THE SYNTHESIS AND STUDY
of
POLYCYCLIC AROMATIC SYSTEMS

THESIS

presented by

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CONTENTS.

SUMMARY.

To suggest that in certain polycyclic aromatic hydrocarbons, the π-electrons are not generally delocalised, but are confined to certain 'benzenoid rings' in aromatic sextets, may be at variance with generally accepted modern chemical theory.

This concept can nevertheless provide a satisfactory basis for the discussion of the chemistry of these substances. Indeed the remarkable properties of the fully benzenoid hydrocarbons, where the localisation is thought to be complete and the hydrocarbons can be written as condensed polyphenyls, must be difficult to account for in a conventional manner.

The ideas described above emphasise the fundamental importance of Robinson's "aromatic sextet" to all aromatic substances.

In the first section the synthesis of 4,5:12,13-dibenzoheptazethrene is described. The unusual basicity of this hydrocarbon illustrates the tendency for all polycyclic hydrocarbons to adopt configurations which have the maximum number of benzenoid rings.

The synthesis of tetrabenzoheptacene has been achieved and this hydrocarbon exhibits all the remarkable stability of all the fully benzenoid hydrocarbons in spite of the extended nature of the molecule. The structure of the tetrabenzoheptacene was fully confirmed by a study of its ultra-violet, infra-red, and phosphorescence spectra.

Dihydro-5,6:13,14-dibenzoheptazethrene has been synthesised by three different routes, but could not be dehydrogenated to the fully aromatic system.

The apparent instability of the 5,6:13,14-dibenzoheptazethrene molecule is explained in terms of the benzenoid ring theory.

Tetrabenzocoronene was synthesised and the absorption spectrum recorded. A study of this, and the properties of the hydrocarbon suggest that this molecule may be sterically strained.

Investigation of the little known chemistry of peropyrene was carried out during unsuccessful attempts to synthesise 5,6 benzoperopyrene. A new route to peropyrene was discovered and several derivatives of the hydrocarbon described.

5,6:12,13-Dibenzoperopyrene was resynthesised by an unambiguous route and its absorption spectrum recorded.

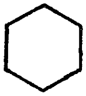
The highly condensed green hydrocarbons resulting from the condensation of anthanthrone were investigated. A separation of the substances was achieved and their absorption spectra recorded. Structures have been suggested, but not proven, for these highly complex hydrocarbons.

In Appendix A an attempt to synthesise the highly basic dinapthoazulene is described.

Finally in Appendix B some preliminary experiments to synthesise a molecule, which must have 'Dewar' structures, are outlined.

Nomenclature.

That used by E.Clar in 'Aromatische Kohlenwasserstoff' is generally employed. Double bonds are usually only written where some special significance is intended.



denotes a fully aromatic benzene ring.

denotes a fully hydrogenated benzene ring.

denotes the 'benzenoid' ring.

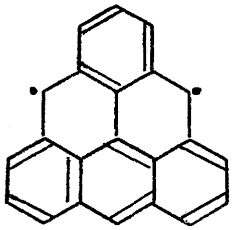
Introduction

Polycyclic aromatic hydrocarbons with their complex banded spectra provide a rich source for the study of absorption spectra, and comparison and correlation of these is an essential means of gaining insight into the nature of aromatic character in general. The first systematic studies of this type were carried out by E.Clar, (1) who had synthesised many of the most important hydrocarbons, and pointed out the family resemblances between the electronic spectra of polycyclic aromatic hydrocarbons.

The significance of Kekule structures and the importance of the aromatic sextet.

The special nature of the electronic state of benzene, and aromatic compounds in general, has long been recognised. Many, and varied, explanations have been offered to account for the absence of bond isomers in disubstituted benzenes. Kekulé's theory involving interchange between two classical structures already involved at least partially nomadic bonds. With the growth of the electronic theory, and the advent of physical tools which proved the benzene molecule to be a regular planar hexagon, the idea of completely delocalised electrons gained acceptance. The three double bonds in benzene were replaced by six π-electrons which were evenly distributed around the ring. That this aromatic sextet was present in all compounds with aromatic character, was first recognised by R.Robinson (2) who showed that it would explain the aromaticity of non-benzenoid substances e.g. the azulenes. The introduction of wave-mechanical theory to theoretical chemistry led to the development of the molecular orbital method, which seeks to describe the behaviour of electrons in terms of probability functions, and classical Kekule structures were not thought to have any real significance; while Pauling's Valence Bond method gave these structures a statistical importance only, and equal weight to all such classical structures.

It is a fact however, that very few molecules do exist which cannot be formulated in classical terms. Great interest is attached therefore, to those structures which can not be given a classical arrangement of bonds but which might conceivably be stable in terms of modern theory. A hydrocarbon of this kind is triangulene, which from the standpoint of classical chemistry has no Kekule structure, and can only be written as a diradical (i). Viewed in molecular orbital terms, structure (ii) might be possible in which the four electrons in the centre could be arranged in paired molecular orbitals.



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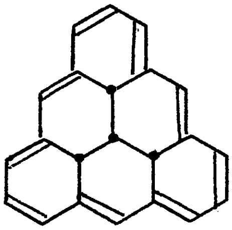
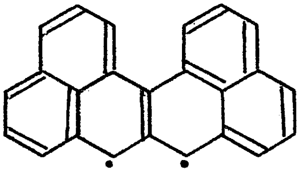


ii

The importance of this molecule was first pointed out by E.Clar,who predicted it would be unstable.(3) Synthetic work by Clar and Stewart (4) later justified this prediction. Hydrogenated derivatives of triangulene failed to yield the parent system upom dehydrogenation by methods which had been successful for the most reactive of polycyclic systems. The molecule exists only as a diradical and polymerises immediately upon formation. This conclusion was arrived at also by Longuet-Higgins (5) and explained in terms of M.O.theory. Several other examples of the same type have since been investigated. The dibenzotetracene (iii) and dibenzopentacene (iv) have been described by Clar and Kemp (6) and shown to exist only as unstable diradicals.



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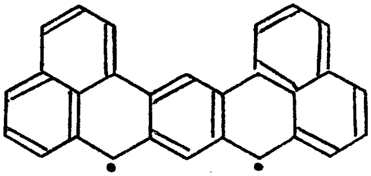
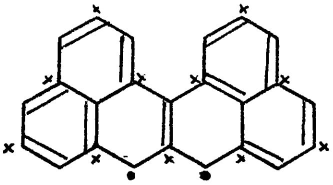


iv

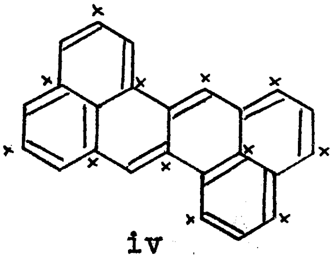
For any polycyclic aromatic hydrocarbon to exist in a stable form it must be possible to formulate it in classical terms. All the above hydrocarbons are alternant in terms of the original definition (7). However when the number of starred and unstarred atoms are counted it is found that they are not equal. It is thus possible to tell at once whether a given polycyclic system will exist as a radical or not. For example consider the systems shown below:-



iii

11 starred
13 unstarred

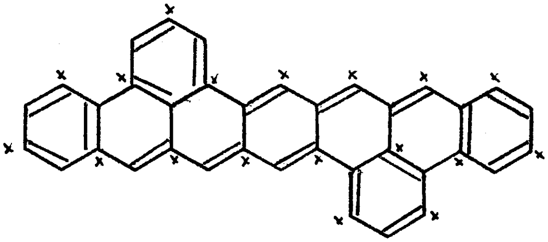
Diradical



iv

12 starred
12 unstarred

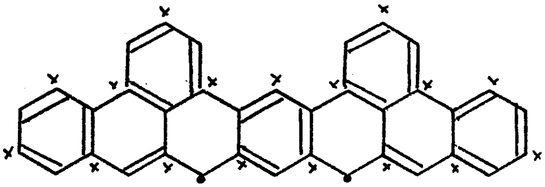
Stable



vi

18 starred
18 unstarred

Stable



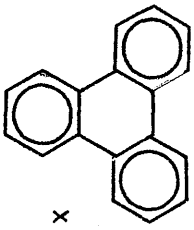
vii

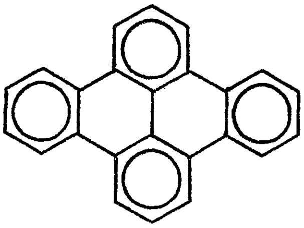
17 starred
19 unstarred

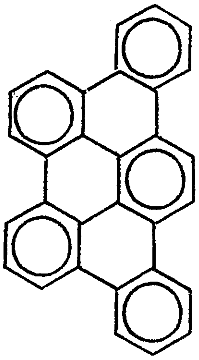
Diradical

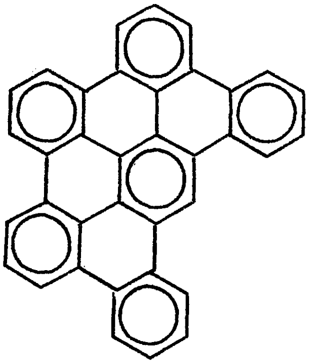
It may be concluded that only alternant hydrocarbons with an equal number of starred and unstarred atoms will be stable. The synthesis of zethrene (v) which has two double bonds fixed in the centre shows that one classical structure is enough to ensure stability (8).

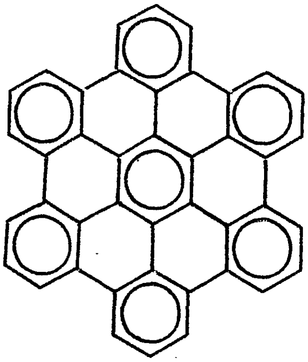
A group of notably stable polycyclic systems with a strictly limited number of Kekule structures has recently been described (9). Examples of these hydrocarbons which can be formulated as condensed polyphenyls are shown below.











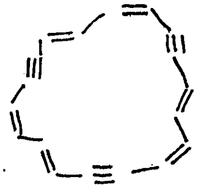
About ten such hydrocarbons are known,and other examples are discussed later. The π-electrons in these fully benzenoid hydrocarbons are thought of as confined to the rings marked with circles. These electrons can be imagined to exist,either as an aromatic sextet,or as the double bonds of two Kekule structures,which are peculiar to those rings alone. Benzenoid hydrocarbons have markedly similar properties,all possessing exceedingly low reactivity and high stability e.g. they do not dissolve even in concentrated sulphuric acid.

The absorption spectrum of each hydrocarbon is the most shifted to the violet of all the isomeric hydrocarbons, except for the corresponding polyphenyl with the same number of rings,and this must be related to the low reactivity.Again all of these hydrocarbons exhibit,long life,intense phosphorescence in solid solution at low temperature.

The preceding facts show that a particularly stable π-electron system must be present in such molecules,and the hypothesis that all the electrons are confined to certain rings in 'inherent sextets' accounts for the experimental observations, although it would seem to be at variance with M.O.theory.

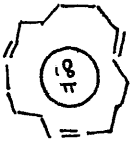
An interesting comparison has been made possible by Sondheimer's synthesis (10) of the polyene (ix) which is said to possess a molecular orbital of the type shown in (ixa). This substance while relatively stable for molecules of this type can not compare in stability with the fully benzenoid triphenylene (x).

Theoretically this hydrocarbon,which also has 18 -electrons could have a molecular orbital of comparable type to the polyene,as shown in (xa). The absorption spectrum of the polyene is markedly shifted to the red in comparison with that of triphenylene. e.g. the β-band of the polyene (11) is at 342mu.while the β-band of triphenylene is at 257mu.

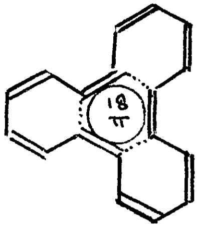


IX

9 Double Bonds.



IXa



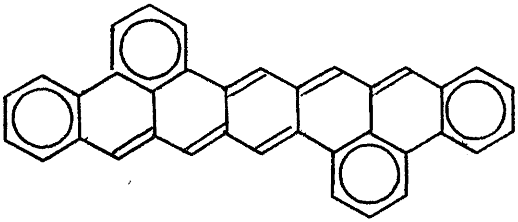
Xa

9 Double Bonds.

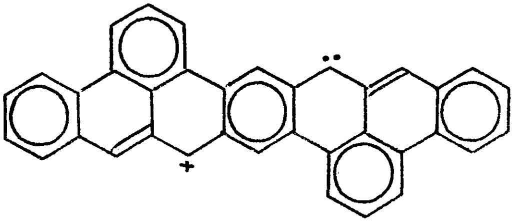
While some of the relative instability of the polyene may be due to hydrogen compression, the extreme differences between the two molecules must be caused by a totally different bonding principle in triphenylene.

The fully benzenoid system is the most stable configuration possible for polycyclic aromatic hydrocarbons and all such hydrocarbons will tend to have the maximum number of benzenoid rings and the minimum of double bonds. This trend is illustrated by several reactions in which the driving force is the fact that the product has gained a benzenoid ring.

Thus when the hydrocarbon dibenzoheptazethrene (xi) is considered it can be seen that a normal arrangement of double bonds could give four benzenoid rings but leave six double bonds fixed in the centre.



xi



xii

However the polarised structure (xii) has five benzenoid rings and the remaining two double bonds could possibly be part of a delocalised ion system.

The synthesis and properties of this hydrocarbon will be fully described later. But it was found that the hydrocarbon was in fact basic, forming a stable hydrochloride and other salts. This is extremely unusual behaviour for a hydrocarbon possessing only six membered rings, and emphasises the importance of the maximum number of benzenoid rings for the stability of polycyclic systems.

Electronic Spectra of Polycyclic Hydrocarbons.

Classification of the band systems.

The numerous absorption bands in the spectra of aromatic hydrocarbons all arise, in the visible and near ultra-violet regions, from three electronic transitions which correspond to three band systems. The classification of these band types in benzene was first made by E.Clar, (1,12) who also showed that the bands occur in all polycyclic hydrocarbons. Such a classification of band types is essential for the logical discussion of the effect of annellation of benzene nuclei upon the spectra of polycyclic systems.

In benzene itself the band groups are as follows:-

β,1790 Å (most intense); para-band 1900-2068 Å (medium intensity), and α band 2300-2600 Å (lowest intensity).

Theoretical accounts of the origin of these band groups in benzene have been given, and a summary of this is given by H.A. Stabbe (13). A similar classification of the electronic transitions in aromatic systems was later made by I.R.Platt (14) and extended to the vacuum ultra-violet. This classification, based upon a drastic simplification of the molecular orbital approach, agreed substantially with Clar's earlier one. A comparison of the two systems is given by Moffit (15).

The three transitions which give rise to the three band groups, i.e α, para, β, were resolved according to their behaviour under various physical conditions. The criteria used are as follows:- The position and intensity of the band, and the direction of the transition moment i.e. polarisation (15). The shift in wavelength on going from room temperature to -180°, (16) and the red shifts on transition from vapour to solution, to the solid state (1,17). Also the vibrational fine structure of the band system is characteristic (18) as are the shifts in different types of solvent (18).

All this data is summarised in Table 1.The alternative Platt symbols are given in parentheses. The term acene is used to denote the linearly annellated series,anthracene, tetracene,pentacene,etc. While the term phene is used for the angularly condensed series;phenanthrene,tetraphene, pentaphene etc.

Table 1.Classification of absorption bands.

	α - bands $^1(L)_b$	para-bands $^1(L)_a$	β -bands $^1(B)_b$
Extinction coefficients (i)	ca.10^2-10^3	ca.10^4-10^5	ca.10^5
Polarisation	Acene:long. Phene:trans.	Acene:trans. Phene:long.	-
Temperature dependence	hypsochromic ca.30-50cm^{-1}	bathochromic ca.300cm^{-1}	bathochromic ca.300cm^{-1}
Red shift			
Vapour→ Solution.	ca.250cm^{-1}	ca.900cm^{-1}	ca.900cm^{-1}
Solution→Solid	ca.700cm^{-1}	ca.1300cm^{-1}	ca.1300cm^{-1}

(i) long.= longitudinal,the transition moment is in the direction of the long molecular axis.

Trans = transverse,transition moment in the direction of the short molecular axis.

Symmetric annellation effects,the Annellation Principle.

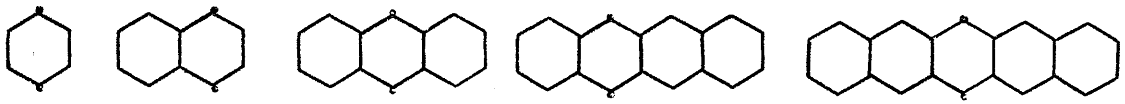
The condensation of benzene nuclei,to form the acene or phene series caused regular and constant shifts in the band systems. Analysis of these shifts enabled E.Clar to relate the position of light absorption to the number of annellated rings in a simple but quantitative manner.(1,12) The results of this Annellation Principle are briefly summarised as follows:-

There are annellation series,e.g.acenes,phenes, in which the difference between corresponding bands of the various members is constant in terms of $\sqrt{\text{Å}}$.

The para-bands of the acenes show a strong red shift upon linear condensation of new rings (positive annellation effect). While the para-bands of the phenes show a slight shift to the violet in comparison with the corresponding acene (negative annellation effect).The α-bands of the phenes show the strong red shift on annellation.

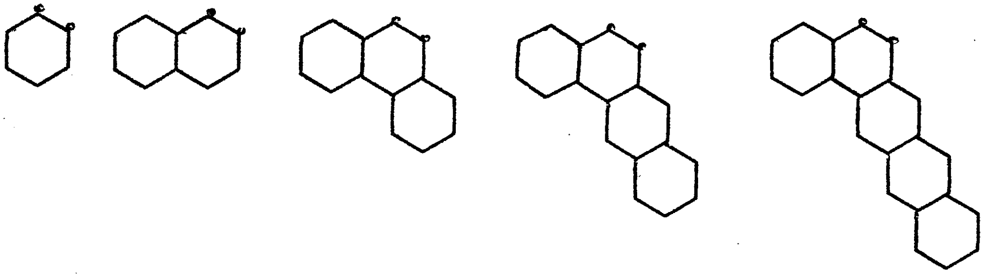
A basic premise of the Annellation Principle is that the electrons which undergo the transitions are located at definite positions in the molecule. The para bands arise from electrons at the para or meso positions of the acenes (marked with dots in figure below). This is also the main site of chemical reaction in these compounds,and the steady advance of the para bands is matched by the steady increase in reactivity at the para position. Reactions such as photo-oxidation,addition of maleic anhydride etc.all occur more readily in the para position of the higher acenes than in the lower acenes.

Acenes.



$$\xrightarrow[\text{increase in para-reactivity}]{\text{increase in para-band wavelength}}$$

Phenes.



$$\xrightarrow[\text{increase in ortho-reactivity}]{\text{increase in } \alpha\text{-band wavelength}}$$

Similarly the 'light absorbing' electrons in the phenes are fixed in the ortho positions (see dots above), and the increase in wavelength of the bands is accompanied by an increase of reactivity at the ortho position. The additional electrons from the annellated rings exert their effect by increasing the screening effect on the nuclear charges retaining the light absorbing electrons. In this manner less energy is needed to cause the electronic transition and the band moves to the red.

The various electronic transitions (α,$\beta$and para) can be represented by an equation, $v \; R=/K^2$ where v is the frequency of the transition, R is a constant,and K is a variable number (Order Number) which increases by a constant amount for each additional ring,and it is a simple function of the number ofπ-electrons.

For example first band of the α absorption in the phenes,can be calculated from $v= R_\alpha /K^2$ where $R_\alpha = 2194600\text{cm}^{-1}$., and the Order Numbers (K) equal $7\frac{1}{2}$,8,$8\frac{1}{2}$,9,$9\frac{1}{2}$ for benzene, napthalene,phenanthrene,tetraphene,pentaphene. Similarly the first β absorption band of acenes can be calculated from $v=R_\beta /K^2$ where K is $8\frac{1}{2}$,9,$9\frac{1}{2}$ and 10 for anthracene,tetracene, pentacene and hexacene. The constant R_β for this series is equal to 2962700cm^{-1}. It can be seen that the constants R and R and therefore the frequencies v_α , v_β are in the ratio:-

$$v_\alpha : v_\beta = \left[\frac{1}{2^2}-\frac{1}{3^2}\right]:\left[\frac{1}{2^2}-\frac{1}{4^2}\right] = 1:1.35$$

This ratio is observed experimentally, and any deviation from it indicates some abnormality such as severe steric strain, in the molecule.

The significance of the Order Number K is that with its help,the two constants R_α and R_β can be related by Rydberg's constant R by the following equations,which are in same form as the well known Rydberg-Mosely equation for atomic spectra:-

$$v_\alpha = \frac{z^2}{K^2} \cdot R\left[\frac{1}{2^2}-\frac{1}{3^2}\right]$$

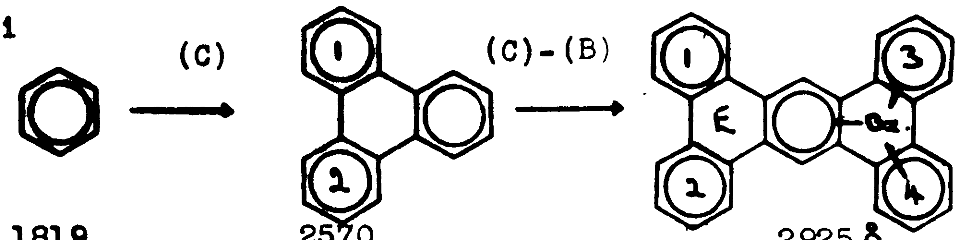
$$v_\beta = \frac{z^2}{K^2} \cdot R\left[\frac{1}{2^2}-\frac{1}{4^2}\right]$$

where the Nuclear Charge (z 12), is double the nuclear charge of carbon (6) and R is Rydbergs Constant.

In the acene series the frequency of the first para-band is calculated from the equation $v = R_p / K_p^2$, where $R_p = 1712800 \text{cm}^{-1}$. In this series however, the Order Number $(K)_p$ does not have the same value as the Order Number K used to calculate the wavelength of the first β-bands of the acenes but is equal to 6,7,8,9,10 and 11 for benzene, napthalene, anthracene, tetracene, pentacene and hexacene. The relationship between the Order Numbers is given by the equation:- $K_p = 2K - 9$ It can also be shown that difference of the aromatic resonance energy between consecutive members of an annellation series, can be related to the differences between the α and β frequency of the bands. The resonance energies calculated in this way are in good agreement with experimental values.

Several other annellation series have been described, these are: the para-bands of the perylenes, the para-bands of the pyrenes, the para-bands of the peropyrenes and the para-bands pf the polyrylenes.

i



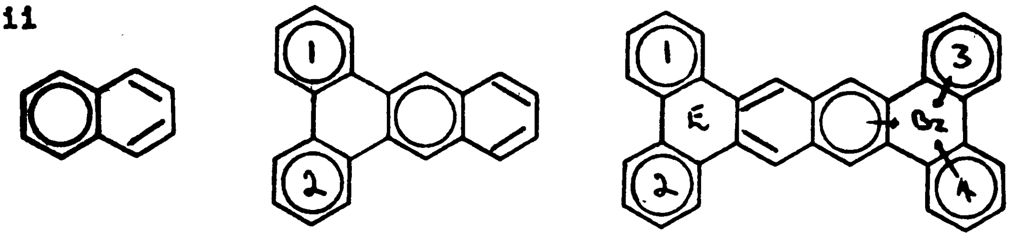
λ_p 1819 2570 2925 Å

+751 +355

$\sqrt{\lambda_p}$ 42.65 50.70 54.10 $\sqrt{Å}$

+8.05 +3.40

ii



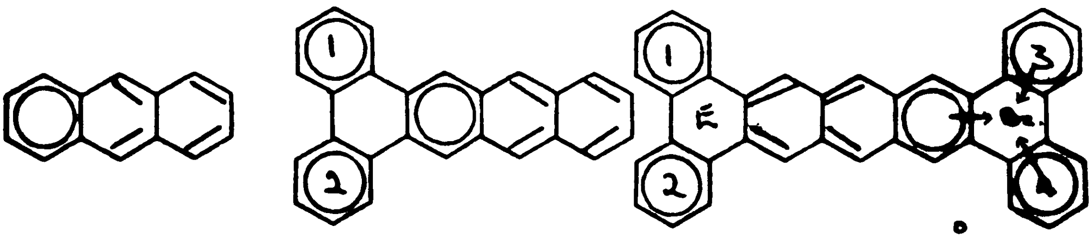
λ_p 2210 2860 3255 Å

+650 +395

$\sqrt{\lambda_p}$ 47.10 53.48 57.05 $\sqrt{Å}$

+6.47 +3.57

iii



λ_p 2515 3130 3460 Å

+615 +330

$\sqrt{\lambda_p}$ 50.15 55.95 58.82 $\sqrt{Å}$

+5.80 +2.87

Asymmetric annellation effects, and the mobile π-electron pair.

All the annellation series discussed above were characterised by regular and constant spectral changes. Recently, series in which unequal or asymmetric shifts of β-bands occur have been described. (19,20,21).

When two diphenylene units (rings 1,2 and 3,4) are successively connected to an acene nucleus the β-bands are displaced by different amounts to the red (see opposite).

In all these cases there is first a large, and then a small positive shift. This could not be accounted for by any theory which supposes an even distribution of π-electrons. It is apparent that there is two distinct processes. The primary one (process C) must be the formation of the bonds between the diphenylene units (rings 1,2 and 3,4.) and the acene nucleus, and the formation of these contact bonds must occur on both occasions.

The secondary process (B), is the formation of an induced benzenoid ring (Bz.) by the transfer of two electrons from the surrounding aromatic sextets. If each sextet can only transfer two electrons, this process (B) can only happen once, and this would account for the observed asymmetric displacements of the β-absorption bands.

Whether the induced ring (Bz.) is formed at the first or second annellation is not certain. A consideration of the energy changes implied by the absorption shifts can be used to show that the induced ring may be formed on the second annellation of the diphenylene unit.

The formation of contact bonds (process C) adds extra electrons which must increase the screening effect without any compensating gain in electron stability.Thus less energy is required to cause the β transition and the absorption band can move to the red. It can also be argued that the formation of an induced ring (process B) resulting as it does in the increase in the benzenoid rings from four to five,must increase the stability of the whole π -electron system. That the gain of one extra benzenoid ring has a profound effect on the π -electron system has been shown earlier. It thus needs more energy to effect the β transition in such a stabilised system and a negative (ultra-violet) shift must occur. This shift is overlaid by the slightly larger positive shift of contact bond formation,and the net result is a slight displacement of the β-absorption to the red.

In Table 2.the various shifts are compared, and it can be seen that when the second,composite shift (C-B), is deducted from the first shift (C),the influence of the contact bonds is eliminated and the effect of the induced ring can be judged.

As is shown below the initial acene system has only been extended by one ring after two annellations, confirming the presence of an empty ring (E).

Table 2.

System	Annellation 1. $\sqrt{A^\circ}$	Annellation 2. $\sqrt{A^\circ}$	Difference. A°
i Benzene → Tetrabenzo-anthracene	+ 8.05	+ 3.40	2237 (β band of Napthalene 2210 A°.)
ii Napthalene → Tetrabenzo-tetracene.	+ 6.47	+ 3.57	2491 (βband of anthracene 2493 A°
iii Tetracene → Tetrabenzo-pentacene	+ 5.80	+ 2.87	2818 (βband of tetracene 2740,2930 A° in heptane 2802A°calc.

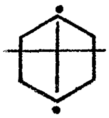
The above arguments do not prove that the first annellation produces the empty ring, and the second annellation the induced benzenoid ring, and indeed the reverse order was favoured at first (19,20,21). It can be claimed however that no other series of events will account for the observed asymmetric shifts, and the meaning of the difference between them.

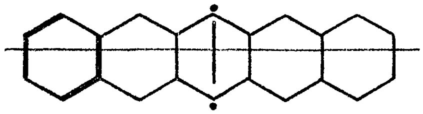
The concept of two π-electrons per aromatic sextet and benzenoid ring, free to migrate through the acene or other system, while the rest of the electrons remain confined to their rings, conflicts with the basic M.O. concept of free movement of all electrons throughout the whole system.

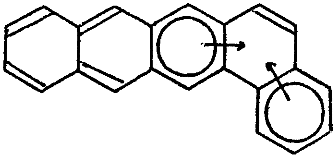
That some delocalisation of the electrons in polycyclic hydrocarbons does occur is shown by the addition of protons, the differing degrees of basicity, and the semiconductivity of these substances. Yet this delocalisation can not be general, since the diamagnetic anisotropic measurements of Akamatu and Matsunaga (22) show a high degree of localisation of electrons in their rings. Indeed they show that in the acenes, the localisation increases with the number of linearly condensed rings. The average orbital of pentacene (1.71Å.) is much smaller than the length of the pentacene molecule (12.14Å.), generalised delocalisation of π-electrons does not seem to occur. In coronene which has three benzenoid rings and therefore three mobile pairs, the average radius increases to 1.94Å, and in ovalene with four benzenoid rings and four mobile pairs it increases to 2.12Å. In both the latter the average π-electron radius is much smaller than the molecule itself.

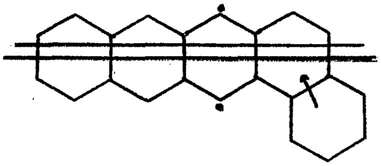
The concept of the mobile π-electron pair reconciles the need for some degree of delocalisation of π-electrons in polycyclic hydrocarbons, with the observed fact that the majority of the π-electrons are highly localised.

In a recent paper E.Clar (23) has used the idea of the mobile pair to explain some hitherto puzzling facts. The para-band absorption can be related to the formation of a para-bond, (marked with dots). This bond could be reinforced and 'compressed' by the two transferable electrons, as indicated by the transverse line in the figures below.









This anti-screening effect is strongest in benzene but decreases with increasing Order Number in the higher acenes, since the same pair has to cover a greater radius. The para-band in the acenes is thus not prevented from moving to the red,as described earlier. If an angular ring is condensed to an acene the new system, a phene,has one more benzenoid ring, shown by the circles above. Now the additional benzenoid ring can provide two more transferable electrons and the four mobile electrons can migrate through the long acene branch (shown by the two transverse lines). The anti-screening effect will be increased and thus the para-transition will require relatively more energy than in the corresponding acene. This is then a simple account of the negative annellation effect observed in the phenes,which had hitherto not been satisfactorily explained.

The anti-screening effect of the mobile pairs also accounts for the fact that the ground state of the para-bands in the phenes is below that of the acenes by the same ratio as that of the levels of the α-bands and β-bands i.e.1:1.35.

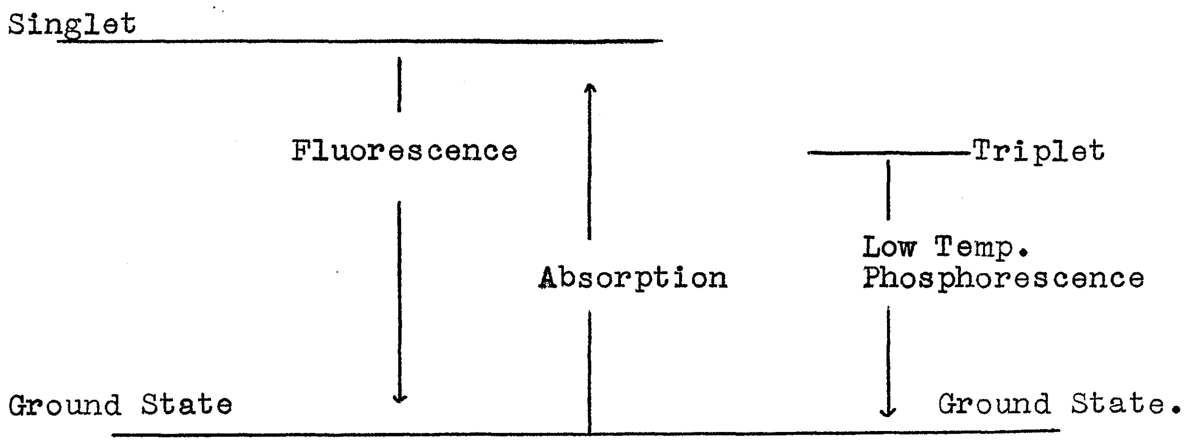
Para-bands must therefore be subdivided into p_α -bands (acene type) and p_β-bands (benzacene or phene type). Transitions calculated on this basis showed very good agreement with experimental values.

Phosphorescence Spectra and the Mobile Electron pair. The phosphorescence emission spectra which can be observed after irradiation of solid solutions of organic molecules at low temperatures are now recognised to be a general property of all unsaturated and aromatic compounds.

The phosphorescent state has an unusually long life-time, but can only be observed under strictly limited conditions which dampen molecular vibrations and reduce molecular interactions. Thus, solid solutions at very low temperature (77K.°) are generally employed.

The relationship between absorption, fluorescence and phosphorescence is shown by the Jablonski diagram (Fig.1).

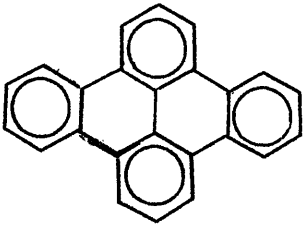
Fig.1.Jablonski Term Scheme

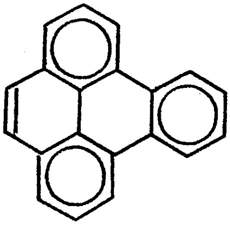


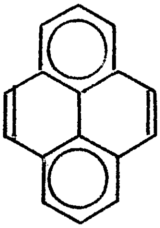
G.N.Lewis and M.Kasha (24) have shown that the low temperature phosphorescence of organic molecules can be attributed to the transition from a Triplet state to the ground state. Such Singlet-Triplet Transitions are highly forbidden and this is the reason for the long life of the phosphorescent state. Lewis and Calvin (25) have made magnetic studies of phosphorescent molecules and found the expected paramagnetism.

Polycyclic aromatic hydrocarbons provide a rich source of phosphorescence spectra. The relationship between the para absorption (Singlet transition) and phosphorescene (Triplet transition) has been investigated by Clar and Zander (26) and the difference between the longest para-band and the shortest phosphorescence band (Singlet-Triplet difference), has been recorded for a large number of polycyclic systems.

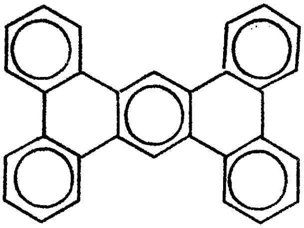
Significant regularities become apparent when these differences are considered in the light of the benzenoid ring theory. The Singlet-Triplet difference is a minimum for fully benzenoid hydrocarbons and increases with the number of non-benzenoid double bonds (See below).

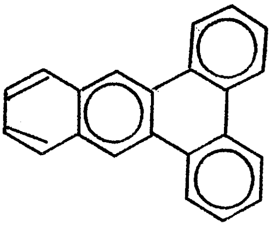


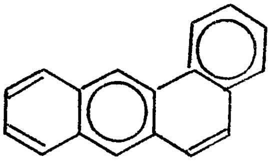




S ⟶ T
Difference cm.$^{-1}$ 10,330 11,650 13,120

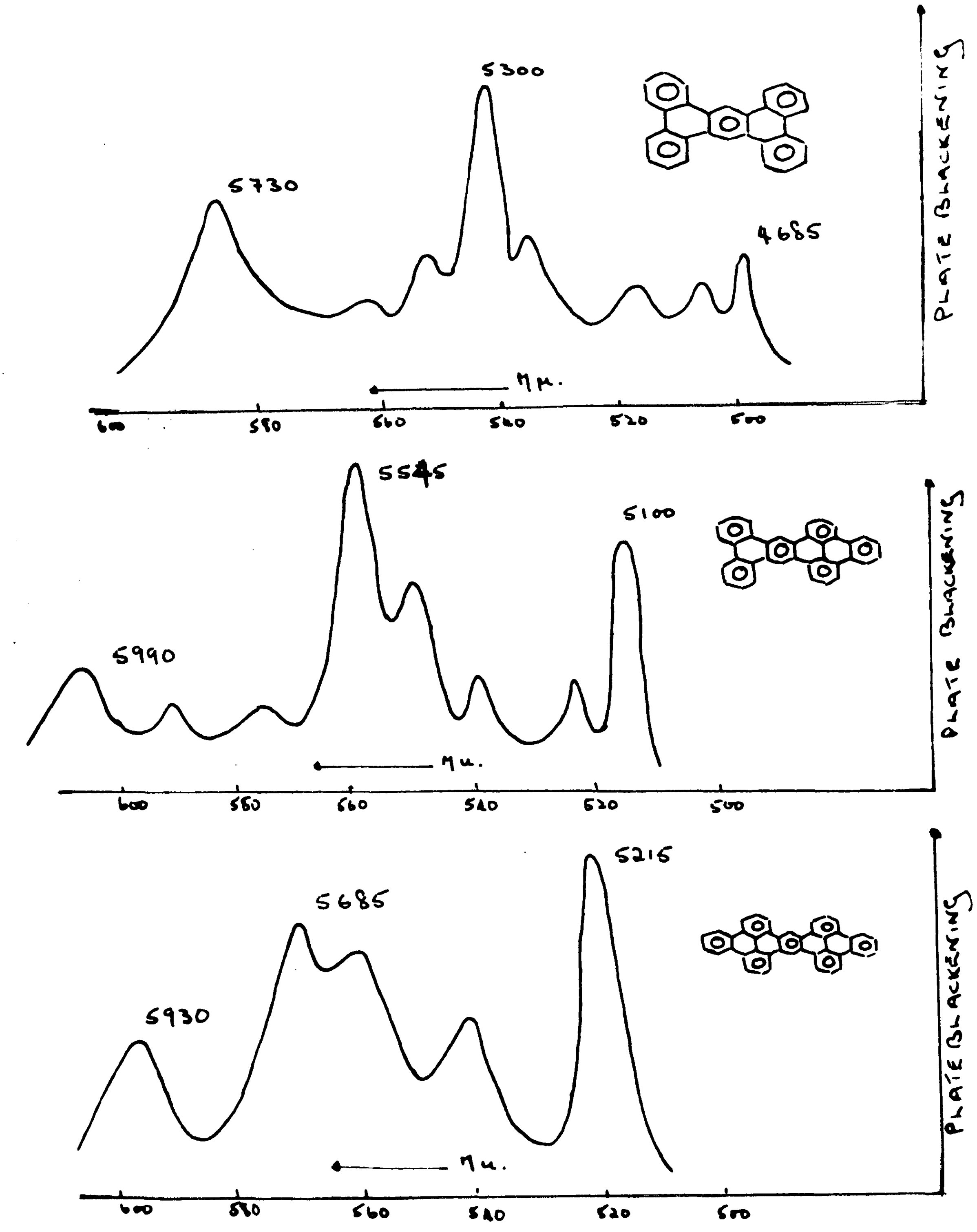






S ⟶ T
Difference cm.$^{-1}$ 9,710 11,180 11,630.

Fig.2 Phosphorescence spectra of fully benzenoid systems.

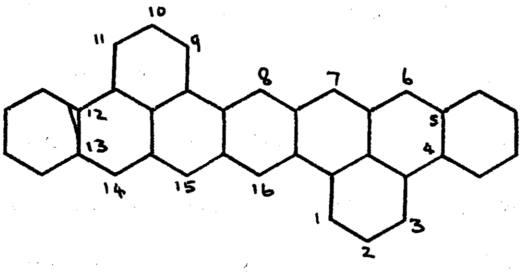


As the double bonds are incorporated into the benzenoid rings, the Singlet-Triplet difference gets smaller, since the phosphorescence bands of the fully benzenoid hydrocarbons lie at much shorter wavelengths than do those of hydrocarbons with 'free' double bonds. This suggests that the phosphorescent state has a connection with the mobile electron pair. In hydrocarbons, like acenes, where a maximum of double bonds are not contained in benzenoid rings, some form of interaction or coupling between the double bond electrons and the mobile pair could occur. This would make the phosphorescence transition easier and the spectrum will shift to the red, thus increasing the Singlet-Triplet difference.

In fully benzenoid systems such coupling is reduced to a minimum and the phosphorescence transition thus requires more energy, the observed bands lie at shorter wave-lengths and the Singlet-Triplet difference becomes a minimum.

Annellation in the acene series only adds extra double bonds thus increasing the coupling effect and allowing the spectra to shift thousands of Angstroms to the red. When a fully benzenoid series is considered, annellation adds no double bonds and relatively small red shifts are found. (Fig. 2.) Long life phosphorescence, which changes little on annellation of benzenoid rings, is thus a very strong indication that a hydrocarbon is fully benzenoid.

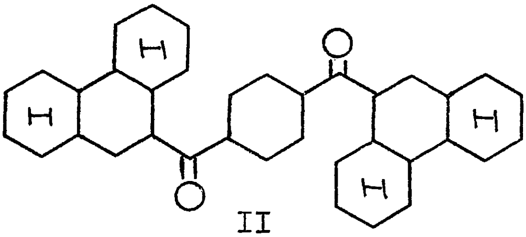
4,5:12,13-Dibenzoheptazethrene



I

Synthesis of 4,5:12,13 -Dibenzoheptazethrene I.

Terephthalyl chloride condensed twice with octahydrophenanthrene in the presence of aluminium chloride to yield 1,4 -di(octahydrophenanthroyl -9) -benzene II.This reaction is analogous to the previously described condensation of benzoyl chloride with octahydrophenanthrene.(27)



II

Pyrolytic condensation of this diketone,after the manner of the Elbs reaction,proceeded smoothly at 400-420, with elimination of water. Very little free hydrogen was detected during the condensation and the main bulk of the reaction product,consisted of highly hydrogenated hydrocarbons. After addition of xylene to the cooled pyrolysis product,a reddish crystalline mixture was deposited. Most of the reaction product remained in solution however,and chromatography gave mainly a viscous oil which was a mixture of highly hydrogenated substances and not investigated further. Small amounts of a yellow crystalline hydrocarbon were obtained from later chromatographic fractions,and proved to be a tetradecahydrodibenzoheptazethrene. The name heptazethrene is used for system III derived from zethrene IV.(28)

Fig. 3

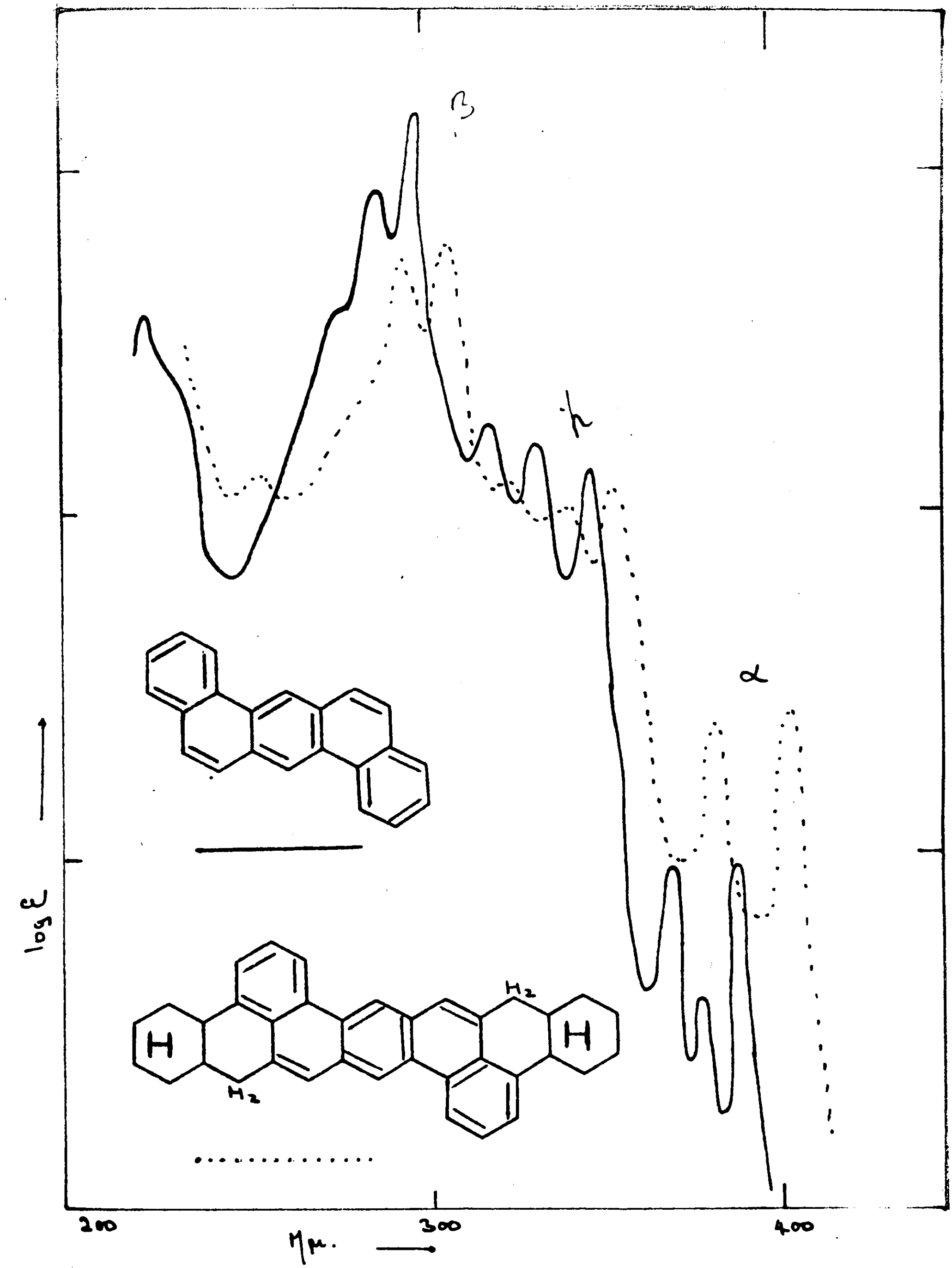
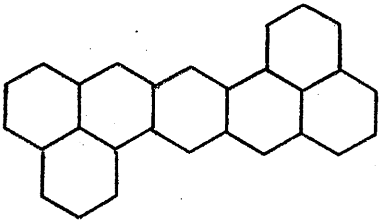


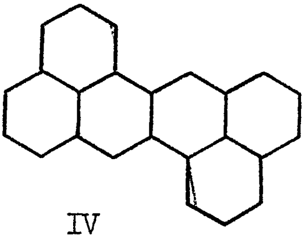
Fig.3 Band Maxima (mu.). inbenzene solution.

(————) α, 395,385,373; p,351,336,322; β,300,299.

(…………) α, 410,388; p, 360,346,330; β,310 .

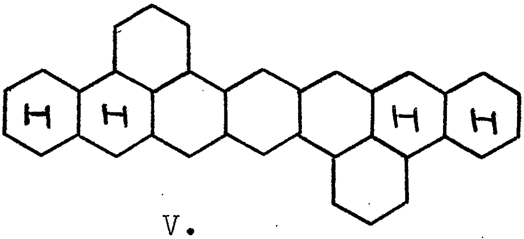


III



IV

The absorption spectrum of the tetradecahydro-hydrocarbon is given in Fig.3, where it is compared to that of 1,2:5,6-dibenzanthracene, the close similarity showing that the hydrocarbon must have structure V.



V.

Addition of copper powder during the pyrolysis, did cause dehydrogenation but because of the sensitivity of the resultant dibenzoheptazethrene to high temperatures, yields by this method were negligible. The reddish solid which crystallised from the diluted pyrolysis product was found to be mainly 6,14-dihydrodibenzoheptazethrene VI with a little octahydro-dibenzoheptazethrene VII.

Fig. 4

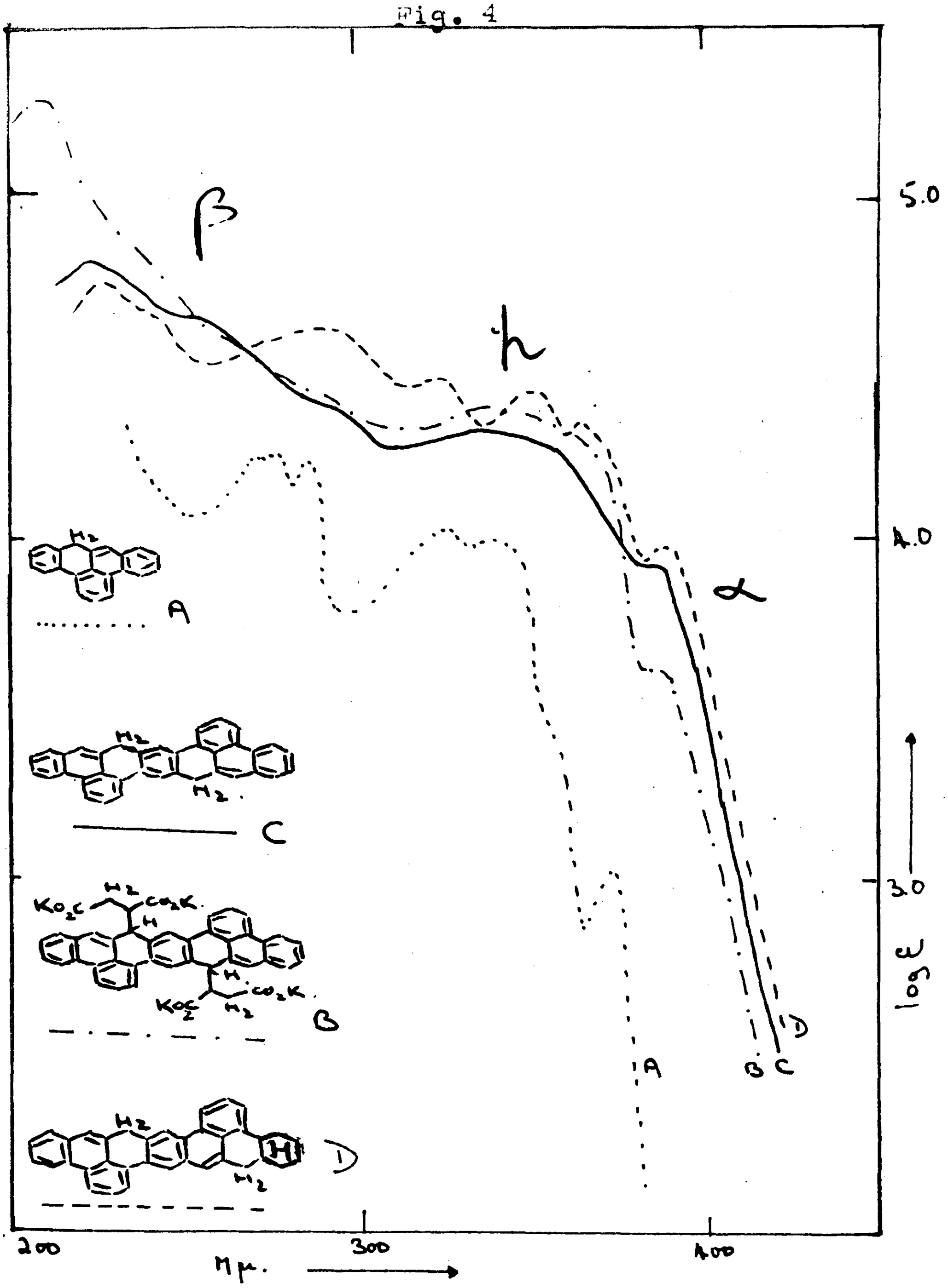


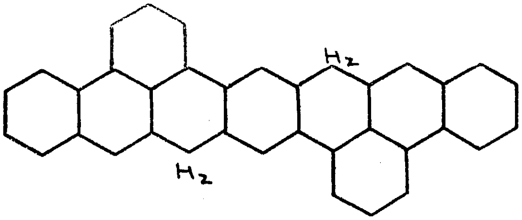
Fig.4 Band Maxima (mu.).

A inalcohol α ,372; p,339,327,3o2: β ,285,276,269.

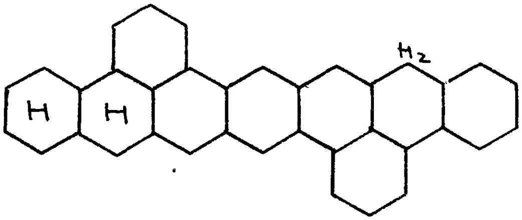
B in 50% alcohol α ,386; p ,340; β ,210.

C in benzene α, 390; p,354,340; in cyclohexane β ,253,222.

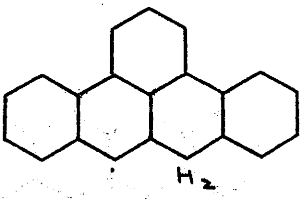
D in benzene α,384; p,36o,344; incyclohexane β,286,210.



VI



VII



VIII

The absorption spectra of the above hydrocarbons, after separation and purification, are shown in Fig.4, in comparison with that of 2,3:7,8-dibenzoperinapthene VIII (27). The similarity is apparent, and the increase in intensity and slight red shift of the spectra of VI and VII in relation to VIII are similar to the changes found on comparison of the spectra of diphenyl and terephenyl. These spectra also eliminate the possibility of the hydrocarbons VI and VII having a 1,2:5,6 -dibenzanthracene complex as in V.

Fig. 5.

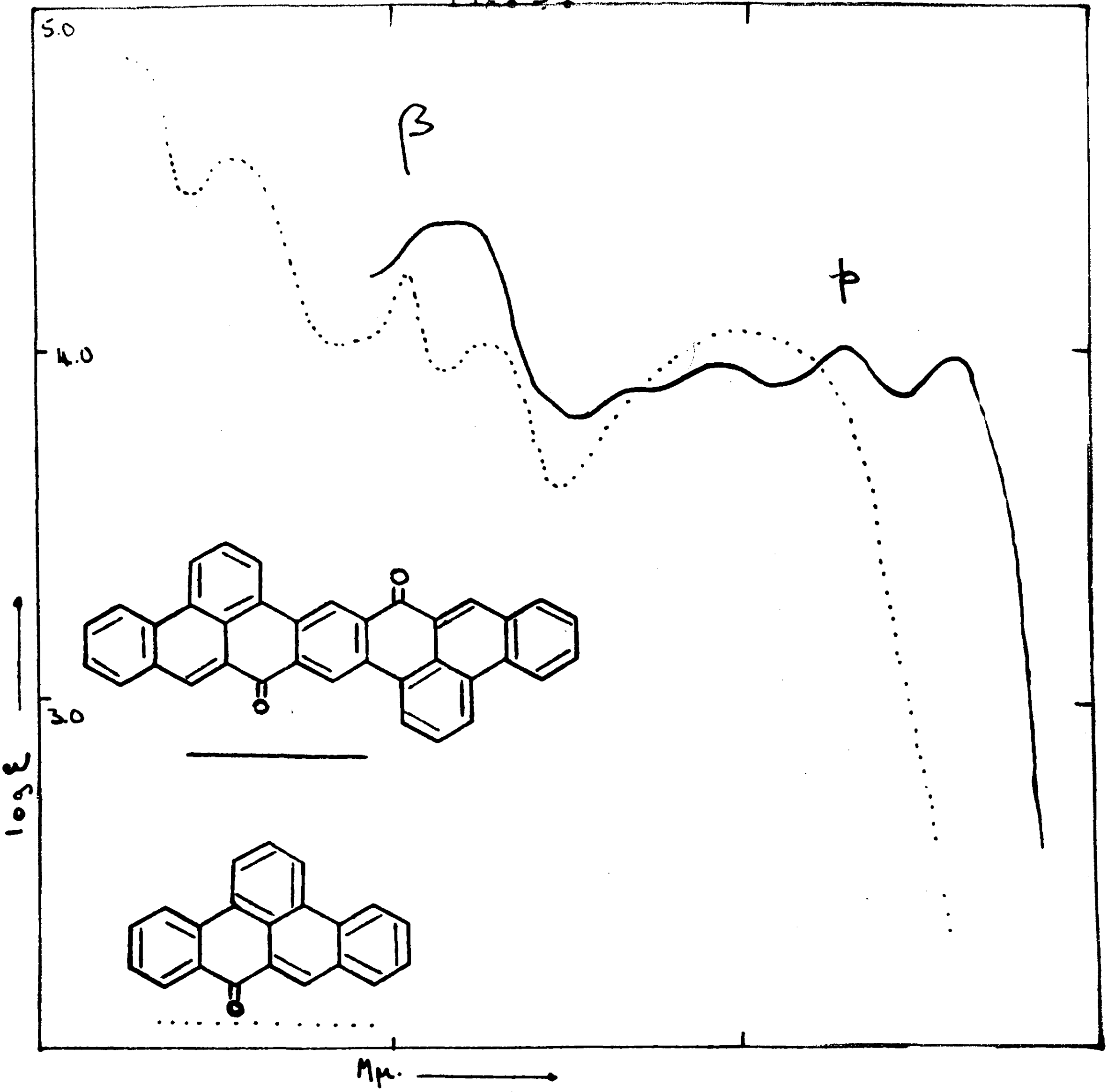
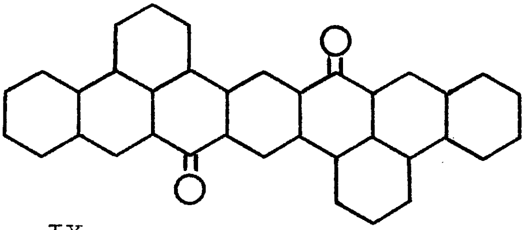


Fig. 5. Band Maxima (mu.)

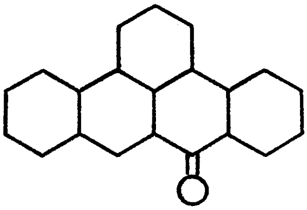
(————) in trichlorobenzene p, 477,455 ; β,340.

(··········) in alcohol p,400,327,303; β,257.

The crystalline mixture of VI and VII was oxidised,with selenium dioxide in nitrobenzene,to dibenzoheptazethrene quinone IX in good yield.

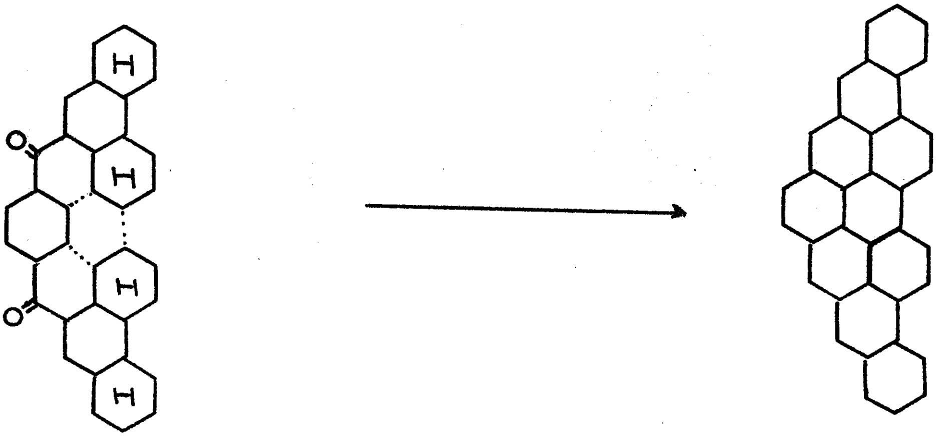


IX



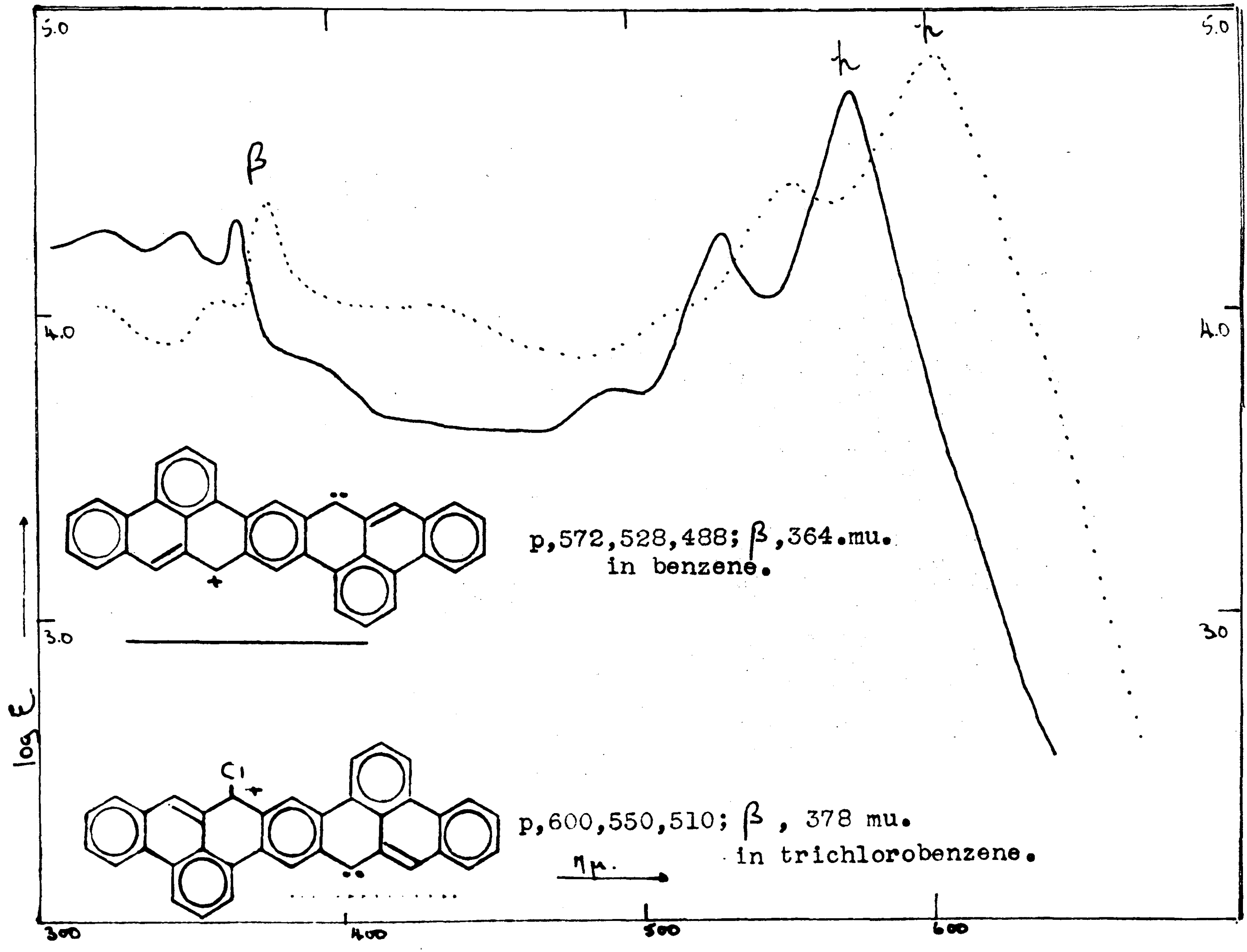
X

The similarity of the absorption spectrum of this quinone to that of 2,3:7,8-dibenzoperinapthenone X is shown in Fig.5 The quinone IX does not form a vat with alkaline sodium dithionite,which is typical behaviour for quinones of the dibenzoperinapthenone type. The structure and properties of this quinone finally excludes the possibility of the alternative condensation to give a hydrocarbon with structure XI,since a quinone of this type would be deeply coloured and form a vat readily.



XI

Fig. 6

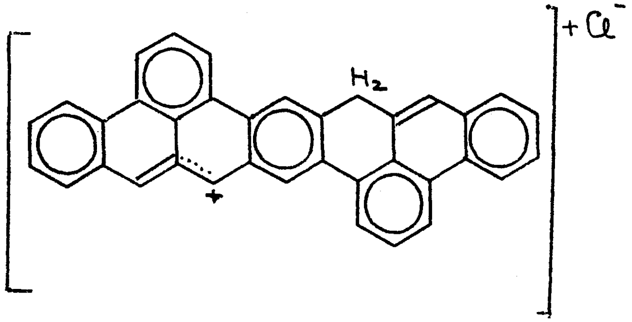


p,572,528,488; β,364.mu.
in benzene.

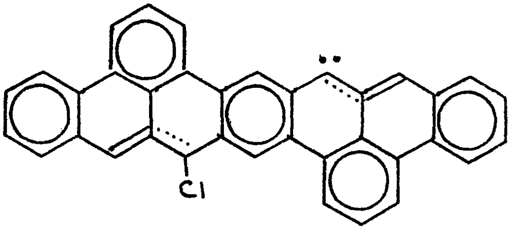
p,600,550,510; β , 378 mu.
in trichlorobenzene.

Dehydrogenation of the mixture of VI and VII by sublimation over preheated palladium charcoal gave needles of dibenzoheptazethrene I in high yield.Simple crystallisation of the mixture from nitrobenzene,or reaction with chloranil in trichlorobenzene also gave crystals of the fully aromatic hydrocarbon I. The crystals of the hydrocarbon were small needles with a shining green surface,which gave red solutions with a yellow fluorescence,and dissolved readily in concentrated sulphuric acid to give violet solutions. The absorption spectrum is given in Fig.6. The hydrocarbon was reactive and not stable at high temperatures. For example sublimation caused a large amount of decomposition,and solutions of the hydrocarbon were photo-oxidisable. Reaction with maleic anhydride took place immediately. While reduction of the hydrocarbon was accomplished in even such a mild medium as zinc dust,pyridine,acetic acid. Quantitative reduction to dihydrodibenzoheptazethrene VI,was complete in a few hours by this method,and indeed this was found to be the best way of obtaining VI in a pure state.

The most remarkable property of dibenzoheptazethrene is its capacity for salt formation. The hydrocarbon is quantitatively removed from trichlorobenzene on shaking with concentrated hydrochloric acid,or by the passage of hydrochloric acid gas through the solution. The violet hydrochloride XII was isolated and gave satisfactory analysis figures,although decomposition of the salt with loss of hydrochloric acid took place within a few hours. The hydrochloride appeared insoluble in most organic solvents, but when a suspension in pyridine was boiled for a few minutes the green crystals of dibenzoheptazethrene were formed on cooling. If a suspension of the hydrochloride in trichlorobenzene was allowed to stand for several days, solutions with the absorption bands of chlorodibenzoheptazethrene XIII, resulted.



XII



XIII

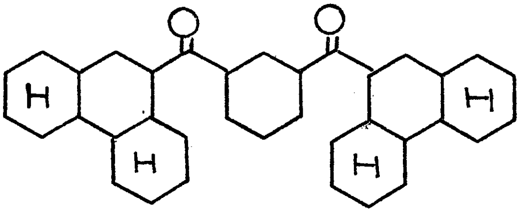
The chloro-hydrocarbon XIII could also be obtained by the action of phosphorous pentachloride on the mixture of hydro-derivatives, VI and VII. The dark blue chlorohydrocarbon did not form salts. This must be due to the chloro group, since similar behaviour in the azulene series has been recorded.(29) The absorption spectrum of the chlorodibenzoheptazethrene XIV is given in Fig.6. Reduction of the chloro-hydrocarbon by the zinc dust, pyridine, acetic acid method, removes the chlorine completely giving pure dihydrodibenzoheptazethrene. On the basis of this result the chlorine atom was placed at the 7 position as shown in XIII.

Dibenzoheptazethrene I formed salts with many acids. Thus a sulphate,phosphate or perchlorate could be formed by shaking solutions of the hydrocarbon with the requisite acid.

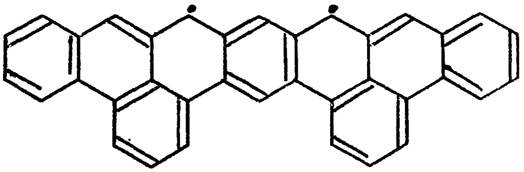
An explanation for the extremely unusual behaviour of this hydrocarbon was given in the introduction,where it was pointed out that the polarised form of the molecule has an extra benzenoid ring and that this must be the driving force of the salt formation.

Isophthalyl chloride condensed twice with octahydrophenanthrene to give 1,3-di-(octahydrophenanthroyl-9) benzene XIV.

Pyrolytic condensation of this diketone could have given products with a skeleton of the type shown in XV. As was noted in the introduction,a hydrocarbon with this structure would be a diradical.

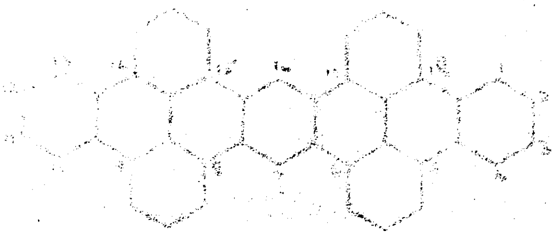


XIV



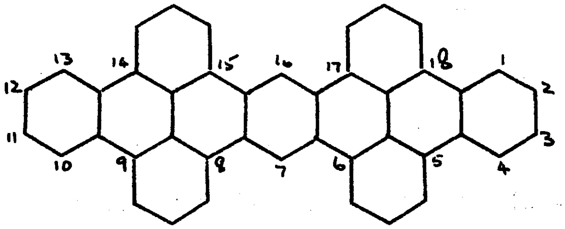
XV

It was found however the reaction product from the pyrolysis of the diketone could be dehydrogenated in high yield to dibenzoheptazethrene I. A rearrangement of the diketone must therefore have occurred during the reaction. Similar rearrangements are known to occur when the resultant hydrocarbon would have the 1,2:7,8 -dibenzanthracene skeleton and a compound with the 1,2:5,6 -dibenzanthracene structure is always formed in its place during pyrolysis reactions.(30)



XVI

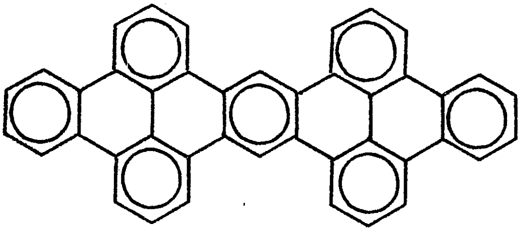
5,6:8,9:14,15:17,18-Tetrabenzoheptacene.



XVI

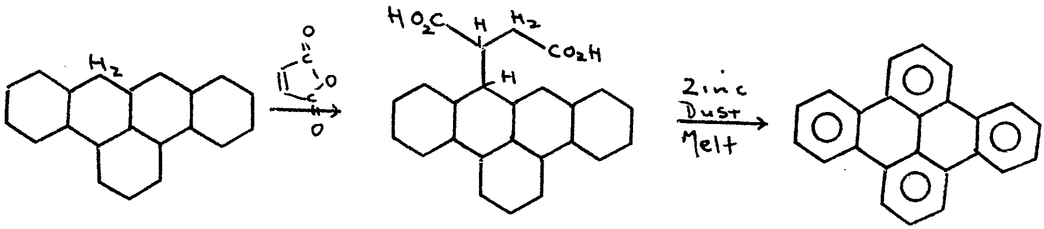
Synthesis of 5,6:8,9:14,15:18 -Tetrabenzoheptacene XVI.

As can be seen from its structure, tetrabenzoheptacene can be written as a fully benzenoid system i.e. as a condensed polyphenyl.



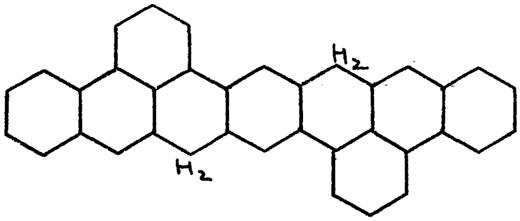
XVI

Thus in spite of the extended nature of the molecule, it was expected that this hydrocarbon would show the stability common to all fully benzenoid systems, and be very much less reactive for example, than dibenzoheptazethrene I described above. That 6,14-dihydrobenzoheptazethrene VI, is analagous to 2,3:7,8-dibenzoperinapthene VIII, has been shown above. Maleic anhydride is known to react with VIII giving an adduct which can be converted to the dicarboxylic acid XVII and then cyclised to the fully benzenoid 1,2:6,7-dibenzpyrene XVIII (27).

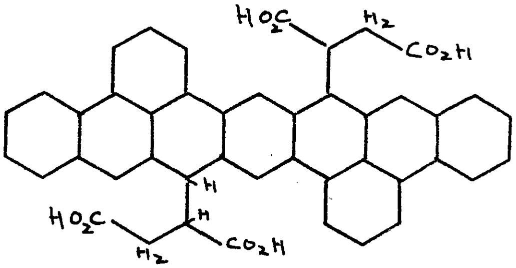


VIII XVII XVIII

As expected the dihydrodibenzoheptazethrene VI also reacted with maleic anhydride to give an adduct which was converted into the tetracarboxylic acid XIX.



VI



XIX

The spectrum of this acid XIX is given in Fig.4,where the close similarity to that of dihydrodibenzoheptazethrene VI shows that no change in aromatic conjugation has taken place during the addition reaction.

When the crude mixture of hydro-hydrocarbons VI and VII was reacted with maleic anhydride for a shorter time,an alkali insoluble residue was left,which after recrystallisation proved to be pure octahydrodibenzoheptazethrene VII. The spectrum of which is given in Fig.4.

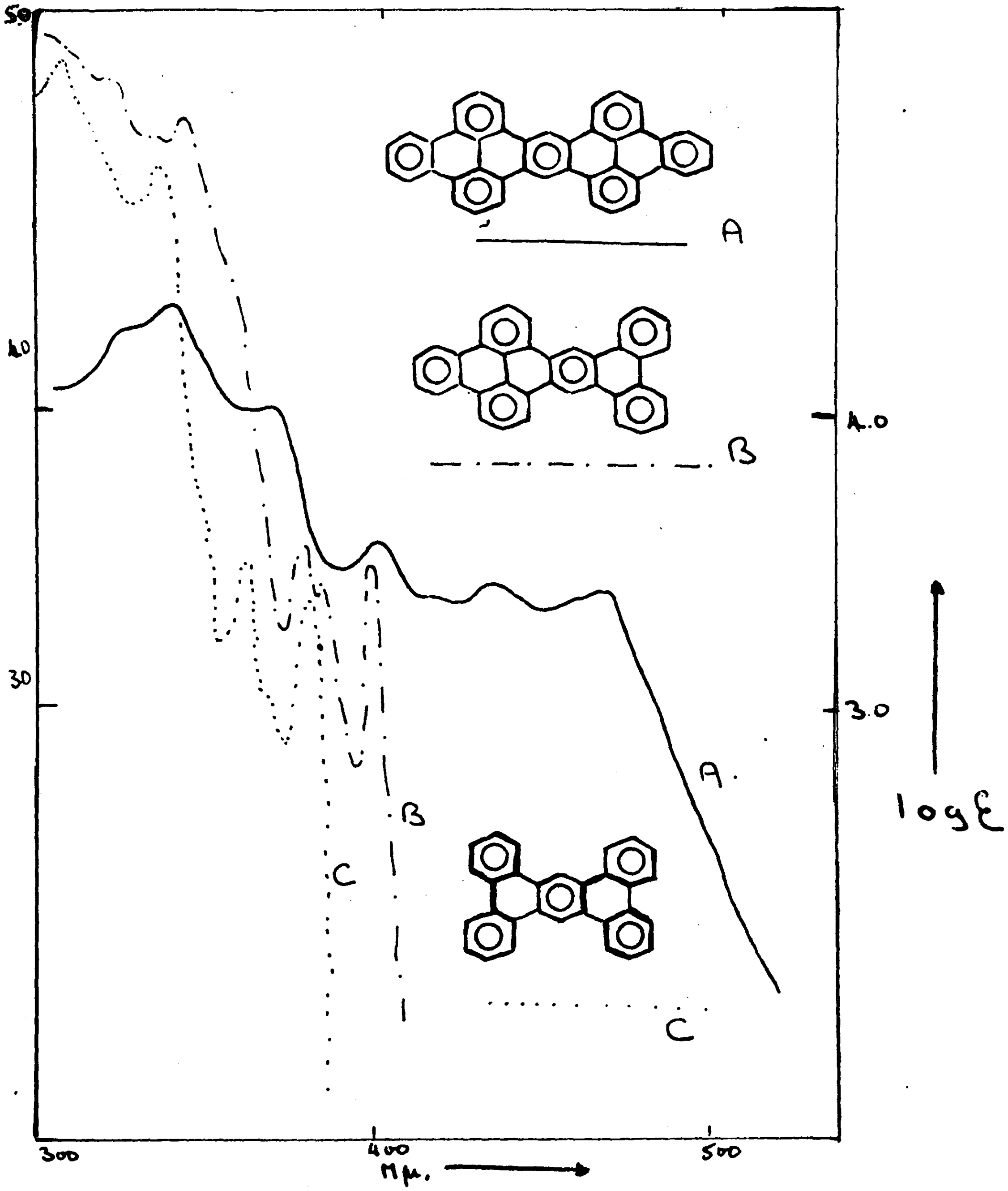
The tetracarboxylic acid XIX was ring-closed and decarboxylated in a zinc dust melt. After thorough extraction of the crude product to remove lower molecular weight impurities,repeated sublimation at high temperatures, followed by crystallisation from methyl napthalene gave the long,thin, pale orange needles of tetrabenzoheptacene.

All the expected properties of a fully benzenoid system were found. Tetrabenzoheptacene does not dissolve in concentrated sulphuric acid, although on slight heating or standing for a few hours in the acid, the crystals turn black on the surface. A solid solution of the hydrocarbon in ethanol at 77°K, showed the expected, intense, long life phosphorescence after irradiation. Tetrabenzoheptacene does not react with maleic anhydride, showing the complete lack of acene character in the molecule. The thermal stability of the molecule was very notable, repeated sublimation at temperatures above 500° did not cause the slightest decomposition of the hydrocarbon.

All the above properties are in remarkable contrast to those of dibenzoheptazethrene, and it is apparent that some special bonding principle must apply in tetrabenzoheptacene.

Although these properties together with the satisfactory analysis and molecular weight estimation, make it reasonably certain that the ring-closure has gone as claimed, additional confirmation of the structure was sought from a study of the ultra-violet, infra-red and phosphorescence spectra of the molecule. The ring-closure of such a complex acid as XIX could theoretically occur in several ways, although it was known that in similar reactions the hydrocarbon with the maximum number of benzenoid rings is formed preferentially (27,31).

Fig. 7.



Band Maxima (mu.)

A (————) In benzene α ,461,426; p,393; β , 329.

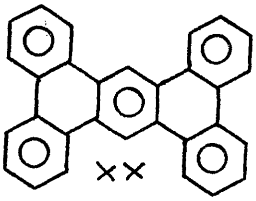
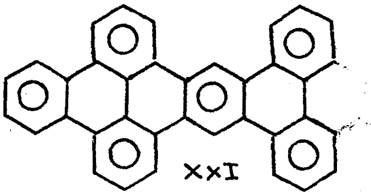
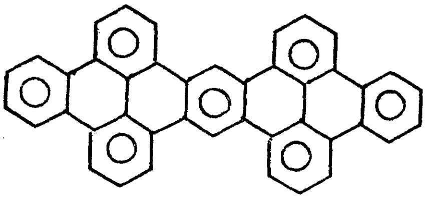
B (—·—·—·—) in trichlorobenzene α,399,386,378; p,344,
323; β , 310,274.

C (········) α , 382,362;p,336; β , 295.

The ultra-violet absorption spectrum of tetrabenzoheptacene II is shown in Fig.7, where it is compared to those of the fully benzenoid tetrabenzanthracene XX and tetrabenzopentacene XXI. The general extension and flattening of the absorption of XVI in relation to XX and XXI is fairly typical in such large molecules. Similar behaviour is seen in the spectrum of circumanthracene when compared to coronene and ovalene.

The regular increase of the β-bands of the three hydrocarbons is shown in Table 3. It can be claimed that these hydrocarbons form a true annellation series, the addition of the o-phenylene unit producing the same small red shift of the band on each occasion.

Table 3.

Hydrocarbon	β-Band Å	β-band $\sqrt{Å}$	Diff. $\sqrt{Å}$
 XX	2950	54.10	
			1.4
 XXI	3100	55.5	
			1.7
 XVI	3290	57.2	

The significance of phosphorescence spectra was discussed in the introduction where it was shown that all fully benzenoid hydrocarbons must have the long life intense phosphorescence which is shown by tetrabenzoheptacene. The phosphorescence emmission spectra of the three benzenoid hydrocarbons are shown in Fig.2. The general similarity of all three is marked. The extremely small shifts observed in the shortest wavelength bands (235Å and 125Å) on progressing from XX to XXI to XVI could only be observed ina fully benzenoid series and must be contrasted with the huge shifts found in other series e.g. the acenes.

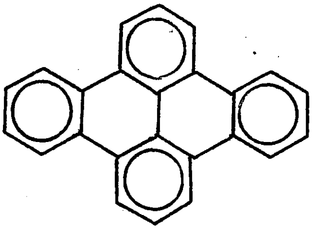
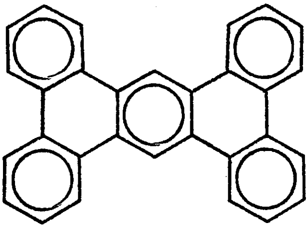
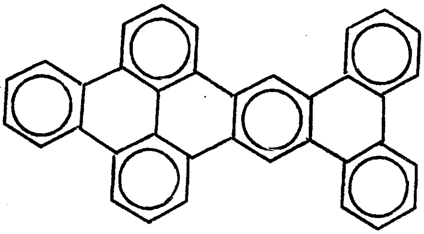
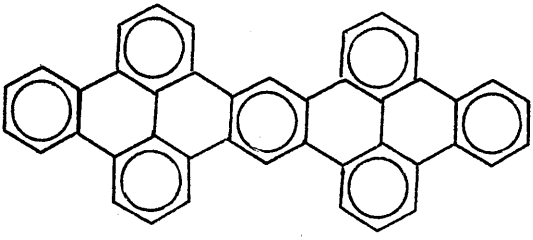
The study of the infra-red spectra of these hydrocarbons is of value, because of the comparison possible between the known, tetrabenzanthracene XX, tetrabenzopentacene XXI and tetrabenzoheptacene XVI, and the similarity of the three spectra is striking.

M.P. Groenwege (32) has shown that the absorption bands in the infra-red spectra of polynuclear hydrocarbons can be assigned to 'sole' (900-860cm.$^{-1}$), 'duo' (860-800cm.$^{-1}$), 'trio' (810-750cm.$^{-1}$) and 'quartet' (770-735cm.$^{-1}$) groups of C-H vibrators. Analysis of the C-H wagging frequencies of polynuclear hydrocarbons on this basis can be used to confirm the constitution of the hydrocarbons.

Thus M. Zander (33) showed that the infra-red spectrum of tetrabenzopentacene XXI was fully consistent with the postulated structure and could exclude alternative reaction products.

Table 4

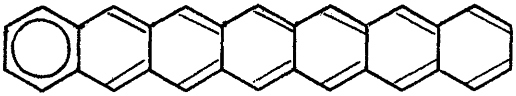
Infra-red Spectra

Hydrocarbons	C-H. vibrations (cm)$^{-1}$ x			
	solo 900-860 cm^{-1}	duo 860-800 cm^{-1}	trio 810-750 cm^{-1}	quartet 700-735 cm^{-1}
 XVIII	-	-	801	744
 XX	870	-	-	749
 XXI	871 863	-	795	746
 XVI	867	-	792	745

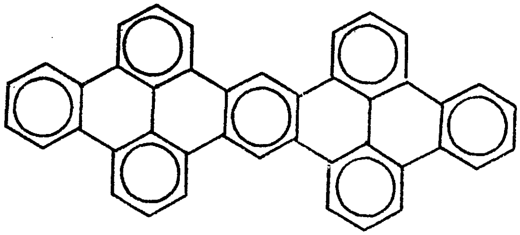
x All spectra in KBr.

In Table 4, The band groups of some relevant hydrocarbons are shown. The close similarity of tetrabenzopentacene XXI and tetrabenzoheptacene is especially marked. Both hydrocarbons having 'solo','trio' and 'quartet' bands at almost identical wavelengths and both having no 'duo' band. Dibenzpyrene XVIII, although also fully benzenoid,has completely different band groups as can be seen in Table 4.

The structure of tetrabenzoheptacene has thus been established by several independent methods. The high stability and chemical inertness of this molecule must be contrasted to that of heptacene itself XXII, which exists only as a dihydro-derivative because of the extreme instability of the fully aromatic system (34). The fact that addition of more rings to this unstable hydrocarbon produces the exceptionally stable tetrabenzoheptacene,can be accounted for by the benzenoid ring theory, but must be difficult to explain on any other basis.

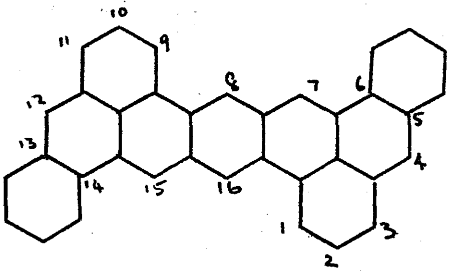


XXII
unstable



XVI
stable

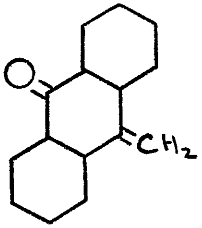
5,6:13,14-Dibenzoheptazethrene.

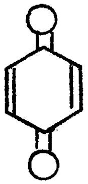


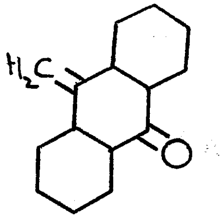
XXIII

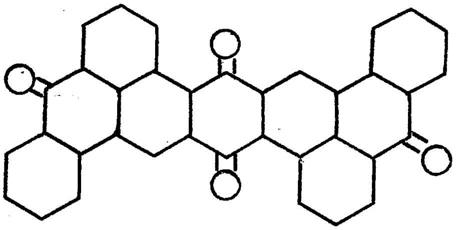
5,6:13,14-Dibenzoheptazethrene XXIII.

Benzoquinone and methylene anthrone condense smoothly in boiling nitrobenzene to give the diquinone XXIV (35).









XXIV

This diquinone could be reduced to dihydro-5,6:13,14-dibenzoheptazethrene by two methods. Prolonged reaction with zinc dust and hydrochloric acid in pyridine or reaction with hydrogen iodide and red phosphorous under pressure were both effective. The purified products from these two methods had almost identical absorption spectra, Fig.8,apart from a slight difference in the weak long-wavelength bands.

As can be seen the absorption spectrum is rather complex, and it is difficult to assign the positions of the hydrogen atoms definitely. The most probable structures are shown below, but the possibility of a combination of these cannot be excluded.

Fig. 8.

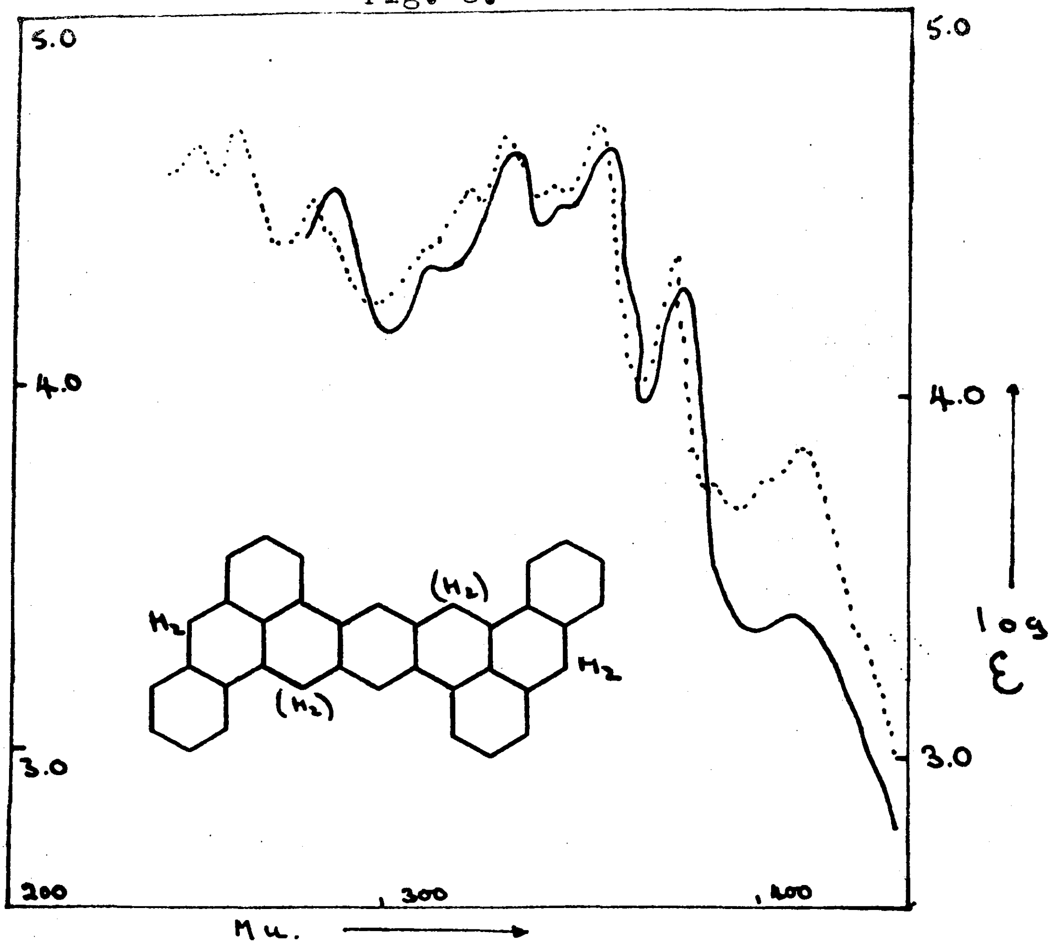


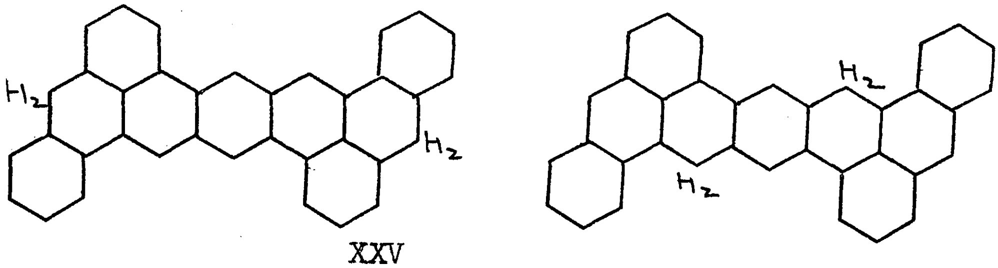
Fig. 8 Dihydro-5,6:13,14-dibenzoheptazethrene.

——— in methyl napthalene, from the zinc dust, pyridine, acetic acid, reduction.

.... in trichlorobenzene, from the hydrogen iodide, red phosphorous reduction.

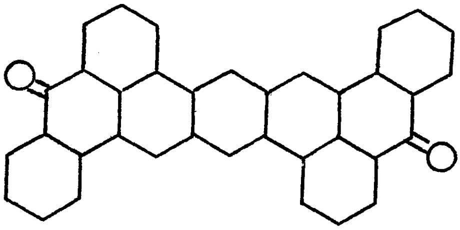
Band maxima (mu.), in trichlorobenzene, 475,437415,405, 391,383,370,361,342,326.

in methyl napthalene, 466,438,417, 406,394,373,346.



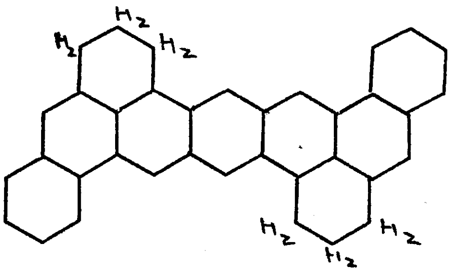
XXV

Although the structure of this dihydro-hydrocarbon is somewhat uncertain, it must be emphasised that the reduction product of the diquinone is not a mixture, but a uniformly crystalline hydrocarbon. Oxidation of the hydrocarbon XXV with selenium dioxide in nitrobenzene, gave a monoquinone XXVI, which most probably has the structure shown, alternative structures being more sterically hindered.

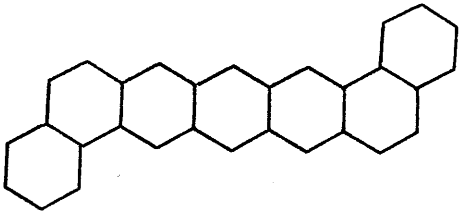


XXVI

The crude reduction product of the diquinone XXIV, by the hydrogen iodide, red phosphorous method, had additional absorption bands at 545mu, and 505mu. which were at first thought to belong to the fully aromatic hydrocarbon XXIII. On chromatography of the crude product however the fractions containing these bands came off the column before the dihydro-hydrocarbon and seemed to belong to a rather readily soluble substance. It is now thought that the bands were those of a more highly hydrogenated hydrocarbon. Possibly the hexahydro-dibenzopentacene XXVII shown below. The red shift of the bands from those of dibenzopentacene XXVIII is of the correct order.



XXVII
545mu,505mu.



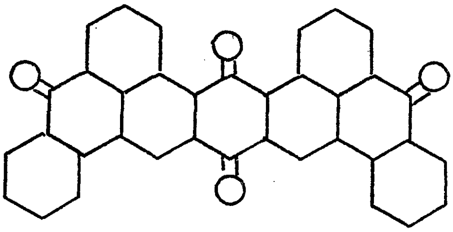
XXVIII
529mu,493mu.

All attempts to dehydrogenate the purified dihydro-hydrocarbon XXV by sublimation over preheated palladium charcoal were unsuccessful. At extremely high temperatures no product at all was obtained,while at more normal reaction temperatures,pure starting material was recovered.

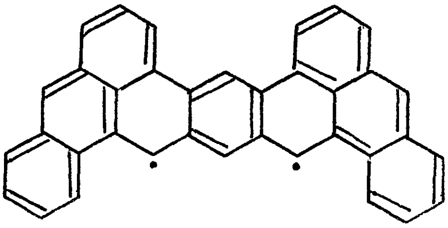
Reaction with chloranil produced no effect when moderately high boiling solvents were used. When trichlorobenzene was employed however, a shift in absorption bands was found. The main part of the reaction product was a black insoluble polymeric material. A very small amount of a crystalline substance was isolated which had sharp absorption bands at 470mu,440mu and 420mu. This could not be the fully aromatic hydrocarbon,but because of the small amounts of the substance isolated no structure can be proposed for it. The reasons for the failure to isolate the fully aromatic hydrocarbon by dehydrogenation of the dihydro-hydrocarbon are two-fold.

Firstly it is possible that 5,6:13,14-dibenzoheptazethrene XXIII, is relatively unstable and could not be isolated under the rigorous conditions which seem necessary to effect the dehydrogenation.

Secondly, while structure XXIV is the most probable for the diquinone, an alternative condensation product XXIX can not be altogether excluded.



XXIX

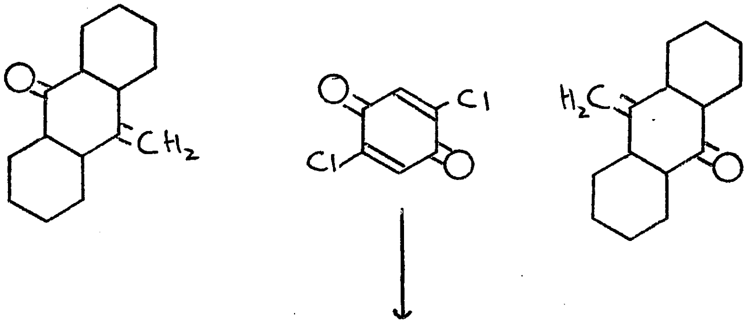


XXX

The fully aromatic system XXX derived from this diquinone would be a diradical and therefore unstable.

In order to decide between these possibilities an unambiguous synthesis of the dihydro-dibenzoheptazethrene XXV was required. This was achieved by two independent routes.

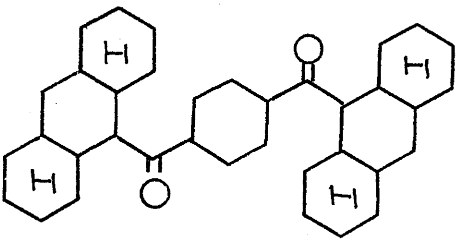
2,5-dichlorobenzoquinone was condensed with methylene anthrone as shown. This condensation must favour the formation of the 'trans' diquinone XXIV and eliminate the formation of the alternative 'cis' structure XXIX.



XXIV

The dihydro-hydrocarbon obtained by reduction of the diquinone obtained in this way was identical to that described above. The absorption spectrum was the same as that shown in Fig.8 and all dehydrogenation reactions failed as before.

Terephthalyl chloride condensed twice with octahydrophenanthrene to give the diketone XXXI in good yield.



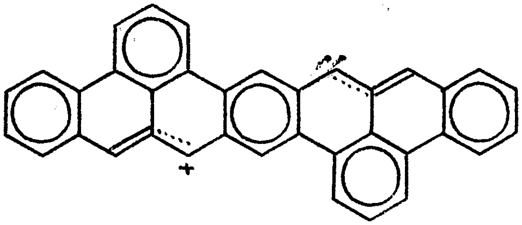
XXXI

Pyrolysis of this diketone in the presence of copper powder gave the dihydro-dibenzoheptazethrene directly, though the yield was very poor. The dihydro-hydrocarbon obtained in this way was identical in all respects to that obtained by the other methods. All attempts to dehydrogenate the hydrocarbon failed as before.

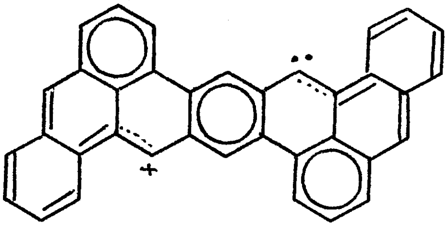
The possibility that the unstable 'cis' structure XXX was responsible for the failure of the dehydrogenation reactions can thus be eliminated. It can only be concluded then that the fully aromatic hydrocarbon is unstable under the experimental conditions employed.

The 5,6:13,14-dibenzoheptazethrene molecule must therefore be less stable than the isomeric 4,5:12,13-dibenzoheptazethrene, which as described above, was isolated under similar conditions.

The reason for the stability of the latter was also shown to be that the polarised form of the molecule had an extra benzenoid ring and the two remaining double bonds incorporated in a delocalised ion system XXXII.



XXXII

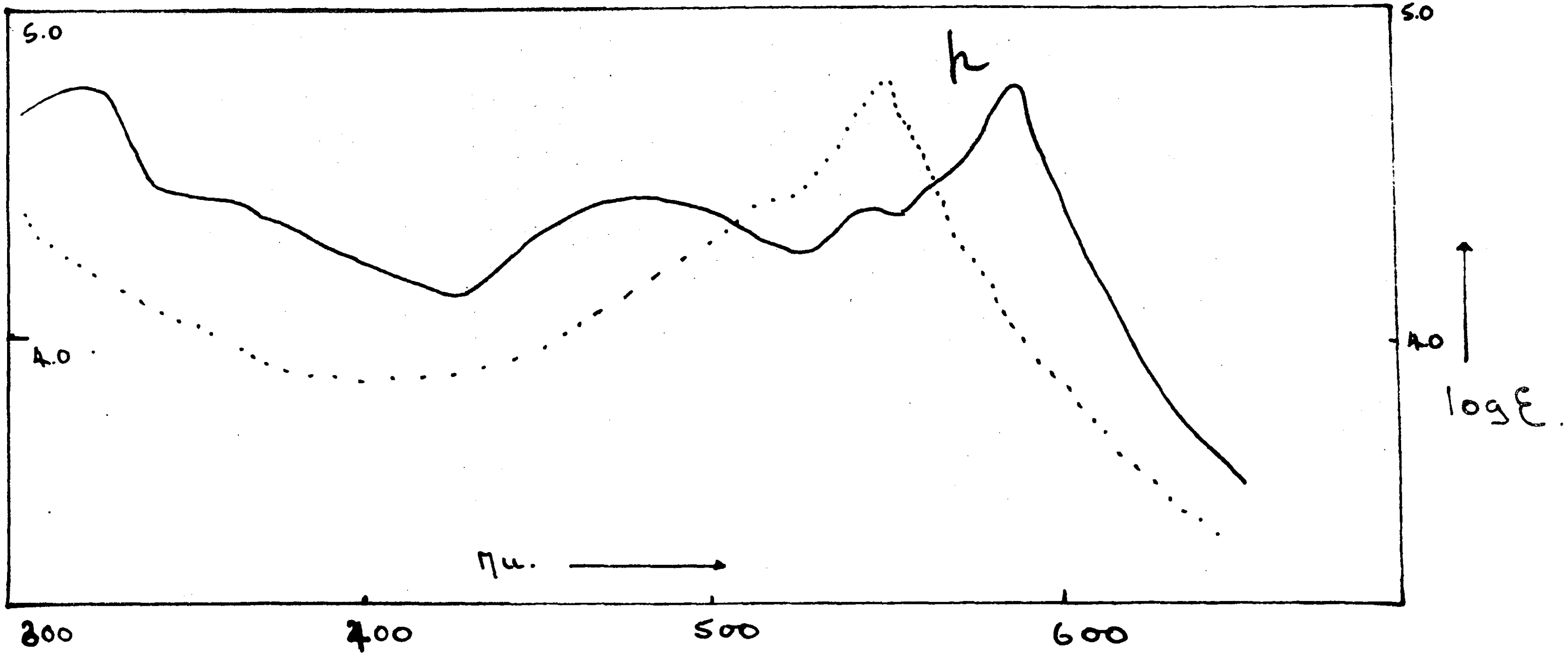


XXXIII

While the polarised form of the angular isomer XXXIII, although having one more benzenoid ring than the normal bond arrangement, only has three benzenoid rings and eight other double bonds.

A comparison of the two molecules on this basis fully supports the observed fact that the angular isomer XXXIII is less stable than the linear one XXXII. Although conventionally

Fig. 9.



Dihydro-5,6:13,14- dibenzoheptazethrene in conc. sulphuric acid

Band maxima (mu.) p, 582,549.

4,5:12,13-Dibenzoheptazethrene in conc. sulphuric acid.

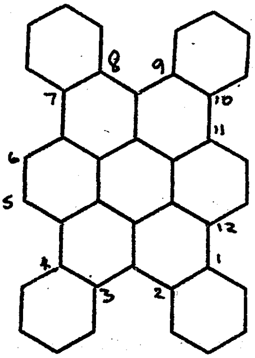
Band maxima (mu.) p, 550,512.

perhaps by comparison with the acenes, one would expect the more extended linear isomer to be the more labile molecule.

Some evidence that 5,6:13,14-dibenzoheptazethrene can exist under specially favourable conditions has been obtained.

The absorption spectrum of the dihydro-hydrocarbon in concentrated sulphuric acid is shown in Fig.9. The close similarity of the spectrum to that of 4,5:12-13-dibenzoheptazethrene may mean that the concentrated sulphuric acid has caused some dehydrogenation and the fully aromatic hydrocarbon is stabilised in the strong acid solution by salt formation.

1,2:3,4:7,8:9,10-Tetrabenzocoronene.

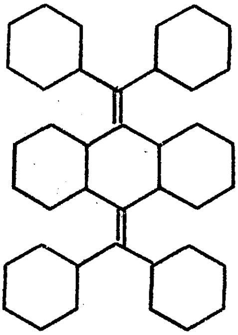


XXXIV

Synthesis of 1,2:3,4:7,8:9,10-Tetrabenzocoronene XXXIV

With the discovery that coronene is readily available from perylene (36) the systematic synthesis of the benzologues of coronene was begun (37,21). As part of this work the synthesis of tetrabenzocoronene XXXIV was undertaken.

The route chosen was the cyclisation of the anthracene derivative XXXV shown below (38)



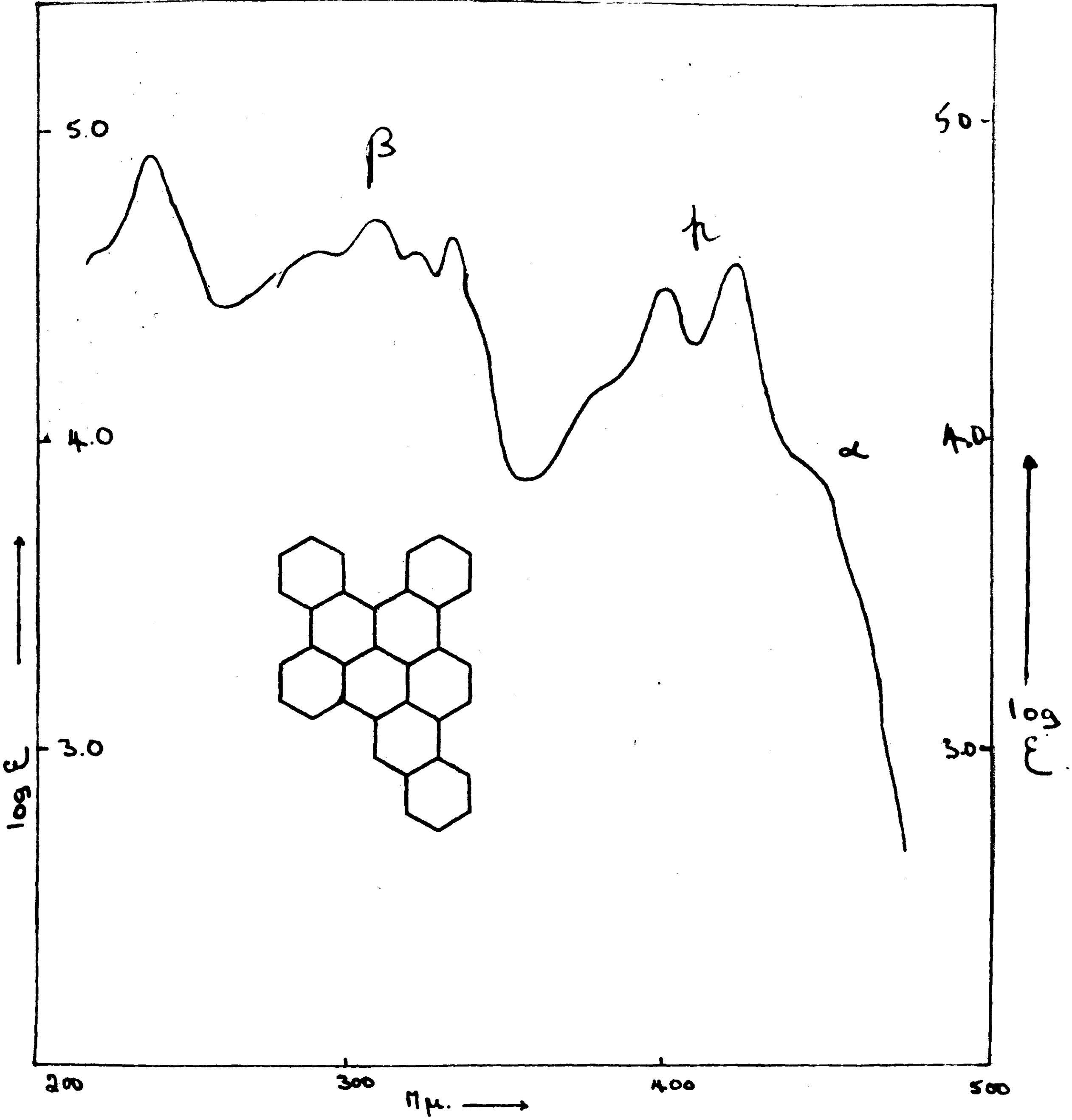
XXXV

All attempts to cyclodehydrogenate this molecule by catalytic means were unsuccessful. Sublimation over freshly prepared copper wire at 500° or over palladium charcoal at 400-450° produced no change in the starting material.

Reaction with aluminium chloride,in benzene, caused some reaction but no useful product was isolated and most of the starting material was unchanged.

Cyclisation of XXXV was however achieved by a melt of aluminium chloride and sodium chloride. The temperature required was rather higher than normal for such reactions and the splitting of phenyl groups and ring closure to five membered ring compounds,which usually occur under

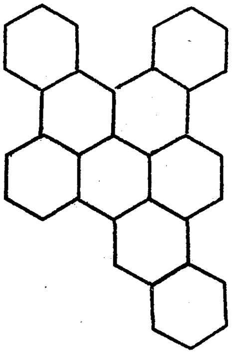
Fig.10.



4,5:10,11-Dibenzo-1,12-o-phenylene perylene, in benzene,

Band maxima (mu.) α, 456; p, 425, 400, 380; β, 335 and in cyclohexane β', 240 these conditions (39) must account for the poor yields. The results of this rather drastic method were somewhat variable, slightly better yields of the final product being obtained if a little stannic chloride was added to the melt.

The crude product was purified by chromatography over alumina, The first fractions yielded a yellow hydrocarbon, which after purification by sublimation, had the absorption spectrum shown in Fig.10. This spectrum is similar in type to those of the perylene series, and structure XXXVI seems probable.

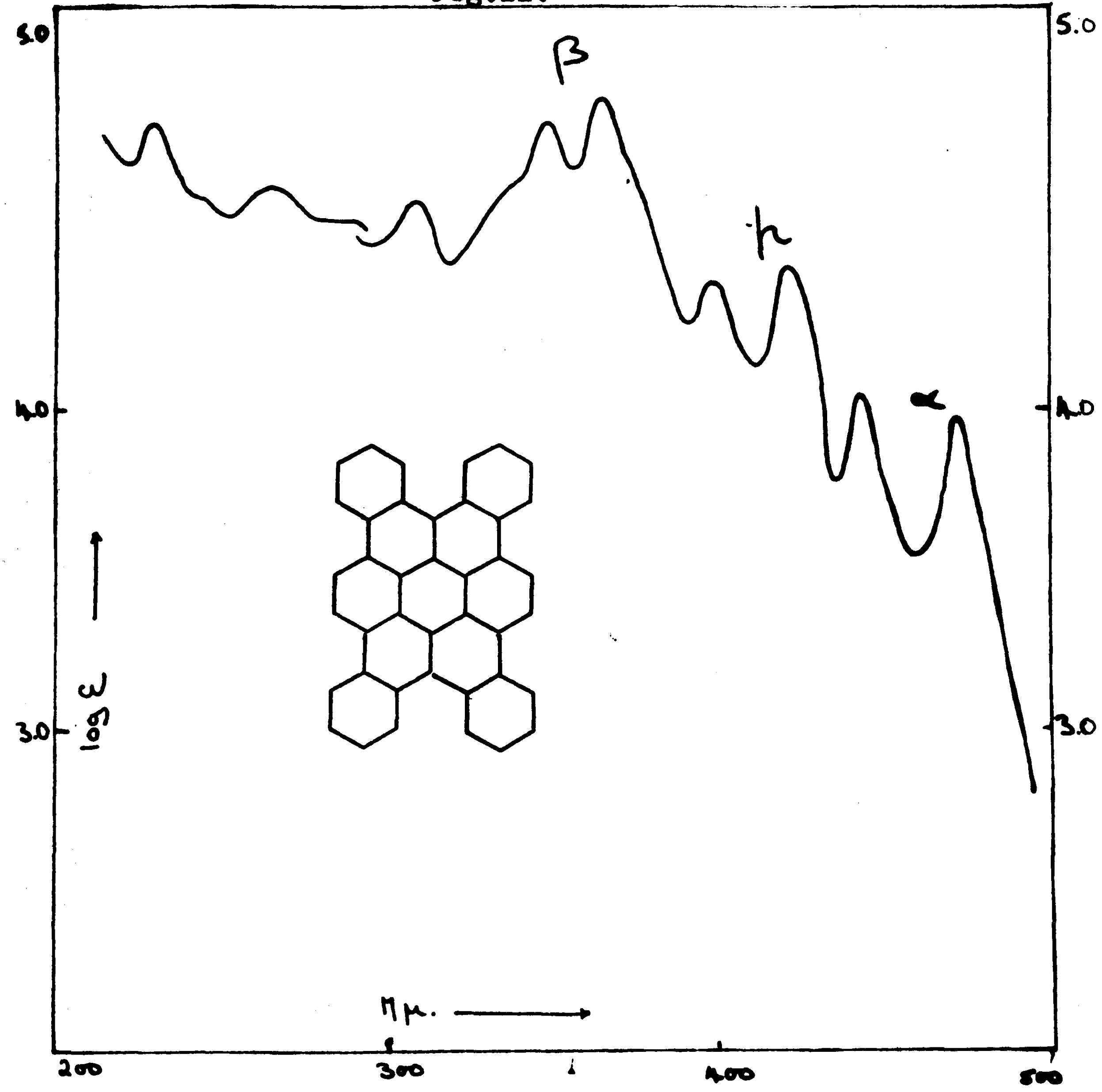


XXXVI

This hydrocarbon must have resulted from splitting off of a phenyl group.

Later fractions from the chromatographic column showed extremely sharp absorption bands at 473mu. and 445mu similar in appearance to the bands shown by all hydrocarbons in the coronene series. Concentration of fractions containing these bands, gave an orange-yellow solid, which after repeated sublimation gave a satisfactory analysis for tetrabenzocoronene XXXIV.

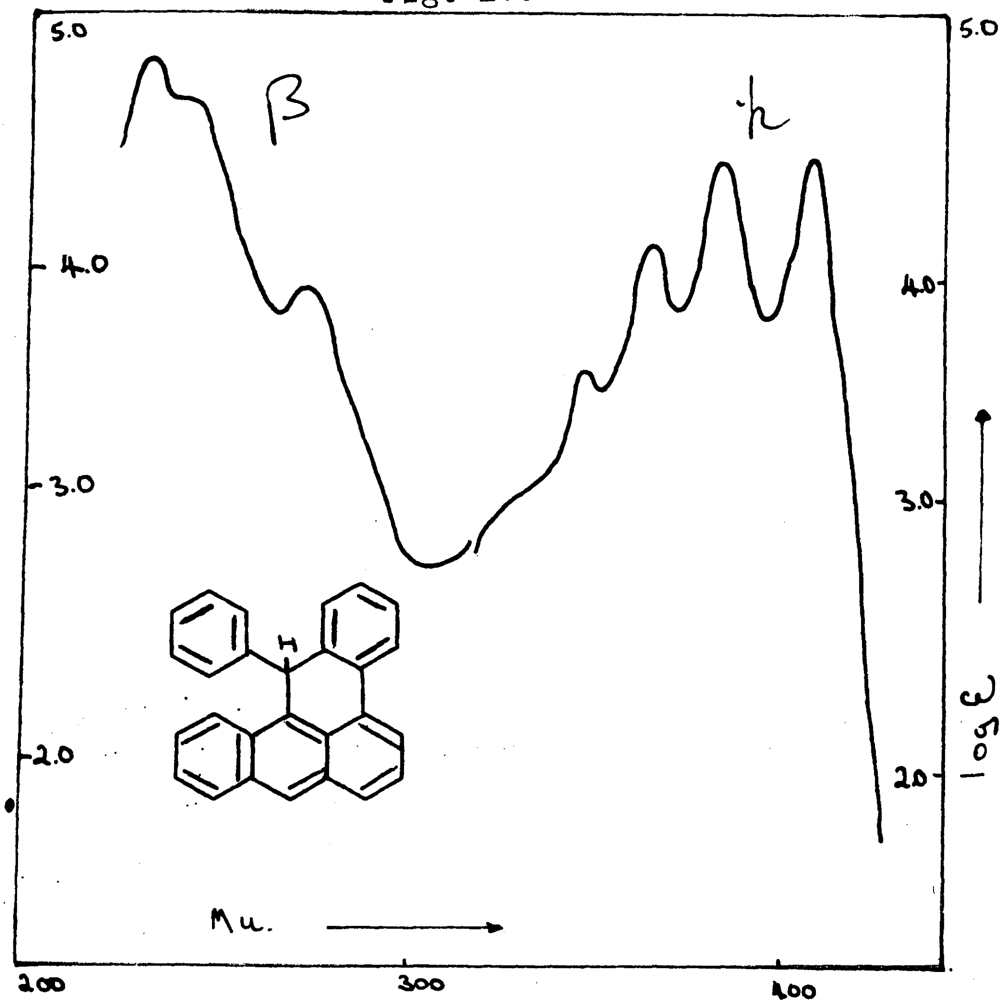
Fig.11.



1,2:3,4:7,8:9,10- Tetrabenzocoronene.

Band maxima (mu.) in benzene, α , 476,446; p, 425. 400; β , 367.

Fig. 12.



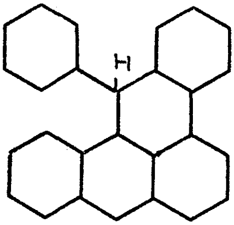
1,2:7,8-Dibenzo-9-phenyl-perinapthene.

Band maxima (mu.) in benzene, p, 404,382,363,345;

and in cyclohexane, β , 294,268,254.

The absorption spectrum of the hydrocarbon is given in Fig.11 and a feature of this spectrum is the ratio of the α : β bands 1:1.29 which differs from the normal ratio 1:1.35 and indicates that there is some steric strain in the molecule (40). This is also evident from the behaviour of the hydrocarbon. Failure to obtain it in a satisfactory crystalline form and the rather low and indistinct melting point may indicate the presence of stereoisomers caused by hydrogen overlap.

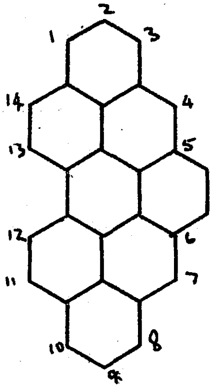
An attempt to synthesise tetrabenzocoronene by another route was made. Reaction of benzophenone chloride and anthracene in the presence of aluminium chloride gave a hydrocarbon which most probably has the structure XXXVII.



XXXVII

The absorption spectrum of this product shown in Fig.12 supports the 9-phenyl -1,2:7,8-dibenzoperinapthene structure XXXVII. The possibility that the substance has a fluoranthene type of structure can not however be altogether excluded. This product failed to react with benzophenone chloride in a satisfactory manner, and thus cannot provide another route to tetrabenzocoronene.

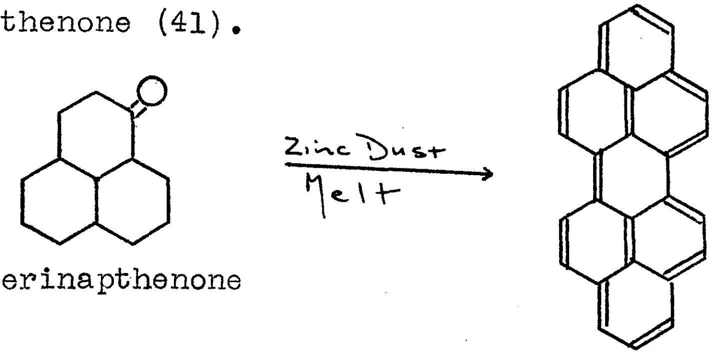
5,6-Benzoperopyrene



XXXVIII

Attempted synthesis of 5,6-benzoperopyrene XXXVIII.

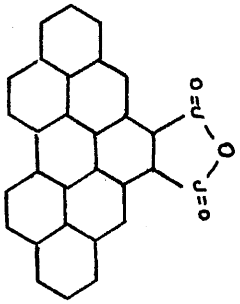
Although many benzologues of peropyrene XXXVIII very few simple ones which are substituted at the 5,6 or 12,13 positions have been described. The synthesis of 5,6-benzoperopyrene was accordingly attempted, the main object being to study the changes in the absorption spectrum in comparison with peropyrene XXXIX. Peropyrene was first synthesised by the bimolecular condensation of perinapthenone (41).



Perinapthenone

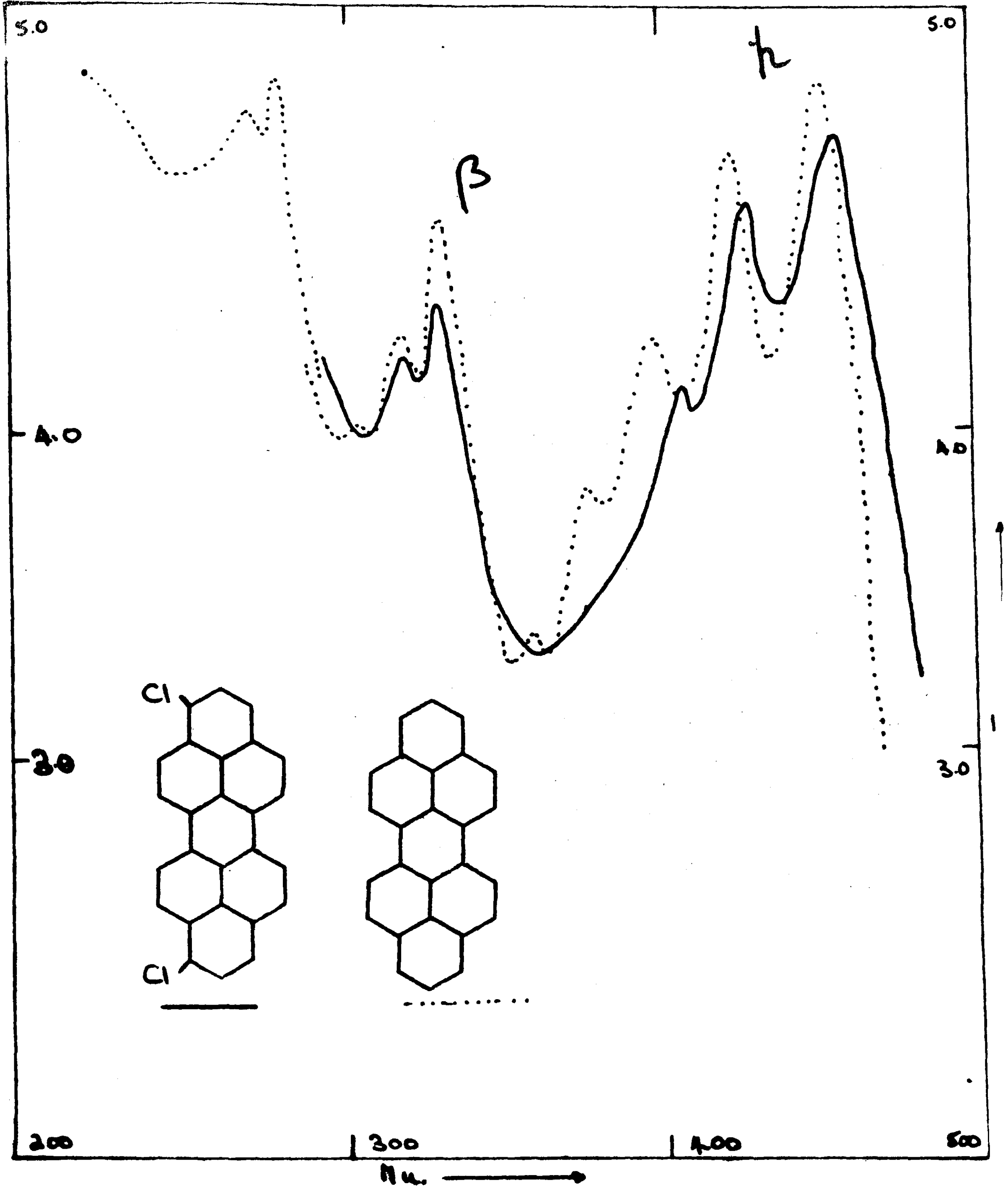
XXXIX

1,2:9,10-dibenzoperopyrene or violanthrene is the parent hydrocarbon of violanthrone the commercially important dyestuff. However very little was known of the chemistry of peropyrene itself. It was thought possible that the molecule might have a bond arrangement like that shown in XXXIX. That is, have a diene system in the centre of the molecule which could react with maleic anhydride, in the same way as perylene does (36) to give an adduct XL which could then be decarboxylated to yield the required hydrocarbon.



XL

Fig. 13.



Band maxima (mu.).

———— Dichloroperopyrene in trichlorobenzene,

p,457,428,423; β , 330.

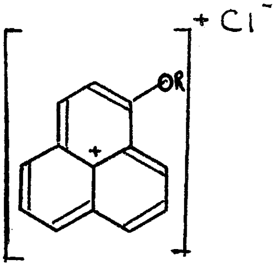
.... Peropyrene in benzene, p, 444,412,392;

β ,326,312.

Prolonged reaction with maleic anhydride and chloranil failed to produce any alkali soluble adduct. Only a small amount of a dichloro-peropyrene could be isolated. The spectrum of this product is shown in Fig.13 where the close similarity to that of peropyrene can be seen. The formation of chlorohydrocarbon through the action of chloranil is rather unusual. A possible mechanism, could be the formation and subsequent decomposition of an unstable peropyrene hydrochloride, in a manner analogous to that described above for chlorodibenzoheptazethrene XIII. Peropyrene does exhibit basic properties although only relatively weakly. When a solution of peropyrene is shaken with a strong acid the intensity of the peropyrene bands diminishes markedly and a violet salt is formed. Violanthrene and isoviolanthrene show similar properties but to a more marked extent.

The reason for the basicity of the peropyrenes must be connected to the two perinapthene systems that the molecule possesses.

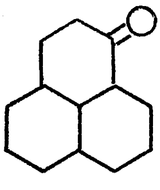
It has been shown (6) that perinapthene systems tend to adopt a centrosymmetric structure, that is one with a frame of alternating double bonds with an odd electron or positive charge in the centre. For example, perinapthone dissolves in hydrochloric acid and can be converted into coloured salts of the type shown below.



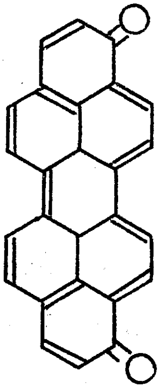
Perinapthenone Salts

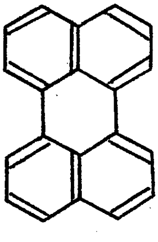
The addition of maleic anhydride also failed with violanthrene and isoviolanthrene, and it was found that oxidation to the quinones of these more highly reactive systems occurred.

A peropyrene quinone was known to be the product of the condensation of perinapthenone in alcoholic potash (42). The dark purple quinone was obtained in good yield and its absorption spectrum, shown in Fig14, indicated that it was not a mixture.



Perinapthenone

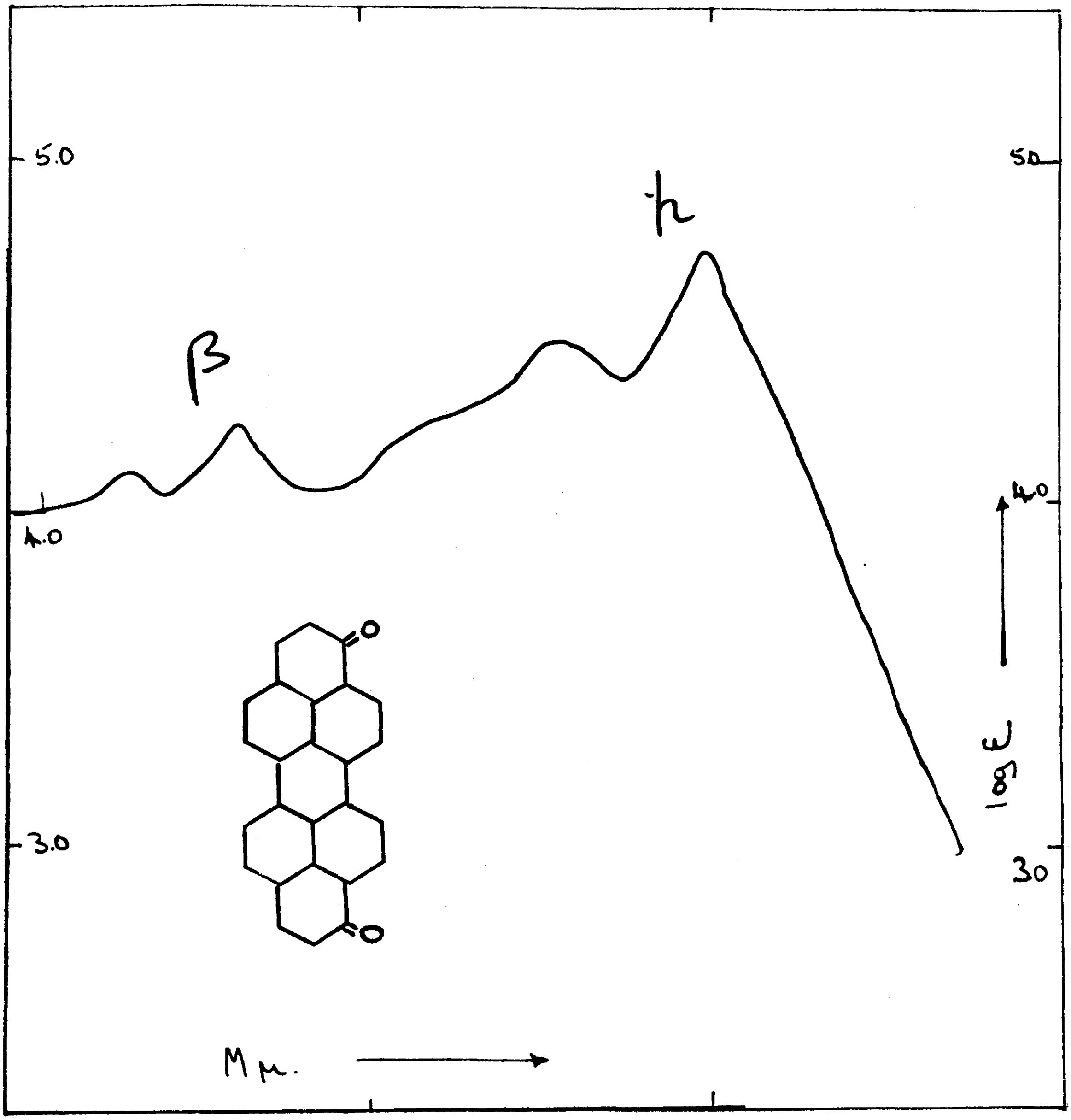




Perylene

XLI

Fig. 14.



Band Maxima (mu.).

Peropyrene-1,10-quinone in trichlorobenzene,

p, 598,556; β , 465.

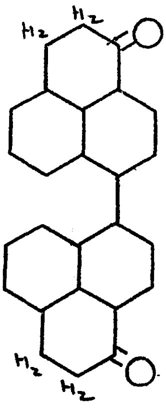
Oxidation of the quinone gave an acid which was decarboxylated to give perylene, thus proving that the carbonyl groups must be in the terminal rings. By analogy with the almost exclusive formation of violanthrone from benzanthrone under similar conditions it was concluded that the quinone had the structure XLI.

As can be seen in XLI, this quinone must have the diene system in the centre of the molecule and it was found that the reaction with maleic anhydride and chloranil proceeded smoothly. The alkali soluble adduct proved difficult to purify because of the ease with which it split to give the quinone. For this reason decarboxylation of this adduct was unsuccessful, as were attempts to reduce the carbonyl groups. Violanthrone formed a similar adduct which behaved in the same way.

Reduction of the quinone in a zinc dust method gave higher yields of peropyrene than the literature method, Another route to peropyrene was found to be by the reduction of perinapthenone with zinc dust in dilute alkali.

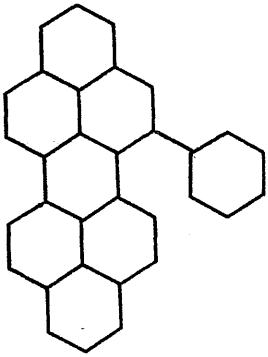
A colourless by-product of the reaction was isolated, which had a strong carbonyl peak at 1675cm^{-1}. (perinapthenone 1635cm^{-1}.), and could be converted in high yield to peropyrene by a zinc chloride-sodium chloride melt and by alcoholic potash to peropyrene quinone.

The dimeric structure XLII seems the most probable for this substance.

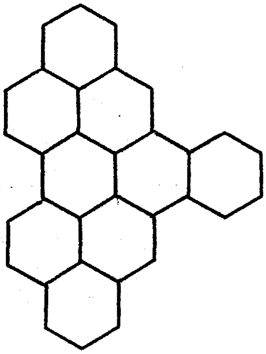


XLII

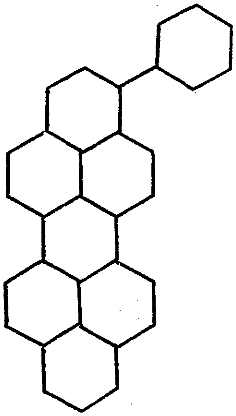
Peropyrene reacted with benzene in the presence of aluminium chloride to give a monophenyl peropyrene. The absorption spectrum shown in Fig.15 is very similar to that of peropyrene. It was hoped that the phenyl group would be in the 5 position as in XLII which could be cyclised to XLIII.



XLII

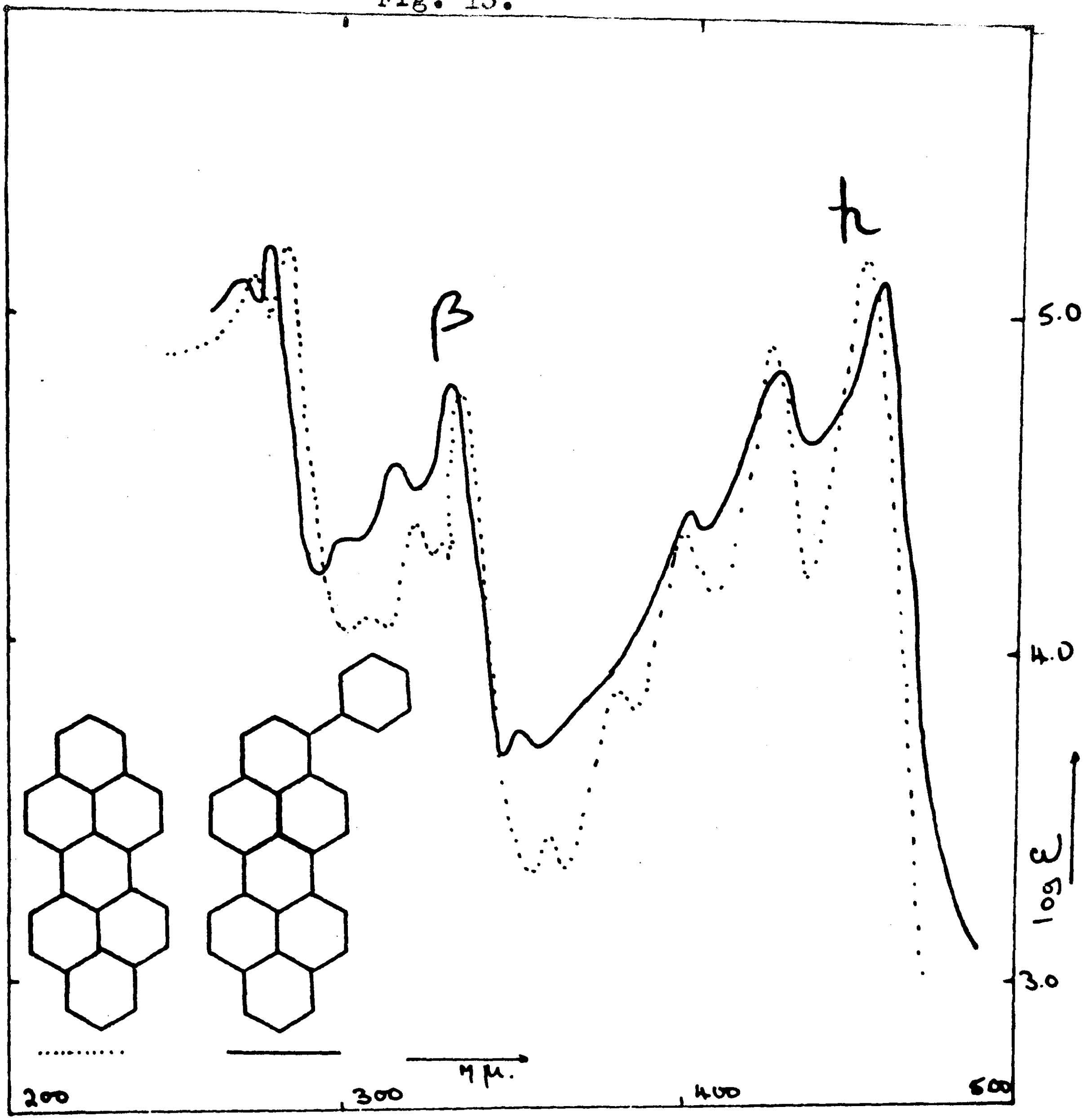


XLIII



XLIV

Fig. 15.



Band maxima (mu.).

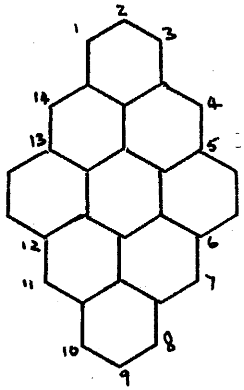
——— 1-Phenyl-peropyrene in benzene, p, 454,422,403; β, 330,316.

······· Peropyrene in benzene, p,444,412,392; β, 326.

However all attempts to cyclise the phenyl group failed at normal reaction temperatures, and when extremely high temperatures were used the phenyl group split off and peropyrene was recovered. The phenyl group is thus most probably at the 1 position.

Although no synthesis of a 5,6-benzoperopyrene has been achieved, some new facts have been established about the chemistry of peropyrene. It can be concluded that, there is no resemblance between the chemistry of perylene and that of peropyrene. The addition of the carbon atoms to the peri-position of perylene resulting as it does in the formation of two perinapthene systems profoundly alters the character of the resultant molecule.

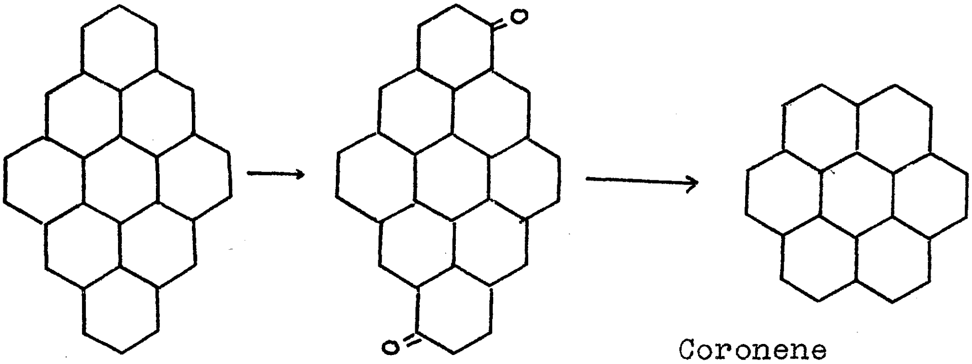
5,6:12,13-Dibenzoperopyrene.



XLV

Synthesis of 5,6:12,13-dibenzoperopyrene XLV.

This hydrocarbon which can also be named 2,3:8,9-dibenzocoronene, was first synthesised by Scholl and Meyer (43) as an intermediate in the synthesis of coronene, as shown below.

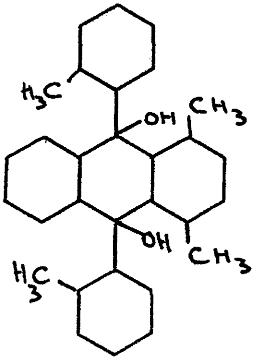


Coronene

XLV

As the absorption spectrum of the hydrocarbon was not recorded and the route used was long and perhaps not wholly unambiguous, it was decided to resynthesise this hydrocarbon by another method.

o-Lithium toluene reacted with 1,4-dimethyl anthraquinone to give the diol XLVI

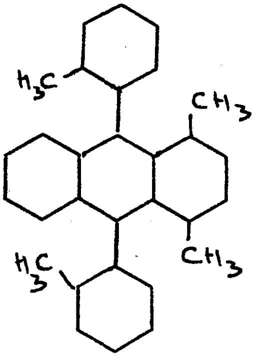


XLVI

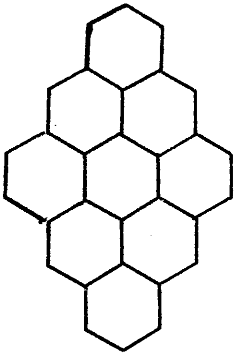
Cyclisation of this diol by simply heating with copper powder under carbon dioxide was not successful although this method was known to succeed in a closely similiar case (44).

Attempts to oxidise the methyl groups of the diol by a variety of methods failed to give useful results. When a crystalline product was isolated the analysis showed a loss of carbon atoms and it is believed that the unsubstituted benzene ring was ruptured under the conditions used.

The diol XLVI was reduced by the action of hydriodic acid in acetic acid to the hydrocarbon XLVII.



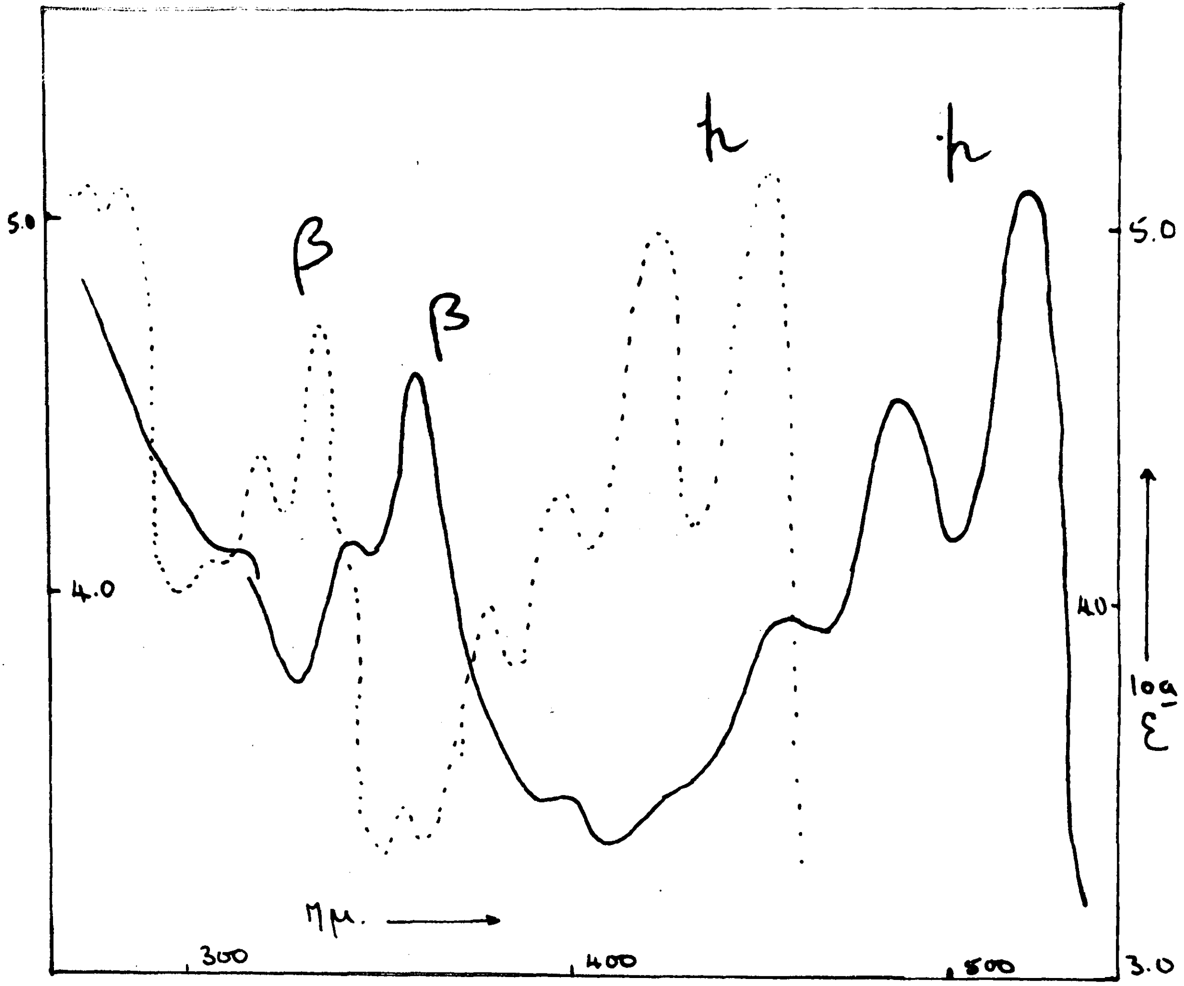
XLVII



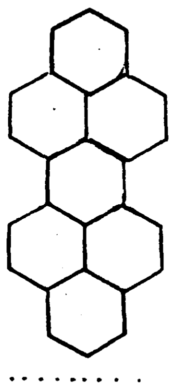
XLV

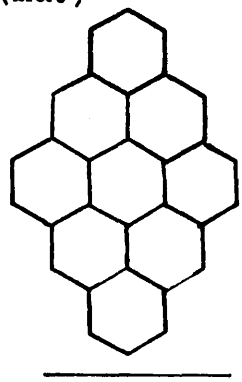
This hydrocarbon was cyclised to the desired hydrocarbon by cyclodehydrogenation over palladium charcoal. However it was found that unusually high temperatures were required to effect the cyclisation and the catalyst became deactivated rather quickly. The small amount of the dibenzoperopyrene XLV which was obtained corresponded exactly to the material described by Scholl and Meyer.

Fig. 16.



Band maxima (mu.)





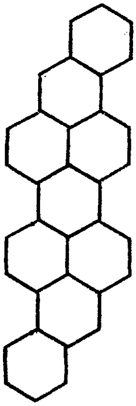
——— 5,6:12:13-Dibenzoperopyrene in methyl napthalene, p, 524,488,458; β , 361.

······· Peropyrene in benzene p, 444,412,392; β,326.

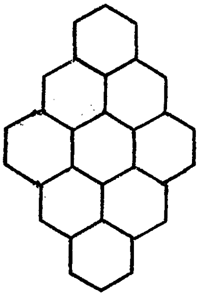
Thus the long thin green needles dissolved to form red solutions with a strong green fluorescence and give identical colours in concentrated sulphuric acid to those described in the literature.

The absorption spectrum of the hydrocarbon is given in Fig.16 where the close similarity of type to that of peropyrene can be seen.

When the values of the principal absorption bands are compared to those of other substituted peropyrenes the interesting fact is discovered that these bands lie at almost identical wavelengths to those of 1,2:8,9-dibenzoperopyrene i.e. isoviolanthrene.



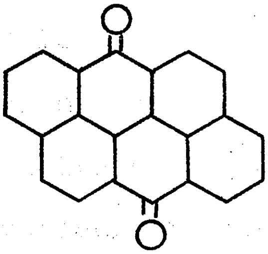
Isoviolanthrene
p,523mu.,488mu.,459mu.
,364mu.
in methyl napthalene



XLV
p,524mu.,488mu.,458mu.
, 458mu.
in methyl napthalene.

The occurrence of band 'isotopy' in all three band systems is unusual. The addition of two carbon items at the 5,6 and 12,13 positions appears to have the same effect on the spectrum of peropyrene as the addition of complete benzene rings at the 1,2 and 8,9 positions.

Condensation products of anthanthrone.



XLVIII.

Condensation products of anthanthrone XLVIII.

Reduction of anthanthrone to anthanthrene by a zinc dust melt, gives rather lower yields than is usual in such reactions. This is due to the formation of bimolecular condensation products during the reduction.

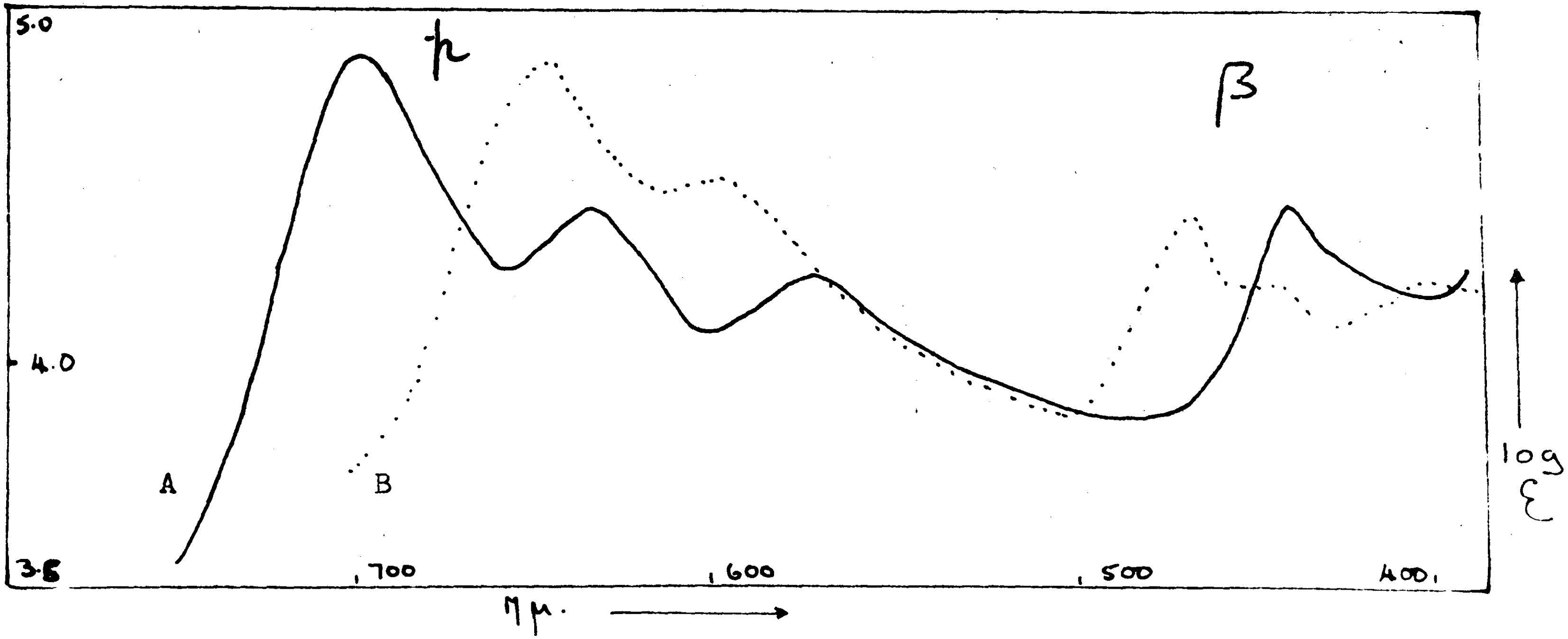
The condensation product is a mixture of two very similar hydrocarbons. One of which has absorption bands at 700mu. and 635mu. and the other with bands at 648mu. and 598mu.

Sublimation of the crude condensation product followed by chromatography over alumina with elution by trichlorobenzene held at 140° gave the 648mu,598mu.hydrocarbon free from the other isomer. This substance formed sparingly soluble bluish-green needles on recrystallisation from trichlorobenzene,and its absorption spectrum is shown in Fig.17. Analysis of this hydrocarbon showed it was $C_{44}H_{20}$ or $C_{44}H_{18}$ the difference of two hydrogen atoms being within the analytical experimental error.

The higher absorbing hydrocarbon (700mu.635mu.) was more soluble and came through the column first,but always mixed with the other isomer.

An alternative method for the preparation of these substances was found. When anthanthrone is reduced with zinc dust,pyridine and acetic acid,the anthanthrol XLIX is formed.

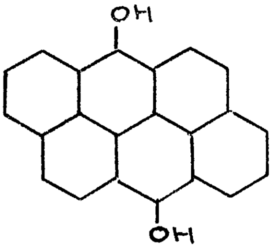
Fig. 17.



Band maxima (mu.) Hydrocarbons from the condensation of anthanthrone.

A ———— , p, 700,635,570; β , 435 inmethyl napthalene.

B ········ , p , 648,598; β , 467 in trichlorobenzene.



XLIX

Self-condensation of this material occurred when it was heated in an inert atmosphere to 300-350°. The product of this condensation was a mixture of extremely insoluble quinones, one of which had absorption bands at 565mu. and 525mu. and the other at 617mu. and 580mu.

Reduction of this mixture of quinones by the zinc dust pyridine,acetic acid method occurred readily and gave green solutions with the mixture of absorption bands described above.

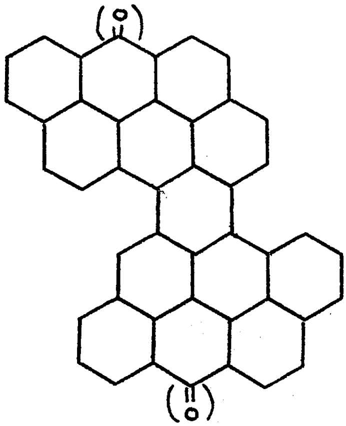
The quinones were separted by chromatography over alumina and elution with trichlorobenzene at 200°. In this way the more soluble of the two quinones was obtained in a pure state and free from the other product. Because of its extreme insolubility the other quinone (617,and 580mu,) was not obtained in a pure state.

The more soluble quinone was recrystallised from trichlorobenzene and formed small brownish-red prisms, which analysed for $C_{44}H_{18,16}O_{2}$. Reduction of this quinone gave the higher absorbing hydrocarbon (700mu,635mu) free from the other hydrocarbon,and its absorption spectrum is given in Fig.17.

Analyses of this hydrocarbon were not satisfactory however, since during recrystallisation some oxidation to the quinone occurs.

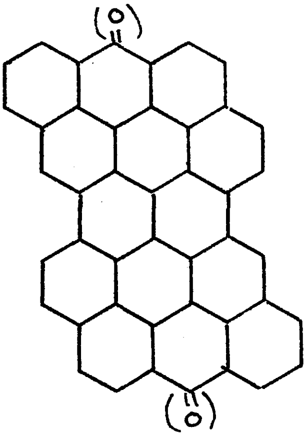
Thus although the two products have been separated and an analysis obtained for each system and the absorption spectra recorded, it is difficult to assign definite structures to these very complex hydrocarbons.

The structures thought to be most likely out of a number of possibilities are shown below.



700mu.,635mu.
(565mu.,525mu.)

more soluble.



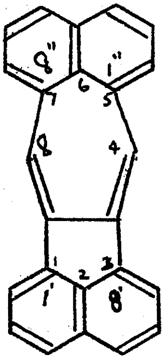
648mu.,635mu.
(617mu.,580mu.)

less soluble.

Appendix A.

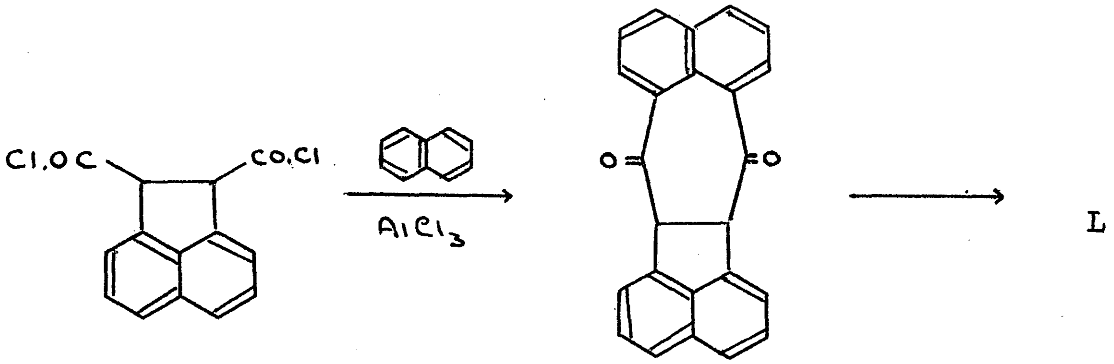
Investigation of a synthetic route to:-

1,3; 5,7- (1',8': 1",8") - Dinapthoazulene L.



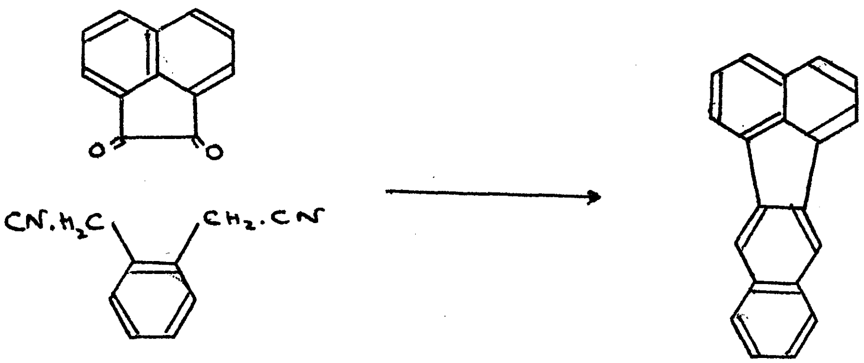
L.

These were based on the attempted synthesis of acenapthene dicarboxylic dichloride LII which could condense with napthalene to give the required structure. Various attempts to synthesise this substance were unsuccessful.



LII

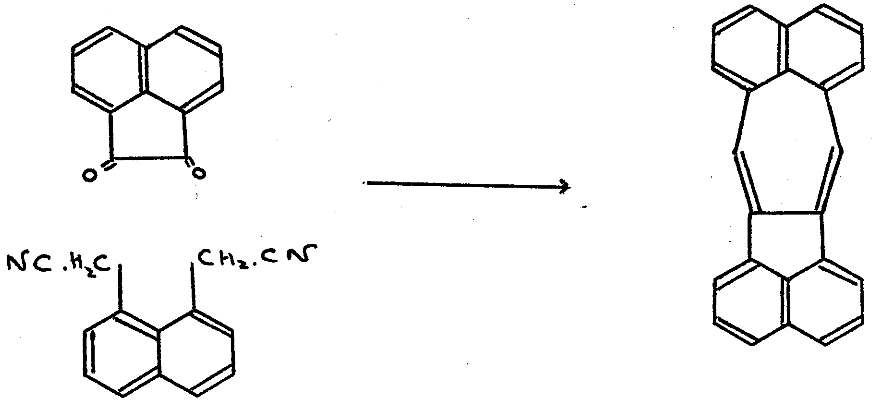
It was therefore decided to investigate a different type of route to the hydrocarbon. It was known that certain dinitriles and ortho-diquinones will condense readily to yield products which could be converted into hydrocarbons. Thus the dinitrile LIII condenses with acenapthene quinone to give a product which was converted to the hydrocarbon LIV (47)



LIII

LIV

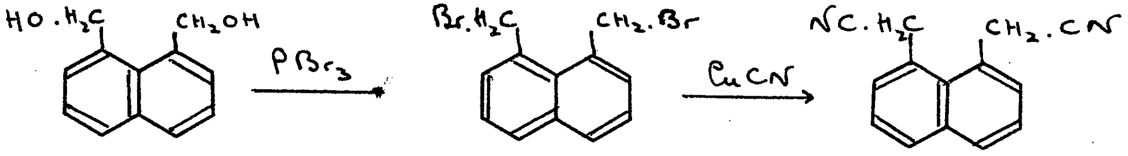
By analogy with this 1,8-bis(cyanomethyl)-napthalene LV should condense with acenapthene quinone to give a product which could be converted to dinapthoazulene.



LV

L

Reduction of napthalic anhydride with lithium aluminium hydride gives 1,8-bis-(hydroxymethyl) napthalene LVI which reacts smoothly with phosphorous tribromide to give the dibromide LVII (48).



LVI

LVII

LV

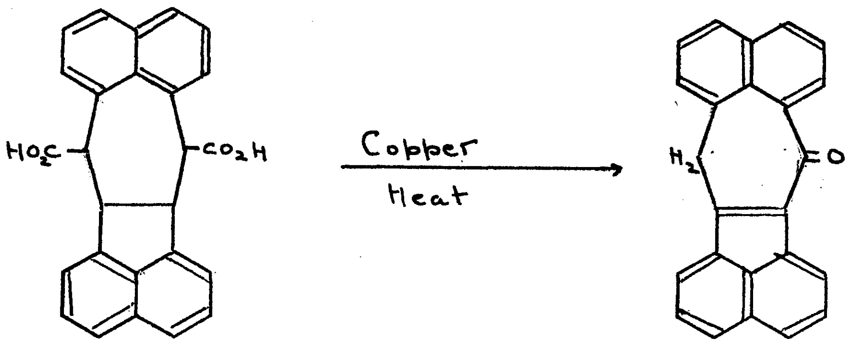
Replacement of the bromine atoms with nitrile groups did not proceed at all smoothly, because of the ease with which the bromide reacted across the 1,8 positions in alkaline media. Even such mildly alkaline reagents as pyridine or dimethyl formamide caused reaction across the 1,8 positions. The dinitrile LV was obtained, although in poor yield, by reaction with cuprous cyanide in dry xylene.

The condensation between the dinitrile LV and acenapthene quinone suffered from much the same difficulties. Thus when the condensing agents described in the literature, piperidine or sodium ethoxide were used, the only reaction which took place was the self-condensation of the dinitrile across the 1,8 positions. This difficulty was never fully overcome although a partially successful condensation was achieved. When the two reactants were finely ground together and excess of a cooled 50% alcoholic potash solution added, under an atmosphere of nitrogen, a brilliant blue colour was developed and a dark violet condensation product was isolated. This substance was insoluble in most organic solvents but did give violet solutions with dilute acetic acid which showed absorption bands at similar wave-lengths to those found for the dinapthoazulene.

It was concluded that at least a portion of the reactants had condensed in the desired manner to give dinitrile or nitrile-amide derivative of the hydrocarbon.

The main portion of the product however was either self - condensation products of the dinitrile or polymeric substances.

Saponification of the crude condensation product by boiling with the strong alcoholic potash solution gave a greenish-red alkaline solution with a strong absorption band at 636mu. and 592mu. Dinapthoazulene itself has absorption bands at 622,573mu. and the alkaline solution was thought to be perhaps the dicarboxylic acid LVIII. Acidification of this alkaline solution gave a very small amount of a red acid which was heated with copper powder under high vacuum,and gave only a trace of a red solid. This dissolved readily in even dilute acetic acid mixed with a little hydrochloric acid,to give violet-blue solutions and in xylene to give solutions with an absorption band at 513mu. This seems similar to the dinaptho-azulene oxide LIX which is a red substance and forms violet solutions with acids and has a band at 500mu.



LVIII

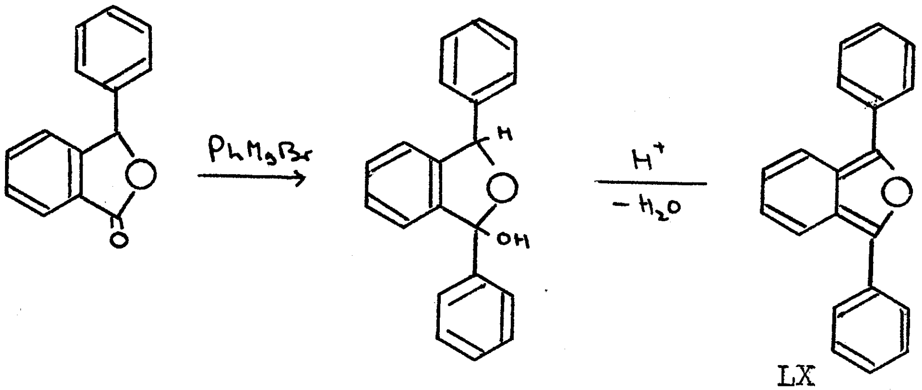
LIX

All the above evidence is only of a qualitative nature and the condensation reaction is not at all a satisfactory route to the dinapthoazulene but the above results do at least provide some indirect support for the constitution of this unusual hydrocarbon since it is impossible that any of the alternative products of the original reaction of fumaryl chloride and napthalene could also be formed in this condensation.

Appendix B.

Preliminary experiments concerning the possibility of synthesising a system which, if only uncharged structures are considered, must contain a 'Dewar' bond.

The isobenzofurans are an interesting class of organic compounds, and one of the earliest examples of this type of molecule was diphenyl isobenzofuran LX, synthesised by Guyot and Catel (49) as shown below.

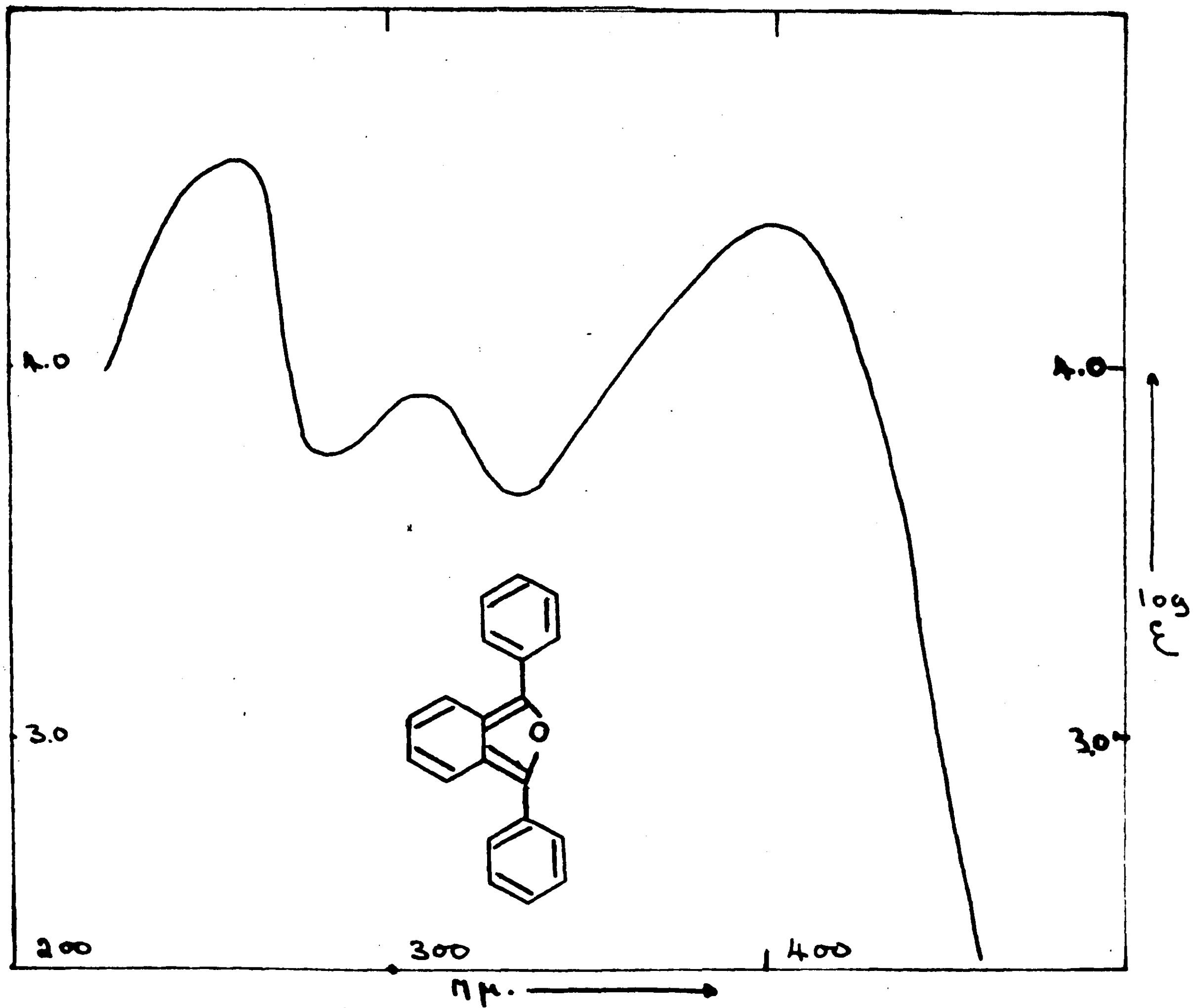


LX

This substance forms bright yellow needles which give intensely yellow solutions which have a strong bluish fluorescence. The molecule is a fairly reactive one and photo-oxidation and addition reactions e.g. of maleic anhydride occur readily. Reduction and oxidation also take place easily. The absorption spectrum is shown in Fig.18.

If this type of structure were to be generated on both sides of a benzene ring, compounds of the type LXI shown below must result. That is molecules which can not be formulated in normal terms and which must, if they exist at all, have an unconventional bond structure and might possibly possess bonds of the 'Dewar' type.

Fig. 18.

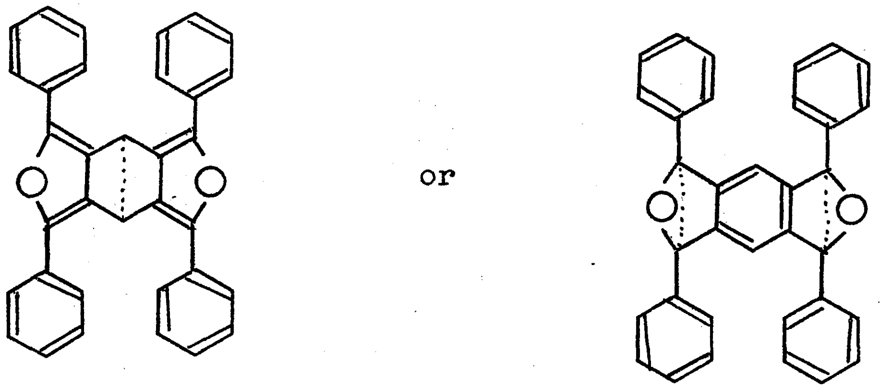


Band maxima (mu)

α,α' - Diphenyl-isobenzofuran in alcohol,

405,310,260.

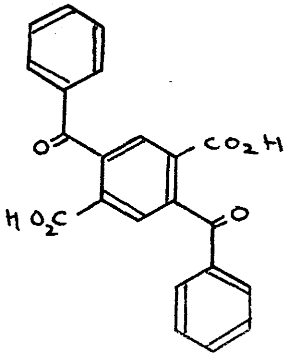
After all Pauling (50) states that Dewar bonds play a part at least in benzene itself, and if no other type of classical bond structures can be written, apart from charged species, might not the long Dewar type of linkage exist?



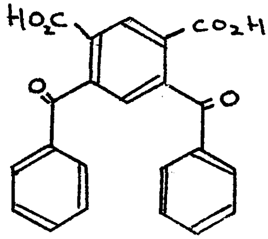
LXI

Accordingly an attempt to synthesise the above type of molecule was made. The route chosen was fully analogous to that used in the original synthesis of diphenylisobenzofuran.

Pyromellitic dianhydride reacts with benzene in the presence of aluminium chloride to give a mixture of the isomeric acids LXII and LXIII (51)

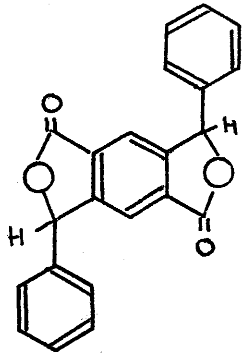


LXII

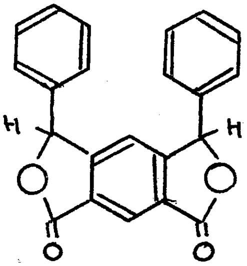


LXIII

When these acids were reduced with dilute alkali and zinc dust it was found, as might be expected, that the 'para' acid LXII, is preferentially reduced. Lactonisation followed by fractional crystallisation enabled a complete separation of the two lactides LXIV and LXV to be made.

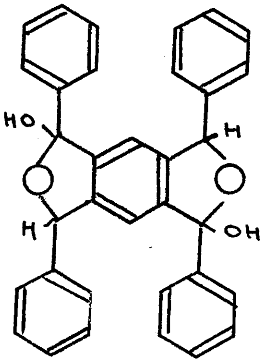


LXIV

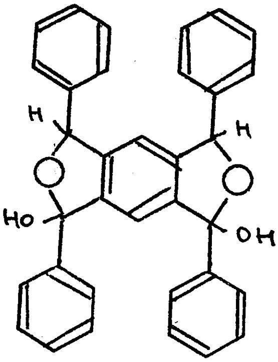


LXV

Reaction of these lactides with phenyl magnesium bromide should give the diols LXVI and LXVII which could be dehydrated to give the required molecule



LXVI



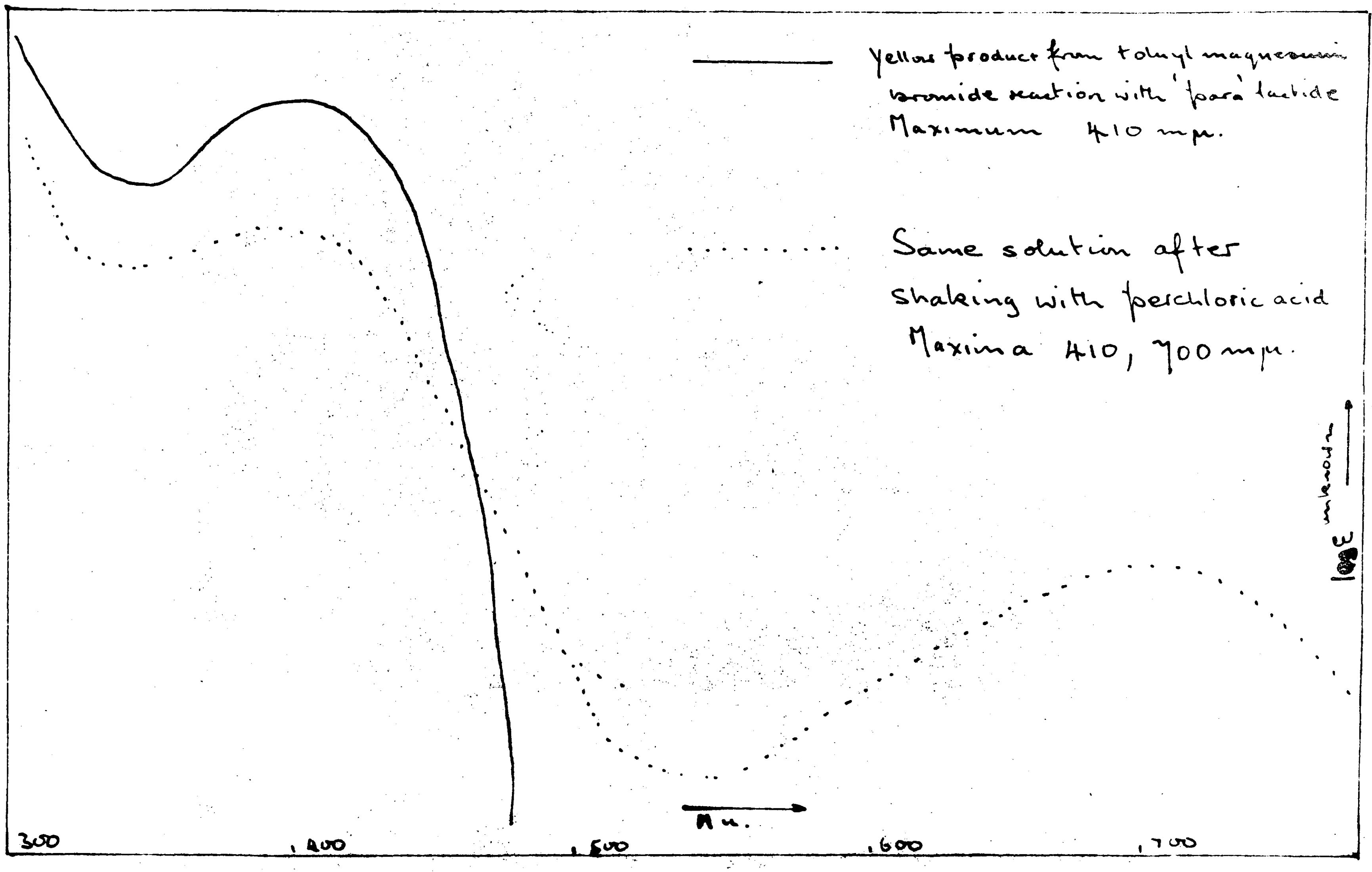
LXVII

Reaction of the 'para' lactide LXVI or of a mixture of the lactides with phenyl magnesium bromide gave a white solid which showed a complete absence of carbonyl peaks in its infra-red spectrum but did have a strong hydroxyl peak. When heated above its melting point the white solid turned bright yellow, and bubbles were formed.

Although the reaction product was insoluble in all non-polar organic solvents,when it was placed in glacial acetic acid with some hydrochloric acid the diol dissolved slowly on boiling, the mixture giving a yellow solution with a strong bluish fluorescence. On cooling white needles were deposited which showed no bands for either carbonyl or hydroxyl in the infra-red spectrum. The ultra-violet spectrum showed that there was no conjugation beyond a benzene system. Furthermore the analysis of this product proved that there was more carbon present than a structure of the required type LXI would require. It must be concluded then that although some of the isobenzofuran type of structure may have been present,as indicated by the typical yellow colours,the Grignard reaction must have taken place more than twice and the whole system undergone a rearrangement.

It was decided therefore to repeat the reaction under somewhat different conditions. Only the 'para' lactide was used and o-toluyl magnesium bromide replaced the phenyl magnesium bromide. It was hoped that the additional methyl group would hinder any rearrangement to some extent at least.

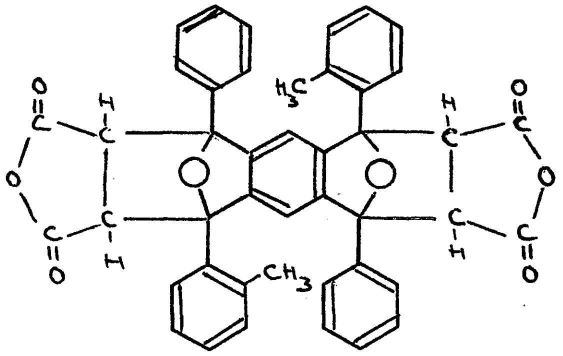
Fig. 19.


Yellow product from tolyl magnesium bromide reaction with 'para' lactide
Maximum 410 mμ.
Same solution after shaking with perchloric acid
Maxima 410, 700 mμ.
log ε
mμ.
300
400
500
600
700

Also in this case the Grignard reagent was added to excess of the lactide in order to prevent the addition occurring more than twice.

Only about half of the lactide reacted under these conditions however. The portion which did react gave a deep yellow solution which on concentration gave a yellowish solid. The absorption spectrum of this solution is shown in Fig.19 and there is some similarity to the spectrum of diphenylisobenzofuran. When this yellow solution was shaken with a strong acid such as perchloric, a brilliant green colour was formed,and the change in absorption is also shown in Fig,19. It was concluded that the Grignard addition had produced at least some of the required diol which had lost the elements of water spontaneously. Recrystallisation of the crude reaction product gave only colourless white needles,the yellow colour remaining in the mother liquors and eventually fading altogether. Once again the analysis of the white product would not support the required structure and the infra-red spectrum showed a lack of hydroxyl or of carbonyl bands. No structure can be suggested for this substance, which must be some form of rearrangement product.

The fact that deep yellow solutions with absorption similar to that of the diphenyl isobenzofurans were formed, and which gave the intense green colours with strong acid,meant that the diphenyl isobenzofuran structure must be present to some extent at least in the crude reaction product. When the product from the Grignard reaction was dissolved immediately in xylene and reacted with excess of maleic anhydride the deep yellow colour faded at once and silky white needles were deposited from the hot solution. This adduct dissolved with difficulty in alkali and its absorption spectrum showed it to be a benzene derivative. The analytical data supported the structure of the double adduct shown below, LXVIII.



LXVIII

The results from the Grignard reactions on the lactides LXVI and LXVII can not be said to be conclusive. In the case of the reaction with toluyl magnesium bromide it can be claimed that at least some of the required structure was formed and while no evidence of the type of bond structure present has been found such a system is not particularly stable and appears to rearrange readily.

Experimental

All melting points were uncorrected and taken in evacuated capillaries. Microanalyses were by Mr Cameron and staff. Visible absorption bands were measured on a Zeiss,diffraction grating spectroscope, and absorption spectra were measured on a Unicam Spectrophotometer.

The palladium charcoal catalyst was prepared by the method of Newmann and Zahn (52) on small lumps of charcoal.

The alumina used for chromatography,unless specially described,was Grade I on the Brockmann scale.

Synthesis of 4,5:12,13-Dibenzoheptazethrene I.

1,4-Di-(octahydrophenanthroyl -9)-benzene II.

Finely powdered terephthalyl chloride (75g.) was mixed with excess of technical octahydrophenanthrene (405g.) and benzene (500ml.). Powdered aluminium chloride (130g.) was added in portions. When the vigorous evolution of hydrochloric acid had ceased,the mixture was decomposed with ice and dilute hydrochloric acid. The crude ketone was filtered off, dissolved in xylene,and combined with the benzene mother liquor. This mixture was washed very thoroughly with hot water, and dilute ammonia. Removal of the xylene-benzene mixture left the crude ketone (200g.),which was used directly for the pyrolysis. Repeated crystallisation of a portion of ketone from xylene,gave small,pale yellow needles m.p.201-202°. The solution in concentrated sulphuric acid was brown at first, later turning orange. (Found: C,85.9;H,7.5. $C_{36}H_{38}O_2$ requires C,86.0; H,7.6%). The infra-red spectrum showed a carbonyl peak at 1660cm.

Pyrolyses of 1,4-Di-(octahydrophenanthroyl-9) -benzene II.

The crude ketone (100g.) was melted,and the temperature raised gradually to 400,water was evolved,and the brownish colour lightened to pale orange with a strong yellow fluorescence. When no more water appeared ($\frac{1}{2}$-$\frac{3}{4}$ hr.),heating was stopped and the mixture was cooled,with the exclusion of air.

Hot xylene (150 ml.) was added, and on cooling a red solid (5g.) was deposited. Further portions (2-3g.) were later obtained from the mother liquor. This crystalline pyrolysate consisted of a mixture of hydrogenated hydrocarbons, mainly the dihydro VI with some octahydro VII, and a trace of the fully aromatic dibenzoheptazethrene I. This crystalline mixture was used directly for subsequent reactions. The mixture dissolved slowly in concentrated sulphuric acid, and gave a violet colour at first which changed to purple. The yields of the crystalline pyrolysate were as described only when excess technical octahydrophenanthrene containing 30% of tetrahydronapthalene was used.

Tetradecahydro -4,5:12,13-dibenzoheptazethrene V.

The filtrate from the above reaction was chromatographed on alumina. Elution with petroleum ether (60-80°) and then benzene, gave several fractions. The major portion was a b) viscous oil which could not be characterised. Later fractions gave a small amount (50mg.) of a yellow crystalline hydrocarbon m.p.438-40°, which gave yellow solutions in concentrated sulphuric acid.

(Found: C, 92.1; H, 7.5. $C_{36}H_{34}$ requires C, 92.6: H, 7.4%)

The absorption spectrum given in Fig.3, shows this hydrocarbon to be a 1,2:5,6 -dibenzanthracene derivative.

4,5:12,13-Dibenzoheptazethrene - 7,15-quinone IX.

The crystalline pyrolysate, that is the mixture of the dihydro and octahydro-hydrocarbons VI and VII, (300mg.) and selenium dioxide (100mg.) boiled in nitrobenzene (10ml) for twenty minutes. The red solution turned purple and then dark brown. On cooling the brown product was filtered off and washed with hot nitrobenzene, then with methanol, and finally with hot water to remove excess selenium dioxide. Purification by sublimation first at 200-50°/0.1mm to remove selenium metal, and then at 400°/0.1mm gave the small brown needles of the quinone (200mg.) M.p. above 450° (dec.) (Found: C,89.5; H,4.3 $C_{36}H_{18}O_2$ requires C,89.6;H,3.8%) The quinone gave a green solution in concentrated sulphuric acid. It did not dissolve in alkaline sodium dithionite solution, to give a 'vat'. The absorption spectrum shown in Fig.5, is similar in type to the dibenzoperinapthenone type.

4,5:12,13-Dibenzoheptazethrene I.

The crystalline pyrolysate (500mg.) was sublimed, in a current of air free carbon dioxide, over 15% palladium charcoal at 300-320°/0.1 mm. Shining green needles (450mg) of the fully aromatic hydrocarbon were formed, dec.pt. above 400°. Solutions of the hydrocarbon in organic solvents were violet-red with a strong red fluorescence. The dibenzoheptazethrene dissolved immediately in concentrated sulphuric acid to give a deep purple solution, which showed absorption bands in the visible region at 550mu.,and 512mu.

(Found: C,95.21; H, 4.71 $C_{36}H_{20}$ requires C,95.55;H,4.46%)

Visible bands,in benzene, 572,528, 488mu. Absorption spectrum is given in Fig.6.

(ii)Dehydrogenation with nitrobenzene.

The pyrolysate (1g.) was suspended in nitrobenzene (15ml.),and refluxed for 2-3 minutes. The brownish red solution turned deep purple with a strong red fluorescence,and on cooling glistening green needles (300mg.) were deposited.

(iii) Dehydrogenation using chloranil in trichlorobenzene.

The pyrolysate (1g.) was suspended in trichlorobenzene (20ml.) and excess chloranil (1g.) added. The mixture was boiled for 2-3 minutes,and on cooling,crystals (200mg.) of the hydrocarbon I were formed.

Salts of 4,5:12,13 -Dibenzoheptazethrene XII.

(i) Hydrochloride

Solutions of the hydrocarbon I in trichlorobenzene,were shaken with concentrated hydrochloric acid. The organic layer was completely decolourised and a violet salt formed. The salt could also be formed by the passage of hydrochloric acid gas. A solution of hydrocarbon (100mg.) in trichlorobenzene (500ml.) was saturated with hydrochloric acid gas. The flocculant violet precipitate was filtered off,washed with dry benzene, and dried in vacuo.

(Found: C,88.0; H,4.3; Cl,6.8. $C_{36}H_{21}Cl$ requires C,88.4; H, 4.3; Cl,7.3%)

The hydrochloride decomposed on standing, turning black, with loss of hydrochloric acid. If a suspension of the salt in trichlorobenzene was allowed to stand for several days, a solution with the absorption bands (594mu.,555mu.) of the chlorodibenzozethrene XIII resulted. The hydrochloride appeared insoluble in most organic solvents. When a suspension of the salt in pyridine was boiled, green crystals of the parent hydrocarbon I were formed. The salt gave purple solutions in concentrated sulphuric acid which had bands at 550mu.and 512mu.

(ii) Sulphate.

Solutions of the dibenzoheptazethrene were completely decolourised on shaking with 80% sulphuric acid. The violet sulphate being formed. Dibenzoheptazethrene gave solutions in concentrated sulphuric acid which showed absorption band at 550mu.,and 512mu., compared to the hydrocarbon in trichlorobenzene solution where the bands were at 572mu.,and 528mu. This shift is indicative of salt formation.

(iii) Perchlorate andPhosphate.

Solutions of dibenzoheptazethrene in trichlorobenzene were also decolourised when shaken with perchloric or phosphoric acid, the violet salts being precipitated.

7-Chloro-4,5-dibenzoheptazethrene XIII.

An excess of phosphorous pentachloride (500mg.) was added to a suspension of the crystalline pyrolsate (300mg.) in boiling xylene. The reddish-brown solution turned a deep blue with a strong red fluorescence, and on cooling the dark blue chlorohydrocarbon (250mg.) was deposited. Recrystallisation from trichlorobenzene gave the pure chlorohydrocarbon, dec.pt above 450°, which dissolved in concentrated sulphuric acid to give a deep purple solution.

(Found: Cl, 7.3 $C_{36}H_{19}Cl$ requires Cl, 7.5%)

6,14-Dihydro-4,5:12,13-dibenzoheptazethrene VI.

Although this substance is the main product of the pyrolysis the best method of obtaining it pure was by reduction of dibenzoheptazethrene or chlorodibenzheptazethrene. Dibenzoheptazethrene (500mgs), or chlorodibenzoheptazethrene (500mgs.) was ground together with zinc dust (2g.) This mixture was suspended in pyridine (100ml.), and refluxed. Acetic acid (80%, 10ml). was added slowly over three hours. The violet solution decolourised immediately becoming a pale yellow with a strong blue fluorescence. After cooling, the solution was filtered into water and boiled. The pale yellow dihydrodibenzoheptazethrene was filtered off, dried and sublimed. m.p. 395-400° (dec.). The colour in concentrated sulphuric acid was violet.

(Found: C, 94.6; H, 5.4 $C_{36}H_{22}$ requires C. 95.1; H4.9%.)

1,3-Di-(octahydrophenanthroyl -9)-benzene XIV.

Procedure was as for diketone II, with isophthalyl chloride in place of terephthalyl chloride.

Crystallisation from benzene, and petroleum ether (100-120°) gave white needles m.p. 172-173°, which dissolved in concentrated sulphuric acid to give a brown solution which later turned orange.

(Found: C,86.0; H,7.9 $C_{36}H_{38}O_2$ requires C,86.0; H,7.6%)

Pyrolysis of 1,3-di(octahydrophenanthroyl-9)-benzene XIV.

The conditions were the same as those described for diketone II. The crude diketone XIV (100g.) gave the same mixture of hydrogenated hydrocarbons (6g.).

The product obtained in this way could be dehydrogenated in good yield to dibenzoheptazethrene I.

Synthesis of 5,6:8,9:14,15:17,18-Tetrabenzoheptacene XVI.

Reaction of maleic anhydride with 6,14-dihydro-4,5:12,13-Dibenzoheptazethrene VI.

The mixture of crystalline hydrocarbons from the pyrolysis of the diketones II or XIV,(5g.) was added to molten maleic anhydride and boiled for fifteen minutes. After cooling the mixture was poured into hot water and digested. The light-brown product was filtered off,dissolved in 15-20% caustic potash solution containing zinc dust to prevent aerial oxidation. The light yellow solution had a strong blue fluorescence and acidification gave the brownish tetracarboxylic acid XIX. A portion of the acid was recrystallised from acetic anhydride m.p.250-5° (dec.)

(Found: C,78.8; H,4.8 $C_{44}H_{28}O_7$ requires C.79.0;H,4.3%)

The analysis figures correspond to a semi-anhydride,and almost identical figures were obtained if precipitated acid was dried under vacuum at 150° for several hours. The acid gave steel-blue solutions in concentrated sulphuric acid which later turned reddish.

The absorption spectrum of the acid is given in Fig.4 and the similarity of this to the spectrum of dihydrodibenzoheptazethrene VI shows that no change in aromatic conjugation has taken place.

Octahydro-4,5:12,13-dibenzoheptazethrene VII.

When the above condensation was carried out for a shorter time there was an alkali insoluble residue (200mg.). Recrystallisation from benzene gave small white needles, m.p. 318-320°. This hydrocarbon could not be dehydrogenated by means of chloranil in trichlorobenzene, but sublimation over 15% palladium charcoal at 300-320° gave dibenzoheptazethrene in quantitative yield. The octahydro hydrocarbon gave a blue solution in concentrated sulphuric acid.

(Found: C, 93.5; H, 6.3 $C_{36}H_{28}$ requires C, 93.9; H, 6.1%)

The absorption spectrum of the hydrocarbon is similar to that of dihydrobenzoheptazethrene VI, and shows that the aromatic complex can not be 1,2:5,6-dibenzanthracene as in the tetradecahydro-hydrocarbon.

5,6:8,9:14,15:17,18-Tetrabenzoheptacene XVI.

The tetracarboxylic acid (5g.) was ground together with zinc dust (5g.) Zinc chloride (50g.), sodium chloride (5gs.), and a little water (2ml.) were added and the temperature of the mixture was raised, with constant stirring to 300-320, for ten minutes. After cooling the mixture was digested with dilute acetic acid and the zinc dust dissolved in dilute hydrochloric acid. The crude product (2g.) was extracted with ether and xylene, to remove impurities of low molecular weight. Repeated sublimation (400-450°/0.1mm.), followed by recrystallisation from methyl napthalene gave yellow needles (300mg.) of tetrabenzoheptacene. m.p. 480-490° (sublim.)

Tetrabenzoheptacene does not dissolve in concentrated sulphuric acid although the surface of the crystals turns black on standing.

(Found: C,95.5; H,4.5 $C_{42}H_{22}$ requires C,95.8; H,4.2%)

The hydrocarbon has a long life phosphorescence in solid ethanolic solution at 77°K,this is shown in Fig.2.

The molecular weight of the hydrocarbon was estimated by the mass spectroscopic method to be 510 ± 5 $C_{42}H_{22}$ requires 526

The ultra-violet absorption spectrum is given in Fig.7 and it is shown in Table 3,that the hydrocarbon forms an annellation series with tetrabenzanthracene XX and tetrabenzopentacene XXI.

The infra-red spectrum of the hydrocarbon is closely similar to that of tetrabenzoanthracene and tetrabenzopentacene. The band groups of tetrabenzoheptacene are given in Table 4. and fully support the structure.

5,6:13,14-Dibenzoheptazethrene XXIII.

5,6:13,14-Dibenzoheptazethrene -4,8:12,16-diquinone XX1V (35)

Methylene anthrone (35) (10g.) was added to boiling nitrobenzene (200ml.) and recrystallised benzoquinone (10g.) added in portions. The brown needles of the quinone XXIV were formed almost immediately. The addition of benzoquinone was completed over 10-15 min. and the product (10g.) filtered off from the hot solution. When chloranil was used in place of benzoquinone the yield of the quinone was much lower.

Dihydro- 5,6:13,14-Dibenzoheptazethrene XXV.

The quinone XXIV (15g.) and zinc dust (30g.) were suspended in pyridine (200ml.) and the mixture boiled. Concentrated hydrochloric acid (70ml.) was added over five hours. The mixture was poured into water and the crude product (10g.) filtered off. Recrystallisation from methyl napthalene gave small brownish-yellow needles, which were sublimed. M.p.435° (rapid heating).

(Found: C, 95.11; H, 4.49. $C_{36}H_{22}$ requires C, 95.12; H, 4.88%)

Absorption spectrum Fig.8

Sulphuric acid colour, green then brown, finally violet.

The quinone XXV was also reduced by hydrogen iodide/ red phosphorous under pressure.

The quinone (4g.) XXIV 55% hydrogen iodide (30ml.) and red phosphorous (1.23g.) were sealed in a Carius tube, which was heated for 6-8 hrs. at 200-10° C. The product (3.5g.) was washed with water, alkaline sodium dithonite solution, and dilute ammonia. The crude product has additional bands at 545mu. and 505mu. in trichlorobenzene solution. When the reaction product was chromatographed over alumina the first fractions contained the long wavelength bands. Concentration of these fractions did not yield a crystalline product, and because of the solubility of this substance it was concluded that the bands belong to a more highly hydrogenated derivative. Elution with hot xylene, gave a yellow fraction, having bands at 413mu, 434mu, 460mu. Concentration of these fractions, sublimation (dec.) and recrystallisation from methyl napthalene yielded the brownish-yellow needles of the dihydro-hydrocarbon XXV. Absorption spectrum Fig.8

(Found: c,95.04; H,4.82. $C_{36}H_{22}$ requires C.95.12;H,4.88%)

Concentrated sulphuric acid colour, as above.

5,6:13,14-dibenzoheptazethrene 4,12-quinone XXVI.

The dihydro-dibenzoheptazethrene XXVI (300mg.) was dissolved in nitrobenzene (10ml.) and selenium dioxide (100mg.added). The mixture was refluxed for 15 min. The crude product was washed with hot water to remove excess selenium dioxide, and sublimed, giving small brown needles, M.p.480° C (dec.)

(Found: C,89.25; H,3.83. $C_{36}H_{18}O_2$ requires C,89.61;H,3.76%)

Concentrated sulphuric acid, colour violet-brown.

The quinone XXVI did not form a vat with alkaline sodium dithionite.

Attempts to dehydrogenate dihydro-5,6:13,14-dibenzoheptazethrene.

With palladium charcoal.

The dihydro hydrocarbon (500mg.) was mixed with 10% palladium charcoal (200mg.) and heated to 300-20° C for 2-3hrs.in an atmosphere of air free carbon dioxide. Sublimation at 380-400° C/ 0. 1mm. gave unchanged dihydro -hydrocarbon XXV. Visible bands: 413mu. 434mu. 460mu. When the dihydro-hydrocarbon was sublimed over lumps of 10% palladium charcoal at 400° C most of it was destroyed,only a little starting material was recovered.

With chloranil in boiling trichlorobenzene.

When pure dihydro dibenzoheptazethrene XXV (1g.) was dissolved in boiling trichlorobenzene (50ml.) and an excess of chloranil (1g.) added the solution darkened at once and a black precipitate formed. The bands of the starting material 413mu.,434mu 460mu.were replaced by bands at 473mu.,440mu.,422mu. After boiling for 15 mins.the black product was filtered off (1.3g.) Sublimation at 400-50° C/0.1mm. gave a very small amount (2-3mg) of a pale orange substance. This crystallised from methyl napthalene as small needles which dissolved very slowly in concentrated sulphuric acid to give a faint blue colour. No structure can be suggested for this small amount of material.

5,6:14,14-Dibenzoheptazethrene -4,8:12,16-diquinone XXIV using 2.5-dichlorobenzoquinone (53)

2,5-dichlorobenzoquinone (5g.)was added to a boiling solution of methylene anthrone (5g.) in nitrobenzene (100ml.) Reddish-brown needles of the quinone XXIV were formed,and filtered off from the hot solution (4.5g.).

Reduction of the quinone by hydrogen iodide/red phosphorous method as described above, gave a hydrocarbon with identical properties to those of the dihydro 5,6:13,14-dibenzoheptazethrene XXV. The absorption spectrum was identical to that shown in Fig.8. Dehydrogenation reactions were also unsuccessful.

1,4-Di(octahydroanthracenoyl -9) -benzene XXXI.

Octahydroanthracene (50g.) and terephthalyl chloride (29g.) were suspended in dry benzene (250ml.) Aluminium chloride (45g.) was added in portions to the mixture. The solution turned red and hydrochloric acid was evolved. The reaction was allowed to proceed for fifteen minutes. Decomposition was carried out by pouring into a mixture of ice and hydrochloric acid. The crude product (35g.) was filtered off, and the concentration of the benzene layer yielded more crude ketone (45g.) Recrystallisation from xylene gave small clumps of very pale yellow needles. M.p. 320-3° C.

(Found: C, 85.57; H, 7.02. $C_{36}H_{38}O_2$ requires C, 86.02; H, 7.60%)

Infra-red, carbonyl group 1660cm^{-1}.

The colour in concentrated sulphuric acid was a brownish-red,

Cyclisation of 1,4-di(octahydroanthracenoyl-9)-benzene XXXI.

With copper powder absent.

The crude ketone XXI (30g.) was melted and the temperature raised gradually to 400°. The melt became a clear brown, later darkening and showing some greenish fluorescence. Water was evolved slowly, no more appearing after 30 min. when heating was stopped. The reaction mixture was allowed to cool, air being excluded. Hot xylene (100ml.) was added but no precipitate was formed, even after allowing the mixture to stand for some time. The crude product had bands at 528mu., 510mu., 500mu., and 456mu. Chromatography over alumina, and elution with pet.ether and benzene gave fractions having bands at 454mu. and 447mu., but concentration gave light brown viscous oils. This mixture of highly hydrogenated hydrocarbons was unaffected by chloranil in trichlorobenzene.

With copper powder present.

The ketone XXXI (35g.) was heated to 400° as above, but copper powder (5g.) was added in portions, and the mixture was held at 400-20 for 45 min. After cooling in the absence of air, xylene (100ml.) was added to the mixture. After standing a black precipitate (1.5g.) was formed. This showed bands at 460mu., 434mu., and 413mu. Sublimation at 380-400° C/0.1mm, with considerable decomposition, gave the dihydrodibenzoheptazethrene XXV (500 mgs.). The absorption spectrum was identical to that given in Fig.8.

(Found: C, 95.00; H, 4.84. $C_{36}H_{22}$ requires C, 95.11; H, 4.88%)

The sulphuric acid colours were identical to those described above. All attempts at dehydrogenation failed as before.

Synthesis of 1,2:3,4:7,8:9,10-Tetrabenzocoronene XXXIV.

Di-(diphenylmethylene) -9,10-dihydroanthracene XXXV (38).

9,10-Dihydroanthracene (18g.) and benzophenone chloride (50g.) were heated together at 250° for 3 hours. Xylene was added to the cooled mixture and after refluxing for some time allowed to cool. The needles deposited were filtered off, washed with benzene and dried (11.7g.) M.p.306-9° (lit.306°)

Colour in sulphuric acid, green.

Attempts to cyclise XXXV by catalytic means

1. Copper wire.

Copper oxide in wire form was reduced to copper by heating during the passage of hydrogen. The anthracene derivative XXXV was sublimed over this catalyst which was held at 500-50°. The starting material was recovered unchanged.

2. Palladium charcoal.

Di-(diphenylmethylene)-9,10-dihydroanthracene was sublimed over palladium charcoal lumps, but even at 400-50° no change in the starting material was found.

Reaction of XXV with aluminium chloride in benzene.

Di-(diphenylmethylene) -9:10-dihydroanthracene (3g.) was suspended in dry benzene (50ml.) and finely ground aluminium chloride (6g.) added in portions. Ten drops of stannic chloride were also added. The mixture turned a dull green colour, and was refluxed for one hour with no further change. Decomposition of the mixture gave starting material (2.5g.) and a small amount of an extremely soluble greenish solid, which was not further investigated.

Cyclisation of di-(diphenylmethylene)-9:10-dihydroanthracene XXXV. in sodium chloride-aluminium chloride melt.

The dihydroanthracene derivative XXXV (5g.) was added to a melt of aluminium chloride (100g.) and sodium chloride (20g.) containing stannic chloride (3g.),and held at 110-120°. A dark reddish colour was formed and as the temperature was raised with constant stirring,the colour darkened,becoming almost black. The melt was held at 140-150° for 8-10 minutes and then raised for a minute to 160-170°. The reaction mixture was allowed to cool and decomposed cautiously with dilute hydrochloric acid.

The product was a brownish solid (4.5g.)

This solid was dissolved in xylene and chromatographed over alumina. Elution with dry benzene gave at first colourless solutions with a strong blue fluorescence,these yielded about 100mg. of starting material. Later benzene fractions showed bands in the visible region at 456-60mu (weak) and 428mu.(strong). Concentration of those fractions containing these bands gave a bright yellow solid (250mg.).Which sublimed at 300°/01mm. M.p.309-12°. The absorption spectrum of this hydrocarbon is given in Fig.10.

The analytical data supports the 4,5:10,11-dibenzo-1,12-o-phenylene perylene structure XXXVI. The hydrocarbon gave a violet colour in sulphuric acid.

(Found: C,96.1;H,4.2 $C_{34}H_{18}$ requires C,95.8;H,3.8%)

The perylene XXXVI reacted with maleic anhydride and chloranil to give a small amount of highly crystalline adduct. This formed bright red needles which precipitated from the reaction mixture. However because of the extremely small amounts (1-2mg.) isolated, this product was not investigated further. But the formation of an adduct with maleic anhydride is typical for hydrocarbons with a perylene structure (36).

When the eluant showed that the bands of the perylene were almost absent, benzene was replaced by xylene as eluant, and eventually hot xylene was used. These later fractions contained very sharp absorption bands at 473mu.and 445mu., all fractions showing that these bands were collected and on concentration yielded a pale orange-yellow solid (300mg.). This hydrocarbon sublimed without decomposition at 300°/01mm. The absorption spectrum shown in Fig.11 was of the coronene type. The analytical data also supported the 1,2:3,4:7,8;9,10-tetrabenzocoronene structure XXXIV.

(Found: C,95.75; H,4.20 $C_{40}H_{20}$ requires C,95.96;H,4.03%)

The hydrocarbon could not be induced to form a satisfactory crystalline state. Even on allowing xylene solutions to cool very slowly it was always in a very finely divided state. The melting point of the hydrocarbon was rather indistinct. A portion of the hydrocarbon first melted at 320° but the whole sample was not molten till about 350°. This behaviour was constant, even after repeated sublimation and recrystallisation. It was concluded that several stereoisomers were present due to hydrogen overcrowding. Evidence of steric strain was obtained from the spectrum. Fig.11.

9-phenyl-1,2:7,8-dibenzoperinapthene XXXVII.

Finely ground anthracene (18g.) was finely ground and suspended in benzene (50ml.) together with benzophenone chloride (25g.) Finely ground aluminium chloride (15g.) was added in portions, the reaction mixture turning violet then olive green. After boiling for 15 mins.the cooled mixture was decomposed in the usual way and the benzene layer steam distilled.Ether was added to the remaining blackish tarry material and the solution allowed to stand for some time. Brownish crystals were deposited and crystallised from xylene as yellow platlets. (2-3g.) M.p.169-170°.

The absorption spectrum shown in Fig.12 appears to be that of an anthracene derivative.

(Found: C,94.54; H,5.22 $C_{27}H_{18}$ requires C,94.70;H,5.30%)

Attempts to react this product further with benzophenone chloride were unsuccessful.

Attempted synthesis of 5,6-Benzoperopyrene XXXVIII.

Peropyrene XXXIX (41).

Perinapthenone (10g.) was condensed in a zinc dust melt as described in the literature. After sublimation of the crude product and recrystallisation from xylene,golden platlets (300mg.) were obtained. M.p. 374-5° (lit.)

Visible bands in xylene: 444,426mu.

Concentrated suplhuric acid colour,bright blue.

Reaction of peropyrene with maleic anhydride and chloranil.

Peropyrene (120mg.) was mixed with excess maelic anhydride (2g.)and cloiranil (500mg.). The mixture was refluxed until the 444mu. band of peropyrene disappeared (½ hr.) and was replaced by one at 452mu. Hot nitrobenzene (50ml.) was added and the crude product (112mg.) filtered off. It was insoluble in alkali. Sublimation 400°/0.1mm., and recrystallisation gave orange-red needles (5mg.) M.p.406-409°.

(Found: C,78.97, H, 3.06 $C_{26}H_{12}Cl_2$ requires C,79.23,H,3.46%)

Visible bands 452,429mu. Spectrum Fig.13

Concentrated sulphuric acid colour, blue.

Reaction of violanthrene with maelic anhydride and chloranil.

Violanthrene (100mg.) was boiled with a mixture of maelic anhydride (1g.) and chloranil (500mg.) after a few minutes the 492mu. band of violanthrene was replaced by the 645,mu., 608 mu. bands of violanthrone.

Reaction with isoviolanthrene,produced isoviolanthrone.

Peropyrene -1-10-quinone XLI. (42).

Perinapthenone (10g.) was added slowly to a hot solution of potassium hydroxide (50g.) in methanol (100ml.) and the temperature raised to 150-160° for five minutes. The melt was digested with hot water, diluted to one litre,and air bubbled through the solution for several hours. The purple precipitate was filtered off and dried (9g.). A portion was crystallised from nitrobenzene,giving a dark purple powder. M.p. sinters above 450°.

(Found: C,86.96; H,3.97% $C_{26}H_{12}O_2$ requires C.87.63; H,3.39%)

The quinone forms a bright red vat with alkaline sodium hydrosulphite.

Visible bands,in nitrobenzene 600mu.,555mu.,490mu., Spectrum Fig.14

Concentrated sulphuric acid colour,blue.

Oxidation of peropyrene- 1-10 -quinone.

Crude quinone (1g.) was suspended in a mixture of chromic anhydride (1.4g.),water (100ml.) and concentrated sulphuric acid (15ml.). This was boiled for one hour,the product filtered off,extracted with dilute alkali,and acidified. The crude acid (200mg.) was heated with soda lime,a small amount of a hydrocarbon sublimed off at 380-400°/0.1mm. The absorption spectrum in benzene was identical with that of perylene.

Visible bands in benzene 439mu. and 412mu.

Reduction of peropyrene - 1 -10-quinone XLI.

The crude quinone (10g.) was ground together with zinc dust (10g.) sodium chloride (10g.),and zinc chloride (50g.) was added. After the addition of water (1ml.) the mixture was melted and the temperature raised with constant stirring,to 290-310°,for five minutes. Digestion with hot water,removal of the zinc dust with acid,and sublimation 350°/0 .02mm.gave peropyrene (3g.).

Visible bands in xylene 444mu.,426mu.

Colour in sulphuric acid,blue.

Reaction of peropyrene -1 -10-quinone,XLI,with maleic anhydride and chloranil.

The quinone (1g.) was ground with maleic anhydride (20g.) and chloranil (1g.). The mixture was heated,the blue coloured solution turned dull red and then golden yellow. After cooling xylene (50ml.) was added and the crude adduct (1.4g.),filtered off. The blackish solid,gave a red coloured alkali solution, which had an absorption band at 480mu.(diffuse). The adduct was insoluble in benzene or xylene,and solvents such as acetic anhydride,dimethyl formamide,trichlorobenzene etc.,gave solutions with the 600mu,555mu,bands of the quinone. When the adduct was boiled in alkali (5-10%) with zinc dust,dissociation to the quinone also occurred. Attempts to decarboxylate the adduct either with soda lime or copper powder/quinoline were unsuccessful. Violanthrone formed a similar adduct. The alkali solution had a band at 510mu.

3-3' di(perinapthenyl -7,8-dihydro-9-one) XLII (Dimeride).

Perinapthenone (10g.) in xylene (50ml.) was added to a boiling mixture of sodium hydroxide (200ml.5%) and zinc dust (5g.). The solution became a deep red colour, which faded after thirty minutes. The xylene was removed by steam distillation, and the zinc dust filtered off. Extraction with xylene gave colourless needles of the <u>dimeride</u> XLII. M.p. 256-257°, (1.5g.). (Found: C,86.09; H,5.01; $C_{26}H_{18}O_2$ requires C.86.16;H,4.9%) The infra-red spectrum showed a strong carbonyl peak at 1675cm. The compound could be distilled at atmospheric pressure, and dissolved in concentrated sulphuric acid to give a bright yellow solution.

Reduction of dimeride XLII to peropyrene XXXIX.

The dimeride XLII (500mg.) was mixed with sodium chloride (1g.) and zinc chloride (5g.), the mixture heated, with constant stirring to 300° for five minutes. After decomposition with dilute acid the crude product was sublimed 300°/0,1mm., giving peropyrene (0.4g.).

Visible bands 444mu, 426mu. Sulphuric acid colour, blue.

Condensation of the dimeride XLII to peropyrene quinone XLI.

The dimeride (100mg.) XLIII was added to a solution of potassium hydroxide (10g.) in methanol (50ml.) and the temperature raised with constant stirring to 150-160°. The typical purple colour of the quinone developed immediately, and after decomposition, the quinone was obtained (90mg.)

Visible bands in trichlorobenzene 595mu.,550mu.

Sulphuric acid colour,blue.

1-phenyl peropyrene XLIV.

Peropyrene (500mg.) was suspended in dry benzene (100ml.), and powdered aluminium chloride (1g.) was added in portions. The mixture was heated on the water bath (1 hr.),the initial strong blue fluorescence changing to blood red. After decomposition in the usual manner,the yellow product (450mg.) was dissolved in xylene,and chromatographed over alumina. Fractions showing the bands at 453mu.,426mu. were collected. Concentration gave the yellow platlets (300mg.) of the phenyl peropyrene. M.p. 310-312°,which sublimed at 300°/0.1mm.

(Found: C,95.16,95.28; H,4.58,4.37 $C_{32}H_{18}$ requires C,95.49; H,4.51%)

Visible bands in xylene 453mu. Spectrum Fig.15. Sulphuric acid colour,blue.

Attempted ring closure of the phenyl peropyrene XLIV.

Phenylperopyrene (100mg.) was added to a melt of aluminium chloride (5g.) and sodium chloride (1g.) at 120°, and the temperature raised to 140° for five minutes. A sample showed that the starting material bands at 453mu. and 423mu. were unchanged. The temperature was then raised to 180-190° for ten minutes,and the mixture decomposed. Sublimation at 320°/0.1mm. gave a mixture which showed a strong band at 444mu,that is of peropyrene, and a weaker one at 453mu. i.e. unchanged phenylperopyrene.

5,6:12,13-Dibenzoperopyrene XLV.

9.10-Dihydro-9:10-dihydroxy-1:4-dimethyl-9,10-Di-o-toluyl. anthracene XLVI.

o-Bromotoluene (0.5M.87.5g.) was added slowly to strips of lithium metal (0.5M.7g.) suspended in dry ether (250ml.) in an atmosphere of nitrogen. The reaction was started by heating the mixture gently,and the ether was kept refluxing,by the addition of more halide. After completion of the reaction (2-3 hrs.),the yellow solution was filtered through a glass wool plug,dry benzene (500ml.) was added and the ether taken off. 1,4 dimethyl anthraquinone (0.125M,30g.) was added as a benzene slurry. The reaction mixture turned brick red as the quinone was added,and after refluxing in an atmosphere of nitrogen (2-3 hr.) it became a dull brown. Decomposition with ice and dilute acetic acid,followed by steam distillation, and extraction with alkaline sodium dithionite (3 times) to remove unreacted quinone,gave the crude diol (35g.) M.p.234-6°. A portion was recrystallised from benzene and gave colourless needles. M.p. 244-6°.

(Found: C,86.03; H,6.43, $C_{30}H_{28}O_2$ requires C,85.68; H, 6.71%). Sulphuric acid colour,brownish-red.

Attempted ring-closure of the diol XLVI.

The diol XLVI (2g.) and copper powder were heated at 400° in carbon dioxide for two hours. An oily red sublimate which had a very weak band at 512mu.was formed. Extraction of the copper powder gave only some oily material with no characteristic absorption.

Attempted oxidation of the diol XLVI.

1.With selenium dioxide.

The diol (3g.) selenium dioxide (12g.) and water (15ml.) were heated under pressure,at 210-20° for 6 hrs. The product was a black solid,insoluble in alkali or any solvent.

2. With dilute nitric acid solution followed by alkaline potassium permanganate solution.

The diol (4.75g.)mixed with nitrobenzene (5ml.) boiled for 48 hrs. with 20% nitric acid (200ml.).After distillation of the nitrobenzene the solid obtained (4g.) was dissolved in dilute sodium hydroxide solution,and powdered potassium permanganate added till its colour persisted for 15 minutes. The filtrate was acidified,and a whiteish acid collected (2g.) A portion was eventually recrystallised from acetic anhydride containing a little nitrobenzene. M.p.250-5°.

(Found:C,64.30;H,3.15 $C_{30}H_{16}O_{08}$ (i.e the fully oxidised diol) requires C,71.43; H,3.20%)

The oxidation had resulted in the loss of carbon atoms,possibly by the rupture of the unsubstituted benzene ring. Attempts to ring-close the crude acid with concentrated sulphuric acid gave no useful result.

1,4-dimethyl-9,10 -di-o-toluyl anthracene XLVII.

The diol XLVI (5g.) was added to a mixture of acetic acid (100ml) and 55% hydrogen iodide (4ml.),and refluxed for 1 hour. The The crude product (4g.) was sublimed,a yellow distillate forming at 180-200°/0.1mm. (3g.). A portion recrystallised from ethanol yielded pale yellow needles.

(Found: C,93.27; H,6.74. $C_{30}H_{26}$ requires C,93.13;6.93%.)

5,6; 12,13-dibenzoperopyrene XLV.

1,4-dimethyl - 9,10-di-o-toluyl anthracene XLVI,(500mg.), was slowly sublimed in an air free carbon dioxide atmosphere, over lumps of 15% palladium charcoal,held at 400. The product was mostly unchanged starting material. When this was removed with benzene,a deposit of the purple dibenzoperopyrene was seen,which was crystallised from methyl napthalene,giving a small amount (2-3mgs.) of long thin green needles. Colour in concentrated sulphuric acid,blue changing to red on standing (lit.) Visible bands in benzene 512mu.,480mu.,452mu. Experiments in which the hydrogen evolved was collected,showed no appreciable amount was given off until the temperature reached at least 400°,and at this temperature the catalyst appears to become quickly deactivated.

Condensation products of anthanthrone XLVIII.

Anthanthrone was reduced by the zinc dust melt method,in the usual manner. After removal of the anthanthrene by sublimation, an increase in temperature to 350-400^{c}/0.1mm. gives the mixture of the green hydrocarbons. This mixture was dissolved in trichlorobenzene and added to a chromatographic column. The column was jacketed by paraffin oil in which a heating coil was immersed. The temperature of the oil was so regulated that the trichlorobenzene issuing from the column was held at 140^{c}. The first fractions contained a mixture of the two hydrocarbons but later ones showed only bands at 648mu. and 598mu. Concentration of these fractions and recrystallisation from trichlorobenzene,followed by sublimation,gave small bluish-green needles,which decomposed at high temperatures without melting.

(Found: C,96.39; H, 3.6 $C_{44}H_{20}$ requires C.96.32; H,3.68%,and $C_{44}H_{18}$ requires C.96.68;H,3.32%)

The absorption spectrum of this hydrocarbon is shown in Fig.17.

Preparation of anthanthrol XLIX.

Anthanthrone (50g.) was powdered together with zinc dust (100g.) and added to pyridine (300-350ml.). The suspension was heated and 2-3ml. of 80% acetic acid added. More dilute acetic acid (10-15ml.) was dropped into the refluxing mixture over 1-2 hours. The dark red solution was decanted into dilute hydrochloric acid. The orange-red precipitate was filtered off and washed with hot water. This material was dried under vacuum and used directly for the condensation.

Condensation of anthanthrol XLIX.

Anthanthrol (20g.)was condensed by heating to 300-50° under carbondioxide. A very dark purple melt was formed which cooled to a glassy solid. This was ground up and heated under vacuum. Anthanthrone sublimed off at 250-300° together with other low molecular weight by-products. The residue (10-15g.) was extracted with trichlorobenzene and the deep purple solutions added,while hot,to the heated chromatographic column. The alumina used was not highly activated (Grade H.) and the temperature was so regulated that the trichlorobenzene issued from the column at 200°. In this way red solutions showing bands at 565mu. and 525mu. were obtained free from any other material. All fractions containing these bands 10 litres) were collected and concentration followed by repeated crystallisation from trichlorobenzene gave small, glittering,brownish-red prisms.(500mg.) M.p.500° (dec.) Colour in sulphuric acid was purple.

(Found: C,91.06;H,3.12 $C_{44}H_{18}O_2$ requires C,91.33; H,3.12% and $C_{44}H_{16}O_2$ requires C,91.64; H,2.8%).

Late fractions from the column showed bands of the other quinone (617mu. 580mu.) but these were always accompanied by bands of the first quinone.

Reduction of the 565mu,525mu.quinone.

The quinone (100mg.) was ground with zinc dust and added to pyridine (100ml.). The mixture was boiled and 80% acetic acid (5ml.) added in portions over three hours. The deep red solution changed almost immediately to clear yellow with an intense green fluorescence. The cooled solution was decanted into hot water and a little hydrochloric acid. After boiling this mixture for some time the resultant dark green hydrocarbon was filtered off and dried (70mg.). The spectrum of this hydrocarbon is shown in Fig.17.(700mu.635mu)

The hydrocarbon was recrystallised from methyl napthalene and gave bluish green crystals. Analysis of these indicated that oxygen must be present and it was concluded that some quinone was formed during the recrystallisation.

Appendix A,Attempted synthesis of Dinapthoazulene I.

1,8-Bis(hydroxymethyl) napthalene LV (54,55).

Reduction of napthalic anhydride was carried out as described in the literature (55).

The crude alcohol recrystallised from acetone as very long colourless needles. M.p. 156-158° (lit.160°).

1,8 Bis -(bromomethyl)napthalene LVII (54).

The alcohol LV (5g.) was suspended in dry benzene (200ml.) and phosphorous tribromide (5g.) added in portions to the gently refluxing mixture. The benzene was decanted and taken off at the water pump,leaving the crude dibromide (5g.) M.p 123-126. Recrystallisation from benzene gave large colourless prisms M.p 129-130° (lit.128-132°).

(Found: C,46.1; H,3.5: Br. 50.6 calculated for $C_{12}H_{10}Br_2$ C,45.9; H,3.2; Br.50.9%)

Yields of the dibromide were higher when ether was used instead of benzene,as described in the literature (54).

1,8-Bis (cyanomethyl)-napthalene LV.

The dibromide LVII (5g.) was dissolved in dry xylene (150ml.) and an~~d~~hydrous cuprous cyanide (5g.),which had been dried at 110 for several hours,was added. This mixture was stirred and refluxed for 10 hours. The xylene solution became dark brown and the cuprous cyanide light brown. The xylene solution was filtered and then concentrated under vacuum to a small volume (10ml). Brownish prisms (650mg.)

crystallised out. Repeated crystallisation and clarification with animal charcoal gave small colourless prisms. M.p.205-208° (Found: C,81.4; H,4.8; N,13.6 $C_{14}H_{10}N_2$ requires C,81.5; H,4.9; N,13.6%).

The infra-red spectrum showed a nitrile peak at 2240cm^{-1}. The yield of the dinitrile could not be improved using this method and alkali media always caused self condensation of the dibromide.

Condensation of the dinitrile LV and acenapthene quinone.

The dinitrile LV (100mg.) and acenapthene quinone (90mg.) were ground very finely together and made into a smooth paste with a little alcohol (5ml.) added. A 50% alcoholic potash solution was added to this mixture at room temperature. An immediate bright blue colour was developed, which persisted for about an hour, gradually fading to a dull green. After allowing the mixture to stand for some time the alkaline solution was filtered into an excess of dilute acid, and a dark violet solid obtained (100mg.) some unreacted dinitrile was recovered (50mg.). The violet solid was insoluble in most organic solvents, but a violet colour develops in 80% acetic acid which showed bands at 578mu,527mu,460mu. The dinapthoazulene has bands at 580mu,544mu,596mu,404mu in 90% acetic acid.

The violet solid was soluble in pyridine or in dimethyl formamide even in the cold. These solutions were deep purple and showed broad absorption bands at 642mu and 586mu. An estimation of the nitrogen content of the violet solid showed that this was much lower than even a diamide derivative would require. All attempts to saponify the violet solid failed. Heating under vacuum with soda-lime gave no result. The condensation was repeated but the alkaline solution was diluted and then boiled after the condensation was completed. The green colour of the condensation mixture faded to a yellow-brown and finally to a dull violet-red. On cooling a dark violet precipitate was formed,which appeared similar to the product described above. The filtered alkaline solution was reddish-green and had a marked red fluorescence. The solution had bands at 636mu. and 592mu. Acidification of this solution gave a little (12mg.)of a red acid. This was ground with some copper powder and heated under vacuum, a trace of red solid was obtained. This dissolved in xylene to give a solution with a band at 513mu. and on shaking this solution acetic acid and hydrochloric acid,a violet-blue colour was formed. This behaviour is similar to that of dinapthoazulene oxide.

Appendix B.

Mixture of 3.6-dibenzoylbenzene -2:5dicarboxylicacid LXII. and 2:6-dibenzoylbenzene -3:5-dicarboxylic acid LXIII.

The method described by Mills and Mills was used (51) Pyromellitic dianhydride (25g.) gave 44g.of the mixture of acids. Attempts to modify the conditions,by using nitrobenzene as solvent were not successful.

1,4-di-(phenyl-hydroxymethyl)-benzene-3,6-dicarboxylic anhydride LXIV.

The mixture of acids LXII,LXIII (15g.) was dissolved in 5% sodium (450ml.) and zinc dust (30g.) was added. The mixture was refluxed until the initial deep red colour faded to a pale yellow (15-20 min.). After cooling the filtered solution was made strongly acid with concentrated hydrochloric acid and boiled for 30 mins.). The resultant dirty white solid was thoroughly ground ,and extracted with dilute sodium carbonate (4-5 times).The insoluble residue was crystalised from glacial acetic acid,until the M.p. remained at over 285°. Repeated crystallisation of these higher melting fractions yielded the colourless plates of LXIV,(3.2g.) M.p. 308-11°.

(Found: C,76.70,76.82; H,4.12,4.09 $C_{22}H_{14}O_4$ requires C,77.18; H,4.12%). Infra-red,lactone peak,1750cm^{-1}.

The carbonate extracts were acidified and the acid put through the same procedure. In this way additional amounts of the lactone were obtained.

1,5-Di-(phenyl-hydroxymethyl)-benzene-3,5-dicarboxylic. anhydride LXV.

The acetic acid mother liquors from the above were collected, and concentrated. After standing a few days a lower melting product crystallised out. Several crystallisations from acetic acid gave the colourless plates of LXV M.p.231-232°. (Found: C,76.45; 77.34; H,4.32,4.40. $C_{22}H_{14}O_4$ requires C,77.18; H,4.12%). Infra-red lactone peak 1760cm.$^{-1}$.

Reaction of 1.4-di-(phenyl-hydroxymethyl)-benzene-3.6-dicarboxylic anhydride with phenyl magnesium bromide.

To a solution of phenyl magnesium bromide in ether, made from bromobenzene (30g.) and activated magnesium (3.5g.) was added a slurry of the higher melting LXIV lactone (2g.) in benzene. The ether was distilled off and the mixture refluxed for 1 hr. The clear brown solution was decomposed with ice and dilute acetic acid, and the product (1.8g.) filtered off. M.p.165-70° (gas evolved, yellow melt formed). The product was insoluble in non-polar organic solvents. The infra-red spectrum showed a strong hydroxyl peak at 3620 cm.$^{-1}$ and no lactone peak. Concentrated sulphuric acid colour was, at first brownish-red then green.

Dehydration of the Grignard reaction product.

1. The product from the Grignard reaction (1g.) was dissolved in the minimum of glacial acetic acid (50ml.) and a few drops of concentrated hydrochloric acid were added. The mixture was refluxed for 15 mins. A pale yellow colour developed with a strong greenish fluorescence. On cooling a pale greenish solid was deposited (450mg.).Recrystallisation from a mixture of benzene and pet.ether (100-120°) gave white rods M.p. 275°. It was sublimed without decomposition at 270°/0.1mm. (Found: C,89.48, 89.23; H,5.78,5.70 $C_{34}H_{22}O_2$ i.e.the expected product LXI requires C,88.29; H,4.79%).
The infra-red spectrum showed no hydroxyl or carbonyl peaks. Concentrated sulphuric acid colour,olive green turning bright green on standing.

2.

Pyrolysis of the Grignard product.

The crude Grignard product was heated under vacuum.At 100° it turned yellow,melting with bubbling at 160-80°,and at 250-280°, a bright yellow glassy sublimate. This was crystallised from pet.ether (100-120°),and gave the whitish rods. M.p.275° as above. Concentrated sulphuric acid colour:as above.

Reaction of the lactide LXIV with o-toluyl magnesium bromide.

O-toluyl magnesium bromide was prepared in ether solution, from o-bromo-toluene (24g.) and activated magnesium (3.5g.) A calculated amount (250ml.) of this solution was added to a suspension of the lactide LVIV (5g.) in benzene (300ml.) The mixture became slightly pink, then light yellow as heat was applied. The ether was taken off, and the reaction mixture refluxed for 1 hr. After cooling the golden-brown solution was decomposed with ice and ammonium chloride, the solution becoming bright yellow. Unreacted lactide (2.5g.) was recovered. The bright yellow solution (spectrum Fig.19) turned deep green on the addition of any strong acid, (spectrum Fig.19). This colour disappeared on addition of water, or alkali. The remainder of the benzene solution was concentrated, and several different products obtained. A yellowish white solid (300mg.) M.p.320-4°, crystallised out first. Further concentration yielded a deeper yellow product (100mg.).M.p.276-280°, and the removal of the rest of the benzene left a sticky orange gum.

Formation of the maleic anhydride adduct LXVIII.

The lower melting yellow solid (200mg.) was immediately dissolved in xylene (10ml.) and a large excess of maleic anhydride (2gm.) added. The mixture was refluxed for 15 mins. and the deep yellow colour of the solution faded rapidly, and fine silky colourless needles (10mg.) were deposited from the hot reaction mixture M.p. 308-12° (dec.)

(Found: C,77.07; H,5.09. $C_{44}H_{30}O_8$ requires C,76.95; H, 4.40%).

This adduct LXVIII was insoluble in organic solvents, but dissolved with difficulty in alkali.

For this reason perhaps the estimations of the equivalent weight were inconsistent.

BIBLIOGRAPHY.

(1) E.Clar, "Aromatische Kohlenwasserstoffe,Polycyclische Systeme",Verlag Springer,1st Edition 1941,2nd.Edition 1952.

(2) J.W.Armit and R. Robinson,J.Chem.Soc.127,1604 (1925).

(3) E.Clar,"Aromatische Kohlenwasserstoffe",Ist.Edition (1941) p.311.

(4) E.Clar and D.G.Stewart,J.Amer.Chem.Soc.75,2667 (1953); 76,3504 (1954).

(5) H.C.Longuet-Higgins, J. Chem. Phys. 18, 265 (1950).

(6) E.Clar,W.Kemp and D.G.Stewart,Tetrahedron 3 ,325 (1958).

(7) C.A.Coulson and H.C.Longuet-Higgins,Proc.Roy.Soc.A192, 16 (1947)

(8) E.Clar,Lang, and Schulz-Kiesow,Chem.Ber.88,1520 (1955)

(9) E.Clar and M.Zander,J.Chem.Soc 1861 (1958);E.Clar and C.T.Ironside,Proc.Chem.Soc.150 (1958);E.Clar,M.Zander and C.T.Ironside,J.Chem.Soc.142 (1959);M.Zander,Chem. Ber. in press (1959).

(10)F.Sondheimer and R.Wolovsky, J.Amer.Chem.Soc. 81 1771 (1959)

(11)D.W.Davies,Tetrahedron Letters,Vol.8,P.4-7 (1959).

(12)E.Clar,Chem.Ber.82,495 (1949); J.Chem.Phys.17,484 (1949)

(13)H.A.Stabbe ,"Einfurung in die Theoretische Organische Chemie", Verlag-Chemie,Weinheim/Bergster 1959 pp.353-361.

(14)H.B.Klevens and I.R.Platt,J.Chem.Phys.17,470,(1949); I.R.Platt,J.Chem.Phys.17,484.(1949)

(15)W.Moffit,J.Chem.Phys.22,320 (1954)

(16) D.S.McClure,J.Chem. Phys.22,1256 (1954).

(17) E.Clar,Spectrochimica Acta 4, 116 (1950).

(18) D.P.Craig,Revs. Pure and Applied Chem.(Australia) 3,207 (1953).
N.D.Coggeshall and A.Pozefsky,J.Chem.Phys.19,980,(1951);
G.M.Badger and R.S.Pearce,Spectrochimica Acta.4,280 (1951)

(19) E.Clar,Tetrahedron,5 , 98 (1958).

(20) E.Clar,Tetrahedron 6, 355 (1959).

(21) E.Clar,C.T.Ironside and M.Zander,Tetrahedron,6,358 (1959)

(22) H.Akamatu and Y.Matsunaga,Bull.Chem.Soc.Japan,29,800 (1956)

(23) E.Clar,IV Meeting on Molecular Spectroscopy,Bologna, Italy,(1959).

(24) G.N.Lewis and M.Kasha,J.Amer.Chem.Soc. 66,2100 (1944);
M.Kasha,Chem.Revs.41, 401 (1947).

(25) G.N.Lewis and M.Calvin,J.Amer.Chem.Soc.67,1232 (1945).

(26) E.Clar and M.Zander,Chem.Ber.89,749 (1956).

(27) E.Clar,Ber.Dtsch.Ges.76,611 (1943).

(28) E.Clar,"Aromatische Kohlenwasserstoffe",P.393 (1952).

(29) W.Kemp,Ph.D. Thesis Glasgow University (1956) p.63

(30) J.W.Cook,J.Chem.Soc. 487 (1931);1472 (1932); 499 (1931);
and F.R.John,Ber.Dtsch.Chem.Ges. 64,981 (1931);
E.Clar,Ber.Dtsch.Chem.Ges. 73,81 (1940).

(31) E.Clar,Chem.Ber.81, 520 (1948).

(32) M.P.Groenwege,Colloquium Spectroscopium Internationale VI,(Amsterdam) (1956).Pergamon Press Ltd,London P.579.

(33) M.Zander,Chem.Ber. in-press (1959).

(34) E.Clar "Aromatische Kohlenwasserstoffe pp.267-270.

(35) I.G.Farbeinindustrie A.G.D.R.P.591496 (1932);
E.Clar,Ber.Dtsch.Ges. 69,1686 (1936).

(36) E.Clar, and M.Zander, J.Chem.Soc. 4616 (1957).

(37) E.Clar and M.Zander,J.Chem Soc.,577 (1958).

(38) Padova,Compt.Rend. 148,291 (1909)

(39) E.Clar and W.Willicks,Chem.Ber. 89,743 (1956)

(40) E.Clar and D.G.Stewart,J.Amer.Soc. 74,6235 (1952).

(41) E.Clar,Chem.Ber. 76,458 (1943)

(42) B.A.D.,D.R.P. 283066 (1913)

(43) Scholl and Meyer,Ber.Chem.Dtsch.Ges. 65,902 (1932); Scholl,Meyer and Winkler,Annalen 494,201 (1932).

(44) E.Clar and J.R.Holker,J.Chem.Soc. 3259 (1951).

(45) E.Clar,private communication published in outline in "Aromatische Kohlenwasserstoffe" 2nd.Edition,p387 et.seq; D.G.Stewart,Ph.D.Thesis,p.41 et seq. Glasgow University (1953).

(46) W.Kemp,Ph.D.Thesis,Glasgow University (1956) p.36 et seq.

(47) Moureu,Chovin and Pivod,Compt.Rend. 223,951 (1946); Bull.Soc.Chim. 13, 106 (1946).

(48) G.Glilardi and G.Kalopissis,Bull.Soc.Chim,217 (1952).

(49) Guyot and Catel,Bull.Soc.Chim. 35,1124 (1906); Compt. Rend.,140,1349 (1905).

(50) L.Pauling,'The Nature of the Chemical Bond' 2nd Edition, (1950) p.146.

(51) Mills and Mills, J.Chem.Soc. 2194 (1912).

(52) M.Newman and Zahn, J.Amer.Chem.Soc.,65,1099 (1943).

(53) Ling, J.Chem.Soc. 61, 558 (1892)

(54) G.Glilardi and G.Kalopissis,Bull.Soc.Chim.,217,(1952)

(55) R.Beyler,and L.Sarett,J.Amer. Chem.Soc. 74,1406 (1952).

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by

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