$

The doubly occupied molecular orbitals of the ground state are $\Phi(A_1)$, $\Phi'(E)$ and $\Phi''(E)$ leading then to the total ground state π-electron energy

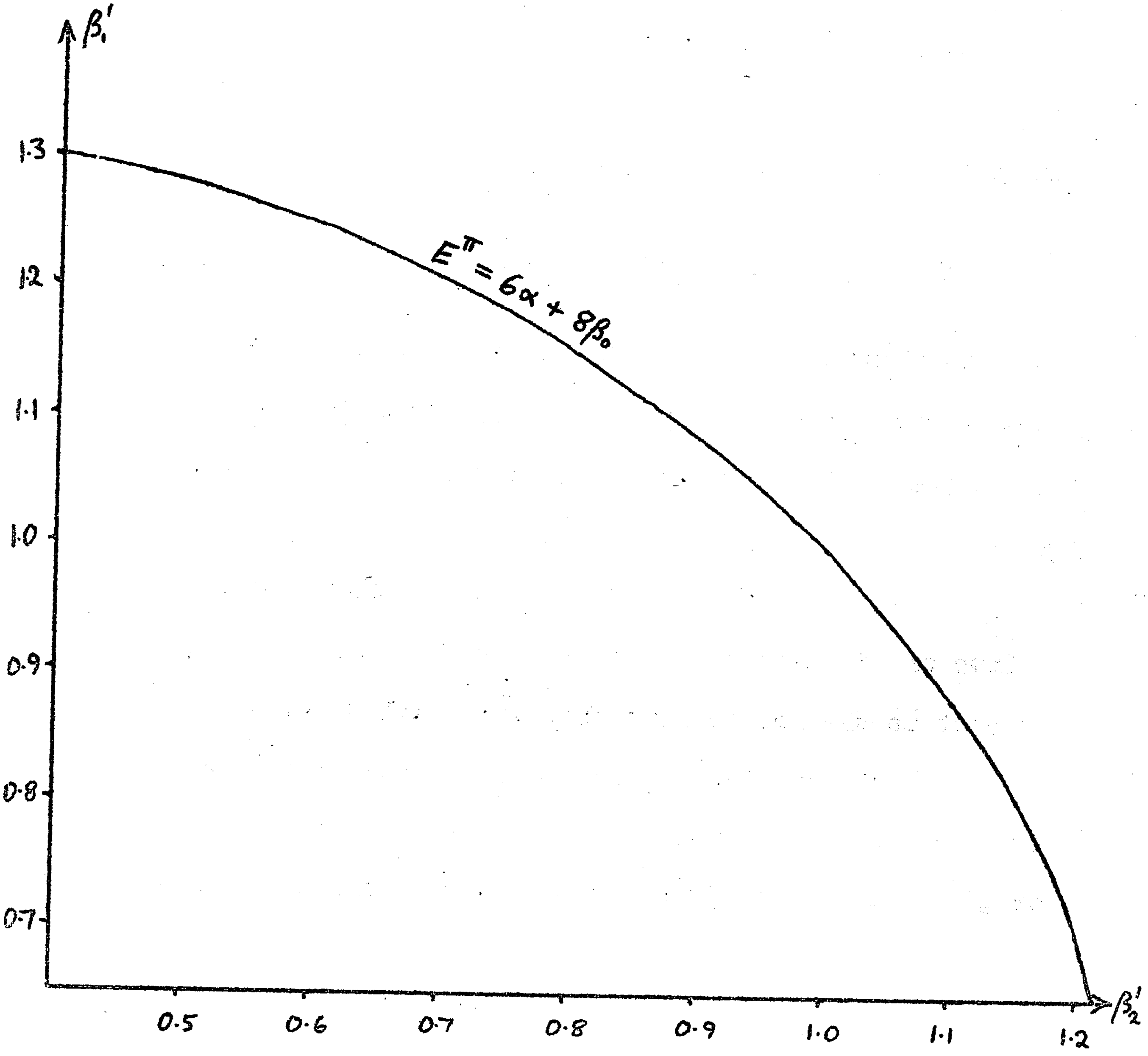
$$\begin{aligned} E(3\underline{v}) &= 2\,\mathcal{E}(A_1) + 4\,\mathcal{E}^{+}(E) \\ &= 6\alpha + 2\left\{\beta_1 + \beta_2 + 2(\beta_1^2 + \beta_2^2 - \beta_1\beta_2)^{\frac{1}{2}}\right\} \quad \ldots\ldots(1) \end{aligned}$$

The π-electron energy of the ground state if all C-C bonds are equivalent (molecular orbital symmetry $\underline{C}_{6\underline{v}}$) is

$$E(6\underline{v}) = 6\alpha + 8\beta_0 \qquad \ldots\ldots(2)$$

where β_0 is the interaction integral for the observed benzene C-C bond length.

Fig. 4: Relationship between β_1' and β_2' to give constant total π electron energy $6\alpha + 8\beta_0$



Equating (1) and (2) we obtain a relationship showing how β_1 and β_2 must change relative to each other, in order to preserve in the C_{3v} model the same total π-electron energy obtained with the C_{6v} model. Since we are concerned with the relative rather than the actual magnitudes of β_0, β_1 and β_2 we shall work in terms of β_1' and β_2' the ratios of β_1 and β_2 to β_0. The required relationship is then

$$\beta_1' = \beta_2' - \frac{4}{3}\left\{1-(4-3\beta_2')^{\frac{1}{2}}\right\} \qquad \ldots.(3)$$

This is plotted out in Fig.4, which is really a single β'-space. For an extended range a family of such contours

β'-space. For an extended range a family of such contours

would be required.

We may now observe the effect of changing the values of adjacent bonds in an annelated benzene ring subject to the requirement that the total π-electron energy of the annellated benzene ring remains constant. Thus, accepting the validity of Clar's explanation of the origin of the β-bands in the spectra of the triphenylenes, we may regard one of the three outer rings of VIII, say ring A, as having bonds of alternately high and low order,

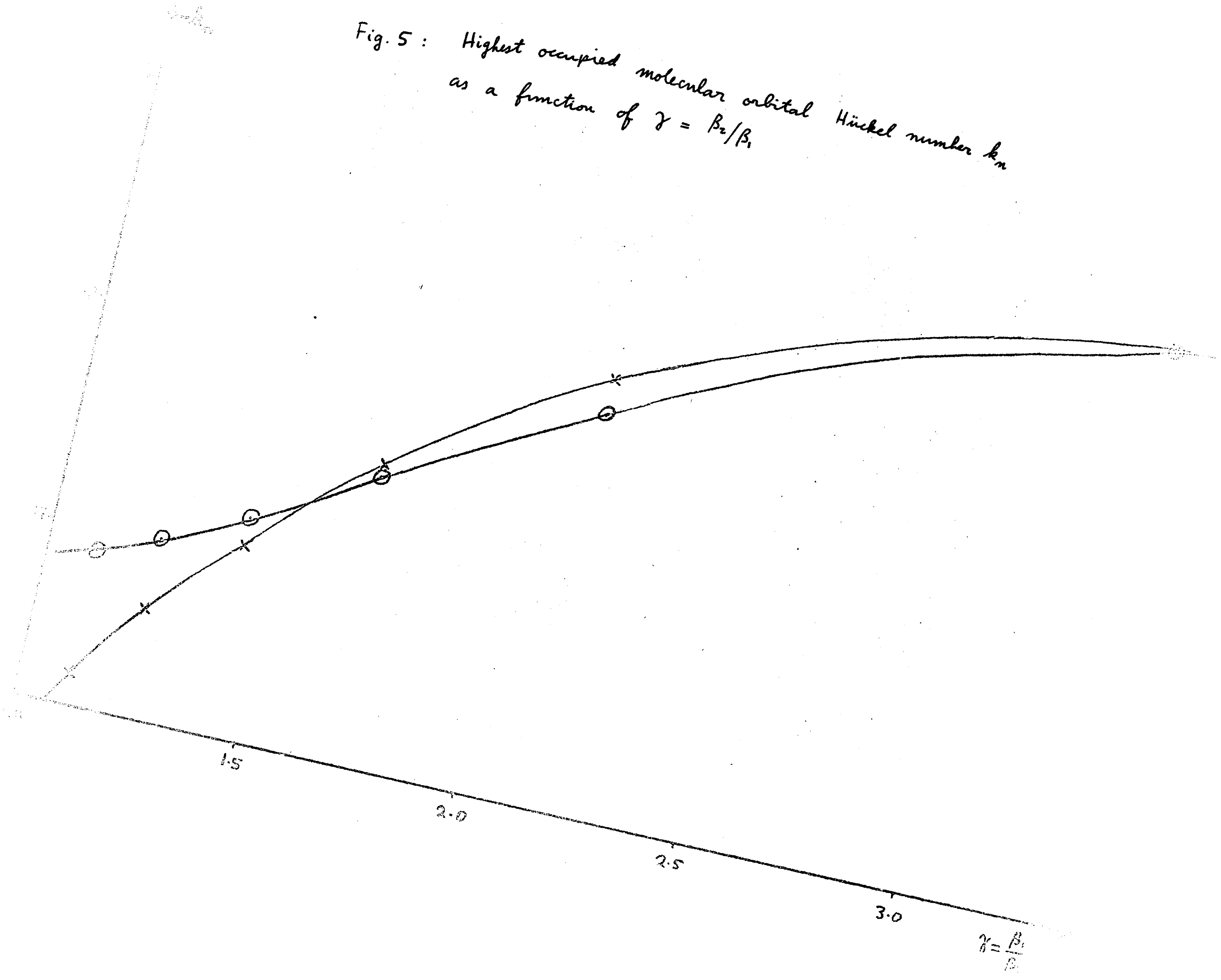
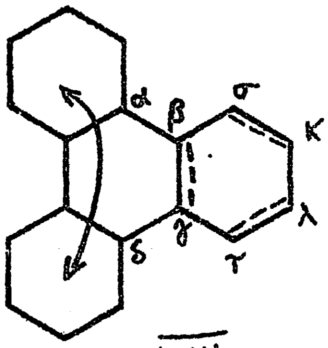
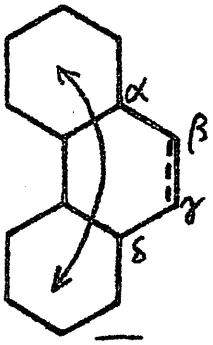


Fig. 5: Highest occupied molecular orbital Hückel number k_n as a function of $\gamma = \beta_2/\beta_1$

while the other rings constitute a phenanthrene system. We may, therefore, vary the β'-values for the bonds in this ring iso-energetically according to (3) and, for simplicity, assume that the β'-values for bonds $\alpha\beta$ and $\gamma\delta$ are the same as those of the low order bonds in ring A. In phenanthrene IX although the bond $\beta\gamma$ is not shared with



VIII



IX

another ring we may still suppose, for purposes of comparison, that the β'-values of bonds $\alpha\beta$, $\beta\gamma$, $\gamma\delta$ are again given by (3).

The results of these calculations are illustrated in Fig.5 where the highest occupied molecular orbital energies have been plotted in units of $-\beta_0$ against $\gamma = \beta_2/\beta_1$. The curves cross at $\gamma = 1.61$ and, using this with (3) we find that $\beta_1 = 0.737$ and $\beta_2 = 1.187$. Substitution of these values into a new Hückel molecular-orbital calculation on phenanthrene and triphenylene leads to k_n equal to $0.7407\beta_0$ and $0.7403\beta_0$ respectively, and so confirms the technique described.

DISCUSSION

We do not claim that the calculations described here yet furnish unassailable proof of Clar's theories of aromaticity. They are in general agreement with the relevant spectra of the known triphenylenes and to this extent corroborate the predictions made on the basis of Clar's models. However, the fact that we are using Hückel molecular-orbitals as bases precludes the acceptance of localised electron-pair models. These can have no meaning in the Hückel theory unless some of the β_{rs} values are assumed to be zero even when r and s are neighbours. For example, if in triphenylene VIII we put the β-values for bonds $\beta\sigma$ and $\gamma\tau$ equal to zero, as would be necessary if these were considered to be pure σ-bonds, we should obviously find the secular determinant factorising to give the π-levels of phenanthrene from the conjugated system to the left of and including $\beta\gamma$ and those of butadiene (or of ethylene if $\kappa\lambda$ also has $\beta = 0$) from the rest of the molecule. In either case the lowest electronic transition energies would therefore be those of phenanthrene. However, there is ample evidence to support the view that between sp^2-hybridised carbon atoms β is a function of bond length and cannot be zero in aromatic hydrocarbons. Further β' appears always to be between 0.7 and 1.2, Our calculations indicate that the relative spectral measurements are predictable by using β -values lying within this range.

CONCLUSION

We conclude that the observations of Clar and his colleagues on the spectra of the triphenylenes are explicable on the basis of molecular orbital calculations such as our series I and II the latter being probably the better. We certainly do not assert that we can explain the spectra in detail or that we are confident that the interaction integrals β are unequivocally determined, indeed we show that it is possible to vary these in a benzene ring without altering the highest occupied levels k_n. We hope to report in a subsequent publication on the result of assuming in the B*m*,*1* portion of the molecule *s*B*m*,*1* that the β's are those of the phene OB*m*,*1*.

We gratefully acknowledge many helpful discussions with Dr. E. Clar and Dr. J. F. Guye-Vuilleme and the award of a D.S.I.R. Maintenance Grant to one of us (D.A.M.-B.) Chemistry Department, University of Glasgow.

References.

(1) AHMED, F.R. and J. TROTTER: Acta Cryst., 1963, **16**, 503.

(2) CLAR, E., A. McCALLUM and R.A. ROBERTSON: Tetrahedron, 1962, **18**, 1471.

(3) COULSON, C.A. and R. DAUDEL: "Dictionary of Values of Molecular Constants", Volume II.

(4) GOODWIN, T.H. and D.A. MORTON-BLAKE: Theoretica Chimica Acta, in press.

(5) HARGREAVES, A. and S. HASAN RIZVI: Acta Cryst., 1962, **15**, 365.

(6) LENNARD-JONES, J.E: Proc.Roy.Soc., 1937, **A.158**, 280.

(7) MULLIKEN, R.S., C. RIEKE and W. G. BROWN: J.Amer.Chem.Soc., 1941, **63**, 48.

(8) PARISER, R: J. Chem. Phys., 1956, **24**, 250.

(9) STREITWIESER, A., Jr.: "Molecular Orbital Theory for Organic Chemists", Wiley, New York, 1961, p.218.