THE SYNTHESIS and STUDY
of
POLYCYCLIC AROMATIC HYDROCARBONS.

THESIS

presented by

Bruce Anson McAndrew, B.Sc. (Glasgow)

for the degree of

DOCTOR OF PHILOSOPHY

of the

University of Glasgow.

May, 1967.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

SUMMARY

The work in this thesis can readily be divided into two parts, the former concerned with the syntheses and absorption spectra of polycyclic aromatic hydrocarbons, and the latter dealing with their NMR spectra.

Naphtho-(2'.3':1.2)-pentacene (I) has been synthesised to complete the annellation series, anthracene, 1.2-benzotetracene, naphtho-(2'.3':1.2)-pentacene. This compound exhibits the typical properties of a pentacene, being readily photo-oxidised and undergoing maleic anhydride addition very readily.

2-Phenyltetracene (II), 2.8-diphenyltetracene (III), 2-phenylpentacene (IV), 2.9-diphenylpentacene (V), and 9-phenyltetraphene (VI) have all been characterised with the exception of (III) which defied synthesis, although a number of possible routes have been investigated. Since β-phenyl and β,β'-diphenyl substituted naphthalenes and anthracenes exhibit an exocyclic quartet of electrons, (II) - (V), the appropriate compounds in the tetracene and pentacene series might also be expected to display this phenomenon. However,

a careful examination of the positions of the absorption maxima suggests that the quartet of electrons has not been formed. (VI) has been synthesised so that a molecule, capable of forming both an induced sextet and an exocyclic quartet, could be investigated. The shifts of the β-bands indicate that both types of interaction exist.

2.3,4.5,8.9,10.11-Tetrabenzoperylene (VII) has been made as an intermediate in the synthesis of 1.2,3.4,7.8,9.10-tetrabenzocoronene (VIII). (VII) is an important hydrocarbon in its own right, and shows some interesting and instructive differences in its reactivity with maleic anhydride when compared with other benzo- and naphthoperylenes. Like its parent compound, perylene, (VII) exists in monomer and dimer crystals, whose colour is slightly different. By twin-fold addition of maleic anhydride, followed by decarboxylation, the coronene homologue (VIII) can be synthesised from (VII); this represents the first unambiguous synthesis of 1.2,3.4,7.8,9.10-tetrabenzocoronene (VIII). A photochemical route to this hydrocarbon has also been investigated: it failed to give positive results.

In studying the UV-spectra of a large number of higher annellated pyrenes, certain anomolous peaks appeared in some of the spectra, apparently belonging to the 3.4-

benzophenanthrene skeleton. To try and gain further information on this problem, 5.6-benzopicene (IX) has been synthesised. In this compound, either the benzophenanthrene or picene moieties could cause the principal absorption maxima; a study of the UV-spectrum of (IX) however, failed to give any unambiguous results. Naphtho-(3'.1':1.14); (3''.1'':4.5);(1'''.3''':7.8);(3''''.1'''':11.12)-pentacene (X), a kind of twin tribenzopyrene, has been synthesised and its UV-spectrum studied with regard to the problems outlined in this paragraph.

The recent work of Buu-Hoi in proving that 1.2,3.4-dibenzopyrene (XI) is, in actual fact, a dibenzofluoranthene has led us to attempt a new synthesis of dibenzopyrene (XI). The desired compound has not been made, and instead a yellow hydrocarbon has been obtained, to which has been assigned an isomeric dibenzofluoranthene structure on UV and mass spectral evidence.

Turning now to the second half of the thesis, the NMR spectra of a large number of polycyclic aromatic hydrocarbons and related compounds have been studied. Methyl derivatives of phenanthrene and pyrene were considered first; methyl substitution in the 9-position in phenanthrene and in the 1- and 6-positions in pyrene caused doublets indicating the high double bond character of these positions. Elsewhere the methyl signal appeared as a singlet, so confirming the benzenoid character of these rings. Further work on methyl derivatives of chrysene, picene, benzophenanthrene and related hydrocarbons has led to more complicated results which for the most part can be explained by the strict application of Robinson's Sextet.

A comprehensive study of the position of particular protons in the NMR spectra of higher annellated pyrenes has yielded results which cannot be correlated with simple ring current theory. To explain these results, a limitation of the conjugation present in these hydrocarbons has been proposed, a concept which receives considerable support from absorption spectroscopy studies.

Finally, the NMR spectra of some twenty compounds related to pyrene have been analysed by 1st order techniques. From the experience thus gained, a new interpretation of the NMR spectrum of pyrene itself has been made; a number of suitably alkylated pyrenes have been examined in an attempt to gain support for this interpretation. In addition, a considerable amount of relatively straightforward synthetic chemistry has been carried out to obtain the necessary hydrocarbons for spectroscopic examination.

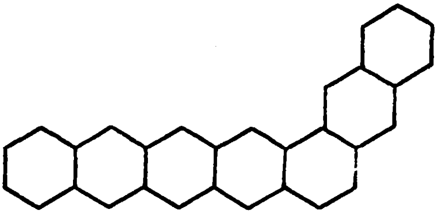
ACKNOWLEDGEMENTS.

I am delighted to have this opportunity to express my appreciation to Professor E. Clar for his guidance throughout the course of this work - his encouragement and enthusiasm have been unfailing.

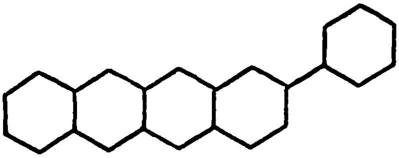
I would like to thank, too, the Scientific Research Council for a subsistence allowance for the last three years. The micro-analyses, and infra-red, NMR and mass spectra have been carried out by the staffs of these laboratories in this Department - I am indebted to them all.

Finally Mr. P.H. McCabe was associated with me in the work described in Chapter 2, and Mr. J. Brown and Mlle. H. Walthert carried out many of the literature preparations required for Chapters 6 and 8; I gratefully acknowledge their industry.

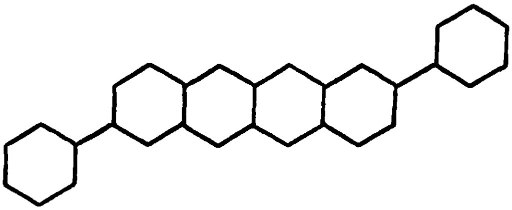
CONTENTS.



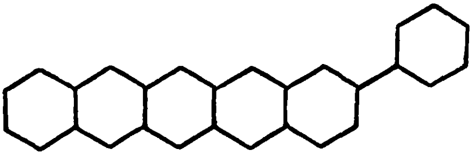
I



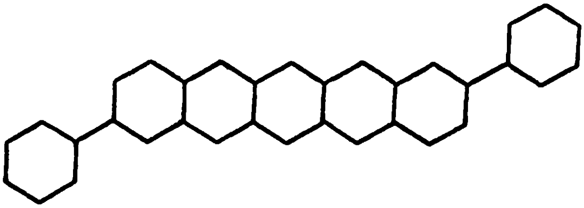
II



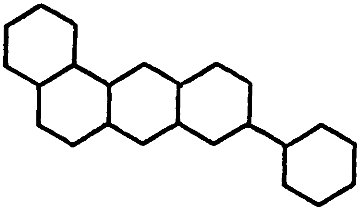
III



IV



V



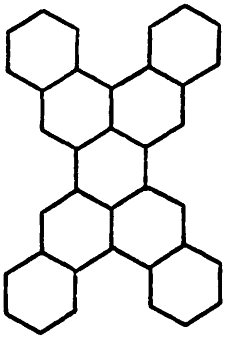
VI

SUMMARY

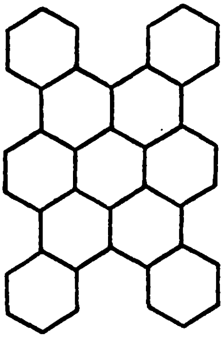
The work in this thesis can readily be divided into two parts, the former concerned with the syntheses and absorption spectra of polycyclic aromatic hydrocarbons, and the latter dealing with their NMR spectra.

Naphtho-(2'.3':1.2)-pentacene (I) has been synthesised to complete the annellation series, anthracene, 1.2-benzotetracene, naphtho-(2'.3':1.2)-pentacene. This compound exhibits the typical properties of a pentacene, being readily photo-oxidised and undergoing maleic anhydride addition very readily.

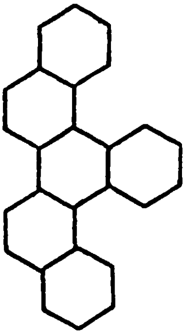
2-Phenyltetracene (II), 2.8-diphenyltetracene (III), 2-phenylpentacene (IV), 2.9-diphenylpentacene (V), and 9-phenyltetraphene (VI) have all been characterised with the exception of (III) which defied synthesis, although a number of possible routes have been investigated. Since β-phenyl and β,β'-diphenyl substituted naphthalenes and anthracenes exhibit an exocyclic quartet of electrons, (II) - (V), the appropriate compounds in the tetracene and pentacene series might also be expected to display this phenomenon. However,



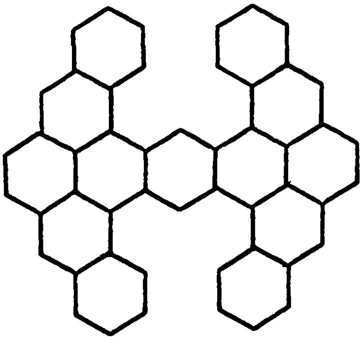
VII



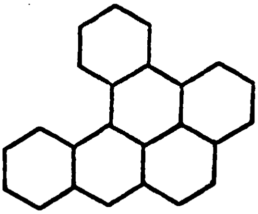
VIII



IX



X



XI

a careful examination of the positions of the absorption maxima suggests that the quartet of electrons has not been formed. (VI) has been synthesised so that a molecule, capable of forming both an induced sextet and an exocyclic quartet, could be investigated. The shifts of the β-bands indicate that both types of interaction exist.

2.3,4.5,8.9,10.11-Tetrabenzoperylene (VII) has been made as an intermediate in the synthesis of 1.2,3.4, 7.8,9.10-tetrabenzocoronene (VIII). (VII) is an important hydrocarbon in its own right, and shows some interesting and instructive differences in its reactivity with maleic anhydride when compared with other benzo- and naphtho-perylenes. Like its parent compound, perylene, (VII) exists in monomer and dimer crystals, whose colour is slightly different. By twin-fold addition of maleic anhydride, followed by decarboxylation, the coronene homologue (VIII) can be synthesised from (VII); this represents the first unambiguous synthesis of 1.2,3.4,7.8,9.10-tetrabenzocoronene (VIII). A photochemical route to this hydrocarbon has also been investigated: it failed to give positive results.

In studying the UV-spectra of a large number of higher annellated pyrenes, certain anomolous peaks appeared in some of the spectra, apparently belonging to the 3.4-

benzophenanthrene skeleton. To try and gain further information on this problem, 5.6-benzopicene (IX) has been synthesised. In this compound, either the benzophenanthrene or picene moieties could cause the principal absorption maxima; a study of the UV-spectrum of (IX) however, failed to give any unambiguous results. Naphtho-(3'.1':1.14); (3''.1'':4.5);(1'''.3''':7.8);(3''''.1'''':11.12)-pentacene (X), a kind of twin tribenzopyrene, has been synthesised and its UV-spectrum studied with regard to the problems outlined in this paragraph.

The recent work of Buu-Hoi in proving that 1.2,3.4-dibenzopyrene (XI) is, in actual fact, a dibenzofluoranthene has led us to attempt a new synthesis of dibenzopyrene (XI). The desired compound has not been made, and instead a yellow hydrocarbon has been obtained, to which has been assigned an isomeric dibenzofluoranthene structure on UV and mass spectral evidence.

Turning now to the second half of the thesis, the NMR spectra of a large number of polycyclic aromatic hydrocarbons and related compounds have been studied. Methyl derivatives of phenanthrene and pyrene were considered first; methyl substitution in the 9-position in phenanthrene and in the 1- and 6-positions in pyrene caused doublets indicating

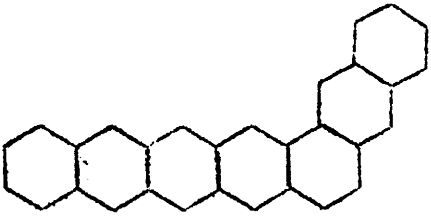
the high double bond character of these positions. Elsewhere the methyl signal appeared as a singlet, so confirming the benzenoid character of these rings. Further work on methyl derivatives of chrysene, picene, benzophenanthrene and related hydrocarbons has led to more complicated results which for the most part can be explained by the strict application of Robinson's Sextet.

A comprehensive study of the position of particular protons in the NMR spectra of higher annellated pyrenes has yielded results which cannot be correlated with simple ring current theory. To explain these results, a limitation of the conjugation present in these hydrocarbons has been proposed, a concept which receives considerable support from absorption spectroscopy studies.

Finally, the NMR spectra of some twenty compounds related to pyrene have been analysed by 1st order techniques. From the experience thus gained, a new interpretation of the NMR spectrum of pyrene itself has been made; a number of suitably alkylated pyrenes have been examined in an attempt to gain support for this interpretation. In addition, a considerable amount of relatively straightforward synthetic chemistry has been carried out to obtain the necessary hydrocarbons for spectroscopic examination.

CHAPTER 1.

NAPHTHO-(2'.3':1.2)-PENTACENE



I

INTRODUCTION:

The hydrocarbon naphtho-(2'.3':1.2)-pentacene (I) has been synthesised and its ultra-violet spectrum compared with that of other members of the phene group, in particular with those of anthracene (IV) and 1,2-benzotetracene (XIII) with which naphtho-(2'.3':1.2)-pentacene (I) forms an annellation series.

DISCUSSION:

Before considering in detail the absorption spectra of naphtho-(2'.3':1.2)-pentacene (I) and related compounds, a very brief account of the classification of the bands in the ultra-violet spectra of polycyclic aromatic compounds seems appropriate.

The earliest classification[1] of the spectra of aromatic hydrocarbons divided the bands into three different types - R bands ($\log \varepsilon < 2$), B bands (benzenoid bands) ($2{\cdot}4 < \log \varepsilon < 3{\cdot}5$), and K bands ($\log \varepsilon > 4$). Polycyclic aromatic compounds were considered to exhibit only B and K bands. This distribution was based on the examination of a limited number of hydrocarbons and never gained complete acceptance in the field of polycyclics.

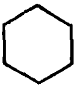
A much improved classification, which took into consideration a much larger number of compounds was introduced by Clar in 1936.[2] It was pointed out by him that there were three main band systems divided into α-bands ($\log \varepsilon = 2$-3), p-bands ($\log \varepsilon \simeq 4$), and β-bands ($\log \varepsilon = 4$-$6$). As well as their characteristic intensities, their shifts on changing phase and their polarisations parallel or perpendicular to the molecular axes were all taken into account in this classification. To emphasise even further the success of this method, it was shown that the existence of an empirical relationship between the position of the absorption maximum of lowest frequency (ν) in either the p- or β-bands would fit an equation of the type

$$\sqrt{\frac{R}{\nu}} = n$$

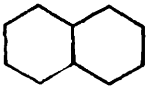
where R is an numerical constant and n is an integer. From this simple relationship an 'Annellation Principle' was built up which allowed the accurate prediction of the bands of an unknown polycyclic aromatic hydrocarbon.

A further classification has since been introduced by Platt;[3] one which is based on the mathematical free-electron theory of conjugated systems and identifies a band as being polarised in a particular direction with respect to the molecular axis. In hydrocarbons of the acene series, the two classifications give identical results. In angular and condensed hydrocarbons, the two concepts diverge strongly on the direction of polarisation of certain bands, and it appears that the annellation concept gives the correct result.[4]

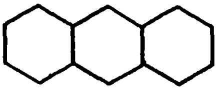
Turning now from the general background to our particular problem, let us look first of all at the linear acene series which has been studied in the greatest detail. Although an immediate difficulty is apparent in the loss of



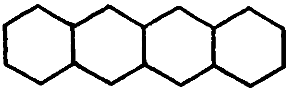
II



III

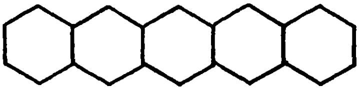


IV

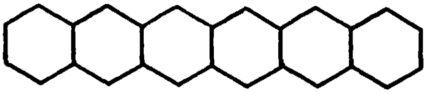


V

λ_β	1852		2210		2515		2740	Å
$\sqrt{\lambda_\beta}$	43·04	$\xrightarrow{3\cdot97}$	47·01	$\xrightarrow{3\cdot15}$	50·16	$\xrightarrow{2\cdot19}$	52·35	√Å
λ_p	2038		2850		3745		4710	Å
$\sqrt{\lambda_p}$	45·14	$\xrightarrow{8\cdot24}$	53·38	$\xrightarrow{7\cdot82}$	61·20	$\xrightarrow{7\cdot43}$	68·63	√Å

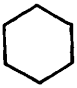


VI

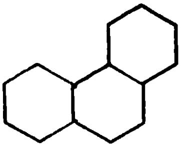


VII

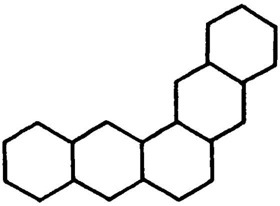
λ_β		3030		-	Å
$\sqrt{\lambda_\beta}$	$\xrightarrow{2\cdot70}$	55·05		-	√Å
λ_p		5820		6930	Å
$\sqrt{\lambda_p}$	$\xrightarrow{7\cdot67}$	76·30	$\xrightarrow{6\cdot96}$	83·26	√Å



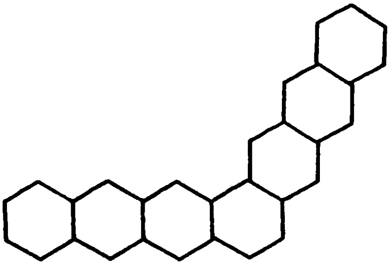
II



VIII



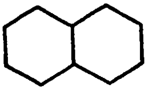
IX



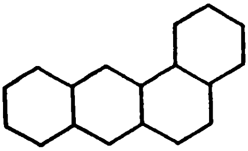
X

λ_β 1852 2510 3145 3910 Å

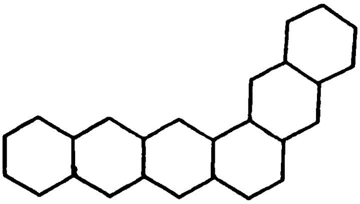
$\sqrt{\lambda_\beta}$ 43·04 $\xrightarrow{7\cdot06}$ 50·10 $\xrightarrow{5\cdot98}$ 56·08 $\xrightarrow{6\cdot45}$ 62·53 $\sqrt{\text{Å}}$



III



XI



XII

λ_β 2210 2900 3580 Å

$\sqrt{\lambda_\beta}$ 47·01 $\xrightarrow{6\cdot85}$ 53·86 $\xrightarrow{5\cdot98}$ 59·84 $\sqrt{\text{Å}}$

the α-bands in certain members of this series, consideration of the other bands gives an extensive amount of information. The most important relationship, which applies to both β- and p-bands is that the red shift for each ring annellation (II - VII) is approximately constant in units of $\sqrt{\text{Å}}$ which is a scale for reciprocal nuclear charges (i.e. the π-electrons which come into the system to counteract nuclear attraction)[5]. Such a stringent rule is found to be applicable to the α- and β-bands of the phene series. Here again the α-band is sometimes hidden, permitting us to look at only the β-bands; consideration of their values shows that the shift difference in $\sqrt{\text{Å}}$ is very approximately constant. In addition, a number of other conclusions can be drawn by carefully looking at the entire absorption spectrum or particular parts of it.

When angular rings are fused on to a benzene nucleus (II → VIII → IX → X), the entire absorption spectrum shifts in a regular fashion to longer wavelengths (figure 1). In a similar way, a second phene series, beginning with naphthalene (III → XI → XII) shows an identical pattern (figure 2). In both cases all three types of bands show hyperchromic shifts as we annellate rings. In the new series (IV → XIII → I) (figure 3) we should expect and indeed find the same results. The characteristic bathochromic

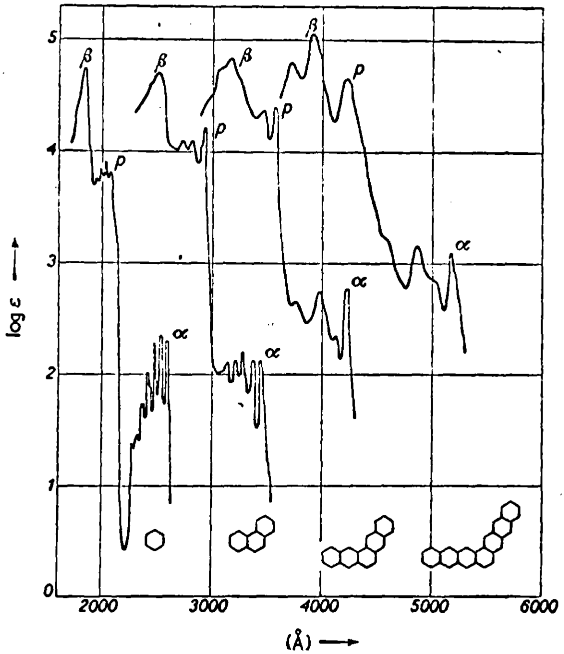


Figure 1

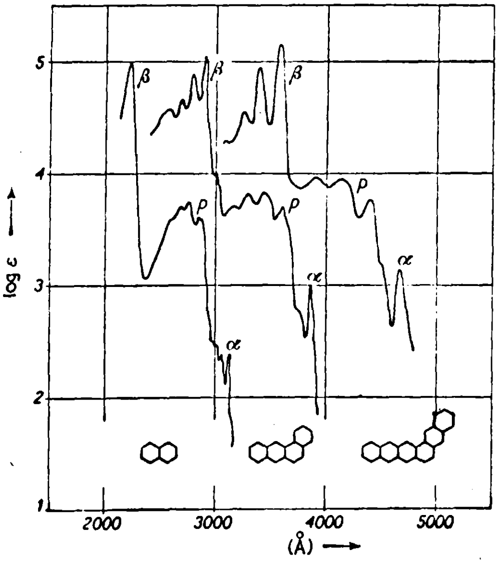
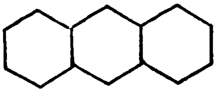
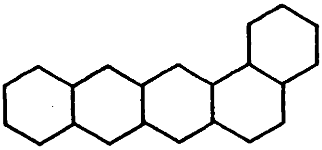


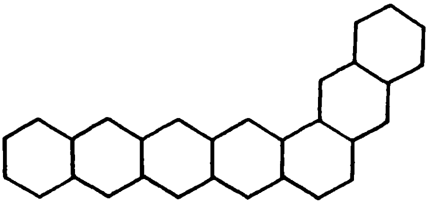
Figure 2



IV

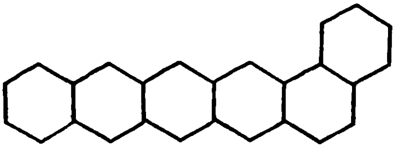


XIII



I

	IV		XIII		I
λ_β	2515		3190		3815 Å
$\sqrt{\lambda_\beta}$	50·16	$\xrightarrow{6\cdot 33}$	56·49	$\xrightarrow{5\cdot 28}$	61·77 √Å



XIV

λ_β = 3480 Å

shifts of the bands can readily be appreciated, and it is particularly noticeable how the vibrational fine structure of the p-band produces five sharp peaks in the spectrum of all three hydrocarbons (IV, XIII, I).

Furthermore, it has been pointed out that hydrocarbons in the acene and phene series with the same number of rings exhibit β-bands at approximately the same wavelength.[5] In hydrocarbons with six rings 1.2-benzopentacene (XIV), λ_β= 3480 Å, and hexaphene (XII), λ_β = 3580 Å, exhibit this property. Until the present work was undertaken, heptaphene (X), λ_β = 3910 Å was the only known member of the next higher series; naphtho-(2'.3':1.2)-pentacene (I), λ_β = 3815 Å, obviously allows us to extend this relationship to hydrocarbons with seven fused rings. In addition to the position, the shape of the β-bands is also quite characteristic.[5] In the acene series, there appears one sharp band, which broadens somewhat in the phene series. In the more strongly asymmetric phenes, like hexaphene (XII) and heptaphene (X), the β-band splits into two or more bands; the four β-bands in naphtho-(2'.3':1.2)-pentacene (I) are therefore indicative of a strongly asymmetric member of this series.

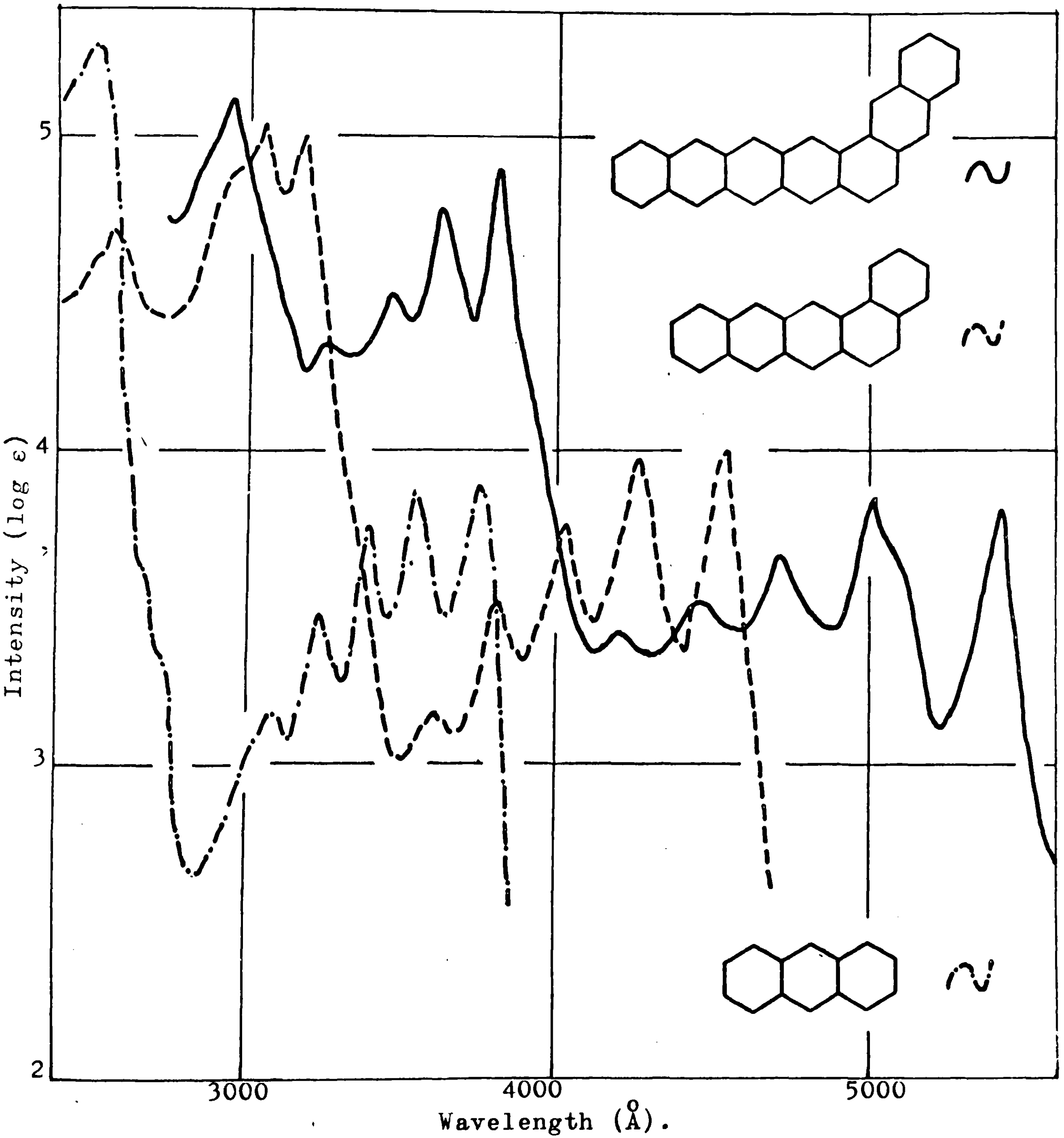
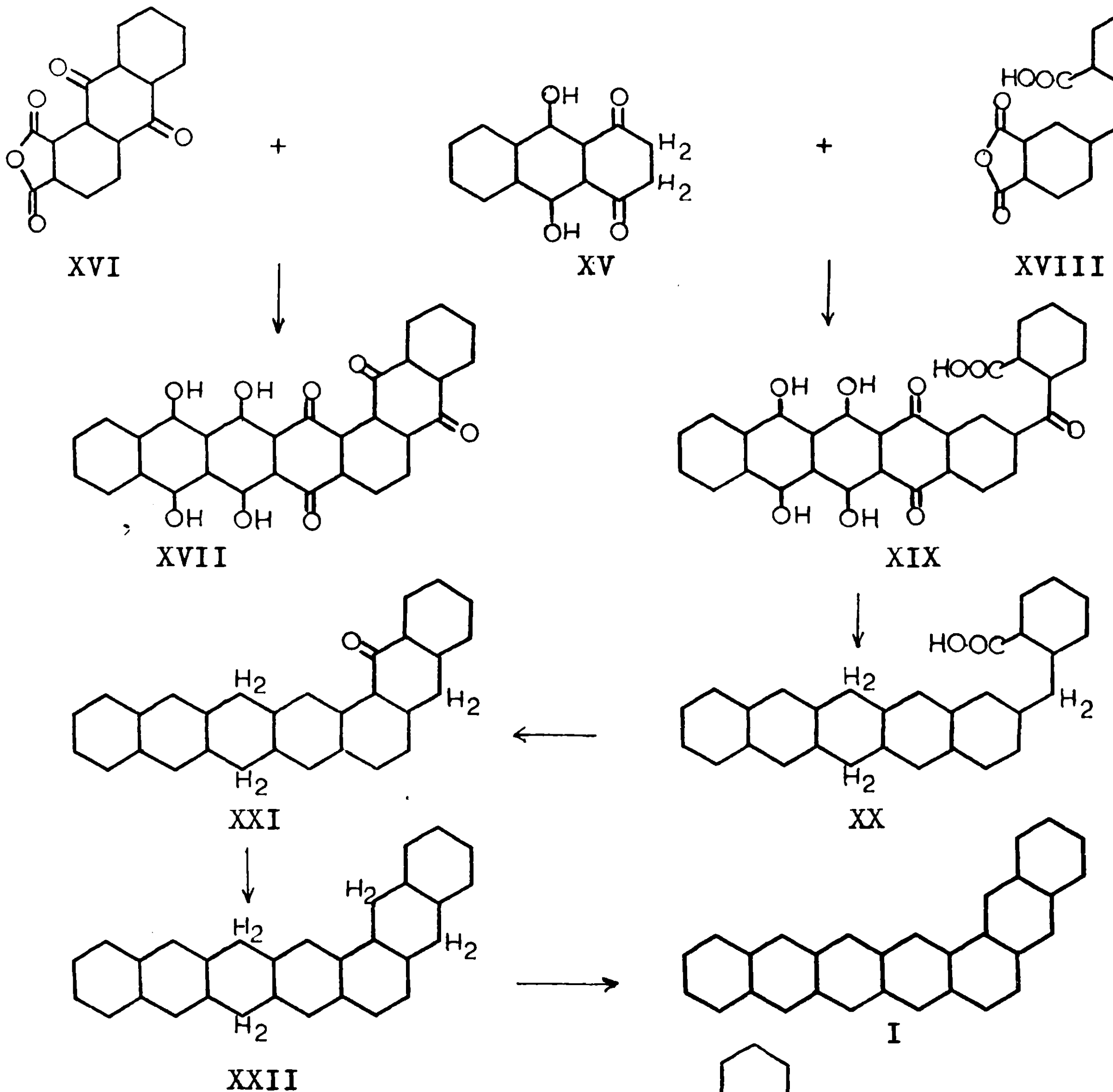
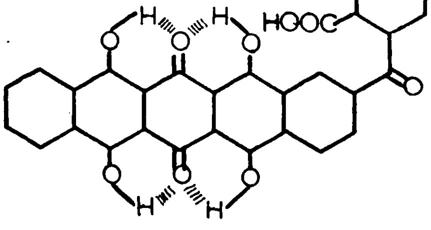


Figure 3. Absorption maxima (Å) and log ε (in parentheses).
Anthracene in alcohol: p, 3745 (3·87), 3545 (3·86), 3380 (3·75), 3230 (3·47), 3080 (3·15); β, 2515 (5·29).
1.2-Benzotetracene in benzene: p, 4525 (4·00), 4250 (3·97), 4010 (3·80), 3800 (3·50), 3620 (3·16); β, 3190 (4·98), 3060 (5·01); in ethanol, β', 2580 (4·72).
Naphtho-(2'.3':1.2)-pentacene in benzene: p, 5420 (3·80), 5025 (3·83), 4705 (3·67), 4450 (3·51), 4215 (3·41); β, 3815 (4·89), 3630 (4·77), 3460 (3·50), 3260 (4·34); β', 2945 (5·11).



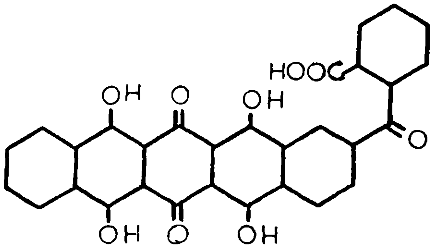


XIXa

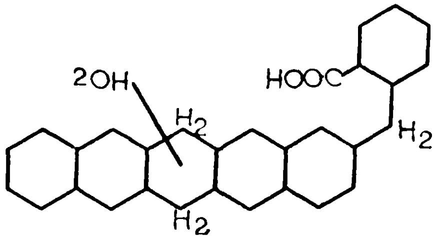
An interesting and inexplicable difference between our new series (IV → XIII → I) and previous phene series is that we do not find increased intensities of the bands as we progress through the members of a group. Finally, a comment may be made regarding the α-bands. They exhibit considerable alternating character depending on whether or not we have a symmetric or non-symmetric arrangement of the rings.[5] Since the α-bands in this series are hidden by the stronger p-bands, we can regretably draw no conclusions as regards their character.

EXPERIMENTAL DISCUSSION.

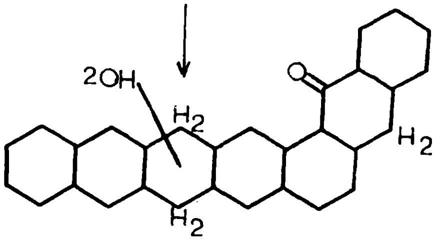
A literature search revealed that the seven-ring system of naphtho-(2'.3':1.2)-pentacene had been synthesised only once before, by Marschalk,[6] who condensed leucoquinizarin (XV)[7] with anthraquinone-1.2-dicarboxylic acid anhydride (XVI) to yield the tetrahydroxydiquinone (XVII). Since the details of the preparation of the anhydride (XVI)[8] were not given, it was decided to approach the synthesis somewhat differently.



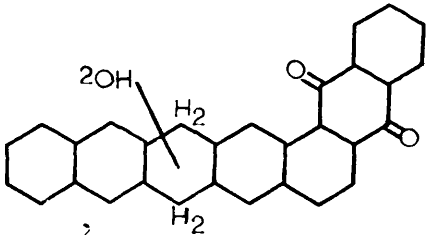
XIXa



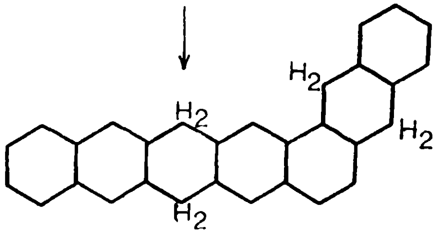
XXIII



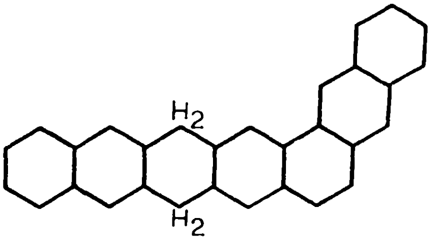
XXIV



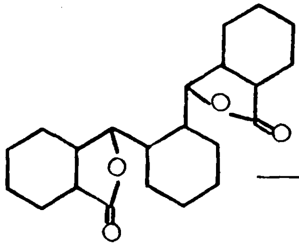
XXV



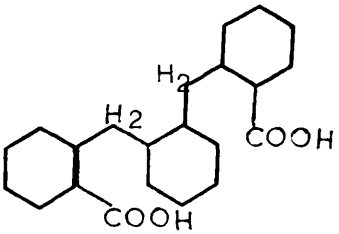
XXII



XXVI

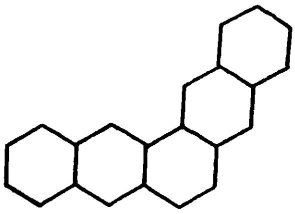


XXVII

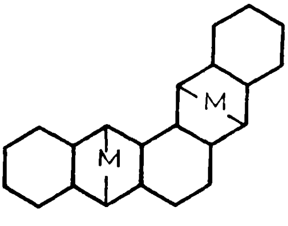


\+

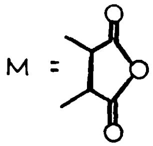
XXVIII

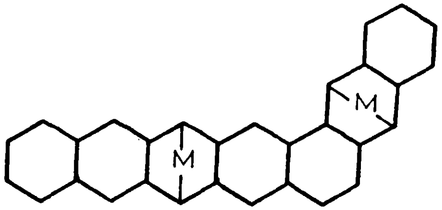


XXIX



XXX





XXXI

The proposed route was to condense leucoquinizarin (XV) with the anhydride (XVIII)[9] to yield the acid (XIX). Reduction would lead to the o-carboxybenzyl-dihydropentacene (XX) which was to be cyclised to the anthrone (XXI). Further reduction to the tetrahydro derivative (XXII), followed by dehydrogenation would then yield the desired naphtho-(2'.3':1.2)-pentacene (I).

Leucoquinizarin (XV), for which an improved method of preparation is given in the experimental section readily condensed with benzophenone-2'.3.4-tricarboxylic acid-3.4-anhydride (XVIII)[9] in the presence of aluminium chloride to yield the extremely stable and highly insoluble acid (XIX), which probably exists in the form (XIXa) where the maximum amount of hydrogen bonding between hydroxyl and carbonyl groups is possible.[10] Reduction of this compound, however, did not lead to the desired o-carboxybenzyl-dihydropentacene (XX) but to a dihydroxy analogue of it (XXIII) in which the positions of the hydroxyl groups are unknown. There does not appear to be any way in which information regarding their position can be gained. Cyclisation with phosphorus oxychloride yielded the corresponding dihydroxyanthrone (XXIV) which, it was suspected, was oxidised to the corresponding quinone (XXV) on attempted crystallisation from nitrobenzene. On reduction by the zinc dust/pyridine/acetic acid method, (XXV) yielded small amounts of a pale yellow compound, which was later shown, by melting point and ultraviolet spectrum to be tetrahydronaphtho-(2'.3':1.2)-pentacene (XXII).

This synthetic route left much to be desired: it involved a dihydroxy acid (XXIII) with hydroxyl groups in unknown positions, and it was impossible to find a suitable solvent for the anthrone (XXIV) which did not oxidise it during crystallisation so preventing complete characterisation. Due to this, it was decided to abandon the route, and to reduce the readily obtainable acid (XIX) by an alternative method. In the red phosphorus/hydriodic acid reduction[11] of o-di-(3-phthalidyl)-benzene (XXVII), as well as the expected 1,2-di-(o-carboxybenzyl)-benzene (XXVIII), small amounts of pentaphene (XXIX) were produced by reductive cyclisation. Treatment of our acid (XIX) with the same reagents might then be expected to yield naphtho-(2'.3':1.2)-pentacene (I) or a hydrogenated derivative of it.

When an intimate mixture of acid (XIX), red phosphorus, and hydriodic acid were heated in a sealed tube for three days at 240° and the xylene extract chromatographed on Grade I Alumina, a small amount of pale yellow hydrocarbon was obtained. The most likely structure for this material is 1'.4'.6.13-tetrahydronaphtho-(2'.3':1.2)-pentacene (XXII); a satisfactory analysis and an ultra-violet spectrum, which was indicative of a tetrasubstituted naphthalene,[12] were obtained (figure 4). The absorption maxima at values greater than 350 mμ would not be expected of a naphthalenic compound, and are probably due to small amounts of 6.13-dihydronaphtho-(2'.3':1.2)-pentacene (XXVI) in which the principal chromophore would be the tetraphene nucleus.

Attempted dehydrogenation of the tetrahydronaphthopentacene (XXII) with phenanthroquinone in boiling nitrobenzene was completely unsuccessful; this is further proof for the tetrahydro (XXII) structure as distinct from the dihydro (XXVI) structure, since this reagent apparently only dehydrogenates dihydro compounds to the parent hydrocarbons.[13] Equally unsuccessful was the use of chloranil in boiling xylene. Nevertheless, a poor yield of dehydrogenated material could be obtained by sublimation of (XXII) over copper powder, naphtho-(2'.3':1.2)-pentacene (I) subliming as beautiful rose-pink pyramids.

Lack of material prevented the parent hydrocarbon being studied in great detail. Its purple solution in trichlorobenzene was rapidly decolourised on standing,

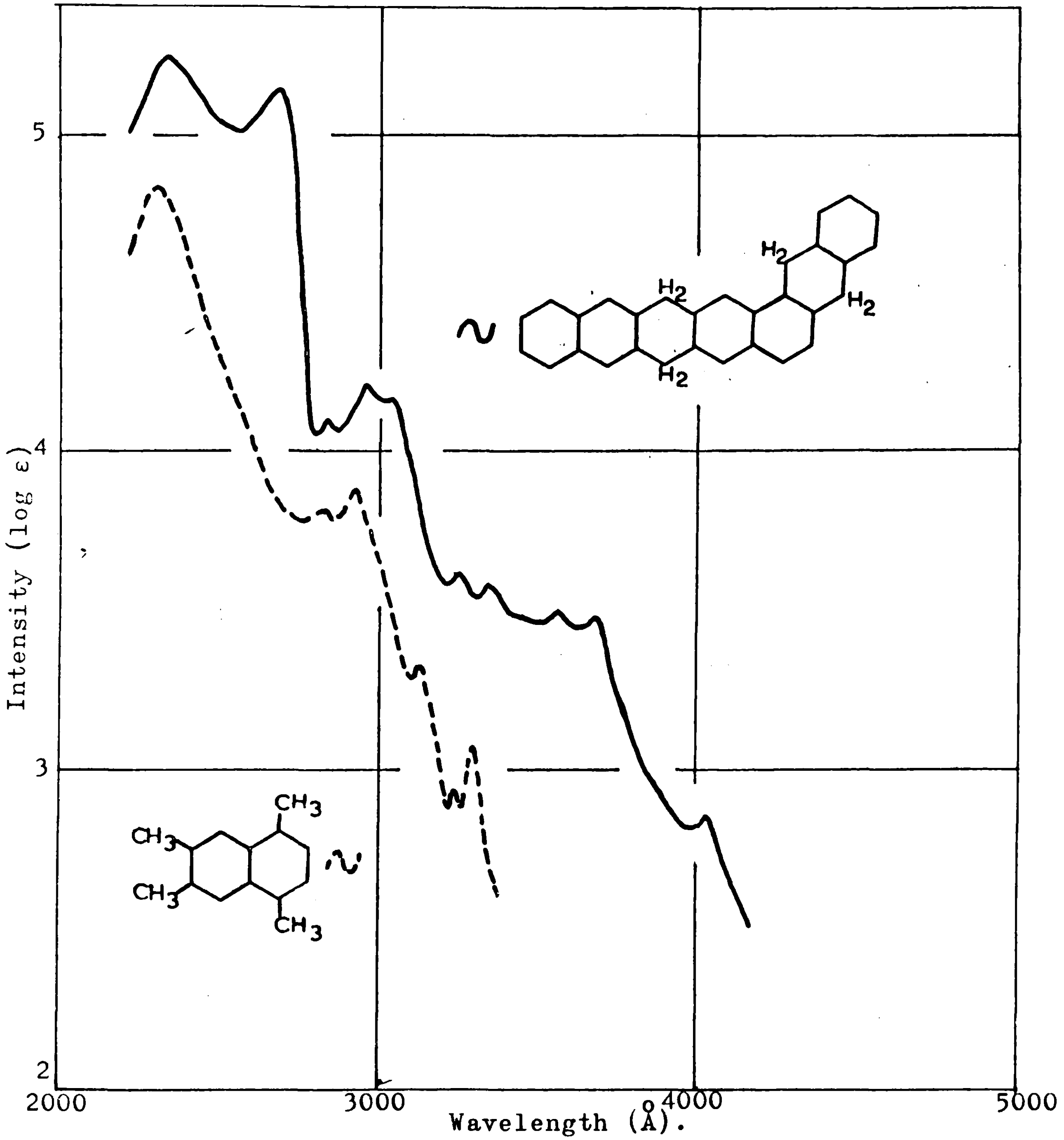


Figure 4. Absorption maxima (Å) and $\log \varepsilon$ (in parentheses).
1.4.6.7-Tetramethylnaphthalene in methanol: α, 3300 (3·09), 3240 (2·92), 3130 (3·32); p, 2920 (3·87), 2840 (3·80); β, 2330 (4·85).
1'.4'.6.13-Tetrahydronaphtho-(2'.3':1.2)-pentacene in ethanol: α, 4030 (2·83), 3680 (3·45), 3565 (3·48), 3340 (3·57), 3250 (3·60); p, 3050 (4·16), 2945 (4·20), 2835 (4·08); β, 2695 (5·15), 2420 (5·29).

presumably with the formation of a photo-oxide.[14] Further, on the addition of (I) to molten maleic anhydride, it dissolved within seconds to give a pale yellow solution. Since pentaphene (XXIX) gave a double adduct (XXX) with maleic anhydride,[15] it can be assumed that naphtho-(2'.3':1.2)-pentacene (I) would give the corresponding di-adduct (XXXI).

EXPERIMENTAL

Leucoquinizarin (XV).

To a boiling solution of sodium carbonate (16 g.) in water (1500 ml.) was added finely ground quinizarin (12 g.); the mixture was vigorously stirred until all the quinizarin had dissolved. To the resulting deep violet solution was added sodium dithionite (4 x 5 g.) until all the leucoquinizarin precipitated out. Additional dithionite (3 g.) was added to complete the reduction, shown by the red-orange colour of the solution. The precipitate was filtered immediately to prevent re-oxidation, and washed with dilute acetic acid until alkali-free. It was then dried for forty-eight hours at 75-80° and used directly in the next stage. (XV) melted at 150-153° (lit. m.pt. 155°)[7].
Yield 11·5 g.

2-(o-Carboxybenzoyl)-5.7.12.14-tetrahydroxy-pentacene-6.13-quinone (XIXa).

A finely ground mixture of leucoquinizarin (XV) (10 g.), freshly prepared benzophenone-2'.3.4-tricarboxylic acid-3.4-anhydride (XVIII) (10 g.)[9] and aluminium chloride (2 g.) in a large Pyrex test-tube was plunged into a metal-bath at 280° and kept at that temperature for thirty minutes.

The resulting dark brown brittle mass was pulverised and extracted with boiling hydrochloric acid (1:1, 1500 ml.) and then with boiling alkaline dithionite (1500 ml.) to remove the soluble by-products. The insoluble residue was extracted with boiling nitrobenzene (1000 ml.) - a few impurities only entered into solution. The condensation product (XIXa) was filtered from the hot nitrobenzene solution, washed thoroughly with ethanol and dried to leave the purple-brown microcrystalline 2-(o-carboxybenzoyl)-5.7.12.14-tetrahydroxypentacene-6.13-quinone (XIXa) (14·4 g.) m.pt. > 500°. This compound imparts a beautiful rose-red colour to organic solvents ($\lambda_{max}^{benzene}$ = 5645, 5530, 5250, 4900; intensities unknown), gives a royal-blue colour with concentrated sulphuric acid, and a purple colour with sodium hydroxide. The analytical sample was prepared by dissolving out any impurities with boiling nitrobenzene.

Found C = 69·42%, H = 3·61%

$C_{30}H_{16}O_9$ requires C = 69·23%, H = 3·10%.

2-(o-Carboxybenzyl)-dihydroxy-6.13-dihydropentacene (XXIII).

2-(o-carboxybenzoyl)-5.7.12.14-tetrahydroxy-pentacene-6.13-quinone (XIXa) (5·2 g.) in sodium hydroxide (5%, 1500 ml.) was reduced with copper-activated zinc dust (5 x 3 g.), added at twenty-four hour intervals. The original purple suspension gradually lightened to a reddish-brown solution over the five day reflux. The hot solution was filtered to remove excess zinc dust, and the hot alkaline filtrate was acidified with concentrated hydrochloric acid to give a brown solid which was filtered off, washed thoroughly with water and dried at 100°. This material was triturated with ether to remove gummy impurities, leaving a yellowish solid which crystallised from glacial acetic acid as tiny golden-yellow needles of 2-(o-carboxybenzyl)-dihydroxy-6.13-dihydropentacene (XXIII) (1·25 g.), m.pt. 248-250°, $\lambda_{max}^{benzene}$ = 4085 (3·67), 4000 (3·68), 3045 (4·70), 2410 (4·14), 2315 (4·12). (XXIII) gave a blue turning to violet-red colour in concentrated sulphuric acid.

Found C = 80·60%, H = 5·12%

$C_{30}H_{22}O_4$ requires C = 80·70%, H = 4·97%.

Dihydroxy-1'-oxo-4'.6.13-trihydronaphtho-(2'.3'.1.2)-pentacene (XXIV) and Dihydroxy-6.13-dihydronaptho-(2'.3':1.2)-pentacene-1'.4'-quinone (XXV).

The reduced acid (XXIII) (1 g.) was refluxed in phosphorus oxychloride (25 ml.) for one hour, the solution developing a red-orange colour. Xylene (50 ml.) was added and the mixture co-distilled until the distillation temperature reached 140°. During distillation the anthrone (XXIV) precipitated out. On attempted crystallisation from nitrobenzene, the orange solution darkened considerably, and a brown compound of probable structure (XXV) crystallised out. (XXV) was not examined in detail, and instead reduced directly.

1'.4'.6.13-Tetrahydronaphtho-(2'.3':1.2)-pentacene (XXII).

The brown material from the previous reaction (·72 g.) was suspended in dry pyridine (75 ml.) and zinc dust (5 g.) added. Acetic acid (80%, 10 ml.) was added dropwise over one hour and the entire reaction mixture refluxed for a further five hours. The hot pyridine solution was filtered to remove excess zinc dust, poured on to dilute hydrochloric acid (1500 ml.), refluxed briefly to coagulate the precipitate, filtered, washed thoroughly with dilute ammonia and water and dried. The dark brown solid was melted (~ 250°) under nitrogen and then sublimed (200-210°/·05 mm.) to give a yellow sublimate (23 mg.), m.pt. 219-223°, λ_{max}^{EtOH} = 3580, 3360, 3270, 2970. This material was identical with the tetrahydronaphtho-(2'.3':1.2)-pentacene (XXII) obtained by the improved procedure now described.

A finely ground mixture of the condensation product (XIXa) (1 g.) and red phosphorus[16] (·67 g.) together with hydriodic acid (45%, 10 ml.) were heated in a sealed tube at 240° for three days. The resulting reddish-brown solid was filtered from the colourless mother liquors and extracted with xylene (1500 ml.). The resulting rose-red solution (colour due to small amounts of dissolved starting material) was filtered to remove unreacted phosphorus and then thoroughly extracted with alkaline dithionite (3 x 500 ml.) to remove any unreduced or uncyclised material. The xylene solution was concentrated and chromatographed on Grade I Neutral Alumina; elution with benzene gave a pale yellow solution, which on concentration yielded yellow prisms of 1'.4'.6.13-tetrahydronaphtho-(2'.3':1.2)-pentacene (XXII) (528 mg. from eight tubes) m.pt. 224-227°. The colour in concentrated sulphuric acid was reddish-brown. The UV spectrum is shown in figure 4.

Found C = 93·97%, H = 5·49%

$C_{30}H_{22}$ requires C = 94·20%, H = 5·80%.

Attempted Dehydrogenation of 1'.4'.6.13-Tetrahydronaphtho-(2'.3':1.2)-pentacene (XXII).

Small scale dehydrogenations were attempted using phenanthroquinone in boiling nitrobenzene, and chloranil in boiling xylene. In both cases, no material crystallised from the hot solution and the filtered solutions failed to exhibit the required ultra-violet absorption.

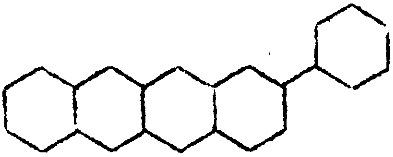
Naphtho-(2'.3':1.2)-pentacene (I).

1'.4'.6.13-Tetrahydronaphtho-(2'.3':1.2)-pentacene (XXII) (500 mg.) was covered with a layer of copper bronze and rapidly sublimed. Yellow material, followed by a reddish-purple sublimate at higher temperatures was obtained. Refluxing benzene was used to remove all the yellow material, while the purple sublimate was collected by scraping. Resublimation at 300-310°/0·01mm. yielded naphtho-(2'.3':1.2)-pentacene (I) as deep rose-pink pyramids (8 mg.), m.pt. 391-394°. (I) gave a green turning to orange-brown solution in concentrated sulphuric acid. The UV spectrum is shown in figure 3.

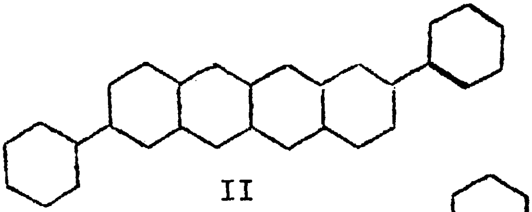
Found	C = 94·93%, H = 4·51%
$C_{30}H_{18}$ requires	C = 95·20%, H = 4·80%.

CHAPTER 2.

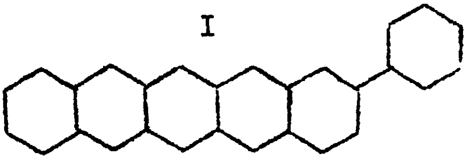
2-PHENYLTETRACENE, 2.8-DIPHENYLTETRACENE, 2-PHENYLPENTACENE, 2.9-DIPHENYLPENTACENE, 9-PHENYLTETRAPHENE.



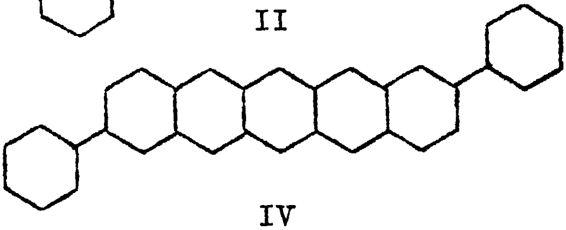
I



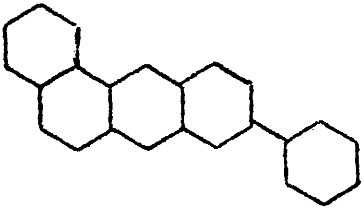
II



III



IV

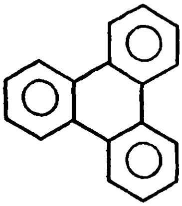


V

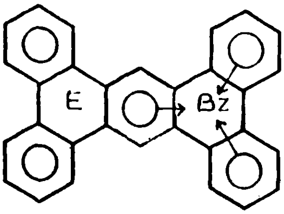
INTRODUCTION:

To explain the asymmetric shifts in the ultra-violet spectra obtained by the substitution of phenyl groups in the β,β'-positions of naphthalene and anthracene, Clar[1] proposed the formation of an exocyclic quartet of electrons.

VI



VII



VIII

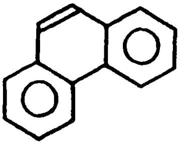
λ_β 1852 $\xrightarrow{718}$ 2570 $\xrightarrow{355}$ 2925 Å

$\sqrt{\lambda_\beta}$ 43·04 $\xrightarrow{7\cdot66}$ 50·70 $\xrightarrow{3\cdot40}$ 54·10 $\sqrt{\text{Å}}$

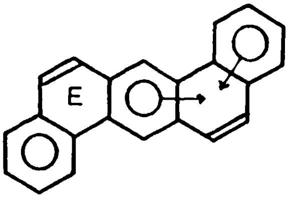
50·70-3·40 = 47·30 ⟶ 2237 Å

λ_β, naphthalene = 2210 Å

VI



IX



X

λ_β 1852 $\xrightarrow{658}$ 2510 $\xrightarrow{460}$ 2970 Å

$\sqrt{\lambda_\beta}$ 43·04 $\xrightarrow{7\cdot06}$ 50·10 $\xrightarrow{4\cdot40}$ 54·50 $\sqrt{\text{Å}}$

50·10-4·40 = 45·70 ⟶ 2089 Å

λ_β naphthalene = 2210 Å

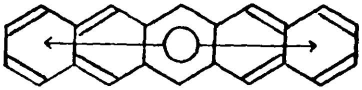
In order to see if this concept could be applied to higher members of the acene series, all the title compounds have been synthesised with the exception of 2.8-diphenyltetracene (II) which defied synthesis, although a number of routes were tried.

DISCUSSION:

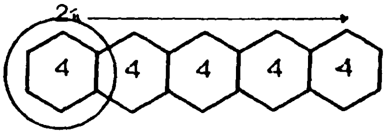
In the previous chapter, it was shown that, when benzene rings are fused together to form polycyclic hydrocarbons of the acene and phene series, strong spectral shifts are found whose values are constant when measured in $\sqrt{\text{Å}}$. A completely different phenomenon occurs when two biphenyl systems are added on to benzene (VI) to form triphenylene (VII) and tetrabenzanthracene (VIII).[2] These two annellations are formally symmetrical and should produce identical bathochromic shifts; in fact they produce two entirely different ones, the first being much larger than the second. This electronic asymmetry can be explained if the second shift is deducted from the β-band (both in $\sqrt{\text{Å}}$) of triphenylene (VII) (Shift Difference Rule), by which means the influence of the biphenyl complexes is eliminated. A β-band at 2237 Å is obtained, which is almost identical with the β-band of naphthalene (XVI), λ_β = 2210 Å. It would therefore seem that one of the two annellations produces an induced benzenoid ring (Bz) which extends the basic conjugation from a single benzene ring to a naphthalene system, whilst the second annellation fails to extend the conjugation to form an anthracene system and instead the centre ring remains empty (E) (VIII).

This asymmetry is not limited to the fusion of biphenyl complexes. If we remove one of the rings and replace it by a double bond, so that we are annellating a styrene-type complex, the series obtained is benzene (VI), phenanthrene (IX) and 1.2,5.6-dibenzanthracene (X).[2] Here again, first a large and then a small shift of the β-band is found and application of the Shift Difference Rule shows that the benzene has been enlarged to a naphthalene system, with the consequent formation of an induced sextet (X).

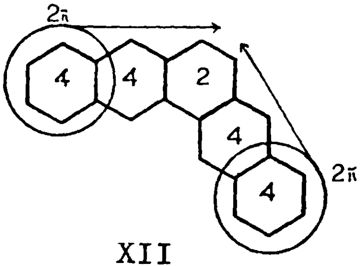
It must be pointed out that this type of electronic asymmetry need not be built up from benzene. Exactly analogous series can be developed from naphthalene, anthracene, and tetracene,[2] indicating that the phenomenon is a very general one. A satisfactory interpretation[3] of these facts can be gained if we consider each ring to have four electrons localised in it, with one pair of mobile π-electrons capable



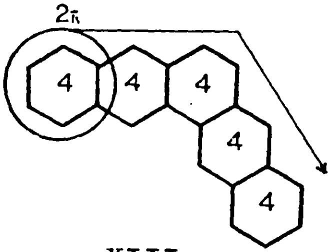
XIa



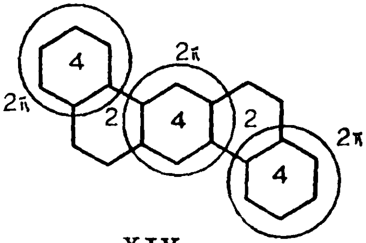
XIb



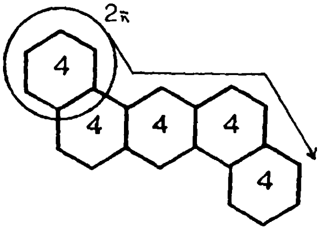
XII



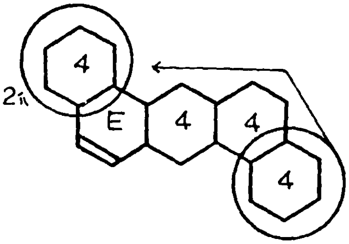
XIII



XIVa

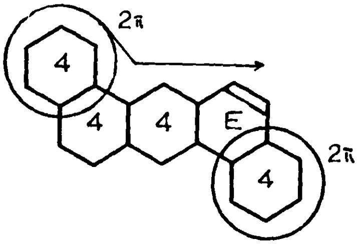


XIVb



XVa

↔

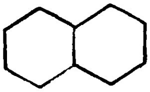


XVb

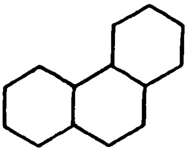
of migrating over the entire molecule as in the acene (XIa, XIb). Phenes can be explained on a similar basis; pentaphene can be formulated as in (XII) with four mobile π-electrons, or alternatively and more uniformly as (XIII). To obtain this more even distribution of electrons in the phene series, it is necessary to break up one sextet; in the centro-symmetrical dibenzacenes, to obtain a similar even distribution (XIVb) from the original one (XIVa) two sextets would need to be split up. This obviously does not happen - only one sextet breaks - leaving us with two equivalent formulae (XVa, XVb) in which there always exists an empty ring to account for asymmetric annellation.

These absorption spectra, then, can be explained by showing that two pairs of transferable π-electrons together with the double-bond in the angle form an induced sextet. It is of interest to see if the same phenomenon occurs in the absence of the fixed double bond - that is to say - is an induced <u>quartet</u> formed in β-substituted and β,β'-disubstituted acenes ?

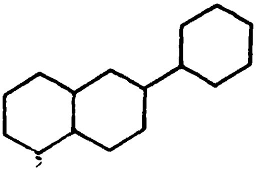
The absorption spectra of phenyl-substituted acenes have been studied in detail by a number of authors.[4,5,6,7,8] The general conclusions[6] reached are that β-phenyl substituents exhibit the Conjugative (C) effect, which produces large



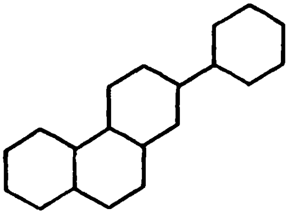
XVI



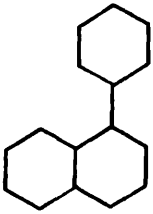
IX



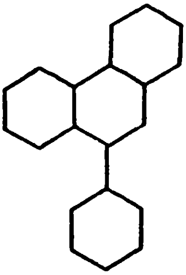
XVII



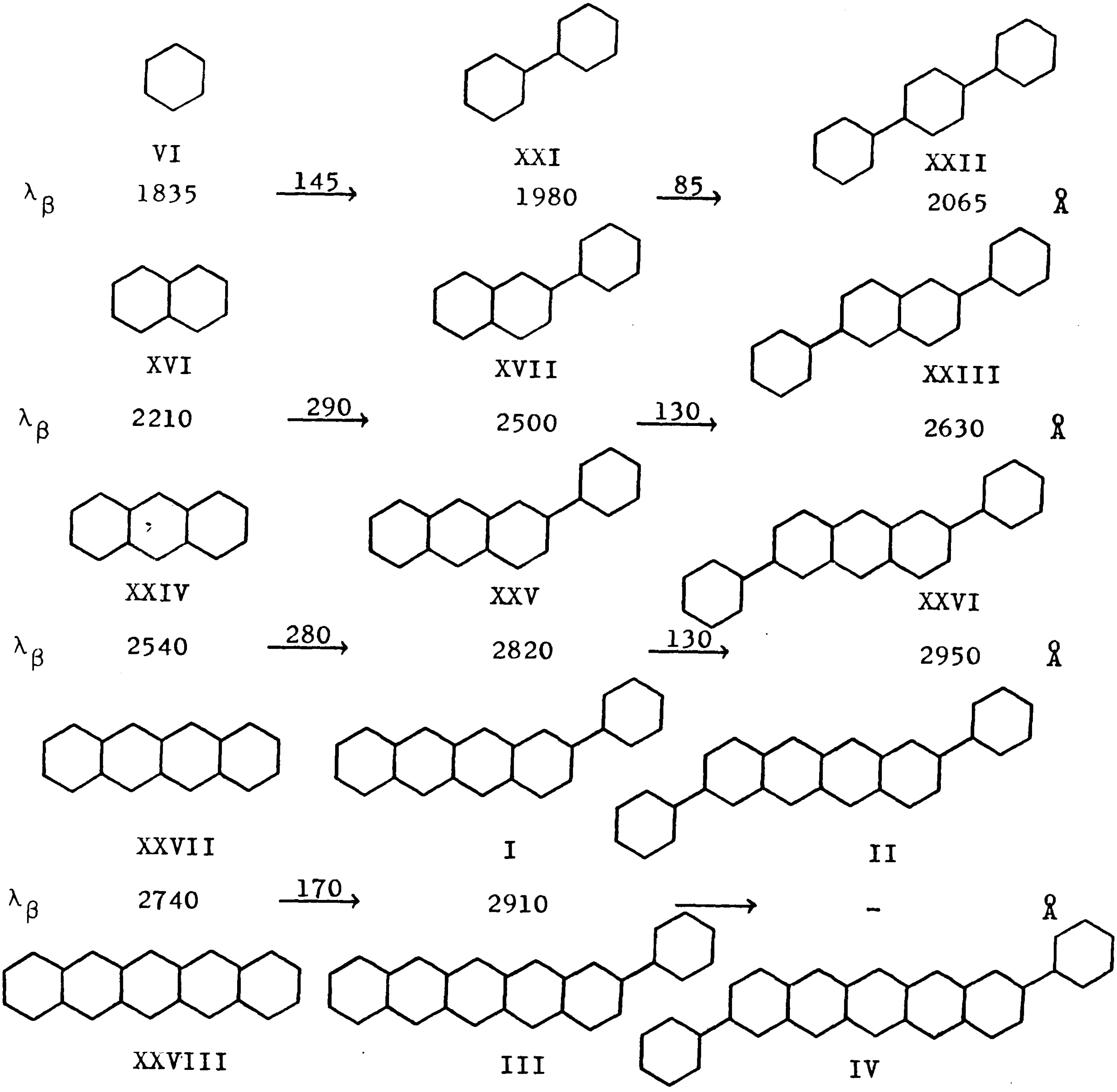
XVIII



XIX



XX



VI XXI XXII

λ_β 1835 $\xrightarrow{145}$ 1980 $\xrightarrow{85}$ 2065 Å

XVI XVII XXIII

λ_β 2210 $\xrightarrow{290}$ 2500 $\xrightarrow{130}$ 2630 Å

XXIV XXV XXVI

λ_β 2540 $\xrightarrow{280}$ 2820 $\xrightarrow{130}$ 2950 Å

XXVII I II

λ_β 2740 $\xrightarrow{170}$ 2910 $\longrightarrow$ - Å

XXVIII III IV

λ_β 3030 $\xrightarrow{170}$ 3200 $\xrightarrow{80}$ 3280 Å bathochromic shifts, decreased fine structure, and increased intensities. Typical examples are that the spectra of 2-phenylnaphthalene (XVII) and 2-phenylphenanthrene (XVIII) do not resemble naphthalene (XVI) and phenanthrene (IX), the differences being due to the extensive conjugation between the two parts of the molecule. Quite contrary to this, α-phenyl substituents show a Steric (S) Effect characterised by small hypsochromic shifts, increased fine structure, and decreased intensities. The spectra of 1-phenylnaphthalene (XIX) and 9-phenylphenanthrene (XX) closely resemble the parent hydrocarbons since the lack of coplanarity due to steric hindrance of the hydrogen atoms prevents conjugation between the two halves.

A somewhat different viewpoint of β-substitution has been adopted by Clar.[1] In the simplest series of benzene (VI) biphenyl (XXI), and p-terphenyl (XXII), the bathochromic shifts of the β-bands are small; however, this series must be considered as a special case since all three hydrocarbons can be written in terms of sextets only, a process which confers on them particular stability.[9] Completely distinct, the series built up from naphthalene (XVI → XVII → XXIII) (figure 1) and anthracene (XXIV → XXV → XXVI) (figure 2) show that the first β-band shift is large in comparison with

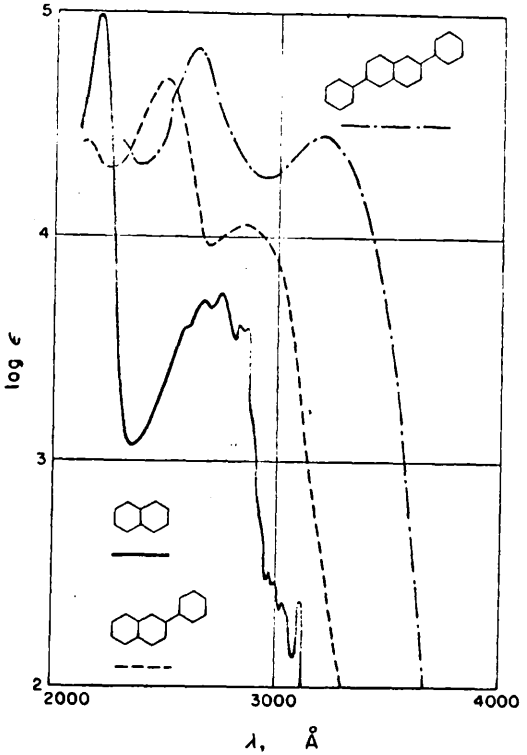


Figure 1

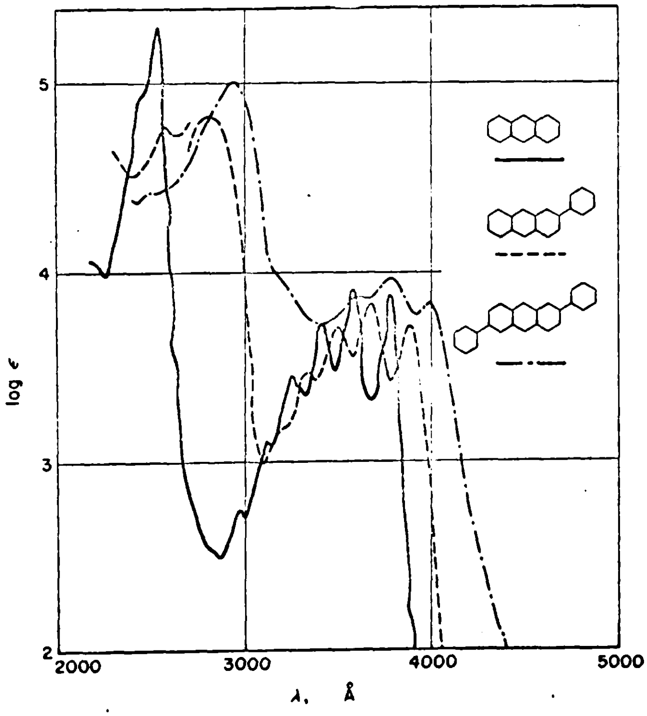


Figure 2.

the second. Now, since the shift involved in annellating a ring in the acene series[10] is of the same magnitude as our larger shift, it suggests that in substituting the first phenyl group, the conjugation present in the molecule is extended by means of an exocyclic quartet of electrons (XVII, XXV). The second phenyl group cannot participate in another quartet since the mobile π-electrons have already been used up, and consequently the shift is smaller. This situation is identical with that already found in the annellation of biphenyl and styrene complexes, and obviously constitutes a new asymmetric annellation series.

In the naphthalene and anthracene series, the formation of an exocyclic quartet extends the conjugation to the anthracene and tetracene moieties respectively. In synthesising the mono- and di-phenyl substituted tetracenes (I, II) and pentacenes (III, IV) the conjugation present will be extended to pentacene and hexacene respectively: and it has been shown that in these higher acenes, this extended conjugation tends to lower their stability.[11] Two conflicting mechanisms then are present, one trying to extend, and the other attempting to limit the conjugation; examination of the β-band shifts in the tetracene series (XXVII → I → II) (figure 3) and the pentacene series

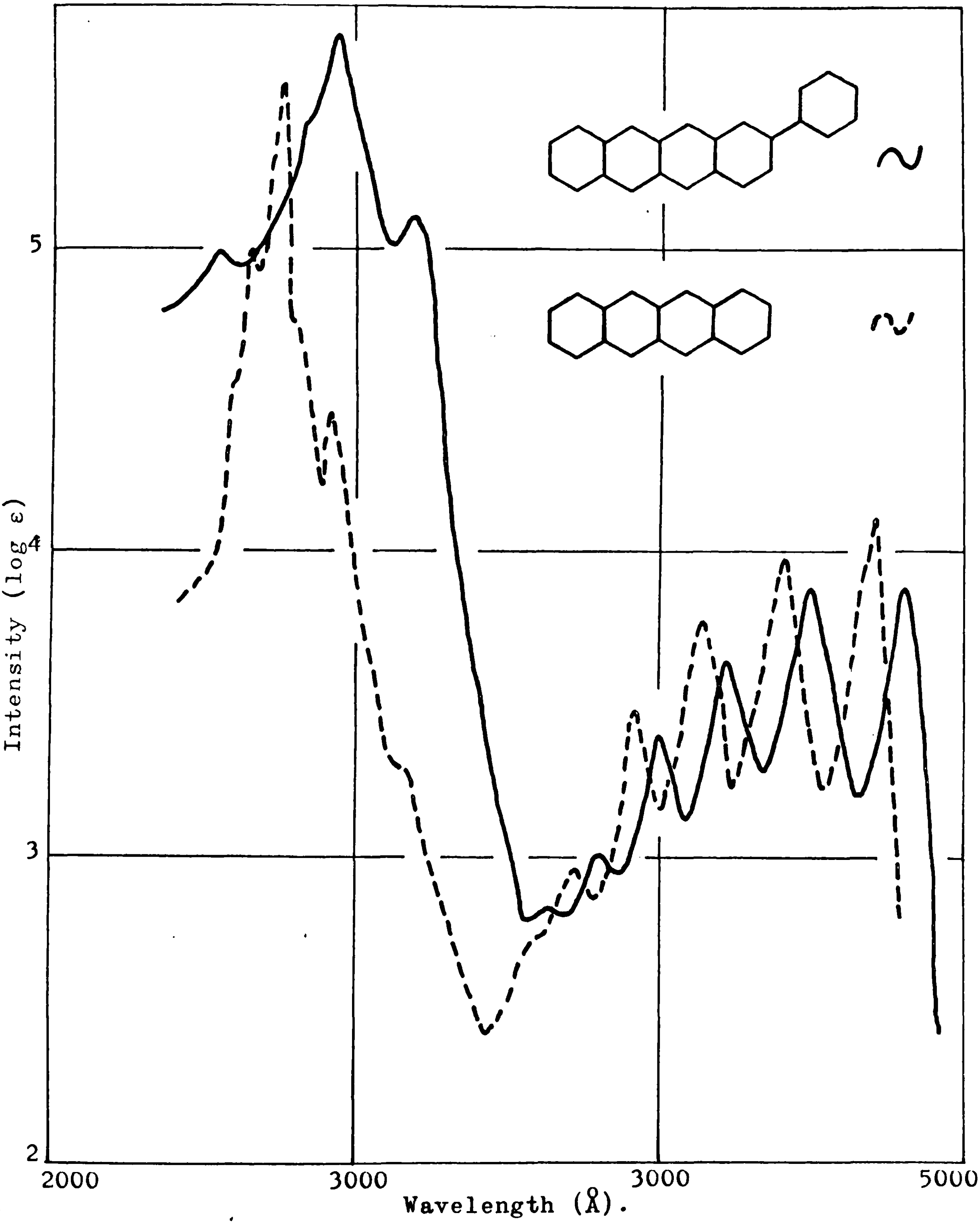


Figure 3. Absorption maxima (Å) and log ε (in parentheses). Tetracene in Alcohol: p, 4710 (4·10), 4410 (3·97), 4150 (3·76), 3930 (3·46), 3730 (2·96); 2930 (4·44); β 2740 (5·53), 2645 (4·99). 2-Phenyltetracene in benzene: p, 4805 (3·88), 4500 (3·89), 4215 (3·64), 4000 (3·38), 3800 (3·00), 3535 (2·82); in cyclohexane, 3180 (5·12); β, 2910 (5·71), 2540 (4·99).

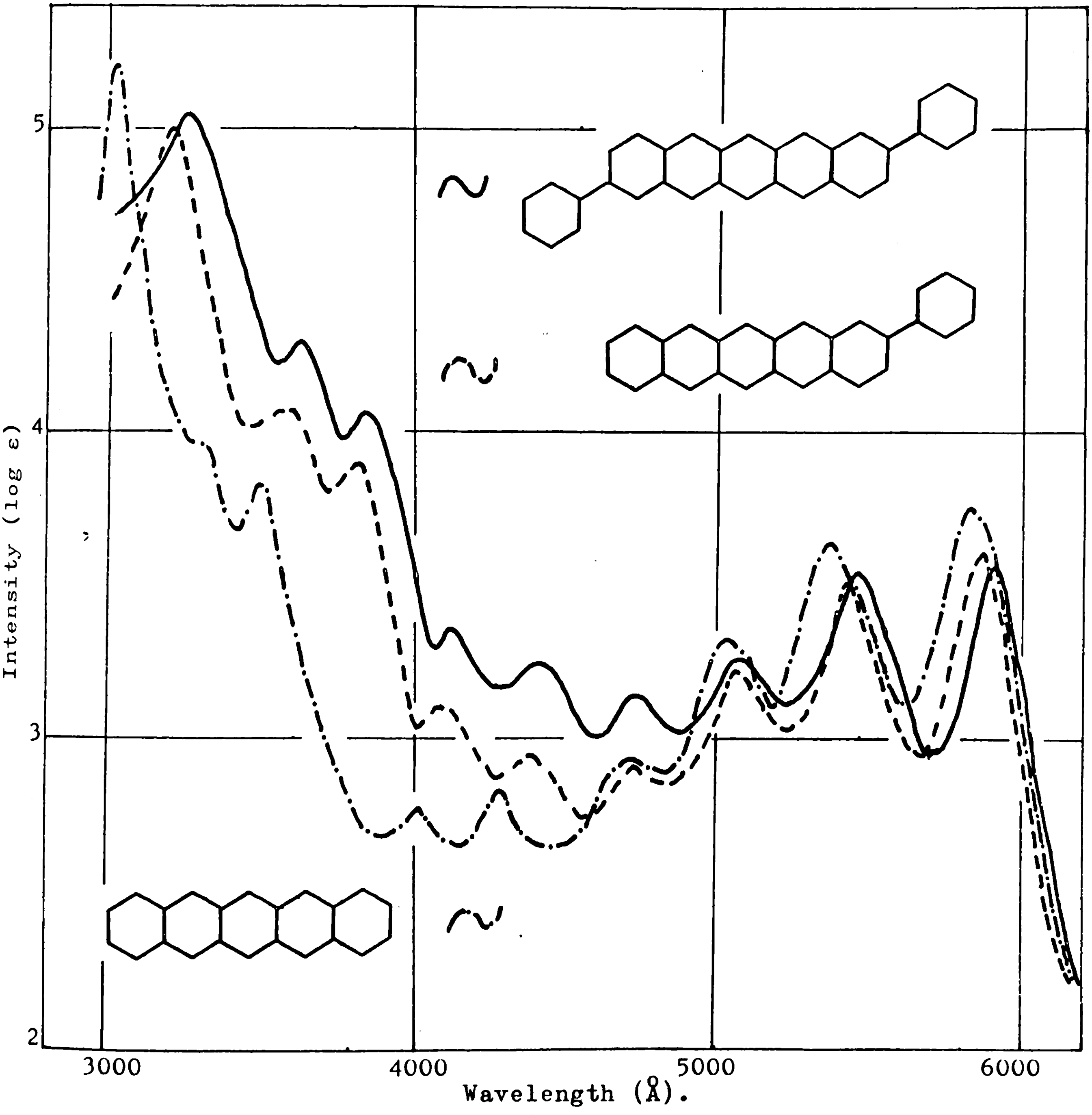
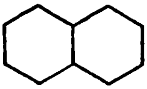
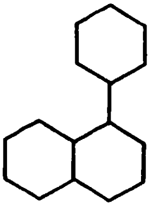
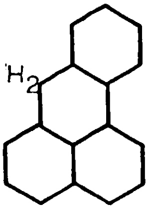
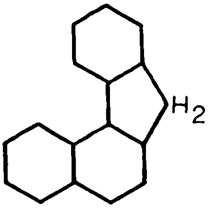
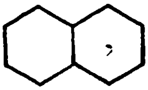
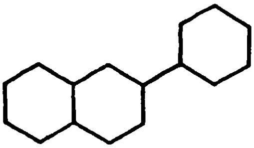
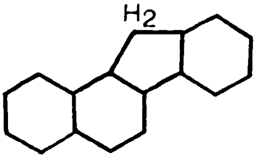
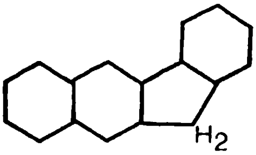


Figure 4. Absorption maxima (Å) and log ε (in parentheses).
Pentacene in trichlorobenzene: p, 5820 (3·76), 5375 (3·63), 5025 (3·32), 4700 (2·94); α, 4280 (2·84), 4030 (2·79); 3500 (3·84), 3320 (3·96); in benzene, β, 3030 (5·20).
2-Phenylpentacene in trichlorobenzene: p, 5880 (3·62), 5440 (3·54), 5070 (3·24), 4730 (2·93); α, 4360 (2·97), 4070 (3·13); 3780 (3·90), 3590 (4·09); in benzene, β, 3200 (5·02).
2.9-Diphenylpentacene in trichlorobenzene: p, 5940 (3·57), 5490 (3·54), 5110 (3·27), 4760 (3·13); α, 4420 (3·25), 4140 (3·37); 3860 (4·07), 3650 (4·30); in benzene, β, 3280 (5·06).

					
	XVI	XX	XXIX	XXX	
λ_β	2210	2260	2280	2310	Å

					
	XVI	XVII	XXXI	XXXII	
λ_β	2210	2500	2620	2630	Å

(XXVIII → III → IV) (figure 4) shows that the shifts involved are still asymmetric but have fallen considerably in absolute value. The mobile π-electrons, capable of forming an exocyclic quartet in the lower members of the acene series, no longer extend their conjugation in this manner in the higher members of the series since their limiting mobility appears to have been reached.

The concept of the transference of π-electrons to form an exocyclic quartet occurs only in the β-position, and cannot take place with α-substituents.[1] This can be appreciated by examining the position of the β-band in naphthalene (XVI) λ_β = 2210 Å and 1-phenylnaphthalene (XIX), λ_β = 2260 Å. A small shift only is involved, (figure 5), and there can, therefore, be no extension of conjugation. Even when methylene groups are added to force the phenyl group into planarity (XXIX, XXX), the further shifts found are too small to be considered asymmetric annellations.[1] The large shift between naphthalene (XVI), λ_β = 2210 Å and 2-phenylnaphthalene (XVII), λ_β = 2500 Å has been explained by the formation of an exocyclic quartet. Here again methylene insertion should make little difference, since all possible conjugation has already occurred. (XXXI) and (XXXII),[12] the appropriate compounds, show only small β-band shifts when compared with 2-phenylnaphthalene (XVII) (figure 6).

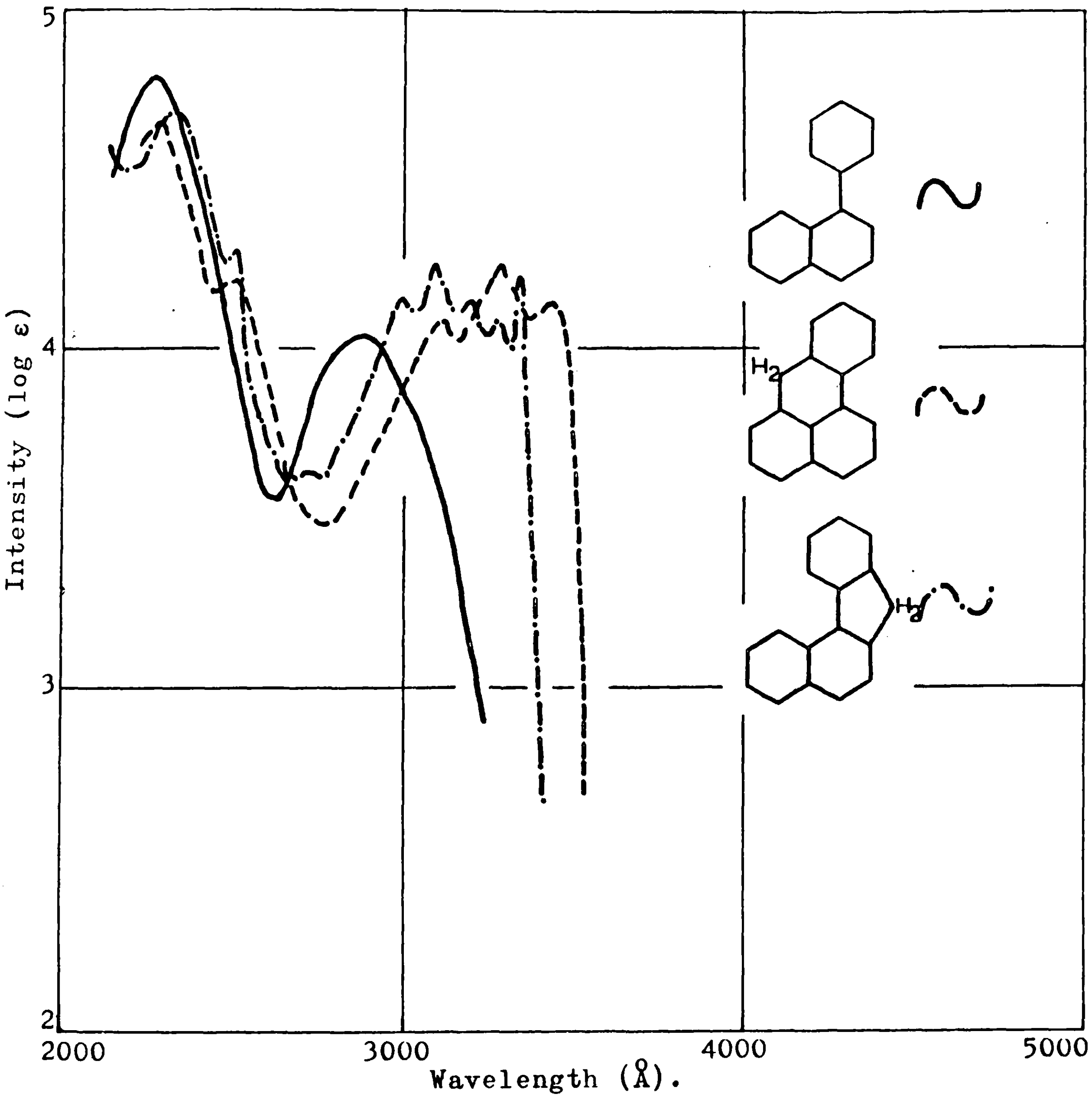
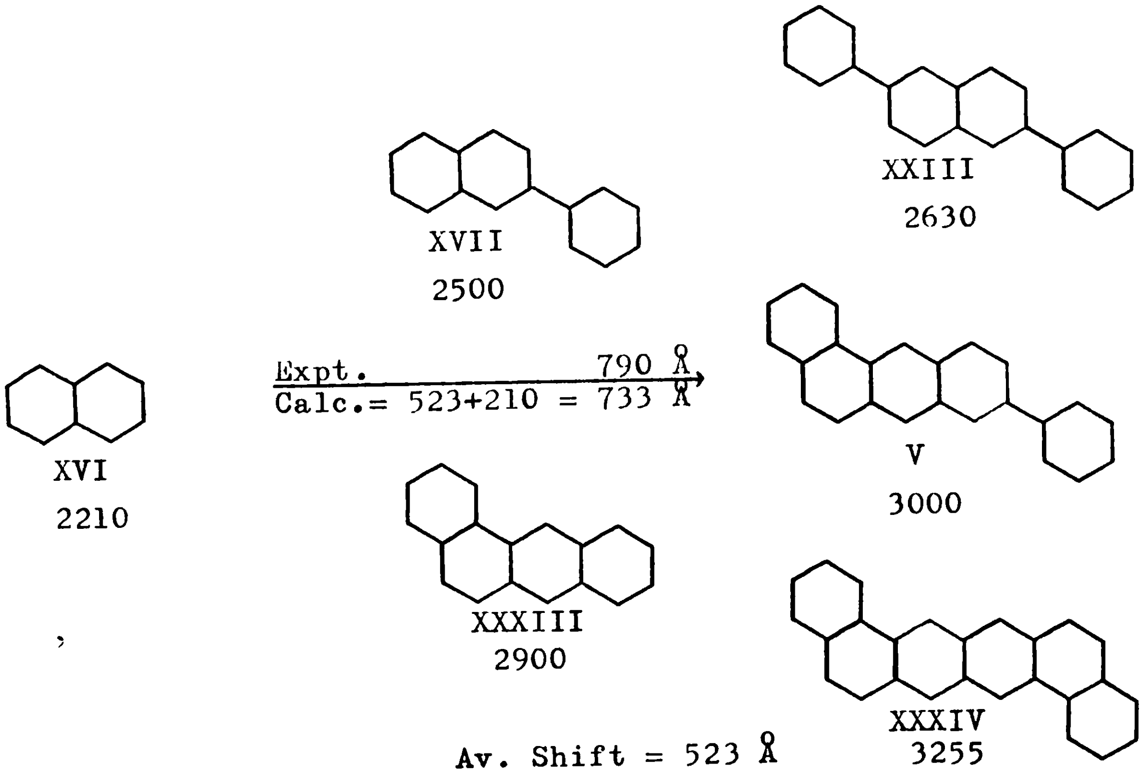


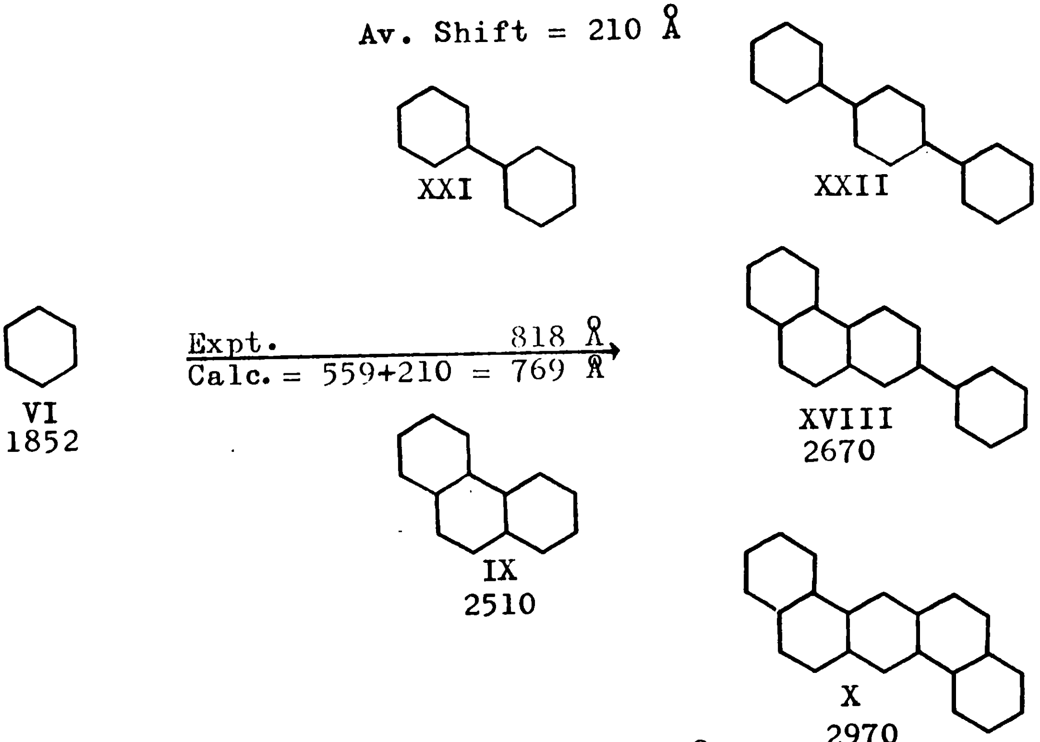
Figure 5. Absorption maxima (Å) and log ε (in parentheses).
1-Phenylnaphthalene in cyclohexane: p, 2900 (4·04); β, 2260 (4·80).
Benzanthrene in ethanol: p, 3440 (4·13), 3290 (4·25), 3120 (4·08); 2500 (4·20); β, 2280 (4·66).
3.4-Benzofluorene in ethanol: p, 3350 (4·20), 3280 (4·08), 3200 (4·14), 3100 (4·24), 3000 (4·10); 2500 (4·29); β, 2310 (4·70).

Av. Shift = 210 Å



Av. Shift = 523 Å

Av. Shift = 210 Å



Av. Shift = 559 Å

9-Phenyltetraphene (V) was synthesised to see what would happen to the spectrum (figure 7) of a molecule which combined in it, a styryl complex able to form an induced sextet and a β-phenyl substituent capable of forming an exocyclic quartet. A direct comparison of the β-band values reveals nothing, but if the average shift for two styryl complexes = $\frac{1}{2}(3255 - 2210) = 523$ Å is added to the average value for the two β-substituted phenyl groups = $\frac{1}{2}(2630 - 2210) =$ 210 Å, a shift of 733 Å is obtained. This value is a mean for the addition of a styrene complex and a β-phenyl group; the experimentally found β-shift is 790 Å (XVI → V) - very satisfactory agreement indeed. Furthermore it is of considerable interest that a similar series from benzene (VI) to 2-phenylphenanthrene (XVIII) can be built up, provided the same figure (210 Å) is used as the average for the formation of an exocyclic quartet; this is a reasonable assumption to make, since the benzene series (VI → XXI → XXII) has been shown to be a special case, and since this figure applies to both the naphthalene and anthracene series where an exocyclic quartet is formed. On the addition of this value to the new mean for styryl complexes = $\frac{1}{2}(2970 - 1852) = 559$ Å, theory predicts the β-band of 2-phenylphenanthrene (XVIII) at 2621 Å; experimentally it is found at 2670 Å.

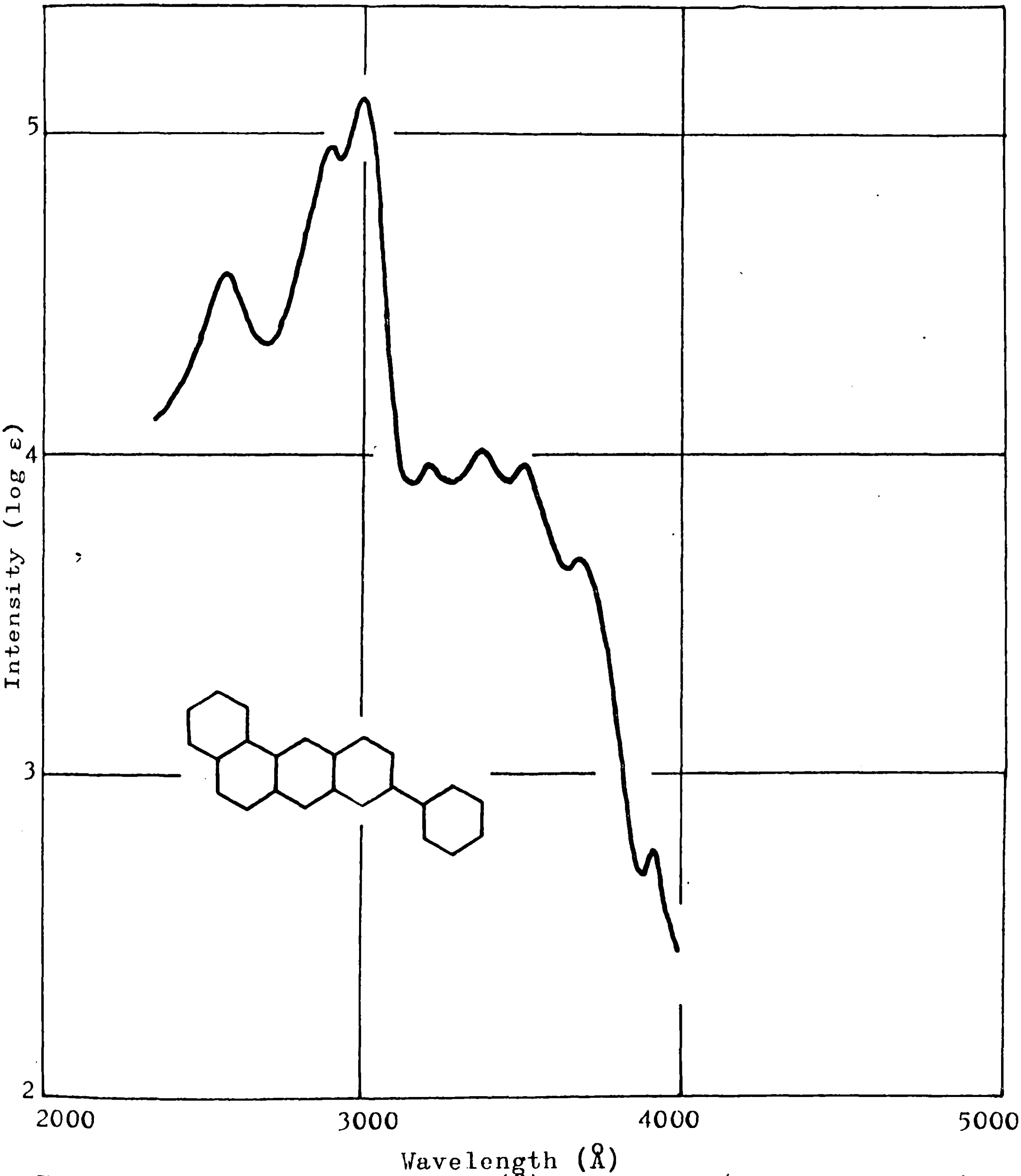
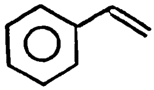
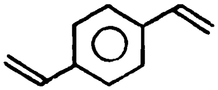


Figure 7. Absorption maxima (Å) and log ε (in parentheses) 9-Phenyltetraphene in cyclohexane: α, 3920 (2·75); 3690 (3·65); p, 3510 (3·97), 3360 (4·01), 3210 (3·96); β, 3000 (5·10), 2900 (4·96), 2570 (4·55).

VI

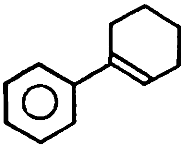


XXXV

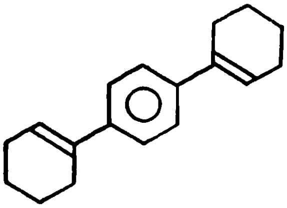


XXXVI

VI



XXXVII



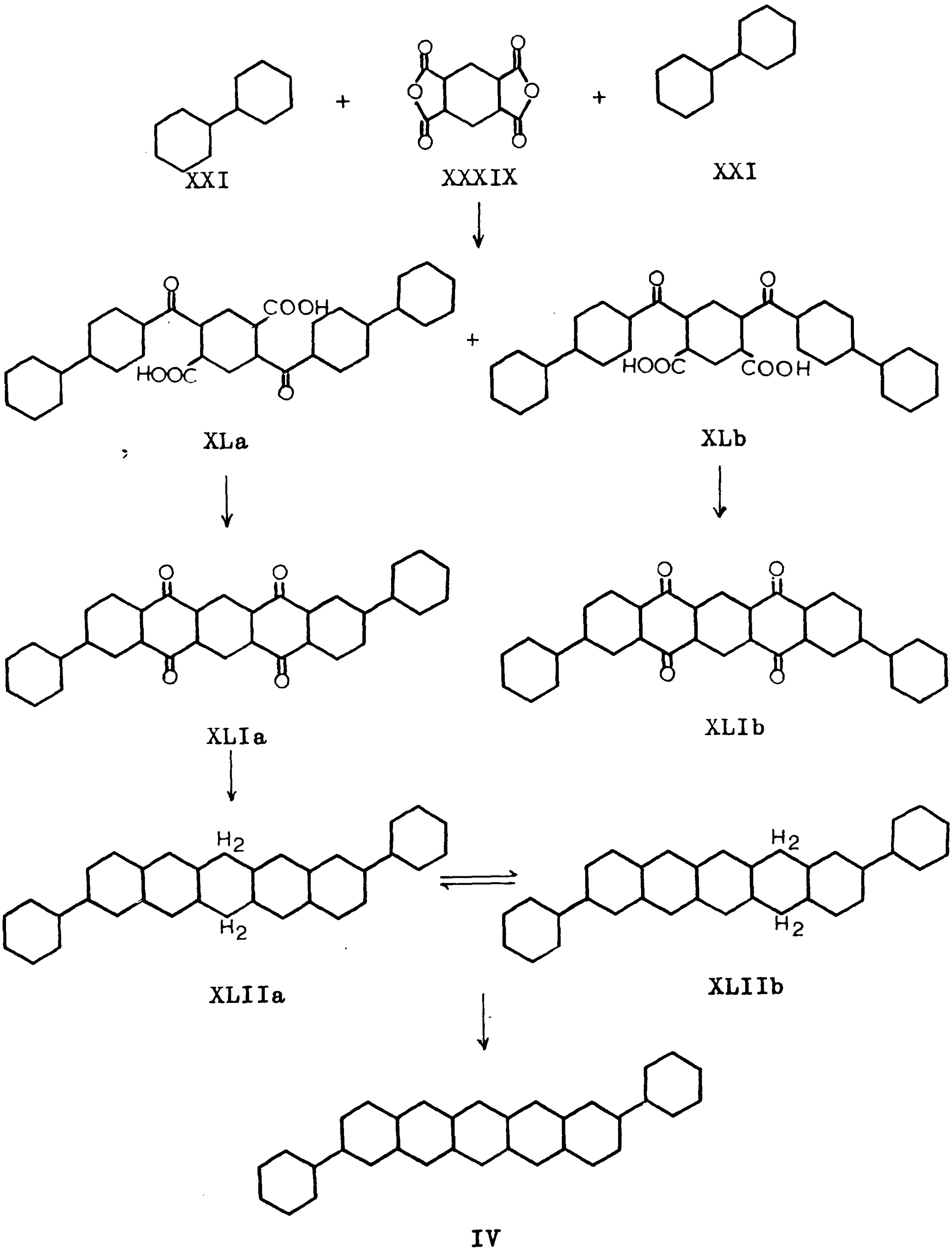
XXXVIII

Until now, the β-bands only have been scrutinised. This is necessary since the p-bands are involved in polarisation transverse to the main molecular axis which lies along the molecule[13] and could not be expected to vary much with a phenomenon which is essentially connected with a longitudinal polarisation.

This interpretation of mono- and di-phenyl substitution is somewhat unusual, yet the shifts involved do seem to fit quite satisfactorily. Further proof of this concept of an exocyclic quartet could be easily gained since a β-substituted phenyl group is not strictly necessary - compounds with an isolated double bond in these positions (e.g. XXXV - XXXVIII) should exhibit all the characteristics of an asymmetric annellation series.

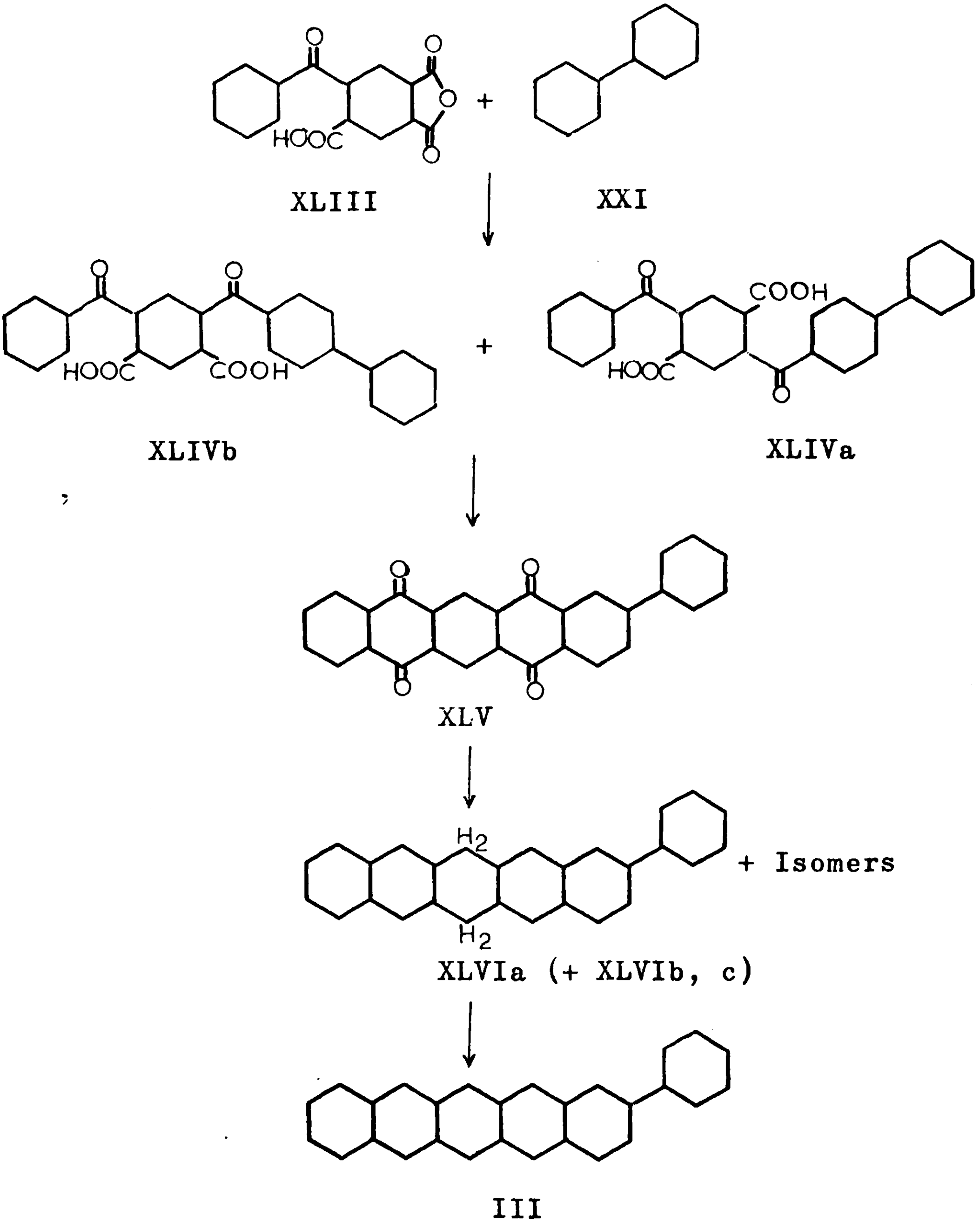
EXPERIMENTAL DISCUSSION:

Friedel-Crafts acylation of biphenyl (XXI) with a variety of anhydrides and acid chlorides was used as the starting point for the synthesis of the title compounds with the exception of 2.8-diphenyltetracene (II). It is therefore of considerable importance to know as much as possible about the position of acylation of biphenyl in these reactions;


XXI
XXXIX
XXI
COOH
HOOC
XLa
HOOC
COOH
XLb
XLIa
XLIb
H2
H2
XLIIa
H2
H2
XLIIb
IV

a recent literature survey[14] has pointed out that the unsubstituted hydrocarbon always acylates in either or both the para positions depending on the conditions used, excess of the hydrocarbon obviously preventing double reaction.

The preparations of the mono- and di-phenylpentacenes (III, IV) were very similar. The disubstituted pentacene (IV) was synthesised first and all the difficulties involved in the route were ironed out in its preparation. A double Friedel-Crafts reaction between biphenyl (XXI) and pyromellitic dianhydride (XXXIX) in tetrachloroethane presented no difficulties and good yields of the isomeric dicarboxylic acids (XLa, XLb) were obtained. Direct cyclisation with concentrated sulphuric acid was not considered since sulphonation of the free phenyl rings would inevitably occur; a milder treatment with sulphuric acid in benzoyl chloride[15] proved unsuccessful. A harsher method seemed therefore to be required, and it was found that when the acids (XL) were treated with phosphorus pentoxide in a melt of phthalic anhydride,[16] a satisfactory yield of the quinones (XLI) was obtained. The quinone (XLIa), since it is the centro-symmetrical isomer would be expected to be the more insoluble and fractional crystallisation yielded it free of its more soluble isomer (XLIb). Preliminary small


HOOC
XLIII
XXI
HOOC
COOH
XLIVb
COOH
HOOC
XLIVa
XLV
H_2
H_2
+ Isomers
XLVIa (+ XLVIb, c)
III

scale reductions of (XLIa) with a view to obtaining diphenylpentacene (IV) directly, did not give encouraging results, and instead it was decided to make diphenyldihydropentacene (XLII), which was obtained by reduction with zinc dust in dilute sodium hydroxide. By analogy with dihydropentacene, it was anticipated that the unsublimed material would possess the 6.13-dihydro-structure (XLIIa) and that on sublimation it would partly isomerise to the 5.14-dihydro-structure (XLIIb). However the ultra-violet spectrum before and after sublimation gave virtually identical maxima, (figure 8), and this can be interpreted as indicating that diphenyldihydropentacene (XLII) contained a mixture of isomers even before sublimation. Dehydrogenation to the parent hydrocarbon, 2.9-diphenylpentacene (IV) was easily accomplished with phenanthroquinone in refluxing nitrobenzene.[17]

The synthesis of 2-phenylpentacene (III) followed an identical pattern. Condensation of the complex anhydride (XLIII)[18] with biphenyl (XXI) gave a mixture of dicarboxylic acids (XLIVa, XLIVb) which were cyclised with phosphorus pentoxide/phthalic anhydride.[16] This time only one quinone (XLV) could be formed, and there was no corresponding difficulty over the separation of isomers. Similar reduction conditions were used to obtain monophenyldihydropentacene (XLVI) which also exhibited the same ultra-violet spectrum before and after sublimation indicating that a complex mixture of dihydro-isomers must be present (XLVIa, b, c) (figure 9). Phenanthroquinone in boiling nitrobenzene[17] again accomplished the dehydrogenation to yield 2-phenylpentacene (III). These two hydrocarbons show a quite remarkable stability over the parent compound (XXVIII) - both could be sublimed without decomposition at temperatures greater than 300° at which temperature pentacene itself (XXVIII) partly decomposed.[19] Further, their solutions in organic solvents did not photo-oxidise when exposed to light and air like those of the parent.[20] This was especially true of the diphenyl compound (IV) whose solution in chloroform was left in the sunlight for one month without any loss of colour.

2-Phenyltetracene (I) was prepared in much the same manner. Condensation of naphthalene-2.3-dicarboxylic acid anhydride (XLVII) with biphenyl (XXI) gave the keto-acid (XLVIII) in high yield. Attempted cyclisation with sulphuric acid in benzoyl chloride[15] gave a dark red isolable complex (XLIX) which could be decomposed to the starting material (XLVIII) with water. This fact, in combination with its strong carbonyl absorption at 1770 $cm.^{-1}$ suggested it might be an ionic complex of the type shown; it

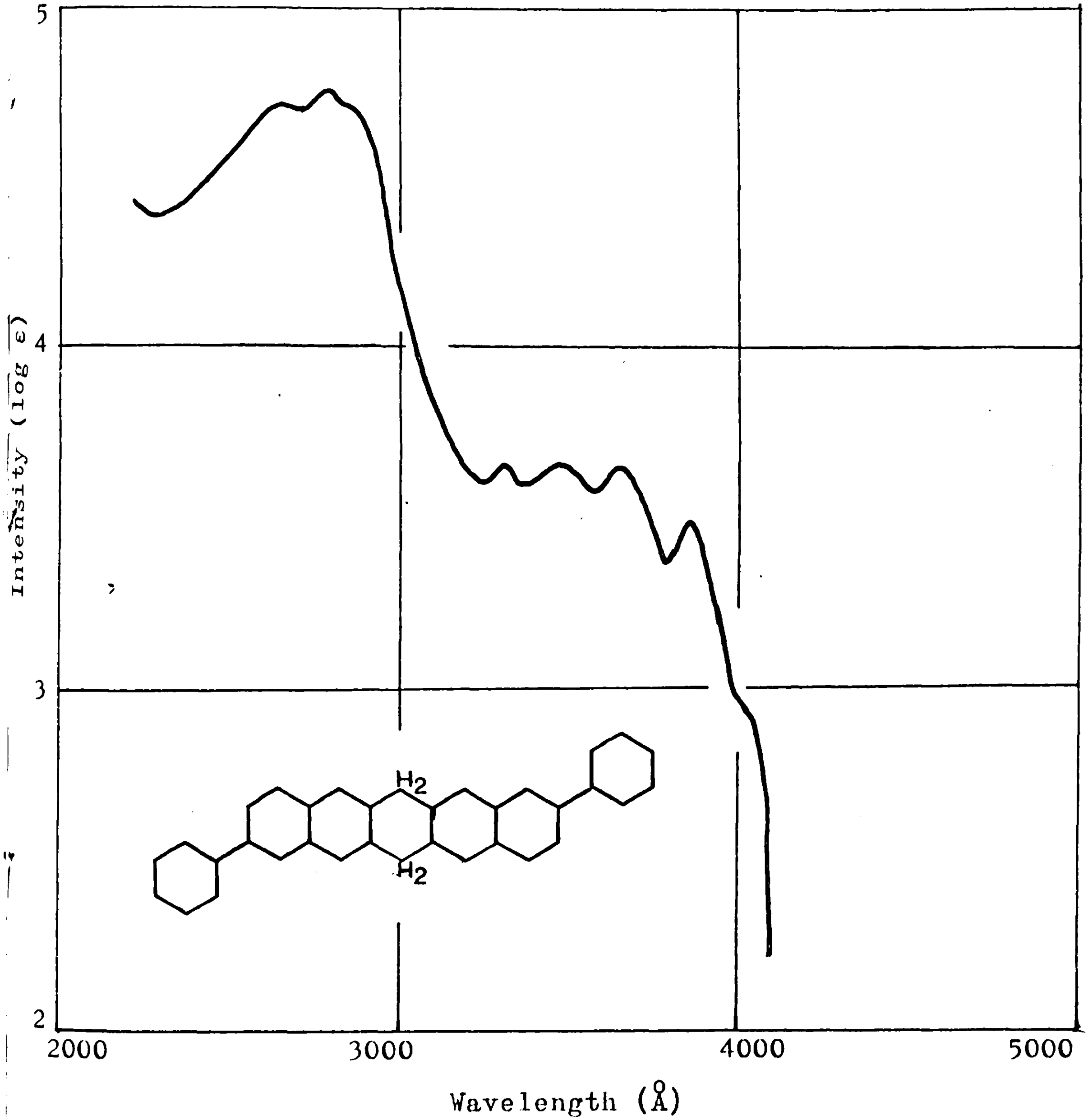


Figure 8. Absorption maxima (Å) and log ε (in parentheses). 2.9-Diphenyldihydropentacene (before sublimation) in cyclohexane: 3860 (3·49); p, 3660 (3·65), 3500 (3·67), 3320 (3·65); β, 2800 (4·77), 2660 (4·73).

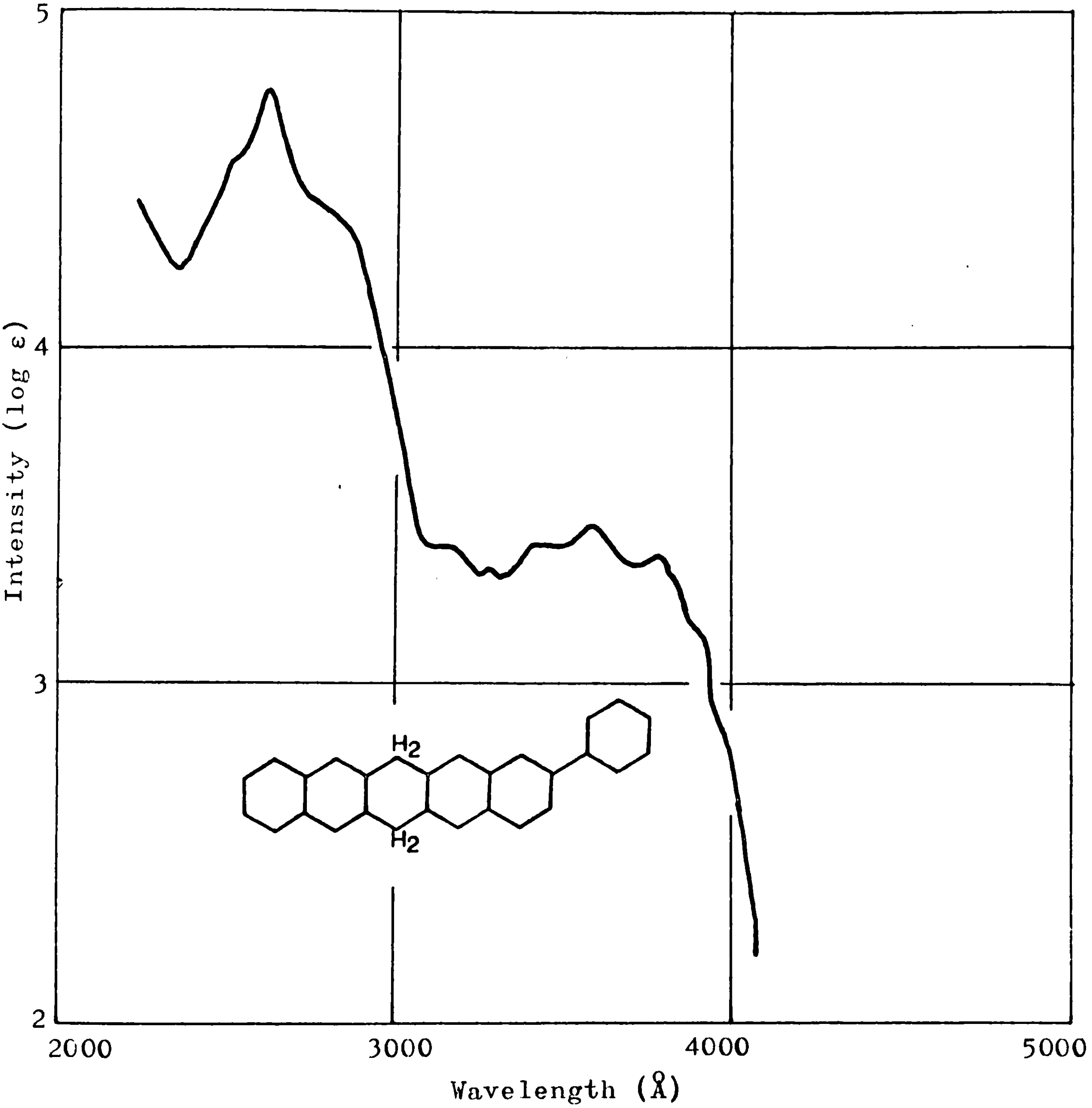
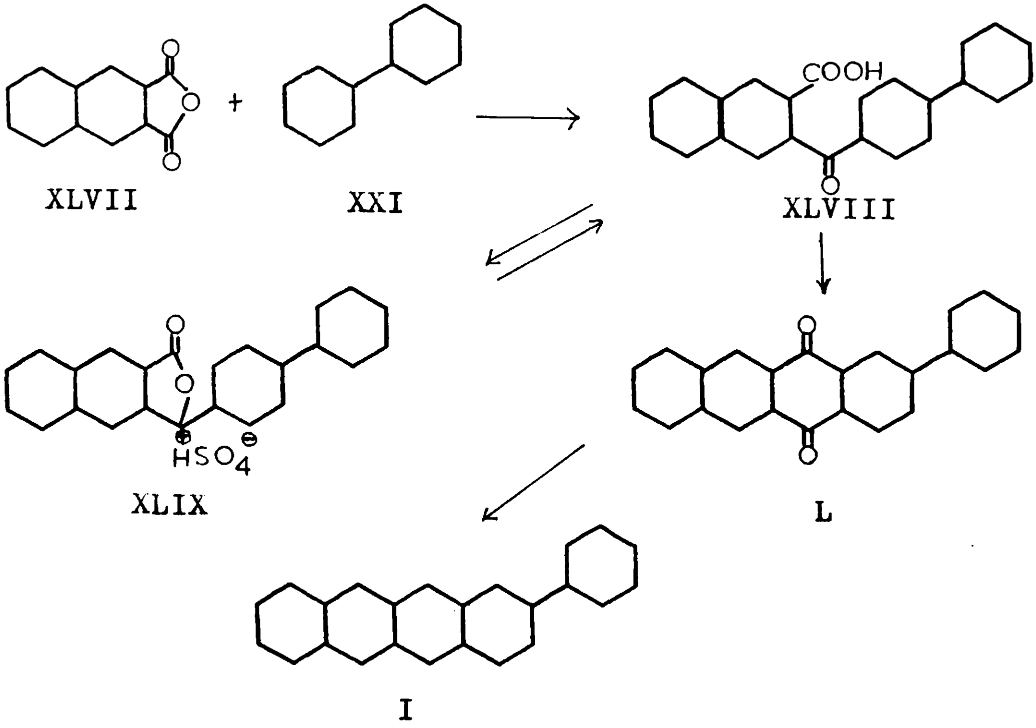
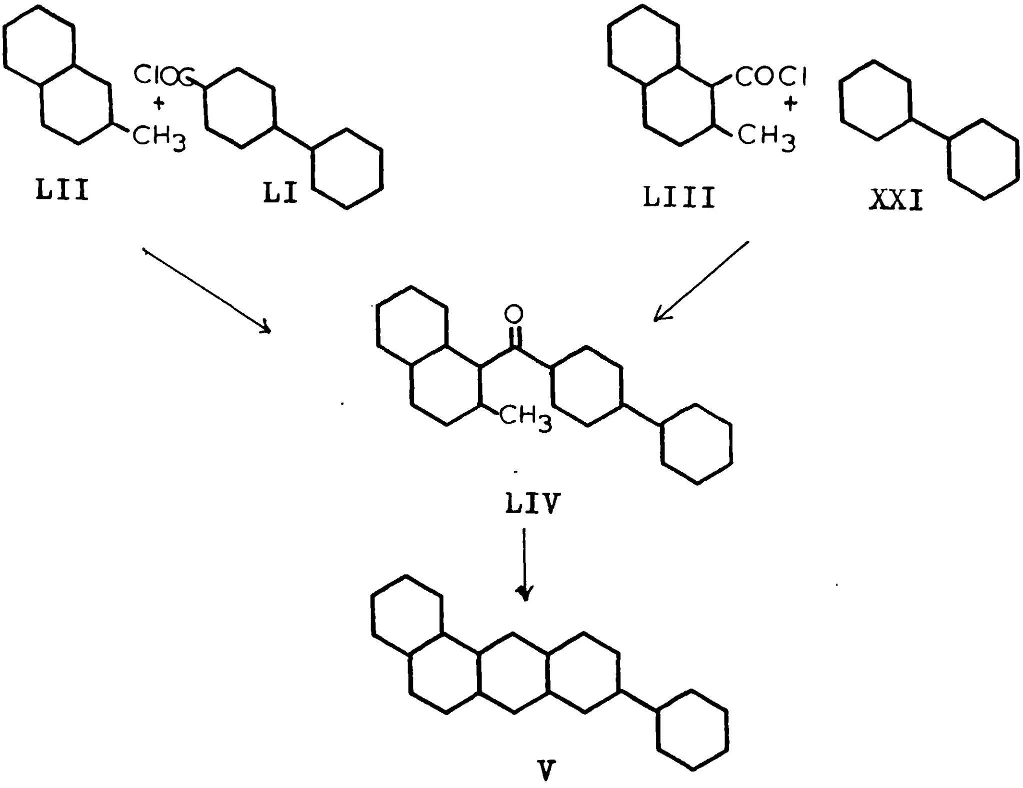


Figure 9. Absorption maxima (Å) and log ε (in parentheses). 2-Phenyldihydropentacene (before sublimation) in cyclohexane: 3780 (3·36); p, 3590 (3·47), 3420 (3·41), 3260 (3·34); β, 2780 (4·41), 2600 (4·77).

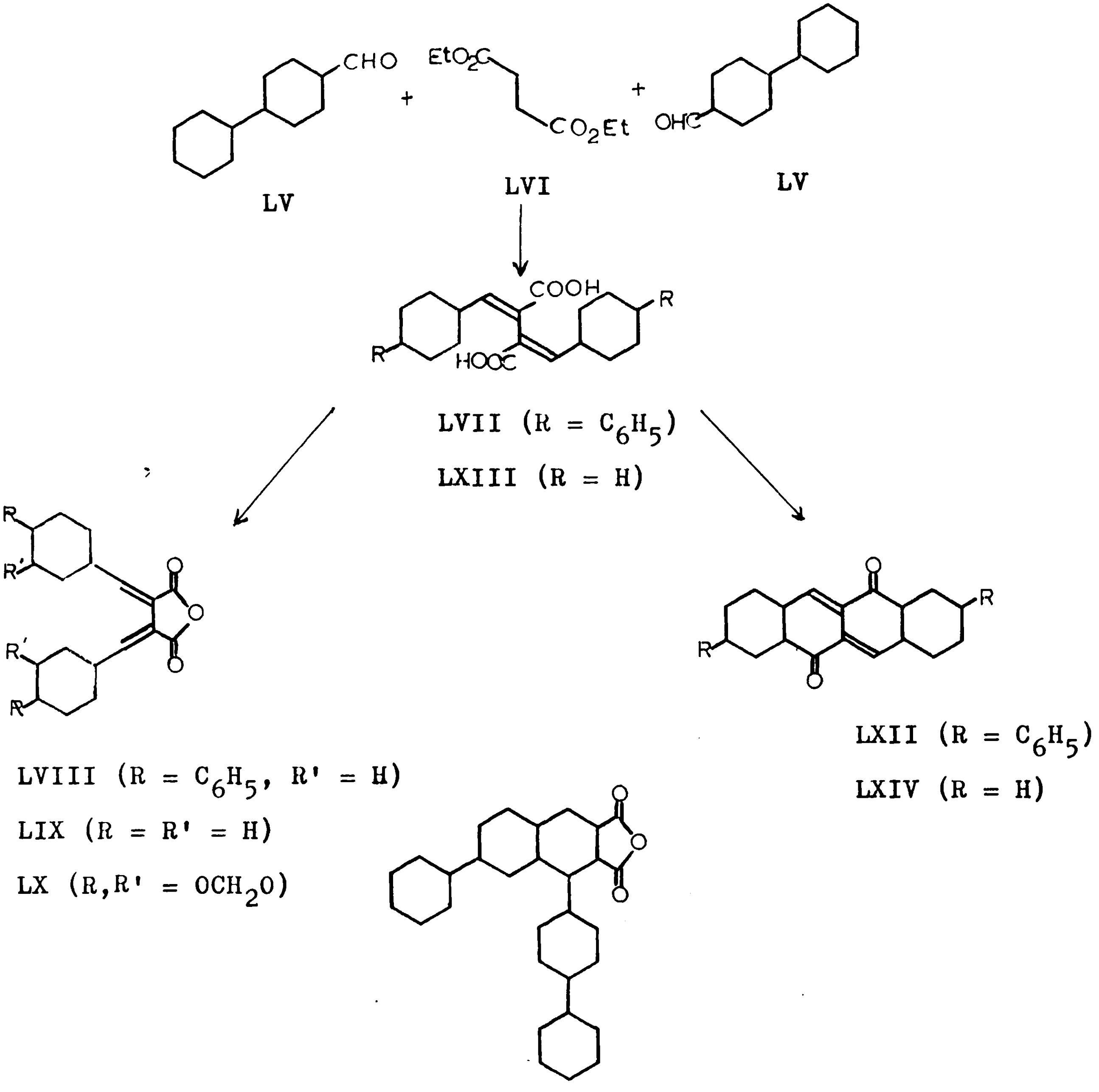

XLVII
XXI
COOH
XLVIII
HSO4
XLIX
L
I


ClOC
CH3
LII
LI
COCl
CH3
LIII
XXI
CH3
LIV
V

was not further investigated. The acid (XLVIII) was successfully cyclised by the now standard phosphorus pentoxide/phthalic anhydride method to the quinone (L) which was directly reduced to the hydrocarbon (I) by zinc dust/pyridine/acetic acid.

9-Phenyltetraphene (V) has been previously synthesised by Cook,[21] but the ultra-violet spectrum was not recorded - hence its repetition. Cook condensed 4-phenylbenzoyl chloride (LI) with 2-methylnaphthalene (LII) to yield the ketone (LIV); this compound was prepared in the present work by reaction of 2-methyl-1-naphthoyl chloride (LIII)[22] with biphenyl (XXI). Both methods resulted in the same material. The Elbs reaction[23] was then used to obtain the required hydrocarbon (V).[21]

2.8-Diphenyltetracene (IV), however, presented a quite different problem. The most direct route appeared to be the double Stobbe condensation[24a,b] of p-phenylbenzaldehyde (LV)[25] with diethyl succinate (LVI) to yield 2.3-di-(p-biphenyl)-fulgenic acid (LVII) which was characterised as its anhydride (LVIII). That this compound (LVIII) has the required structure was proved beyond doubt by physical techniques - it exhibited $\nu_{max}^{KBr} = 1762, 1819\ cm.^{-1}$ and $\lambda_{max}^{dioxan} = 2570(4{\cdot}26), 2640(4{\cdot}28), 3100(4{\cdot}47), 4040(3{\cdot}96)$.



LV LVI LV

LVII (R = C_6H_5)

LXIII (R = H)

LVIII (R = C_6H_5, R' = H)

LIX (R = R' = H)

LX (R,R' = OCH_2O)

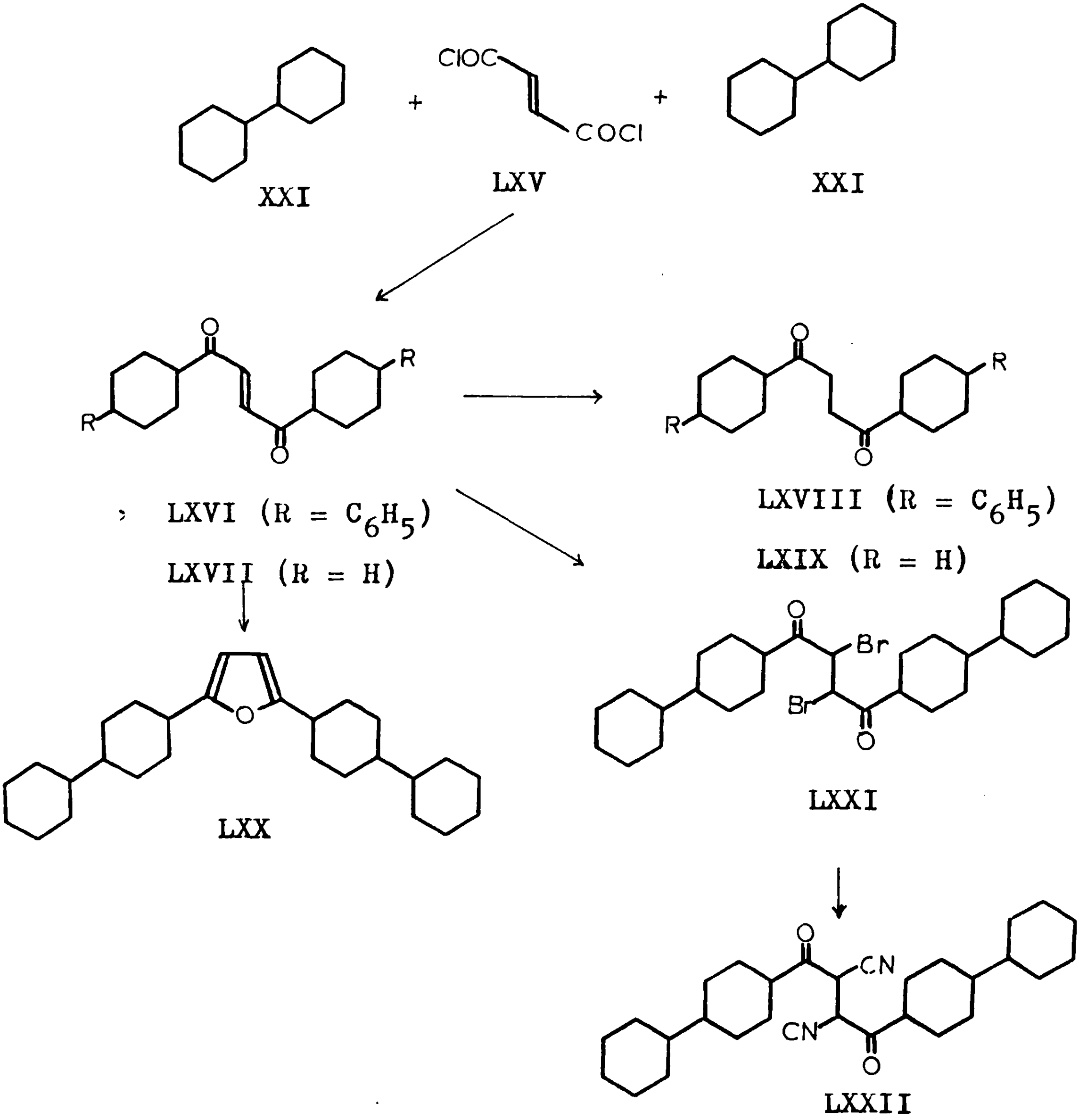
LXII (R = C_6H_5)

LXIV (R = H)

LXI

The infra-red values compared well with the parent compound (LIX) with ν_{max} = 1754, 1812 cm.$^{-1}$.[26] Although the ultra-violet spectrum could not be compared with that of (LIX), a suitable comparison could be made with the recently prepared related anhydride (LX), λ_{max}^{dioxan} = 2640(4·12), 3090(4·15), 4250(4·18).[27] Furthermore every precaution was taken to prevent cyclisation to a naphthalene derivative (LXI).[28]

The next step in the synthetic route was the cyclisation of the fulgenic acid (LVII) to the so-called diaquinone(LXII).[29] The unsubstituted acid (LXIII) could readily be cyclised with sulphuric acid[29,30] to the parent quinone (LXIV) whose ultra-violet spectrum has been reported by a variety of authors.[29,31,32] Marschalk's figures,[32] in which both solvent and intensities were reported seem most likely to be correct - $\lambda_{max}^{CHCl_3}$ = 270 (> 4·5), 435 (3·8), 455 (3·9), 490 (3·8). Ring closure of the disubstituted fulgenic acid (LVII) was not successful though a large variety of methods - polyphosphoric acid, liquid hydrogen fluoride, phosphorus pentoxide in refluxing xylene - were all tried. The only method which gave even an iota of success was the inverse acid-chloride method[33] from which was obtained a solution which showed $\lambda_{max}^{PhNO_2}$ = 463, 493, 528 (intensities unknown); these values showed a fairly constant bathochromic


ClOC
COCl
+
+
XXI
LXV
XXI
R
R
R
R
LXVI (R = C_6H_5)
LXVII (R = H)
LXVIII (R = C_6H_5)
LXIX (R = H)
O
LXX
Br
Br
LXXI
CN
CN
LXXII

shift from the parent diaquinone (LXIV). In order to repeat this type of ring closure under different conditions, more fulgenic acid (LVII) was required. Unfortunately, the double Stobbe condensation could not be repeated, even though a variety of condensing agents (e.g. sodium hydride, potassium t-butoxide),[24b] and the newest high temperature methods were tried.[27]

Since it was essential to obtain this hydrocarbon (IV) to complete the series, a new approach was tried. Friedel-Crafts reaction between fumaroyl chloride (LXV)[34] and biphenyl (XXI) yielded the well known diketone (LXVI).[35a,b] It was then proposed to reduce (LXVI) to the corresponding ethane derivative (LXVIII) followed by alkylation of the active methylene groups to obtain the required number of carbon atoms. Reduction of 2-ene-1.4-diones (LXVII) to 1.4-diones (LXIX) has been accomplished with alkaline dithionite[36] and tin amalgam.[37] Since the former used ethanol as solvent, in which (LXVI) was insoluble, the latter was tried, and instead of yielding the desired (LXVIII), ring closure took place to give a new 2.5-disubstituted furan (LXX).[38] An alternative method involved bromination of the double bond,[35a] followed by cyanide exchange,[39] and cyclisation.[40] The dibromo compound (LXXI) was successfully characterised, but attempts to cyclise the crude dicyano compound (LXXII) were hopeless, and this route too had to be abandoned.

EXPERIMENTAL

2.5-Di-(p-phenylbenzoyl)-benzene-1.4-dicarboxylic acid (XLa) and 2.4-Di-(p-phenylbenzoyl)-benzene-1.5-dicarboxylic acid(XLb)

To a solution of biphenyl (XXI) (35 g.) in tetrachloroethane (240 ml.), was added an intimate mixture of fused, powdered pyromellitic dianhydride (XXXIX) (23 g.) and aluminium chloride (81 g.). The resulting dark green suspension was heated at 50 - 60° for four hours, and then decomposed by pouring on to excess dilute hydrochloric acid Xylene (240 ml.) was added to make the organic layer less viscous, and the precipitated acids (XL) were filtered off and dried. The crude reaction product was dissolved in aqueous ammonia, any base-insoluble material filtered off, excess concentrated hydrochloric acid added to precipitate the acid mixture which was filtered, washed with hot water and dried. Crystallisation from nitrobenzene yielded almost colourless prisms of (XLa, b) (32 g.), m.pt. 359-363°. The acid mixture gave a dark green colour with concentrated sulphuric acid.

Found C = 77·61%, H = 4·39%

$C_{34}H_{22}O_6$ requires C = 77·55%, H = 4·21%.

2.9-Diphenylpentacene-5.14,7.12-diquinone (XLIa)

To the mixed acids (XLa, b) (30 g.) in a melt of phthalic anhydride (280 g.) was added phosphorus pentoxide (40 g.); the pale yellow melt immediately turned dark green and gradually darkened over four hours reflux. The cooled, still mobile, melt was poured on to excess dilute sodium hydroxide, boiled to remove all the phthalic anhydride and the resulting suspension was filtered, washed with water, and dried to leave a greenish-brown residue of quinone (XLIa, b). This residue was dissolved in nitrobenzene (3 l.) and crystalline fractions were collected at the following volumes: 3 l.; 2 l.; 1 l. No further crystalline material was then obtained till the volume was reduced to 250 ml. The three crystalline fractions were then recrystallised repeatedly from nitrobenzene as fine, bright yellow needles of 2.9-diphenylpentacene-5.14,7.12-diquinone (XLIa) (7·5 g.) m.pt. 380-381°. (XLIa) gave a violet colour with concentrated sulphuric acid, and a transient violet changing to brownish-yellow vat with alkaline dithionite.

Found C = 83·20%, H = 3·64%

$C_{34}H_{18}O_4$ requires C = 83·25%, H = 3·70%.

2.9-Diphenyl-6.13-dihydropentacene (XLIIa) and 2.9-Diphenyl-5.14-dihydropentacene (XLIIb).

Finely powdered 2.9-diphenylpentacene-5.14,7.12-diquinone (XLIa) (4·5 g.) and copper-activated zinc dust (45 g.) were refluxed in sodium hydroxide (5%, 450 ml.) for eight hours. The hot suspension was rapidly filtered to give a light grey residue and a filtrate which turned green. The residue was treated with concentrated hydrochloric acid to remove the excess zinc dust, and the solid remaining was filtered off, washed with dilute ammonia and dried. (XLIIa,b) were crystallised from xylene as light tan-coloured crystals (3·5 g.) m.pt. 292-297°. The dihydro isomers sublimed readily and gave a golden-brown colour on warming with concentrated sulphuric acid. The UV-spectrum is shown in figure 8.

Found C = 94·14%, H = 5·44%

$C_{34}H_{24}$ requires C = 94·40%, H = 5·60%.

2.9-Diphenylpentacene (IV)

The dihydro isomers (XLIIa, b) (1 g.) were dissolved in nitrobenzene (20 ml.). Phenanthroquinone (0·5 g.) was added and the solution heated for twenty seconds till the violet colour of (IV) was visible. The solution was allowed to cool slowly in the absence of light, and when cool, the violet precipitate was filtered off, washed with benzene and dried to give crude diphenylpentacene. Sublimation (280-300°/·005 mm.) under carbon dioxide yielded the pure compound as purple-blue platelets (0·6 g.) m.pt. 394-395°. (IV) gave a golden-brown colour on warming with sulphuric acid. The UV-spectrum is shown in figure 4.

Found C = 94·69%, H = 5·48%

$C_{34}H_{22}$ requires C = 94·84%, H = 5·16%.

2-Benzoyl-5-(p-phenylbenzoyl)-benzene-1.4-dicarboxylic acid (XLIVa) and 2-Benzoyl-4-(p-phenylbenzoyl)-benzene-1.5-dicarboxylic acid (XLIVb).

An intimate mixture of freshly prepared benzophenone-2.4.5-tricarboxylic acid-4.5-anhydride (XLIII) (60 g.)[18] and aluminium chloride (81 g.) was added to a solution of biphenyl (XXI) (31 g.) in tetrachloroethane(400ml.).

The dark green suspension was warmed at 70-80° for three hours, and then decomposed by pouring on to excess dilute hydrochloric acid. Steam distillation removed the tetrachloroethane, and the excess water was decanted off. The greasy reaction product was triturated with xylene, filtered, washed with benzene and dried. The crude reaction product was then dissolved in aqueous ammonia, any base-insoluble material removed by filtration, excess concentrated hydrochloric acid added to precipitate the acid mixture, which was filtered, washed with hot water, and dried. Crystallisation from nitrobenzene yielded cream-coloured prisms of (XLIVa, XLIVb) (56 g.), m.pt. 320-323°. The dicarboxylic acids gave an immediate dark green colour with concentrated sulphuric acid.

Found C = 74·74%, H = 4·16%

$C_{28}H_{16}O_6$ requires C = 74·66%, H = 4·03%.

2-Phenylpentacene-5.14,7.12-diquinone (XLV).

To the mixed acids (XLIVa, b) (27 g.) in a melt of phthalic anhydride (250 g.) was added phosphorus pentoxide (30 g.); the yellowish melt immediately turned green and gradually darkened over four hours reflux. The cooled melt was poured on to excess dilute sodium hydroxide, boiled to dissolve the phthalic anhydride and the resulting suspension was filtered, washed with water and dried. Crystallisation from xylene gave orange-yellow prisms of 2-phenylpentacene-5.14,7.12-diquinone (XLV), (13·5 g.) m.pt. 340-341°. (XLV) gave a violet colour with concentrated sulphuric acid, and a violet changing to red vat with alkaline dithionite.

Found C = 81·15%, H = 3·26%

$C_{28}H_{14}O_4$ requires C = 81·15%, H = 3·40%.

2-Phenyl-6.13-dihydropentacene (XLVIa), 2-Phenyl-7.12-dihydropentacene (XLVIb) and 2-Phenyl-5.14-dihydropentacene (XLVIc)

Finely powdered 2-phenylpentacene-5.14,7.12-diquinone (XLV) (2 g.) and copper activated zinc dust (20 g.) were refluxed in sodium hydroxide (5%, 200 ml.) for seven hours. The hot suspension was filtered,and the residue treated with concentrated hydrochloric acid to remove the excess zinc dust. The remaining solid was filtered off, washed with dilute ammonia and dried. (XLVIa, b, c) were crystallised from xylene as tan-coloured crystals (1·4 g.) m.pt. 243-247°. A red, becoming brown colour was obtained with concentrated sulphuric acid. The UV-spectrum is shown in figure 9.

Found C = 94·04%, H = 5·85%

$C_{28}H_{20}$ requires C = 94·34%, H = 5·66%.

2-Phenylpentacene (III).

The mixed dihydro compounds (XLVIa, b, c) (1 g.) were dissolved in nitrobenzene (20 ml.). Phenanthroquinone (0·5 g.) was added and the solution was boiled till the violet pentacene colour was observed. The solution was allowed to cool in the absence of light, the violet precipitate filtered off, washed with benzene and dried. Sublimation (280-290°/·001 mm.) under carbon dioxide gave pure purple-blue platelets of 2-phenylpentacene (III) (0.5 g) m.pt. 365-366°. (III) gave a violet, turning to brown colour in concentrated sulphuric acid. The UV-spectrum is shown in figure 4.

Found C = 94·61%, H = 4·99%

$C_{28}H_{18}$ requires C = 94·88%, H = 5·12%.

3-(p-Phenylbenzoyl)-2-naphthoic acid (XLVIII).

An intimate mixture of freshly fused, powdered naphthalene-2.3-dicarboxylic acid anhydride (XLVII) (20 g.) and aluminium chloride (40 g.) was added to a solution of biphenyl (XXI) (15·4 g.) in tetrachloroethane (150 ml.). The deep green suspension was held at 60-65° for ninety minutes, and then decomposed with dilute hydrochloric acid.

Steam distillation removed the tetrachloroethane, and on standing overnight the oily keto-acid hardened to a waxy solid. The aqueous solution was decanted, the solid dissolved in aqueous ammonia, any base-insoluble material filtered off, and excess concentrated hydrochloric acid added to the chilled basic solution whereby (XLVIII) was precipitated as a pale yellow voluminous precipitate. Crystallisation from glacial acetic acid yielded glittering prisms of 3-(p-phenylbenzoyl)-2-naphthoic acid (XLVIII) (30 g.) m.pt. 205-206°. The acid gave a transient green colour in concentrated sulphuric acid which changed to red-violet almost immediately, and then to red on standing.

Found $C = 81{\cdot}70\%$, $H = 4{\cdot}58\%$

$C_{24}H_{16}O_3$ requires $C = 81{\cdot}80\%$, $H = 4{\cdot}58\%$.

Attempted Cyclisation with Sulphuric Acid/Benzoyl Chloride.

3-(p-Phenylbenzoyl)-2-naphthoic acid (XLVIII) (10 g.) and concentrated sulphuric acid (2 drops) in benzoyl chloride (25 ml.) were refluxed for thirty minutes. On the addition of glacial acetic acid (50 ml.) a dark red precipitate was obtained, which was collected, washed with xylene and dried (500 mg.) m.pt. 225-230° (dec). This material showed a strong carbonyl absorption at 1770 cm.$^{-1}$ and could be decomposed to starting material (XLVIII) on boiling with water; this suggested it might be an ionic complex of the type shown (XLIX). The filtrate, on decomposition with water followed by the usual work up gave starting material (9·1 g.).

2-Phenyltetracene-5.12-quinone (L).

To 3-(p-phenylbenzoyl)-2-naphthoic acid (XLVIII) (20 g.) in a melt of phthalic anhydride (150 g.) was added phosphorus pentoxide (8·5 g.); the yellow melt went almost black over the three hour refluxing period. The cooled melt was poured on to excess dilute sodium hydroxide, boiled to dissolve the phthalic anhydride, and the resulting suspension was filtered, washed with water, and dried. The greenish residue was extracted with xylene (2 x 1 l.), and this extract on concentration gave dark yellow crystals of quinone. Purification was accomplished by sublimation (200-210°/·002 mm.) to give pale yellow crystals of 2-phenyltetracene-5.12-quinone (L) (14 g.) m.pt. 244-247°. The quinone gave an ultramarine colour with concentrated sulphuric acid, and a yellow-green vat with alkaline dithionite.

Found C = 86·40%, H = 4·34%

$C_{24}H_{14}O_2$ requires C = 86·21%, H = 4·22%

2-Phenyltetracene (I).

To an intimate mixture of 2-phenyltetracene-5.12-quinone (L) (7 g.) and zinc dust (21 g.) in dry refluxing pyridine (200 ml.) was added water (3 drops). The original yellow-green colour rapidly changed - maroon, brown, green, and finally to yellow-green. Acetic acid (90%, 100 ml.) was then added over a period of four hours during which time the solution became yellow and clear. The hot solution was filtered, and the yellow filtrate poured on to dilute acetic acid (500 ml.). The resulting precipitate was filtered, washed with water and dried (3 g.).

An intimate mixture of this solid and copper powder (6 g.) was heated under carbon dioxide at 300° for five minutes. Sublimation (180-195°/·001 mm.) gave a red-orange solid which crystallised from xylene as orange-red plates of 2-phenyltetracene (I) (230 mg.) m.pt. 257-259°. In concentrated sulphuric acid, (I) gave a reddish-violet turning to olive-green colouration. The UV-spectrum is shown in figure 3.

Found C = 94·45%, H = 5·42%

$C_{24}H_{16}$ requires C = 94·70%, H = 5·30%.

1-(p-Phenylbenzoyl)-2-methylnaphthalene (LIV).

2-Methyl-1-naphthoyl chloride (LIII) (30 g.)[22] in tetrachloroethane (50 ml.) was added dropwise over thirty minutes to a suspension of biphenyl (XXI) (23·2 g.) and aluminium chloride (50 g.) in tetrachloroethane (100 ml.). The reaction mixture was kept at 70-75° for one hour, and then decomposed with dilute hydrochloric acid. Steam-distillation removed the organic solvent, and the oil remaining was dissolved in benzene, washed with aqueous sodium hydroxide, and water, and then dried over magnesium sulphate. Concentration of this solution failed to yield crystalline material and the solution had to be chromatographed on Grade I Neutral Alumina (750 g.). Elution with benzene gave a yellow solution which on concentration gave a pale yellow solid m.pt. 105-108°. Recrystallisation from methanol gave colourless prisms of 1-(p-phenylbenzoyl)-2-methylnaphthalene (LIV) (7·5 g.) m.pt. 109-110° (lit. 109-110°).[21] (LIV) gave a cherry-red colour with concentrated sulphuric acid, identical with the original material.[21] Further elution (50% ether/benzene) yielded on concentration golden crystals of a by-product; these were recrystallised from benzene as gleaming colourless plates m.pt. 237-239°. Colour in sulphuric acid: yellow. These were not further investigated.

9-Phenyltetraphene (V).

1-(p-Phenylbenzoyl)-2-methylnaphthalene (LIV) (6 g.) was dissolved in dry xylene (50 ml.). The xylene was distilled off, and the dark coloured residue heated at 420-425° for five minutes under carbon dioxide. On cooling, the black mass was thoroughly extracted with xylene and the concentrated extract chromatographed on Grade I Alumina (150 g.). Elution with benzene gave an orange solution with a green fluorescence. The eluate was evaporated to dryness and the solid repeatedly crystallised from ethyl acetate as pale yellow leaflets of 9-phenyltetraphene (V) (254 mg.) m.pt. 238-240° (lit. 240-241°).[21] In sulphuric acid, the following colour changes were observed: crimson to purple to blue on standing. The UV-spectrum is shown in figure 7.

Found	C = 94·41%, H = 5·56%
$C_{24}H_{16}$ requires	C = 94·70%, H = 5·30%.

2.3-Di-(p-biphenyl)-fulgenic acid (LVII) and 2.3-Di-(p-biphenyl)-fulgide (LVIII).

To a chilled suspension (dry cold/carbon tetrachloride bath) of alcohol - free sodium ethoxide, prepared from sodium (2·53 g.) and absolute alcohol (5·06 g.) in dry ether (75 ml.) was added, with vigorous stirring over thirty minutes, p-phenylbenzaldehyde (LV) (20 g.)[15] and freshly distilled diethyl succinate (LVI) (9·57 g.) in dry ether (150 ml.). The mixture was stirred at -15° for three days and then for a further three days at room temperature. During the addition, a yellow suspension was obtained, which darkened to red-orange over the remaining reaction time. Water (250 ml.) was then added, and the suspended material dissolved. Acidification of the aqueous layer gave a red-orange oil which solidified on standing, and was collected by filtration. Repeated crystallisation of this material from glacial acetic acid eventually gave colourless needles or prisms of 2.3-di-(p-biphenyl)-fulgenic acid (LVII) (10·5 g.) m.pt. 180-183°, $\nu_{max}^{KBr} = 1682$ cm.$^{-1}$ (C=O). The colour in concentrated sulphuric acid was yellow-green.

Dicarboxylic acid (LVII) (1·75 g.) was refluxed in acetic anhydride (20 ml.) for thirty minutes, the solution concentrated to small volume and allowed to cool. Golden-brown glistening crystals of the anhydride were obtained, which crystallised as large orange prisms of 2.3-di-(p-biphenyl)-fulgide (LVIII) (1·25 g.) m.pt. 200-201°, ν_{max}^{KBr} = 1762, 1819 cm.$^{-1}$ (O=C-O-C=O) and λ_{max}^{dioxan} = 2570(4·26), 2640(4·28), 3100(4·47), 4040(3·96). (LVIII) gave a yellow turning to green colour in concentrated sulphuric acid.

Found C = 84·45%, H = 4·65%

$C_{30}H_{20}O_3$ requires C = 84·09%, H = 4·70%.

All attempts to repeat this reaction failed. Even when different condensing agents[24b] and different reaction conditions[27] were tried, successful isolation of (LVII) or (LVIII) was never accomplished.

Attempted Cyclisations of 2.3-Di-(p-biphenyl)-fulgenic acid (LVII).

1) With polyphosphoric acid. (LVII) (1 g.) was warmed on a steam bath with polyphosphoric acid (50 ml.) for one hour. No colour developed and starting material was obtained on dilution with water.

2) With hydrogen fluoride. (LVII) (1 g.) was dissolved in anhydrous hydrogen fluoride. An immediate

purple colour developed which darkened on standing overnight. This solution, when poured on to ice gave a yellow solid, identified as impure starting material.

3) With phosphorus pentoxide. (LVII) (1 g.) was dissolved in refluxing xylene (25 ml.) and phosphorus pentoxide (3 g.) was added. After ten minutes refluxing the black solution was poured on to water. No recognisable product was isolated.

2.8-Diphenyltetracene-6.12-quinone (LXII).

2.3-Di-(p-biphenyl)-fulgenic acid (LVII) (3 g.), phosphorus pentachloride (3 g.) and dry benzene (50 ml.) were refluxed together for one hour, by which time all evolution of hydrogen chloride had ceased. The pale yellow solution was evaporated to dryness, dry benzene (50 ml.) added and the solvent removed under reduced pressure; this last procedure was repeated until all traces of phosphorus oxychloride had been removed. The acid chloride was then dissolved in tetrachloroethane (25 ml.), transferred to a dropping funnel, and added slowly to a stirred ice-cold suspension of aluminium chloride (2·5 g.) in tetrachloroethane (50 ml.). The dark green complex was stirred for twelve hours. A small portion was removed, and worked up in the usual fashion - no trace of ring closed material was found. To try and force cyclisation, the solution was warmed for four hours at 75-80°C. Decomposition with dilute hydrochloric acid, followed by steam distillation to remove tetrachloroethane left a reddish-brown solid, which was collected by filtration, and washed thoroughly with dilute sodium hydroxide, which dissolved the greater part of the residue. What remained was dissolved in nitrobenzene and showed $\lambda_{max}^{PhNO_2} = 463, 493, 528$; these absorption maxima probably belong to 2.8-diphenyltetracene-6.12-quinone (LXII) .

Reduction of Trans-di-(p-phenylbenzoyl)-ethylene (LXVI).

To a refluxing solution of trans-di-(p-phenylbenzoyl)-ethylene (LXVI) (4 g.)[35a,b] and tin amalgam (10 g.)[37] in acetic acid (500 ml.) was added concentrated hydrochloric acid (20 ml.). After thirty minutes, the solution had appreciably lightened; it was filtered, and the acetic acid was removed under vacuum. Crystallisation from xylene gave not the substituted ethane (LXVIII), but beautiful plates of pale yellow 2.5-di-(p-biphenyl)-furan (LXX) (3·7 g.) m.pt. 276-278°, $\lambda_{max}^{dioxan} = 2720(4{\cdot}32), 3560(4{\cdot}79)$.[41] The colour obtained in concentrated sulphuric acid was red-violet on warming.

Found C = 90·28%, H = 5·78%

$C_{28}H_{20}O$ requires C = 90·29%, H = 5·42%.

Sym-di-(p-phenylbenzoyl)-dibromoethane (LXXI).

Bromine (1·5 ml.) in chloroform (50 ml.) was added to a refluxing solution of trans-di-(p-phenylbenzoyl)-ethylene (LXVI) (10 g.) in chloroform (1000 ml.). The solution was refluxed for one hour to ensure complete addition of the bromine. Chloroform (750 ml.) was distilled off, and the resulting solution allowed to stand overnight; crystals of (LXXI) were obtained, filtered off, and dried. Crystallisation from chloroform yielded colourless needles of sym-di-(p - phenylbenzoyl)-dibromoethane (LXXI) (6 g.) m.pt. 244° dec. (lit. 218°).[35a] (LXXI) did not dissolve in concentrated sulphuric acid. Concentration of the mother liquors, followed by the addition of methylene chloride yielded a further portion of (LXXI) (5·5 g.).

Found C = 61·52%, H = 3·81%

$C_{28}H_{20}O_2Br_2$ requires C = 61·33%, H = 3·68%.

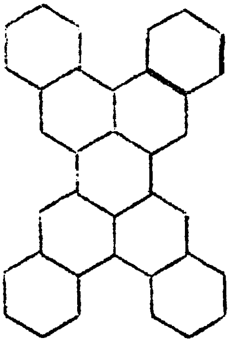
Sym-di-(p-phenylbenzoyl)-dicyanoethane (LXXII) and Attempted Cyclisation.

A finely powdered intimate mixture of the dibromo compound (LXXI) (3 g.) and copper cyanide (4 g.) was refluxed in dry pyridine (50 ml.) for three hours. The resulting dark brown solution was poured on to dilute hydrochloric acid (1000 ml.); this suspension was boiled to dissolve pyridine hydrochloride and any copper salts. The residue was removed by filtration, washed with water and dried. Recrystallisation from benzene/methanol gave pale yellow needles of sym-di-(p-phenylbenzoyl)-dicyanoethane (LXXII) (1·5 g.) m.pt. 229-231^{o} ν_{max}^{KBr} = 2555 cm.$^{-1}$ (C≡N).

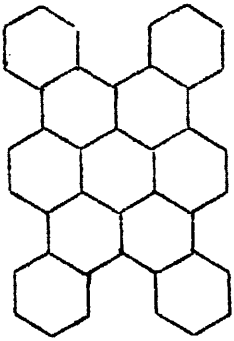
(LXXII) (250 mg.) was stirred with ice-cold concentrated sulphuric acid (2·5 ml.) for five minutes. The reddish-brown solution was then poured on to ice-water. The insoluble material was filtered off and on thorough examination no cyclised products could be recognised. Other attempts using lengthier times or higher temperatures invariably resulted in water-soluble sulphonated compounds.

CHAPTER 3.

2.3,4.5,8.9,10.11-TETRABENZOPERYLENE AND 1.2,3.4,7.8,9.10-TETRABENZOCORONENE.



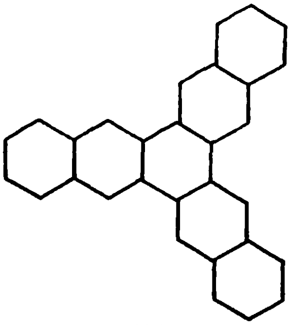
I



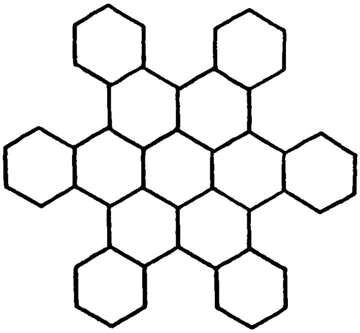
II

INTRODUCTION.

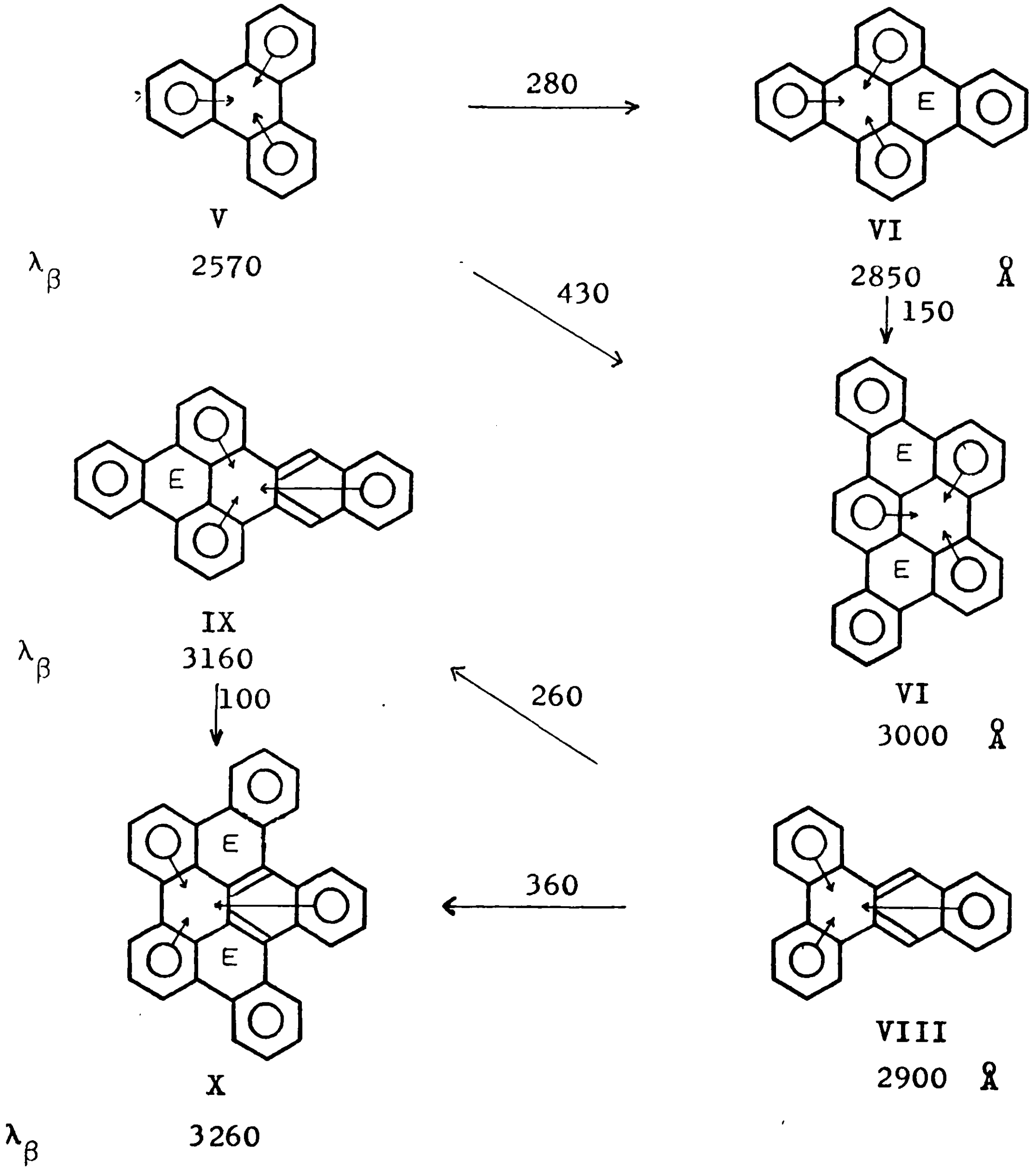
In discussing the absorption spectrum of 1.2,3.4,5.6,7.8,9.10,11.12-hexabenzocoronene (IV),[1a,b] this hydrocarbon was considered to have been built up from naphtho-(2'.3':6.7)-pentaphene (III) by the annellation of



III



IV

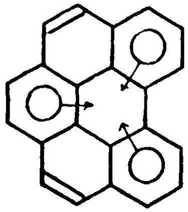


V
λ_β
2570
280
VI
2850 Å
430
150
IX
λ_β
3160
100
VI
3000 Å
260
360
X
λ_β
3260
VIII
2900 Å
E

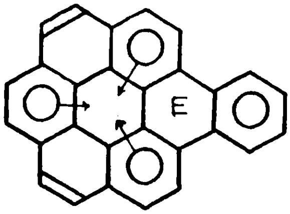
three o-phenylene complexes. It appeared equally possible that (IV) might be thought of as 2.3,4.5,8.9,10.11-tetrabenzoperylene (I) with the addition of two o-phenylene complexes and to examine this possibility, (I) has been synthesised. Easily obtained from (I) is 1.2,3.4,7.8,9.10-tetrabenzocoronene (II), an hitherto unknown benzologue of coronene.

DISCUSSION.

The addition of an o-phenylene complex to a polycyclic aromatic hydrocarbon is associated with one or other of two entirely different shifts. When triphenylene (V) is compared with 1.2,6.7-dibenzopyrene (VI) and 1.2,3.4-dibenzanthracene (VIII) with 1.2-benzonaphtho-(2".3":6.7)-pyrene (IX), the bathochromic shifts involved are 280 Å and 260 Å respectively. A somewhat smaller red shift of 170 Å is recorded when 1.12-benzoperylene (XI) is o-phenylated to 1.2-benzocoronene (XII). These are typical examples of o-phenylation in which the observed shift is due entirely to the formation of single bonds, the new benzenoid ring taking no part in the conjugation present in the hydrocarbon.

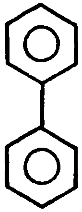


→

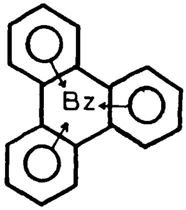


XI **XII**

λ_β 3030 $\xrightarrow{170}$ 3200 Å

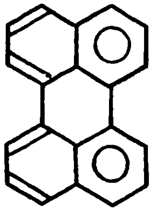


→

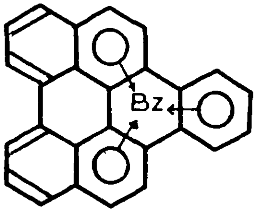


XIII **V**

λ_β 1980 $\xrightarrow{590}$ 2570 Å



→

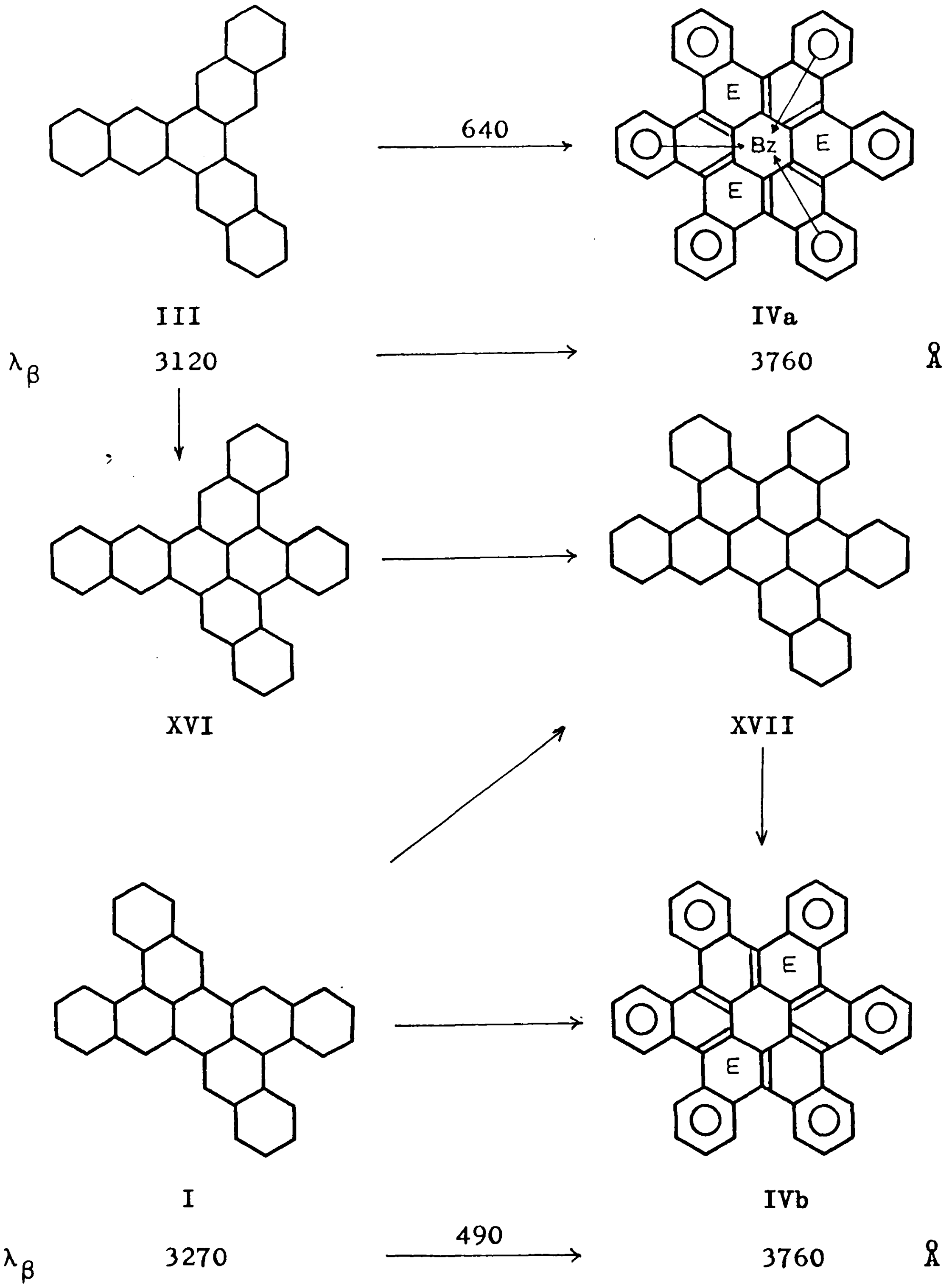


XIV **XV**

λ_β 2510 $\xrightarrow{595}$ 3105 Å

In complete contrast is the shift observed in a 'benzenogenic annellation'.[2] In passing from biphenyl (XIII) to triphenylene (V) and from perylene (XIV) to 1.12-o-phenylene-perylene (XV), bathochromic shifts of 595 Å and 590 Å are found. This figure exceeds by far the value for single bonds and can only be explained by the fact that an induced benzenoid ring (Bz) has been formed. The difference in value between the shift associated with single bonds and that connected with a 'benzenogenic annellation' is so great that it is not possible to confuse the two. Consequently it is possible to say whether the annellation of a hydrocarbon has taken place with or without the formation of an induced sextet from the magnitude of the annellation effect.

The experimentally found red shift for the tri-o-phenylation of naphtho-(2'.3':6.7)-pentaphene (III) to give 1.2,3.4,5.6,7.8,9.10,11.12-hexabenzocoronene (IV) is 640 Å.[1a,b] If an equal contribution from each annellation is assumed, the value for a single o-phenylation is 213 Å. An apparently very similar picture can be drawn when the di-o-phenylation of 2.3,4.5,8.9,10.11-tetrabenzoperylene (I) (figure 1) to give 1.2,3.4,5.6,7.8,9.10,11.12-hexabenzocoronene (IV) is considered; the shift found is 490 Å and,


640
E
Bz
E
E
III
IVa
λ_β
3120
3760
Å
XVI
XVII
I
IVb
E
E
λ_β
3270
490
3760
Å

again assuming equal contributions, the value for a single o-phenylation has increased slightly to 245 Å; both values, nevertheless, lie well within the range associated with single bonds only. However, closer examination of hexabenzocoronene (IVa, IVb) is merited. In (IVa), the hydrocarbon appears to have three empty (E) rings, and a central ring with induced benzenoid (Bz) character; on the other hand, in (IVb) hexabenzocoronene has two empty (E) rings and a central ring with no induced benzenoid character. This anomaly can be resolved to a certain extent since the possibly unwarranted assumption, that each o-phenylation contributes an equal amount to the shift of the β-bands, has been made. In the much simpler systems (V → VI → VII) and (VIII → IX → X), the second o-phenylation does induce a much smaller red shift, but this decrease on di- or tri-o-phenylation need not necessarily apply in the 'synthesis' of 1.2,3.4,5.6,7.8,9.10,11.12-hexabenzocoronene (IV); this point cannot be fully resolved until all the appropriate hydrocarbons (XVI, XVII) have been synthesised.

The whole ultra-violet spectrum of sterically overcrowded molecules is affected in a characteristic way; comparison of 2.3,4.5,8.9,10.11-tetrabenzoperylene (I) with the closely related 2.3,8.9-dibenzoperylene (XVIII) (figure 1)

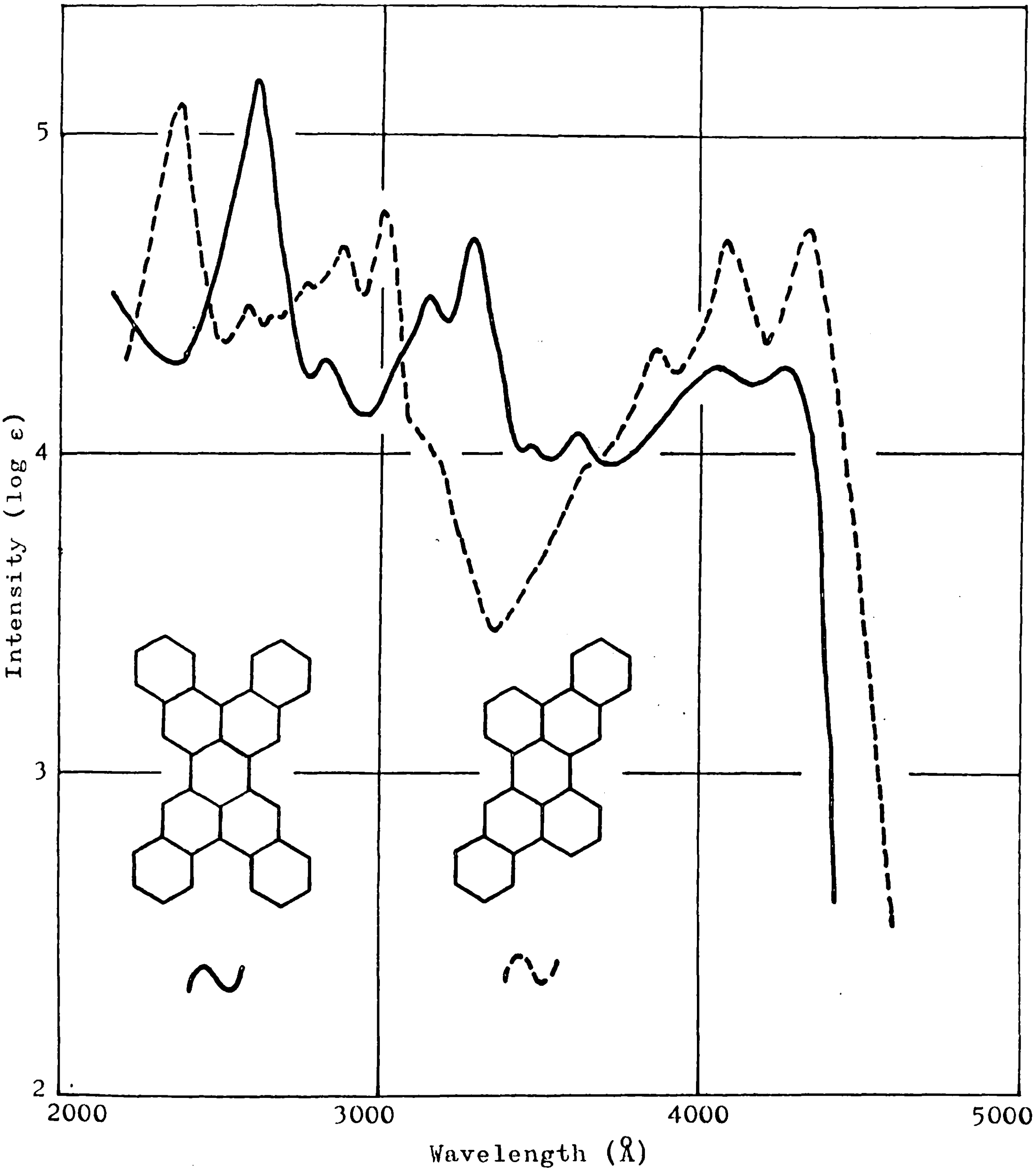
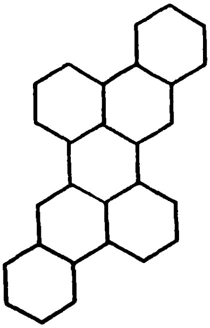
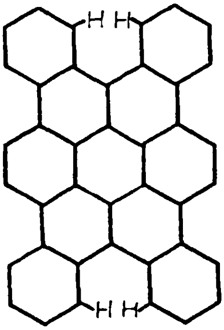


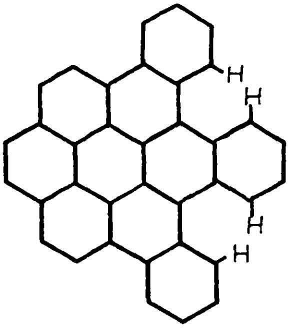
Figure 1. Absorption maxima (Å) and log ε (in parentheses).
2.3,4.5,8.9,10.11-Tetrabenzoperylene in benzene: p, 4250 (4·28), 4040 (4·30), 3600 (4·07); β, 3270 (4·68), 3130 (4·51), 2860 (4·28); in cyclohexane, β', 2605 (5·16).
2.3,8.9-Dibenzoperylene in benzene: p, 4335 (4·71), 4080 (4·66), 3860 (4·32), 3655 (3·96); β, 3035 (4·77), 2910 (4·60); in cyclohexane, β, 2755 (4·52), 2575 (4·45); β', 2380 (5·08).



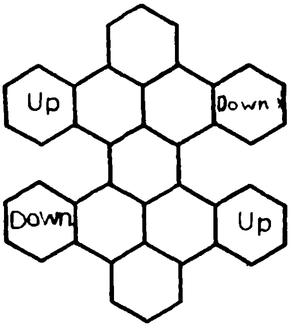
XVIII



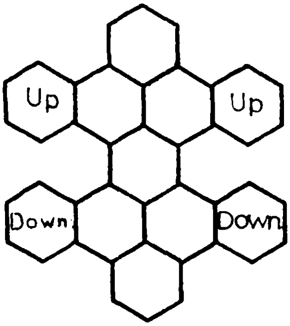
II



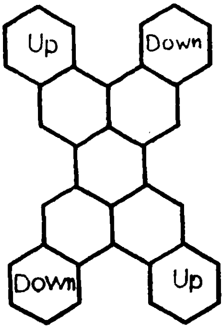
XIX



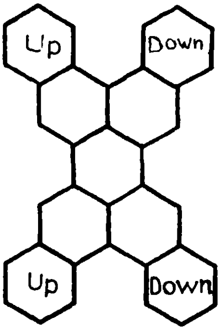
XXa



XXb



XXIa



XXIb

shows this particularly well. The steric hindrance brings about a general broadening of the bands and a hypochromic shift in the absorption maxima. Unfortunately the $\nu_\alpha:\nu_\beta$ ratio,[3] which gives a quantitative measurement of overcrowding, cannot be calculated since the α-bands are hidden by the stronger p-bands, as is typical of most perylenes. This ratio, however, can be calculated for 1.2,3.4,7.8,9.10-tetrabenzocoronene (II) (figure 2) - $\nu_\alpha:\nu_\beta = 1:1\cdot31_8$; this agrees extremely well with 1.2,3.4,5.6-tribenzocoronene (XIX)[4] - $\nu_\alpha:\nu_\beta = 1:1\cdot31_1$ - the steric strain in the two molecules would be expected to be virtually identical. In fact, the positions of the highest α- and β-band are almost superposable - 4660 Å and 3535 Å for (II) and 4640 Å and 3540 Å for (XIX). As anticipated this ratio drops to $1:1\cdot29_3$ for hexabenzocoronene (IV);[1a,b] all these figures should, of course, be compared with the ratio of 1:1·35 for planar hydrocarbons.[3] That the agreement between 1.2,3.4,7.8,9.10-tetrabenzocoronene (II) and 1.2,3.4,5.6-tribenzocoronene (XIX) is so good, is particularly satisfactory, since a previous claim has been made to the synthesis of tetrabenzocoronene.[5] Its ultra-violet spectrum (figure 3) is not atypical of a coronene homologue though the α-bands appear to be exceptionally intense. Also, the positions of the α- and β-

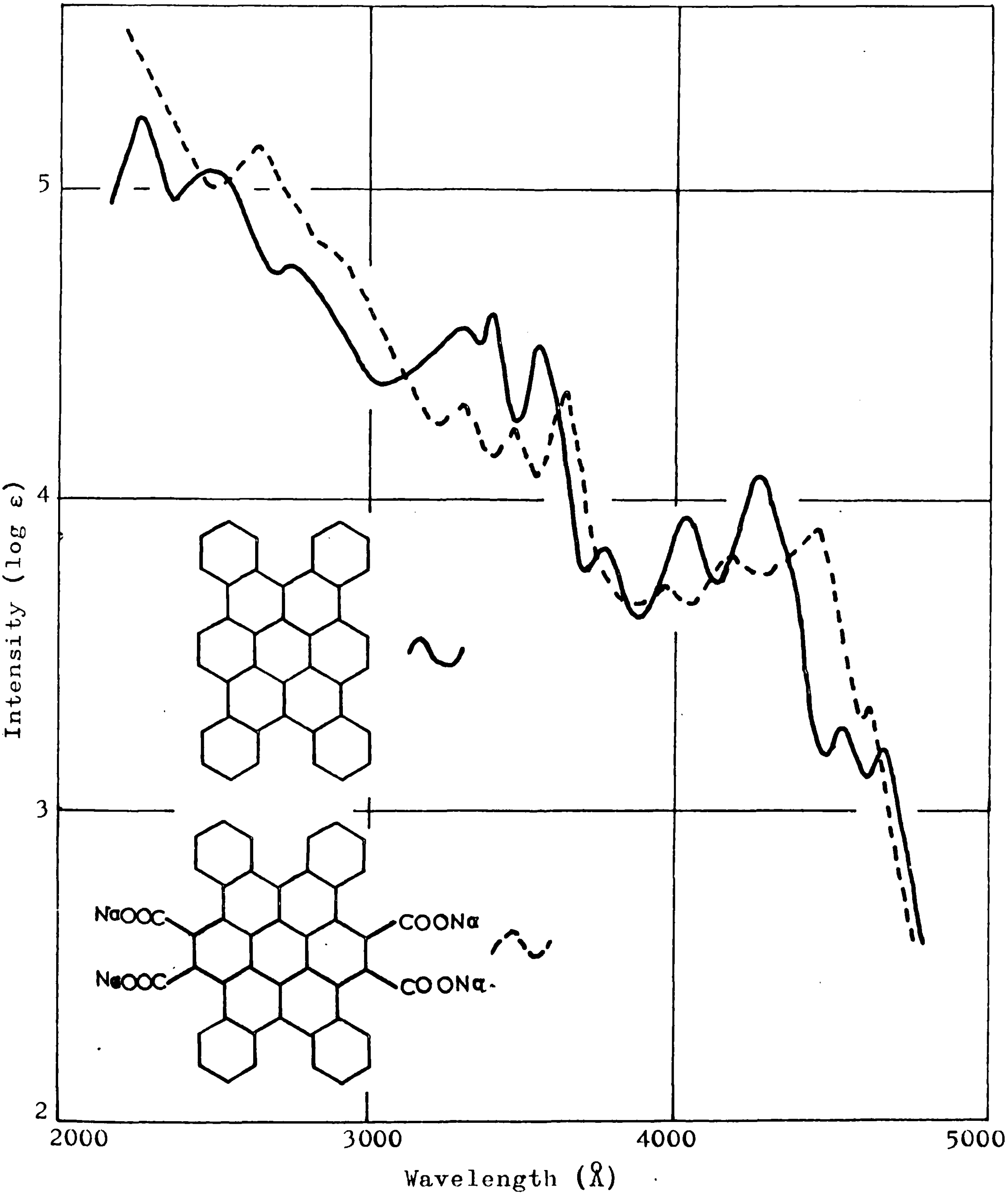


Figure 2. Absorption maxima (Å) and log ε (in parentheses). 1.2,3.4,7.8,9.10-Tetrabenzocoronene in trichlorobenzene: α, 4660 (3·48), 4535 (3·26); p, 4260 (4·07), 4020 (3·93), 3770 (3·83); β, 3535 (4·48), 3380 (4·58), 3300 (4·54); in cyclohexane, 2730 (4·75); β', 2475 (5·06), 2250 (5·23). Tetrasodium-1.2,3.4,7.8,9.10-tetrabenzocoronene-5.6,11.12-tettetracarboxylate in 50% ethanol: α, 4620 (3·34); p, 4440 (3·92) 414180 (3·84), 3965 (3·73); β, 3625 (4·35), 3450 (4·23), 328285 (4·31); β', 2630 (5·16).

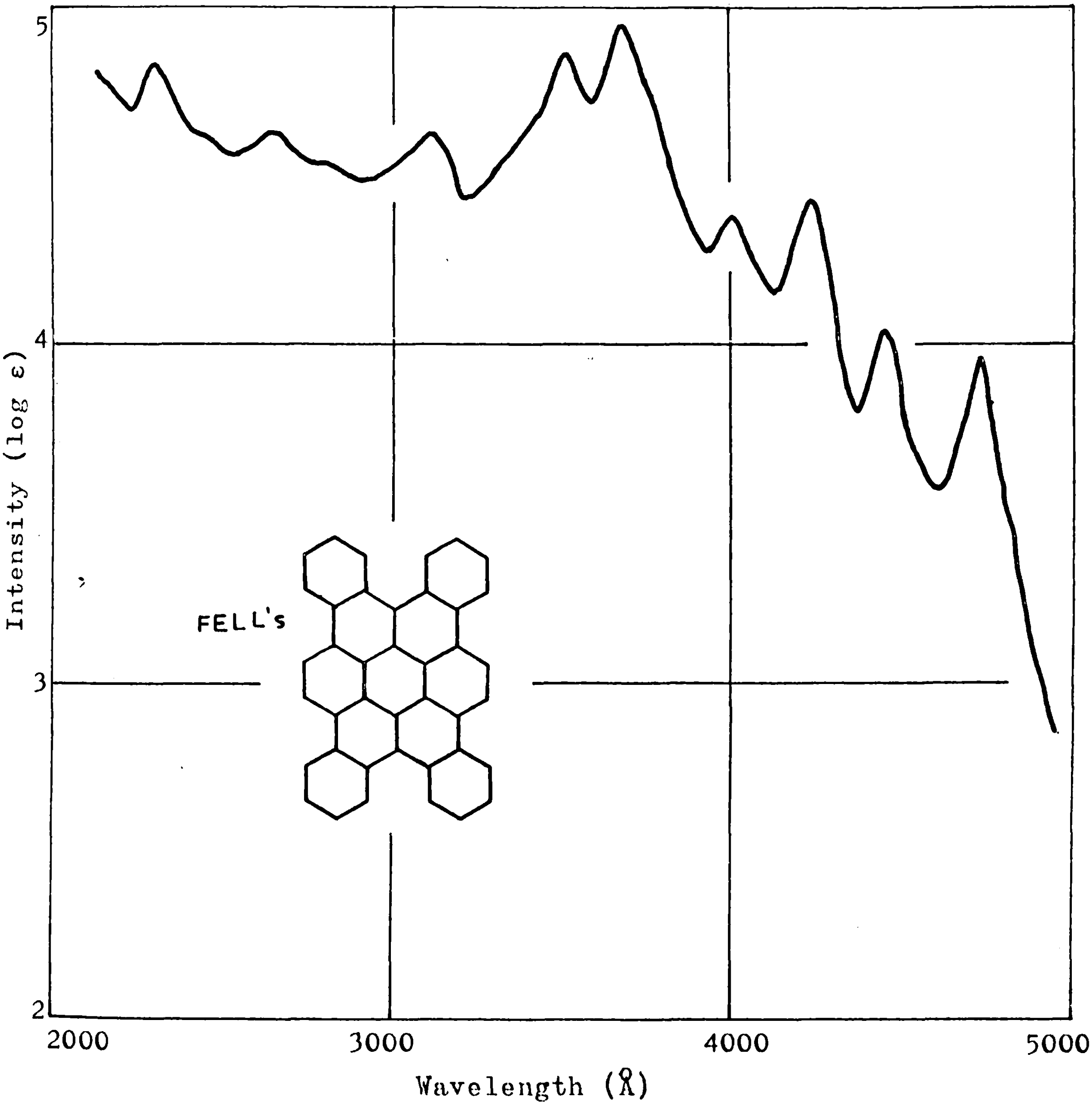
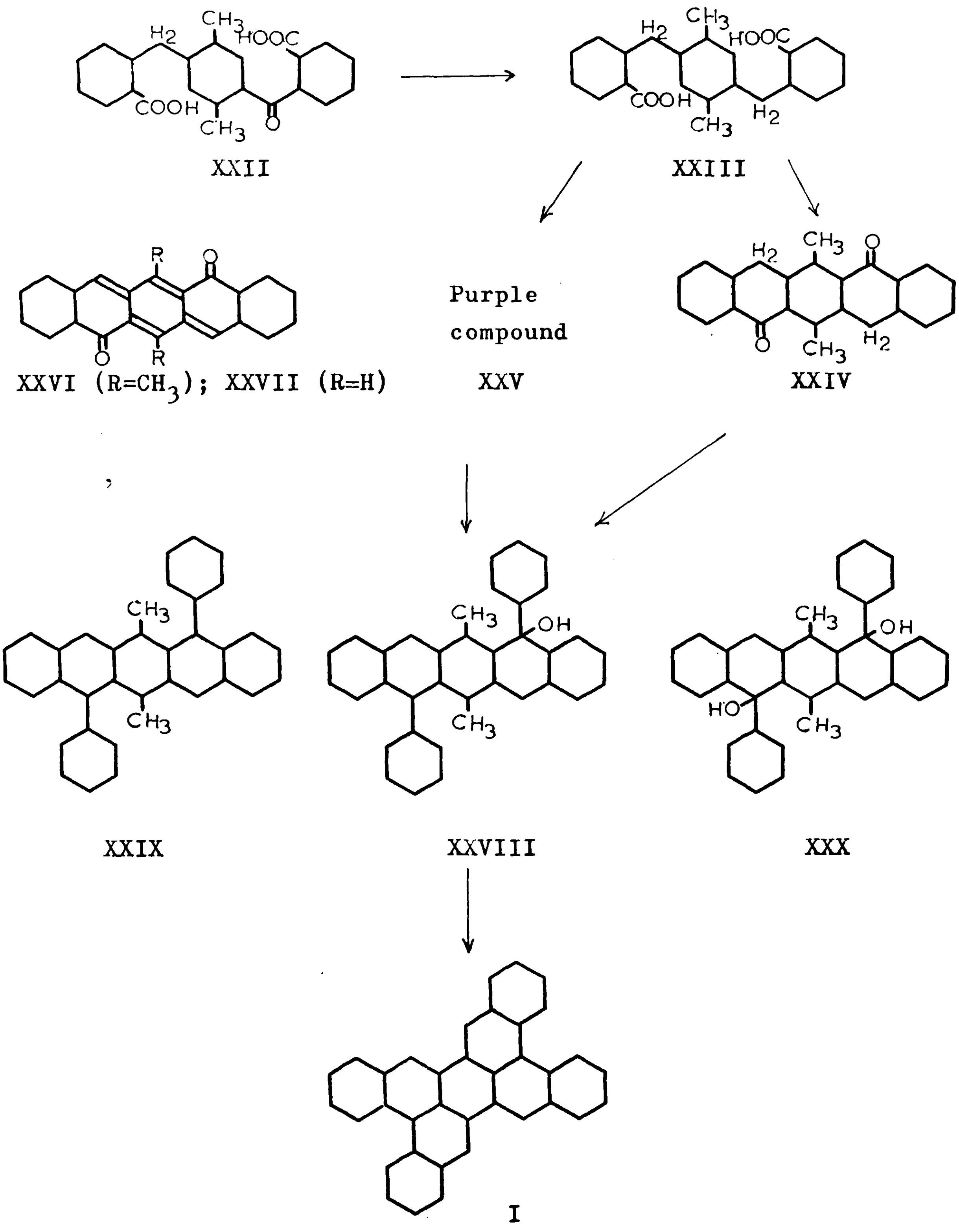


Figure 3. Absorption maxima (Å) and log ε (in parentheses). Fell's coronene in benzene: α, 4760 (3·96), 4460 (4·03); p, 4250 (4·42), 4000 (4·37); β, 3670 (4·94), 3515 (4·86), 3115 (4·63); in cyclohexane, β', 2640 (4·64), 2295 (4·83).

bands (4760 Å and 3670 Å) appear rather further to the red than expected and the ratio $\nu_\alpha:\nu_\beta = 1:1{\cdot}29_7$ seems surprisingly low.

This property of steric overcrowding[6] is a very interesting one, since it could be relieved in a variety of ways - variation in bond lengths, variation in bond angles, vertical movement of the overcrowded atoms only, or buckling of the entire molecule. X-ray crystallography has shown that the last concept is the correct one,[6] a result supported by theory.[7] In particular theoretical considerations of 4.5,6.7,11.12,13.14-tetrabenzoperopyrene (XX)[8] have shown that there are two possible structural isomers (XXa, XXb), of which (XXa) seems to be favoured on energy calculations. A similar situation exists in 2.3,4.5,8.9,10.11-tetrabenzoperylene (XXIa, XXIb), but, in this case, since the two regions of overcrowding are at opposite ends of the molecule, the two possible structures might have very similar energies. Experimentally, two different crystals of 2.3,4.5,8.9,10.11-tetrabenzoperylene (I) can be isolated - long yellow-green needles and shorter orange blades. Although the above explanation is a possibility, there is another more attractive one. Tanaka[9] has pointed out that perylene (XIV) exists in two different crystal modifications: an α-form

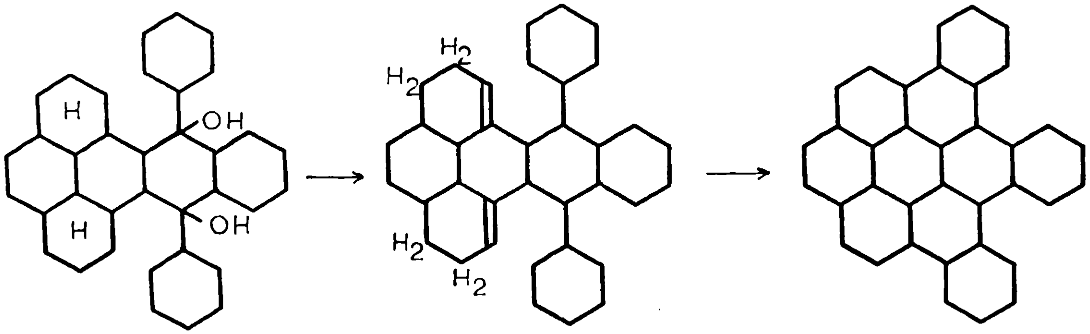

H2
CH3
HOOC
COOH
CH3
O
XXII
H2
CH3
HOOC
COOH
CH3
H2
XXIII
R
O
O
R
XXVI (R=CH3); XXVII (R=H)
Purple compound
XXV
H2
CH3
O
O
CH3
H2
XXIV
CH3
CH3
XXIX
CH3
OH
CH3
XXVIII
CH3
OH
HO
CH3
XXX
I

($a = 11{\cdot}35$, $b = 10{\cdot}87$, $c = 10{\cdot}31$ Å, $\beta = 100{\cdot}8^{\circ}$) and a β-form ($a = 11{\cdot}27$, $b = 5{\cdot}88$, $c = 9{\cdot}65$ Å, $\beta = 92{\cdot}1^{\circ}$); obviously the α-form is a 'dimer' crystal and the β-form a 'monomer'. Since 2.3,4.5,8.9,10.11-tetrabenzoperylene (I) has the same symmetry as perylene (XIV) itself, the two crystalline structures of (I) could correspond to 'monomer' and 'dimer' crystals.

EXPERIMENTAL DISCUSSION.

The keto-acid (XXII)[1a,b] was reduced to 1.4-di-(o-carboxybenzyl)-2.5-dimethylbenzene (XXIII) by zinc dust in dilute sodium hydroxide; the progress of the reaction was readily followed by the loss of carbonyl absorption at 1678 $cm.^{-1}$. Cyclisation of (XXIII) with refluxing phosphorus oxychloride yielded the double anthrone (XXIV) as orange-brown prisms in fairly good yield; however, if the cyclisation was carried out using the inverse acid chloride method,[10] beautiful reddish-purple needles of unknown structure (XXV) were obtained. It was initially thought that in the course of the latter cyclisation, the double anthrone (XXIV) had been dehydrated to the corresponding quinone (XXVI), which would be expected to have a deep colour due to its more highly conjugated chromophore. Comparison of the ultraviolet spectrum of (XXV) with that of the parent quinone (XXVII)[11] showed no close relationship, and this idea had to be shelved. That compounds (XXIV, XXV) were very closely related was shown by a number of facts - they had the same melting point and identical patterns in the fingerprint region of the infra-red, and both analysed for $C_{24}H_{18}O_2$. Although both showed parent molecular ions at 338 in the mass spectrum, the break-down patterns did differ; accurate analysis of these failed to give information of value. Also, the NMR spectra, obtained with some difficulty due to solubility problems, differed: the methyl region was identical, but at 6·3 τ, where (XXIV) correctly showed a methylene signal, (XXV) failed to show any absorption. These facts make it difficult to assume a classical equilibrium on the anthrone-anthranol pattern.

Both (XXIV) and (XXV) were treated with phenyl lithium. The absorption maxima of the reaction mixtures were identical; this constituted an important piece of evidence for the similarity of structure of (XXIV) and (XXV) since the spectra obtained are of the pentacene variety and are very susceptible to substitution differences. Work up of both reaction mixtures yielded the same mono-ol (XXVIII).

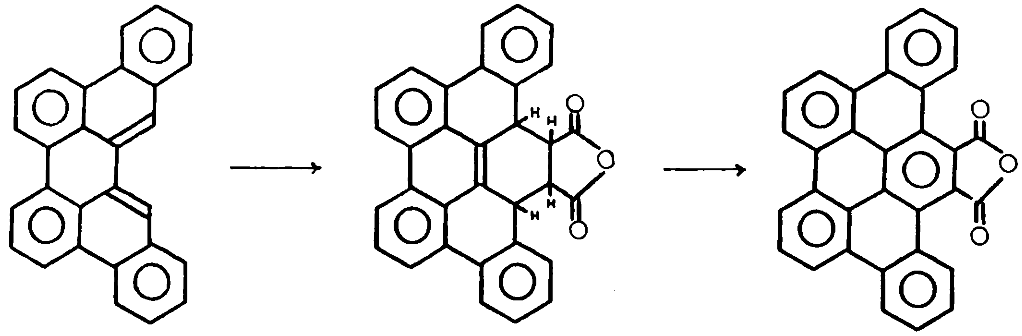


XXXII XXXIII XIX

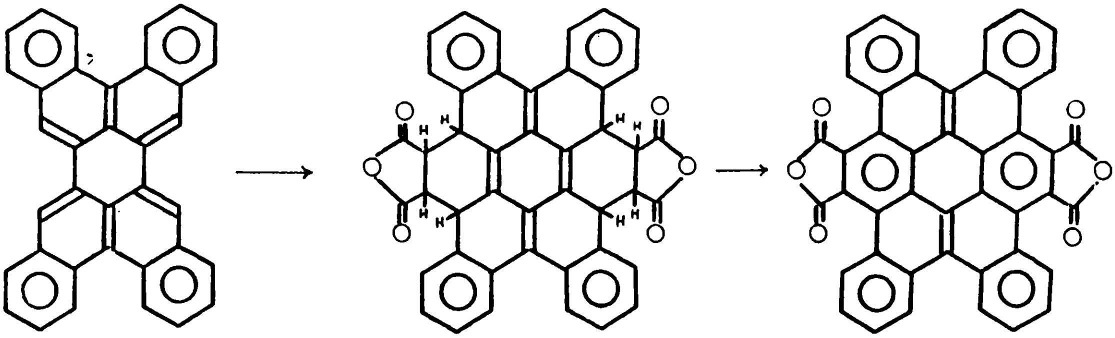
No trace of either the hydrocarbon (XXIX) or the diol (XXX) were found, although these were theoretically possible products from the reaction of phenyl lithium on the double anthrone.[12]

The initial step in the cyclodehydrogenation of this type of molecule has been shown to be the elimination of water (XXXII → XXXIII → XIX),[4] followed by cyclisation and dehydrogenation; now since (XXVIII) only contained one hydroxyl group, good yields of the cyclodehydrogenated product (I) could not be anticipated, and nor were they found. The two different crystal structures of 2.3,4.5,8.9,10.11-tetrabenzoperylene (I) have already been discussed.

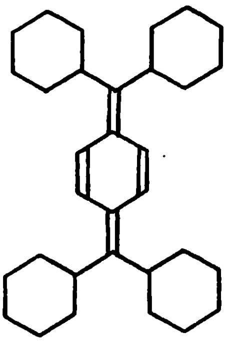
The reaction of maleic anhydride with 2.3,4.5,8.9, 10.11-tetrabenzoperylene (I) and with the closely related 2.3,10.11-dibenzoperylene (XXXIV) provided some interesting comparisons. (XXXIV), on refluxing in excess maleic anhydride, formed the hydrogenated adduct (XXXV) which dissociated in high boiling solvents. Addition of chloranil immediately dehydrogenated (XXXV) to give the fully aromatic adduct (XXXVI). No signs of any di-addition product were found.[13] Tetrabenzoperylene (I), on refluxing in maleic anhydride, slowly dissolved - no adduct (XXXVII) separated, but on the addition of chloranil, dark red plates of the fully



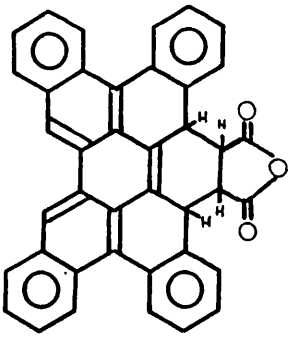
XXXIV XXXV XXXVI



I XXXVII XXXVIII



XXXIX



XL

aromatic adduct (XXXVIII) crystallised. That a di- and not a mono-adduct was formed can readily be appreciated if the ultra-violet spectrum of the solution be inspected before the addition of chloranil. It showed only one broad maximum at 331 mμ (~ 4·0), typical of a highly alkylated benzoquinone-bis-diphenylmethide (XXXIX) (figure 4),[14] and not the complicated spectrum of an alkyl pentaphene which would be obtained from the mono-adduct (XL). The fully aromatic adduct (XXXVIII) showed the expected close relationship to the parent hydrocarbon in its absorption spectrum (figure 2). An interesting new theoretical treatment of the 'dienophilicity' of polycyclic aromatic hydrocarbons[15] has shown that 2.3,10.11-dibenzoperylene (XXXIV) would be expected to add only one molecule of maleic anhydride; tetrabenzoperylene (I) was unfortunately not considered in this work.

The fully aromatic di-adduct (XXXVIII) could only be decarboxylated to 1.2,3.4,7.8,9.10-tetrabenzocoronene (II) with soda-lime, and even then only in exceptionally poor yields, so low in fact that enough material for an analytical sample could not be obtained. The mass spectrum showed, however, the parent ion and base peak at 500, confirming the structure. Earlier material, claimed to be tetrabenzocoronene (II)[5] was subjected to mass spectral analysis

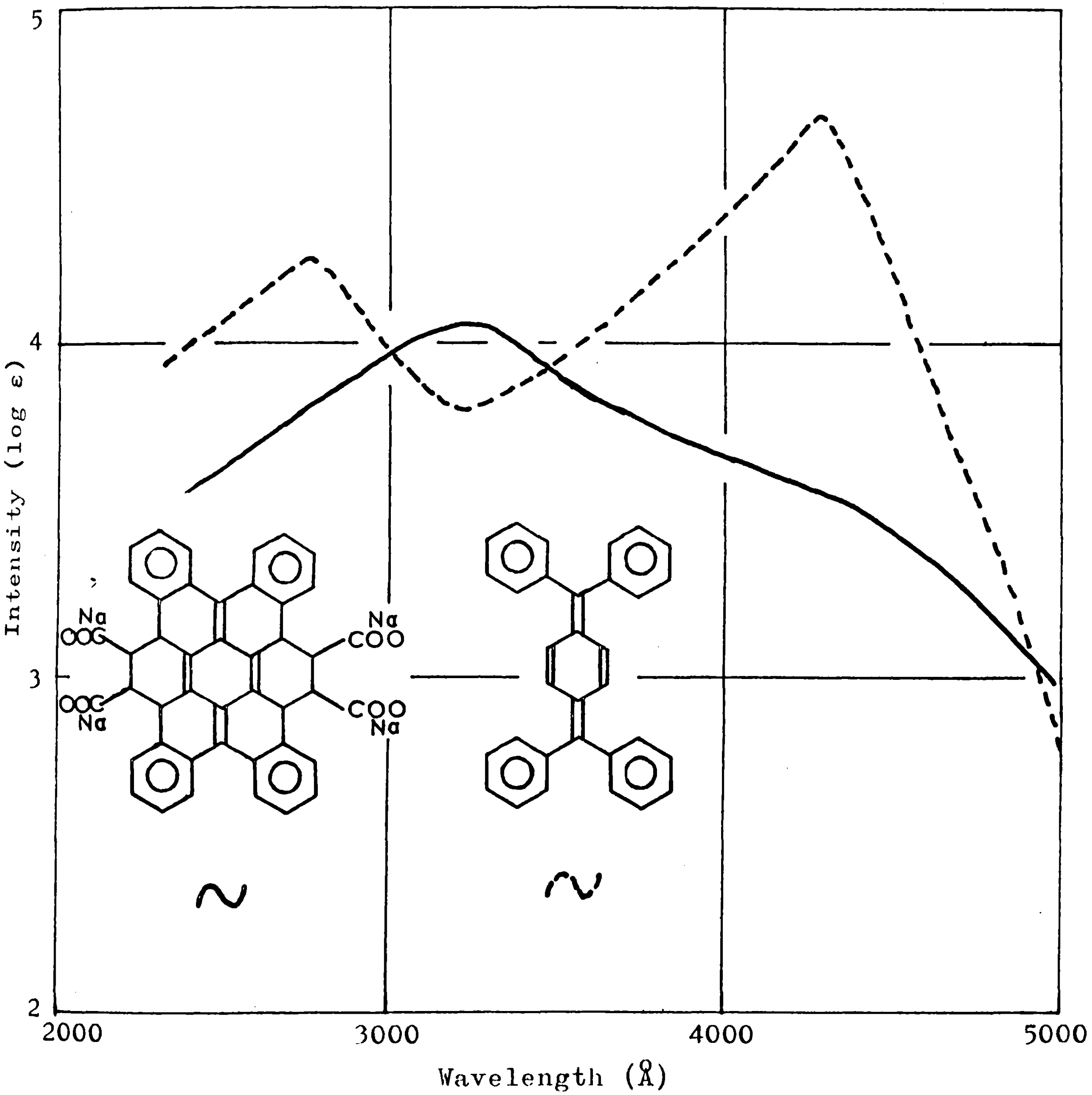
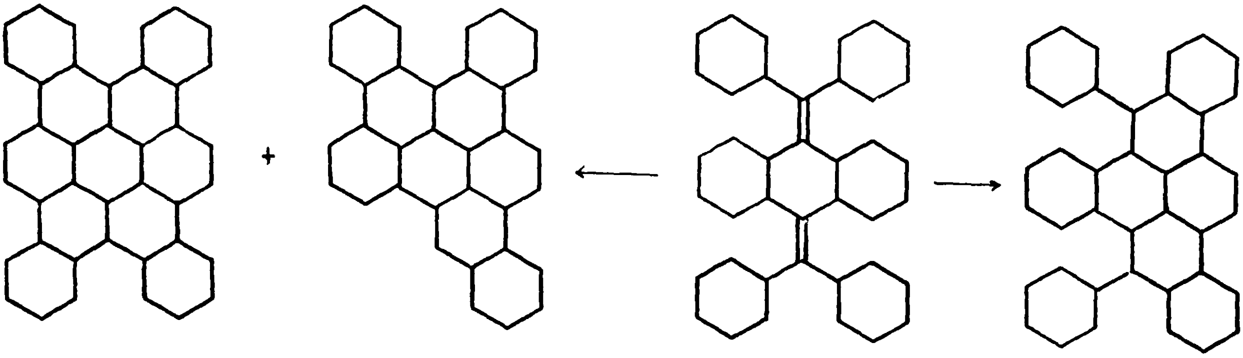


Figure 4. Absorption maxima (Å) and log ε (in parentheses).
Tetrasodium-4a.5.6.6a.10a.11.12.12a-octahydro-1.2,3.4,7.8,9.10-tetrabenzocoronene-5.6,11.12-tetracarboxylate in water:
3310 (~4·0).
Benzoquinone-(1.4)-bis-diphenylmethide in cyclohexane:
4260 (4·69), 2760 (4·25).

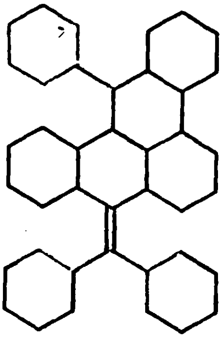


II

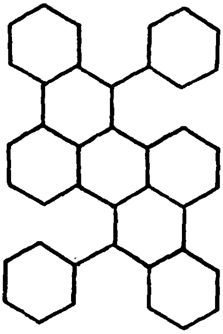
XLII

XLI

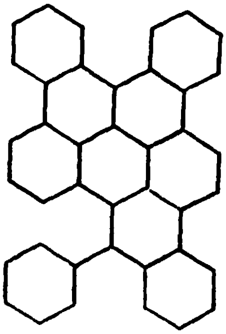
XLIV



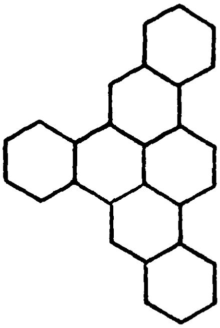
XLIII



XLV



XLVI



XLVII

also - the parent ion at 500 was found again, but the base peak of the spectrum had moved to 426, indicating the loss of a phenyl group, and suggesting that 2.3,8.9-dibenzo-1.12-o-phenyleneperylene (XLII) was present. Treatment with maleic anhydride also separated Fell's material into two components.

To obtain his material, Fell cyclised anthraquinone-bis-diphenylmethide (XLI)[16] in an aluminium chloride/stannic chloride melt.[5] In an attempt to gain more 1.2,3.4,7.8,9.10-tetrabenzocoronene (II), (XLI) was subjected to photochemical cyclisation.[17] After ten days irradiation, the solution was chromatographed and yielded a small amount of 3.10-diphenyl-1.2,4.5,8.9-tribenzopyrene (XLIV), easily recognised from the other possible products (XLIII, XLV, XLVI) by the close relationship of its ultra-violet spectrum to the parent hydrocarbon (XLVII) (figure 5).[18]

Mention must also be made of one further point, regarding the usefulness of 2.3,4.5,8.9,10.11-tetrabenzo-1.12-o-phenyleneperylene (XVII) as an intermediate in the 'synthesis' of 1.2,3.4,5.6,7.8,9.10,11.12-hexabenzocoronene (IV). Double ring closure of the keto-acid,(XXII) followed by treatment with phenyl lithium and cyclodehydrogenation should yield (XVII). However, although mono-cyclisation of (XXII) can be accomplished[1a,b] no success was achieved in the double cyclisation.

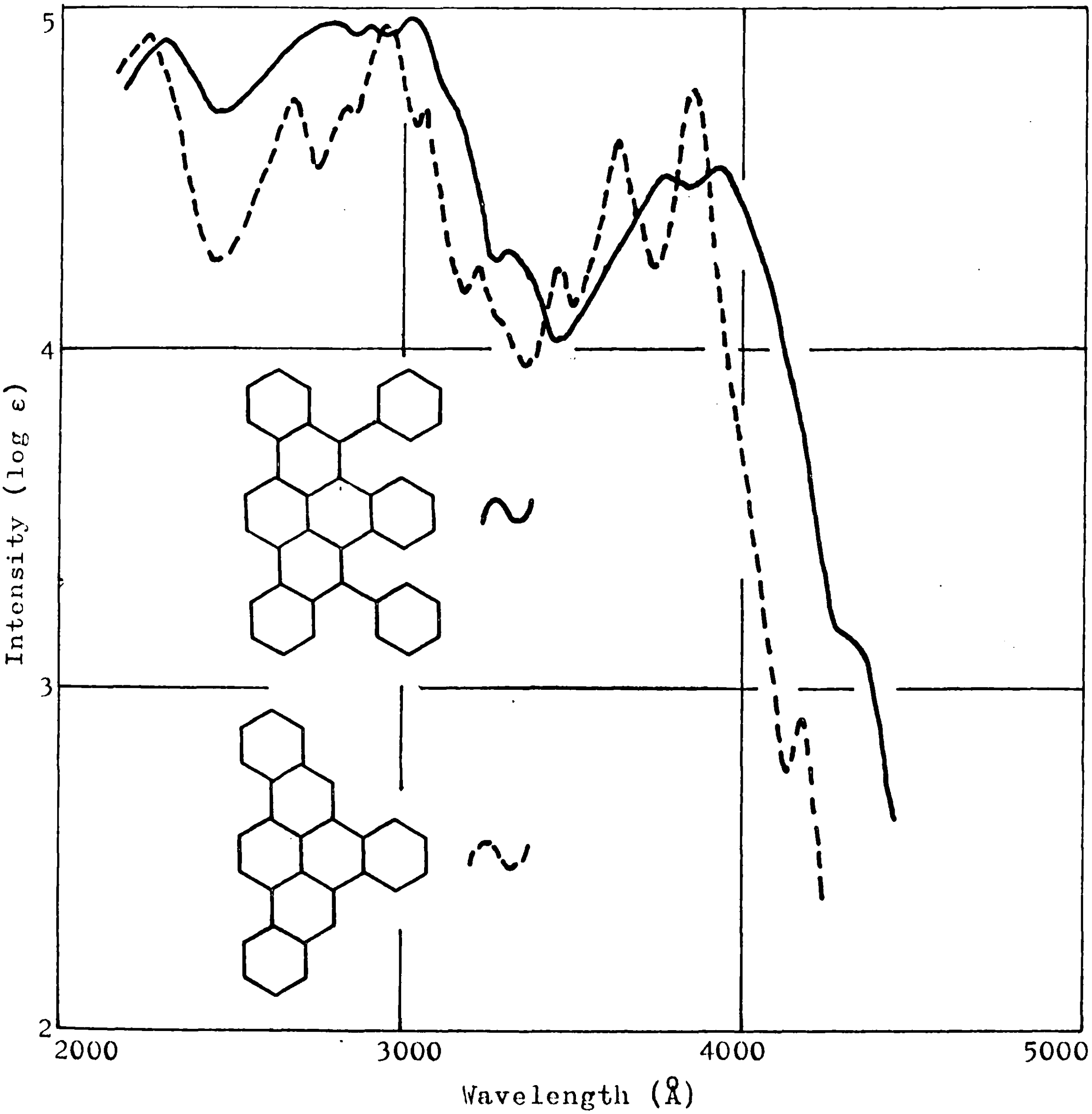


Figure 5. Absorption maxima (Å) and log ε (in parentheses).
3.10-Diphenyl-1.2,4.5,8.9-tribenzopyrene in cyclohexane:
p, 3960 (4·53), 3775 (4·49); 3310 (4·28); β, 3020 (4·97),
2910 (4·95), 2800 (4·96); β', 2320 (4·91).
1.2,4.5,8.9-Tribenzopyrene in cyclohexane: α, 4180 (2·86);
p, 3850 (4·76), 3640 (4·60), 3465 (4·24); 3230 (4·26),
3070 (4·70); β, 2965 (4·94), 2850 (4·70); 2680 (4·73);
β', 2260 (4·92).

EXPERIMENTAL

1-(o-Carboxybenzyl)-4-(o-carboxybenzoyl)-2.5-dimethylbenzene (XXII).

(XXII) was prepared by the method of Clar and Stephen[1b] as colourless needles, m.pt. 249-250°, (lit. m.pt. 249-250°)[1b] ν_{max}^{KBr} = 1695 cm.$^{-1}$ (acid C=O), 1678s cm.$^{-1}$ (ketone C=O).

1.4-Di-(o-carboxybenzyl)-2.5-dimethylbenzene (XXIII).

1-(o-Carboxybenzyl)-4-(o-carboxybenzoyl)2.5-dimethylbenzene (XXII) (250 g.) was reduced with copper-activated zinc dust (375 g.) in sodium hydroxide (8%, 3500 ml.) by refluxing for six days. The zinc dust was added in portions (5 x 75 g.) at intervals of twenty-four hours. The hot alkaline solution was then filtered from the excess zinc, acidified with concentrated hydrochloric acid, and the precipitated reduced acid (XXIII) collected by suction filtration. The dicarboxylic acid crystallised from glacial acetic acid as colourless needles of 1.4-di-(o-carboxybenzyl)-2.5-dimethylbenzene (XXIII) (150 g.) m.pt. 304-305°, ν_{max}^{KBr} = 1690 cm.$^{-1}$ (C=O). With concentrated sulphuric acid (XXIII) gave a red-orange solution, which turned green on warming.

Found C = 77·00%, H = 6·10%
$C_{24}H_{22}O_4$ requires C = 76·98%, H = 5·92%.

7.14-Dihydro-6.13-dimethylpentacene-5.12-dione (XXIV).

1.4-Di-(o-carboxybenzyl)-2.5-dimethylbenzene (XXIII) (37·4 g.) and phosphorus pentachloride (39 g.) were refluxed in freshly distilled phosphorus oxychloride (500 ml.) for thirty minutes. While copious quantities of hydrogen chloride were evolved, the colour of the solution changed from yellow to orange to red, and finally to dark green. Phosphorus oxychloride (250 ml.) was distilled off, and dry xylene was added as 'chaser solvent' till the distillation temperature rose to 135-140^{o}, by which time, the reaction product had begun to precipitate. It was collected by filtration, washed with benzene and dried. Crystallisation from benzene/ethanol and then from dioxan yielded orange-brown clusters of prisms of 7.14-dihydro-6.13-dimethylpentacene-5.12-dione (XXIV) (25·5 g.), m.pt. 334-336^{o}, ν_{max}^{KBr} = 1655 cm.$^{-1}$ (C=O); λ_{max}^{EtOH} = 3430 (3·62), 2970 (4·32), 2640 (4·15), M.S. molecular ion m/e = 338; calc. M.W. = 338. (XXIV) gave a yellow turning to green colour in concentrated sulphuric acid.

Found	C = 85·41%, H = 5·23%
$C_{24}H_{18}O_2$ requires	C = 85·18%, H = 5·36%.

Inverse Acid Chloride[10] cyclisation of (XXIII).

1.4-Di-(o-carboxybenzyl)-2.5-dimethylbenzene (XXIII) (37·4 g.) and phosphorus pentachloride (39 g.) were warmed on the steam bath for one hour. All the resulting phosphorus oxychloride was removed at the water pump, and the residual acid chloride was suspended in dry benzene (250 ml.) and transferred to a dropping funnel. This suspension was dropped on to finely divided aluminium chloride (32 g.) in dry benzene (250 ml.), the temperature during addition never being allowed to rise above 10°C. The reddish-brown complex was refluxed with stirring for twelve hours, decomposed with dilute hydrochloric acid, and then steam-distilled to remove all organic solvent. The reddish solid was collected by filtration, dried and crystallised from xylene as lustrous reddish-purple needles of unknown structure (XXV) (10·5 g.), m.pt. 335-336°, ν_{max}^{KBr} = 1645 cm.$^{-1}$ (C=O), $\lambda_{max}^{benzene}$ = 5590 (3·50), 5200 (3·35), 4910 (2·98), 3490 (3·95), 3360 (3·94), 3020 (4·91), 2910 (4·93), M.S. molecular ion m/e = 338; calc. M.W. = 338. A yellow turning to green solution was obtained in concentrated sulphuric acid.

Found	C = 85·02, 85·06%	H = 5·22, 5·09%
$C_{24}H_{18}O_2$ requires	C = 85·18%,	H = 5·36%

5-Hydroxy-5.12-diphenyl-5.14-dihydro-6.13-dimethylpentacene (XXVIII).

Bromobenzene (15·7 g.) was added to strips of lithium metal (1·4 g.) suspended in dry ether (250 ml.) in a nitrogen atmosphere and the mixture refluxed until all the lithium had dissolved (3-4 hours). The ethereal solution of phenyl lithium was then filtered through glass wool into a very finely divided suspension of 7.14-dihydro-6.13-dimethylpentacene-5.12-dione (XXIV) (8·4 g.) in dry benzene (250 ml.). The reaction mixture, which was greenish-black (λ_{max} = 6325, 5840, 5435, 4105, 3920, 3695Å)was refluxed for twelve hours. Decomposition with ice and dilute acetic acid, followed by steam distillation to remove the organic solvents left a buff-coloured residue. This material was triturated with ether and yielded a dark yellow solid. Repeated crystallisation from benzene/petrol gave the mono-ol (XXVIII) as pale yellow crystals, (7·5 g.), m.pt. 194-199°dec., $\lambda_{max}^{C_6H_{12}}$ = 3730 (3·57), 3200 (3·88), 3060 (3·85), 2580 (4·22), 2340 (4·16). Evaporation of the ether yielded further material (4 g.). Colour in sulphuric acid was greenish-brown.

Found C = 90·59%, H = 5·95%

$C_{36}H_{28}O$ requires C = 90·72%, H = 5·92%.

An identical experiment was carried out on the purple material (XXV) of unknown structure. The reaction mixture showed λ_{max} = 6330, 5845, 5425, 4095, 3890, 3685 Å. After decomposition and work up, the product obtained was identical in all respects with (XXVIII).

2.3,4.5,8.9,10.11-Tetrabenzoperylene (I).

5-Hydroxy-5.12-diphenyl-5.14-dihydro-6.13-dimethylpentacene (XXVIII) (2 g.) and copper powder (15 g.) were pyrolysed in a carbon dioxide atmosphere at 400-410° for two hours. The hydrocarbon produced was extracted with boiling xylene and chromatographed on Grade I Neutral Alumina (60 g.). Elution with benzene gave firstly, a yellow, closely followed by an orange, solution. Concentration of the yellow eluate gave long yellow-green needles of 2.3,4.5,8.9,10.11-tetrabenzoperylene (I) (28 mg.) and concentration of the orange eluate gave orange blades of (I) (11 mg.). Final purification was accomplished by sublimation at 310-320°/·04 mm. Both forms melted at 367-368° and gave an apple-green colour in warm sulphuric acid. The UV spectrum is shown in figure 1.

Found (needles) C = 95·28%, H = 4·69%
Found (blades) C = 95·81%, H = 4·37%
$C_{36}H_{20}$ requires C = 95·55%, H = 4·45%.

1.2,3.4,7.8,9.10-Tetrabenzocoronene-5.6,11.12-tetracarboxylic acid dianhydride (XXXVIII).

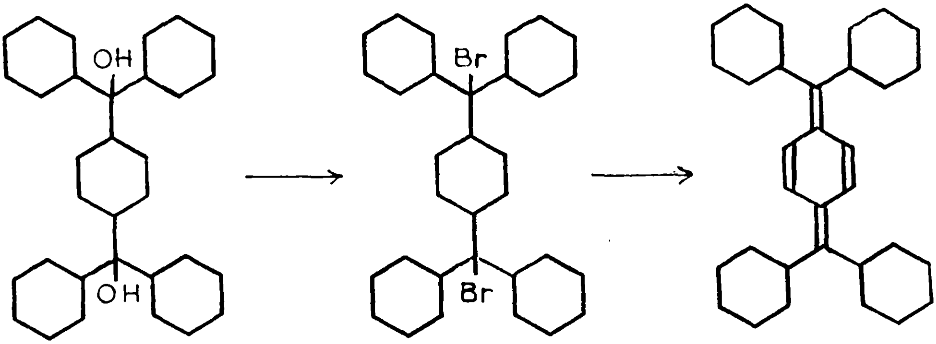
2.3,4.5,8.9,10.11-Tetrabenzoperylene (I) (75 mg.) and maleic anhydride (2·0 g.) were refluxed for thirty minutes by which time all the hydrocarbon had dissolved. An aliquot was removed, dissolved in warm water, and its ultraviolet spectrum recorded: it showed only one maximum at 3310Å($\sim$ 4·0), which indicated the presence of 4a.5.6.6a.10a.11.12.12a-octahydro-1.2,3.4,7.8,9.10-tetrabenzocoronene-5.6,11.12-tetracarboxylic acid dianhydride (XXXVII). Addition of chloranil (150 mg.), followed by a further thirty minutes reflux, allowed the adduct (XXXVIII) to crystallise from the hot solution. Dry xylene was added, the adduct filtered off and washed with benzene to yield dark red platelets of the fully aromatic 1.2,3.4,7.8,9.10-tetrabenzocoronene-5.6,11.12-tetracarboxylic acid dianhydride (XXXVIII) (90 mg.) m.pt. 440-445°. In concentrated sulphuric acid, (XXXVIII) gave an orange-red colour on warming. The UV-spectrum is shown in figure 2.

Found		C = 80·89%, H = 2·70%
$C_{44}H_{16}O_4$ (fully aromatic adduct)	requires	C = 82·45%, H = 2·52%
$C_{44}H_{24}O_4$ (hydrogenated adduct)	requires	C = 81·47%, H = 3·73%.

Correct analytical figures for this compound, which could not be crystallised or sublimed, are very difficult to obtain since the presence of very small amounts of chloranil or fumaric acid have a large influence on the analytical figures. The figures obtained, however, do suggest that the compound is the fully aromatic adduct.

1.2,3.4,7.8,9.10-Tetrabenzocoronene (II).

1.2,3.4,7.8,9.10-Tetrabenzocoronene-5.6,11.12-tetracarboxylic acid dianhydride (XXXVIII) (60 mg.) was ground together with soda-lime (250 mg.) and heated to 350° under nitrogen for one hour. Sublimation (380-395°/0·03mm.) yielded a dull orange film of hydrocarbon, which was dissolved in trichlorobenzene. Concentration allowed 1.2,3.4,7.8,9.10-tetrabenzocoronene (II) (<1 mg.) to crystallise as bright orange-brown needles or plates, m.pt. 396-397°, M.S. molecular ion m/e = 500, calc. M.W. = 500. The hydrocarbon gave a yellow-green colour with a faint green fluorescence in concentrated sulphuric acid. The UV-spectrum is shown in figure 2.



XLVIII XLIX XXXIX

Benzoquinone-(1.4)-bis-diphenylmethide (XXXIX).

The UV-spectrum of (XXXIX) was required for comparison purposes. ω,ω,ω',ω'-tetraphenyl-p-xylylene glycol (XLVIII) (2·5 g.)[19] was dissolved in hot glacial acetic acid (20 ml.), and hydrobromic acid in glacial acetic acid (50%, 5 ml.) was rapidly added. The original yellow colour darkened appreciably and the dibromide crystallised out. The solution was refluxed for thirty minutes, cooled, filtered, and the residue washed with acetic acid and ether. The solid was recrystallised from ethylene bromide as beautiful colourless tablets of ω,ω,ω',ω'-tetraphenyl-p-xylylene dibromide (XLIX) (1·5 g.), m.pt. 270-272° (lit. m.pt., 270-272°).[20]

Dehydrobromination was accomplished with molecular silver according to the method of Thiele and Balhorn.[20] Benzoquinone-(1.4)-bis-diphenylmethide (XXXIX) was obtained as glittering orange needles m.pt. 240-242° (lit.m.pt., 250-254°, preheated bath).[21] The UV-spectrum is shown in figure 4.

Reinvestigation of Fell's Tetrabenzocoronene.[5]

The hydrocarbon obtained by Fell (10 mg.)[5] was refluxed with maleic anhydride (250 mg.) for three hours, by which time it appeared that all the hydrocarbon had dissolved. Dilute sodium hydroxide was added to dissolve any adduct formed and to precipitate any unreacted hydrocarbon. The aqueous solution was filtered through a sinter - λ_{max} = 456, 425, 400, 380, 335 mμ. The material caught in the sinter was dissolved in xylene - λ_{max} = 472, 440, 412, 402, 360, 320, 308 mμ. This result suggested Fell's material was not homogeneous; further support was provided by the mass spectrum which exhibited strong peaks at 500 and 426, and was not identical with the mass spectrum of the material obtained by the unambiguous route already described.

Photochemical Cyclisation[18] of Anthraquinone-bis-diphenylmethide: 3.10-Diphenyl-1.2,4.5,8.9-tribenzopyrene (XLIV).

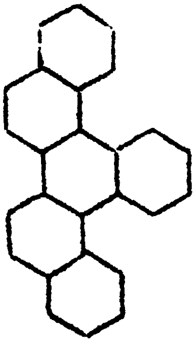
Anthraquinone-bis-diphenylmethide (XLI) (540 mg.)[17] was irradiated in dry benzene (500 ml.) with a mercury vapour lamp in the presence of iodine. The course of the reaction was followed by removing a standard portion and examining the ultra-violet spectrum. At the end of ten days, the reaction appeared to be complete. The benzene was removed under vacuum, the residue dissolved in the minimum amount of trichlorobenzene and chromatographed on Grade I Neutral Alumina (25 g.). Elution with xylene gave a yellow-green band with a strong blue-violet fluorescence which on concentration yielded pale yellow needles of 3.10-diphenyl-1.2,4.5,8.9-tribenzopyrene (XLIV) (52 mg.) m.pt. 332-334°. (XLIV) gave a bright blue colour in concentrated sulphuric acid. The UV-spectrum is shown in figure 5.

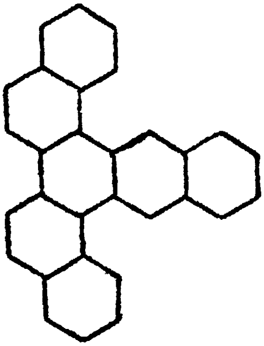
Found C = 94·95%, H = 5·19%

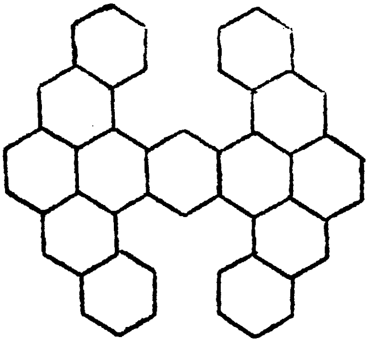
$C_{40}H_{24}$ requires C = 95·21%, H = 4·79%.

CHAPTER 4.

5.6-BENZOPICENE, NAPHTHO-(2'.3':5,6)-PICENE AND TETRANAPHTHO-(3'.1':1.14);(3''.1'':4.5);(1'''.3''':7.8);(3''''.1'''':11.12)-PENTACENE.

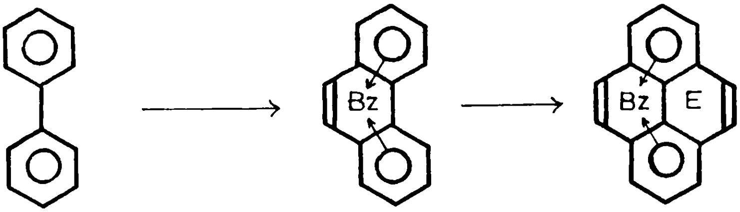

I


II


III

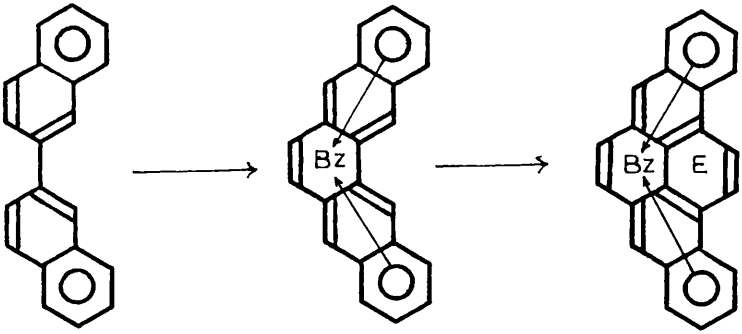
INTRODUCTION:

An extensive study of the ultra-violet spectra of certain higher annellated pyrenes revealed certain interesting and unusual results which made it essential that 5.6-benzopicene (I) and naphtho-(2'.3':5.6)-picene (II) be



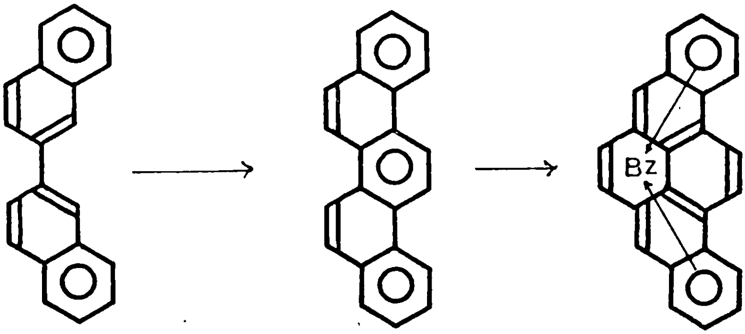
IV V VI

λ_β 2100 $\xrightarrow{430}$ 2530 $\xrightarrow{210}$ 2740 Å



VII VIII IX

λ_β 2550 $\xrightarrow{595}$ 3145 $\xrightarrow{175}$ 3320 Å



VII X IX

λ_β 2550 $\xrightarrow{295}$ 2845 $\xrightarrow{475}$ 3320 Å synthesised. After a number of false starts, a small amount of the former has been obtained, and a route to the latter found. Lack of time together with very poor yields have prevented a more satisfactory completion of this project. In addition, tetranaphtho-(3'.1':1.14);(3''.1'':4.5);(1'''.3''':7.8); 3''''.1'''':11.12)-pentacene (III) has been synthesised and its ultra-violet spectrum compared with those of pentaphene (VIII) and 1.2,3.4,9.10-tribenzopyrene (XII).

DISCUSSION:

In building up pyrene (VI) from biphenyl (IV) via phenanthrene (V) by the fusion of two ethylenic bridges, the annellation effect is found to be highly asymmetric. Therefore one of the central rings must have induced benzenoid character (Bz) and the other must be empty (E).[1]

In the same way, 3.4,9.10-dibenzopyrene (IX) (figure 1) can be derived from 2.2'-dinaphthyl (VII). If the first ethylenic bridge is connected across the 3.3'-positions the series 2.2'-dinaphthyl (VII), pentaphene (VIII), 3.4,9.10-dibenzopyrene (IX) is obtained. The values of the shifts (595 Å and 175 Å) are highly asymmetric, and therefore during the first annellation an induced benzenoid ring (Bz)

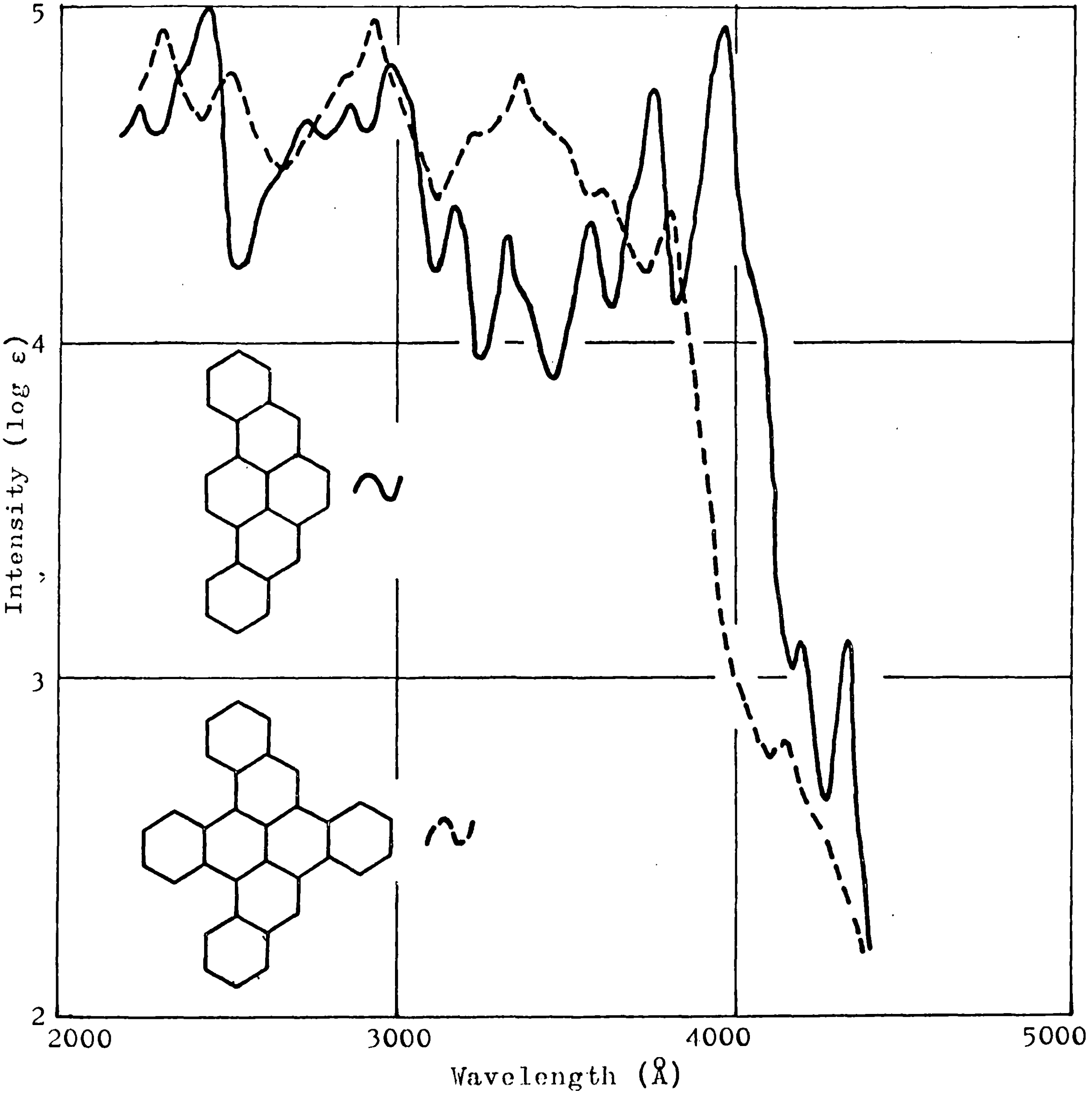
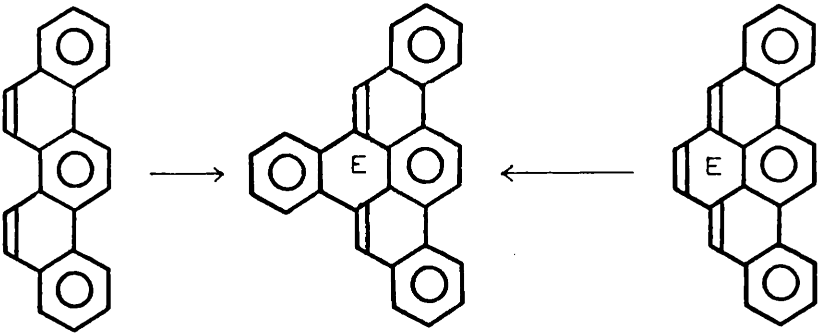


Figure 1. Absorption maxima (Å) and log ε (in parentheses). 3.4,9.10-Dibenzopyrene in benzene: α, 4330 (3·10), 4190 (3·10); p, 3970 (4·94), 3750 (4·74), 3565 (4·34); β, 3320 (4·32), 3170 (4·40); β', 2970 (4·84), 2850 (4·70); in ethanol, β'', 2720 (4·63); β''', 2420 (5·00), 2220 (4·70).
1.2,3.4,6.7,9.10-Tetrabenzopyrene in cyclohexane: α, 4140 (2·80); p, 3800 (4·40), 3620 (4·46); β, 3360 (4·80), 3240 (4·63); β', 2920 (4·96), 2820 (4·80); β'', 2480 (4·82), 2280 (4·94).

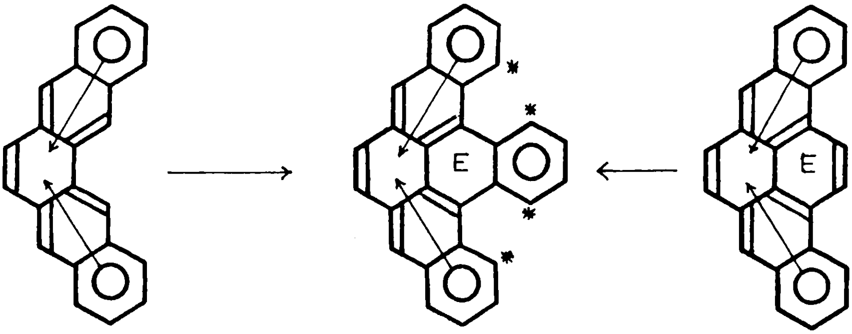
must be formed while the second produces an empty ring (E).[1] Alternatively, the 1.1' positions can be joined first with the production of the series 2,2'-dinaphthyl (VII), picene (X), 3.4,9.10-dibenzopyrene (IX). The first shift (295 Å) is the smaller, and hence the new ring does not have induced benzenoid character (although it has of course benzenoid character). The second, and larger, shift (475 Å) must then produce an induced benzenoid ring (Bz). Now the fact that 3.4,9.10-dibenzopyrene (IX) can be derived from both pentaphene (VIII) and picene (X) by annellation of an ethylenic bridge suggests these two types of conjugation might co-exist within the molecular framework of 3.4,9.10-dibenzopyrene (IX), causing the spectrum of (IX) to be represented by a superposition of the spectra of pentaphene (VIII) and picene (X). The spectrum of 3.4,9.10-dibenzopyrene (IX) exhibits a β-band at 3320 Å and a β'-band at 2970 Å, these bands being shifted 175 Å and 125 Å respectively from the β-band of pentaphene (VIII) at 3145 Å and that of picene (X) at 2845 Å, confirming these ideas. The shifts are caused by the single bonds of the ethylenic bridges.

Having analysed the spectrum of 3.4,9.10-dibenzopyrene (IX) satisfactorily, it is natural to turn our attention to the isomeric tribenzopyrenes - 1.2,4.5,8.9-



X XI IX

λ_β 2845 $\xrightarrow{105}$ 2950 $\xleftarrow{-20}$ $\lambda_{\beta'}$ 2970 Å



VIII XII IX

λ_β 3145 $\xrightarrow{90}$ corr. $\begin{array}{r}3375\\ \underline{-140}\\ 3235\end{array}$ $\xleftarrow{-85}$ 3320 Å tribenzopyrene (XI) (figure 2) and 1.2,3.4,9.10-tribenzopyrene (XII) (figure 2) to substantiate our arguments. 1.2,4.5,8.9-Tribenzopyrene (XI) can be derived from picene (X) by adding an o-phenylene complex to the 12.13-positions. The β-band shift is only 105 Å, well below the maximum value for the formation of single bonds only, and hence the newly formed ring must be empty (E); the basic conjugation in 1.2,4.5,8.9-tribenzopyrene (XI) is therefore of the picene type. In an analogous manner, 1.2,3.4,9.10-tribenzopyrene (XII) can be built up from pentaphene (VIII) by connecting an o-phenylene complex to the 13.14-positions. The β-band shift, after the usual correction of the starred carbon atoms for overcrowding[2] is only 90 Å, again well below the maximum value for the formation of single bonds and here also, the newly formed ring must be empty (E). The conjugation in this hydrocarbon (XII) is therefore of the pentaphene type.

Comparison of the positions of the β- and β'-bands of 3.4,9.10-dibenzopyrene (IX) with the β-bands of the two tribenzopyrenes (XI, XII) shows some important features. Since it is well known that very small shifts are indicative of fixed double bonds at the positions where new rings have been fused,[3] it can easily be appreciated that the values involved here (-20 Å and -85 Å) do constitute very small shifts,

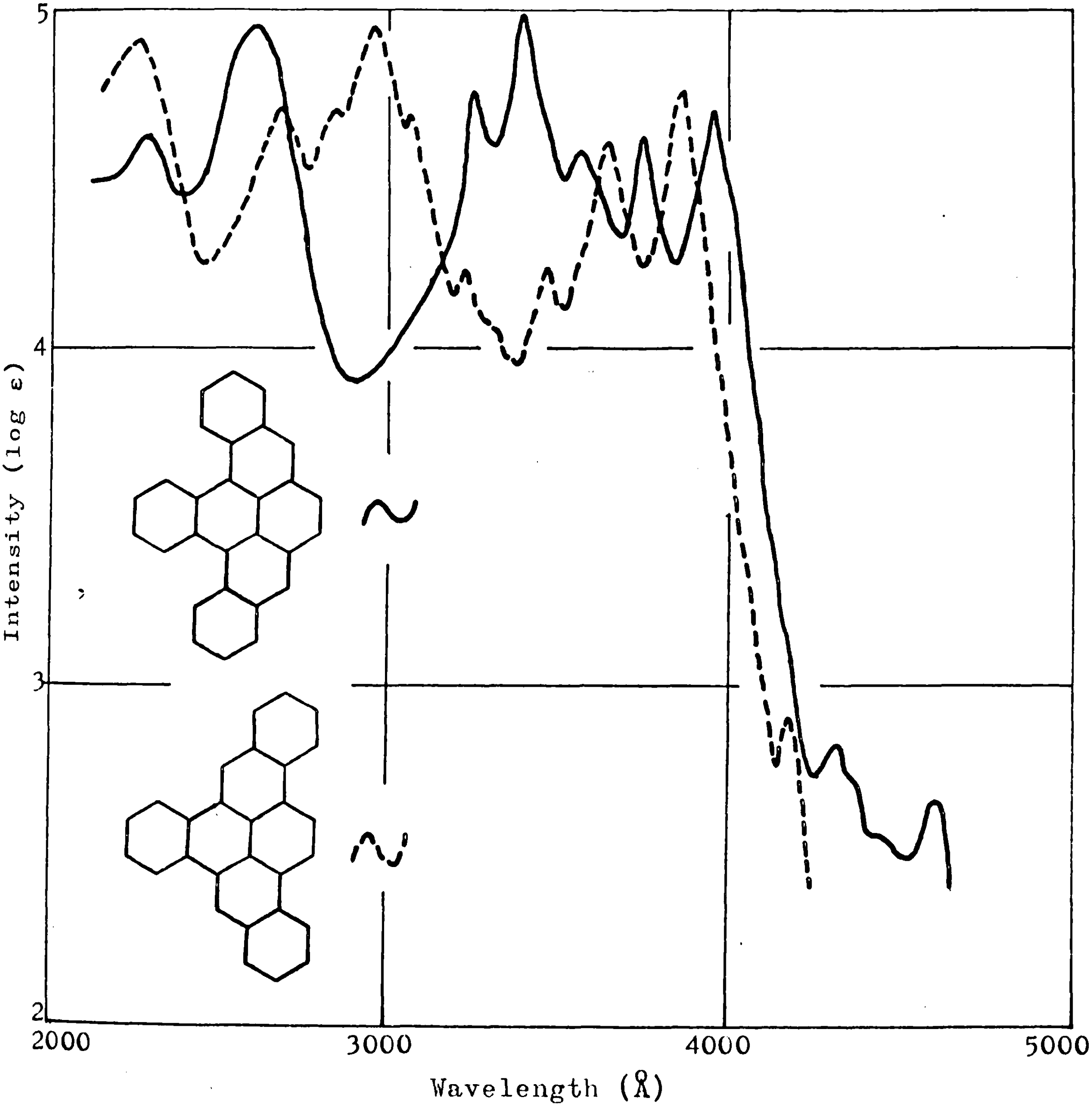
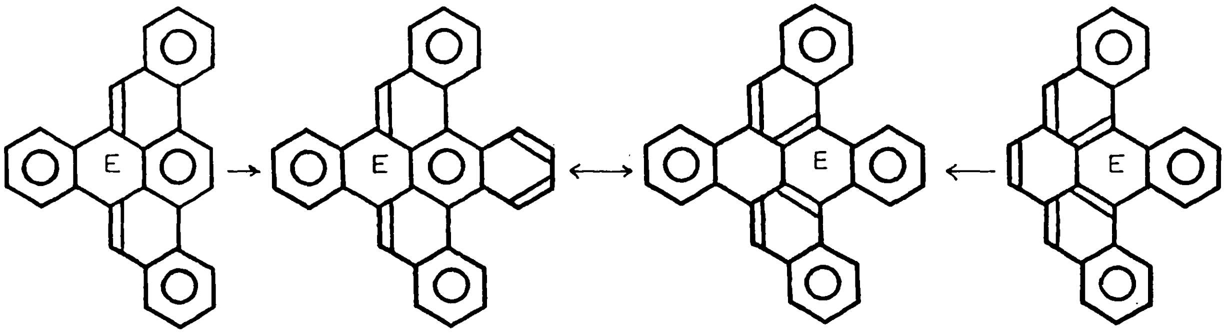
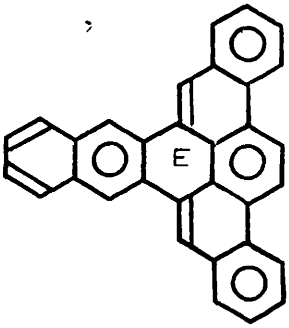


Figure 2. Absorption maxima (Å) and log ε (in parentheses). 1.2,3.4,9.10-Tribenzopyrene in ethanol: α, 4160 (2·88), 4340 (2·98); p, 3930 (4·78), 3730 (4·58), 3540 (4·56); β, 3375 (5·00), 3220 (4·76); β', 2600 (4·96), 2290 (4·62). 1.2,4.5,8.9-Tribenzopyrene in cyclohexane: α, 4180 (2·86); p, 3850 (4·76), 3640 (4·60), 3465 (4·24); 3230 (4·26), 3070 (4·70); β, 2965 (4·94), 2850 (4·70); 2680 (4·73); β', 2260 (4·92).

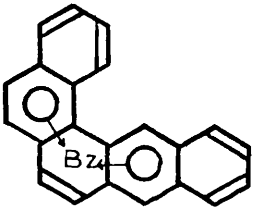


XI XIIIa XIIIb XII

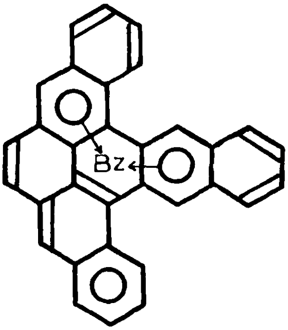
λ_β 2950 $\xrightarrow{-30}$ $\lambda_{\beta'}$ 2920 λ_β 3360 $\xleftarrow{-15}$ λ_β 3375 Å



XIV



XVI



XV

λ_β 2980 3080 3120 Å

and so form additional evidence for the restriction of electronic conjugation in 1.2,4.5,8.9-tribenzopyrene (XI) and 1.2,3.4,9.10-tribenzopyrene (XII).

Yet further evidence of this electronic restriction can be provided. The two possible electronic configurations in 3.4,9.10-dibenzopyrene (IX), although they are lost in the tribenzopyrenes (XI, XII), should reappear in 1.2,3.4,6.7,9.10-tetrabenzopyrene (XIII) (figure 1).[4] Hence this hydrocarbon should exhibit an absorption maximum very close to 2950 Å if it adopts configuration (XIIIa) and another close to 3375 Å if configuration (XIIIb) is adopted; it is very satisfactory to find this hydrocarbon has $\lambda_{\beta'}$ = 2920 Å and λ_{β} = 3360 Å.

Having successfully shown that there is a 'duality' of electronic arrangement in 3.4,9.10-dibenzopyrene (IX) and 1.2,3.4,6.7,9.10-tetrabenzopyrene (XIII), the next step is to provide further evidence that there is only one electronic configuration in hydrocarbons derived from the two tribenzopyrenes (XI, XII). Since 1.2,4.5,8.9-tribenzopyrene (XI) has been shown to exist as a substituted picene, removal of the o-phenylene complex and replacement by a 2.3-naphthylene unit with the consequent formation of 4.5,8.9-dibenzo-naphtho-(2'''.3''':1.2)-pyrene (XIV) (figure 3) should have very little

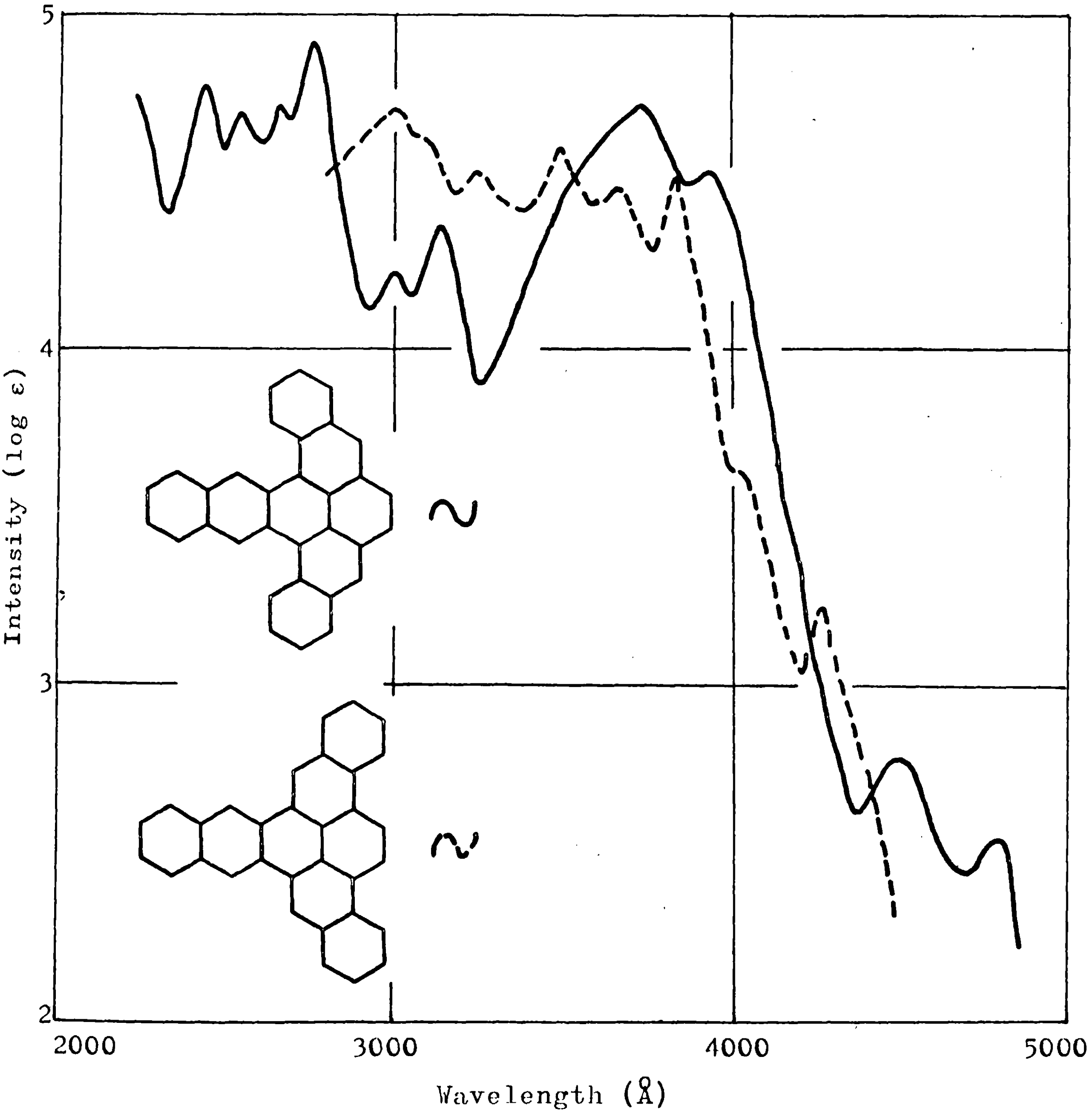
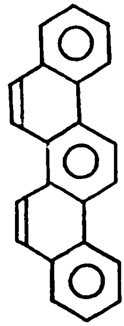
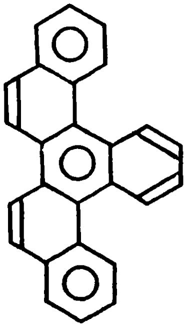


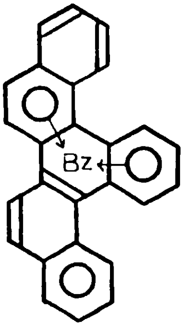
Figure 3. Absorption maxima (Å) and log ε (in parentheses).
3.4,9.10-Dibenzo-naphtho-(2'''.3'''.1.2)-pyrene in benzene: α, 4810 (2·54), 4520 (2·77); p, 3950 (4·54), 3730 (4·74); β, 3120 (4·37), 2990 (4·22); in cyclohexane, β', 2740 (4·94), 2640 (4·73), 2530 (4·72), 2420 (4·80).
4.5,8.9-Dibenzo-naphtho-(2'''.3'''.1.2-pyrene in trichlorobenzene: α, 4260 (3·24); 4010 (3·66); p, 3840 (4·52), 3640 (4·51); 3470 (4·62), 3220 (4·54); in benzene, β, 2980 (4·74).



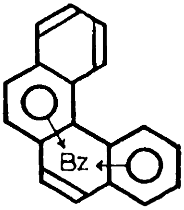
X



Ia

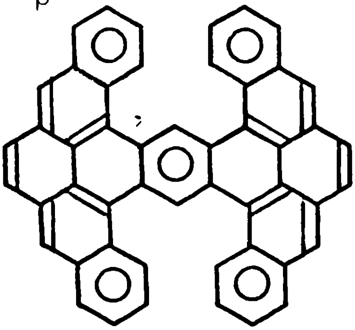


Ib

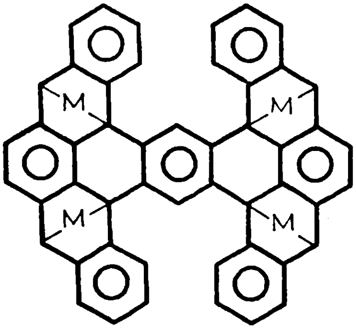


XVII

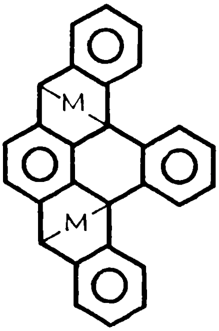
λ_β 2845 2830 ↔ 2830 2810 Å



XVIII

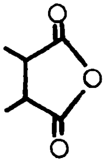


XIX



XX

M =



effect on the position of the β-band. This is found – 1.2,4.5,8.9-tribenzopyrene (XI) exhibits λ_β = 2950 Å while (XIV) shows λ_β = 2980 Å. Using the same argument, 3.4,9.10-dibenzo-naphtho-(2'''.3''':1.2)-pyrene (XV) (figure 3)[5] should exhibit an absorption maximum very close to the β-band of 1.2,3.4,9.10-tribenzopyrene (XII) at 3375 Å. Unfortunately the β-band of this dibenzonaphthopyrene (XV) appears at 3120 Å, and so cannot be correlated with absorption maxima of either the pentaphene or the picene series. A new type of conjugation would therefore seem to be of premier importance in 3.4,9.10-dibenzo-naphtho-(2'''.3''': 1.2)-pyrene (XV). Now if the conjugation in (XV) were of the 1.2-benzotetraphene (XVI)[6] type, then the β-band of (XV) will be moved slightly, since the double bond of the induced benzenoid ring (Bz) will cut off the other rings from the principal conjugation. In fact, the β-bands of (XV) and (XVI) are in almost identical positions, one occurring at 3080 Å, and the other at 3120 Å.

A complete departure from conjugation of the pentaphene and picene types having been found in 3.4,9.10-dibenzo-naphtho-(2'''.3''':1.2)-pyrene (XV) it became necessary to examine this phenomenon in greater detail. The obvious starting points are 5.6-benzopicene (I) (figure 4) and naphtho-(2'.3':5.6)-picene (II). Now the former can exist

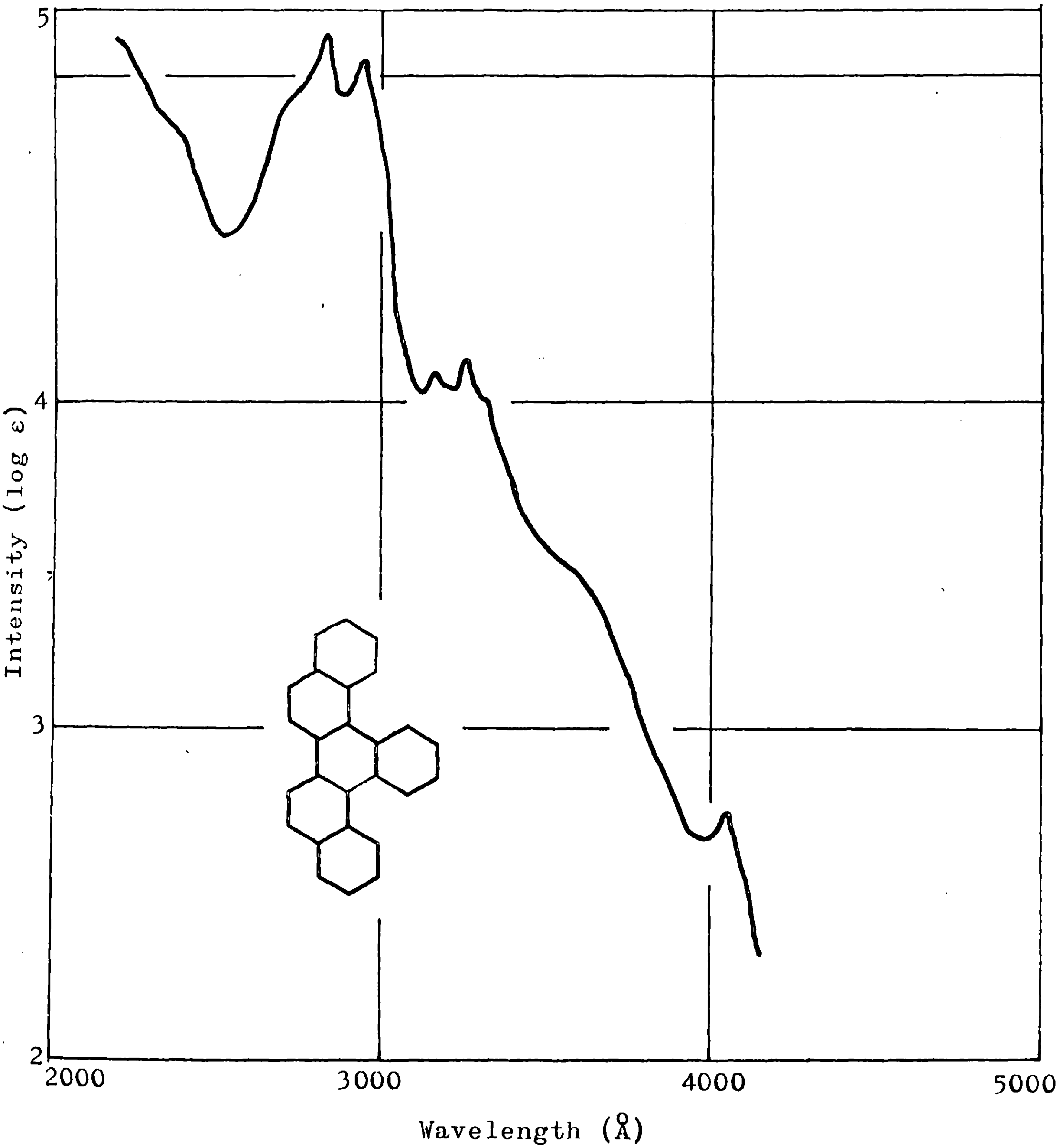


Figure 4. Absorption maxima (Å) and log ε (in parentheses). 5.6-Benzopicene in ethanol: α, 4030 (2·73); p, 3245 (4·16), 3160 (4·09); β, 2950 (5·04), 2830 (5·12).

with two different electronic patterns (Ia, b) derived from picene (X), (λ_β = 2845 Å) and 3.4-benzophenanthrene (XVII) (λ_β = 2810 Å). The experimentally found position of the β-band of 5.6-benzopicene (I) is at 2830 Å, a figure lying mid-way between the β-bands of 3.4-benzophenanthrene (XVII) and picene (X), so making it impossible to draw any definite conclusions as regards the principal chromophore. The problem can therefore only be satisfactorily resolved when the synthesis of naphtho-(2'.3':5.6)-picene (II) has been completed.

Another hydrocarbon which has been examined is tetranaphtho-(3'.1':1.14);(3''.1'':4.5);(1'''.3''':7.8);(3''''.1'''':11.12)-pentacene (III) (figure 5), which should allow some interesting comparisons with pentaphene (VIII) and 1.2,3.4,9.10-tribenzopyrene (XII). If our ideas regarding the limitation of electronic conjugation are correct, this material should bear a similarity to pentaphene (VIII) since it can formally be considered as two pentaphene moieties attached to a single benzene ring (XVIII). Comparing the ultra-violet spectra of pentaphene (VIII) with that of the tetranaphthopentacene (III) shows there is a fairly constant shift to longer wavelength of about 750 Å, though of course there is much less fine structure due to overcrowding.

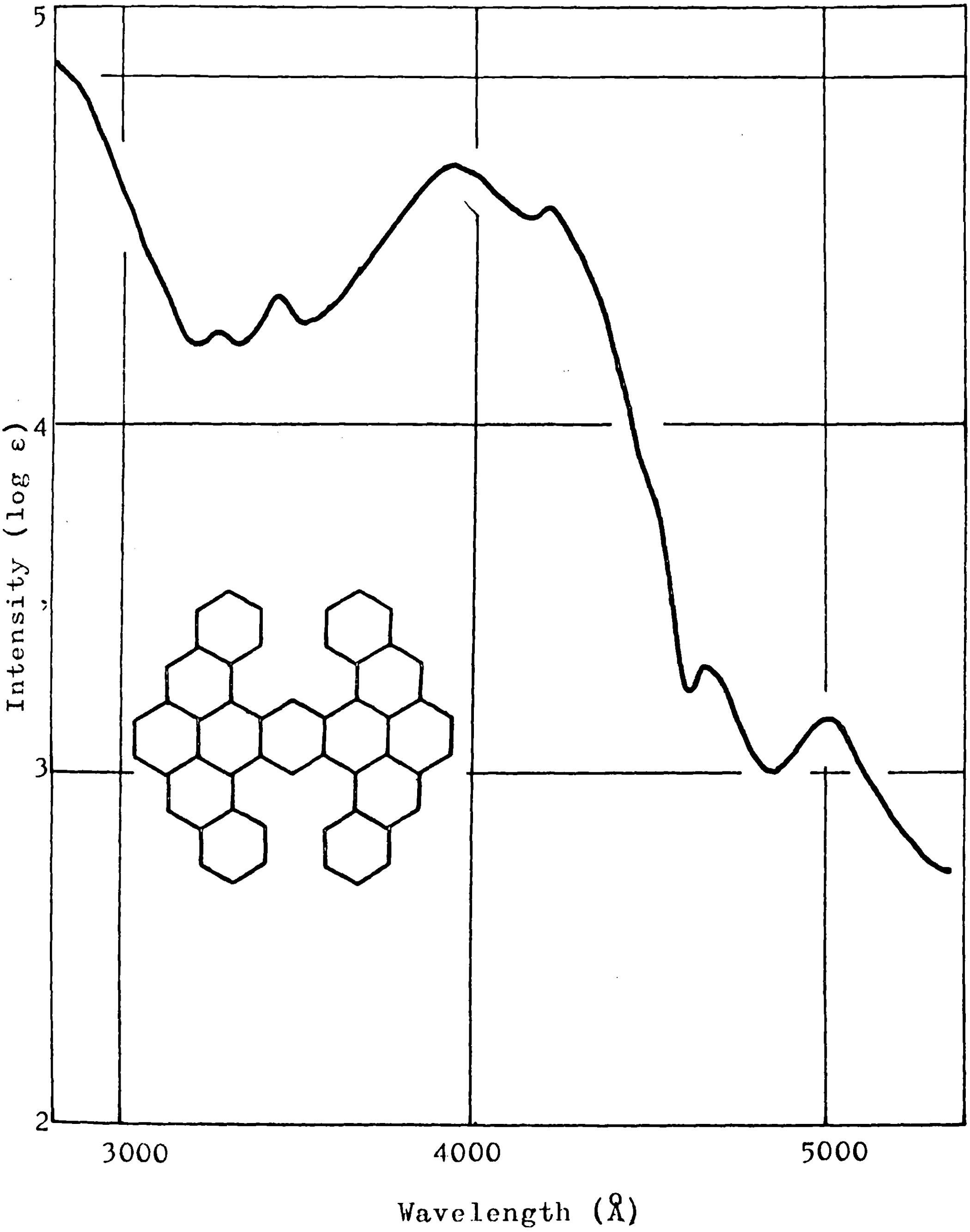


Figure 5. Absorption maxima (Å) and log ε (in parentheses). Tetranaphtho-(3'.1':1.14);(3''.1'':4.5);(1'''.3''':7.8); (3''''.1'''':11.12)-pentacene in trichlorobenzene: α, 5010 (3·16), 4680 (3·30); p, 4220 (4·62), 3940 (4·76); in benzene, β, 3410 (4·36), 3250 (4·27).

Additional evidence that this type of conjugation is the principal chromophore comes from the spectrum of the maleic anhydride adduct of (III) which has only one peak at 2650 Å; the only possible way to obtain a spectrum of this sort is by the formation of the tetra-adduct(XIX) (figure 6). Now the maleic anhydride adduct of 1.2,3.4,9.10-tribenzopyrene (XX) (figure 6) is virtually identical - a single peak at 2640 Å. Since both hydrocarbons form the same type of adduct, the only possible conclusion is that the electronic arrangements must be very similar.

Two further points are worthy of a brief comment. Considerably more information about the conjugation present in these higher annellated pyrenes can be gained by examining their <u>polarised</u> ultra-violet spectra:[7] it had been hoped to carry out some work on these lines but the necessary apparatus proved too difficult to assemble. However, further evidence on the fine structure of these hydrocarbons has been gained from NMR studies, which are discussed at some length in Chapter 7.

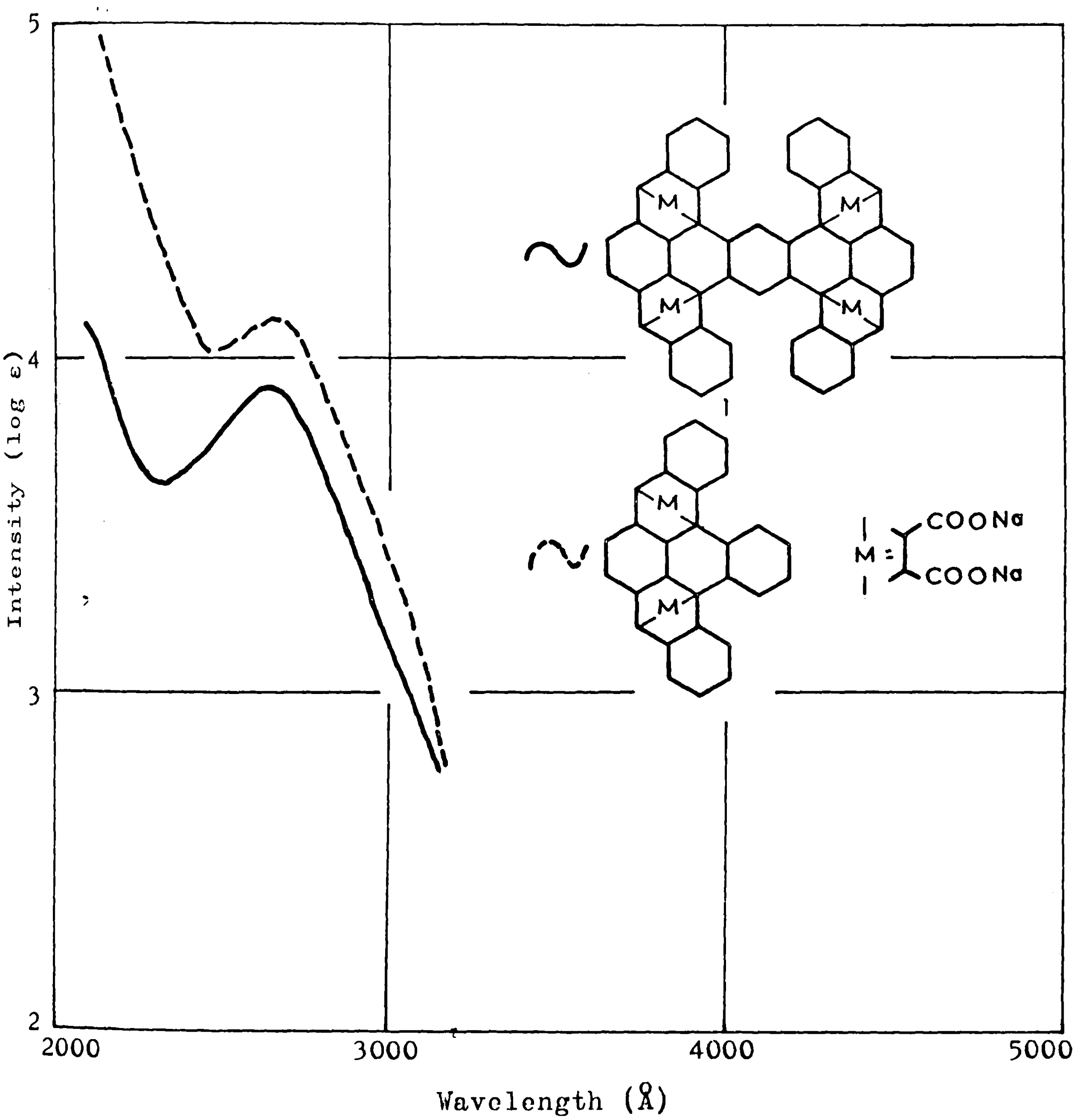
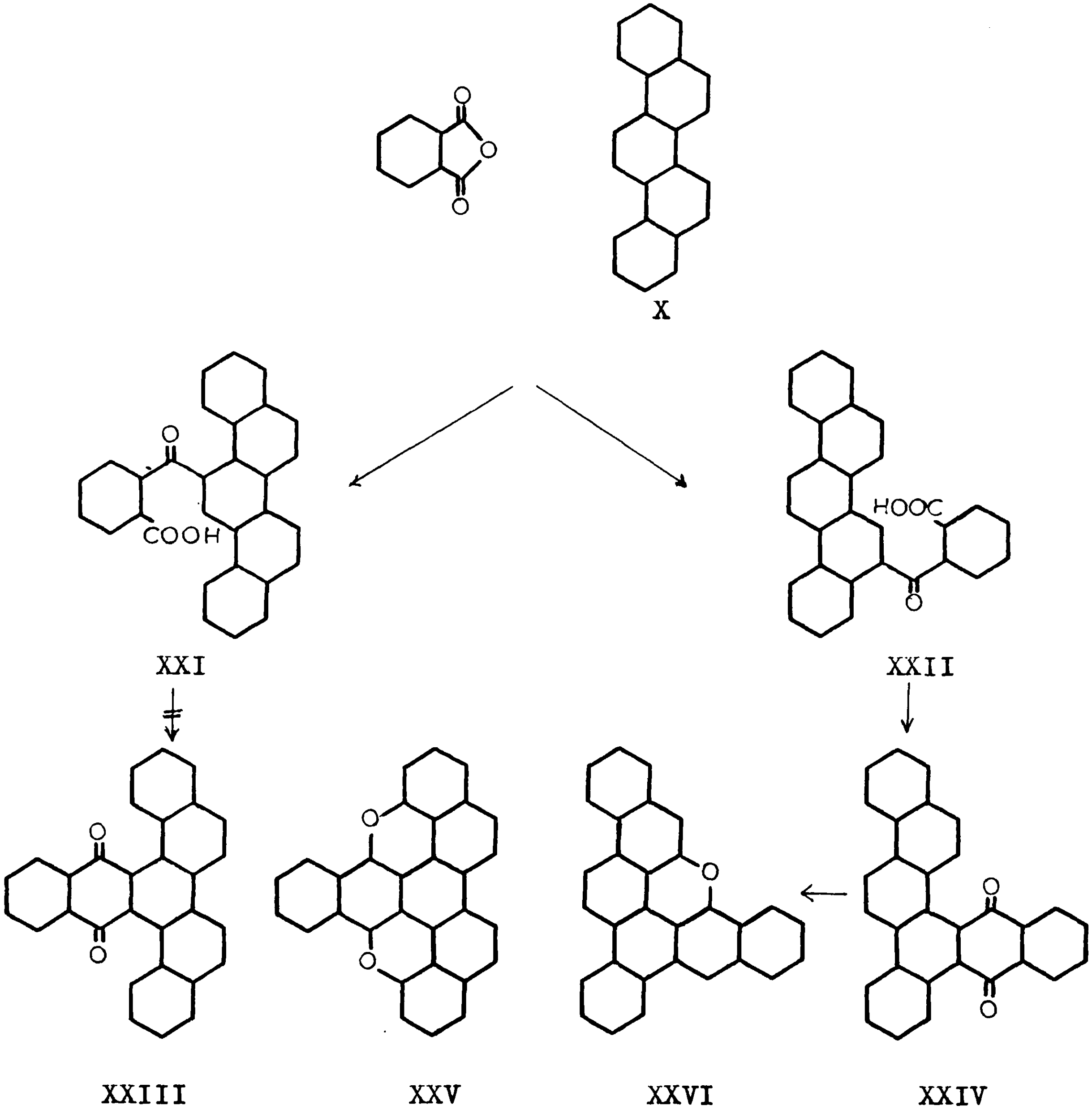
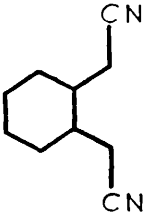
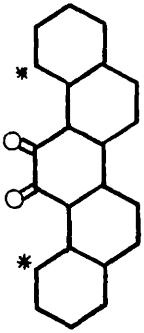


Figure 6. Absorption maxima (Å) and log ε (in parentheses). Tetranaphthopentacene adduct with maleic anhydride in 50% aqueous ethanol: 2650 (3·92).
1.2,3.4,9.10-Tribenzopyrene adduct with maleic anhydride in 50% aqueous ethanol: 2640 (4·11).

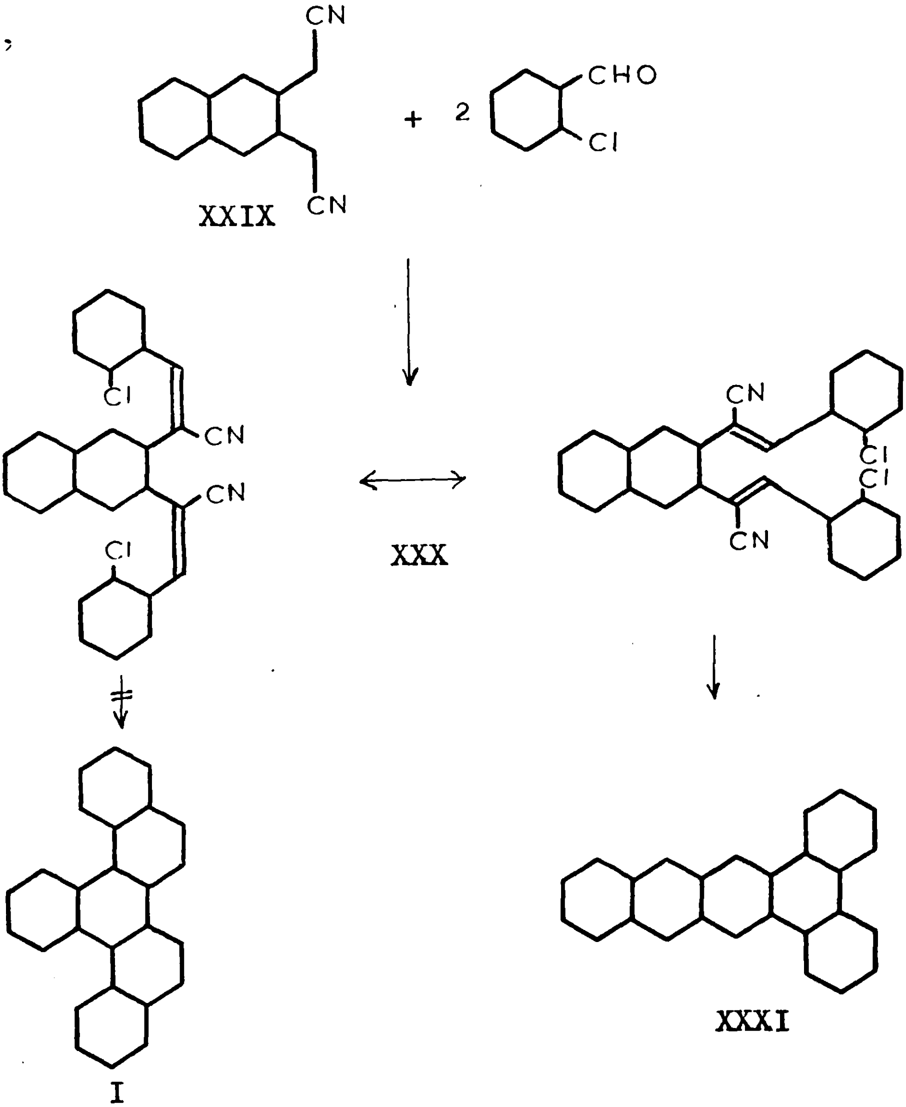

X
XXI
COOH
HOOC
XXII
XXIII
XXV
XXVI
XXIV



XXVIII



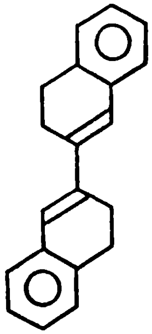
XXVII



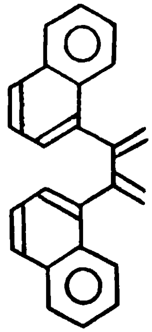
EXPERIMENTAL DISCUSSION:

The initial object of the experimental work was the preparation of naphtho-(2'.3':1.2)-picene (II). To this end, Stephen, who began this project, condensed picene (X) with phthalic anhydride to obtain the isomeric 5- and 11-o-carboxybenzoylpicenes (XXI, XXII).[4] Cyclisation with concentrated sulphuric acid/benzoyl chloride[8] yielded only one quinone, 11.12-phthaloylpicene (XXIV), for which structural proof was obtained by a zinc dust melt reduction which yielded only a mono-oxido compound (XXVI); if the required quinone, 5.6-phthaloylpicene (XXIII) had been obtained, reduction would, of course, have yielded a di-oxido compound (XXV).[4]

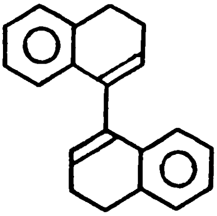
Our own earliest attempt to synthesise naphtho-(2'.3':1.2)-picene (II) involved the condensation[9] of picene-5.6-quinone (XXVII)[10] with benzene-1.2-diacetonitrile (XXVIII);[11] however, no reaction could be induced between them, probably because of steric hindrance between the cyanide groups and the starred carbon atoms. Another possible approach, this time to 5.6-benzopicene (I), was to react naphthalene-2.3-diacetonitrile (XXIX)[12] with o-chlorobenzaldehyde to obtain the complex dinitrile (XXX). Cyclisation, followed by decarboxylation, should yield the



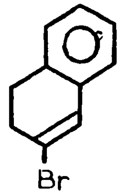
XXXII



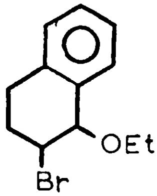
XXXIII



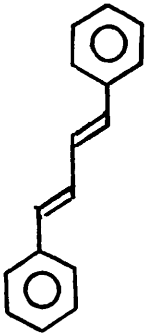
XXXIV



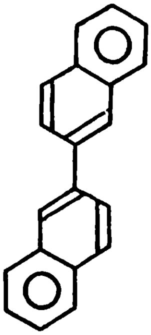
XXXV



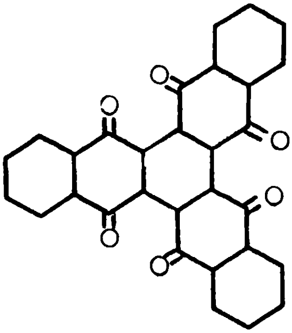
XXXVI



XXXVII



XXXVIII



XXXIX

desired 5.6-benzopicene (I). Orange-yellow needles of a hydrocarbon were indeed obtained, but on careful examination these proved to be 1.2,3.4-dibenzotetracene (XXXI).[13]

Since these early attempts had ended so disappointingly, it was decided to approach the problem from a different angle - from the standpoint of a Diels-Alder reaction which could be used to build up the required carbon skeleton. There were two dienes which could be used - 3.4,3'.4'-tetrahydro-2.2'-dinaphthyl (XXXII) and 2.3-di-(1-naphthyl)-buta-1.3-diene (XXXIII). The former has been mentioned twice in the literature, but the yields reported were poor.[14,15] To obtain (XXXII) in better yield, a new synthetic route was tried - the dimerisation of β-tetralone: even although α-tetralone can be dimerised in high yield to 3.4,3'.4'-tetrahydro-1.1'-dinaphthyl (XXXIV),[16,17] no success at all was experienced in the corresponding reaction with β-tetralone. Another approach, the 'Grignard dimerisation'[18,19] of the bromo-dialin (XXXV)[15] also failed to yield the required product, forcing us to return to the original starting material, 2-bromo-1-ethoxytetralin (XXXVI) of von Braun;[14] using improved techniques[19] in the dimerisation step, 3.4,3'.4'-tetrahydro-2.2'-dinaphthyl (XXXII) was finally obtained in satisfactory amounts. That this material had the required structure has been investigated in some detail. Its ultra-violet spectrum (figure 7) showed considerably more fine structure than the corresponding 1.1'-compound (XXXIV)[20] (figure 7) and in this respect approached as might be expected the spectrum of trans,trans-1.4-diphenylbutadiene (XXXVII).[20] In addition, the NMR spectra of the two dienes (XXXII, XXXIV) have been analysed, since both the position and the coupling constant of the vinylic proton are characteristic. This vinylic proton should be found at lower field in 3.4,3'.4'-tetrahydro-2.2'-dinaphthyl (XXXII) than in 3.4,3'.4'-tetrahydro-1.1'-dinaphthyl (XXXIV),[21] and in addition, in (XXXII) the coupling constant should be very small since only long-range allylic coupling can occur. On the other hand, a much larger coupling with the methylene protons of the α-carbon atom can be anticipated in (XXXIV).[22] These predictions have been borne out by the spectra - the vinylic protons' position in (XXXII) is at $3{\cdot}25\ \tau$ and the coupling cannot be resolved whereas in (XXXIV) the τ value found is $3{\cdot}91$ and the coupling constant is $4{\cdot}2$ c/s.

Diels-Alder condensation of 3.4,3'.4'-tetrahydro-2.2'-dinaphthyl (XXXII) with maleic anhydride has already been reported.[15] Now, since the steric requirements of benzoquinone and naphthoquinone are little different from

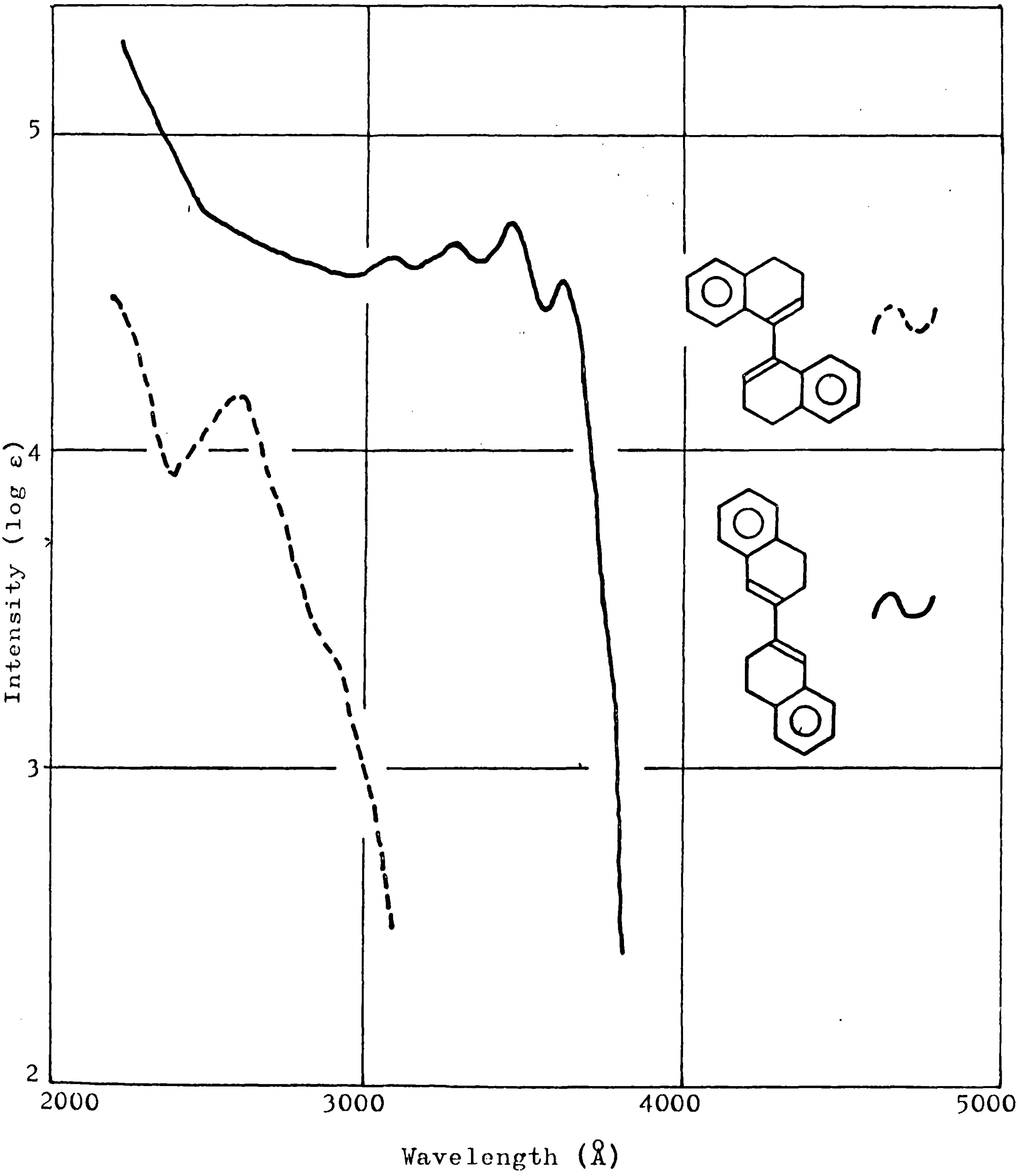
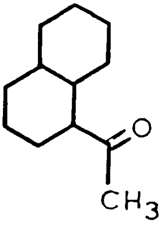
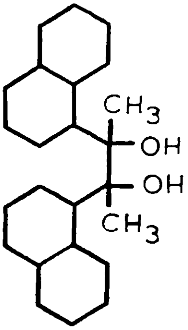


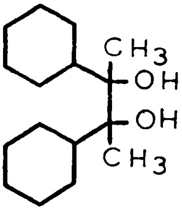
Figure 7. Absorption maxima (Å) and log ε (in parentheses).
3.4,3'.4'-Tetrahydro-2.2'-dinaphthyl in ethanol: 3620 (4·54), 3440 (4·71), 3270 (4·69), 3090 (4·61).
3.4,3'.4'-Tetrahydro-1.1'-dinaphthyl in ethanol: 2600 (4·20).



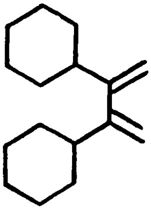
XL



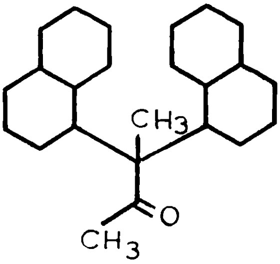
XLI



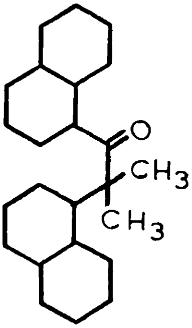
XLII



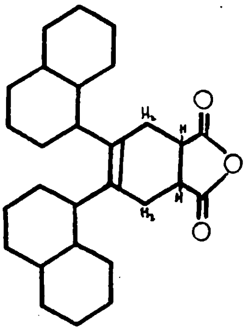
XLIII



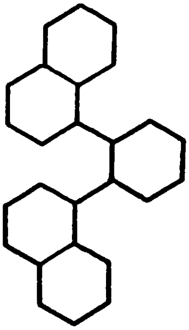
XLIV



XLV



XLVI



XLVII

maleic anhydride, it was anticipated that condensation would occur without any great difficulty. However, after trying these condensations under a variety of reaction conditions, none of the desired adducts were ever isolated. The principal products from the reaction of (XXXII) with benzoquinone were 2.2'-dinaphthyl (XXXVIII)[14] and hydroquinol; with (XXXII) and naphthoquinone the starting materials were returned unchanged, except in one instance when triphthaloylbenzene (XXXIX)[23] was obtained.

This left no alternative but to turn to the other diene, 2.3-di-(1-naphthyl)-butadiene (XXXIII) which has been synthesised starting from methyl-1-naphthyl ketone (XL). Dimerisation of this ketone (XL) by Newman's method[17] yielded 2.3-di-(1-naphthyl)-butane-2.3-diol (XLI), which interestingly crystallised from aqueous solvents as a dihydrate;[24] this compound could not be dehydrated to the required diene (XXXIII) in good yield. The closest analogy that could be found was the conversion of 2.3-diphenylbutane-2.3-diol (XLII) to 2.3-diphenylbutadiene (XLIII) with potassium bisulphate;[25] use of this method did yield (XXXIII) in small amounts (figure 8) together with much larger quantities of either of two possible pinacol-pinacolone rearrangement products (XLIV, XLV) - the double methyl signal in the NMR spectrum indicating

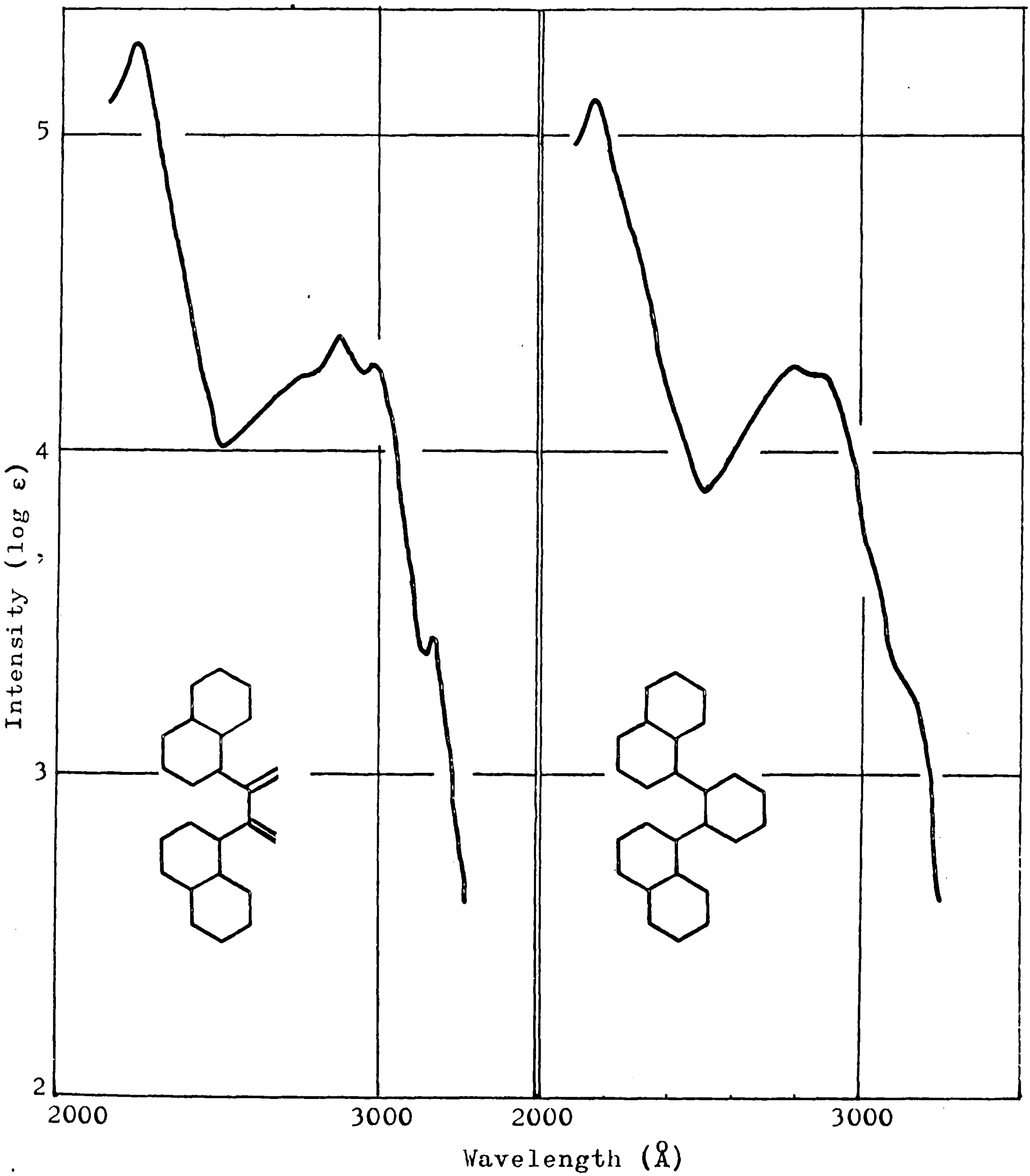
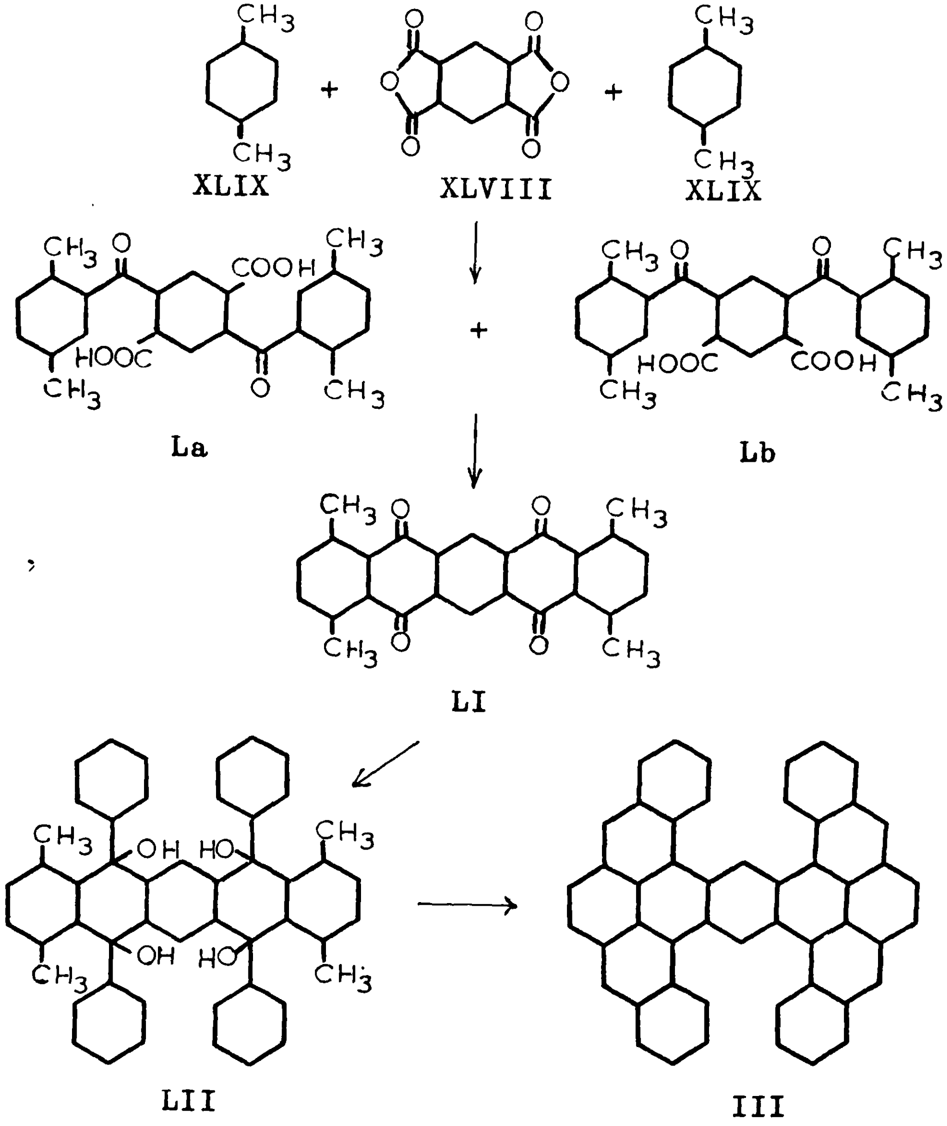


Figure 8. Absorption maxima (Å) and log ε (in parentheses). 2.3-Di-(1-naphthyl)-buta-1.3-diene in ethanol: α, 3140 (3·42); β, 2945 (4·28), 2840 (4·37), 2750 (4·35); β, 2210 (5·29). o-Di-(1-naphthyl)-benzene in ethanol: p, 2910 (4·23), 2820 (4·28); β, 2180 (5·11).

that (XLIV) rather than (XLV) had been formed. Any other methods of dehydration always failed to yield the required diene (XXXIII).[26] 2.3-Dinaphthylbutadiene (XXXIII) readily reacted with maleic anhydride to form the expected adduct (XLVI) which could be decarboxylated and dehydrogenated in one step to o-di-(1-naphthyl)-benzene (XLVII) (figure 8) with lead dioxide in decalin.[27] It is worth mentioning that an attempt has been made to surmount the problem of having to isolate the butadiene (XXXIII). Campbell has successfully reacted certain dimethyldiols with maleic anhydride to yield adducts of type (XLVI) directly;[28] reaction of our diol (XLI) with maleic anhydride gave none of the required product (XLVI).

Photochemical cyclisation[29] of o-di-(1-naphthyl)-benzene (XLVII) yielded a mixture of starting material (XLVII) and the required product, 5.6-benzopicene (I). After chromatography, which did not separate the two hydrocarbons satisfactorily, the 5.6-benzopicene enriched fractions were treated with sym-trinitrobenzene (TNB) to yield a single TNB complex. Decomposition of this material yielded the pure 5.6-benzopicene (I) which could not be induced to crystallise, due no doubt to the large amount of steric overcrowding present in the hydrocarbon.


CH3
CH3
XLIX
O
O
O
O
O
O
XLVIII
CH3
CH3
XLIX
CH3
O
COOH
CH3
HOOC
CH3
O
CH3
La
+
CH3
O
O
CH3
HOOC
COOH
CH3
CH3
Lb
CH3
O
O
CH3
CH3
O
O
CH3
LI
CH3
OH
HO
CH3
OH
HO
CH3
CH3
LII
III

The synthesis of tetranaphthopentacene (III) was quite straightforward. Double Friedel-Crafts reaction between pyromellitic dianhydride (XLVIII) and p-xylene (XLIX) yielded the isomeric acids (La, b).[30] Cyclisation with concentrated sulphuric acid gave the desired diquinone (LI) which on reaction with phenyl lithium followed by cyclodehydrogenation gave tetranaphthopentacene (III) as golden-yellow needles.

EXPERIMENTAL

Attempted Condensation[9] of picene-5.6-quinone (XXVII) with benzene-1.2-diacetonitrile (XXVIII).

1) in presence of solvent. Picene-5.6-quinone (XXVII) (200 mg.)[10] and benzene-1.2-diacetonitrile (XXVIII) (100 mg.)[11] were refluxed for twenty-four hours in dry pyridine (25 ml.) containing piperidine (1 ml.). On allowing to cool, crystals of the starting quinone slowly precipitated.

2) in absence of solvent. Picene-5.6-quinone (XXVII) (200 mg.) and benzene-1.2-diacetonitrile (XXVIII) (100 mg.) were made into a paste with a few drops of piperidine. This paste was kept molten for thirty minutes and then allowed to solidify. Addition of benzene (75 ml.) followed by crystallisation gave only starting material (XXVII).

Di-(o-chlorobenzylidene)-naphthalene-2.3-diacetonitrile (XXX).

Naphthalene-2.3-diacetonitrile (XXIX) (20 g.)[12] and o-chlorobenzaldehyde (28 g.) were dissolved in hot ethanol (500 ml.). Sodium hydroxide (33%, 75 ml.) was added, and the mixture shaken. The solution rapidly darkened, became much warmer, and the product crystallised from the hot solution. After cooling, the condensation product was filtered off, washed with ethanol and dried. Crystallisation from glacial acetic acid yielded colourless prisms of di-(o-chlorobenzylidene)-naphthalene-2.3-diacetonitrile (XXX) (19·5 g.) m.pt. 197-198°, which did not dissolve in concentrated sulphuric acid.

Found	C=74·33%, H=3·55%, N=6·08%
$C_{28}H_{16}N_2Cl_2$ requires	C=74·51%, H=3·57%, N=6·20%.

Cyclisation and Decarboxylation of di-(o-chlorobenzylidene)-naphthalene-2.3-diacetonitrile (XXX): 1,2,3.4-Dibenzotetracene (XXXI).

Di-(o-chlorobenzylidene)-naphthalene-2,3-diacetonitrile (XXX) (2 g.) was dissolved in dry quinoline (30 ml.) and potassium hydroxide (4 g.) was added to the refluxing solution. The two phase mixture immediately darkened and was refluxed under nitrogen for two hours. On cooling, the reaction mixture was poured on to dilute hydrochloric acid (100 ml.) and the dark brown solid obtained was collected by filtration, washed with water and dried (750 mg.). No attempt was made to isolate a pure compound at this stage - decarboxylation was carried out directly on the crude material.

The solid was ground together with soda-lime (2·5 g.), made into a thick paste with saturated potassium hydroxide solution, and then heated at 275-300° in an nitrogen atmosphere for five minutes. Sublimation (240-260°/·03 mm.) gave a yellow sublimate which was dissolved in benzene and chromatographed on Grade I Neutral Alumina (10 g.). Elution with benzene gave a pale yellow solution which on concentration yielded long orange-yellow needles of 1.2,3.4-dibenzotetracene (XXXI) (24 mg.) m.pt. 260-263° (lit. m.pt. 265-266°).[13] (XXXI) dissolved in concentrated sulphuric acid forming a red solution.[13]

Found	C = 94·93%, H = 5·20%
$C_{26}H_{16}$ requires	C = 95·09%, H = 4·91%.

<u>Attempted Dimerisation of β-tetralone.</u>

A mixture of freshly scraped aluminium foil (12 g., 1 sq.cm. squares), freshly distilled β-tetralone (20 g.),[31] dry ethanol (150 ml.), dry benzene (100 ml.) and mercuric chloride (0·5 g.) were refluxed under nitrogen for twenty-four hours. After cooling, decomposition was accomplished with excess dilute hydrochloric acid, and the aqueous phase was extracted with benzene/ether (1:1); the combined organic phases were washed with dilute hydrochloric acid and water, dried over magnesium sulphate and all the organic solvent removed. The yellow-orange oil remaining was dissolved in glacial acetic acid (50 ml.) and acetic anhydride (50 ml.) and dehydration of the pinacol carried out by refluxing for three hours. After concentration to small volume and standing overnight, no crystalline material was obtained. GLC examination of the product showed the presence of three recognisable compounds: naphthalene, 2.2'-dinaphthyl (XXXVIII) and 3.4,3'.4'-tetrahydro-2.2'-dinaphthyl (XXXII). A large number of other unidentifiable components were also present.

Attempted Dimerisation of 2-bromo-3.4-dihydronaphthalene (XXXV)

2-Bromo-3.4-dihydronaphthalene (XXXV) (20 g.)[15] and magnesium (2·3 g.) were refluxed in dry tetrahydrofuran (100 ml.) for three hours under nitrogen. The Grignard reagent so formed was then added to a suspension of ethyl bromide (10 g.) and water-free cobalt chloride (2·1 g.) in dry tetrahydrofuran (100 ml.) and the green reaction mixture refluxed for a further three hours. It was decomposed with hydrochloric acid, and thoroughly extracted with ether; the ethereal extract was dried over magnesium sulphate and all the solvent removed by vacuum distillation to leave a clear oil. An ethanolic solution of this oil eventually deposited a small amount of colourless solid which was collected and recrystallised repeatedly from ethanol as colourless prisms of 3.4,3'.4'-tetrahydro-1.1'-dinaphthyl (XXXIV) (460 mg.) m.pt. 141-142^{o} (lit. m.pt. 141^{o}).[16]

There does not appear to be a rational explanation for the preparation of a 1.1'-diene (XXXIV) from a 2-bromo compound (XXXV) by a simple coupling reaction.

Dimerisation of 2-bromo-1-ethoxytetralin : 3.4,3'.4'-Tetrahydro-2.2'-dinaphthyl (XXXII).

2-Bromo-1-ethoxytetralin (XXXVI) (80 g.)[14] and magnesium (7·68 g.) were refluxed in dry tetrahydrofuran (500 ml.) for three hours under nitrogen. The Grignard complex obtained was added to ethyl bromide (34·9 g.) and water-free cobalt chloride (7·1 g.) in dry tetrahydrofuran (500 ml.) and the mixture refluxed for a further three hours. The green reaction mixture was then decomposed with dilute hydrochloric acid, extracted thoroughly with ether and the ethereal extract dried over magnesium sulphate. After the removal of all organic solvent by vacuum distillation, the crude reaction product was taken up in ethanol (250 ml.) and dilute sulphuric acid (100 ml.), refluxed for three hours and the reaction product extracted by the procedure just described. The pale yellow oil thus obtained was dissolved in ethanol/ cyclohexane and on standing almost colourless needles of 3.4,3'.4'-tetrahydro-2.2'-dinaphthyl (XXXII) (34·5 g.) m.pt. 156-158° (lit. m.pt. 158-159°)[15] were deposited. All solutions of (XXXII) in organic solvents exhibited a strong blue fluorescence; the diene dissolved in concentrated sulphuric acid to produce a yellow colour. The UV-spectrum is shown in figure 7. NMR spectrum: 2·78 τ (aromatic CH, multiplet, 8 protons), 3·25 τ (vinylic CH, singlet, 2 protons) and 7·18 τ (methylene CH_2, multiplet, 8 protons).

3.4,3'.4'-Tetrahydro-1.1'-dinaphthyl (XXXIV)

(XXXIV) was prepared from α-tetralone by the method of Altman and Ginsburg[16] - colourless prisms from ethanol, m.pt. 141-142° (lit. m.pt. 141°).[16] The UV-spectrum is shown in figure 7. NMR spectrum: 2·85 τ (aromatic CH, multiplet, 8 protons), 3·91 τ (vinylic CH, triplet, 2 protons), 7·05 τ (methylene CH_2, multiplet, 4 protons) and 7·62 τ (methylene CH_2, multiplet, 4 protons).

Attempted Diels-Alder Reaction between 3.4,3'.4'-tetrahydro-2.2'-dinaphthyl (XXXII) and benzoquinone.

(1) mild conditions. Diene (XXXII) (2·5 g.), benzoquinone (2·2 g.) and chloranil (5·0 g.) were refluxed in dry xylene (25 ml.) for twelve hours. On standing, the red reaction mixture deposited a small amount of orange material which on crystallisation from ethanol gave colourless plates of 2.2'-dinaphthyl (XXXVIII) (0·5 g.) m.pt. 185-186° (lit. m.pt. 186°).[14]

(2) sealed tube. Diene (XXXII) (0·5 g.), benzoquinone (2·5 g.) and xylene (5 ml.) were heated in a sealed tube at 200°C for twelve hours. From the red reaction mixture only 2.2'-dinaphthyl (XXXVIII) and hydroquinol could be isolated and characterised.

(3) in nitrobenzene.[32] Diene (XXXII) (0·5 g.) and benzoquinone (2·5 g.) were refluxed in nitrobenzene (5 ml.) for twelve hours. After steam distillation to remove the organic solvent, 2.2'-dinaphthyl (XXXVIII) was obtained as the principal reaction product.

Attempted Diels-Alder Reaction between 3,4,3'.4'-tetrahydro-2.2'-dinaphthyl (XXXII) and naphthoquinone.

(1) mild conditions. Diene (XXXII) (2·5 g.), naphthoquinone (3·0 g.) and chloranil (5·0 g.) were refluxed in dry xylene (25 ml.) for twelve hours. On standing no adduct was deposited; the solution was concentrated, and a mixture of solids slowly deposited. These could be recognised as the starting materials.

(2) sealed tube. Diene (XXXII) (0·5g.) naphthoquinone (1·5 g.) and xylene (5 ml.) were heated in a sealed tube at 200°C for twelve hours. From the dark brown reaction mixture only starting materials could be isolated.

(3) in nitrobenzene.[32] Diene (XXXII) (0·5 g.) and naphthoquinone (1·5 g.) were refluxed in nitrobenzene (5 ml.) for twelve hours. When cool, this solution deposited some brownish-yellow crystalline material, which was collected and dried. Crystallisation from a large volume of o-dichlorobenzene yielded sheaves of bright yellow needles of triphthaloylbenzene (XXXIX) (280 mg.) m.pt. ~ 450° (lit. m.pt. 450-460°);[23] M.S. molecular ion m/e = 468; calc. M.W. = 468. Our material gave the required yellow colour in concentrated sulphuric acid.[23]

2.3-Di-(1-naphthyl)-butane-2.3-diol (XLI).

Methyl-1-naphthyl ketone (XL) (180 g.) was dissolved in absolute alcohol (750 ml.) and dry benzene (750 ml.) in a 3-necked flask fitted for reflux with stirring. To this was added aluminium foil (27 g., 1 sq. cm. squares, freshly scraped) and mercuric chloride (1 g.). On gentle warming, a vigorous reaction started which could be left for three hours. The reaction mixture was then stirred and refluxed for a further twelve hours. When cool, the mixture was treated with excess dilute hydrochloric acid, and the product extracted with benzene/ether (1:1). The combined extracts were washed with dilute hydrochloric acid, water, sodium carbonate and finally water, and then dried over magnesium sulphate. The organic solvents were removed by vacuum distillation, leaving a yellow-orange oil, to which was added an equal volume of ice-cold methanol. On standing overnight at 0°C, the diol crystallised out as colourless needles (65 g.).

Crystallisation from methanol yielded 2.3-di-(1-naphthyl)-butane-2.3-diol as needles of its dihydrate m.pt. 102-104°.

Found C = 76·08%, H = 6·93%

$C_{24}H_{22}O_2.2H_2O$ requires C = 76·17%, H = 6·92%.

Alternatively, crystallisation from benzene/petrol gave colourless prisms of the anhydrous material, m.pt. 184-186°, ν_{max}^{KBr} = 3558 cm.$^{-1}$ (O-H). (XLI) gave an olive-green colour in concentrated sulphuric acid.

Found C = 84·03%, H = 6·20%

$C_{24}H_{22}O_2$ requires C = 84·18%, H = 6·48%.

A varying amount of further diol could be obtained on concentrating the methanolic mother liquors and allowing them to stand at 0°C for one month (5-10 g.).

2,3-Di-(1-naphthyl)-buta-1,3-diene (XXXIII)

2.3-Di-(1-naphthyl)-butane-2.3-diol (XLI) (20 g.) and freshly dried sodium bisulphate (0·5 g.)[25] were gently refluxed (200°/1·5 mm.) for thirty minutes. When cool, the resulting melt was dissolved in the minimum amount of benzene, and chromatographed on Grade I Basic Alumina (800 g.). Elution with petroleum ether (40-60°) gave a colourless solution with a strong blue-violet fluorescence. The petroleum ether was removed and the solid obtained crystallised from ethanol as colourless platelets of 2.3-di-(1-naphthyl)-buta-1.3-diene (XXXIII) (0·5 g.) m.pt. 174-175°, ν_{max}^{KBr} = 915 cm.$^{-1}$ (C-H). The UV-spectrum is shown in figure 8. (XXXIII) gave a golden-yellow colour in concentrated sulphuric acid.

Found C = 93·80%, H = 6·13%

$C_{24}H_{18}$ requires C = 94·08%, H = 5·92%.

Further elution with 2% chloroform/petroleum ether (40-60°) gave a clear solution which exhibited a strong carbonyl absorption. The organic solvents were removed, and the material crystallised from ethyl acetate as colourless prisms of 3.3-di-(1-naphthyl)-butan-2-one (XLIV) (8·3 g.) m.pt. 158-159°, ν_{max}^{KBr} = 1702 cm.$^{-1}$ (C=O). NMR spectrum: 1·95 τ (aromatic CH, multiplet, 6 protons), 2·44 τ (aromatic CH, multiplet, 8 protons), 7·56 τ (methyl CH_3, singlet, 3 protons) and 7·87 τ (methyl CH_3, singlet, 3 protons). (XLIV) gave a blue-violet colour in concentrated sulphuric acid.

Found C = 88·65%, H = 6·13%

$C_{24}H_{20}O$ requires C = 88·85%, H = 6·22%.

Repetition of this preparation gave 1·62 g. of 2.3-di-(1-naphthyl)-butadiene (XXXIII) from 60 g. of starting diol (XLI).

Attempted Dehydration of 2.3-Di-(1-naphthyl)-butane-2.3-diol (XLI) by a Cis-Elimination Reaction.[26]

Although 2.3-di-(1-naphthyl)-butadiene (XXXIII) had been prepared and characterised, the yield was very poor; an alternative method was sought for its preparation involving a cis-elimination reaction.

To an ice-cold solution of diol (XLI) (3·4 g.) in dry pyridine (30 ml.) was added dropwise ethyl chloroformate (12·5ml.). The reaction mixture was stirred for fifteen minutes at 0°C, then sealed in a nitrogen atmosphere and left overnight at 0°C. The mixture was poured on to excess dilute sulphuric acid, extracted rapidly with ether, the ethereal solution dried (magnesium sulphate) and the ether then removed to leave the oily bis-carbonate ester, ν_{max}^{film} = 1744 $cm.^{-1}$ (C=O), 1275 $cm.^{-1}$ (C-O).

This material was directly pyrolysed at 250-275° for ten minutes to accomplish the elimination. The brown tar thus obtained was dissolved in the minimum amount of toluene and chromatographed. Elution with benzene gave a colourless solution which yielded crystals of pinacolone (XLIV) on concentration.

1.2-Di-(1-naphthyl)-cyclohex-1-ene-4.5-dicarboxylic acid anhydride (XLVI).

2.3-Di-(1-naphthyl)-buta-1.3-diene (XXXIII) (1·53 g.) and maleic anhydride (0·44 g.) were refluxed in dry xylene (10 ml.) for one hour. The solution was concentrated to yield the required adduct which was collected by filtration. Crystallisation from benzene/acetic anhydride yielded colourless asterisks of 1.2-di-(1-naphthyl)-cyclohex-1-ene-4.5-dicarboxylic acid anhydride (XLVI) (1·22 g.) m.pt. 213^{o}, ν_{max}^{KBr} = 1778, 1842 cm.$^{-1}$ (O=C-O-C=O). (XLVI) gave a pale yellow colour in concentrated sulphuric acid.

Found C = 83·26%, H = 5·16%

$C_{28}H_{20}O_3$ requires C = 83·15%, H = 4·99%.

An attempt was made to prepare this anhydride by the direct condensation[28] of the diol (XLI) with maleic anhydride, in order to eliminate the isolation of the dinaphthylbutadiene (XXXIII). Diol (1 g.) and maleic anhydride (2 g.) were refluxed in diethyl phthalate for ten minutes. The major part of the solvent was then removed by vacuum distillation, and the remaining portion was diluted first with ethyl acetate and then with petrol. No adduct (XLVI) was isolated.

o-Di-(1-naphthyl)-benzene (XLVII).

A finely powdered mixture of anhydride (XLVI) (1·0g.) and lead dioxide (4 g.) in freshly distilled decalin (20 ml.) were placed in a 100 ml. flask equipped with a glass inlet tube leading to the surface of the reaction mixture, and an outlet tube leading to a solution of barium hydroxide. The mixture was refluxed for five hours in a nitrogen atmosphere while carbon dioxide was being evolved. The reaction over, xylene (50 ml.) was added, refluxed briefly and filtered; this procedure was repeated three times to ensure all the hydrocarbon was obtained in solution. The united extracts were distilled to small volume and chromatographed on Grade I Neutral Alumina (30 g.). Elution with petroleum ether (40-60°) yielded a colourless solution with a strong violet fluorescence. Crystallisation from benzene/ethanol yielded o-di-(1-naphthyl)-benzene (XLVII) as colourless plates (237 mg.) m.pt. 155° (soften 145°). The UV-spectrum is shown in figure 8. A colourless solution was obtained with concentrated sulphuric acid.

Found C = 94·21%, H = 5·69%

$C_{26}H_{18}$ requires C = 94·51%, H = 5·49%

5.6-Benzopicene (I).

o-Di-(1-naphthyl)-benzene (XLVII) (220 mg.) and iodine (22 mg.) were irradiated in cyclohexane (500 ml.) for forty-eight hours in the presence of a steady stream of air. The cyclohexane was removed, the resulting oil dissolved in a small amount of xylene and chromatographed on Grade I Neutral Alumina (10 g.). It was found impossible to obtain a satisfactory separation of starting material (XLVII) and product (I). Therefore the 5.6-benzopicene enriched fractions were transformed into the TNB complex in benzene solution. Only one crystalline complex was obtained - stout orange rods, m.pt. 179-180°.

Found N = 11·30%

$C_{26}H_{16}.C_{12}H_6O_{12}N_6$(1:2) requires N = 11·14%.

The complex was decomposed by passing it down an Alumina column to yield a yellow solution of 5.6-benzopicene (I) which could not be induced to crystallise; mass spectral analysis showed that 5.6-benzopicene had indeed been obtained: M.S. molecular ion m/e = 328; calc. M.W. = 328.

A further attempt was made to obtain 5.6-benzopicene (I) as a solid by the formation and decomposition of its picrate - bright red-orange needles, m.pt. 162-163°. This proved equally unsuccessful.

Found N = 10·62%

$C_{26}H_{16}.C_{12}H_6O_{14}N_6$(1:2) requires N = 10·68%.

1,4,8,11-Tetramethylpentacene-5.14,7.12-diquinone (LI).

Large quantities of this material were required, and since the original method of preparation[30] was not satisfactory, the following method was eventually found to be suitable for the preparation of (LI) in bulk.

The mixed dicarboxylic acids (La, b) (40 g.)[30] were stirred with concentrated sulphuric acid (300 ml.) at 50° till all the solid material had dissolved. The reddish-brown solution was then warmed to 100°C and scraped vigorously until a precipitate was obtained. The reaction mixture was then decomposed with ice to give a light green precipitate which was filtered, washed with water, dilute ammonium hydroxide and water and then dried. 1,4,8,11-Tetramethylpentacene-5.14 7.12-diquinone (LI) (24·0 g.) m.pt. $>340^{\circ}$ required no further purification.

5,7,12,14-Tetraphenyl-5,7,12,14-tetrahydroxy-5,7,12,14-tetrahydro-1,4,8,11-tetramethylpentacene (LII).

The above diquinone (LI) (20 g.) was added as a very finely divided dry benzene slurry (350 ml.) to an ethereal solution (450 ml.) of phenyl lithium, prepared from bromobenzene (63 g.) and lithium chips (5·7 g.) .

On mixing, the solution went immediately blue-green, changing to a yellowish-brown colour over five minutes. The mixture was shaken with glass beads for thirty-six hours, decomposed with ice and dilute acetic acid, and then steam - distilled to remove the organic solvents. The reddish-brown solid obtained was triturated with ether, and on filtration gave a pale green solid. On allowing the ethereal solution to partially evaporate, further solid material was collected. Recrystallisation from ether gave colourless rods of tetra-ol (LII) (8·6 g.) m.pt. 275-278° dec., which dissolved in concentrated sulphuric acid to produce a blue colour.

Found C = 84·80%, H = 6·17%

$C_{50}H_{42}O_4$ requires C = 84·96%, H = 5·99%.

Tetranaphtho-(3'.1':1.14);(3''.1'':4.5)(1'''.3''':7.8);(3''''. 1'''': 11.12)-pentacene (III).

Tetra-ol (LII) (2 g.) was thoroughly ground with copper bronze (20 g.) and the intimate mixture pyrolysed for three hours at 400-420° in an atmosphere of carbon dioxide. The resulting material was extracted with xylene to remove any partially condensed material, and then with trichlorobenzene to ensure the desired hydrocarbon was taken into solution. The trichlorobenzene extract was concentrated and chromatographed on Grade I Neutral Alumina. Elution with the same solvent yielded a faintly fluorescent yellow solution which deposited tiny, deep golden-yellow needles of tetranaphthopentacene (III) (44 mg.) m.pt. > 500°, on concentration. (III) gave a violet, turning to brown colour in concentrated sulphuric acid. The UV-spectrum is shown in figure 5.

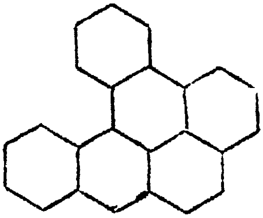
Found C = 95·66%, H = 4·38%

$C_{50}H_{26}$ requires C = 95·82%, H = 4·18%.

A colourless adduct with maleic anhydride could be obtained when the hydrocarbon (III) was warmed for thirty minutes in a melt of the anhydride. The UV-spectrum is shown in figure 6.

CHAPTER 5

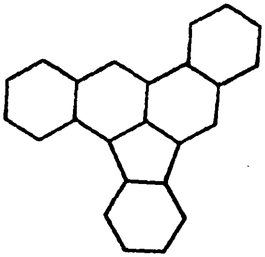
1.2,3.4-DIBENZOPYRENE



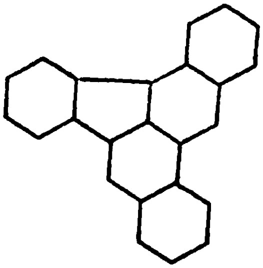
I

INTRODUCTION:

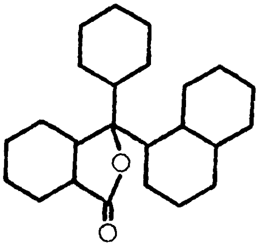
In the earlier part of 1966, Buu-Hoi[1a, b] showed that the hydrocarbon 1.2,3.4-dibenzopyrene (I) did not have this structure but was in fact 2.3,5.6-dibenzofluoranthene (II). It was therefore of interest to see if this simple hydrocarbon (I) could be synthesised in an unambiguous manner, since there is a considerable probability of its having strong carcinogenic activity.



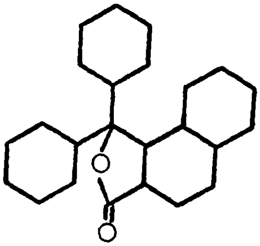
II



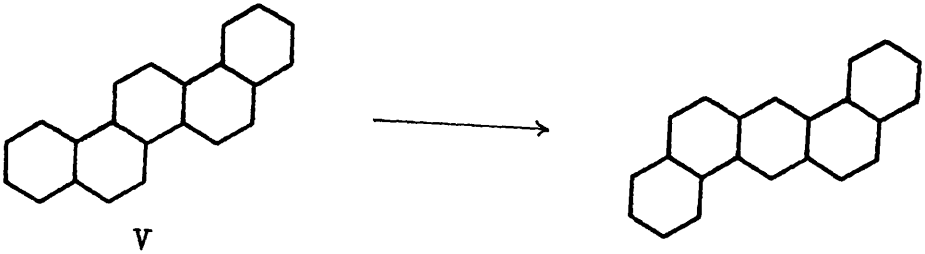
II



III

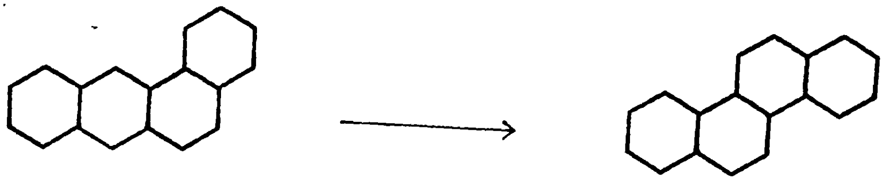


IV



V

VI



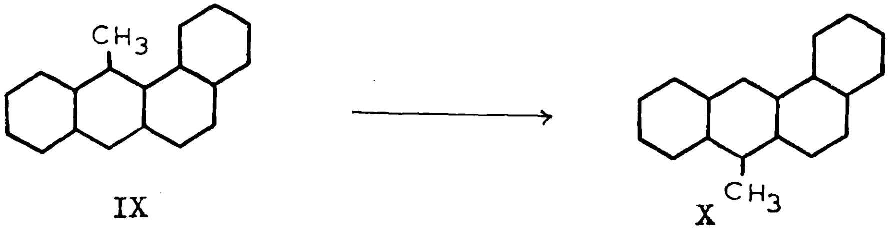
VII

VIII

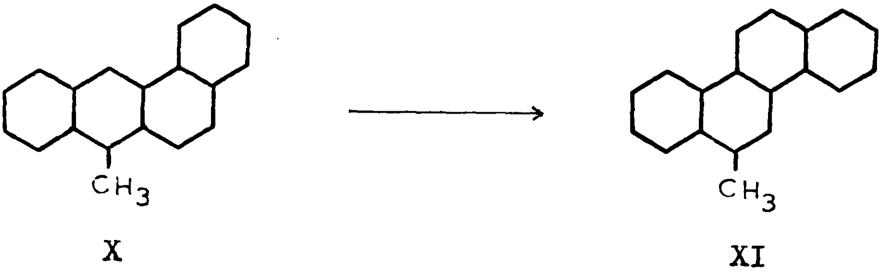
DISCUSSION:

The first synthesis of 1.2,3.4-dibenzopyrene (I) was accomplished by Clar[2] from 3-phenyl-3-(1-naphthyl)-phthalide (III). The synthetic route involved could have resulted in the formation of isomeric hydrocarbons, and in order to confirm the structure, Clar and Stewart[3] resynthesised this hydrocarbon from the isomeric phthalide (IV). A further synthesis and the simplest of all involved the treatment of tetraphene with aluminium chloride in refluxing benzene.[4] The general acceptance of these synthetic routes was shown by the fact that a considerable number of simple alkyl derivatives have been made by one or other of these methods.

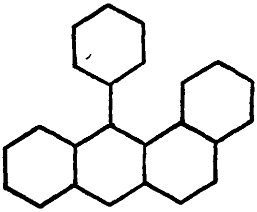
A number of reasons can be advanced to cast doubt on the structure of 1.2,3.4-dibenzopyrene (I). The first of these is the surprisingly low reactivity of the meso-anthracene position (i.e. position 5) in the Vilsmeier reaction.[5] Secondly, and most important, is the fact that all the synthetic routes involve the use of aluminium chloride which is capable of isomerising polycyclic systems under fairly mild conditions.[6] A typical example of this is the isomerisation of picene (V) to 1.2,5.6-dibenzanthracene (VI), where a phenanthrene complex becomes an anthracene complex. Unfortunately the reverse type of rearrangement also occurs

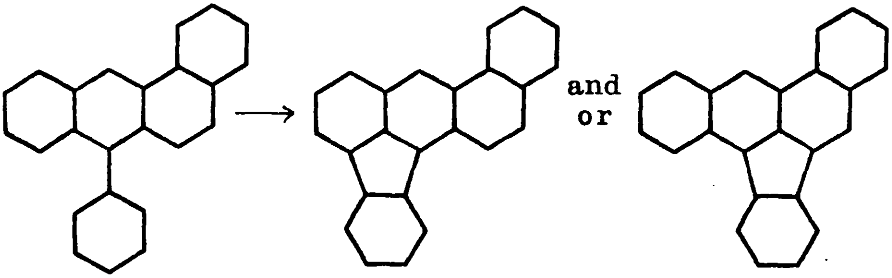


IX X

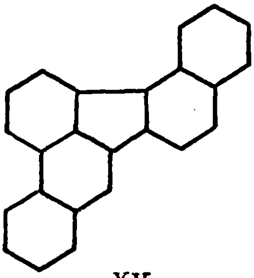


X XI





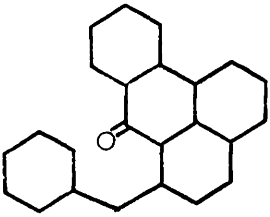
XII XIII XIV II



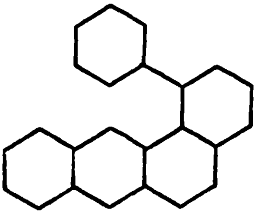
XV

when tetraphene (VII) rearranges to chrysene (VIII). To complicate matters still further, simple derivatives also undergo these reactions with either substituent migration (IX → X) or with skeletal rearrangement (X → XI). It is therefore quite obvious that any synthetic route involving the use of aluminium chloride is open to serious doubt.

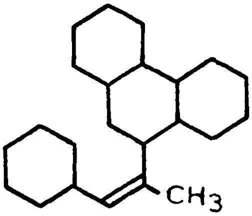
In order to prove the true structure of 1.2,3.4-dibenzopyrene (I), it was shown that 12-phenyltetraphene (XII) and 7-phenyltetraphene (XIII) gave the same hydrocarbon on cyclodehydrogenation.[1b] Cyclodehydrogenation of (XIII) could lead to either naphtho-(2'.1':2.3)-fluoranthene (XIV), which is not identical with our dibenzopyrene due to its prior synthesis,[7] or to the hitherto unknown 2.3,5.6-dibenzofluoranthene (II). This hydrocarbon was synthesised by Buu-Hoi[1b] along with the isomeric 3.4,10.11-dibenzofluoranthene (XV). Now since it is most unlikely that 7-phenyltetraphene (XIII) can undergo skeletal rearrangement to give 3.4,10.11-dibenzofluoranthene (XV), the only conclusion left to us is that dibenzopyrene is in fact 2.3,5.6-dibenzofluoranthene (II). Further proof is obtained from the fact that the melting point, ultra-violet spectrum (figure 2) and halochromism in sulphuric acid are identical .



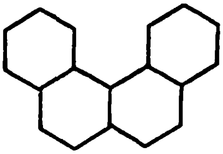
XVI



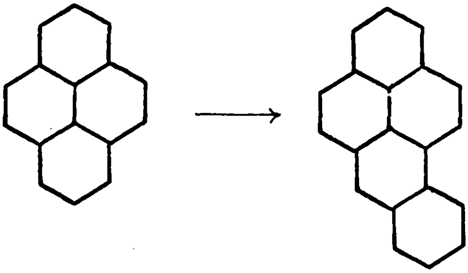
XVII



XVIII

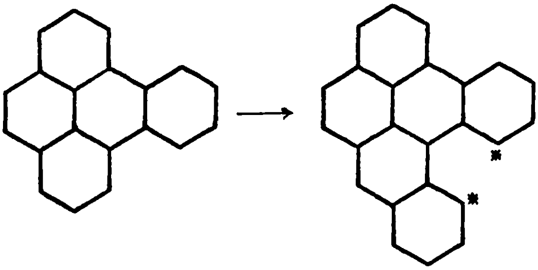


XIX



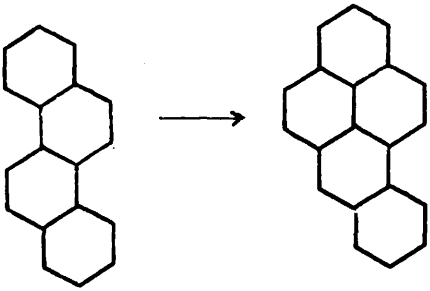
XX XXI

λ_β 2720 $\xrightarrow{245}$ 2965 Å



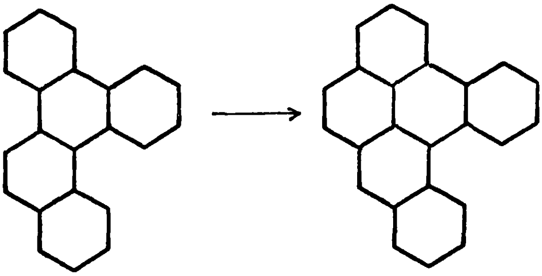
XXII I

$$2890 \xrightarrow{230} \begin{array}{r} 3190 \\ \text{corr.}\ -70 \\ \hline 3120 \end{array}\ \text{Å}$$



VIII XXI

λ_β 2670 $\xrightarrow{295}$ 2965



XXIII I

2860 $\xrightarrow{330}$ 3190 Å

Having thus established that dibenzopyrene is not a pyrene homologue but instead a dibenzofluoranthene, it follows that it is of interest to synthesise the true 1.2,3.4-dibenzopyrene (I). The first attempt was the Bradsher-type[8] cyclisation of 6-benzylbenzanthrone (XVI); no cyclised material was obtained.[1b] However, by cyclisation of 1-phenyltetraphene (XVII),[9] a pale yellow hydrocarbon, m.pt. 162-163°, was obtained which, although no evidence is presented, might well have the correct structure. The successful cyclisation of (XVII) without rearrangement can be explained by the dehydrogenation involving the active 12-position in the tetraphene nucleus and by the fact that the phenyl ring in (XVII) is less hindered than that in (XII). A successful synthesis with satisfactory structural evidence has since appeared.[10] From the styryl-phenanthrene (XVIII), in a series of unambiguous steps, Carruthers obtained 1.2,3.4-dibenzopyrene (I) as pale yellow plates m.pt. 163-164°, whose ultra-violet spectrum is shown in figure 1.

A preliminary study of this spectrum shows the characteristic sharp peaks of a pyrene homologue. Now since the hydrocarbon is overcrowded, we can expect the ratio of $\nu_\alpha : \nu_\beta$ to be considerably less than 1:1·35;[11] indeed we find $\nu_\alpha : \nu_\beta$ is 1:1·315 which compares well with the closely related

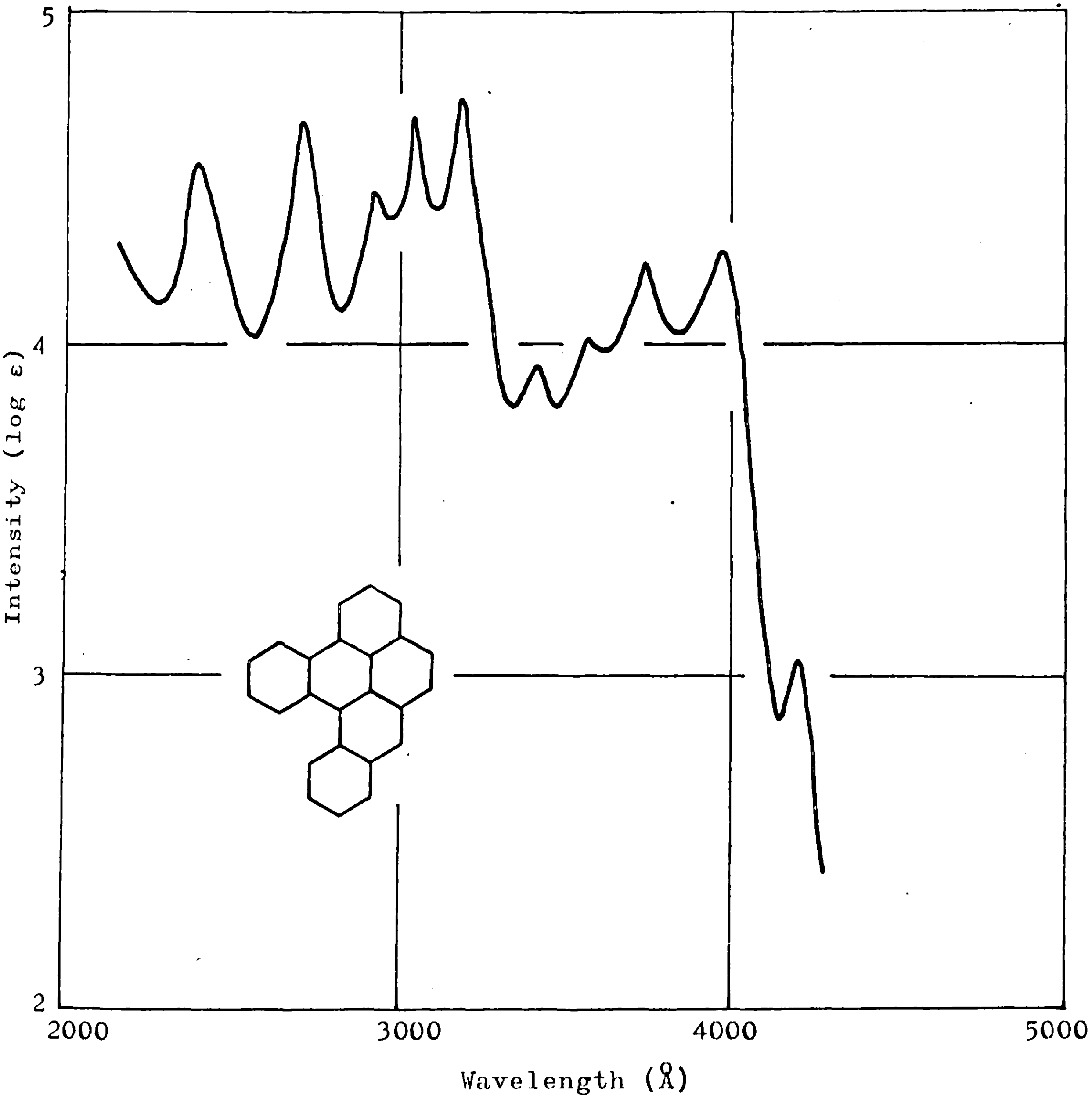


Figure 1. Absorption maxima (Å) and log ε (in parentheses). 1.2,3.4-Dibenzopyrene in ethanol: α, 4200 (3·04); p, 3970 (4·27), 3750 (4·25), 3600 (4·02), 3410 (3·85); β, 3190 (4·74), 3050 (4·69), 2940 (4·44); β', 2710 (4·64), 2400 (4·54).

3.4-benzophenanthrene (XIX) with $\nu_\alpha : \nu_\beta = 1:1{\cdot}324$. In complete contrast with this, the spectrum of 2.3,4.5-dibenzofluoranthene (II) (figure 2) shows the much broader peaks of a fluoranthene derivative and has $\nu_\alpha : \nu_\beta = 1:1{\cdot}37$ showing an absence of overcrowding. Turning now to the positions of the bands, the bathochromic shift involved in annellating a ring to the 3.4-position of a pyrene nucleus is 245 Å (XX → XXI). An identical shift should be found on comparing 1.2-benzopyrene (XXII) with 1.2,3.4-dibenzopyrene (I). The difference found is 300 Å, but from this value it is necessary to subtract 70 Å for the overcrowding of the two starred atoms[12] leaving a difference of 230 Å which is in good agreement with the 245 Å shift above. An even better comparison, which does not include a correction for overcrowding, involves the red shift of 295 Å between the β-bands of chrysene (VIII) and 2.3-benzopyrene (XXI). Correspondingly the β-band shift from 1.2-benzochrysene (XXIII) to (I) is 330 Å - proof again that the hydrocarbon prepared by Carruthers[10] is beyond doubt 1.2,3.4-dibenzopyrene (I).

The rationale behind our own synthetic work was to treat the phthalide (XXV) in an aluminium chloride/sodium chloride melt. If, under the acidic conditions of the melt, the phthalide rearranges, then the oxygen atoms will be

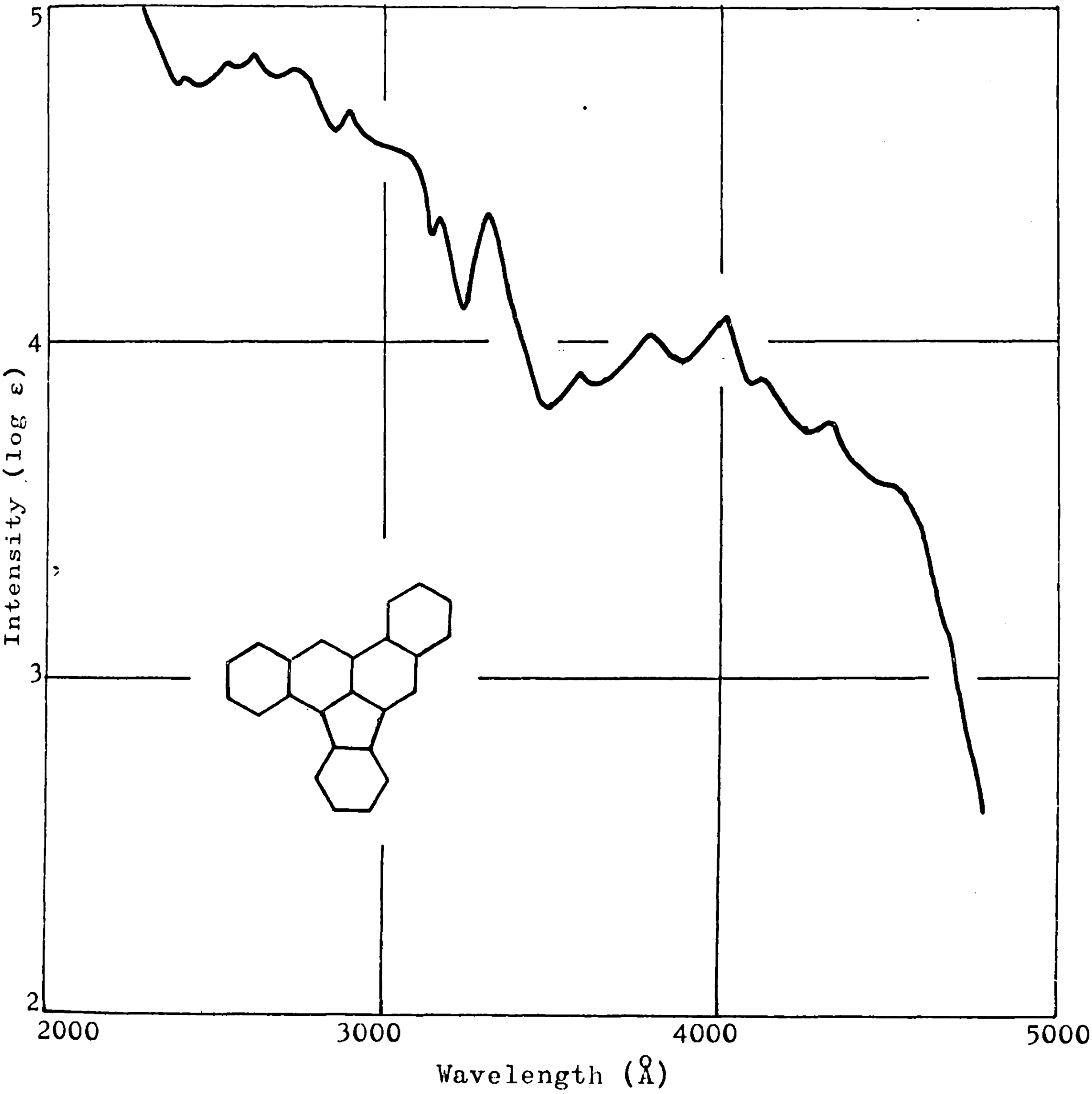
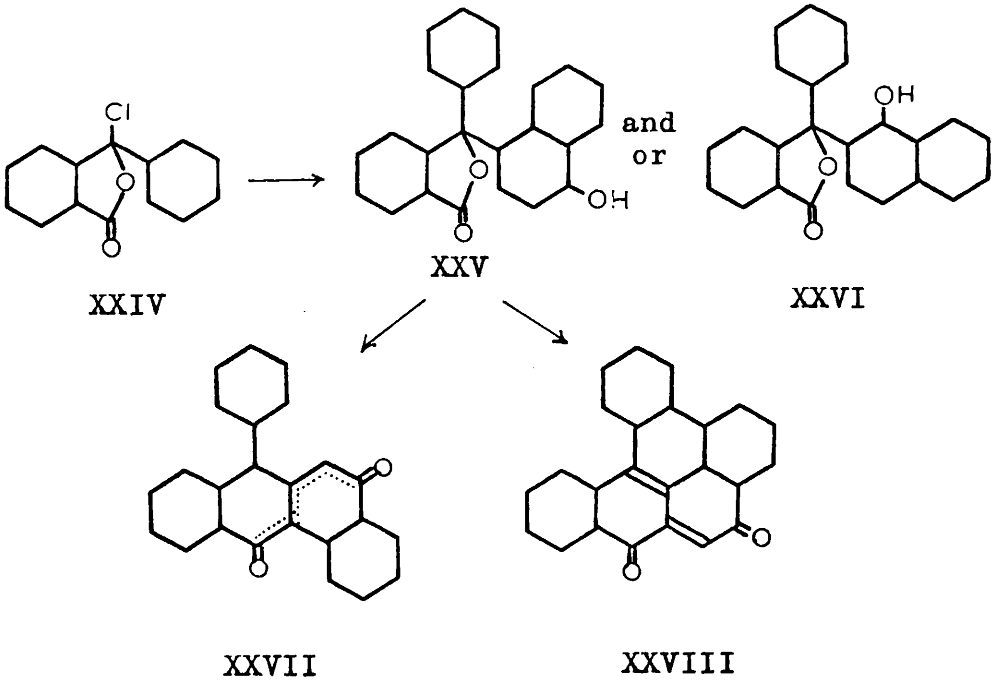
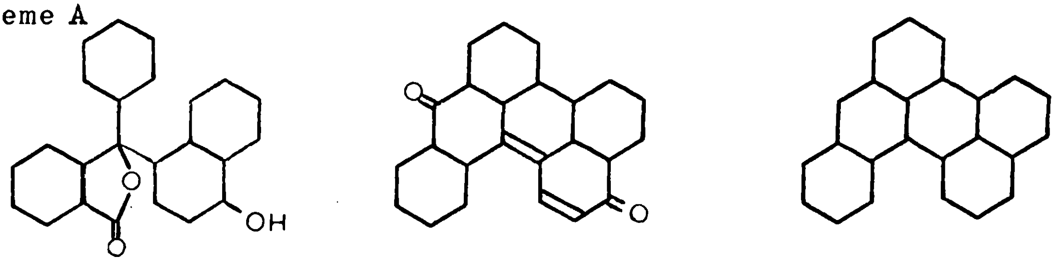


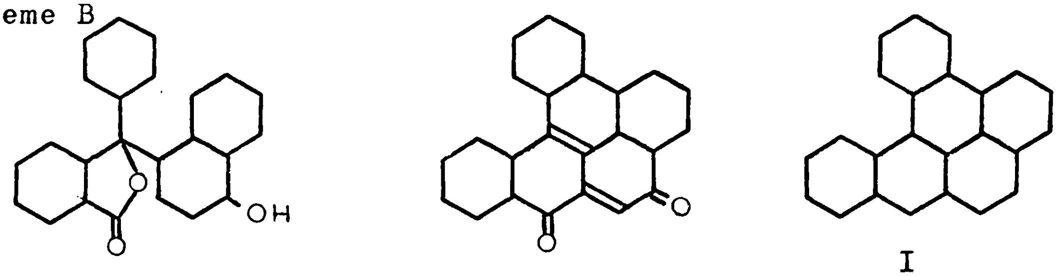
Figure 2. Absorption maxima (Å) and log ε (in parentheses). 2.3,5.6–Dibenzofluoranthene in ethanol: α, 4540 (3·56), 4330 (3·76), 4120 (3·88); p, 4010 (4·08), 3790 (4·02), 3590 (3·90); β, 3305 (4·38), 3150 (4·36), 3010 (4·58), 2890 (4·68), 2710 (4·80), 2610 (4·85), 2530 (4·83), 2400 (4·78).


Cl
O
O
XXIV
O
O
OH
XXV
and
or
OH
O
O
XXVI
O
O
XXVII
O
O
XXVIII

Scheme A

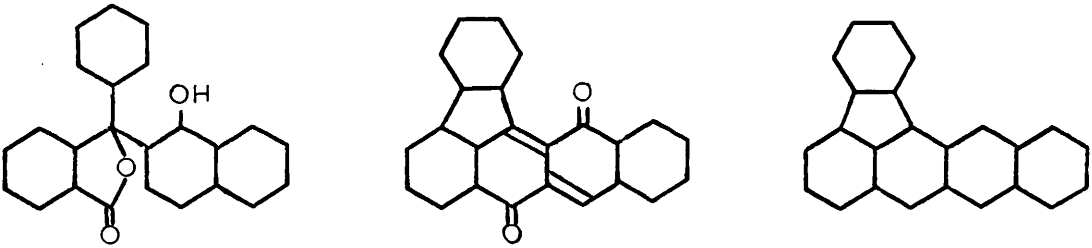


Scheme B



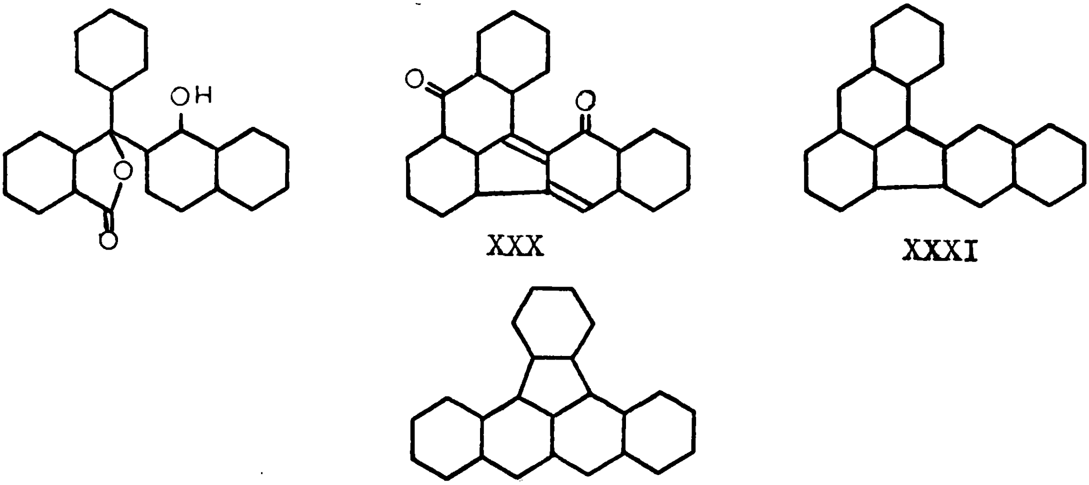
I

Scheme C



XXIX

Scheme D



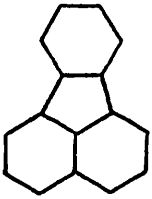
XXX

XXXI

XXXII

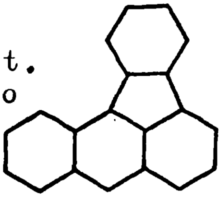
obtained with five carbon atoms between them, so eliminating the possibility of quinone formation (XXVII). On the other hand, if no rearrangement occurs, the phthalide (XXV) will be cyclised and oxidised to the polycyclic quinone (XXVIII). Reduction of (XXVIII) should then give the required 1.2,3.4-dibenzopyrene (I); in actual fact, reduction of the quinone obtained gave orange platelets of a hitherto unknown hydrocarbon, m.pt. 219-220°.

To explain this, we must consider any ambiguities in our synthetic route. Reaction of the pseudo-acid chloride (XXIV) with α-naphthol can yield either (XXV) or (XXVI).[13] Cyclisation in an acidic melt can then occur at the benzene ring or at the naphthalene nucleus deactivated by a meta-hydroxyl group. All the possibilities are taken into account in Schemes A - D. No further alternatives are possible since the quinone must have formula $C_{24}H_{12}O_2$ (analysis, mass spectrum) and the hydrocarbon $C_{24}H_{14}$ (analysis, mass spectrum). Consideration of each of these schemes in detail eliminates Scheme A immediately, since both the quinone and the hydrocarbon are well known compounds.[14] Scheme B can also be neglected since the hydrocarbon which we have obtained is not identical with the authentic material synthesised by Carruthers.[10] Turning now to the



m. pt.
110°

XXXIII

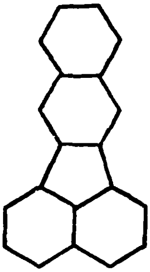


m. pt.
144-145°

XXXIV

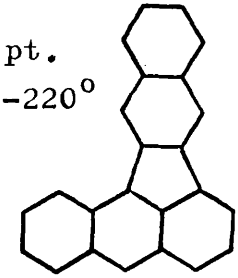
λ_{β} 2870 $\xrightarrow{-310}$ 2560 Å

λ_{p} 3585 $\xrightarrow{+695}$ 4280 Å



m. pt.
217°

XXXV

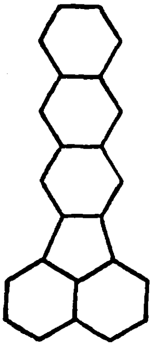


m. pt.
219-220°

XXXI

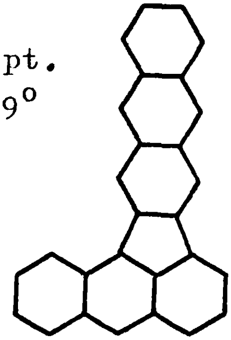
λ_{β} 3080 $\xrightarrow{-340}$ 2740 Å

λ_{p} 4000 $\xrightarrow{+705}$ 4705 Å



m. pt.
301-303°

XXXVI



m. pt.
319°

XXXVII

λ_{β} 3340 $\xrightarrow{-360}$ $\lambda_{\beta'}$ 2980 Å

λ_{p} 4380 $\xrightarrow{+670}$ 5050 Å alternative phthalide (XXVI), cyclisation and reduction could lead to either naphtho-(2'.3':2.3)-fluoranthene (XXIX) (Scheme C) or 2.3,11.12-dibenzofluoranthene (XXXI) (Scheme D).

The ultra-violet spectrum of our material (figure 3) indicates that naphtho-(2'.3':2.3)-fluoranthene (XXIX) need not be considered further. Like 2.3,6.7-dibenzofluoranthene (XXXII), naphtho-(2'.3':2.3)-fluoranthene (XXIX) consists of an o-phenylene complex annellated to tetracene, and thus we can expect their p-bands to be at approximately the same position i.e. at 5710 Å.[3,15] The p-band of our synthetic material (figure 3) is at 4705 Å. 2.3,11.12-Dibenzofluoranthene (XXXI) (from Scheme D) merits a much more rigorous examination, however, and stands up to this surprisingly well. An examination of the longer wavelength p-bands, shows that the annellation of a benzene ring to the 2.3-position of a fluoranthene produces a bathochromic shift of almost 700 Å (XXXIII → XXXIV) and (XXXVI → XXXVII). Thus we should expect a similar shift on annellating a ring in this position to 11.12-benzofluoranthene (XXXV) to give 2.3,11.12-dibenzofluoranthene (XXXI). A shift of 705 Å is found which fits extremely well. In an identical way, the β-bands all suffer a hypsochromic shift whose value varies over a somewhat larger range. Of importance also is the way in which the melting

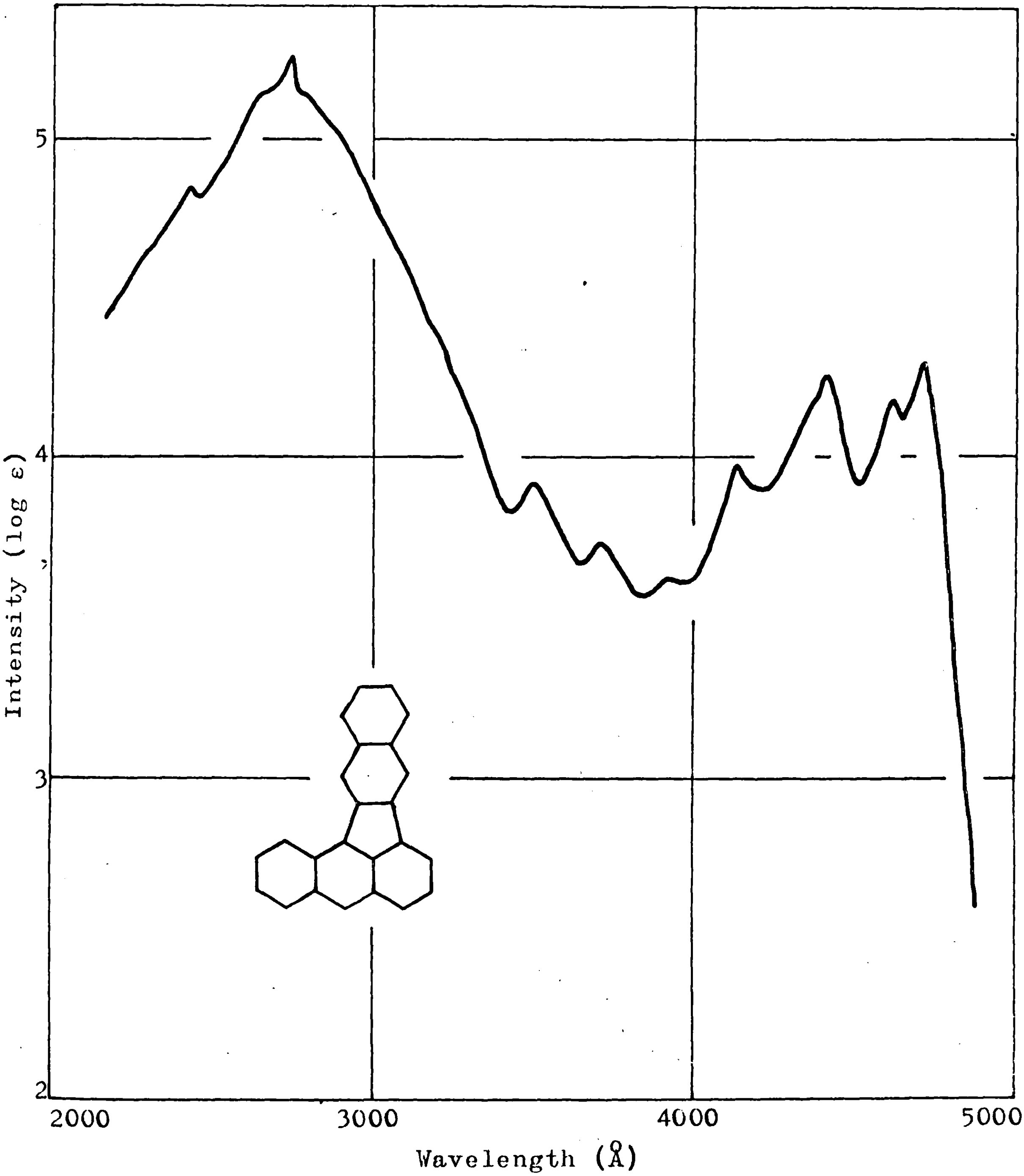
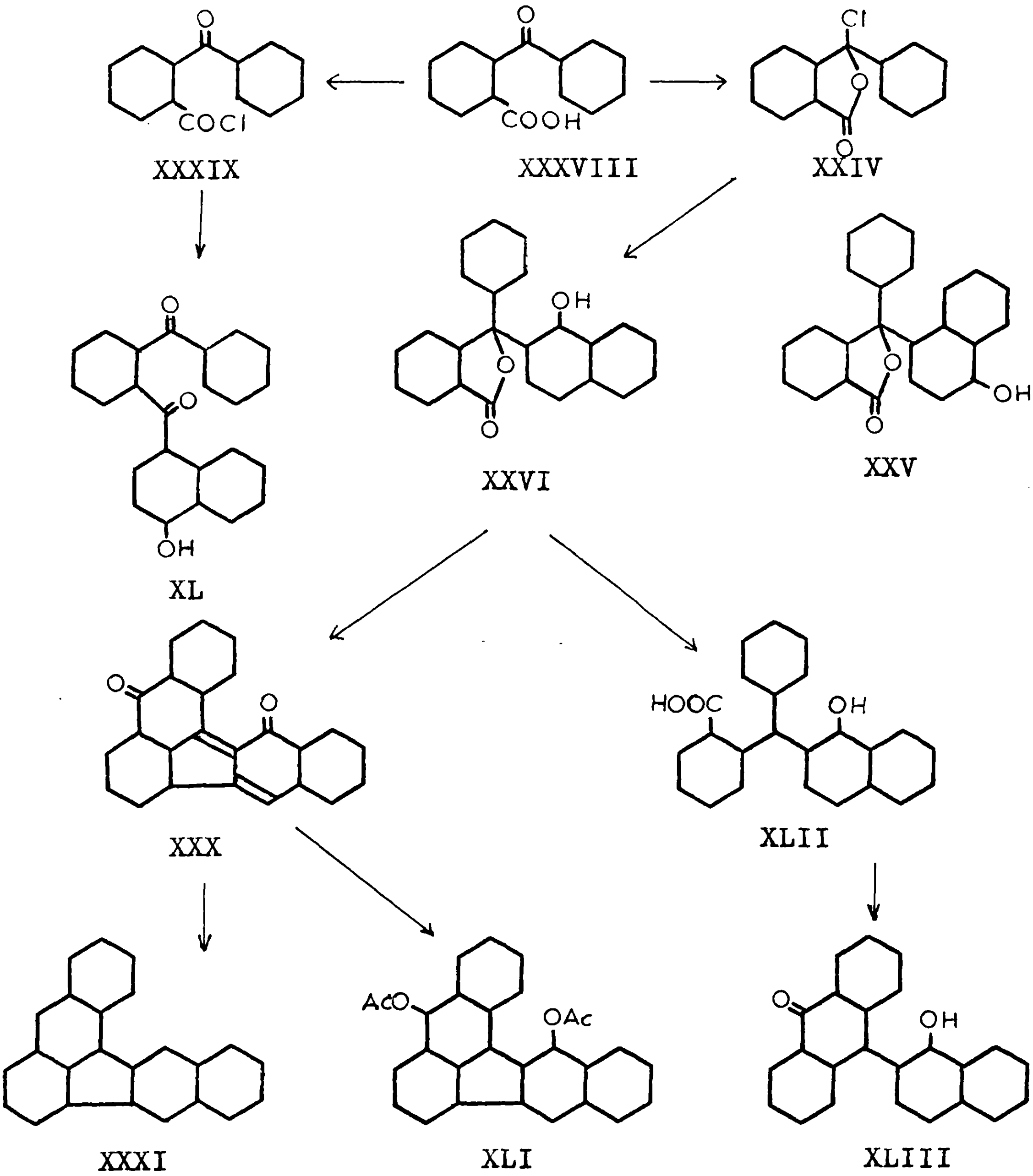


Figure 3. Absorption maxima (Å) and log ε (in parentheses). 2.3,11.12-Dibenzofluoranthene in cyclohexane: p, 4705 (4·28), 4630 (4·18), 4400 (4·25), 4140 (3·96), 3905 (3·61); 3715 (3·74), 3400 (3·91); β, 2740 (5·24), 2425 (4·84).


COCl
XXXIX
COOH
XXXVIII
Cl
XXIV
OH
XL
OH
XXVI
OH
XXV
HOOC
OH
XXX
XLII
AcO
OAc
OH
XXXI
XLI
XLIII

point of (XXXI) fits into the series as can be seen from the values opposite. Any other physical techniques applied failed to give any information of value, except for the aforementioned mass spectrum, which showed a large molecular ion at 302, requiring $C_{24}H_{14}$ as our hydrocarbon's formula.

Thus we are left in the somewhat unsatisfactory position that our attempted synthesis of 1.2,3.4-dibenzopyrene (I) has resulted in the production of a hydrocarbon which is suspected of being 2.3,11.12-dibenzofluoranthene (XXXI), but for which we have incomplete evidence for a full structure elucidation.

EXPERIMENTAL DISCUSSION

Normally carboxylic acids can be transformed into the corresponding acid chlorides with a wide variety of reagents: in the case of aromatic carboxylic acids with o-keto substituents (XXXVIII) there are two possibilities - formation of the normal acid chloride (XXXIX) and of the pseudo-acid chloride (XXIV) (actually a chloro-phthalide). Treatment of o-benzoylbenzoic acid (XXXVIII) with phosphorus pentachloride in carbon disulphide leads to the normal product (XXXIX)[16] while thionyl chloride gives the desired pseudo-acid chloride (XXIV).[17] The structural proof for both of these compounds was provided by Meyer,[18a] although at a later date this was challenged.[18b]

Consideration of the literature reactions of α-naphthol brings us to the conclusion that it can condense in either the 2- or 4-position[13] with the formation of the appropriate two phthalides (XXV) and (XXVI). That a phthalide is formed, and not a diketone (XL), which would result from reaction of the normal acid chloride with α-naphthol, is readily shown by examination of the IR-spectrum which shows a strong ν(C=0) at 1743 cm.$^{-1}$ characteristic of an α,β-unsaturated lactone in a 5-membered ring.[19] After one crystallisation of the crude material, TLC showed that only one phthalide had been formed, probably (XXVI) as has been shown from our earlier argument. There does not seem to be any simple way of distinguishing between the two phthalides by chemical or physical means.

The aluminium chloride/sodium chloride melt on the phthalide (XXVI) was carried out in the usual way, fairly short reaction times improving the yield of quinone (XXX), whose purification was accomplished via its beautiful emerald-green vat.

To prepare what might be a sensitive hydrocarbon, it was decided to reduce (XXX) by the mild zinc dust/water/ sealed tube method. Chromatography, after the initial work-up, showed the presence of two hydrocarbons, one with bands at 374 and 354 mμ and the other at 470 and 463 mμ. To ascertain which was the principal product a zinc dust/acetic anhydride reduction was carried out, the diacetate (XLI) produced,[20] showing absorption bands at 479 and 472 mμ, indicating that the second eluate from the chromatogram contained the important material. Since the zinc dust/water/ sealed tube method along with the zinc dust/pyridine/acetic acid method gave poor yields, it was decided to revert back to the normal zinc dust melt type of reduction, which resulted in improved yields. Chromatography yielded three fractions - (a) colourless crystals (374, 354 mμ), probably highly hydrogenated material (b) a red gum which could not be crystallised (448, 422, 397 mμ + 374, 354 mμ) and (c) orange platelets of (XXXI) (470, 463 mμ). Purification of the third fraction by sublimation gave the pure hydrocarbon which has been tentatively assigned the structure 2.3,11.12-dibenzofluoranthene (XXXI) since it did not prove to be identical with the authentic material made by Carruthers.[10]

To obtain further information on the structure of the quinone (XXX) and the hydrocarbon (XXXI), reduction of the phthalide, (XXVI) to the corresponding acid (XLII) was carried out using zinc dust in dilute sodium hydroxide. Our intention was then to cyclise (XLII) to the anthrone (XLIII) and then form the quinone (XXX) by oxidative cyclisation in an aluminium chloride/sodium chloride melt. Unfortunately cyclisation of (XLII) with hydrogen fluoride or polyphosphoric acid was unsuccessful, since the starting material was obtained unchanged. After its removal by crystallisation, TLC showed the presence of some much less polar and hence presumably cyclised material, whose quantity was insufficient for further synthetic studies.

EXPERIMENTAL

3 - Phenyl - 3-(2-naphth-1-ol)-phthalide (XXVI)

,Thionyl chloride (200 ml.) was added dropwise to finely powdered o-benzoylbenzoic acid (XXXVIII) (46 g.) in a cooled 1-litre 3-necked flask, the temperature of the reaction mixture being kept below 50°C. A vigorous reaction ensued with the evolution of hydrogen chloride. After the initial reaction had subsided and all the acid was in solution, the reaction mixture was refluxed for five minutes. The excess thionyl chloride was removed at the water pump, and the pseudo-acid chloride (XXIV), a yellow oil, was dissolved in glacial acetic acid (200 ml.). α-Naphthol (31 g.) was added, and the mixture refluxed for thirty minutes; glacial acetic acid (100 ml.) was then distilled off, and on standing overnight the phthalide (XXVI) crystallised out and was collected by suction filtration. Recrystallisation from xylene yielded colourless platelets of 3-phenyl-3-(2-naphth-1-ol)-phthalide (XXVI) (60 g.), m.pt. 226-228°, $\nu_{max}^{KBr} = 1743$ cm.$^{-1}$ (C=O). (XXVI) gave a purple colour with concentrated sulphuric acid.

Found C = 81·89%, H = 4·43%

$C_{24}H_{16}O_3$ requires C = 81·80%, H = 4·58%.

2.3,11.12-Dibenzofluoranthene-4.13-quinone (XXX)

3-Phenyl-3-(2-naphth-1-ol)-phthalide (XXVI) (10 g.) was added at 140° to a melt of sodium chloride (10 g.) and aluminium chloride (50 g.). The melt turned immediately deep red-brown and was kept at 140° for two minutes. The melt was allowed to cool and then poured on to dilute hydrochloric acid (1500 ml.) giving rise to a brownish-purple precipitate which was collected and thoroughly washed with hot water. The solid was then dissolved in dilute sodium hydroxide (1500 ml., pH=9) with sodium dithionite (35 g.) present. On gentle warming (28°-30°), a deep emerald-green vat was obtained which was filtered from all solid impurities. The vat was then stirred extremely vigerously for twelve hours to allow aerial oxidation to take place; the reddish-brown quinone (XXX) was filtered, washed with dilute sodium hydroxide and dried. Purification by sublimation (240°-260°/·025 mm.) yielded dark red feathery needles of 2.3,11.12-dibenzofluoranthene-4.13-quinone (XXX) (4 g.), m.pt. 278-280°, ν_{max}^{KBr} = 1661cm^{-1}(C=O), M.S. molecular ion m/e = 332, calc. M.W. = 332.(XXX) gave a turquoise colour with concentrated sulphuric acid.

Found	C = 86·86%, H = 3·51%
$C_{24}H_{12}O_2$ requires	C = 86·73%, H = 3·64%.

Reduction by zinc dust/water in a sealed tube.

Quinone (XXX) (250mg.) and zinc dust (2·5 g.) were ground together and placed in a Carius tube with the addition of water (3 drops). The tube was evacuated, sealed and heated at 300° for forty-eight hours. On cooling, the contents were extracted with xylene (250 ml.), the extracts concentrated and chromatographed on Grade I Neutral Alumina (30 g.). Elution with hexane gave a colourless eluate with a violet fluorescence, λ_{max} = 374, 354, 337, 317, 252 mμ. Further elution with benzene gave a lemon-coloured eluate with a green fluorescence λ_{max} = 470, 463, 440, 414, 390 mμ.

Reduction by zinc dust in acetic anhydride.

Quinone (XXX) (100 mg.) and zinc dust (1·0 g.) were ground together and refluxed for five minutes in acetic anhydride (5 ml.). Filtration removed the excess zinc dust; examination of the filtrate showed λ_{max} = 479, 472 mμ, suggesting that the lemon-coloured eluate from the previous experiment is the important one.

Reduction by zinc dust/pyridine/acetic acid.

Quinone (XXX) (250 mg.) was dissolved in dry pyridine (30 ml.). Zinc dust (2 g.) was added, and then acetic acid (80%, 3 ml.) added dropwise over two hours. The reddish-brown colour of the solution changed slowly to yellow-green over five hours refluxing. The reaction mixture was filtered to remove the excess zinc dust, and poured on to excess dilute hydrochloric acid. The finely divided precipitate was collected, washed with water, dilute ammonia, and finally water, and then dried at 80°. The dry solid was melted under nitrogen and then sublimed to give a dark red oily sublimate, which was dissolved in xylene and chromatographed on Grade I Neutral Alumina (30 g.). Development of the column gave bands identical with those obtained in the zinc dust/water/sealed tube reduction.

Reduction by zinc dust melt: 2.3,11.12-Dibenzofluoranthene (XXXI).

Quinone (XXX) (2 g.), zinc dust (2 g.), sodium chloride (2 g.), and moist zinc chloride (10 g.) were ground together and melted at about 200°. The temperature was increased to 310-320° with stirring and kept at this temperature for five minutes: a reddish-brown melt was obtained. It was decomposed with dilute acetic acid, excess zinc removed with concentrated hydrochloric acid, and filtered to give a dark red solid which was thoroughly washed with water, dilute ammonia, and water. It was then dissolved in xylene and chromatographed on Grade I Neutral Alumina (100 g.). Elution with hexane yielded a colourless solution with a violet fluorescence; further elution with cyclohexane gave an orange-red solution with a very similar fluorescence. These were combined since they showed identical bands in the UV-spectrum. Concentration yielded a red gum which would not crystallise. Sublimation at 140-150° gave colourless prisms m.pt. 165-173°; λ_{max} = 374, 354, 337, 317, 252 mμ. They gave no colour in concentrated sulphuric acid, and most probably are highly hydrogenated material. Further sublimation at 200-225°/·02 mm. gave a red oil which would not crystallise, λ_{max} = 448, 422, 397, 346, 323, 311 mμ and 374, 354, 337, 317, 252 mμ. With concentrated sulphuric acid an olive-green colour was obtained.

Further development of the column with benzene gave a lemon-coloured solution with a green fluorescence. Concentration then yielded orange prisms of hydrocarbon which were sublimed at 195-205°/·03 mm. to give orange platelets of

2.3,11.12-dibenzofluoranthene (XXXI) (50 mg.), m.pt. 219-220°, M.S. molecular ion m/e = 302, calc. M.W. = 302. This hydrocarbon gave a purple surface colour followed by an ultramarine solution with concentrated sulphuric acid. The UV-spectrum is shown in figure 3.

Found C = 95·02%, H = 4·87%

$C_{24}H_{14}$ requires C = 95·33%, H = 4·67%.

1-Phenyl-1-(o-carboxyphenyl)-2-(naphth-1-ol)methane (XLII).

3-Phenyl-3-(2-naphth-1-ol)-phthalide (XXVI) (20 g.) was added to a boiling mixture of sodium hydroxide (5%, 400 ml.) and copper-activated zinc dust (75 g.) with some cyclohexanol added to reduce foaming. The mixture was refluxed for three hours during which time the colour of the solution changed from yellow to brown to pale green. The hot solution was filtered, and the excess zinc thoroughly washed with dilute sodium hydroxide. The reduced acid was precipitated by the addition of excess concentrated hydrochloric acid and the voluminous precipitate coagulated by boiling. The aqueous mother liquors were decanted off, and the acid crystallised from xylene. Recrystallisation from benzene yielded 1-phenyl-1-(o-carboxyphenyl)-2-(naphth-1-ol) methane (XLII) as clusters of prisms (14·5 g.), m.pt. 157-158°, $\nu_{\mathrm{max.}}^{\mathrm{KBr}}$ = 1700cm.$^{-1}$(C=0). In concentrated sulphuric acid (XLII) gave an initial orange surface colour giving way to a yellow-green solution which turned emerald-green on standing.

Found C = 81·14%, H = 5·44%

$C_{24}H_{18}O_3$ requires C = 81·33%, H = 5·12%

Attempted Cyclisation with Polyphosphoric Acid.

The acid (XLII) (2 g.) was warmed overnight on a steam-bath with polyphosphoric acid (100 ml.). The viscous solution which developed a deep red-brown colour overnight, was poured on to ice-water (500 g.) and the suspended solid collected by filtration and dried. TLC (3% methanol/benzene) showed the presence of starting material in large amounts, and less polar cyclised material in small amounts. Fractional crystallisation from benzene/ethanol yielded (XLII) (1·65 g.) identified by m.pt., IR, and H_2SO_4 colour). The reddish mother-liquors yielded on further concentration orange-brown needles of presumably the anthrone (XLIII) (10 mg.), m.pt. 85-91°, $\nu_{\mathrm{max}}^{\mathrm{KBr}}$ = 1678cm.$^{-1}$(C=0). Colour in sulphuric acid was yellowish-green.

Attempted Cyclisation with Hydrogen Fluoride.

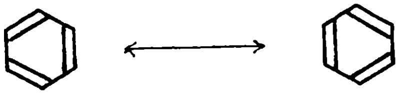
The acid (XLII) (2 g.) was dissolved in liquid hydrogen fluoride (80 ml.). A dark red solution was obtained, which was allowed to stand until all the hydrogen fluoride had evaporated. Ice-water (250 g.) was added, and the pale yellow solid obtained was filtered and dried. TLC (3% methanol/benzene) showed identical results to the polyphosphoric acid cyclisation. After the removal of starting material (XLII) (1·8 g.) (identified as previously), concentration of the mother liquors yielded a pale yellow gum, $\nu_{max}^{film} = 1670$ cm.$^{-1}$ (C=O), which could not be crystallised.

CHAPTER 6.

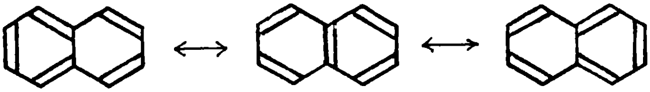
THE ESTABLISHMENT OF DOUBLE BOND CHARACTER IN METHYL DERIVATIVES OF POLYCYCLIC AROMATIC HYDROCARBONS

INTRODUCTION:

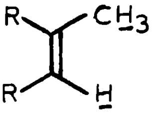
The establishment of high double bond character in certain bonds of polycyclic aromatic hydrocarbons has been proved by studying the NMR spectra of various methyl derivatives. The position of this type of double bond in the molecule can be anticipated by strict application of Robinson's sextet,[1] but cannot be correlated with either valence bond or molecular orbital theory.[2]



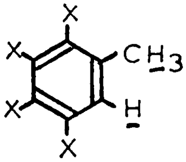
Ia Ib



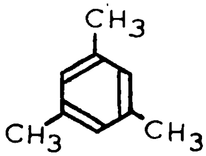
IIa IIb IIc



III



IV (X=Hal)
V (X=Cl)



VI

DISCUSSION:

The classical Kekule description of benzene (Ia, b) requires that the two positions ortho to any substituent be completely equivalent. Rigorous extension of this idea to naphthalene then demands that the double bonds should oscillate between the three possible structures (IIa, b, c). Before the turn of the century, however, it had been pointed out that there existed a remarkable difference between the two positions ortho to a β-naphthalene substituent, the 1-position being invariably favoured in a variety of reactions;[3] this result was interpretated as indicating the presence of the double bond in the 1.2-position and not in the 2.3-position - that is to say the double bonds in naphthalene were not mobile, but fixed in the symmetrical structure (IIb). Since these early experiments, a vast amount of time and energy has been spent trying either to verify or villify this concept.[4]

With the advent of NMR spectroscopy, a new tool became available to study this problem. In its formativo years, the proton chemical shift seemed to be the most important criterion available to organic chemists, but with the arrival of more sophisticated instruments, the phenomenon of spin-spin coupling took on an ever increasing role.

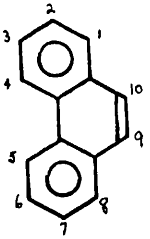
In our particular work, the long range spin-spin coupling in allylic systems[5] is of paramount importance, but before examining our results, it is necessary to consider the spin-spin coupling constants in the two extreme cases - that is $J(\underline{H}\text{-C=C-C}\underline{H}_3)$ of simple alkenes (III) and compare it with the same coupling constant in substituted benzenes (IV). Examination of some propenes shows that J = 1·7-1·8 c/s is the usual value in the former case,[6,7] while the magnitude in the latter, aromatic type of compound, exemplified by 2.3.4.5-tetrachlorotoluene (V) and mesitylene (VI) is J = 0·6 c/s.[8]

All our results are illustrated in the accompanying tables. If, firstly, the position of the methyl signal is examined, it was shown a number of years ago, there existed a relationship of sorts between the <u>aromatic</u> proton shift and the magnitude of the ring current.[9] Further work on this problem revealed that the position of the aromatic proton was affected by numerous factors - steric and solvent effects, and spin-spin coupling - hence it was much better to use the aromatic methyl resonance, which was not similarly affected, but which did change position with ring current size.[10] Another improvement, that ring currents were much better calculated for each individual hydrocarbon, and not addatively from benzene became apparent soon after.[11]

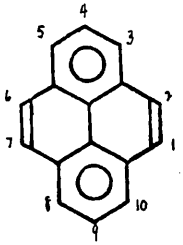
Combining these improvements, Lewis[12] has shown that there exists a good linear relationship between the position of the methyl resonance and the computed aromatic proton shift. Our results, dealing with a much wider variety of ring systems provide a considerable amount of experimental data for which there are as yet no corresponding calculations.

Having dealt with the position of the methyl signal obtained from the basic spectrum, examination of the expanded methyl resonance reveals the presence of two types of signal-singlets, which constitute the majority, and doublets. The value of the coupling constant in the latter case only varies from 1·0-1·3 c/s (with the exception of methylcoronene = 0·9 c/s), a value lying midway between the limiting cases already discussed, suggesting that the bond order of the bond separating the methyl group and the aromatic proton with which it couples is intermediate in character between an ethylenic double bond and a benzenoid double bond. Special mention must be made of two cases, 4-methylpyrene and 4.9-dimethylpyrene which both show triplets (J = 0·7 c/s) caused by coupling with the equivalent ortho ring protons; the size of the coupling constant indicates there is a very close relationship to the benzene rings of (V) and (VI).

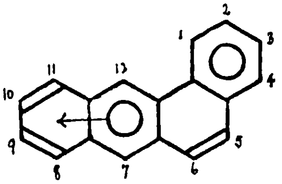
It now seems appropriate to discuss our findings in relation to the current theories available for dealing with these molecules, in particular to see if there is any connection between the occurrence of the splitting of the methyl signal and the percentage of double bond character of the CH_3-C=CH- system as calculated by valence bond (VB) and molecular orbital (MO) theories. The method used to calculate the percentage double bond character for VB theory is a simplified one - the number of Kekule structures with the double bond in any position (or positions) is divided by the total possible number of Kekule structures; this gives the values listed in the tables. For the MO method, the readily available literature values have been taken.[13] Careful examination of the experimental findings and the calculated double bond character fails to reveal any relationship. Indeed, the problem goes much deeper. Both VB and MO theories predict a percentage of double bond character for every bond in a polycyclic aromatic hydrocarbon, a concept which has been convincingly proved by X-ray crystallography.[14,15] Our results, on the other hand, suggest that there are two definite types of unsaturation in polycyclic aromatics - benzenoid rings and 'fixed' double bonds, which approach ethylene in character. Application of this sextet and fixed



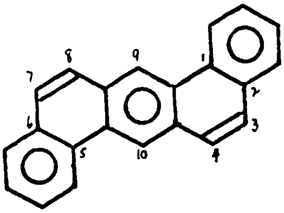
VII



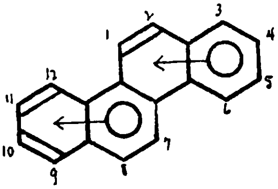
VIII



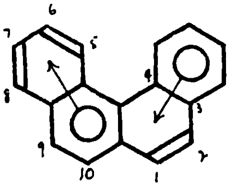
IX



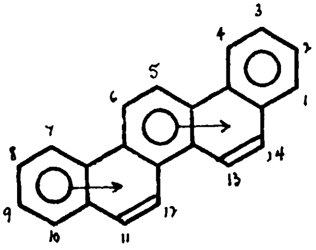
X



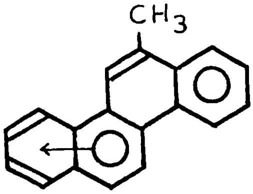
XI



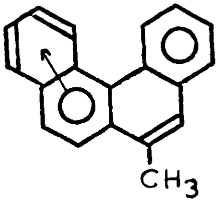
XII



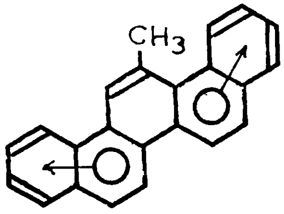
XIII



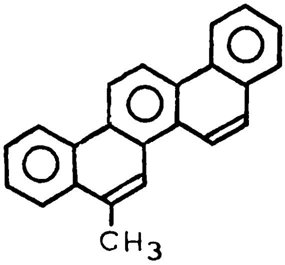
XIV



XV



XVI



XVII

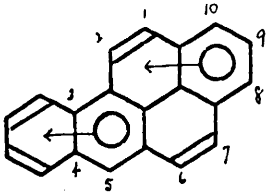
double bond concept, long advocated by Clar,[16] goes a long way to explaining our results.

If phenanthrene (VII) is written with the maximum number of sextets, then a methyl substituent in the 9-position is attached to an ethylenic type of double bond and consequently the signal appears as a doublet. Substituents in the 1-, 2-, and 3-positions all appear as singlets since they are attached to aromatic sextets. Chemical evidence, too, supports high double bond character in the 9.10-position, exemplified by the smooth addition of bromine to form phenanthrene dibromide. Substituted pyrenes (VIII) confirm these ideas. 1-Methyl- and 1.6-dimethylpyrene attached to formal double bonds both exhibit doublets, while in the closely related 1.2-dimethylpyrene, the methyl resonance appears as a singlet, since the hydrogen with which coupling takes place has been removed. Substituents in any other position appear as singlets, since they are attached to benzenoid rings, with the exception of 4-methyl and 4.9-dimethylpyrene (triplets), which have already been discussed. To consolidate these results, methyl substituted tetraphenes (IX) and 1.2,5.6-dibenzanthracenes (X), both of which contain a phenanthrene type double bond in the 'angle' were examined. 5-Methyltetraphene and 4-methyl-1.2,5.6-

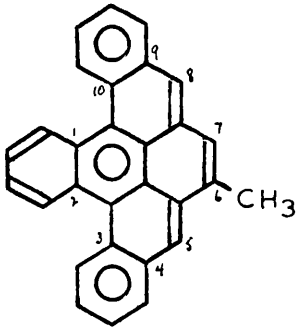
dibenzanthracene produce doublets since the methyl group is attached to the double bond in the 'angle'; substituents in other positions show the expected singlet. Methyl signals from substituted polycyclic aromatic hydrocarbons have been seldom reported in the literature[17,18,19,20] but what results there are, especially those on methyltetraphenes,[20] substantiate our own conclusions.

Turning now to methyl derivatives of chrysene (XI), 3.4-benzophenanthrene (XII) and picene (XIII), a new situation arises since the sextets can migrate from one ring to another. Monomethyl substitution in any of the 'central' rings produces a doublet, suggesting high double bond character at these positions. However, what may be happening is that the substituent is forcing the molecule to adopt a phenanthrene type of arrangement of the electrons (XIV - XVII), with high double bond character in the desired position. Dimethyl substitution fails to give instructive results - 2.8-dimethylchrysene shows a singlet and 2.9-dimethyl-3.4-benzophenanthrene produces a doublet - obviously more compounds must be studied before any conclusions can be drawn.

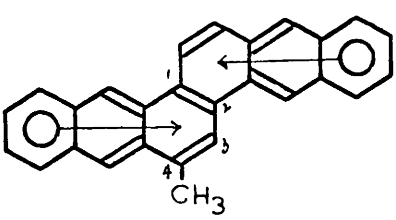
Before discussing certain hydrocarbons synthesised for specific purposes, the triplet methyl resonance of 4-methyl and 4.9-dimethylpyrene was further investigated.



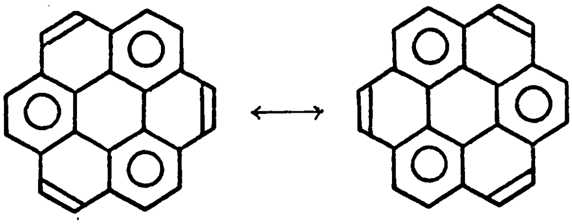
XVIII



XIX

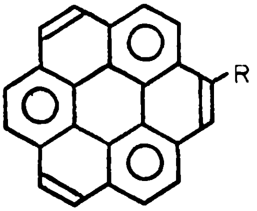


XX



XXIa

XXIb



XXII ($R=CH_3$)

XXIII ($R=CH_2CH_3$)

This triplet (J = 0·7 c/s) is obviously caused by coupling with the two equivalent ortho protons, and as has already been mentioned mesitylene (VI) shows exactly the same effect with a very similar coupling constant (J = 0·6 c/s).[8] Toluene, too, might be expected to exhibit this effect, but unfortunately good resolution of the expanded methyl signal could not be satisfactorily obtained, possibly because the meta and para protons also couple with the methyl signal so broadening it and eliminating the fine structure. However, another possibility must be considered: Bryce-Smith[21] has recently shown that alkylbenzenes and maleic anhydride react at specific positions in the ring, indicating that a particular bond in the ring has high double bond character. In the case of toluene this would obviously destroy the plane of symmetry through the methyl group, carbon 1 and carbon 4, and cause a broad unresolvable methyl signal in the NMR. Analogous effects are observed in the spectra of three monomethyl-3.4-benzopyrenes (XVIII), all of which show singlet methyl signals. The ring protons can therefore no longer be equivalent, caused in this case by the fact that the sextets are able to migrate in the manner shown (XVIII) and confer different double bond order to the 8.9 and 9.10 bonds.

6-Methyl-1.2,3.4,9.10-tribenzopyrene (XIX) was synthesised, because by sextet theory, the 6.7 bond should have exceptionally high double bond character; the expected methyl doublet is found, but the value of the coupling constant (1·2 c/s) does not show an abnormally high value. 4-Methylanthraceno-(2',1':1.2)-anthracene (XX) has also been synthesised; even though the 3.4-position has high double bond character, the fact that it can be part of an aromatic sextet probably accounts for the singlet methyl resonance in this hydrocarbon.

The NMR spectra of the aromatic protons of coronene (XXI) shows only a single sharp peak, which gives absolutely no indication of splitting at the highest expansions. If coronene is formulated with three sextets and three rings of the type of the middle ring of phenanthrene, then obviously a delocalisation mechanism must exist which equates all the ring protons and produces a sharp singlet (XXIa, b). The same mechanism cannot operate for methylcoronene (XXII), since the methyl signal appears as a doublet, typical of a methyl group attached to a fixed double bond. Now the C - C bond length should be affected by the presence or absence of this delocalisation mechanism; if it is present, the 1.2, 3.4,5.6,7.8,9.10, and 11.12 bonds should all be equal, a result well authenticated by the X-ray investigation of coronene.[22] On the other hand, if delocalisation is absent, as is suspected in methylcoronene, then the 1.2,5.6, and 9.10 bonds should be equal, but should not be the same length as the 3.4,7.8 and 11.12 bonds. A successful X-ray examination could not be carried out because the crystals exist with an average distribution of the methyl group round the coronene nucleus.[23]

The aromatic protons of methylcoronene (XXII) produce nine distinct peaks. Assignments can be made - the hydrogen atom in position 2 gives rise to the broad band at 1·54 τ, the hydrogen atoms in positions 11 and 12 ought to produce a quartet, part of which is at 1·20 and 1·22 τ, the other bands being superimposed by stronger bands. This leaves eight protons which cause the appearance of three doublets. The NMR spectrum of ethylcoronene (XXIII) shows a similar splitting of the aromatic protons; in both cases the appearance of these three doublets cannot be explained in conventional terms.

Hydrocarbon Substituent	τ	Signal Coupling Constant	Double Bond Character			Solvent Machine Expansion	Text Figure
			VB	Bond	MO		
<u>PHENANTHRENE (VII)</u>							
1-Methyl	7·34	Singlet				CS_2/60/x6	Fig.1
2-Methyl	7·53	Singlet				CS_2/60/x6	Fig.2
9-Methyl	7·45	Doublet 1·1c/s	0·80	9:10	0·77	CS_2/60/x6	Fig.3
3.6-Dimethyl	7·48	Singlet				CS_2/60/x12	
<u>PYRENE (VIII)</u>							
1-Methyl	7·11	Doublet 1·3c/s	0·83	1:2	0·78	$CDCl_3$/60/x6	Fig.4
1.6-Dimethyl	7·20	Doublet 1·2c/s	0·67	1:2	0·78	CS_2/60/x6	Fig.5
3-Methyl	7·20	Singlet				CS_2/60/x12	Fig.6
4-Methyl	7·34	Triplet 0·7c/s				CS_2/100/x20	Fig.7
4.9-Dimethyl	7·18	Triplet 0·7c/s				CS_2/100/x20	
1.2-Dimethyl	7·36	Singlet				CS_2/100/x10	Fig.8
3.8-Dimethyl	7·17	Singlet				CS_2/100/x20	
<u>TETRAPHENE (IX)</u>							
3-Methyl	7·53	Singlet				CS_2/100/x20	Fig.9
5-Methyl	7·48	Doublet 1·2c/s	0·86	5:6	0·78	CS_2/100/x20	Fig.10
9-Methyl	7·52	Singlet				CS_2/100/x20	
3.9-Dimethyl	7·56	Singlet				CS_2/100/x20	
<u>1.2,3.4-DIBENZANTHRACENE (X)</u>							
3'-Methyl	7·49	Singlet				CS_2/100/x20	Fig.11
4-Methyl	7·25	Doublet 1·1c/s	0·83	3:4	0·78	CS_2/100/x20	Fig.12

Hydrocarbon Substituent	τ	Signal Coupling Constant	Double Bond Character			Solvent Machine Expansion	Text Figure
			VB	Bond	MO		
CHRYSENE (XI)							
2-Methyl	7·32	Doublet 1·0c/s	0·75	1:2 or	0·75	CS_2/100/x20	Fig.13
2.8-Dimethyl	7·26	Singlet	0·50	7:8	0·75	CS_2/100/x20	Fig.14
3.4-BENZOPHENANTHRENE (XII)							
1-Methyl	7·40	Doublet1·05c/s	0·75	1:2 or	0·76	CS_2/100/x20	
2.9-Dimethyl	7·35	Doublet 1·0c/s	0·50	9:10	0·76	CS_2/100/x20	Fig.15
6-Methyl	7·44	Singlet				CS_2/100/x20	
7-Methyl	7·49	Singlet				CS_2/100/x20	Fig.16
PICENE (XIII)							
5-Methyl	7·60	Doublet1·05c/s	0·70	5:6	0·73	CS_2/100/x10	
11-Methyl	7·21	Doublet 1·1c/s	0·77	11:12	0·76	CS_2/100/x4	
3.4-BENZOPYRENE (XVIII)							
8-Methyl	7·15	Singlet				CS_2/60/x24	
9-Methyl	7·24	Singlet				CS_2/60/x24	
10-Methyl	7·12	Singlet				CS_2/60/x24	
1.2,3.4,9.10-TRIBENZOPYRENE (XIX)							
6-Methyl	7·33	Doublet 1·2c/s	0·92	6:7	-	CS_2/100/x20	
ANTHRACENO-(2'.1':1.2)-ANTHRACENE (XX)							
4-Methyl	7·41	Singlet	0·89	3:4	-	CS_2/100/x4 CAT.	
CORONENE (XXI)							
Methyl	6·76	Doublet 0·9c/s	0·70	1:2	0·75	CS_2/100/x10	Fig.17
Ethyl	-	-				CS_2/100/x10	Fig.18

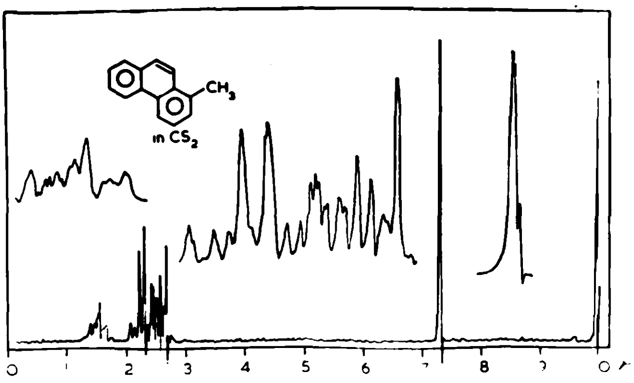


Figure 1.

1-Methylphenanthrene

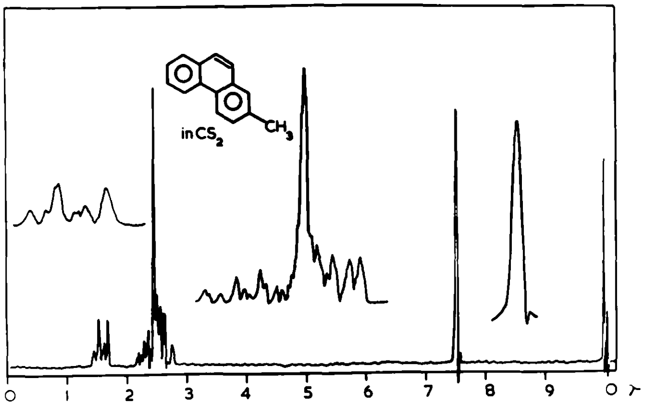


Figure 2.

2-Methylphenanthrene

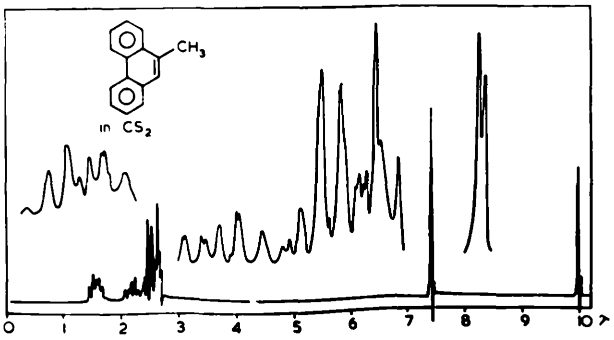


Figure 3.

9-Methylphenanthrene

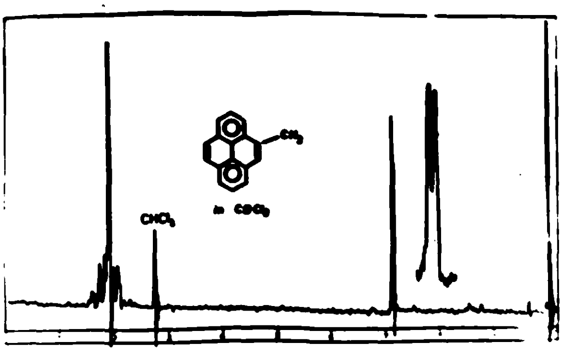


Figure 4.
1-Methylpyrene

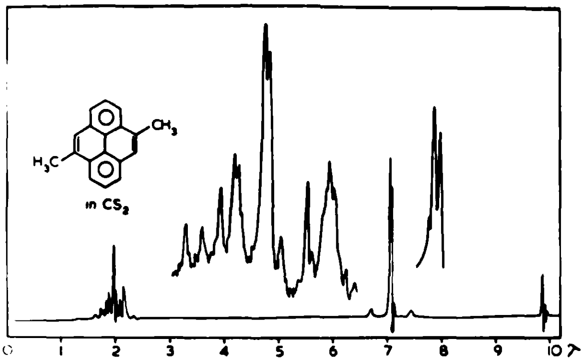


Figure 5.
1,6-Dimethylpyrene

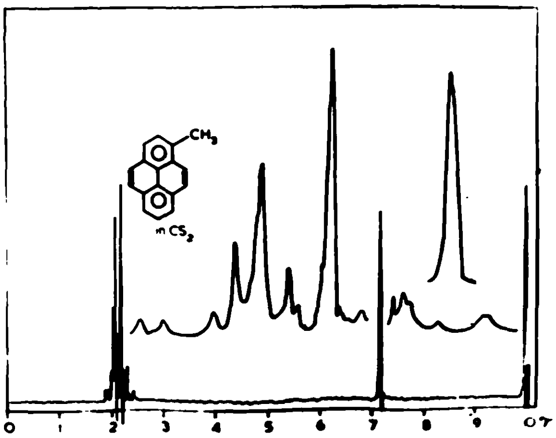


Figure 6.
3-Methylpyrene

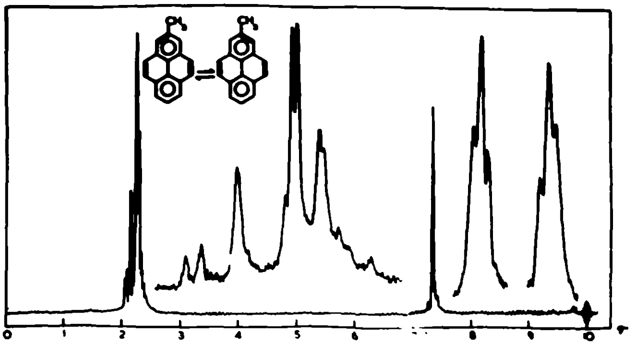


Figure 7.
4-Methylpyrene

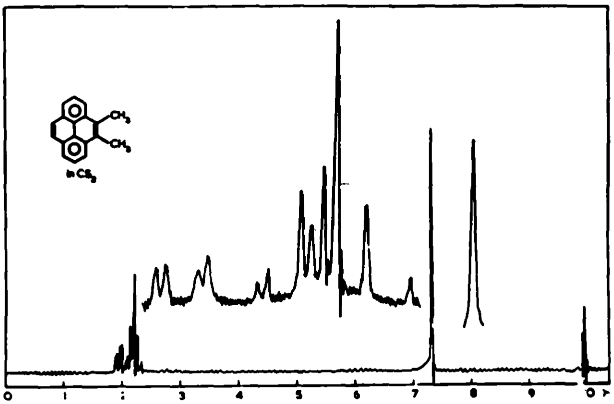


Figure 8.
1.2-Dimethylpyrene

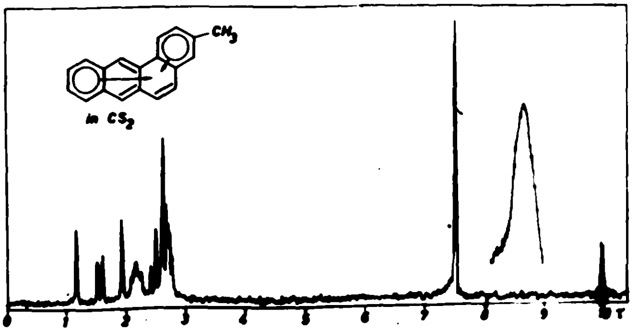


Figure 9.
3-Methyltetraphene

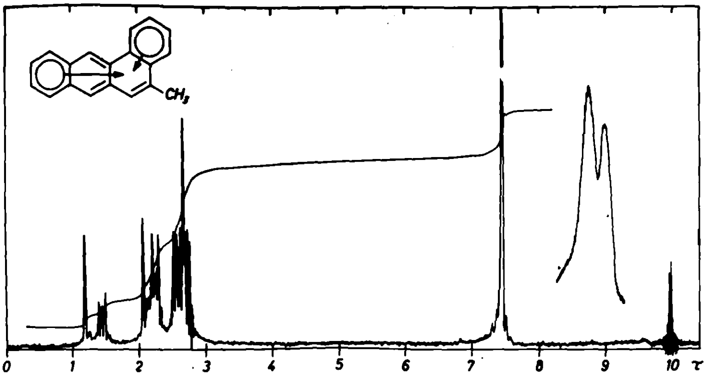


Figure 10.

5-Methyltetraphene

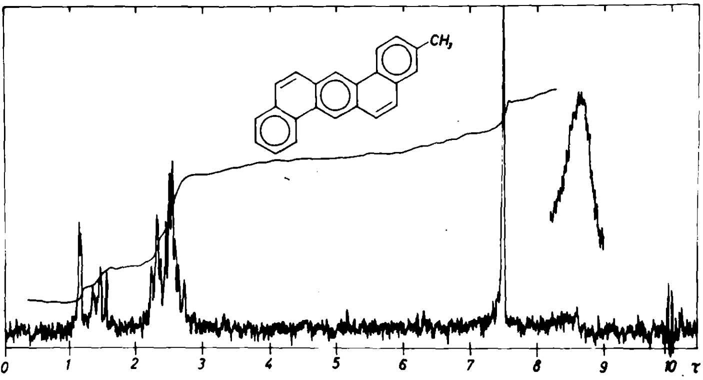


Figure 11.

3'-Methyl-1.2,3.4-dibenzanthracene

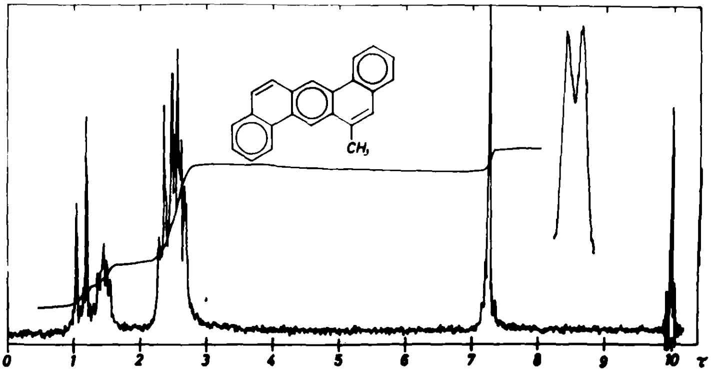


Figure 12.

4-Methyl-1.2,3.4-dibenzanthracene

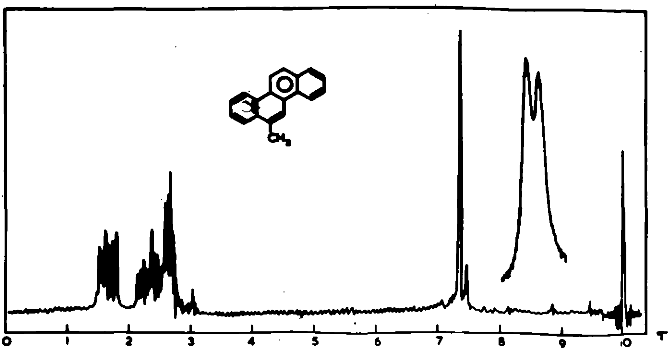


Figure 13.
2-Methylchrysene

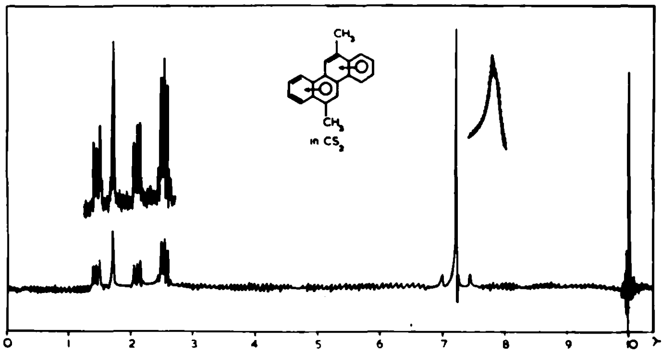


Figure 14.
2.8-Dimethylchrysene

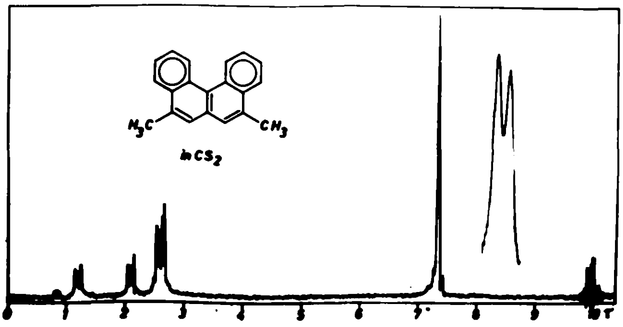


Figure 15.
2.9-Dimethyl-3.4-benzophenanthrene

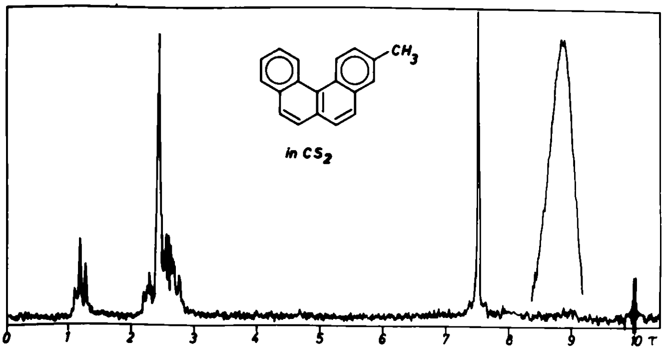


Figure 16.
7-Methyl-3.4-benzophenanthrene

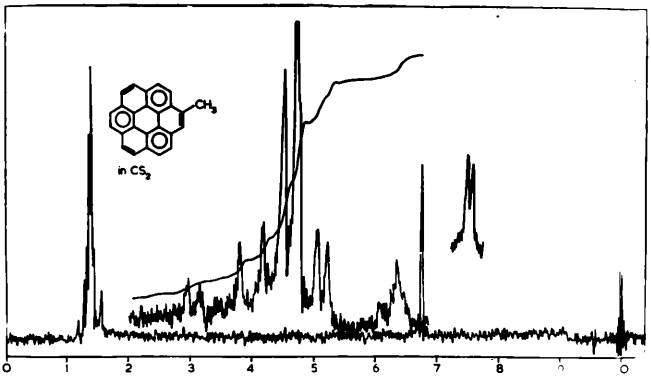


Figure 17.
Methylcoronene

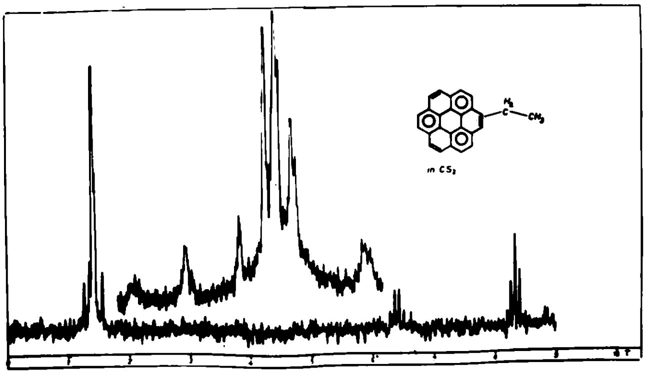
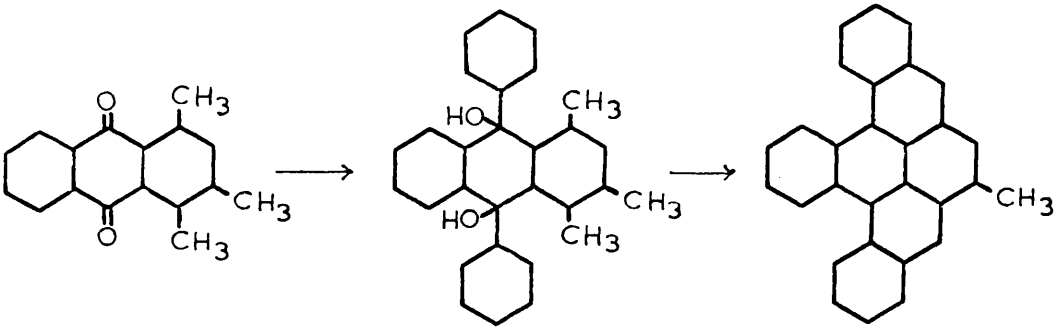
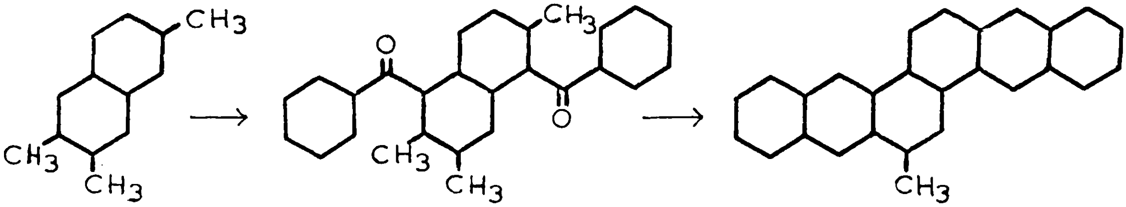


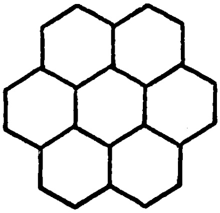
Figure 18.
Ethylcoronene



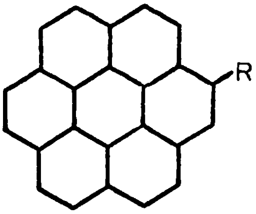
XXIV XXV XIX



XXVI XXVII XX



XXI



XXII ($R=CH_3$)

XXIII ($R=CH_2CH_3$)

XXVIII ($R=COCH_3$)

XXIX ($R=COC_6H_5$)

XXX ($R=CH_2C_6H_5$)

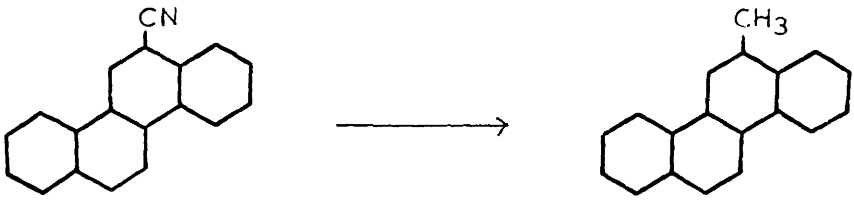
EXPERIMENTAL DISCUSSION:

The majority of the compounds whose NMR spectra have been investigated were gifts from a wide variety of chemists, to whom proper acknowledgement has been given in the experimental section.

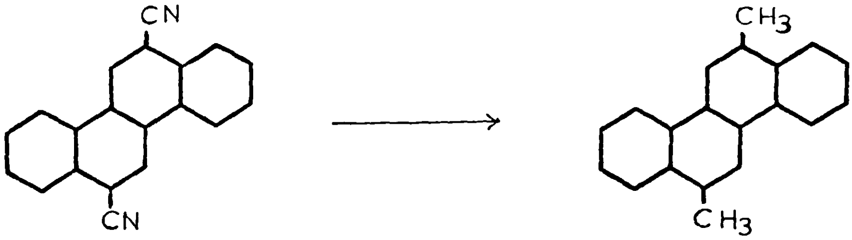
2-Methylchrysene (XXXII),[24] 2.8-dimethylchrysene (XXXIV),[25] and 1.6-dimethylpyrene (XXXVIII)[26] have all been made by the same series of reactions - bromination, cyanide exchange, and reduction - a reaction sequence which was a considerable improvement on their previous syntheses. 3.8-Dimethylpyrene, the only other pyrene which was synthesised, was made according to the method of Martin.[27]

6-Methyl-1.2,3.4,9.10-tribenzopyrene (XIX) was synthesised by following closely the route to the parent hydrocarbon.[28] 1.2.4-Trimethylanthraquinone (XXIV)[29] reacted with phenyl lithium to give the expected diol (XXV) which was cyclodehydrogenated to the desired hydrocarbon (XIX) with copper powder at 400-410°.[28] The synthesis of 4-methyl-anthraceno-(2'.1':1.2)-anthracene (XX) also closely followed one of the routes to the parent hydrocarbon.[30] Double Friedel-Crafts acylation of 2.3.6-trimethylnaphthalene (XXVI) with benzoyl chloride gave the diketone (XXVII) which was ring closed to the required hydrocarbon (XX) by the Elbs Reaction.

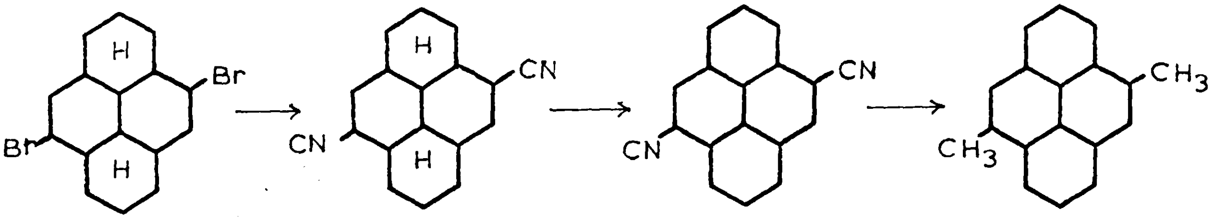
Coronene (XXI) was readily acetylated to give acetylcoronene (XXVIII);[31] reduction by the Huang-Minlon method[32] yielded ethylcoronene (XXIII), which was easily purified by chromatography. Because the NMR spectra of methylcoronene (XXII) and ethylcoronene (XXIII) showed such interesting features, it was decided to synthesise benzylcoronene (XXX) also. Benzoylation of coronene to give benzoylcoronene (XXIX)[31,33] could not be carried out satisfactorily, since an analytically pure sample of (XXIX) could not be obtained; mass spectral analysis always showed the presence of some dibenzoylated material. Nevertheless, the mixed product was reduced to a mixture of monobenzyl and dibenzylcoronene which could not be separated by fractional crystallisation or chromatography, mass spectral measurements invariably showing the presence of both hydrocarbons. The possibility that a mixture had been obtained in the preparation of ethylcoronene (XXIII) was fortunately eliminated by mass spectroscopy.



XXXI XXXII



XXXIII XXXIV



XXXV XXXVI XXXVII XXXVIII

EXPERIMENTAL

2-Methylchrysene (XXXII).

Chrysene-2-nitrile (XXXI) (100 mg.),[34] hydrazine hydrate (2·5 ml.) and xylene (1 ml.) were heated in a sealed tube at 200°C for thirty hours. The resulting pale yellow solid was filtered from the hydrazine/xylene mixture which was then diluted with water, the xylene separated and combined with a xylene solution of the residue. The concentrated, dried solution was chromatographed on Grade I Neutral Alumina. Elution with benzene gave a colourless solution which on concentration yielded colourless needles of 2-methylchrysene (XXXII) (40 mg. from four tubes), m.pt. 159-160° (lit. m.pt. 160-161°).[24] (XXXII) dissolved in concentrated sulphuric acid to give a colourless solution.

2.8-Dimethylchrysene (XXXIV).

Crysene-2.8-dinitrile (XXXIII) (100 mg.)[35] was reduced in exactly the same manner as (XXXI),. Crystallisation from benzene after chromatography gave colourless needles of 2.8-dimethylchrysene (XXXIV) (100 mg. from four tubes), m.pt. 235-237° (lit. m.pt. 238°).[25] (XXXIV) gave a bluish colour on warming with concentrated sulphuric acid.

1.6-Dicyano-3.4.5.8.9.10-hexahydropyrene (XXXVI).

This material was prepared by a modified version of Vollmann's method:[36] 1.6-dibromo-3.4.5.8.9.10-hexahydropyrene (XXXV) (40 g.)[36] and copper cyanide (25 g.) were ground together, suspended in quinoline (500 ml.) and refluxed for 3½ hours. The reaction mixture was allowed to cool, the precipitate filtered off, washed thoroughly with ethanol and dried. The brown precipitate was extracted with boiling nitrobenzene, the copper salts filtered off and the solution concentrated. The yellow solid crystallised from nitrobenzene as colourless needles of 1.6-dicyano-3.4.5.8.9.10-hexahydropyrene (XXXVI) (25 g.) m.pt. 303° (lit. m.pt. 303°).[36] (XXXVI) sublimed at 240-250°/0·025mm. and dissolved in concentrated sulphuric acid with a yellow-green colour.

Found	N = 10·88%
$C_{18}H_{14}N_2$ requires	N = 10·85%.

Pyrene-1.6-dinitrile (XXXVII).

1.6-Dicyano-3.4.5.8.9.10-hexahydropyrene (XXXVI) (20 g.) selenium (20 g.) and dibenzofuran (60 g., solvent) were refluxed for twenty hours. At the end of the reaction time, the excess selenium which had formed a lump was removed, and the filtrate was then allowed to solidify. Separation of dibenzofuran and pyrene-1.6-dinitrile (XXXVII) was achieved by vacuum sublimation. (XXXVII) sublimed at 300-310°/·02 mm. and was crystallised from trichlorobenzene as yellow needles (4 g.) m.pt. 401-403° (lit. m.pt. 406°).[36] It did not dissolve in concentrated sulphuric acid.

Found N = 11·20%

$C_{18}H_8N_2$ requires N = 11·11%.

1.6-Dimethylpyrene (XXXVIII).

Pyrene-1.6-dinitrile (XXXVII) (100 mg.) was reduced with hydrazine hydrate (2·5 ml.) and xylene (1 ml.) in a sealed tube in the same way as crysene-2-nitrile (XXXI). Crystallisation from benzene after chromatography gave colourless plates of 1.6-dimethylpyrene (XXXVIII) (96 mg. from four tubes) m.pt. 195° (lit. m.pt. 190-192°).[26] (XXXVIII) gave a yellowish-green colour with concentrated sulphuric acid.

Found C = 93·67%, H = 6·03%

$C_{18}H_{14}$ requires C = 93·88%, H = 6·12%.

9.10-Diphenyl-9.10-dihydroxy-9.10-dihydro-1.2.4-trimethylanthracene (XXV).

Bromobenzene (40 g.) was added to strips of lithium metal (3 g.) suspended in dry ether (500 ml.) in a nitrogen atmosphere and the mixture refluxed until all the lithium had dissolved (four hours). The ethereal solution was filtered through glass wool into a suspension of 1.2.4-trimethylanthraquinone (XXIV) (14 g.)[29] in dry benzene (300 ml.). The reaction mixture was refluxed with stirring for twenty minutes, and then decomposed with ice and dilute acetic acid; after steam distillation, the reaction product was obtained as a yellow-orange oil. This material was extracted with ether, the ethereal extract washed with aqueous dithionite, dried over magnesium sulphate and concentrated. On standing, a light yellow solid slowly precipitated; this crystallised from benzene as almost colourless platelets of diol (XXV) (12·5 g.) m.pt. 278-279°. (XXV) dissolved in concentrated sulphuric acid to give a yellow-brown colour.

Found	C = 85·84%, H = 6·62%
$C_{29}H_{26}O_2$ requires	C = 85·68%, H = 6·45%.

6-Methyl-1.2,3.4,9.10-tribenzopyrene (XIX).

Diol (XXV) (4 g.) and activated copper powder (30 g.)[37] were thoroughly mixed and pyrolysed in an atmosphere of carbon dioxide at 400-410° for three hours. The reaction mixture was thoroughly extracted with xylene, the extract concentrated and chromatographed on Grade I Neutral Alumina (130 g.). Elution with benzene gave a greenish-yellow solution which failed to yield crystals on concentration. On dilution with petrol, greenish-yellow needles of 6-methyl-1.2,3.4,9.10-tribenzopyrene (XIX) (55 mg.) m.pt. 212-213° were obtained. An apple green colour was obtained with concentrated sulphuric acid.

Found C = 94·77%, H = 5·32%

$C_{29}H_{18}$ requires C = 95·05%, H = 4·95%.

1.5-Dibenzoyl-2.3.6-trimethylnaphthalene (XXVII).

Benzoyl chloride (140·5 g.) was added dropwise over fifteen minutes to a finely powdered mixture of 2.3.6-trimethylnaphthalene (XXVI) (57 g.) and aluminium chloride (133 g.) in carbon disulphide (350 ml.). After the initial vigorous reaction had subsided and the reaction mixture had become still (~ one hour), the dark complex was decomposed with ice and dilute hydrochloric acid. The carbon disulphide was removed by steam distillation, and the reaction product was collected, washed thoroughly with boiling water and dried to give the crude diketone. Crystallisation from xylene yielded colourless prisms of 1.5-dibenzoyl-2.3.6-trimethylnaphthalene (XXVII) (45 g.) m.pt. 212-214°. (XXVII) gave an orange surface colour with concentrated sulphuric acid and slowly dissolved forming a pale yellow solution.

Found C = 85·69%, H = 5·68%

$C_{27}H_{22}O_2$ requires C = 85·69%, H = 5·86%.

4-Methylanthraceno-(2'.1':1.2)-anthracene (XX).

1.5-Dibenzoyl-2.3.6-trimethylnaphthalene (XXVII) (25 g.) in xylene (150 ml.) was gently distilled to remove the xylene, and then heated vigorously at 430-440° for twenty minutes until there were no traces of water left. The cooled mixture was dissolved in the minimum amount of pseudocumene and chromatographed on Grade I Neutral Alumina (1 kg.). Elution with benzene yielded an almost colourless solution whose UV-spectrum was characteristic of a substituted tetraphene. Further elution with xylene gave a deep yellow solution which on concentration yielded yellow rosettes of

4-methylanthraceno-(2'.1':1.2)-anthracene (XX) (314 mg.) m.pt. 315-318°. In concentrated sulphuric acid, (XX) gave a purple-black surface colour and a dark yellow solution with a faint fluorescence.

Found C = 94·73%, H = 5·18%

$C_{27}H_{18}$ requires C = 94·70%, H = 5·30%.

Acetylcoronene (XXVIII).

To a finely ground mixture of coronene (XXI) (1 g.) and aluminium chloride (4 g.) in nitrobenzene (50 ml.) was added acetyl chloride (1 ml.) in nitrobenzene (10 ml.). The solution, which changed from yellow to reddish-brown, was shaken for ten hours with glass beads and then decomposed with dilute hydrochloric acid. The nitrobenzene was removed by steam distillation, and the residue repeatedly crystallised from xylene. Acetylcoronene (XXVIII) (0·95 g.) formed yellow needles m.pt. 207-208° (lit. m.pt. 206-207°)[31] M.S. molecular ion m/e = 342, calc. M.W. = 342, which gave a reddish-orange colour in concentrated sulphuric acid. The UV spectrum is shown in figure 19.

Found C = 90·99%, H = 4·38%

$C_{26}H_{14}O$ requires C = 91·20%, H = 4·67%.

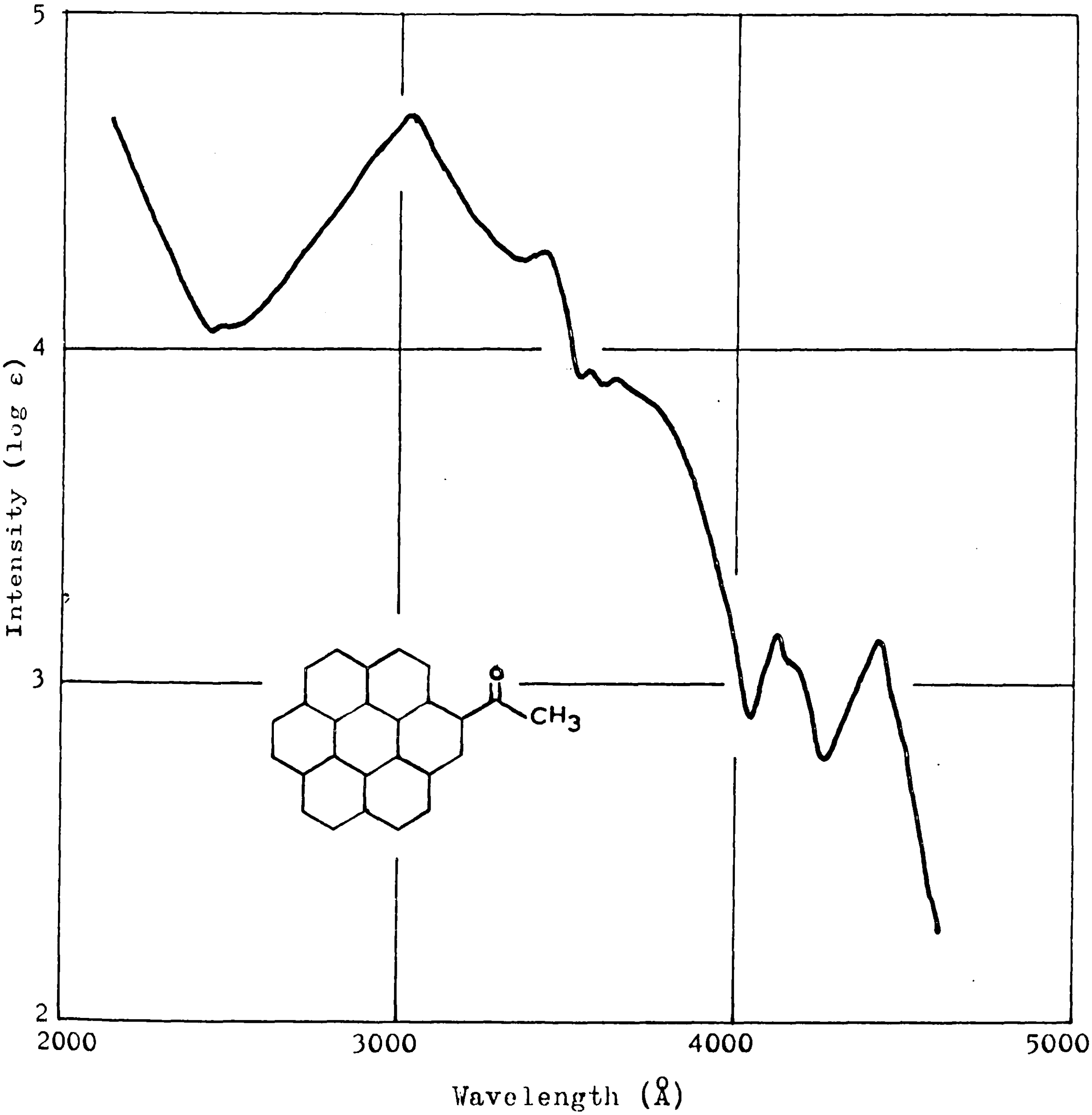


Figure 19. Absorption maxima (Å) and log ε (in parentheses). Acetylcoronene in benzene: α, 4415 (3·13), 4145 (3·14); p, 3650 (3·90), 3570 (3·92), 3445 (4·27); β, 3040 (4·90); in cyclohexane, –.

It is worth noting that acetylcoronene in pyridine readily formed a hydrazone with hydrazine hydrate and piperidine. If water was added this hydrolysed gradually back to acetylcoronene. In this way any trace of unreacted coronene could be removed.

Ethylcoronene (XXIII).

Acetylcoronene (XXVIII) (0·5 g.), sodium hydroxide (0·18 g.), hydrazine hydrate (80%, 0·3 ml.) in diethylene glycol (10 ml.) were refluxed for one hour. Water and excess hydrazine were then distilled off until the temperature rose to 200°. The mixture was then refluxed for a further three hours, water added, and the hydrocarbon filtered off and washed. It was chromatographed on Grade I Neutral Alumina (20 g.). Concentration of the eluate gave yellow needles which were purified through the picrate - dark red needles m.pt. 224-226° dec.

The picrate was decomposed with ammonia, and repeated crystallisation from xylene gave long pale yellow needles (0·3 g.) of ethylcoronene (XXIII) m.pt. 203-204°, M.S. molecular ion m/e = 328, calc. M.W. = 328, which did not dissolve in concentrated sulphuric acid. The UV-

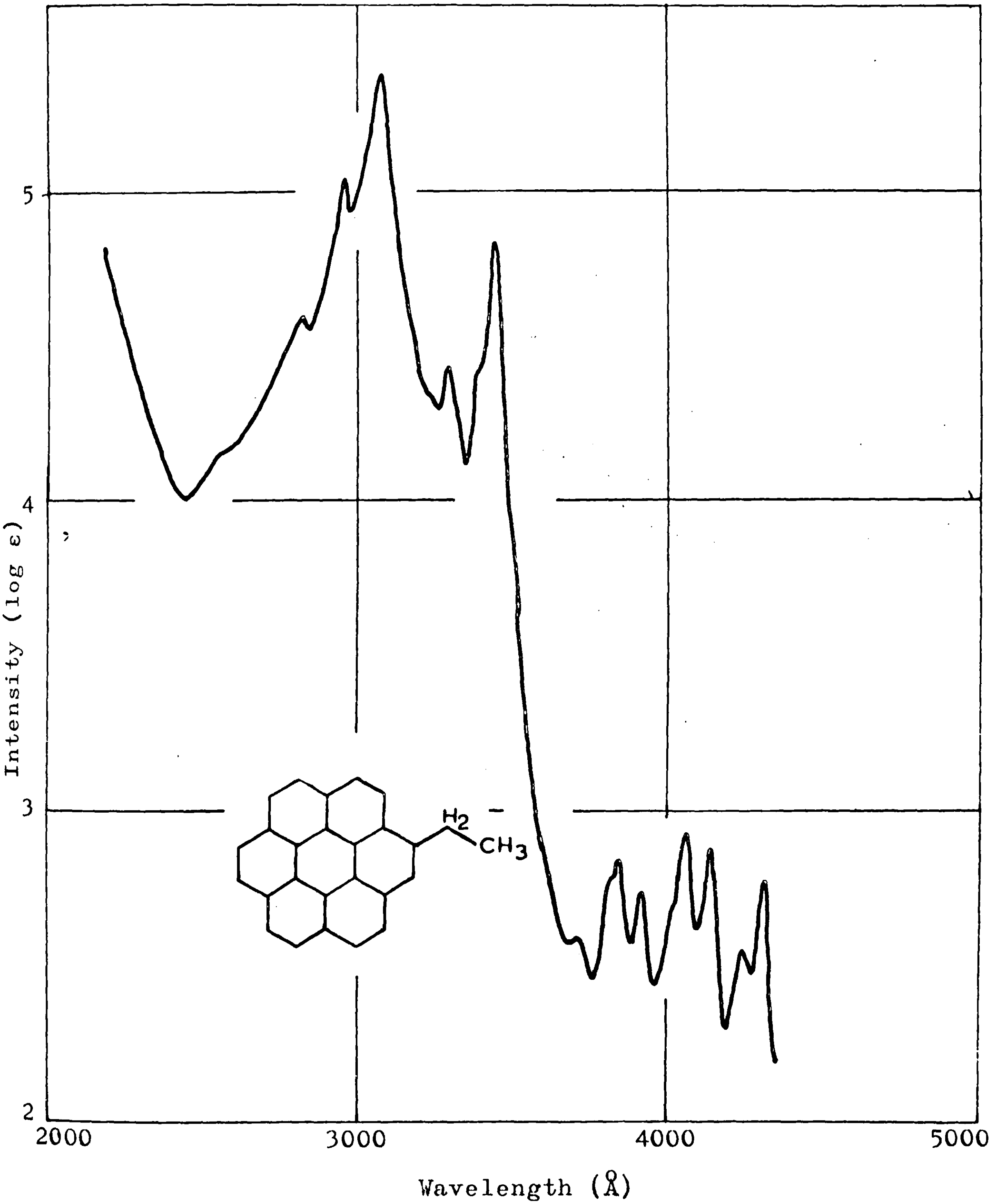


Figure 20. Absorption maxima (Å) and log ε (in parentheses). Ethylcoronene in benzene: α, 4300 (2·78), 4245 (2·56), 4130 (2·89), 4065 (2·95), 3915 (2·74), 3835 (2·85), 3710 (2·60); in cyclohexane, p, 3420 (4·84), 3275 (4·44); β, 3050 (5·38), 2940 (5·04), 2825 (4·60), 2535 (4·15).

spectrum is shown in figure 20.

Found $C = 94{\cdot}93\%$, $H = 4{\cdot}70\%$

$C_{26}H_{16}$ requires $C = 95{\cdot}09\%$, $H = 4{\cdot}91\%$.

Attempted Preparation of Benzoylcoronene (XXIX) and Benzylcoronene (XXX).

To a finely ground mixture of coronene (XXI) (1 g.) and aluminium chloride (4 g.) in nitrobenzene (50 ml.) was added benzoyl chloride (1 ml.). The solution's initial green colour changed to garnet-red over the three-day shaking period with glass beads. Decomposition with dilute hydrochloric acid and steam distillation to remove the nitrobenzene followed. The residue was repeatedly crystallised from xylene; needles of m.pt. 223-225° were obtained (lit. m.pt. 224-225°, 224°).[31,33] M.S. showed strong ions at 404 and 508 due to monobenzoyl and dibenzoylcoronene.

The mixed benzoyl and dibenzoyl compounds were reduced in the same way as acetylcoronene (XXVIII). Fractional crystallisation, chromatography and attempted crystallisation of the picrates were all unsuccessful in separating the two hydrocarbons.

Acknowledgements.

Thanks are due to Messrs. Rutkerswerke and Teerverwertung for samples of all the phenanthrenes, 3-methylpyrene, 4-methylpyrene and 4.9-dimethylpyrene, to Professor H. Dannenberg for 1.2-dimethylpyrene, to Dr. W. Carruthers for 1-methylpyrene, to Professor J. Cook for the methyldibenzanthracenes, to Professor M.S. Newman for the methylpicenes, to Professor G.H. Daub for the methylbenzopyrenes, and finally to Dr. J.L. Monkman of the Occupational Health Laboratory, Canadian Department of Health and Welfare for the methyltetraphenes and the methylbenzophenanthrenes.

CHAPTER 7.

RING CURRENTS: THEORY AND EXPERIMENT.

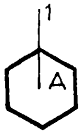
INTRODUCTION:

The experimentally found resonance signal of an identically positioned proton in a number of higher annellated pyrenes and related hydrocarbons cannot be correlated with the position as calculated by simple ring current methods.[1] A satisfactory explanation, however, can be made in terms of sextet theory. These results, together with some earlier ultra-violet measurements give some insight into the principle aromatic conjugation present in these hydrocarbons.

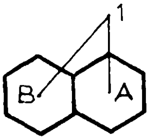
DISCUSSION:

A qualitative explanation of the fact that protons attached to a benzene ring are found at much lower field positions than ethylenic protons, which formally at least have the same environment, is that there are induced ring currents flowing round closed conjugated paths in the former case.

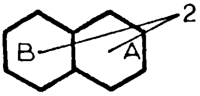
Examination of some polycyclic aromatic compounds[1] has shown that aromatic protons in slightly different environments have different chemical shifts. Application of this ring current model to these hydrocarbons has satisfactorily predicted the order in which these protons should appear in the NMR spectrum, but was somewhat erroneous in anticipating the magnitude of the shift involved. Since this pioneering paper, a number of improvements in the theoretical concepts have been made - first the simple π-electron current model has been replaced by two current loops equally spaced above and below the benzene ring,[2] and somewhat more important, it has been pointed out that benzene ring currents are not all of the same magnitude,[3,4] but that each individual ring has its own particular current. Theoretical and experimental results, therefore, are now in better agreement.[5]



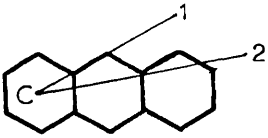
I



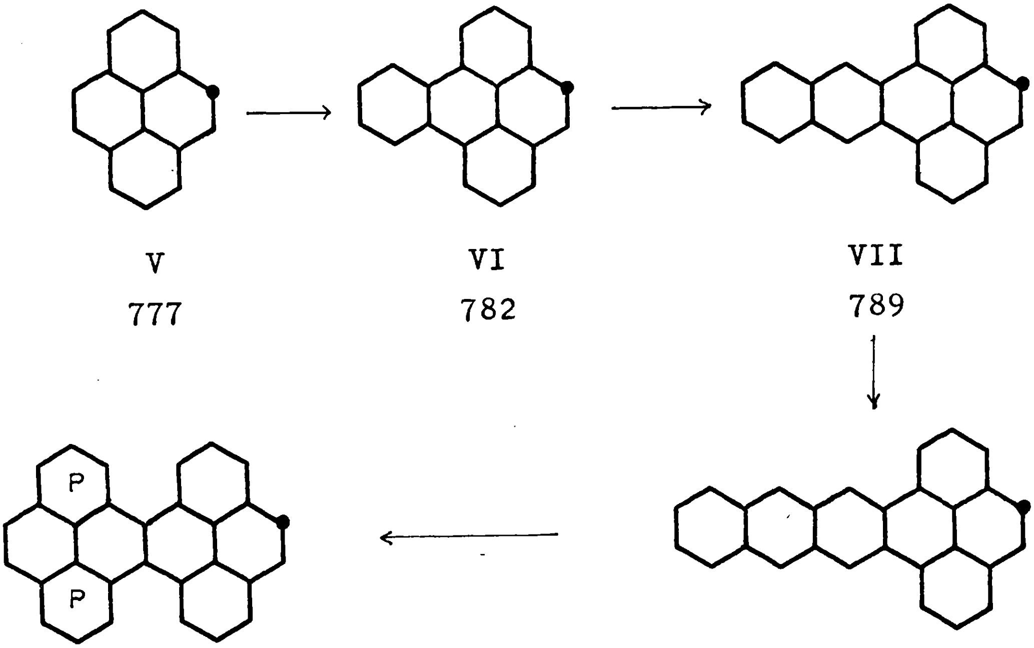
II



III



IV



V
777

VI
782

VII
789

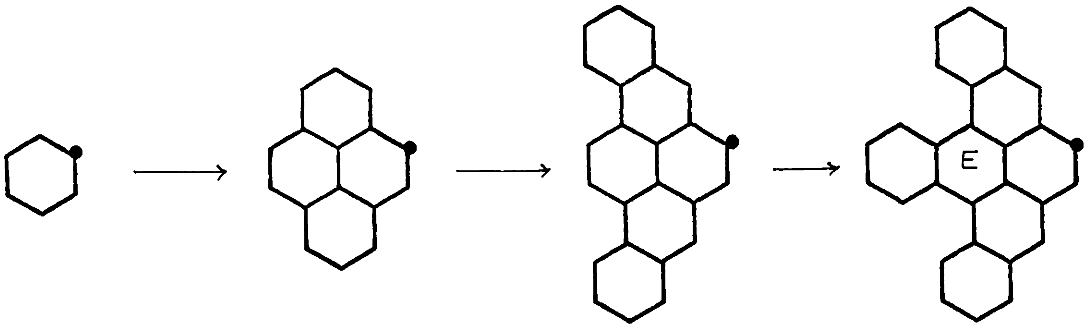
VIII
785

IX
796

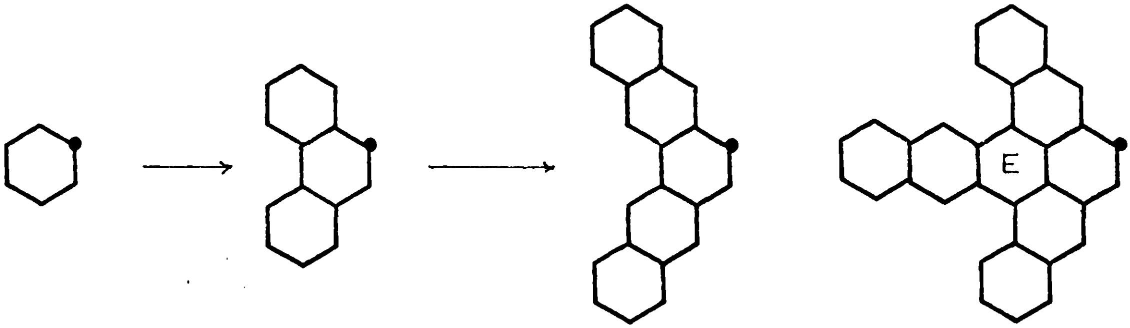
Notwithstanding all these improvements, it must be remembered that the simplest ring current model can predict the order in which the protons should appear by the use of the following equation - the chemical shift of a particular proton (δ) is given by

$$\delta = - \frac{e^2a^2}{2mc^2} \sum_i R_i^{-3}$$

where R_i = distance to the proton from the centre of the i th hexagon, and a = radius of the current ring. In the following explanatory calculation, the C-H and C-C bond lengths are taken to be the same, and equal to a. Now with a = 1·25 cms., the chemical shift of the protons in benzene (I) is -1·41 ppm., relative to ethylene. For naphthalene it is apparent that four measurements are involved - A1, B1 in (II) and A2, B2 in (III). Applying our equation, the chemical shifts due to the ring current are δ_1 =-2·01 ppm., and δ_2 =-1·64 ppm., that is -0·60 ppm., and -0·23 ppm., relative to benzene. Obviously the effect of B1 is greater than that of B2, since the distance involved is shorter. In an exactly analogous manner, the effect of C1 is greater than C2 (V), but both, it must be emphasised are much smaller than B1 or B2. Application of this idea to large condensed polycyclic molecules follows easily -



	I	V	X	XI
marked meso	720	777	772 820	762 817



	I	XIII	XIV	XII
marked meso	720	743	754	762 816

by adding the various distances involved, it should be possible to predict the order in which the same proton in each molecule of a series of related hydrocarbons should appear, and compare it with the experimental value.

Examination of the position of the marked proton in a series of 1.2-benzo substituted pyrenes shows that there is a low-field shift as the series (V → IX) is ascended with the exception of (VIII) which travels slightly in the reverse direction. Theory of course predicts movement to lower field as the higher annellated pyrenes are reached, the value of the shift decreasing in amount with increasing distance.(Table 1) Experiment and theory, in this group agree satisfactorily with the inexplicable exception of (VIII).

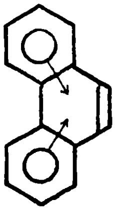
Quite contrary to this, theory and experiment totally disagree for pyrenes annellated in other positions. On annellating a butadiene complex to phenanthrene (XIII) and pentaphene (XIV), pyrene (V) and 3.4,9.10-dibenzopyrene (X) are formed. The resonance signal of the proton moves downfield as expected, but the size of the shifts involved are so different, that between (XIV) and (X) being so small, the signal from 3.4,9.10-dibenzopyrene (X) is now at <u>higher</u> field than that of pyrene (V) itself, a result in total disagreement with theory.(Table 2) Examination of the two

TABLE 1.

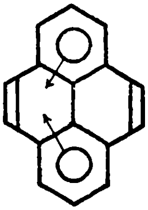
COMPOUND	DISTANCE INVOLVED	THEORETICAL FIELD POSITION
V	A1 + B1 + 2B2	HIGHEST
VI	A1 + B1 + 2B2 + C2	↓
VII	A1 + B1 + 2B2 + C2 + D2	↓
VIII	A1 + B1 + 2B2 + C2 + D2 + E2	↓
IX	A1 + B1 + 2B2 + C2 + D2 + 2P2	LOWEST

TABLE 2.

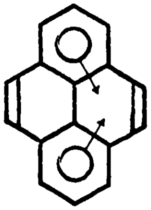
COMPOUND	DISTANCE INVOLVED	THEORETICAL FIELD POSITION
I	A1	HIGHEST
XIII	A1 + B1 + B2	↓
XIV	A1 + B1 + B2 + C1 + C2	↓
V	A1 + B1 + 2B2	↓
X	A1 + B1 + 2B2 + C1 + C2	↓
XI	A1 + B1 + 2B2 + C1 + 2C2	↓
XII	A1 + B1 + 2B2 + C1 + 2C2 + D2	LOWEST



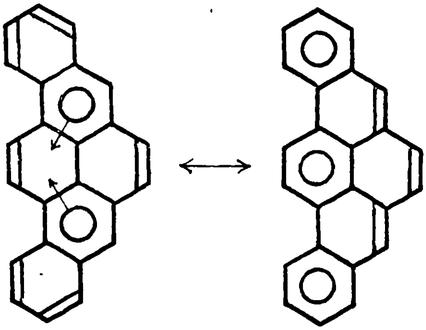
XIII



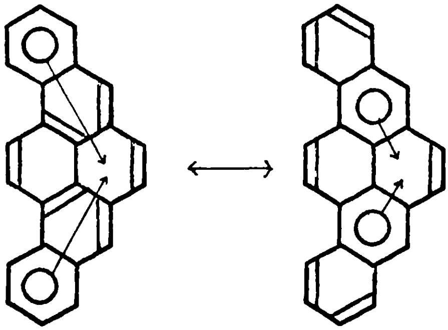
XVa



XVb



XVIa

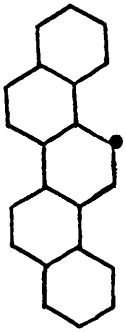


XVIb

other pyrene homologues (XI, XII) shows that they have moved to even higher field, also contrary to theory.

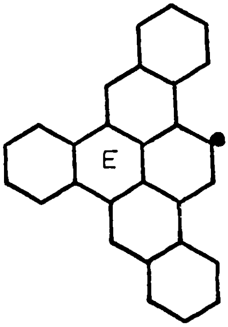
Now, the theoretical reason for the movement of the proton resonance signal is that with the presence of more benzene rings, the ring current is enlarged, and so moves the signal to lower field. If this process is reversed, and the proton signal moves in the opposite direction, the ring current must be less, and the only conceivable way of decreasing the ring current is to assume that some of the rings exert no influence on it. Application of the 'aromatic sextet' and 'fixed double bond' concept[6] can provide a suitable explanation. If phenanthrene (XIII) is drawn with two sextets and a fixed double bond, then the centre ring contains an 'induced' sextet as indicated by the arrows. Now pyrene (V) with two rings of the type of the middle ring of phenanthrene (XIII) can have either of its central rings with induced benzenoid character (XVa, b); this oscillating mechanism must then confer more 'aromaticity' to pyrene (V) in the sense that the position of the proton being examined has moved to lower field. In the same way, 3.4,9.10-dibenzopyrene (X) is more 'aromatic' in this sense than pentaphene (XIV), but the shift in this case is not so large suggesting that one or other of the two possible electronic configurations (XVIa, b) might be preferred to some extent. Confirming this idea the proton position for 3.4,9.10-dibenzopyrene (X) is at higher field than that of pyrene (V) indicating that the 'oscillating' mechanism is no longer in operation. Additional evidence that this is the correct explanation comes from 1.2,3.4,9.10-tribenzopyrene (XI) and 3.4,9.10-dibenzo-naphtho-(2''.3'':1.2)-pyrene (XII) both of which exhibit resonance at exactly the same position to even higher field so that the conjugation causing the ring current must be the same in both molecules. The only way that this can possibly occur is by having the rings marked (E) contain no π-electrons, so cutting off one annellation limb. That the position of the resonance signal is only 8 c/s from that of pentaphene (XIV) itself is a strong indication that (XI) and (XII) should be considered as 13.14-substituted pentaphenes.

As to these figures being accurately measured, there can be very little doubt, since the position of the meso-proton signal (positions 5 and 8), which should be almost equivalent in the three hydrocarbons (X, XI, XII) was carefully noted - the figure varies over only 4 c/s.



XVII

881



XVIII

869

Other measurements confirm this limitation of conjugation in certain hydrocarbons. The resonance position of the marked proton in picene (XVII) and 1.2,4.5,8.9-tribenzopyrene (XVIII) are found at 881 c/s and 869 c/s respectively. Since theory predicts that the proton from the tribenzopyrene (XVIII) should be at lower field than that of picene (XVII), and the experimental finding shows the opposite to be the case, some localisation of the π-electrons must be occurring. The value of the shift (11 c/s) is not much different to that found on annellating an o-phenylene complex to pentaphene (XIV) to form (XI) (8 c/s) and so 1.2,4.5,8.9-tribenzopyrene (XVIII) is best considered as a picene with a 12.13-o-phenylene complex attached to it. Unfortunately (XVII) and (XVIII) cannot be compared with the identical position in 3.4,9.10-dibenzopyrene (X) since (X) was run in carbon disulphide, and (XVII) and (XVIII) were run in arsenic tribromide because of solubility problems.

The ultra-violet spectra of these and related hydrocarbons have already been discussed in an earlier chapter, and quite independently almost identical conclusions were reached. The fact that the results from two such dissimilar branches of spectroscopy can be explained in the same fashion is highly significant, and suggests that our understanding of the fine structure of polycyclic aromatic hydrocarbons may be reaching a turning point.

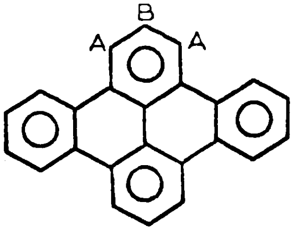
One final point must be mentioned. Dailey,[7] in a recent comprehensive paper on the theoretical aspects of this subject, pointed out there exists a paradox - the chemical shifts due to the ring currents are theoretically proportional to Δ_χ, the anisotropy in the diamagnetic susceptibility; yet the experimental values of Δ_χ are much larger than the theoretically calculated ones, while the experimental chemical shifts are substantially smaller than the theoretical ones. When it is remembered that the π-orbital radius, calculable from the anisotropy varies with the shape of the molecule,[8] and that this could indicate a certain amount of π-electron localisation, there would appear to be evidence accruing from all sides to support the ideas outlined in this chapter.

CHAPTER 8.

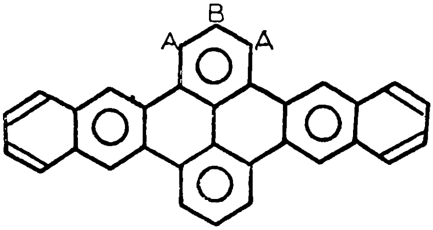
NMR STUDIES ON PYRENE AND RELATED COMPOUNDS.

INTRODUCTION:

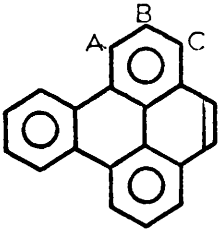
Although the NMR spectrum of pyrene (XX) has always been considered as a good example of an A_2B system,[1] by examination of a number of allied compounds, a large body of evidence has been collected which suggests that the spectrum is better interpreted as an $AA'B$ system, with two separate coupling constants whose values indicate a certain amount of double bond fixation.



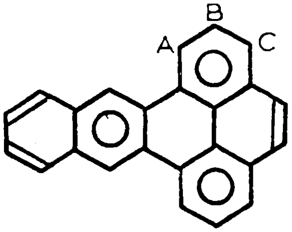
I



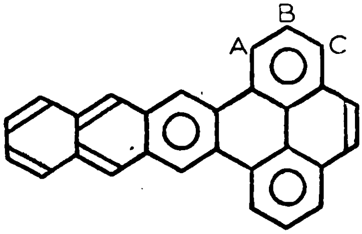
II



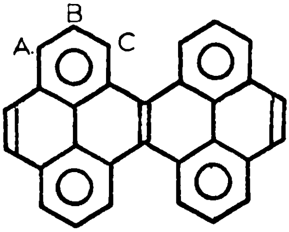
III



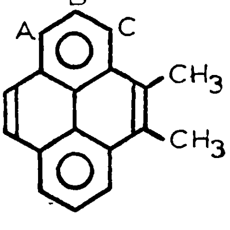
IV



V



VI



VII

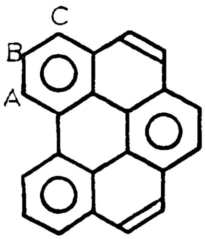
DISCUSSION:

In this chapter only the parts of the NMR spectrum which contain a portion of the three spin system from the three adjacent protons on a benzene ring have been closely examined. For the sake of simplicity, these three protons are denoted by ABC, even though they obviously belong to an AX_2, AMX, or related system. In addition, all the values given in the tables have been obtained by direct measurement of the spectra; in no case has any kind of second order treatment been applied to them. It therefore seems imperative that pyrene (XX) be interpreted by first order techniques also, and not, as previous analyses of the compound,[1] as a strongly coupled A_2B system. As might be expected, the two analyses markedly differ: this chapter describes the results leading to a new interpretation of the NMR spectrum of pyrene (XX), and also what support can be gained for it from an examination of some alkylated derivatives of this polycyclic aromatic hydrocarbon.

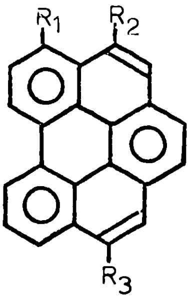
The simplest spectra which have been obtained in our studies are those of 1.2,6.7-dibenzopyrene (I) (figure 1) and dinaphtho-(2'.3':1.2);(2".3":6.7)-pyrene (II), both of which can be interpreted as AX_2 systems. They show only five peaks, a doublet due to the A protons and a triplet due to the B proton. The reason for their simplicity is that the

A protons being in overcrowded positions are shifted to much lower field; this causes a decrease in the J/Δν ratio and allows a simple interpretation of the spectra. The size of the coupling constants are important - the ortho coupling constant, J_{AB} = 7·6 or 8·0 c/s being typical of aromatic systems[3] and the meta coupling constant being absent because of the equivalence of the A protons. This infers, of course, that the ring being examined is completely benzenoid and can be written with a sextet.[4]

The next, logical step is the examination of some asymmetrically substituted pyrenes - 1.2 -benzopyrene (III), naphtho-(2'.3':1.2)-pyrene (IV), anthraceno-(2'.3':1.2)-pyrene (V), pyreno-(1'.2':1.2)-pyrene (VI) and 1.2-dimethylpyrene (VII) (figures 2-4) - all of whose ABC protons exhibit the same pattern of eleven peaks, quartets from A and C, and a triplet from B. On inspection of the coupling constants, it is found that $J_{AB} = J_{BC}$ in all these hydrocarbons causing the expected B quartet to degenerate into a triplet.[2] The ortho coupling constants J_{AB} and J_{BC} all have values typical of aromatic systems[3] and with the non-equivalence of A and C in these compounds, meta coupling can now of course be identified; the values of both ortho and meta coupling constants are typical of completely benzenoid rings,[3] allowing us to write sextets[4] as shown (III-VII).



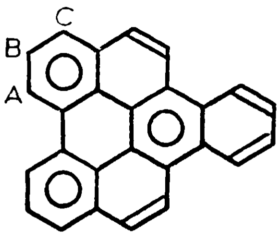
VIII



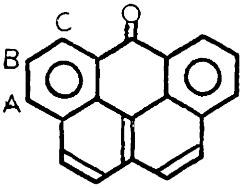
IX R_1=Me, R_2=R_3=H

X R_2=Me, R_1=R_3=H

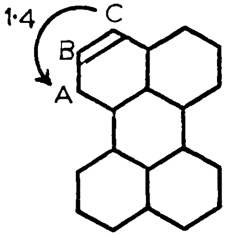
XI R_1=H, R_2=R_3=Me



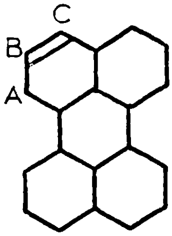
XII



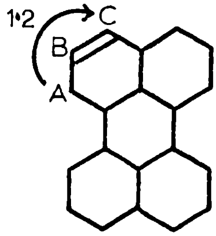
XIII



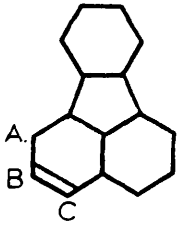
XIVa



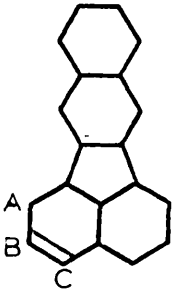
XIV



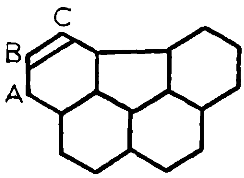
XIVb



XV



XVI

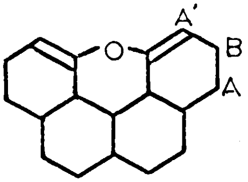


XVII

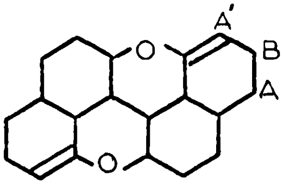
Two other hydrocarbons show this type of 'deceptively simple' spectrum - 1.2-benzoperylene (VIII) and 1.12-o-phenyleneperylene (XII) (figures 5 & 7). From the arguments in the previous paragraph, these hydrocarbons can also be written in terms of sextets and fixed double bonds. Interesting confirmation of the correctness of this idea has been obtained by studying some methyl derivatives of 1.12-benzoperylene (VIII). When the fully aromatic ring is substituted (IX), the methyl signal appears as a singlet but when the fixed double bond is substituted (X, XI), the methyl signal is obtained as a doublet ($J = 1{\cdot}0 - 1{\cdot}1$ c/s) (figure 6). These results substantiate our arguments here and the work already described in Chapter 6.

At this point, it must be emphasised that not only hydrocarbons exhibit this type of spectrum. For instance, naphthanthrone (XIII) (figure 8) shows an eleven line spectrum from its ABC protons. Both ortho and meta coupling constants are of the correct magnitude for fully benzenoid rings.

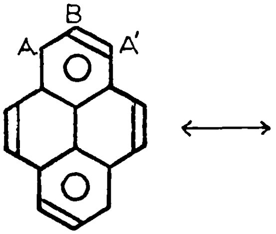
In the next group of hydrocarbons, the expected twelve line spectrum from the three adjacent protons is found; due to the fact that J_{AB} is no longer equal to J_{BC}, the B proton now exhibits its expected quartet,[2] Perylene (XIV), fluoranthene (XV), 11.12-benzofluoranthene (XVI) and 2.13-benzofluoranthene (XVII) (figures 9-12) are typical examples. This difference in the values of the ortho coupling constants found in these compounds is of fundamental importance to our argument; since these values are tending to move outwith the limits for fully aromatic rings ($J = 7{\cdot}0{-}8{\cdot}4$ c/s),[3] it is believed that this is due to a difference in double bond character round the ring. To be more explicit, the greater the coupling constant, the greater the double bond character of the C-C bond between the protons being examined. If perylene (XIV) is considered as an example, $J_{BC} > J_{AB}$, and hence a double bond must occur between the B and C protons. It follows that all four BC positions have high double bond character, and consequently perylene (XIV) must have an electronic arrangement like a double naphthalene. In an exactly analogous manner it is possible to fix double bonds in the appropriate positions in fluoranthene (XV) and its benzologues (XVI, XVII); in all three cases, the high double bond character is in the expected position. There are two further points of interest in these spectra. First, the two meta coupling constants in perylene (XIV) are unequal - $J_{AC} = 1{\cdot}2$ c/s and $J_{CA} = 1{\cdot}4$ c/s. A possible explanation which supports our argument is that the coupling is stronger



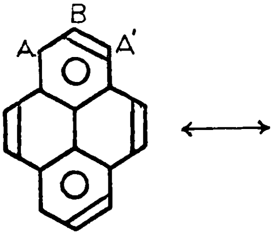
XVIII



XIX



XXa



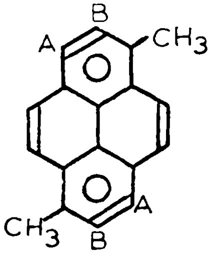
XXb

from C to A than from A to C since in the former case the coupling involves the electrons of the double bond before the single bond (XIVa) while in the latter the reverse is the case (XIVb). No explanation can be given for the absence of this feature in the NMR spectra of the fluoranthenes (XV-XVII). Secondly, by chance, fluoranthene (XV) exhibits only ten peaks (instead of twelve) since parts of the A and C quartets overlap to give a multiplet of six peaks. Because of this overlap, the mid-points of the A and C quartets are obviously very close together, a mere 8 c/s separating them, which makes the $J/\Delta\nu$ ratio equal to approximately one; therefore a second order treatment should theoretically be required but it is quite obvious the spectrum can be successfully interpreted without this more mathematical treatment.

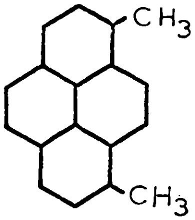
Before discussing the NMR spectrum of pyrene (XX) itself, it is necessary to consider the spectra of naphthoxanthene (XVIII) and dinaphthylene dioxide (XIX), since they provide the key to the interpretation of the pyrene spectrum. An entirely new pattern of peaks is obtained, numbering seven in all, the expected quartet from B but only three peaks from the other two protons. Our interpretation of these three peaks is that they belong to two doublets (four peaks) which have degenerated into three peaks due to the superposition of one peak from each doublet with the formation of the asymmetric triplet shown (figures 13, 14). The coupling constants J_{AB} and $J_{A'B}$ are much smaller than usual and must be associated with single bonds only. If it is accepted that the six π-electrons from a benzene ring exist on two levels, two on the lower and four on the higher,[4] then the lower level π-electrons must be fixed in the positions shown (XVIII, XIX) if any sense is to be made of the coupling constants. Application of Schmidt's Rule,[5] which states that the bond next to a double bond is a particularly strong one, then allows us to tentatively assign the larger coupling constant to the A'B bond, and the smaller to the AB bond. The other four π-electrons must exist on energy levels which have little effect on the NMR spectrum.

A definite conclusion can be drawn from these two spectra: small coupling constants associated with single bonds confer an unusual pattern on the NMR spectrum. Now pyrene (XX) (figure 15) shows a pattern very similar to these oxido compounds (XVIII, XIX). A quartet due to the B proton is obtained as usual, but this time two doublets are found for the A and A' protons. The asymmetry of the two doublets is easily recognised as being almost identical with the triplet found in (XVIII, XIX). An interesting feature is the complete absence of any meta coupling, a factor which also occurs in the aforementioned oxido compounds (XVIII, XIX). However, one immediate difference is apparent - inspection of the coupling constants ($J_{A'B} = 9{\cdot}0$ c/s, $J_{AB} = 5{\cdot}5$ c/s) suggests the presence of a single bond and a double bond unlike the two single bonds described in the previous paragraph. Hence it is felt that the NMR spectrum of pyrene (XX) has now been analysed at its face value, the analysis depending on correlations drawn from a variety of other compounds. It is, in our opinion, best formulated in either a centrosymmetrical or a plane-symmetrical form both of which must oscillate or 'flip' to preserve the symmetry of the molecule (XXa, b).

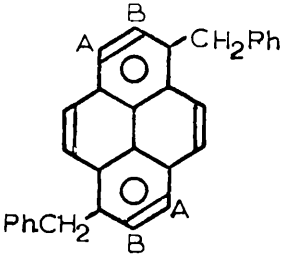
This new interpretation of the pyrene spectrum must of course be compared with the earlier one which considered pyrene (XX) as an A_2B system with a single coupling constant of 7·6 c/s.[1] An important point in the interpretation of pyrene in this manner is the recognition of the ninth, combination band. Now in all our spectra, which are better resolved than those in the earlier investigation, this combination band has never been spotted; this constitutes an important piece of evidence for the inexactitude of the earlier interpretation. To further clarify our ideas, it was thought that at higher temperatures any bond fixation



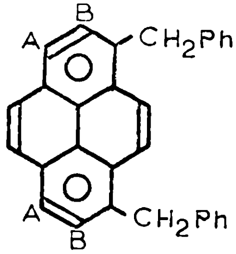
XXI



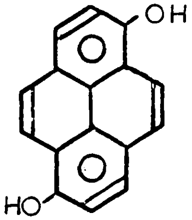
XXII



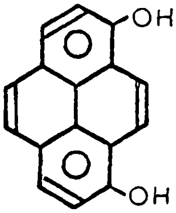
XXIII



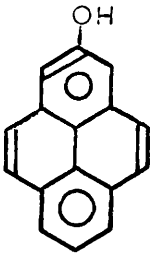
XXIV



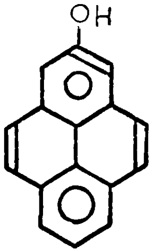
XXV



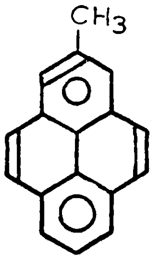
XXVI



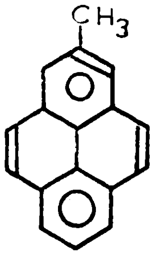
XXVIIa



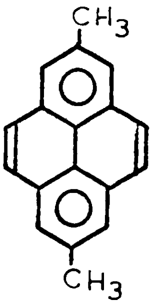
XXVIIb



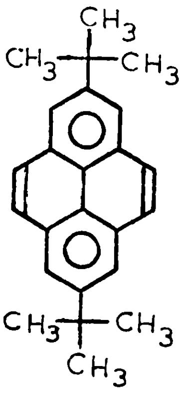
XXVIIIa



XXVIIIb



XXIX



XXX

might be lost and a different spectrum be obtained. A temperature study from $-30^\circ C$ to $+130^\circ C$ was therefore carried out on pyrene (XX). Low temperatures had no effect, but high temperatures caused a number of small shifts, whose direction was such that, had they been much larger, a five line AX_2 type of spectrum like that of 1.2,6.7-dibenzopyrene(I) would have been obtained. It would therefore seem that a considerable amount of energy is required to overcome the bond fixation.

In order to find out if one or other of the plane-symmetrical or centrosymmetrical form was favoured, it was decided to examine some 3.8- and 3.10-disubstituted pyrenes. 3.8-Dimethylpyrene (XXI) was successfully prepared from 3.8-dibromopyrene,[7] but 3.10-dimethylpyrene (XXII) could not be synthesised since 3.10-dibromopyrene, although described in the literature,[6,7] could not be obtained. In fact the only pair of 3.8- and 3.10-derivatives synthesised were the dibenzyl compounds. . 3.8-Dimethylpyrene (XXI) and 3.8-dibenzylpyrene (XXIII) (figures 16, 17), both show two quartets, the one from the AB protons having a coupling constant of 8·0 c/s in both cases; this value suggests some degree of fixed double bond character as shown (XXI, XXIII). It might be pointed out that the interpretation of these spectra and of a considerable number of those described earlier is based on examination of the spectra taken on both 60 Mc/s and 100 Mc/s machines. In this way, although the overall pattern generally changes, peaks coupled together always remain the same number of cycles per second apart and are easily recognised. The only 3.10-derivative examined, 3.10-dibenzylpyrene (XXIV) shows a quartet from the AB protons and two singlets from the C and D protons. The coupling constant, J_{AB}, in this instance, is 7·9 c/s, again suggesting a limited amount of fixed double bond character. Chemical evidence supports this idea - the isomeric 3.8-dihydroxypyrene (XXV) and 3.10-dihydroxypyrene (XXVI) fail to enter into the diazo-coupling reaction. This, of course, means the hydroxyl group is 'alcoholic' rather than 'phenolic' - and the only way to explain this is by assuming the double bond takes up a position away from the substituent (XXV, XXVI). In 4-hydroxypyrene (XXVIIa, b), where the double bond cannot adopt a position distant from the substituent, the diazo-coupling reaction takes place quite normally.[8] The only possible conclusion to be drawn from these results is that there is no preference for either symmetry form.

Since 3.8- and 3.10-substituents have been shown to have definite fixation character on both spectroscopic and chemical evidence, it is necessary to consider the effect of 4-substituents. 4-Methylpyrene (XXVIIIa, b) shows the same AA'B pattern of peaks as pyrene (XX), an important point which shows that the high symmetry of pyrene confers no special properties. However, the methyl signals of (XXVIII) and 4.9-dimethylpyrene (XXIX) show triplets which means that oscillation must be taking place very rapidly to attain the necessary equivalence of the two ortho protons. Further evidence of this equivalence is obtained from 4.9-di-t-butylpyrene (XXX) which shows no meta coupling at the highest expansions.

In conclusion, therefore, it seems possible to differentiate between two types of pyrene derivative; those in which the double bond appears to be fixed (3.8- and 3.10-derivatives) and those in which it oscillates very rapidly (4.9-derivatives). Pyrene (XX) must lie somewhere between the two extremes.

Hydrocarbon	No of Peaks	Position	Multiplicity	Coupling Constant c/s	
1.2,6.7-Dibenzopyrene (I)	5	A_2 898·7	doublet	$J_{AB}=7\cdot6$	AsBr$_3$:
		B 812·8	triplet		CAT.
					Fig.1.
Dinaphtho-(2'.3':1.2);(2''.3'':6.7)-pyrene (II)	5	A_2	doublet	$J_{AB}=8\cdot0$	AsBr$_3$:
		B	triplet		CAT.
1.2-Benzopyrene (III)	11	A 866·8	quartet	$J_{AB}=J_{BC}=7\cdot5$	CS$_2$:
		B 777·5	triplet	$J_{AC}=1\cdot6$	Fig.2.
		C 795·0	quartet		
Naphtho-(2'.3':1.2)-pyrene (IV)	11	A 885·3	quartet	$J_{AB}=J_{BC}=7\cdot5$	CS$_2$:
		B 789·1	triplet	$J_{AC}=1\cdot7$	CAT
		C 800·4	quartet		
Anthraceno-(2'.3':1.2)-pyrene (V)	11	A 885·0	quartet	$J_{AB}=J_{BC}=7\cdot2$	CS$_2$:
		B 786·0	triplet	$J_{AC}=1\cdot7$	CAT.
		C 799·5	quartet		
Pyreno-(1'.2':1.2)pyrene (VI)	11	A 911·2	quartet	$J_{AB}=J_{BC}=7\cdot5$	CS$_2$:
		B 792·9	triplet	$J_{AC}=1\cdot5$	CAT.
		C 808·8	quartet		Fig.3.
1.2-Dimethylpyrene (VII)	11	A 803·1	quartet	$J_{AB}=J_{BC}=7\cdot5$	CS$_2$:
		B 785·1	triplet	$J_{AC}=1\cdot8$	Fig.4.
		C 770·8	quartet		
1.12-Benzoperylene (VIII)	11	A 887·2	quartet	$J_{AB}=J_{BC}=7\cdot5$	CS$_2$:
		B 787·0	triplet	$J_{AC}=1\cdot4$	Fig.5.
		C 808·8	quartet		
3.10-Dimethyl-1.12-benzoperylene (XI)	11	A 885·3	quartet	$J_{AB}=J_{BC}=7\cdot5$	CS$_2$:
		B 790·5	triplet	$J_{AC}=1\cdot2$	Fig.6.
		C 816·2	quartet		
1.12-o-Phenyleneperylene (XII)	11	A 871·0	quartet	$J_{AB}=J_{BC}=7\cdot7$	CS$_2$:
		B 780·0	triplet	$J_{AC}=1\cdot4$	CAT.
		C 803·5	quartet		Fig.7.

Hydrocarbon	No of Peaks	Position	Multi-plicity	Coupling Constant c/s	
Naphthanthrone (XIII)	11	A 868·1	quartet	$J_{AB}=J_{BC}=7{\cdot}5$	CS_2:
		B 776·1	triplet	$J_{AC}=1{\cdot}5$	CAT.
		C 816·7	quartet		Fig.8.
Perylene (XIV)	12	A 804·5	quartet	$J_{AB}=7{\cdot}0$; $J_{BA}=7{\cdot}6$	CS_2:
		B 732·2	quartet	$J_{CB}=8{\cdot}4$; $J_{BC}=8{\cdot}7$	CAT.
		C 756·0	quartet	$J_{AC}=1{\cdot}2$; $J_{CA}=1{\cdot}4$	Fig.9.
Fluoranthene (XV)	(10)	A 779·4	sextet	$J_{AB}=6{\cdot}7$	CS_2:
		B 750·3	quartet	$J_{BC}=8{\cdot}4$	Fig.10.
		C 771·9	sextet	$J_{AC}=1{\cdot}0$	
11.12-Benzofluoranthene (XVI)	12	A 788·9	quartet	$J_{AB}=6{\cdot}6$	CS_2:
		B 755·9	quartet	$J_{BC}=8{\cdot}2$	CAT.
		C 774·5	quartet	$J_{AC}=1{\cdot}2$	Fig.11.
2.13-Benzofluoranthene (XVII)	12	A 786·1	quartet	$J_{AB}=6{\cdot}8$	CS_2.
		B 744·1	quartet	$J_{BC}=8{\cdot}0$	Fig.12.
		C 769·0	quartet	$J_{AC}=0{\cdot}6$	
Naphthoxanthene (XVIII)	7	A 720·4	triplet	$J_{AB}=3{\cdot}2$	CS_2.
		A' 721·6	triplet	$J_{A'B}=5{\cdot}6$	Fig.13.
		B 682·7	quartet		
Dinaphthylene dioxide (XIX)	7	A 695·3	triplet	$J_{AB}=3{\cdot}6$	CS_2:
		A' 696·0	triplet	$J_{A'B}=5{\cdot}1$	CAT.
		B 653·3	quartet		Fig.14.
Pyrene (XX)	8	A 780·6	doublet	$J_{AB}=5{\cdot}5$	CS_2.
		A' 781·7	doublet	$J_{A'B}=9{\cdot}0$	Fig.15.
		B 763·1	quartet		

Hydrocarbon	No of Peaks	Position	Multi-plicity	Coupling Constant c/s	
3.8-Dimethyl-pyrene (XXI)	8	A B	quartet	J_{AB}=8·0	CS_2. Fig.16.
3.8-Dibenzyl-pyrene (XXIII)	8	A B	quartet	J_{AB}=8·0	CS_2. Fig.17
3.10-Dibenzyl-pyrene (XXIV)	8	A B	quartet	J_{AB}=7·9	CS_2
4-Methylpyrene (XXVIII)	8	A 788·6	doublet		
		A' 790·1	doublet		CS_2. Fig.18.
		B	quartet		
4.9-Dimethyl-pyrene (XXIX)	2	768·3	doublet	J=0·6	CS_2
4.9-Di-t-butyl-pyrene (XXX)	1	807·6	singlet	-	CS_2

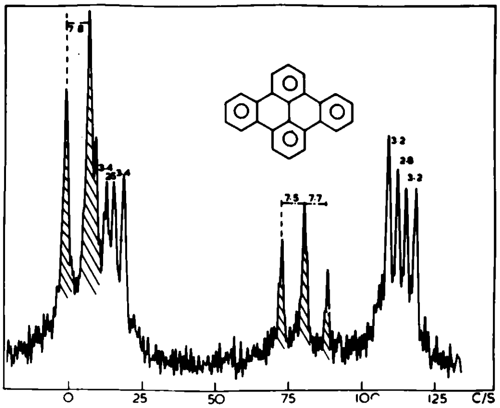


Figure 1.

1.2,6.7-Dibenzopyrene

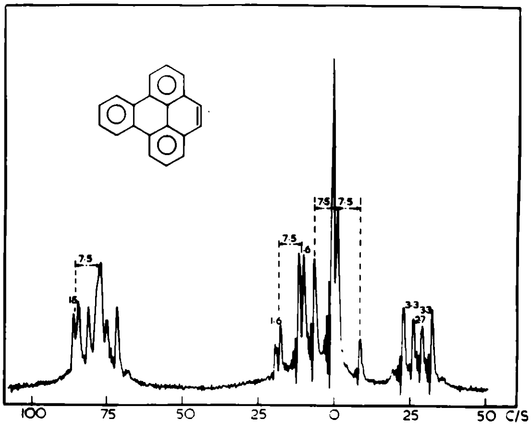


Figure 2.

1.2-Benzopyrene

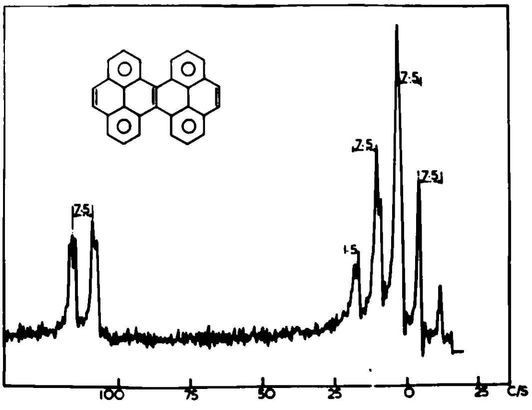


Figure 3.

Pyreno-(1'.2':1.2)-pyrene

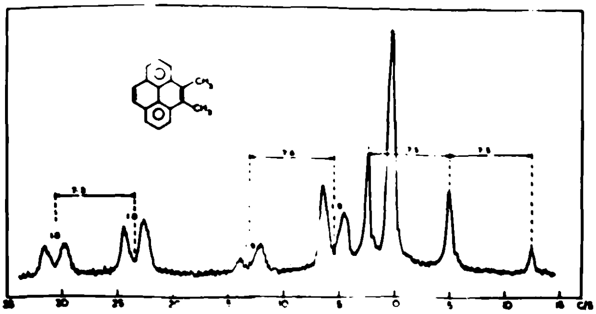


Figure 4.

1.2-Dimethylpyrene

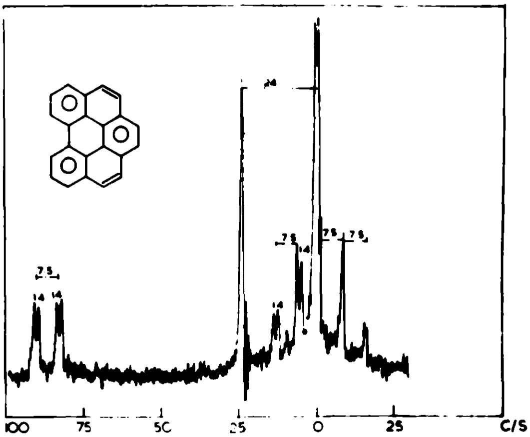


Figure 5.

1.12-Benzoperylene

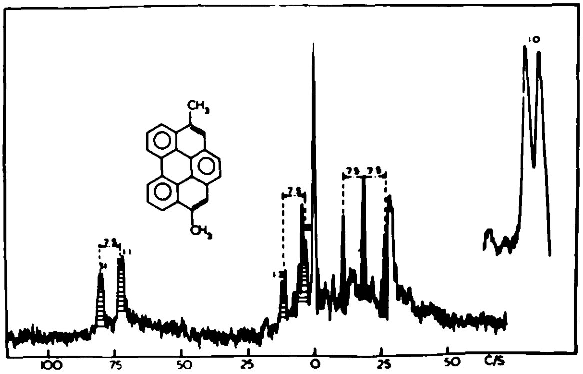


Figure 6.

3.10-Dimethyl-1.12-benzoperylene

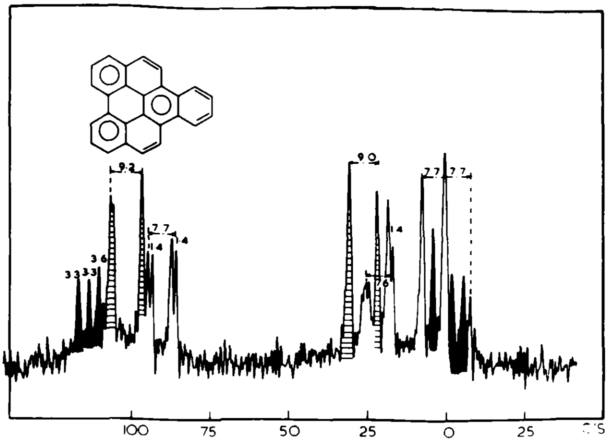


Figure 7.

1.12-o-Phenyleneperylene

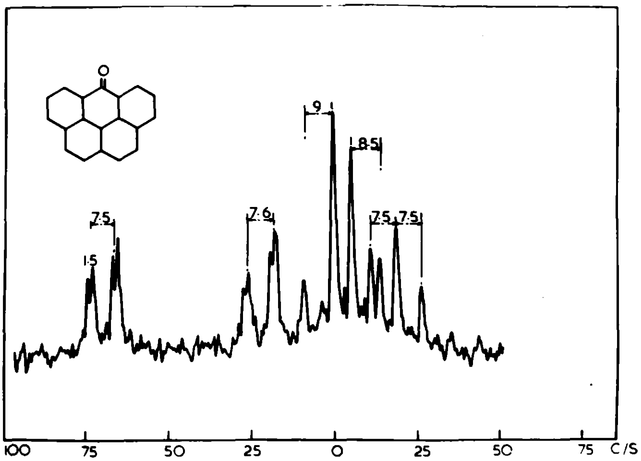


Figure 8.

Naphthanthrone

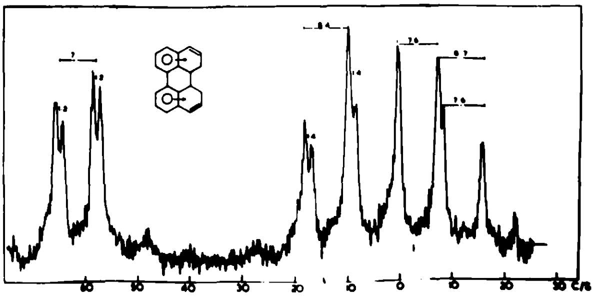


Figure 9.

Perylene

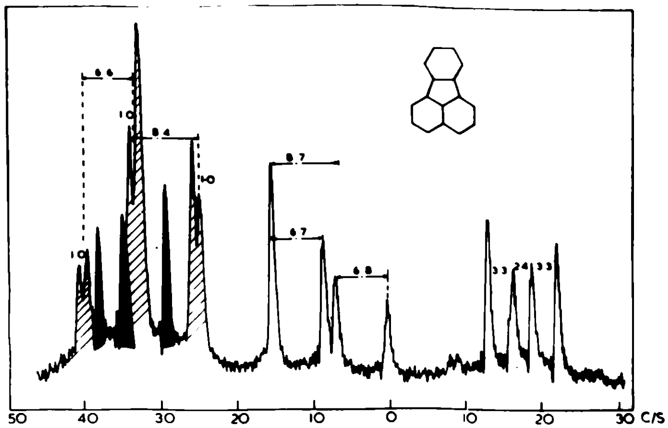


Figure 10.

Fluoranthene

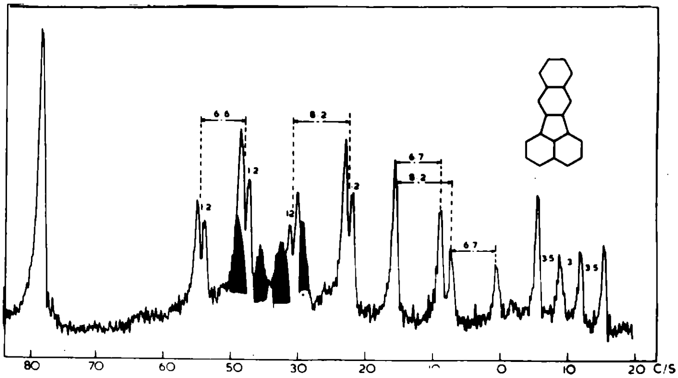


Figure 11.

11.12-Benzofluoranthene

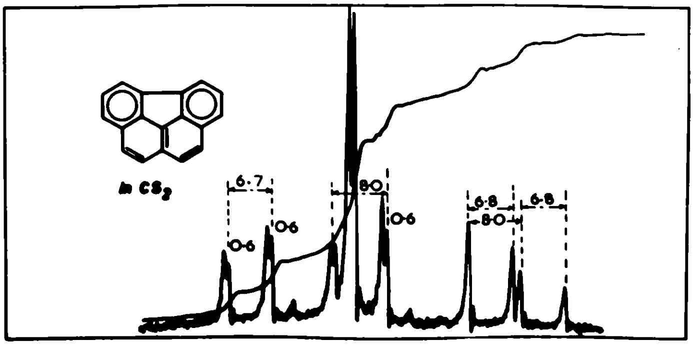


Figure 12.

2.13-Benzofluoranthene

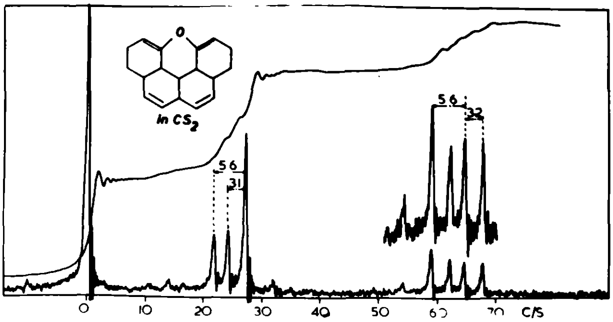


Figure 13.

Naphthoxanthene

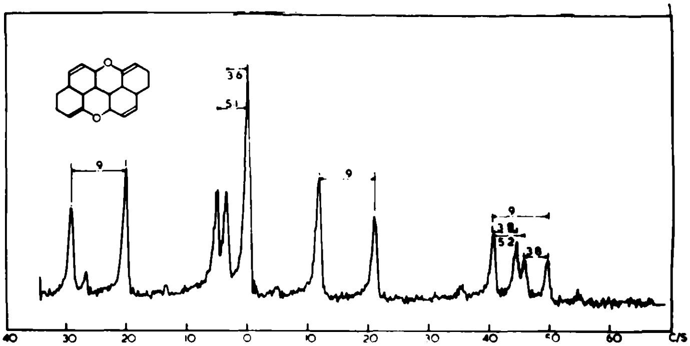


Figure 14.

2.8',8.2'-Dioxido-1.1'-dinaphthyl

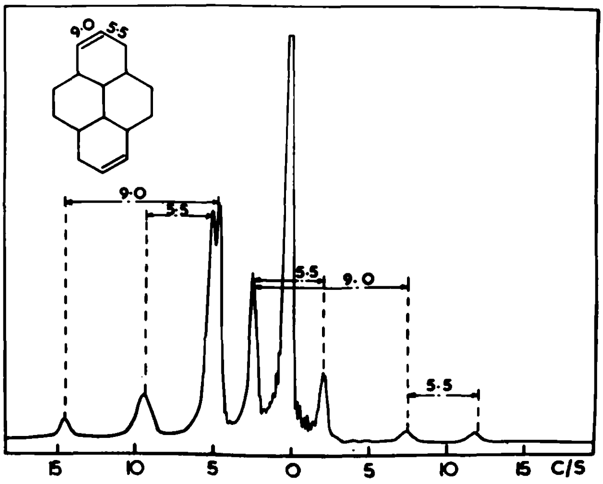


Figure 15.

Pyrene

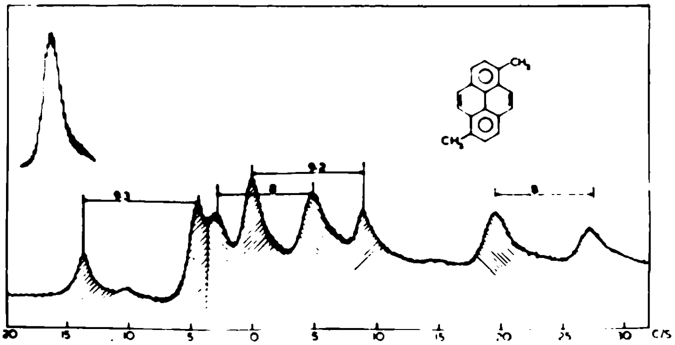


Figure 16.

3.8-Dimethylpyrene

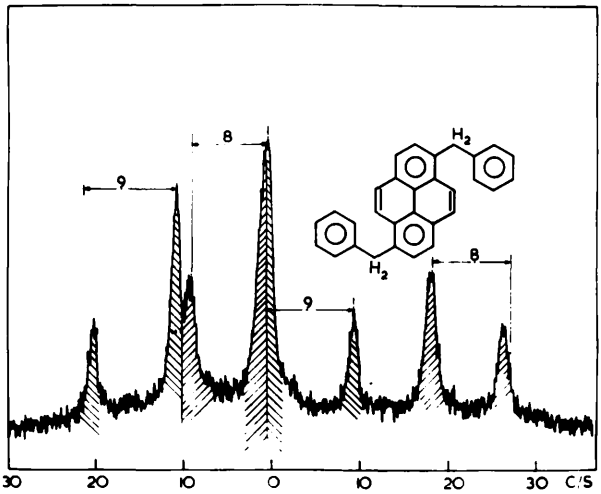


Figure 17.

3.8-Dibenzylpyrene

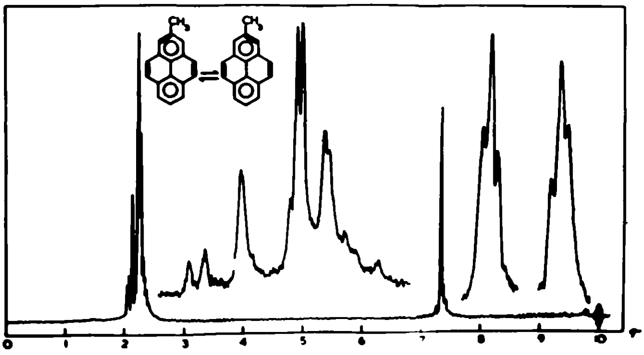
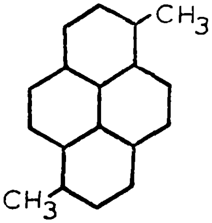
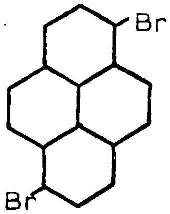


Figure 18.

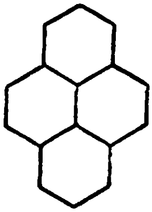
4-Methylpyrene



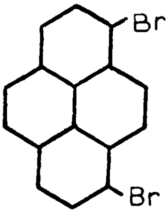
XXI



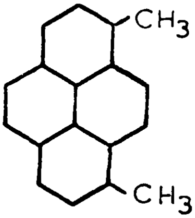
XXXI



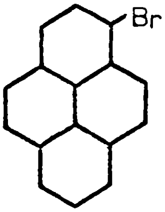
XX



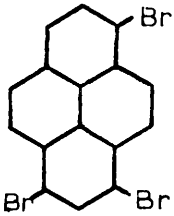
XXXII



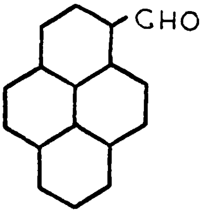
XXII



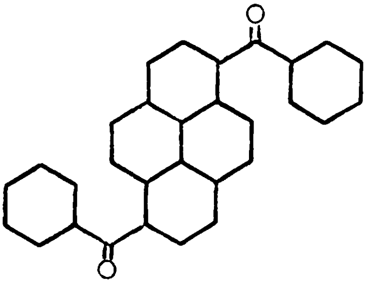
XXXIII



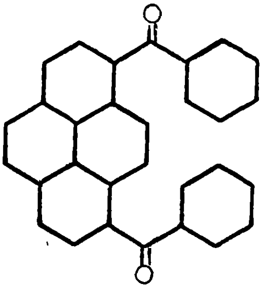
XXXIV



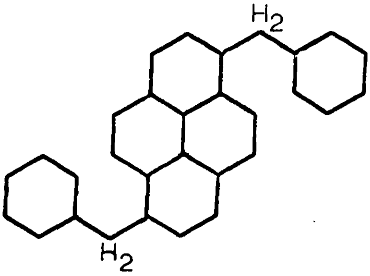
XXXV



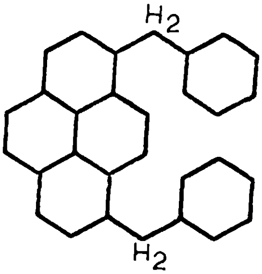
XXXVI



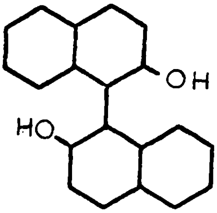
XXXVII



XXIII



XXIV



XXXVIII

EXPERIMENTAL DISCUSSION:

Naphthanthrone (XIII) was prepared from pyrene (XX), glycerin, and concentrated sulphuric acid,[9] but the method adopted involved the use of nitrobenzene,[10] an improvement which allowed lower reaction temperatures and yielded purer material. 2.8',8.2'-Dioxido-1.1'-dinaphthyl (XIX) was prepared by the earliest method of Pummerer and Frankfurter,[11] but was modified in that the purification of the dioxide was accomplished by chromatography. The ultra-violet spectra of naphthoxanthene (XVIII) and 2.8',8.2'-dioxido-1.1'-dinaphthyl (XIX) have been recorded for the first time (figures 19, 20).

The greater part of the experimental work, however, consisted of various attempts to obtain isomeric 3.8- and 3.10-dialkylpyrenes. Before discussing this work in detail, mention must be made of the three hitherto unknown methyl substituted 1.12-benzoperylenes (IX, X, XI) prepared by Drs. U. Sanigok and M. Zander; the preparative work, as distinct from the spectroscopic results, will be described elsewhere.

The simplest 3.8- and 3.10-disubstituted pyrenes are the two dimethyl compounds (XXI, XXII). 3.8-Dimethylpyrene (XXI) has already been synthesised - by bromination of pyrene (XX) to form 3.8-dibromopyrene (XXXI) followed by a

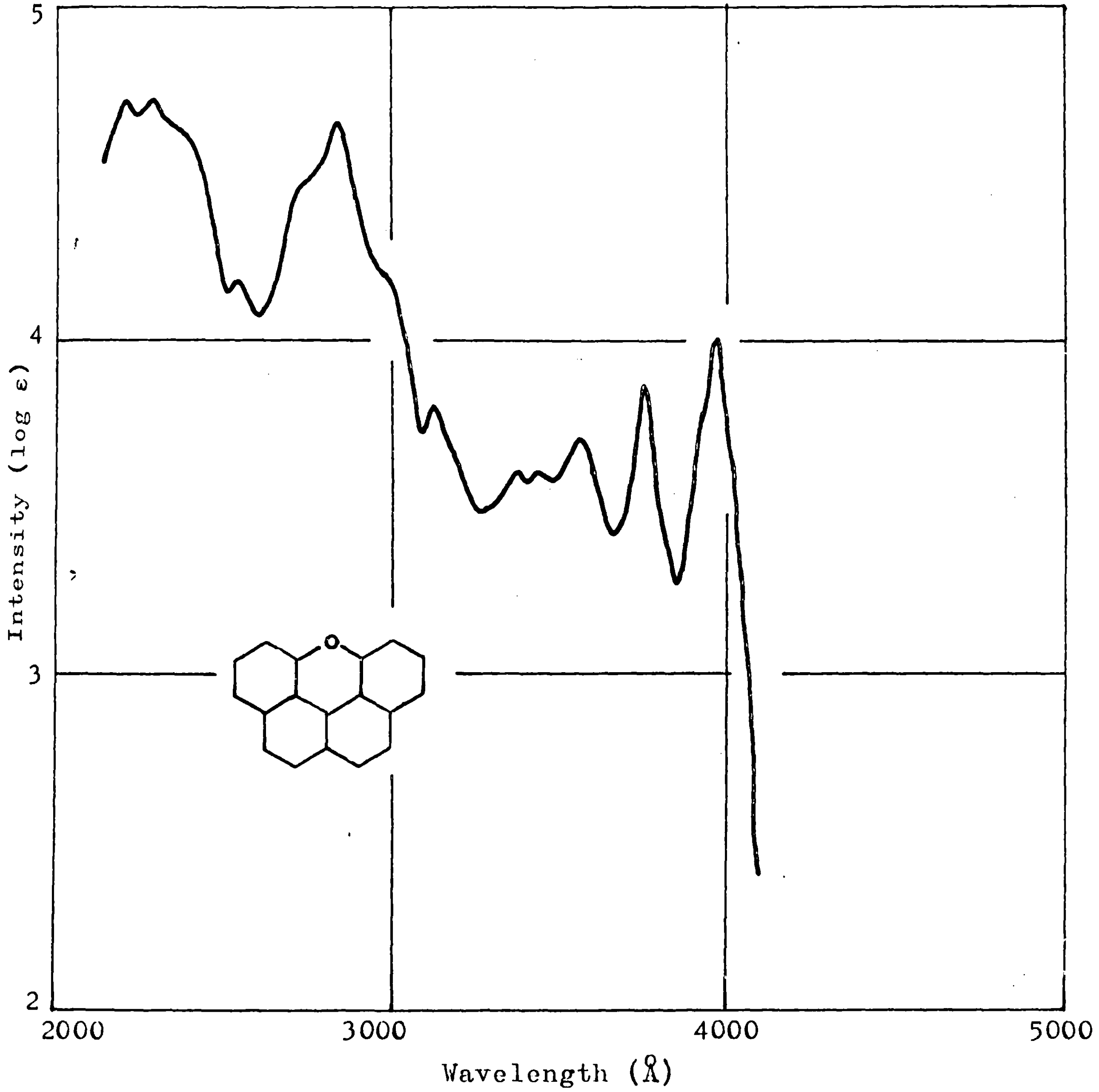


Figure 19. Absorption maxima (Å) and log ε (in parentheses). Naphthoxanthene in ethanol: 3960 (4·00), 3755 (3·87), 3560 (3·70), 3445 (3·60), 3355 (3·60), 3105 (3·80), 2820 (4·64), 2520 (4·18), 2275 (4·73), 2195 (4·71).

modified Grignard reaction to yield 3.8-dimethylpyrene (XXI).[7] Now, Martin[7] had no success in preparing 3.10-dimethylpyrene (XXII) by this route since it was found impossible to obtain 3.10-dibromopyrene (XXXII) in a pure state, even although Lock, a number of years earlier, had isolated, purified, and characterised both dibromopyrenes (XXXI, XXXII).[6] In our hands, in a variety of experiments, bromination of pyrene (XX) has yielded 3-bromopyrene (XXXIII),[6] 3.8-dibromopyrene (XXXI) and 3.5.8-tribromopyrene (XXXIV);[12] in not a single instance has 3.10-dibromopyrene (XXXII) ever been obtained in a pure state.

Since the simplest route had proved unsuccessful, another had to be found. Recently, double Vilsmeier reactions[13] have been accomplished on simple substrates and it was thought that a double reaction of this type might occur in the 3.8- and 3.10-positions in pyrene (XX) if more forcing reagents - dichloromethylalkyl ethers and Lewis acids[14] - were used. All the attempts at this double formylation were equally useless, pyrene-3-aldehyde (XXXV) being the only identifiable material.

The next stage of the preparative work was an approach to the synthesis of the isomeric diethylpyrenes rather than the dimethyl compounds. Friedel-Crafts reaction of pyrene (XX) with excess acetyl chloride should yield the required diacetylpyrenes but after the usual type of work-up, an intractable black tar was obtained from which no pure compounds could be isolated. However, benzoylation was much more successful. The two isomeric dibenzoylpyrenes (XXXVI, XXXVII) were prepared and separated according to the method of Vollmann et al.;[15] reduction by the Huang-Minlon technique gave the isomeric dibenzylpyrenes (XXIII, XXIV) which proved quite satisfactory for NMR studies.

EXPERIMENTAL

Naphthanthrone (XIII).

Naphthanthrone (XIII) was prepared according to the method of Ironside;[10] (XIII) was obtained as orange-brown prisms from glacial acetic acid, m.pt. 242-243° (lit. m.pt. 243°).[15]

2.8',8.2'-Dioxido-1.1'-dinaphthyl (XIX).

A solution of β-dinaphthol (XXXVIII) (2 g.)[11] in dry benzene (100 ml.) was treated with silver oxide (4 g.) for one hour on a steam bath. The hot dark solution was filtered to remove the inorganic material, concentrated and chromatographed on Grade I Neutral Alumina (50 g.). Elution with 10% chloroform/benzene gave a bright yellow eluate which on concentration yielded glistening yellow plates of 2.8',8.2'-dioxido-1.1'-dinaphthyl (XIX) (175 mg.), m.pt. 239-240°, (lit. m.pt. 240°).[16,17]

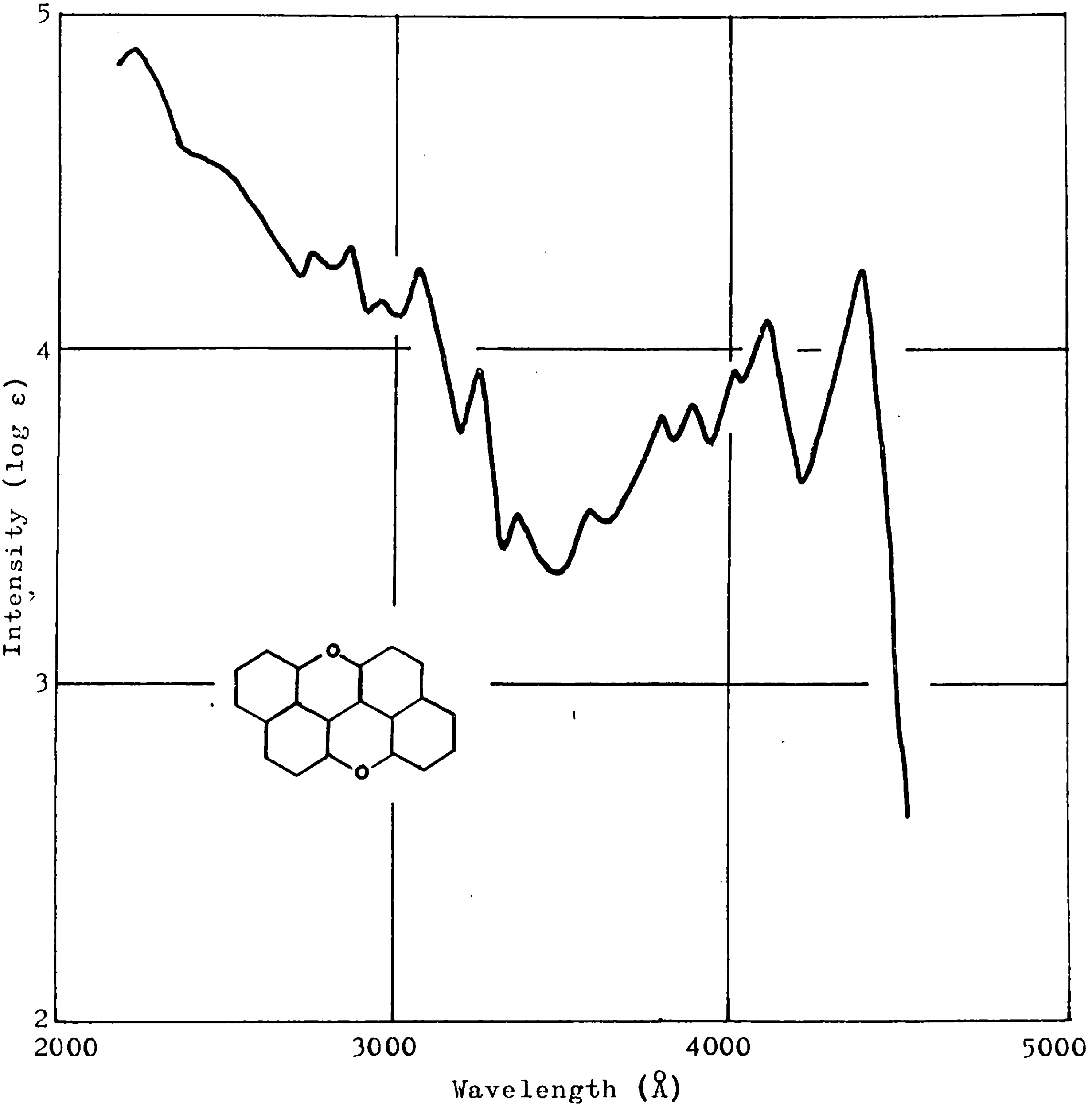


Figure 20. Absorption maxima (Å) and log ε (in parentheses). 2.8',8.2'-Dioxido-1.1'-dinaphthyl in ethanol: 4400 (4·23), 4125 (4·10), 4025 (3·94), 3900 (3·84), 3805 (3·80), 3590 (3·53), 3410 (3·60), 3250 (3·95), 3080 (4·25), 2965 (4·14), 2860 (4·31), 2750 (4·29), 2220 (4·90).

Bromination of Pyrene (XX).

Pyrene (40 g.) was dissolved in dry carbon tetrachloride (600 ml.) at room temperature and bromine (64 g.) in dry carbon tetrachloride (600 ml.) was added dropwise over ninety minutes. The reaction mixture was allowed to stand overnight, and the resulting white precipitate was filtered off and dried (48 g.) m.pt. 187-200°.

This solid was crystallised first from carbon tetrachloride and then from toluene until long colourless needles of 3.8-dibromopyrene (XXXI) m.pt. 225° (lit. m.pt. 223°)[7] were obtained.

Found C = 53·56%, H = 2·54%

$C_{16}H_8Br_2$ requires C = 53·37%, H = 2·24%.

The filtrate was concentrated to 200 ml. and the resulting precipitate removed by filtration. This filtrate should now contain a large proportion of the more soluble 3.10-isomer. The solution was therefore further concentrated and chromatographed on Mallinckrodt Silicic Acid (200 g.). Elution with benzene gave a small portion of pure material, followed by a mixture of two compounds. TLC showed the pure material was 3.8-dibromopyrene (XXXI) and the mixture contained 3.8-dibromopyrene (XXXI) and presumably 3.10-dibromopyrene (XXXII). Preparative TLC also failed to separate these two compounds.

A further large scale experiment was carried out, using less than the required amount of reagent for double bromination. Pyrene (40 g.) was dissolved in dry carbon tetrachloride (1000 ml.) at -10°C and bromine (48 g.) in dry carbon tetrachloride (600 ml.) was added slowly over ninety minutes. The reaction mixture was again allowed to stand overnight, and the resulting precipitate was filtered off and dried (42 g.) m.pt. 189-204°. On attempted crystallisation from carbon tetrachloride, a small portion failed to dissolve. It was filtered off and repeatedly crystallised from a large volume of xylene as stout needles of 3.5.8-tribromopyrene (XXXIV) m.pt. 258-260° (lit. m.pt. 259-260°).[12] The carbon tetrachloride soluble material was crystallised from this solvent, and then from toluene to yield long colourless needles of 3.8-dibromopyrene (XXXI) m.pt. 225°, identical in all respects to the material obtained from the earlier experiment.

The filtrate was again concentrated to 200 ml. and the resulting precipitate removed by filtration. The filtrate was evacuated to dryness, the resulting light brown solid dissolved in benzene and excess picric acid added. A picrate was formed - bright red-orange prisms, m.pt. 170° (lit. m.pt. 172°).[6] After decomposition with aqueous ammonia and crystallisation from ethanol, colourless leaflets of 3-bromopyrene (XXXIII) m.pt. 95° (lit. m.pt. 95°)[6] were identified.

The second crop of crystals not previously examined, showed on TLC examination to be a mixture of 3.8-dibromopyrene (XXXI) and 3.10-dibromopyrene (XXXII). These results confirm that 3.10-dibromopyrene (XXXII) cannot be prepared in a pure state.[7]

3.8-Dimethylpyrene (XXI).

This hydrocarbon was prepared exactly as described by de Clercq and Martin.[7] To purify our material, the garnet-red picrate, m.pt. 204-205° (lit. m.pt. 205°) was crystallised from benzene until long needles were obtained. These were then decomposed with aqueous ammonia, (XXI) crystallised from benzene, and then sublimed as almost colourless platelets of 3.8-dimethylpyrene (XXI), m.pt. 165-166° (lit. m.pt. 165-166°).[7]

Found C = 93·62%, H = 6·35%

$C_{18}H_{14}$ requires C = 93·87%, H = 6·13%.

Formylation of Pyrene.[14]

To a stirred solution of pyrene (10 g.) and dichloromethyl-n-butylether (24 g.) in carbon disulphide (250 ml.) was slowly added titanium tetrachloride (38 g.). The deep reddish-violet solution was stirred for twenty-four hours at room temperature, decomposed with ice and dilute hydrochloric acid, then steam-distilled to remove the organic solvent. The oily organic layer was separated from the aqueous phase by decantation, washed thoroughly with water, and then dissolved in ether. On standing, a dark yellow solid precipitated, which crystallised from ethanol as yellow needles of pyrene-3-aldehyde (XXXV), (8·1 g.), m.pt. 124-126° (lit. m.pt. 125-127°).[14] No indication of the presence of any dialdehyde was found.

A similar experiment using aluminium chloride (45 g.) and tetrachloroethane (100 ml.) held at 50°C for three hours was carried out to see if these harsher conditions would force double formylation. A dark intractable oil was obtained after the usual work up and even after chromatography no solid material could be obtained.

Acetylation of Pyrene.

To a suspension of pyrene (10 g.) and aluminium chloride (20 g.) in carbon disulphide (250 ml.) was added as rapidly as possible acetyl chloride (13·5 g.). A vigorous reaction ensued with the evolution of large quantities of hydrogen chloride. The reddish-brown reaction mixture was decomposed after three hours with ice and dilute hydrochloric acid, and a dark yellow-green oil was obtained which slowly hardened. This material was washed thoroughly with water, dissolved in glacial acetic acid and an attempt made to fractionally crystallise the less soluble 3.8-isomer. This met with no success; the acetic acid solution was therefore evacuated to dryness, and the minimum amount of xylene added to dissolve the reaction product. Chromatography of this solution on Grade I Neutral Alumina failed to separate the isomers also.

Benzoylation of Pyrene:[15] 3.8-Dibenzoylpyrene (XXXVI) and 3.10-Dibenzoylpyrene (XXXVII).

These two isomeric diketones were prepared by the method of Vollmann et al.[15]; 3.8-dibenzoylpyrene (XXXVI) crystallised as deep yellow prisms from xylene, m.pt. 239°

(lit. m.pt. 239°)[15] and 3.10-dibenzoylpyrene (XXXVII) crystallised as pale yellow needles from acetone, m.pt. 164-165° (lit. m.pt. 165°).[15]

3.8-Dibenzylpyrene (XXIII).

3.8-Dibenzoylpyrene (XXXVI) (2·5 g.) and hydrazine hydrate (90%, 1·5 ml.) were refluxed for three hours in diethylene glycol (25 ml.). As the orange hydrazone formed, water and excess hydrazine were removed. Sodium hydroxide (1 g.) was added, and the solution refluxed for a further three hours. The cooled greenish-brown solution was poured on to excess water, the precipitated hydrocarbon collected, washed with water and dried. (XXIII) crystallised from xylene as long colourless needles (2·4 g.) m.pt. 195°. It did not dissolve in concentrated sulphuric acid.

Found C = 94·26%, H = 5·73%

$C_{30}H_{22}$ requires C = 94·21%, H = 5·79%.

3.10-Dibenzylpyrene (XXIV).

3.10-Dibenzoylpyrene (XXXVII) (2·5 g.) and hydrazine hydrate (90%, 1·5 ml.) were refluxed for three hours in diethylene glycol (25 ml.). As the orange hydrazone formed, water and excess hydrazine were removed. Sodium hydroxide (1 g.) was added, the solution refluxed for a further three hours. The cooled red-brown solution was poured on to excess water, the precipitated hydrocarbon collected, washed with water and dried. (XXIV) crystallised from benzene as colourless needles (2·4 g.) m.pt. 188°, and gave a pale green colour in concentrated sulphuric acid.

Found C = 94·34%, H = 5·74%

$C_{30}H_{22}$ requires C = 94·21%, H = 5·79%

Acknowledgements.

Thanks are due to Professor A. Berg for a gift of 4.9-di-t-butylpyrene, to Professor H. Dannenberg for 1.2-dimethylpyrene, and to Dr. M. Zander of Messrs. Rutkerswerke and Teerverwertung for 4-methylpyrene, 4.9-dimethylpyrene, naphthoxanthene and 2.13-benzofluoranthene.

BIBLIOGRAPHY.

Chapter 1.

1. A.E. Gillam and E.S. Stern, An Introduction to Electronic Absorption Spectroscopy, Arnold, 1954, Chapters 8, 9.
2. E. Clar, Ber. Dtsch. Chem. Ges., 1936, 69, 607.
3. J.R. Platt, J. Chem. Phys., 1949, 17, 484; J.R. Platt (Ed.), Systematics of the Electronic Spectra of Conjugated Molecules, Wiley, 1964.
4. H. Zimmermann and N. Joop, Zeit. fur Electrochem., 1961, 65, 61, 66, 138; E. Clar, C.T. Ironside and M. Zander, Tetrahedron, 1966, 22, 3527.
5. E. Clar, Polycyclic Hydrocarbons, Academic Press and Springer-Verlag, 1964, Vol. 1, Ch. 7.
6. Ch. Marschalk, Bull. Soc. Chim. Fr., 1941, [5^{e}], 8, 354.
7. E. Grandmougin, J. Prakt. Chem., 1907, [2], 76, 124.
8. F.C. Whitmore and F.L. Carnahan, J. Am. Chem. Soc., 1929, 51, 856.
9. E. Clar, Ber. Dtsch. Chem. Ges., 1942, 75, 1283.

10. Ch. Marschalk, Bull. Soc. Chim. Fr., 1939, [5^e], 6, 1112.

11. E. Clar and D.G. Stewart, J. Chem. Soc., 1951, 3215.

12. W.L. Mosby, J. Am. Chem. Soc., 1953, 75, 3348.

13. E. Clar and F. John, Ber. Dtsch. Chem. Ges., 1930, 63, 2967; K.F. Lang and M. Zander, Chem. Ber., 1961, 94, 1871.

14. G.M. Badger, The Structure and Reactions of the Aromatic Compounds, Cambridge University Press, 1957, Ch. 9.

15. E. Clar, Ber. Dtsch. Chem. Ges., 1931, 64, 2194.

16. A.I. Vogel, Practical Organic Chemistry, Longmans, 1956, p. 193.

Chapter 2.

1. E. Clar, Tetrahedron, 1961, 16, 113.

2. E. Clar, ibid., 1959, 5, 98; 1959, 6, 355; 1960, 9, 202.

3. E. Clar, Polycyclic Hydrocarbons, Academic Press and Springer-Verlag, 1964, Vol. 1, Ch. 8.

4. R.N. Jones, Chem. Revs., 1943, 32, 1.

5. R.A. Friedel, M. Orchin and L. Reggel, J. Am. Chem. Soc., 1948, 70, 199.

6. R.A. Friedel and M. Orchin, Ultraviolet Spectra of Aromatic Compounds, Wiley, 1951, p. 18, 21.

7. B.D. Pearson, Tetrahedron, 1961, 12, 32.

8. V. Balasubramaniyan, Chem. Revs., 1966, 66, 567.

9. E. Clar, Polycyclic Hydrocarbons, Academic Press and Springer-Verlag, 1964, Vol. I, p. 37-39.

10. E. Clar, ibid.,,p. 49, 58.

11. E. Clar, ibid., p. 32-34.

12. R.A. Friedel, App. Spect., 1957, 11, 13.

13. E. Clar, Polycyclic Hydrocarbons, Academic Press and Springer-Verlag, 1964, Vol. 1, p. 51.

14. P.H. Gore in G.A. Olah (Ed.), Friedel-Crafts and Related Reactions, Interscience, 1964, Vol. III, part I, p. 62.

15. IG Farbenindustrie AG, German Patent 590579, Chem. Zbl., 1934, II, 3846; H. Waldmann, J. Prakt. Chem., 1938, [2], 150, 121.

16. H. de Diesbach and V. Schmidt, Helv. Chim. Acta., 1924, 7, 644; IG Farbenindustrie AG, British Patent 368930, Chem. Zbl., 1932, II, 777.

17. E. Clar and Fr. John, Ber. Dtsch. Chem. Ges., 1930, 63, 2967.

18. E. Clar, Chem. Ber., 1948, 81, 63.

19. E. Clar, Polycyclic Hydrocarbons, Academic Press and Springer-Verlag, 1964, Vol. 1, p. 425.

20. G.M. Badger, The Structure and Reactions of the Aromatic Compounds, Cambridge University Press, 1957, Chapter 9.

21. J.W. Cook, J. Chem. Soc., 1930, 1087.

22 R. Adams and L.O. Binder, J. Am. Chem. Soc., 1941, 63, 2773.

23. L.F. Fieser, Organic Reactions, 1942, 1, 129.

24.a. H. Stobbe and P. Naoum, Ber. Dtsch. Chem. Ges., 1904, 37, 2240; H. Stobbe, Annalen, 1911, 380, 1; H. Stobbe, G. Ljungren and J. Freyberg, Ber. Dtsch. Chem. Ges., 1926, 59, 265.

24.b. W.S. Johnson and G.H. Daub, Organic Reactions, 1951, 6, 1.

25. N.H. Cromwell and R.P. Cahoy, J. Am. Chem. Soc., 1958, 80, 5524; A. Rieche, H. Gross and E. Hoft, Chem. Ber., 1960, 93, 88.

26. M. Masumura, Nippon Kagaka Zasshi, 1956, 77, 497, Chem. Abs., 1958, 52, 316h.

27. D.P. Chakraborty, T. Sleigh, R. Stevenson, G.A. Swoboda and B. Weinstein, J. Org. Chem., 1966, 31, 3342.

28. H. Stobbe, Ber. Dtsch. Chem. Ges., 1907, 40, 3372; F.G. Baddar, L.S. El-Assal and M. Gindy, J. Chem. Soc., 1948, 1270; L.S. El-Assal and A.H. Shehab, ibid., 1963, 2983.

29. S. Dufraisse and J. Houpillart, Compt. Rendu., 1938, 206, 756.

30. E. Bergmann and A. Weizmann, ibid., 1939, 209, 539.

31. L.N. Goldyrev and I.Y. Postovskii, Zh. obshch. Khim., 1941, 11, 451, Chem. Abs., 1941, 35, 6589; I.Y. Postovskii and R.G. Beiles, ibid., 1943, 13, 823, Chem. Abs., 1945, 39, 928.

32. Ch. Marshalk, Bull.Soc. Chim. Fr., 1948, [5^e], 15, 777.

33. W.S. Johnson, Organic Reactions, 1944, 2, 114; W.S. Johnson and H.J. Glenn, J. Am. Chem. Soc., 1949, 71, 1092.

34. L.P. Kyrides, Coll. Org. Syn., 1955, 3, 422.

35.a. H.G. Oddy, J. Am. Chem. Soc., 1923, 45, 2156.

35.b. R. Adams and M.H. Gold, ibid., 1940, 62, 2038.

36. J.B. Conant and H.B. Cutter, ibid., 1922, 44, 2651.

37. J.P. Schaefer, J. Org. Chem., 1960, 25, 2027.

38. R.E. Lutz and R.J. Rowlett, J. Am. Chem. Soc., 1948, 70, 1359.

39. H. Vollmann, H. Becker, M. Corell and H. Streeck, Annalen, 1937, 531, 1.

40. IG Farbenindustrie AG, French Patent 694890, Chem. Zbl., 1931, I, 3290; British Patent 353113, Chem. Zbl., 1931, II, 2664.

41. S.M. King, C.R. Bauer and R.E. Lutz, J. Am. Chem. Soc., 1951, 73, 2253.

Chapter 3.

1.a. J.F. Stephen, Ph.D. Thesis, Glasgow, 1964.

1.b. E. Clar and J.F. Stephen, Tetrahedron, 1965, 21, 467.

2. E. Clar, C.T. Ironside and M. Zander, ibid., 1959, 6, 358.

3. E. Clar and D.G. Stewart, J. Am. Chem. Soc., 1952, 74, 6235.

4. E. Clar and A. McCallum, Tetrahedron, 1964, 20, 507.

5. G.S. Fell, Ph.D. Thesis, Glasgow, 1959.

6. G. Ferguson and J.M. Robertson, Adv. Phys. Org. Chem., 1963, 1, 203.

7. C.A. Coulson and S. Senent, J. Chem. Soc., 1955, 1813, 1819.

8. M.A. Ali and C.A. Coulson, ibid., 1959, 1558.

9. J. Tanaka, Bull.Chem. Soc. Jap., 1963, 36, 1237.

10. W.S. Johnson and H.J. Glenn, J. Am. Chem. Soc., 1949, 71, 1092.

11. E. Clar, Ber. Dtsch. Chem. Ges., 1940, 73, 409.

12. Y. Hirschberg and L. Haskelberg, Trans. Far. Soc., 1943, 39, 45; S.C. Dickerman, L. de Souza and P. Wolf, J. Org. Chem., 1965, 30, 1981.

13. E. Clar and M. Zander, J. Chem. Soc., 1958, 1861.

14. A. Pullman, B. Pullman, E.D. Bergmann, G. Berthier, E. Fischer, D. Ginsburg and Y. Hirshberg, Bull. Soc. Chim. Fr., 1951, [5e], 18, 707.

15. O.E. Polansky and G. Derflinger, in press.

16. M.R. Padova, Ann. Chim.et Phys., 1910, [8e], 19, 432.

17. C.S. Wood and F.B. Mallory, J. Org. Chem., 1964, 29, 3373.

18. E. Clar, J. Chem. Soc., 1949, 2168.

19. F. Ullmann and C. Schlaepfer, Ber.Dtsch.Chem. Ges., 1904, 37, 2003.

20. J. Thiele and H. Balhorn, ibid., 1904, 37, 1463.

21. G. Wittig and H. Krohne, Annalen, 1937, 529, 142.

Chapter 4.

1. E. Clar, Polycyclic Hydrocarbons, Academic Press and Springer-Verlag, 1964, Vol. 1, Ch. 9.

2. E. Clar, Tetrahedron, 1960, 9, 202.

3. E. Clar, Polycyclic Hydrocarbons, Academic Press and Springer-Verlag, 1964, Vol. 1, Ch. 8.

4. J.F. Stephen, Post-Graduate Research Report, Glasgow, 1965.

5. J.F. Stephen, Ph.D. Thesis, Glasgow, 1964.

6. C.L. Hewett, J. Chem. Soc., 1938, 1286.

7. J.H. Eggers and E.W. Thulstrup, Lecture presented to the 8th European Congress on Molecular Spectroscopy, Copenhagen, 1965.

8. H. Waldmann, J. Prakt. Chem., 1938, [2], 150, 121.

9. H. Moureu, P. Chovin and G. Rivoal, Bull. Soc. Chim. Fr., 1946, [5^e], 13, 106.

10. W. Davies and B.C. Ennis, J. Chem. Soc., 1959, 915.

11. C.W. Moore and J.F. Thorpe, ibid., 1908, 165.

12. W. Reid and H. Bodem, Chem. Ber., 1956, 89, 708.

13. E. Clar, ibid., 1948, 81, 68.

14. J. von Braun and G. Kirschbaum, Ber. Dtsch. Chem. Ges., 1921, 54, 597.

15. H.A. Weidlich, ibid., 1938, 71, 1201, 1203.

16. Y. Altman and D. Ginsburg, J. Chem. Soc., 1959, 466.

17. M.S. Newman, J. Org. Chem., 1961, 26, 582.

18. M.S. Kharasch and E.K. Fields, J. Am. Chem. Soc., 1941, 63, 2316.

19. H.A. Staab and F. Binnig, Chem. Ber., 1967, 100, 293.

20. R.A. Friedel and M. Orchin, Ultraviolet Spectra of Aromatic Compounds, Wiley, 1951, Nos. 121, 129.

21. N.S. Bhacca, L.F. Johnson and J.N. Shoolery, NMR Spectra Catalogue, Varian Associates, 1962, Nos. 305, 306.

22. J.A. Pople, W.G. Schneider and H.J. Bernstein, High Resolution Nuclear Magnetic Resonance, McGraw-Hill, 1959, p. 238-247.

23. Elsevier's Encyclopaedia of Organic Chemistry, Elsevier, 1951, Series III, Vol. 14, Supplement, p. 857; E. Rosenhauer, F. Braun, R. Pummerer and G. Riegelbauer, Ber. Dtsch. Chem. Ges., 1937, 70, 2281.

24. H.H. Hatt, Rev. Pure Appl. Chem., 1956, 6, 153.

25. K. Alder and J. Haydn, Annalen, 1950, 570, 201.

26. C.H. DePuy and R.W. King, Chem. Revs., 1960, 60, 431.

27. W. von E. Doering, M. Farber and A. Sayigh, J. Am. Chem. Soc., 1952, 74, 4370.

28. N. Campbell and R.S. Gow, J. Chem. Soc., 1949, 1555.

29. C.S. Wood and F.B. Mallory, J. Org. Chem., 1964, 29, 3373; M. Scholz, M. Muhlstadt and F. Dietz, Tet. Let., 1967, 665.

30. E. Philippi and R. Seka, Sitzung., 1922, 131, 567.

31. M.D. Soffer, M.P. Bellis, H.E. Gellerson and R.A. Stewart, Coll. Org. Syn., 1963, 4, 903.

32. F. Bergmann, H.E. Eschinazi and M. Neeman, J. Org. Chem., 1943, 8, 179.

Chapter 5.

1.a. D. Lavit-Lamy and N.P. Buu-Hoi, Chem. Comm., 1966, 92.

1.b. ibid., Bull. Soc. Chim. Fr., 1966, 2613.

2. E. Clar, Ber. Dtsch. Chem. Ges., 1930, 63, 112.

3. E. Clar and D.G. Stewart, J. Chem. Soc., 1951, 687.

4. M. Zander, Chem. Ber., 1959, 92, 2749.

5. G.A. Olah and S.J. Kuhn in G.A. Olah (Ed.), Friedel-Crafts and Related Reactions, Interscience, 1964, Vol. III, part 2, p. 1211-1240.

6. N.P. Buu-Hoi and D. Lavit-Lamy, Proc. Chem. Soc., 1960, 120; Bull. Soc. Chim. Fr., 1961, 1657; 1962, 1398; 1966, 2619.

7. L.F. Fieser and A. Seligman, J. Am. Chem. Soc., 1935, 57, 2174.

8. C.R. Bradsher, J. Am. Chem. Soc., 1940, 62, 486.

9. F.A. Vingiello, J. Yanez and E.J. Greenwood, Chem. Comm., 1966, 375.

10. W. Carruthers, Chem. Comm., 1966, 548.

11. E. Clar and D.G. Stewart, J. Am. Chem. Soc., 1952, 74, 6235.

12. E. Clar, Tetrahedron, 1960, 9, 202.

13. Elsevier's Encyclopaedia of Organic Chemistry, Elsevier, 1951, Series III, Vol. 12B, p. 1156.

14. E. Clar and H. Frommel, Chem. Ber., 1949, 82, 46.

15. E. Clar and D.G. Stewart, J. Chem. Soc., 1952, 4783.

16. A. Haller and A. Guyot, Bull. Soc. Chim. Fr., 1901, [3^{e}], 25, 54.

17. H. Meyer, Monatshefte, 1904, 25, 478, 1183.

18.a. H. Meyer, **ibid.**, 1907, 28, 1235; 1913, 34, 71.

18.b. H.C. Martin, J. Am. Chem. Soc., 1916, 38, 1142.

19. J.F. Grove and H.A. Willis, J. Chem. Soc., 1951, 877.

20. H. Brockmann, Fort. Chem. Org. Natur., 1957, 14, 141; A.I. Scott, Interpretation of the Ultra-Violet Spectra of Natural Products, Pergamon Press, 1964, p. 294.

Chapter 6.

1. J.W. Armit and R. Robinson, J. Chem. Soc., 1925, 1604.

2. C.A. Coulson, Valence, Oxford University Press, 1961.

3. W. Marckwald, Annalen, 1893, 274, 331; 1894, 279, 1.

4. G.M. Badger, The Structure and Reactions of the Aromatic Compounds, Cambridge University Press, 1957, Chapter 5.

5. S. Sternhell, Rev. Pure Appl, Chem., 1964, 14, 15.

6. A.A. Bothner-By and C. Naar-Colin, J. Am. Chem. Soc., 1961, 83, 231.

7. R.W. Fessenden and J.S. Waugh, J. Chem. Phys.,1959, 30, 944.

8. H. Rottendorf and S. Sternhell, Aust. J. Chem., 1964, 17, 1315.

9. J.A. Pople, W.G. Schneider and H.J. Bernstein, High Resolution Nuclear Magnetic Resonance, McGraw-Hill, 1959, p. 252.

10. C. Maclean and E.L. Mackor, Mol. Phys., 1961, 4, 241.

11. N. Jonathan, S. Gordon and B.P. Dailey, J. Chem. Phys., 1962, 36, 2443.

12. I.C. Lewis, J. Phys. Chem., 1966, 70, 1667.

13. C.A. Coulson and A. Streitwieser, Supplemental Tables of Molecular Orbital Calculations, Pergamon Press, 1965, 2 Vols.

14. A. Streitwieser, Molecular Orbital Theory for Organic Chemists, Wiley, 1961, p. 169.

15. J.M. Robertson, Organic Crystals and Molecules, Cornell University Press, 1953, Chapter 8.

16. E. Clar, Polycyclic Hydrocarbons, Academic Press and Springer-Verlag, 1964, Vol. I, Ch. 6.

17. R.H. Martin, N. Defay, F. Geerts-Evrard and H. Figeys, Bull. Soc. Chim. Belg., 1964, 73, 199.

18. R.H. Martin, M. Flammang and M. Arbaoui, ibid., 1965, 74, 418.

19. R.H. Martin, N. Defay and F. Geerts-Evrard, Tetrahedron, 1965, 21, 2421.

20. P. Durand, J. Parello, N.P. Buu-Hoi and L. Alais, Bull. Soc. Chim. Fr., 1963, 2438.

21. D. Bryce-Smith, personal communication to Professor E. Clar.

22. J.M. Robertson and J.G. White, J. Chem. Soc., 1945, 607.

23. G. Ferguson, private communication.

24. M.S. Newman, J. Am. Chem. Soc., 1938, 60, 2947.

25. L. Golberg and R. Robinson, J. Chem. Soc., 1941, 575.

26. M. Moyle and E. Ritchie, Aust. J. Chem., 1958, 11, 211.

27. M. de Clercq and R.H. Martin, Bull. Soc. Chim. Belg., 1955, 64, 367.

28. E. Clar and J.R. Holker, J. Chem. Soc., 1951, 3259.

29. K. Elbs, J. Prakt. Chem., 1890 [2], 41, 123.

30. E. Clar, H. Wallenstein and R. Avenarius, Ber. Dtsch. Chem. Ges., 1929, 62, 950.

31. H. Reimlinger, J.P. Golstein, J. Jadot and P. Jung, Chem. Ber., 1964, 97, 349.

32. Huang-Minlon, J. Am. Chem. Soc., 1946, 68, 2487.

33. A. Zinke, F. Hanus and O. Ferrares, Sitzung ,1948, 157, 343.

34. IG Farbenindustrie AG, French Patent No. 779893, Chem. Zbl., 1936, I, 4075.

35. K. Funcke, E. Muller and L. Vadasz, J. Prakt. Chem., 1936, [2], 144, 265.

36. H. Vollmann, H. Becker, M. Corell and H. Streeck, Annalen, 1937, 531, 145.

37. A.I. Vogel, Practical Organic Chemistry, Longmans-Green, 1956, p. 192.

Chapter 7.

1. H.J. Bernstein, W.G. Schneider and J.A. Pople, Proc. Roy. Soc., 1956, [A], 236, 515.

2. J.S. Waugh and R.W. Fessenden, J. Am. Chem. Soc., 1957, 79, 846.

3. C.E. Johnson and F.A. Bovey, J. Chem. Phys., 1958, 29, 1012.

4. J.D. Memory, ibid., 1963, 38, 1341.

5. N. Jonathan, S. Gordon and B.P. Dailey, ibid., 1962, 36, 2443.

6. E. Clar, Polycyclic Hydrocarbons, Academic Press and Springer-Verlag, 1964, Vol. 1, Ch. 8.

7. B.P. Dailey, J. Chem. Phys., 1964, 41, 2304.

8. H. Akamatu and Y. Matsunaga, Bull. Chem. Soc. Jap., 1953, 26, 364; 1956, 29, 800.

Chapter 8.

1. N. Jonathan, S. Gordon and B.P. Dailey, J. Chem. Phys., 1962, 36, 2443.

2. E.O. Bishop in D.W. Mathieson (Ed.), Nuclear Magnetic Resonance for Organic Chemists, Academic Press, 1967, Chapter 5.

3. A.A. Bothner-By, Adv. in Magnetic Resonance, 1965, 1, 195.

4. E. Clar, Polycyclic Hydrocarbons, Academic Press and Springer-Verlag, 1964, Vol. 1, Ch. 5.

5. O. Schmidt, Ber. Dtsch. Chem. Ges., 1934, 67, 1870, 2078.

6. G. Lock, ibid., 1937, 70, 926.

7. M. de Clercq and R.H. Martin, Bull. Soc. Chim. Belg., 1955, 64, 367.

8. L.F. Fieser and M. Fieser, Topics in Organic Chemistry, Reinhold, 1963, p. 33-35.

9. R. Scholl and H.K. Meyer, Ber. Dtsch. Chem. Ges., 1936, 69, 152.

10. C.T. Ironside, Ph.D. Thesis, Glasgow, 1959.

11. R. Pummerer and F. Frankfurter, Ber. Dtsch. Chem. Ges., 1914, <u>47</u>, 1472.

12. E. Clar, ibid., 1936, <u>69</u>, 1671, 1686.

13. Ch. Grundmann and J.M. Dean, Angew. Chem. Int. Ed., 1965, <u>4</u>, 955.

14. A. Rieche, H. Gross and E. Hoft, Chem. Ber., 1960, <u>93</u>, 88.

15. H. Vollmann, H. Becker, M. Corell and H. Streeck, Annalen , 1937, <u>531</u>, 1.

16. R. Pummerer, E. Prell and A. Rieche, Ber. Dtsch. Chem. Ges., 1926, <u>59</u>, 2159.

17. A. Corbellini and F. Vietti, Gass. Chim. Ital., 1928, <u>58</u>, 766.