

THE SYNTHESIS AND STUDY

OF

POLYCYCLIC AROMATIC HYDROCARBONS.

THESIS

presented by

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for the degree of

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of the

University of Glasgow.

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Finally, I would to thank my parents for unfailing help and encouragement throughout my educational career.

PUBLICATIONS.

The following papers have been published or are about to be published:

1. The Non-existence of a Threefold Aromatic Conjugation in Linear Benzologues of Triphenylene (Starphenes).

E. Clar and A. Mullen.

Tetrahedron, 24, 6719, (1968)

2. The Location of Double Bonds in Fluoranthene, Perylene and 1,1'-Dinaphthyl by N.M.R.

E. Clar, A. Mullen and Ü. Sanigök.

Tetrahedron, 25, 5639, (1969).

3. Benzologues of Terrylene.

E. Clar and A. Mullen.

Tetrahedron, in press.

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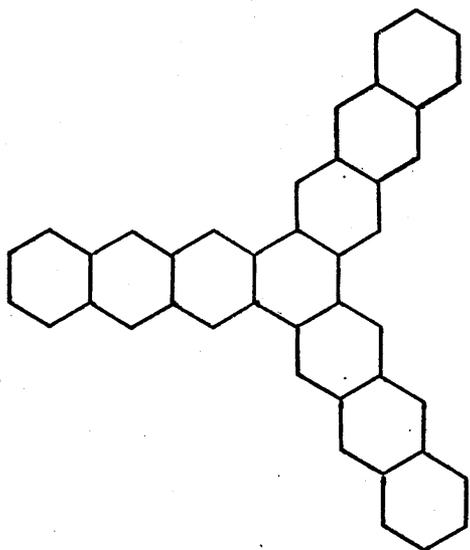
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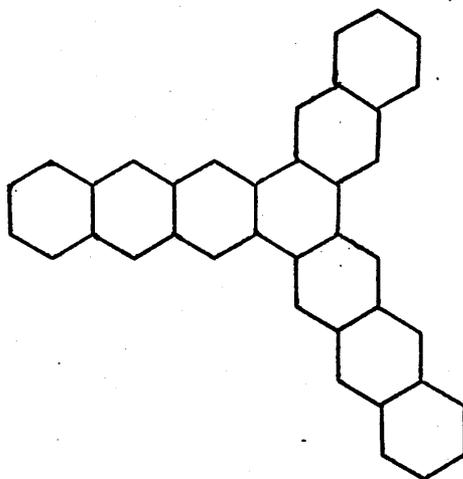
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( i )



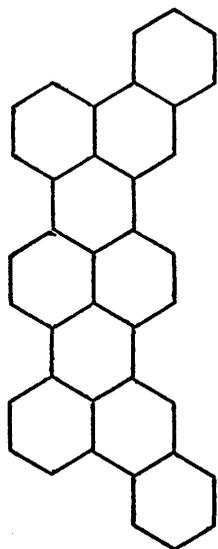
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S U M M A R Y

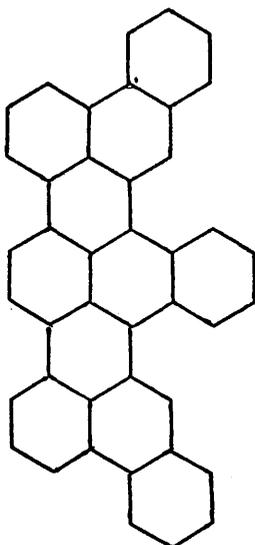
The work in this Thesis mainly concerns the syntheses of polycyclic aromatic hydrocarbons and study of their u.v. spectra with special regard to the Annellation Principle<sup>1</sup> and strict application of Robinson's aromatic sextet<sup>2</sup>.

We have proposed the name 'starphenes' for benzologues of triphenylene, and the numbering system follows a principle introduced recently<sup>13</sup>. The figures give the number of rings in each of the three branches annellated linearly and radiating from the central ring. The total number of rings is the sum of the three figures plus one, as indicated by the name of the starphene.

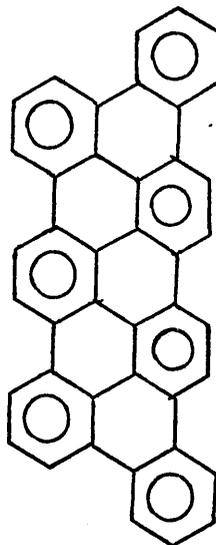
Decastarphene<sup>3</sup> — (3,3,3) (i) and nonastarphene — (2,3,3) (ii) were synthesised. It was found that in any one moment of time conjugation only took place in two branches of the molecule. The third branch was effectively cut off from conjugation. The spectral results could be explained by postulating that in any aromatic ring the pair of  $\pi$  electrons on the lowest level belongs to a double bond. This party cuts off conjugation as in the above crossconjugated case. In the case of benzene, the double bond is freely mobile. The remaining four  $\pi$  electrons are divided into two levels, where one pair remains delocalised within the ring and a third pair is delocalised outside the ring<sup>4</sup> and capable of migrating from one ring to the



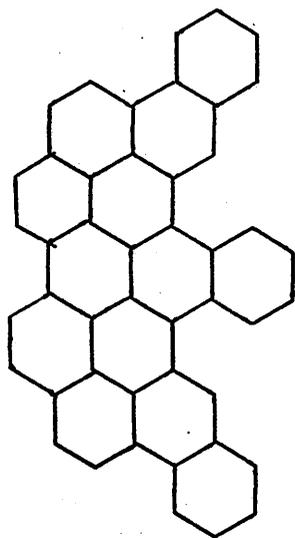
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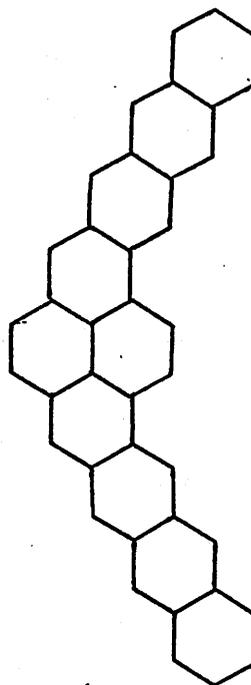
(iv)



(v)



(vi)

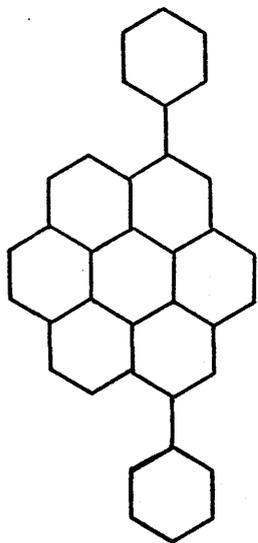


(vii)

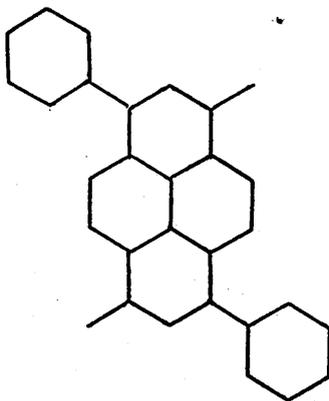
next. It is this electron pair which accounts for the conjugation<sup>4</sup>. 2,3:12,13-Dibenzoterrylene(iii), 2,3:12,13:15,16-tribenzoterrylene(iv), 1,16:2,3:12,13:14,15-tetrabenzoterrylene(v) and 2,3:6,7:8,9:12,13:15,16-pentabenzoterrylene(vi) were synthesised. Their u.v. spectra exhibited the expected absorption bands applicable to the formulae derived by using aromatic sextets<sup>2</sup>.

Tetrabenzoterrylene (v) is a fully benzenoid<sup>5</sup> hydrocarbon with seven aromatic sextets and it possesses the typical properties of a condensed polyphenyl type hydrocarbon<sup>5</sup>. The terrylene benzologues were compared with their perylene analogues<sup>11</sup> and a remarkable similarity in both their reactions with maleic anhydride and their u.v. absorption spectra was found.

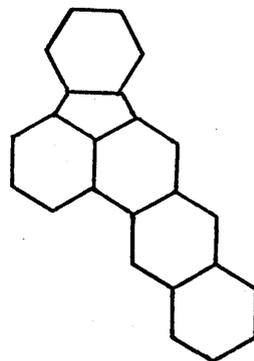
Dianthraceno(2':3',3:4);(2":3",9:10)pyrene (vii) was synthesised and its u.v. absorption spectra compared with other lower benzologues of pyrene<sup>12</sup>. It was found that, although two types of conjugation, a phene and a picene type, were obviously present in the lower benzologues<sup>7</sup> only a picene type was present in dianthracenopyrene (vii). This is readily explained by the fact that the picene arrangement has three sextets<sup>2</sup> whereas the phene arrangement only has two sextets<sup>2</sup>. As conjugation is extended, the two sextets<sup>2</sup> in the phene arrangement become more diluted relative to the picene. Thus the latter arrangement is favoured, as the molecule is less reactive and would retain



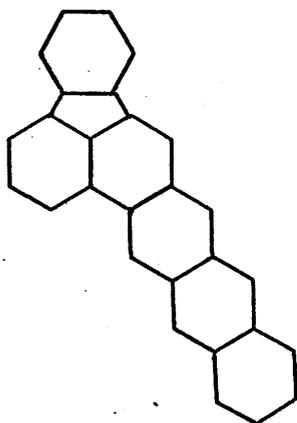
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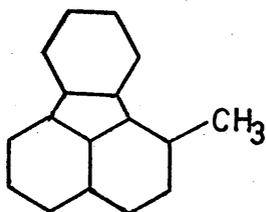
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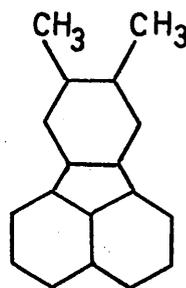
(x)



(xi)



(xiii)



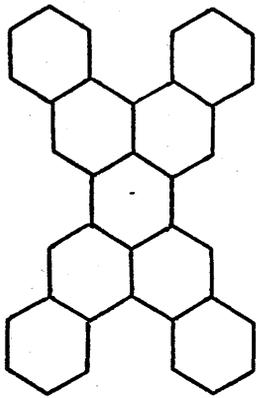
(xii)

its  $\pi$  electrons in a more aromatic distribution. 2,9-Diphenylcoronene (viii) was synthesised and its spectral properties examined in order to ascertain whether there was any extension of conjugation. This would be expected if the substitution affected the superaromaticity<sup>8</sup> of coronene and caused it to behave like  $\alpha$  and  $\beta$  substituted naphthalene fused units. No extension of conjugation was found indicating that the superaromatic<sup>8</sup> nature of coronene is still evident in this derivative, and is not affected by the substitution of two phenyl groups.

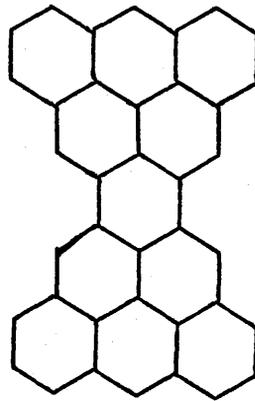
3,8-Diphenyl-5,10-dimethylpyrene (ix) could not be obtained in a crystalline form, despite the fact that a correct microanalysis of the crystalline picrate was obtained.

Naphtho (2':3',2:3) fluoranthene (x) was synthesised and its u.v. absorption spectrum compared with those of 2,3-benzofluoranthene<sup>9</sup> and fluoranthene<sup>9</sup>, indicating a gradual dominance of phene character in the series. Anthraceno (2':3',2:3) fluoranthene (xi) defied synthesis, attempted decarboxylation of the hydrolysed 1',4'-dicyanoanthraceno (2':3',2:3) fluoranthene with soda lime, resulted in the decomposition of the starting material.

1-Methylfluoranthene (xiii) and 8,9-dimethylfluoranthene (xii) were synthesised using modifications of established techniques. Together with other methylfluoranthene derivatives prepared by other workers<sup>10</sup>,



(xiv)



(xv)

a comprehensive study was made of the nature of the electronic arrangements in fluoranthene.

Using methyl signal splitting in the N.M.R. as an indication of the degree of double bond character in a polycyclic hydrocarbon, fixed double bond character was found at the 2,3,4,5 and 8,9 positions in fluoranthene.

2,3:4,5:8,9:10,11-Tetrabenzoperylene (xiv) and dianthraceno(1':8', 2:5);(1":8",8:11)perylene (xv) both defied synthesis, due mainly to difficulty experienced in attempting to open the lactone rings of the intermediates. This snag coupled with the time factor involved prohibited a satisfactory completion of the project.



(i)

All hexagons (i) symbolise aromatic rings.

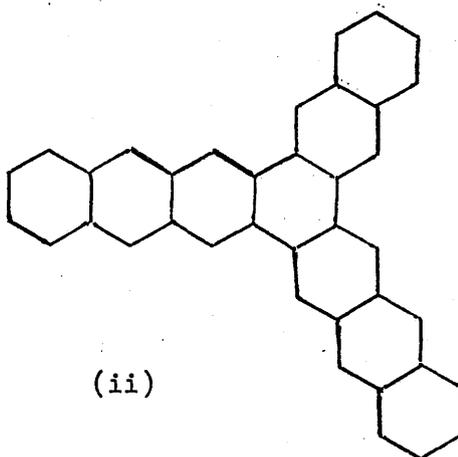
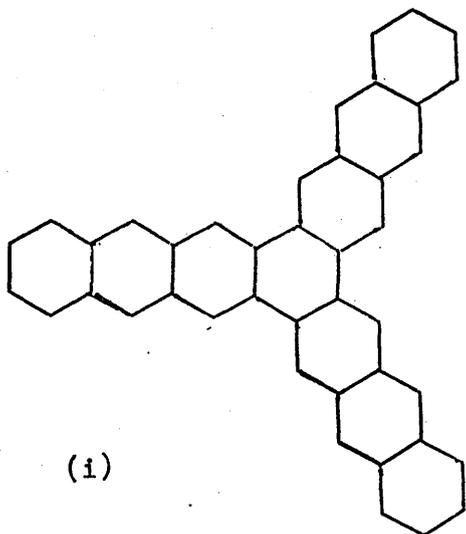
Double bond and sextet<sup>2</sup> (ii) symbols are only used if any significance is intended.



(ii)

## CHAPTER I

### Syntheses of Decastarphene — (3,3,3) and Nonastarphene — (2,3,3)



#### Introduction:

The hydrocarbons deca-starphene — (3,3,3) (i) and nona-starphene — (2,3,3) (ii) have been synthesised and their u.v. absorption spectra compared with heptaphene<sup>1</sup> (xvi) and octa-starphene<sup>2</sup> — (1,3,3) (xvii) (also known as 7,8 — benzoheptaphene). The results show that only two branches of the starphene molecule can be in conjugation at any one time.

Discussion:

Before considering the results obtained a short account of the u.v. bands in polycyclic hydrocarbons will be given.

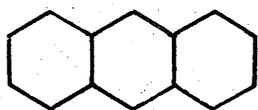
The earliest comprehensive classification of the u.v. bands in polycyclic aromatic hydrocarbons was carried out by Clar<sup>3</sup> in 1936, who classified them according to their intensity, position, effect of annellation and shifts at low temperature.

Other workers studying the u.v. absorption of substituted benzene compounds used various types of nomenclature which are listed below and correlated to Clar's  $\beta$ ,  $\rho$  and  $\alpha$  bands.

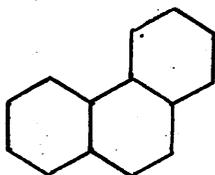
$\beta$	$\rho$	$\alpha$	
-	K	B	4
A	B	C	5
Primary"	Primary'	Secondary	6
-	Principal	-	7

Polycyclic hydrocarbons generally absorb light in the 2000-4000 Å region, corresponding to an energy increase of 70-140 k.cals/mole.

This energy value is intermediate between that required for the ionisation of a single covalent bond and that required for vibrational or rotational transitions.



(iii)



(iv)

Quanta of this magnitude are involved in the displacement of mobile electrons<sup>8</sup>.

The absorption regions of molecules are broad due to the variety of initial and final vibrational and rotational states, all belonging to the same electronic transition. The intensity of absorption is related to the probability of that transition and the wavelength is dependent on the energy involved<sup>8</sup>.

Clar<sup>9</sup> classified his  $\beta$ ,  $\rho$  and  $\kappa$  bands in the following manner:-

$\beta$  Bands: Generally the most intense group with  $\log \epsilon = 4 - 6$ , and lie much more in the u.v. than the other band types. With increasing temperature they are displaced to the violet and with decreasing temperature to the red. The bathochromic shift obtained in changing from gaseous phase to solution, in either alcohol or hexane, amounts to  $900 \text{ cm.}^{-1}$ . The  $\beta$  bands are never hidden or masked by other transitions and are thus invaluable for comparison purposes, and are always observed independent of the symmetry of the molecule.

Hydrocarbons with the same number of rings in the phenes and acenes exhibit  $\beta$  bands at approximately the same wavelength. The acenes, linear benzologues e.g. anthracene (iii) have one narrow  $\beta$  band which broadens in the phenes, angular benzologues e.g. phenanthrene (iv)

and divides into two bands in strongly asymmetric hydrocarbons. Constant shifts in  $\sqrt{\lambda}$ , scale of reciprocal nuclear charges<sup>9</sup>, are observed between each member in the acene and phenes series.

The  $\beta$  bands form a half number series and their frequency can be calculated from the Rydberg equation<sup>7</sup>:

$$\nu_{\beta} = \frac{12^2 R}{K^2} \left( \frac{1}{2^2} - \frac{1}{4^2} \right)$$

K = order number which changes by  $\frac{1}{2}$  per additional ring

starting from benzene (i) = 6.

R = Rydberg constant

Or the wavelength from:

$$\lambda_{\beta} = \frac{27R}{K^2}$$

The above equations are really only applicable to the less complicated hydrocarbons of the acene and phenes type.

$\rho$  Bands: They have an intensity of  $\log \epsilon = \sim 4$  and are displaced with increasing temperature to the violet and with decreasing temperature to the red. A bathochromic shift of  $900 \text{ cm}^{-1}$  is obtained in going from the gaseous state into solution in either hexane or alcohol.

With linear annellation in the acenes the  $\rho$  bands experience a strong constant red shift, measured in  $\sqrt{\lambda}$  and a much weaker shift in the phenes series. The difference in wavelength goes parallel with a significant prominence or decrease in the reactivity of the para position e.g. by photo-oxidation, addition of maleic anhydride and other addition reactions. There are numerous indications that the  $\rho$  bands are connected with a localisation of two  $\pi$  electrons in the para positions<sup>9</sup> and that the longest branch of a hydrocarbon is responsible for the  $\rho$  bands.

The whole acene series can be represented by:-

$$\lambda_{\rho} = \frac{D^2}{16R}$$

Where D is the number of reciprocal nuclear charges 6,7,8,9,10 and 11 in the acene series<sup>9</sup>.

$\alpha$  Bands: Their intensities usually lie in the range  $\log \epsilon = \sim 2 - 3$ . With increasing temperature weak red shifts are observed and with decreasing temperature weak violet shifts. A bathochromic shift of  $250 \text{ cm.}^{-1}$  is observed in going from a gaseous state to a solution in hexane or alcohol. It is the first band type seen in benzene and the phenes, where the difference between individual members is constant in  $\sqrt{\text{Å}}$ . In the acenes, it is generally superimposed by the more intense  $\rho$  bands.

Asymmetric arrangements of the two branches of a phene affect the  $\alpha$  much more than the  $\rho$ , and the  $\alpha$  becomes hidden in the phenes also.

$$\lambda_{\alpha} = \frac{20R}{K^2}$$

$K = 7\frac{1}{2}$  for benzene, and the order number increased by  $\frac{1}{2}$  per additional ring.

Clar found that there was good agreement between the aromatic energy and the value obtained from:

$$E = \nu_{\beta} - \nu_{\alpha} = \frac{7R}{K^2}$$

It was also found that:

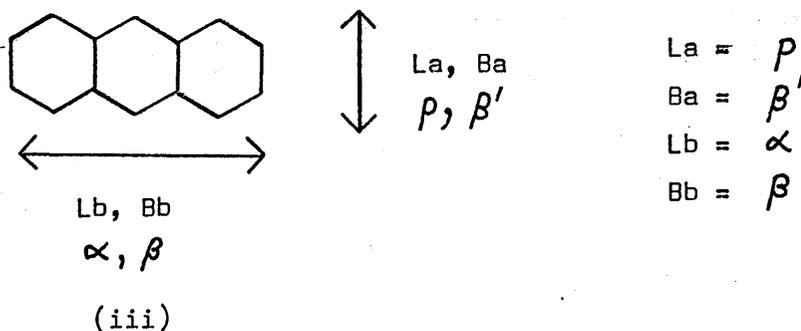
$$\frac{\nu_{\beta}}{\nu_{\alpha}} = \sim 1.35$$

This latter ratio is often of value in determining the origin of bands especially during purification, when isomers may be present.

Clevens and Platt<sup>10</sup> introduced classification of the bands based on the molecular axes of the molecule, and a band being polarised in a particular direction with respect to the molecular axis.

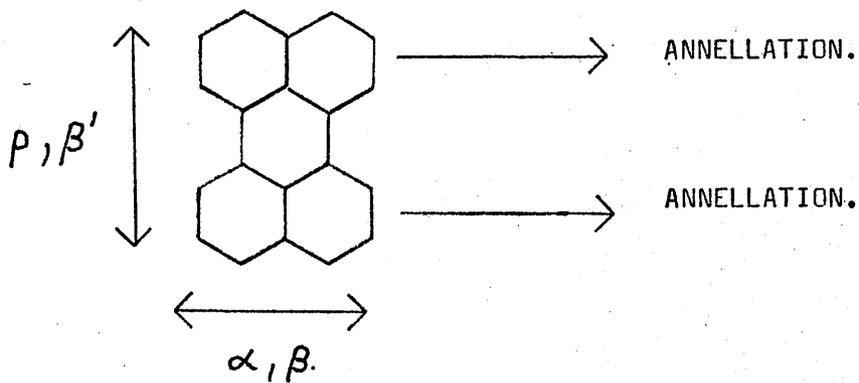
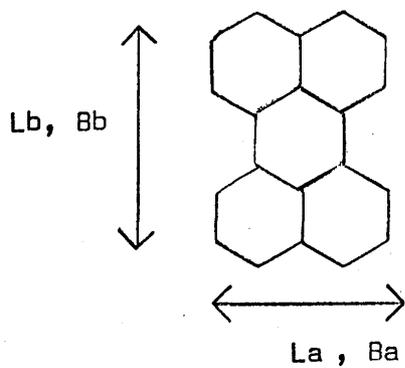
The long molecular axis was designated a and the short axis b, and the absorption bands La, Ba, Lb and Bb.

In the acenes, the La and B $\overset{\alpha}{\beta}$  bands are polarised transversely and the Lb, Bb longitudinally as shown.



Since in the above case, the annellation and molecular axes coincide the only difference is that of nomenclature. This is not the case with angular hydrocarbons, in the case of perylene (v) the prediction

of polarisation of the bands differs by  $90^\circ$  between the two classifications. The classification based on the annellation axis gives the correct results<sup>11</sup>.



(v)

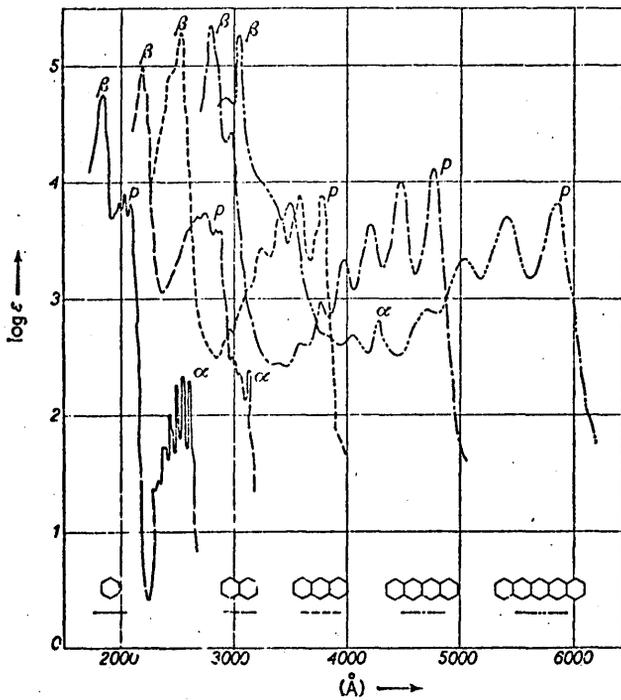


Fig. 1.

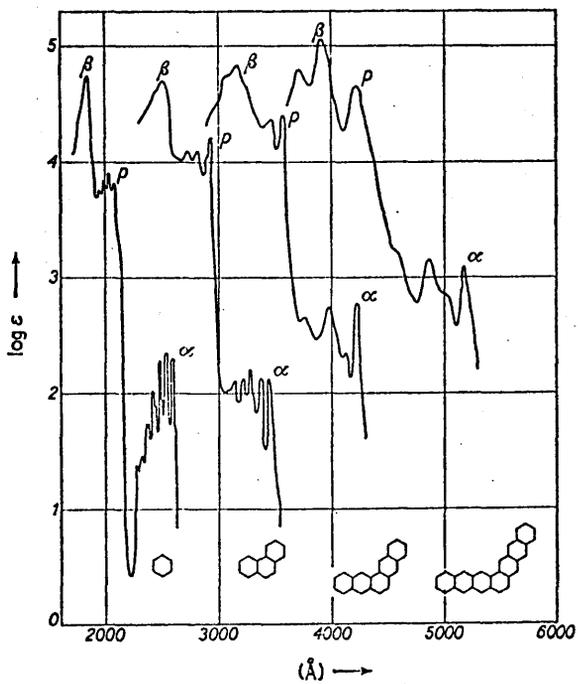


Fig. 2.

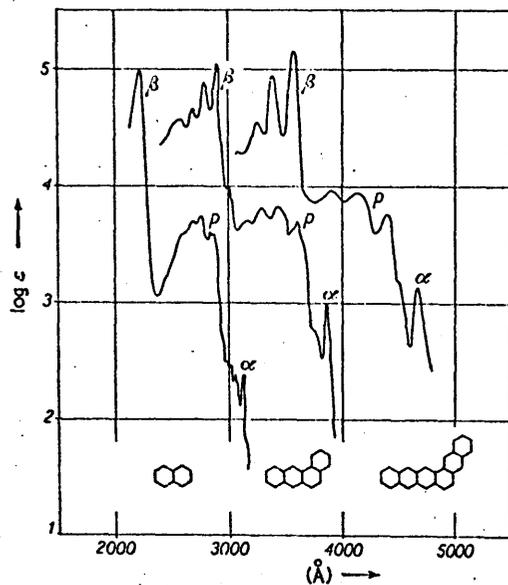
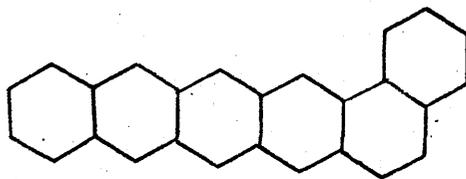


Fig. 3



(vi)

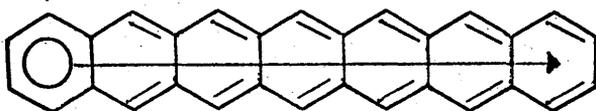
The Annellation Principle<sup>9</sup> is demonstrated on the opposite page for the acenes (fig. 1). The shift is constant in  $\sqrt{\lambda}$  for the  $\beta$  and  $\rho$  bands. The  $\alpha$  bands disappear under the  $\rho$  bands with anthracene (---) and reappear behind the  $\rho$  bands in pentacene (----).

A similar constant  $\sqrt{\lambda}$  for the  $\beta$  bands is obtained with the phenes (fig. 2 and 3). With angular annellation of rings the whole spectrum shifts in a regular manner and the characteristic band pattern of benzene is retained with the  $\alpha$  bands first followed by the  $\rho$  and  $\beta$  bands resp.

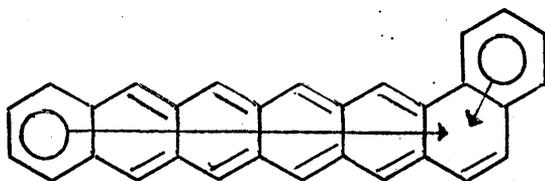
However, if asymmetry in the phenes goes to an extreme as in 1,2-benzopentacene<sup>12</sup> (vi), then the  $\rho$  bands overtake the  $\alpha$  and hide them as in the acenes.

The Annellation Principle<sup>9</sup> has been invaluable in its use for predicting and analysing the spectra of unknown hydrocarbons.

Robinson<sup>13</sup>, introduced a circle inside a hexagon to represent the 6  $\pi$  electrons of benzene, thus avoiding a detailed discussion of the fine structure. Clar<sup>14</sup> has introduced the sextet concept into polycyclic systems to help explain the reactivity and spectral properties of polycyclic hydrocarbons.



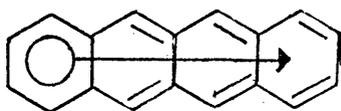
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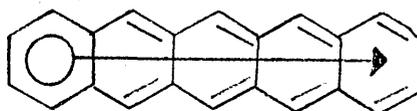
(x)

This concept has recently been strengthened by H.M.O. calculation conducted by Polansky and Derflinger<sup>34</sup>.

In acenes, in order to allow aromatic character in all rings one must assume the mobility of  $2\pi$  electrons which can migrate from ring to ring throughout the whole system. This can be symbolised by an arrow, which represents the mobility of  $2\pi$  electrons (vii & viii).



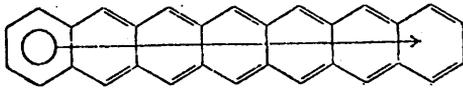
(vii)



(viii)

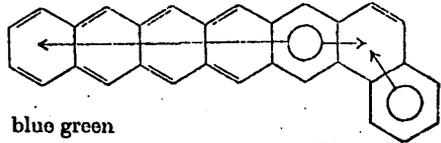
There is thus only one inherent sextet in an acene independent of its length. The sharing of the sextet results in a dilution of the benzenoid character and in higher acenes, the sextet is so diluted that they behave as cyclic polyenes. Greenish-black Heptacene<sup>15</sup> (ix) cannot be obtained in the pure state, one sextet is shared between seven rings. However, if one of its rings is rearranged angularly bluish green 1,2 - benzoheptacene<sup>16</sup> (x) is obtained.

As the angular ring would contain three double bonds, it must be represented as a sextet by definition. This second sextet should increase benzenoid character and lower the reactivity of the molecule<sup>14</sup>. 1,2 - Benzoheptacene<sup>16</sup> (x) can be obtained in a pure state and is much



dark green

(ix)

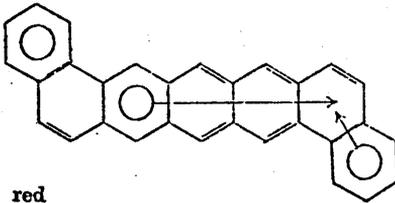


blue green

$\lambda_p = 6510$

$\xrightarrow{-1280}$

(x)

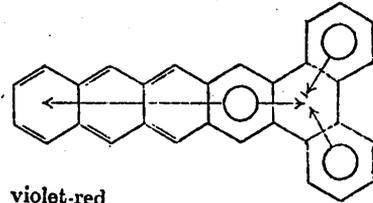


red

$\lambda_p = 5230$

$\lambda_\beta = 3470$

$\xrightarrow{+155}$   
 $\xrightarrow{-40}$

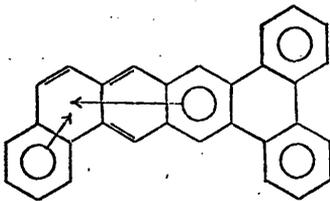


violet-red

$= 5385 \text{ \AA}$

$= 3430 \text{ \AA}$

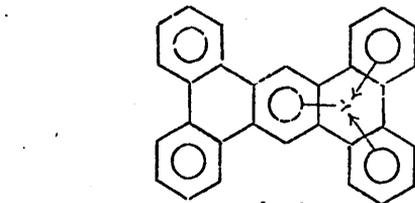
$\xrightarrow{-1155}$   
 $\xrightarrow{-160}$



yellow

$\lambda_p = 4230$

$\lambda_\beta = 3280$

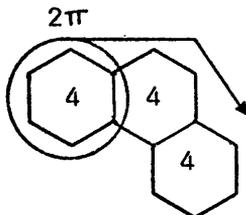


colourless

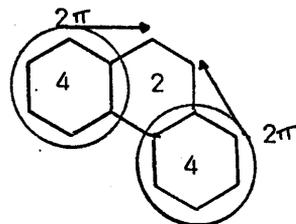
$\xrightarrow{-895}$   $3335 \text{ \AA}$

$\xrightarrow{-330}$   $2950 \text{ \AA}$

(xi)



(iva)



(ivb)

more stable than heptacene<sup>15</sup> (ix).

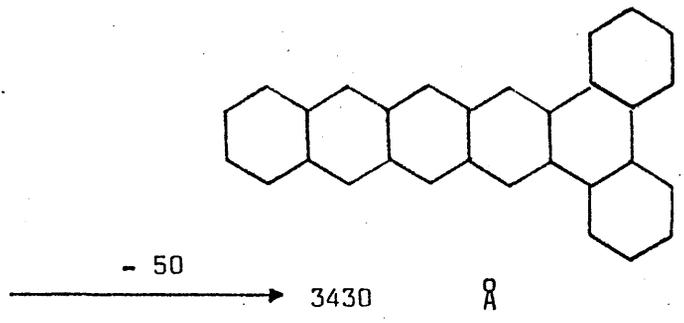
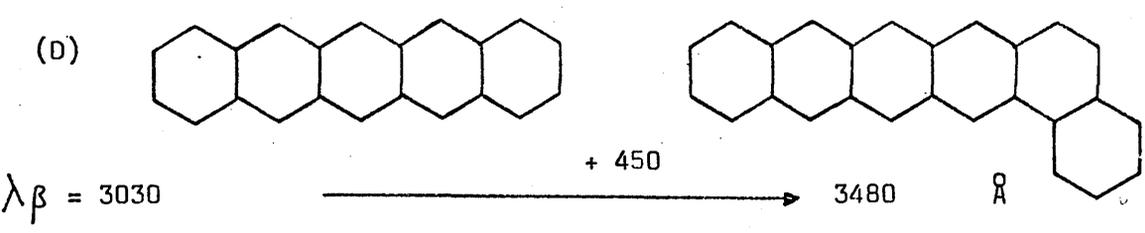
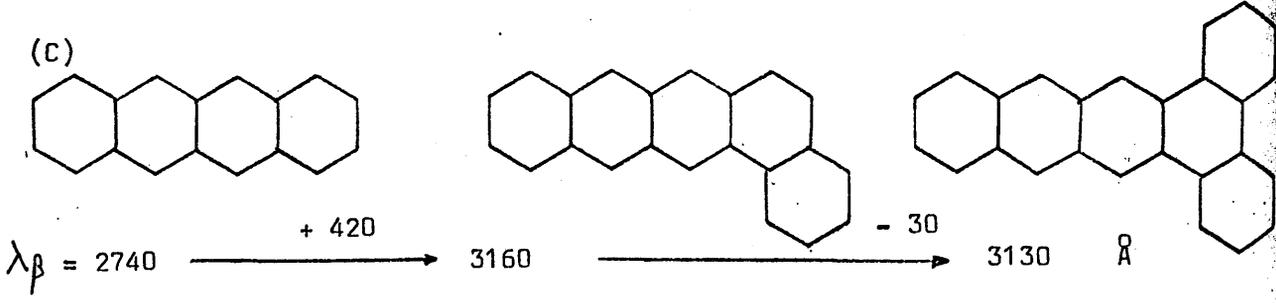
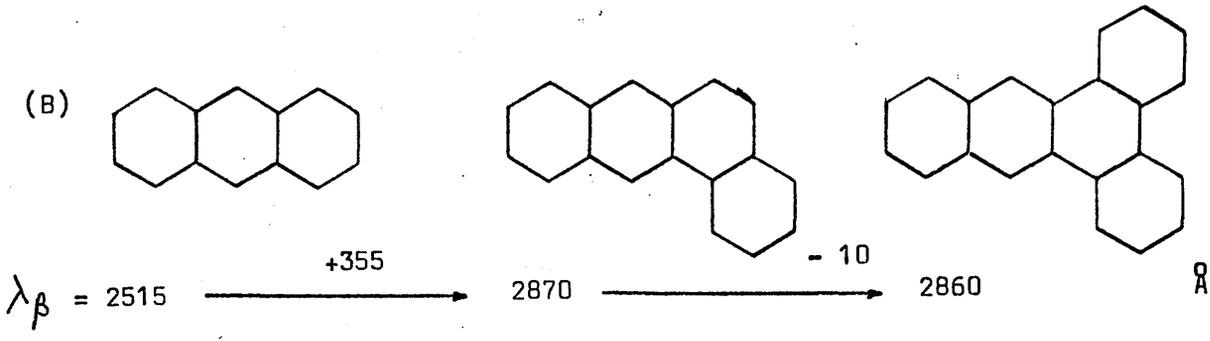
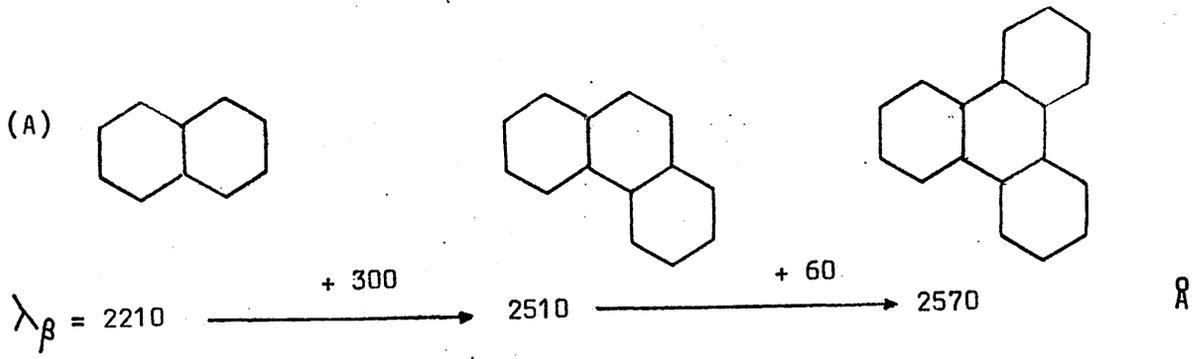
As is shown opposite, the isomer with the greatest number of sextets is the most stable, and the colourless tetrabenzanthracene<sup>17</sup> (xi) neither reacts with maleic anhydride nor dissolves in con.  $H_2SO_4$  - it has five sextets. This hydrocarbon can be classified as fully benzenoid<sup>18</sup>.

An inherent benzenoid ring<sup>14</sup> must have approximately the stability of benzene and aromatic rings which share a sextet can have the stability of naphthalene or as in a polyacene<sup>9</sup>.

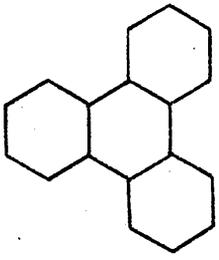
The same 'sextet relationship' is found between anthracene (iii) and phenanthrene (iv). In this case phenanthrene (iv) has 7-12 k.cals. more aromatic energy than anthracene (iii) due to the fact that it has two sextets<sup>14</sup>. N.M.R. studies of methyl phenanthrenes<sup>19</sup> show a high degree of double bond character in the 9,10 bond.

Phenanthrene (iv) can be represented by, (iva) and (ivb).

Obviously arrangement (ivb) with two sextets is the preferred, where the two sextets cause a localisation of the 9,10 bond<sup>19</sup>.



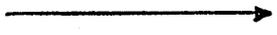
(E)



$$\lambda_{\beta} = 2570$$

(xii)

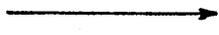
$$+ 300$$



$$2870$$

(xiii)

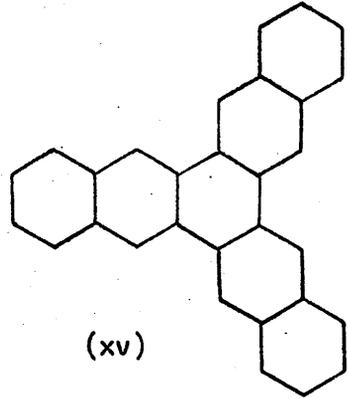
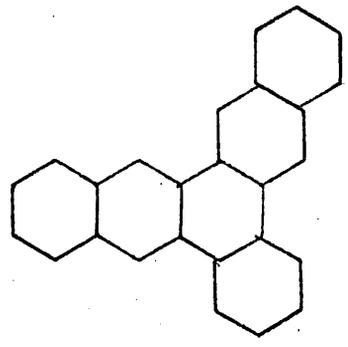
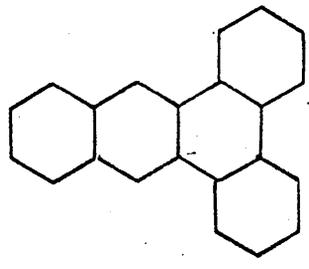
$$+ 270$$



$$3140$$

(xiv)

R



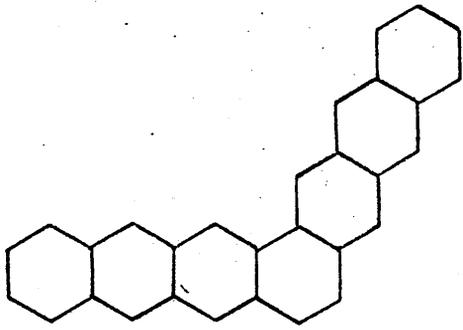
(xv)

$$- 20$$

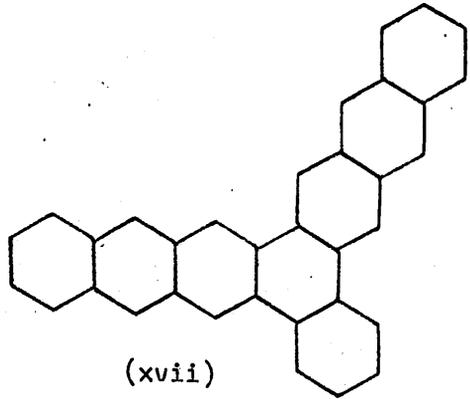


$$3120$$

R

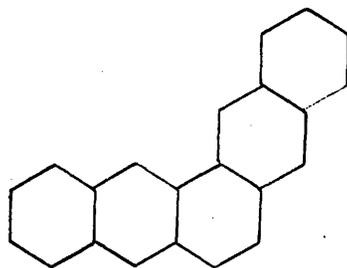
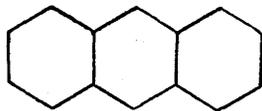
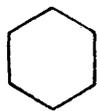


(xvi)



(xvii)

(F)



$\lambda_p =$

1852

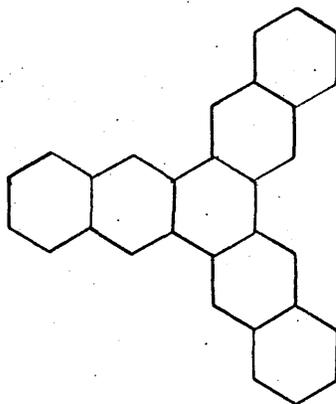
+ 663

→ 2515

+ 630

→ 3145

R



- 25

→ 3120

R

(A)-(D)

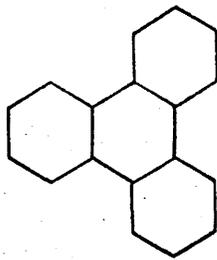
In the series of examples shown opposite there is a strong asymmetric annellation effect<sup>20</sup>, which is obtained when a butadiene complex is fused to the central ring of the phenene. This produces a ring with three formal double bonds. It was thus thought that the asymmetric annellation effect<sup>24</sup> (60Å) was due to the formation of this new sextet<sup>20</sup>. ( For the three branched system produced, the name starphene has been proposed, the numbering follows a principle introduced recently<sup>27</sup>.)

If this were the case then a normal annellation effect should be observed on further linear annellation as no new sextet would be formed<sup>9</sup>.

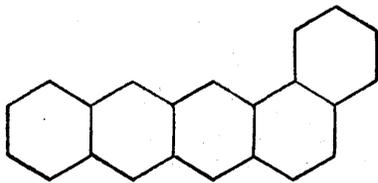
In the series (E), it was found that in going from triphenylene (xii) to 1,2:3,4-dibenzanthracene (xiii) and 6,7-benzopentaphene (xiv), there are shifts of + 300Å and + 270Å resp.<sup>20</sup> This is the normal annellation effect<sup>9</sup>.

However, a further annellation to naphthopentaphene (xv) gives a small hypsochromic shift (20Å). The series (F) is an excellent example of this asymmetric annellation phenomenon<sup>20</sup>.

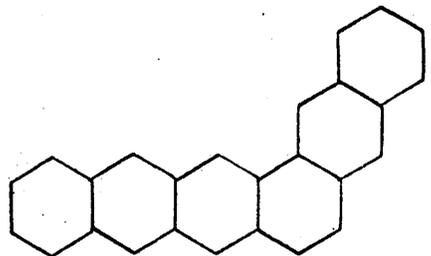
In order to study the next higher series, decastarphene-(3,3,3) (i) and nonastarphene-(2,3,3) (ii) were synthesised and their u.v. absorption spectra compared with heptaphene<sup>1</sup>(xvi) and octastarphene-(1,3,3)<sup>2</sup>



(xii)



(xviii)



(xix)

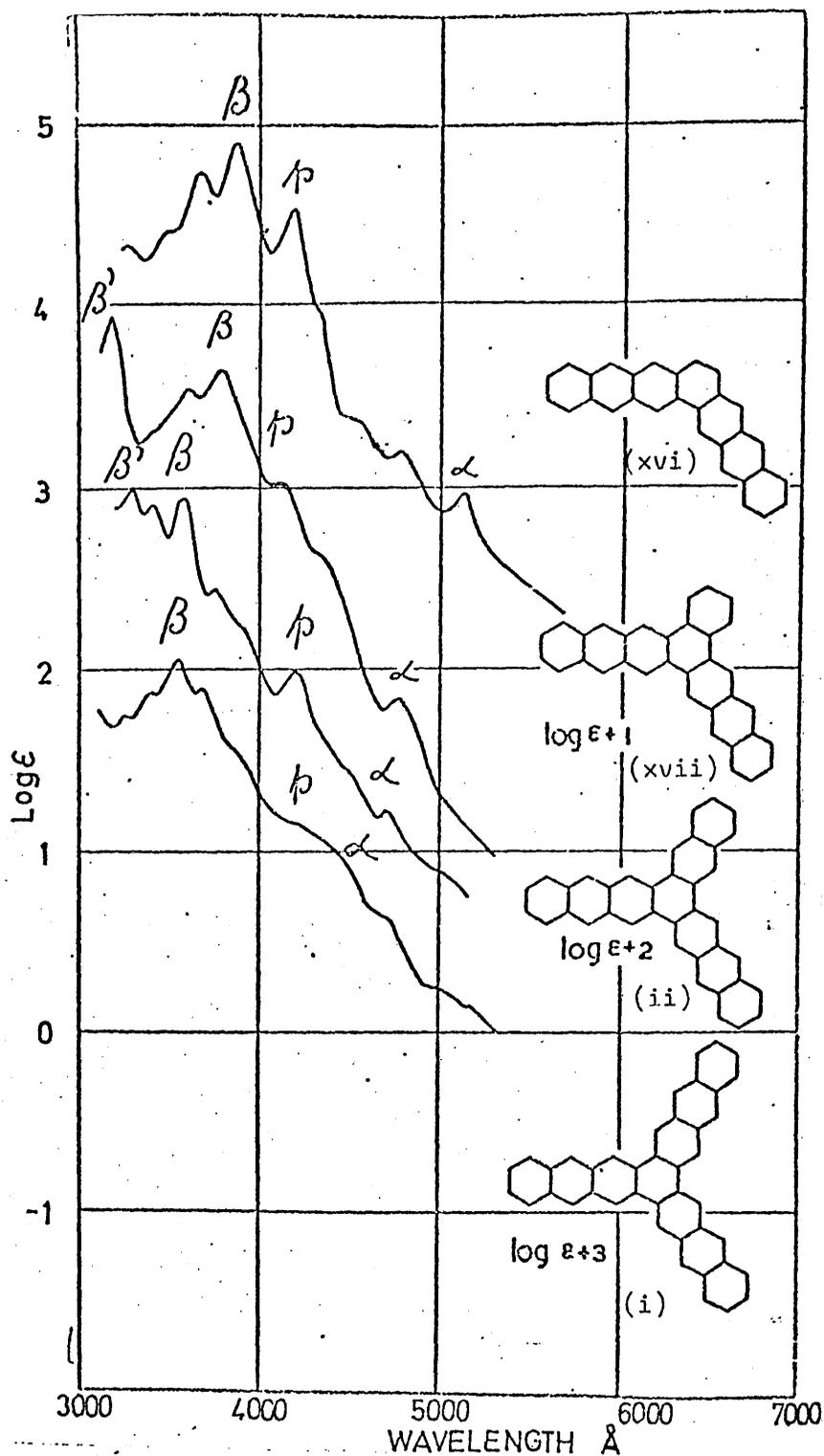


FIG. 4. Absorption spectra in trichlorobenzene with max ( $\text{\AA}$ ) and  $\log \epsilon$  in (parentheses).  
 Heptaphene:  $\alpha$ : 5190 (2.94), 4870 (3.16), 4570 (3.34); p: 4220 (4.47);  $\beta$ : 3900 (4.83), 3700 (4.67).  
 Octastarphene-(1,3,3):  $\alpha$ : 4850 (2.82); p: 4170 (4.02);  $\beta$ : 3840 (4.60), 3660 (4.49);  $\beta'$ : 3220 (4.88),  
 Nonastarphene-(2,3,3):  $\alpha$ : 4700 (3.22); p: 4200 (3.99); 3760 (4.44);  $\beta$ : 3590 (4.95), 3420 (4.90);  
 $\beta'$ : 3310 (4.99).  
 Decastarphene-(3,3,3):  $\alpha$ : 4700 (3.66)?; p: 4250 (4.08)?; 3670 (4.89);  $\beta$ : 3540 (5.04), 3350 (4.88).

(xvii) - see fig. 4.

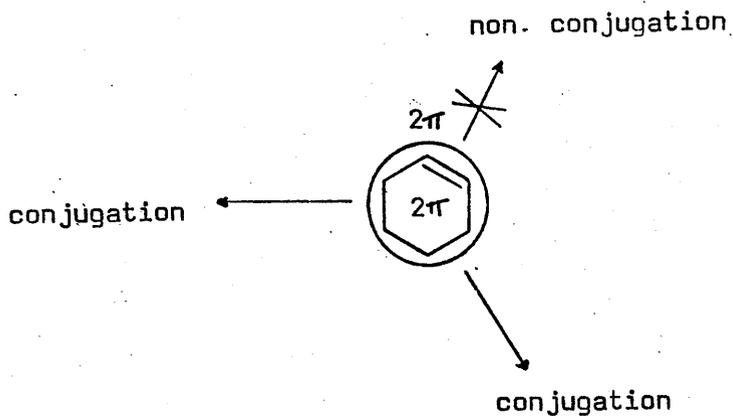
The  $\alpha$  and  $\beta$  bands do not shift towards the red but show small hypsochromic shifts. A normal annellation of the phene type in the case of decastarphene-(3,3,3) (i) would require a shift of more than  $1000\text{\AA}$ .<sup>9</sup>

As expected, the  $\rho$  bands are not greatly affected by the annellations to the central ring of heptaphene<sup>1</sup> (xvi) as in the phene series the  $\rho$  bands are accounted for by the longest linear branch<sup>9</sup>.

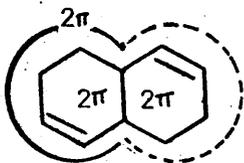
A  $\beta'$  band is seen in the octastarphene-(1,3,3)<sup>2</sup> (xvii) spectrum at  $3220\text{\AA}$ , which corresponds to the  $\beta$  band of 1,2-benzotetracene<sup>21</sup> (xviii) at  $3190\text{\AA}$ . In nonastarphene-(2,3,3) (ii) the  $\beta'$  band is at  $3310\text{\AA}$  which corresponds to the  $\beta$  band of hexaphene<sup>22</sup> (xix) at  $3580\text{\AA}$ .

Thus the two longest branches of the starphene molecule account for the  $\beta$  band absorption whilst the conjugation of a long and short branch accounts for the  $\beta'$  band.

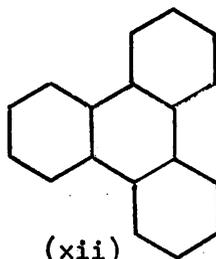
Thus only two branches can be in conjugation at any one time, but the N.M.R. gives only one record for triphenylene<sup>23</sup> (xii). Therefore, there must be a constant switching over of conjugation between the different branches, which can be measured by u.v. but not by N.M.R.



(xx)



(xxi)



(xii)

There must be a strong reason why conjugation is limited to two branches at any point in time. The simplest explanation is that the pair of  $\pi$  electrons on the lowest level in the central ring belong to a double bond. This partly cuts off conjugation.

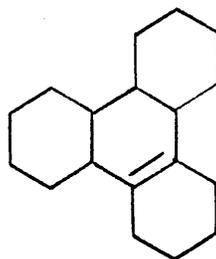
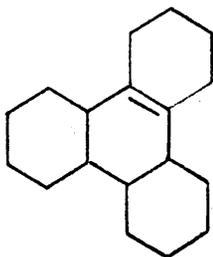
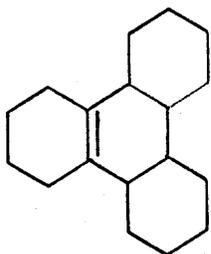
The  $\pi$  electrons of the aromatic sextet could be considered to subdivide into three levels<sup>24</sup>. One pair of  $\pi$  electrons is localised in a double bond within the ring, a pair on the next level within the ring and the remaining pair on an orbital outside the ring and capable of migrating from one ring to the next<sup>24</sup>.

Goodwin and Morton-Blake<sup>27</sup> have shown recently that a satisfactory explanation can be given for the restriction to a twofold aromatic conjugation by a simple M.O. study.

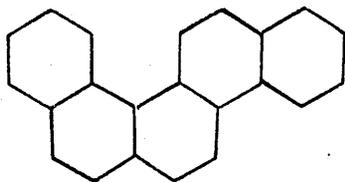
Benzene could be represented as in (xx) where the double bond is freely mobile.

There may be restrictions of this double bond mobility in compounds which show the Mills-Nixon effect<sup>25</sup>. There are also restrictions in naphthalene (xxi) where the double bonds are localised between any  $\alpha, \beta$  position.

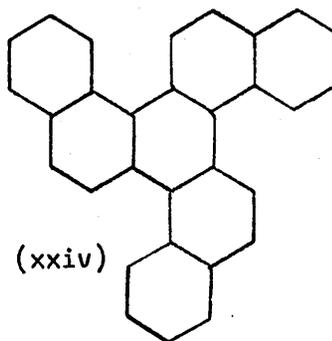
The double bond in triphenylene (xii) can be in three positions as



(xxi)



(xxiii)



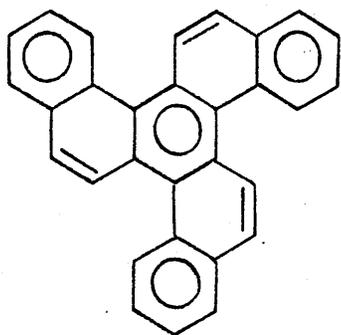
(xxiv)

$\lambda_{\beta} = 2925$

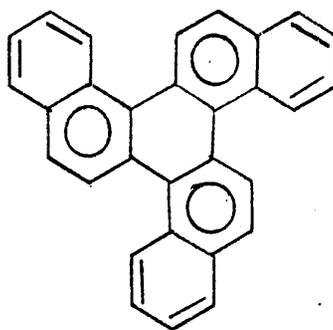
+ 262

3187

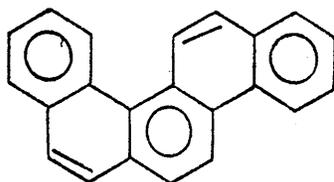
8



(xxiva)



(xxivb)



(xxiiiia)

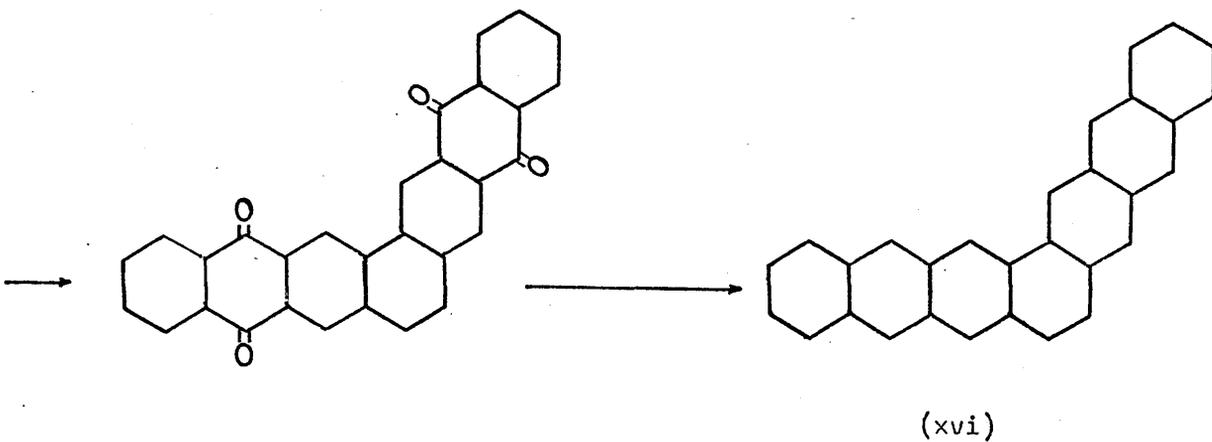
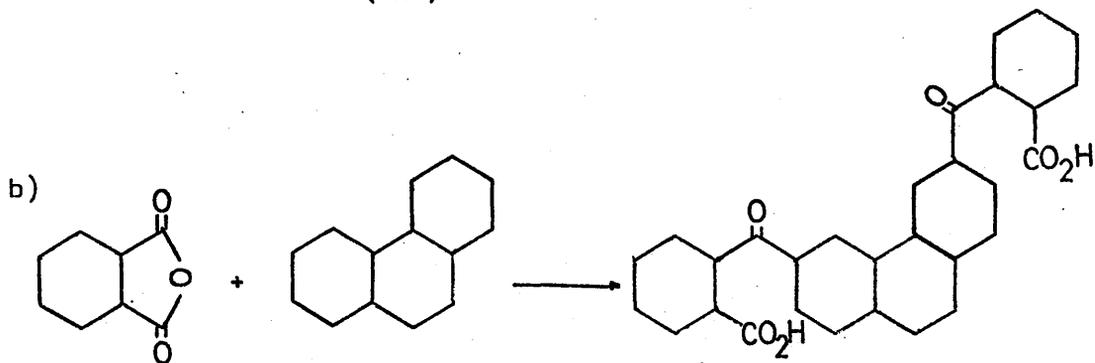
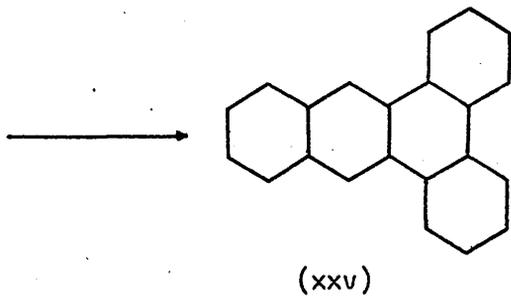
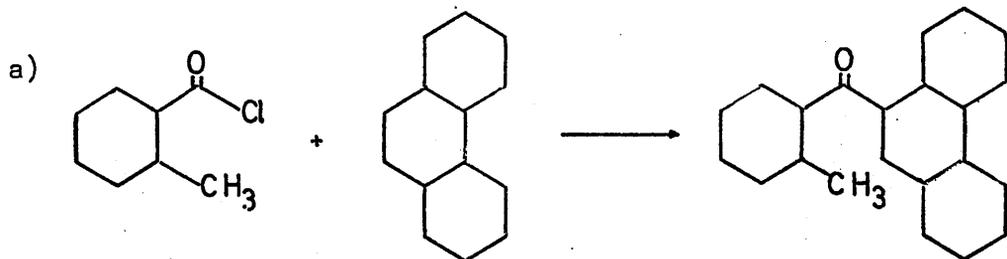
shown (xxii), (the other double bonds are not marked). The double between the two rings always excludes one ring from aromatic conjugation.

In a recent publication<sup>26</sup> 1,2:5,6:9,10-tribenzophenylene (xxiv) was synthesised and its u.v spectrum recorded. Relative to the two branched structure 5,6-benzochrysene<sup>28</sup> (xxiii), there is a large bathochromic shift (262Å), evidence of a normal extension of conjugation<sup>9</sup>.

This apparently contradictory result with regard to the starphene findings is readily explained by strict application of Robinson's aromatic sextet<sup>13</sup>. Tribenzophenylene (xxiv) can be represented by (xxiva) and (xxivb).

The sextets can move through the whole system, causing conjugation to take place in the three branches. The third branch is fused to a sextet (xxiiia) in this case, and not to a fixed double bond as in the starphenes - thus allowing an extension of conjugation.

A non threefold aromatic conjugation is only present in the linear benzologues of triphenylene.



Experimental Discussion:

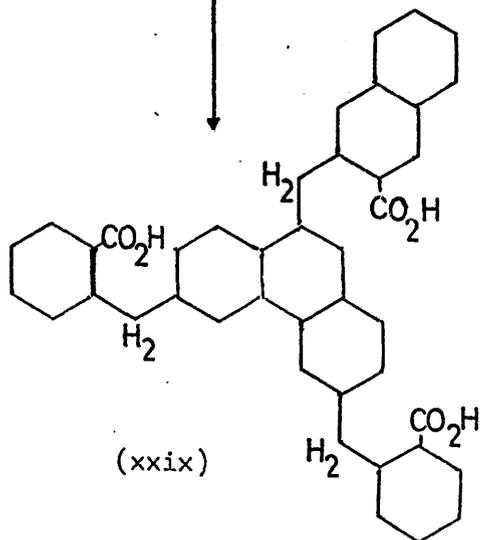
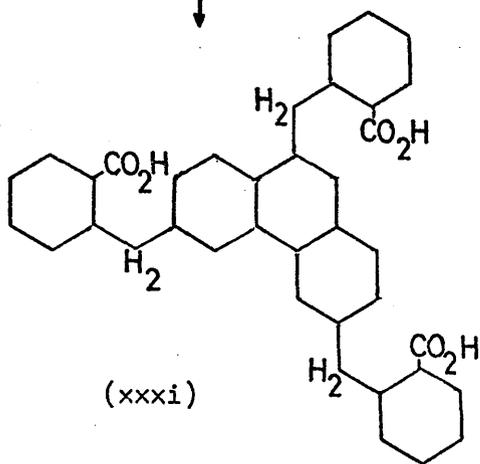
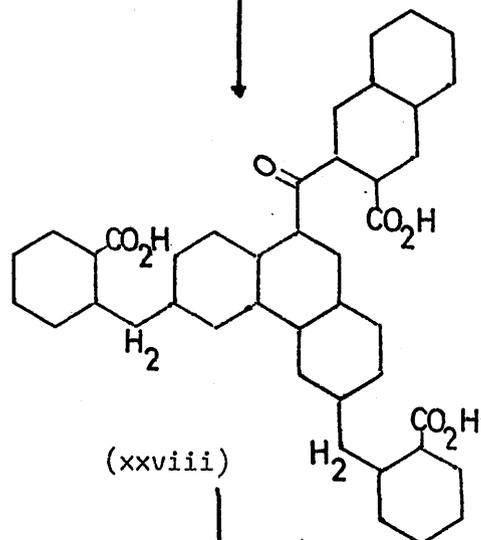
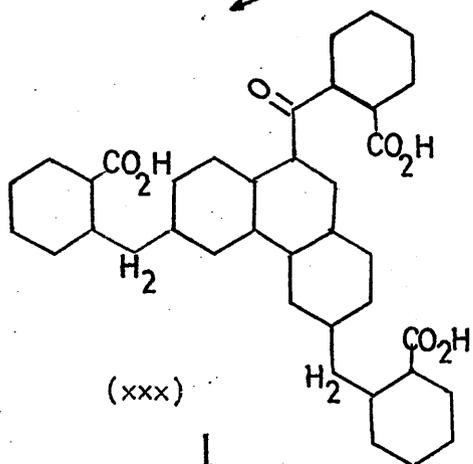
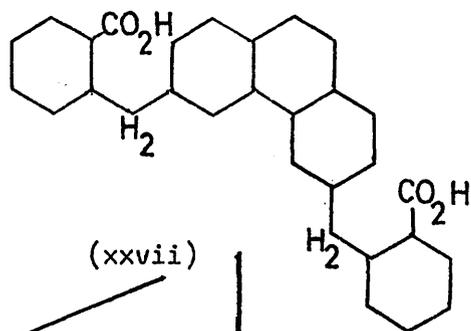
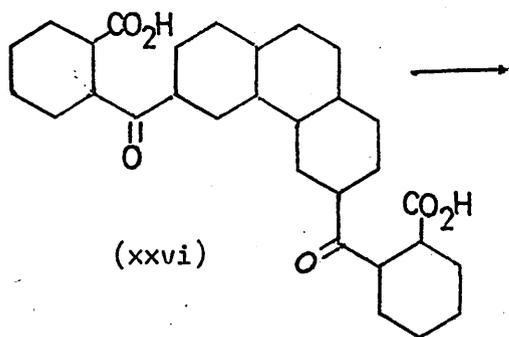
A literature search revealed that the syntheses of many starphenes (linear benzologues of triphenylene) had been based on either phenanthrene<sup>29</sup> (iv) or triphenylene<sup>29</sup> (xii).

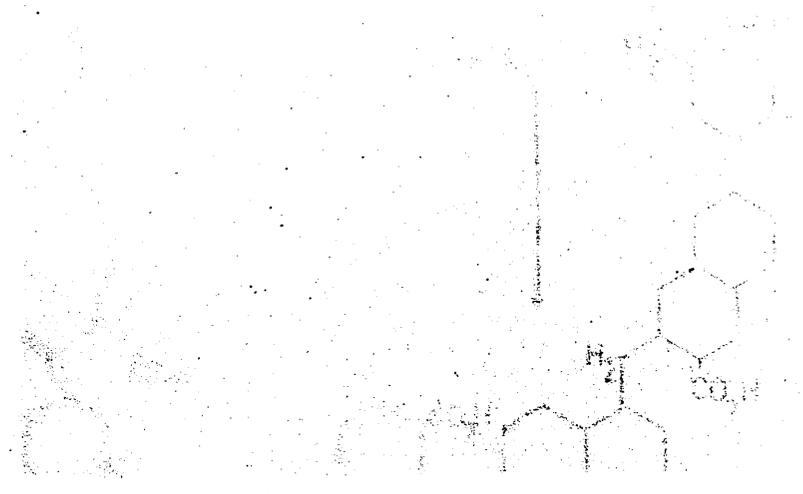
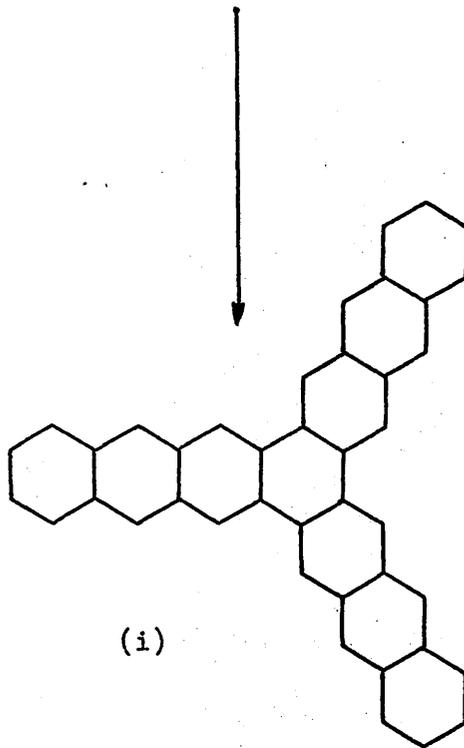
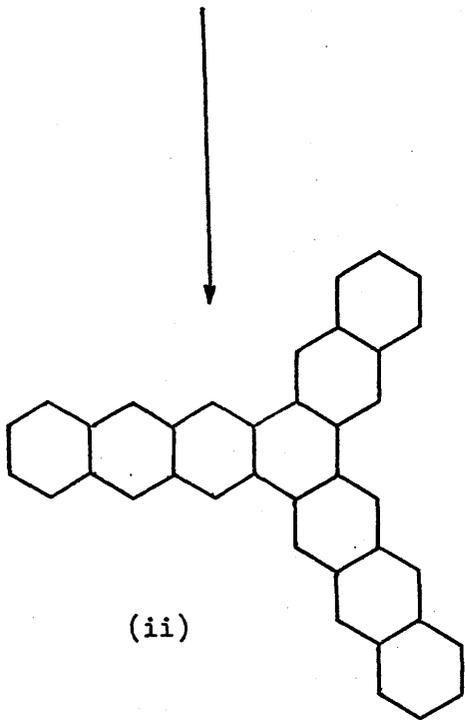
The syntheses of 1,2:3,4-dibenzanthracene<sup>30</sup> (xxv) and hetaphene<sup>1</sup> (xvi) were of particular interest and are shown opposite (a and b respectively).

The heptaphene<sup>1</sup> (xvi) synthesis (b) is of interest as it would give two of the three branches of the required starphenes.

A third anhydride molecule could be introduced into the 9 position in phenanthrene (as in a) opposite) to give the remaining branch.

The molecule could then be cyclised and reduced to yield the required starphene. 3,6-Di-o-carboxy-benzoyl-phenanthrene (xxvi) was synthesised following Clar and Kelly's method<sup>1</sup>. In order to introduce a third anhydride molecule at the 9 position in (xxvi) it is necessary to remove the deactivation effect of the ketones on the phenanthrene nucleus by reducing them.





An unsuccessful attempt was made using the Huang-Minlon technique<sup>31</sup>, however the ketones were reduced using KOH/Zn, giving a good yield of 3,6-di-o-carboxy-benzyl-phenanthrene (xxvii).

More drastic conditions were used to introduce the third anhydride molecule, the total reaction time being increased to 20 hr. The condensing of one molecule of phthalic anhydride and 2,3 - naphthalene-dicarboxylic acid anhydride completed the formation of the skeletons (xxx) and (xxviii) of nonastarphene - (2,3,3) (ii) and decastarphene - (3,3,3) (i) respectively.

Before any cyclisation attempts were made, the remaining ketone group in (xxviii) and (xxx) was reduced using KOH/Zn as before. The zinc dust melt<sup>32</sup> reaction generally goes to completion with the formation of the hydrocarbon when the keto acid is reduced to the acid, otherwise the reduction may not be completed and stop at the anthrone stage<sup>33</sup>.

As in the synthesis of heptaphene<sup>1</sup>, cyclisation with H<sub>2</sub>SO<sub>4</sub> was attempted, which in this case gave very poor yields. The product was reduced using Zn/HOAC and pyridine<sup>33</sup>. The spectra of the hydrocarbons produced were examined showing the presence of nonastarphene-(2,3,3) (ii) and decastarphene-(3,3,3) (i) respectively.

However, as the yields were very poor, cyclisation was attempted using

a zinc dust melt<sup>32</sup>. At the usual temperature recorded for the melt 200°- 310°, cyclisation was incomplete and complete cyclisation was only achieved when a temperature of 380° was employed.

The zinc dust melt<sup>32</sup> gave a much higher yield of hydrocarbon than the H<sub>2</sub>SO<sub>4</sub> method. It had the disadvantage that due to the high temperature of the melt some cleavage of the hydrocarbon inevitably took place.

EXPERIMENTAL

3,6-Di-o-carboxybenzoyl-phenanthrene (xxvi)

(xxvi) was prepared by the method of Clar and Kelly<sup>1</sup>, as colourless prismatic crystals, m.pt. 299-301<sup>o</sup> (lit. m.pt. 299-301<sup>o</sup>)<sup>†</sup>

$\int_{\text{max}}^{\text{KBr}} = 1695\text{cm.}^{-1}$  (acid C=O),  $1678\text{cm.}^{-1}$  (diaryl ketone C=O)

3,6-Di-o-carboxybenzyl-phenanthrene (xxvii)

3,6-Di-o-carboxybenzoyl-phenanthrene (xxvi) (7g) was dissolved in dilute aq. KOH (2000ml., 5%) and a crystal of copper sulphate added. The surface of the mixture was covered with amyl alcohol (50ml.) to avoid frothing. Zinc dust was added in portions of 20g at 24 hour intervals and the mixture refluxed. 4x20g of zinc dust were added at the appropriate periods and the mixture refluxed for a total of one week. The amyl alcohol was distilled off, the solution filtered and acidified with hydrochloric acid. The residue with the zinc dust was thoroughly washed with hot water until acidification with hydrochloric acid gave no more precipitate. The combined acidified suspensions were boiled, filtered and washed with hot water, yield 6g. A further small portion was obtained by dissolving the zinc in hydrochloric acid. The crude product was crystallised four times from acetic acid as colourless prisms of m.pt. 241<sup>o</sup>.

$\int_{\text{max}}^{\text{KBr}} = 1685\text{cm.}^{-1}$  (acid C=O). With conc. sulphuric acid, (xxvii) gave

an orange yellow solution which became green on heating. The N.M.R. spectrum confirmed the symmetrical structure of the molecule.

Found: C, 80.7 ; H, 5.0%

$C_{30}H_{22}O_4$  requires C, 80.7 ; H, 5.0%

3,6-Di-o-carboxybenzyl-9-(3'-carboxy-2'-naphthyl)-phenanthrene (xxviii)

3,6-Di-o-carboxybenzyl-phenanthrene (xxvii) (1g) was powdered with naphthalene-2,3-dicarboxylic acid anhydride and suspended in tetrachloroethane (10ml.). The mixture was shaken for 10 min. and  $AlCl_3$  (5g) added. The dark brown mixture was gently heated before being shaken for 3 hours. After standing for 18 hours, it was decomp. with dilute hydrochloric acid and the tetrachloroethane distilled off with steam. The crude product was repeatedly extracted with boiling water to ensure that the excess naphthalene-2,3-dicarboxylic acid was removed. The acid was dissolved in dilute ammonia leaving a small amount of insoluble material. Acidification, first with acetic acid and then with dilute hydrochloric acid gave the acid (xxviii) (1.02g) which, after repeated crystallisation from acetic acid yielded colourless prismatic crystals, m.pt.  $261^{\circ}$ .  $\int_{max}^{KBr} = 1690cm^{-1}$  (acid C=O)  
In conc. sulphuric acid, (xxviii) was initially leaf green becoming violet on standing.

Found: C, 78.5 ; H, 4.5%

$C_{42}H_{28}O_7$  requires C, 78.3 ; H, 4.4%

3,6-Di-o-carboxybenzyl-9-(3'-carboxylic-2'-naphthylmethyl)-phenanthrene

(xxix)

The acid (xxix) was prepared as described for (xxvii). The yield was 1.4g of (xxix) from 1.9g of (xxviii). The crude product had a m.pt.  $280^{\circ}$  which rose to  $295^{\circ}$  after three crystallisations from nitrobenzene, yielding colourless prismatic crystals. The acid (xxix) dissolved in conc. sulphuric acid to form a wine red solution which became red on heating.  $\nu_{\text{max}}^{\text{KBr}} = 1683\text{cm}^{-1}$  (C=O acid)

Found: C, 80.0 ; H, 4.7%

$C_{42}H_{30}O_6$  requires C, 80.0 ; H, 4.8%

Decastarphene-(3,3,3) (i)

3,6-Di-o-carboxybenzyl-9-(3'-carboxylic-2'-naphthylmethyl)-phenanthrene (xxix) (0.1g) was thoroughly powdered with zinc dust (2g), then mixed with sodium chloride (2g) and crystalline zinc chloride (10g). The mixture was heated with stirring to  $380^{\circ}$  and kept at this temperature for 2 min. After cooling the melt was dissolved in dilute acetic

acid and the residue treated with dilute hydrochloric acid. The insoluble part was filtered off and washed with hot water and dilute ammonia. The crude hydrocarbon (0.072g) was powdered with soda lime (0.5g) and heated under nitrogen to 310° until all traces of humidity had been removed. The pressure was then reduced to  $3 \times 10^{-3}$  mm. Sublimation up to 440° yielded decastarphene (i) as orange red needles.

The sublimate was first extracted with boiling xylene and the insoluble part recrystallised from 1,2,4-trichlorobenzene. It formed flat dark yellow needles, decomp. 500°, which dissolved in conc. sulphuric acid to give a violet solution which became yellowish brown on standing.

Found                    C, 95.3 ; H, 4.6%

$C_{42}H_{24}$  requires C, 95.4 ; H, 4.6%

Mol. wt.            Found:                    m/e = 529

                          Calc.:                    m/e = 528.6

### 3,6-Dicarboxybenzyl-9-o-carboxybenzoylphenanthrene (xxx)

3,6-Di-o-carboxybenzyl-phenanthrene (xxvii) (1g) was powdered with phthalic anhydride (1.5g) and suspended in tetrachloroethane (10ml). The mixture was shaken for 10 min. and  $AlCl_3$  (5g) added. The brown

mixture was gently heated before being shaken for 3 hours. After standing for 18 hours, it was decomposed with dilute hydrochloric acid and the tetrachloroethane distilled off with steam. The residue was repeatedly extracted with boiling water to ensure removal of the excess phthalic acid. The acid (xxx) was dissolved in dilute ammonia leaving a small amount of insoluble material. Acidification, first with acetic acid and then with dil. hydrochloric acid gave the acid (xxx) (0.98g). After repeated crystallisations from acetic acid, colourless prisms of m.pt.  $274-5^{\circ}$  were obtained. The acid (xxx) dissolved in conc. sulphuric acid to give a violet solution which became yellow on heating.  $\nu_{\text{max}}^{\text{KBr}} = 1688\text{cm}^{-1}$  (C=O acid)

Found: C, 76.6 ; H, 4.4%

$\text{C}_{38}\text{H}_{26}\text{O}_7$  requires C, 76.8 ; H, 4.1%

3,6,9-Tri-o-carboxybenzylphenanthrene (xxxi).

(xxxi) was obtained from 3,6-dicarboxybenzyl-9-o-carboxybenzoyl-phenanthrene (xxx) in the manner described for the preparation of 3,6-di-o-carboxybenzyl-phenanthrene (xxvii). The yield was 0.4g of (xxxi) from 0.5g of (xxx). The acid was recrystallised three times from acetic acid, yielding colourless prisms m.pt.  $287^{\circ}$ . In sulphuric acid the acid (xxxi) dissolved to form a bright red soln.

which became yellowish brown at  $50^{\circ}$ .  $\nu_{\text{max}}^{\text{KBr}} = 1688\text{cm}^{-1}$  (C=O acid)

Found: C, 78.4 ; H, 4.8%

$\text{C}_{38}\text{H}_{28}\text{O}_7$  requires C, 78.6 ; H, 4.9%

Nonastarphene-(2,3,3) (ii)

3,6,9-Tri-*o*-carboxybenzylphenanthrene (xxxii) (0.1g) was thoroughly powdered with zinc dust (2g) and then mixed with sodium chloride (2g) and crystalline zinc chloride (10g). The mixture was heated with stirring to  $380^{\circ}$  and kept at this temperature for 2min. After cooling the melt was dissolved in acetic acid and the residue treated with conc. hydrochloric acid. The insoluble part was filtered off and washed with hot water and dilute ammonia. The crude dried hydrocarbon was powdered with soda lime (0.5g) and heated under nitrogen to  $310^{\circ}$  until all traces of humidity were removed. The pressure was then reduced to  $3 \times 10^{-3}$  mm. Sublimation up to  $420^{\circ}$  yielded the orange yellow hydrocarbon (ii), which after crystallisation from xylene gave dark yellow clustered needles, m.pt.  $310-15^{\circ}$ . In conc. sulphuric acid a dark brown solution was obtained with (ii), on standing the solution became yellow brown in colour.

Found: C, 95.4 ; H, 4.6%

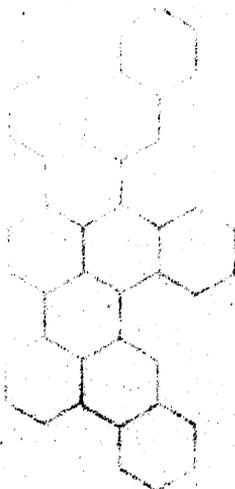
$C_{38}H_{22}$  requires C, 95.4 ; H, 4.4%

Mol. wt. Found: m/e = 478

Calc.: m/e = 478.5



(i)



(ii)



(iii)



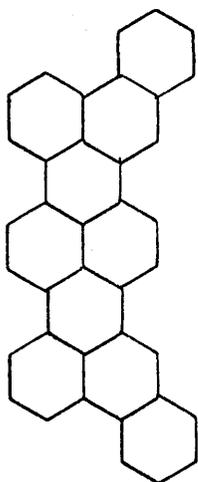
(iv)

Product List:

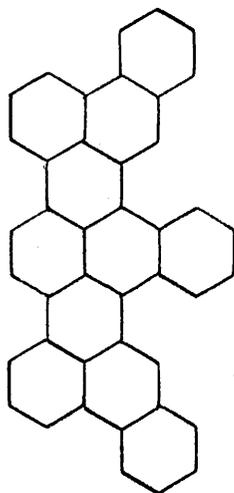
1,17-benzoperace 7, 8:12, 13-dimethylarylene (i)  
 1,10:2, 3:12, 13:14, 15-tetramethylarylene (ii), 1,16:2, 3:12, 13:14, 15-tetramethylarylene (iii), 1,10:2, 3:12, 13:14, 15-tetramethylarylene (iv)

CHAPTER II

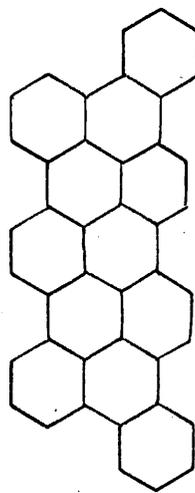
Benzologues of Terrylene.



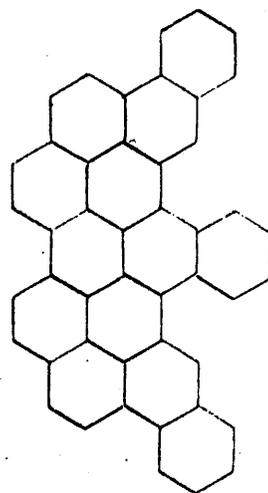
(i)



(ii)



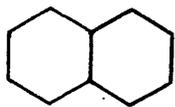
(iii)



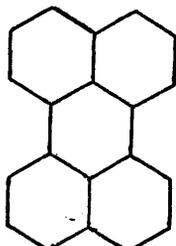
(iv)

Introduction:

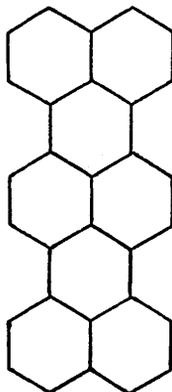
The terrylene (vii) benzologues 2,3:12,13-dibenzoterrylene (i), 2,3:12,13:15,16-tribenzoterrylene (ii), 1,16:2,3:12,13:14,15-tetrabenzoterrylene (iii) and 2,3:6,7:8,9:12,13:15,16-pentabenzoterrylene (iv) have been synthesised. Their u.v. spectra have been compared with terrylene (vii) and its benzologues. The spectra show the expected shifts derived from the formulae with aromatic sextets<sup>2</sup>. Their physical and chemical properties have also been compared with perylene<sup>3</sup>(vi) and its benzologues - showing a remarkable similarity.



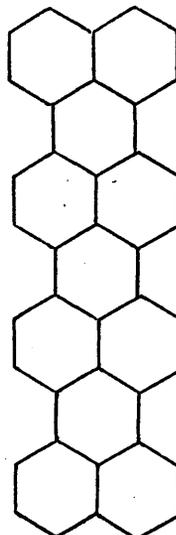
(v)



(vi)



(vii)



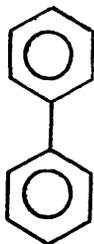
(viii)

$$\lambda_{\beta} = 2210 \xrightarrow{300} 2510 \xrightarrow{260} 2770$$

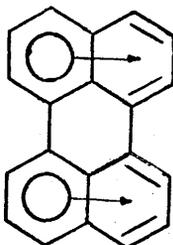
$$\lambda_{\rho} = 2850 \xrightarrow{1490} 4340 \xrightarrow{1260} 5600 \xrightarrow{1100} 6700$$

⌘

⌘



(ix)



(vi')

Discussion:

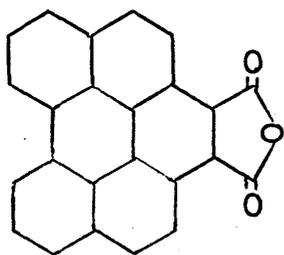
The x-ray structures of the molecules in the peri-condensed series perylene<sup>3</sup> (vi), terrylene<sup>1</sup> (vii) and quarterrylene<sup>1</sup> (viii) show a remarkable similarity. The molecules consist of naphthalene (v) units connected together by quasi-single bonds of length between 1.50 and 1.53 Å. The bonds within the naphthalene complexes show a marked resemblance to their length in naphthalene itself<sup>4</sup>.

There are strong regular shifts towards the red in the series naphthalene<sup>5</sup> (v), perylene<sup>3</sup> (vi), terrylene<sup>1</sup> (vii) and quarterrylene<sup>1</sup> (viii) (see opposite).

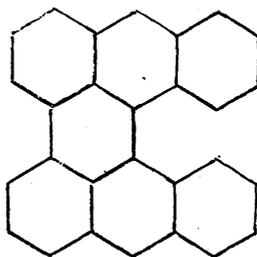
Thus, obviously conjugation takes place between these naphthalene units<sup>12</sup>.

It would seem appropriate at this point to give a brief account of the properties of perylene<sup>3</sup> (vi), and its benzologues<sup>3</sup>, as their properties have been thoroughly examined<sup>3</sup> and perylene (vi) is the preceding member to terrylene (vii) in the series.

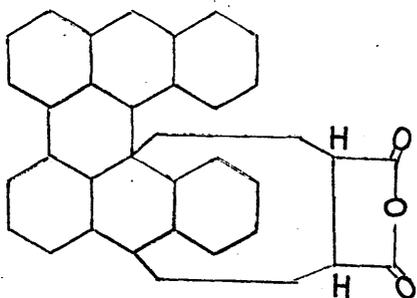
Perylene<sup>3</sup> (vi) is derived from diphenyl (ix) by the fusing of two rings, which results in a large bathochromic shift. This is to be expected as two rings have been annellated and no new sextets<sup>2</sup> have been formed<sup>6</sup>. Perylene is a fairly reactive yellow compound as is shown by its reaction



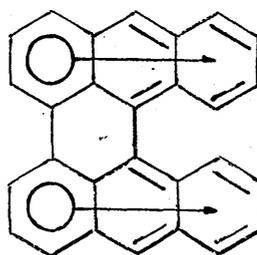
(xi)



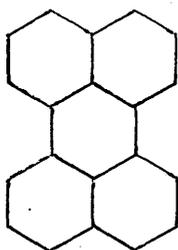
(xii)



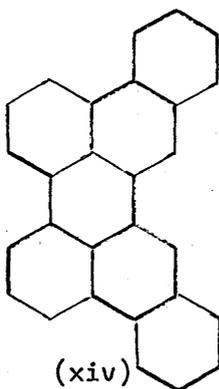
(xiii)



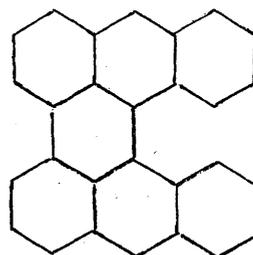
(xii')



(vi)



(xiv)



(xii)

$\lambda_{\beta}$	=	2510	3020	3130	Å
$\lambda_{\rho}$	=	4340	4400	5580	Å

with maleic anhydride (x) and chloranil<sup>7</sup> (as dehydrogenating agent) resulting in the formation of the adduct<sup>8</sup> (xi).

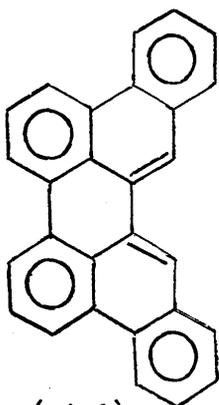
1,2:11,12-Dibenzoperylene<sup>3</sup> (xii) is much more reactive than perylene (vi) as would be expected if the formula is derived with strict application of the aromatic sextet concept<sup>2</sup>.

In dibenzoperylene<sup>3</sup> (xii'), the two sextets<sup>2</sup> present in perylene (vi) are further diluted, and the reactivity of the molecule resembles two fused anthracene complexes. The immediate reaction with maleic anhydride to form the endocyclic adduct (xiii) is indicative of this increased reactivity<sup>9</sup> and its acene character<sup>10</sup>.

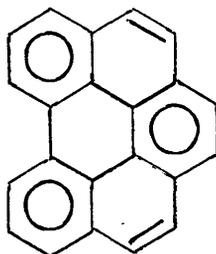
Dibenzoperylene<sup>9</sup> (xii') is violet in colour in comparison with perylene (vi) as would be expected by the fusing of two rings with no new sextet<sup>2</sup> or sextets<sup>2</sup> being formed<sup>6</sup>. In striking contrast to this, 2,3:10,11-dibenzoperylene<sup>11</sup> (xiv) is yellow in colour, although it is an isomer of dibenzoperylene<sup>9</sup> (xii).

This contrast can be more quantitatively seen if the  $\beta$  and  $\rho$  bands of perylene<sup>3</sup> (vi), and the two dibenzoperylene isomers (xii)<sup>9</sup> and (xiv)<sup>11</sup> are compared.

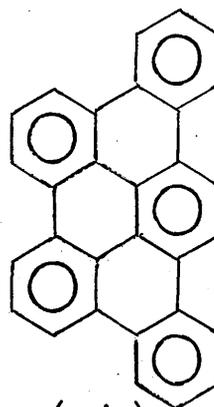
In 2,3:10,11-dibenzoperylene<sup>11</sup> (xiv) the  $\alpha$  bands are hidden under the



(xiv')

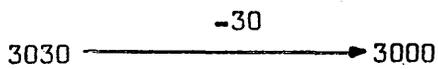


(xv)



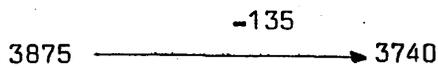
(xxiv)

$\lambda_{\beta} = 3020$

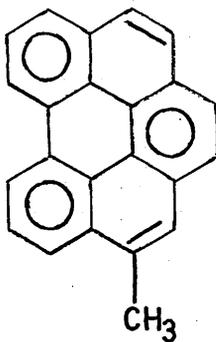


R

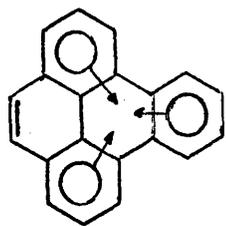
$\lambda_{\rho} = 4400$



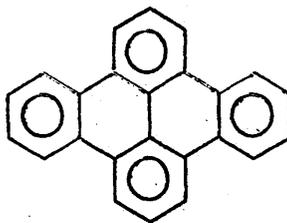
R



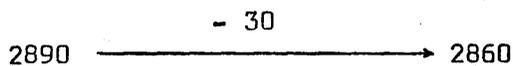
(xvi)



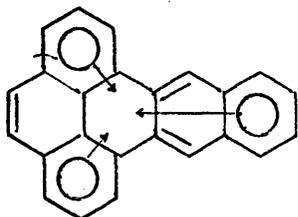
(xvii)



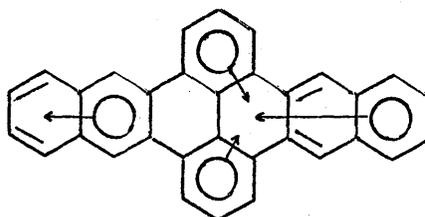
(xviii)

 $\lambda_{\beta} =$ 

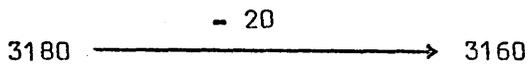
R



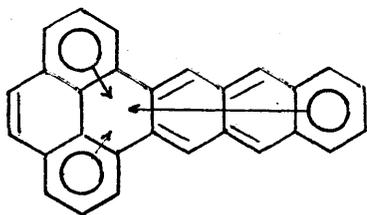
(xix)



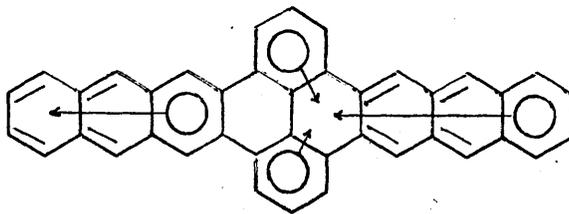
(xxi)

 $\lambda_{\beta} =$ 

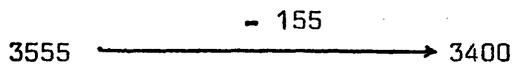
R



(xxii)



(xxiii)

 $\lambda_{\beta} =$ 

R

$\rho$  bands as would be expected of a system consisting of two fused phenanthryl complexes<sup>12</sup>. Whereas in 1,2:11,12-dibenzoperylene<sup>9</sup> (xii'), the  $\alpha$  bands are already the second group of bands to appear in the spectrum as would be expected of the dianthracene type complex present.<sup>12</sup>

The four aromatic sextets<sup>2</sup> in 2,3:10,11-dibenzoperylene<sup>11</sup> (xiv') readily account for its u.v. absorption spectrum being at much shorter wavelength relative to 1,2:11,12-dibenzoperylene<sup>9</sup> (xii) which, although an isomer has only two sextets<sup>2</sup>.

1,12-Benzoperylene<sup>11</sup> (xv) which is pale yellow can be written with three sextets<sup>2</sup> and two fixed double bonds<sup>13</sup>. The N.M.R. spectrum of 3-methyl-1,12-benzoperylene<sup>14</sup> (xvi) showed that the methyl resonance signal consisted of a doublet of separation 1c/s. This corroborates the concept of their being a 'fixed double bond'<sup>13</sup> at the 2,3 position. Certainly, if there is a fixed double bond in the 9,10 position in phenanthrene<sup>15</sup>, this must also be the case here.

Clar has found that annellation to a fixed double bond<sup>16</sup> in a polycyclic hydrocarbon produces a small hypsochromic shift if any at all<sup>16</sup>. Some examples of this type of annellation are shown opposite<sup>17</sup> (xvii-xxiii).

When rings are fused to the fixed double bonds<sup>16</sup> in 1,12-benzoperylene (xv) forming 1,12:2,3:10,11-tribenzoperylene<sup>18</sup> (xxiv) a small hypsochromic

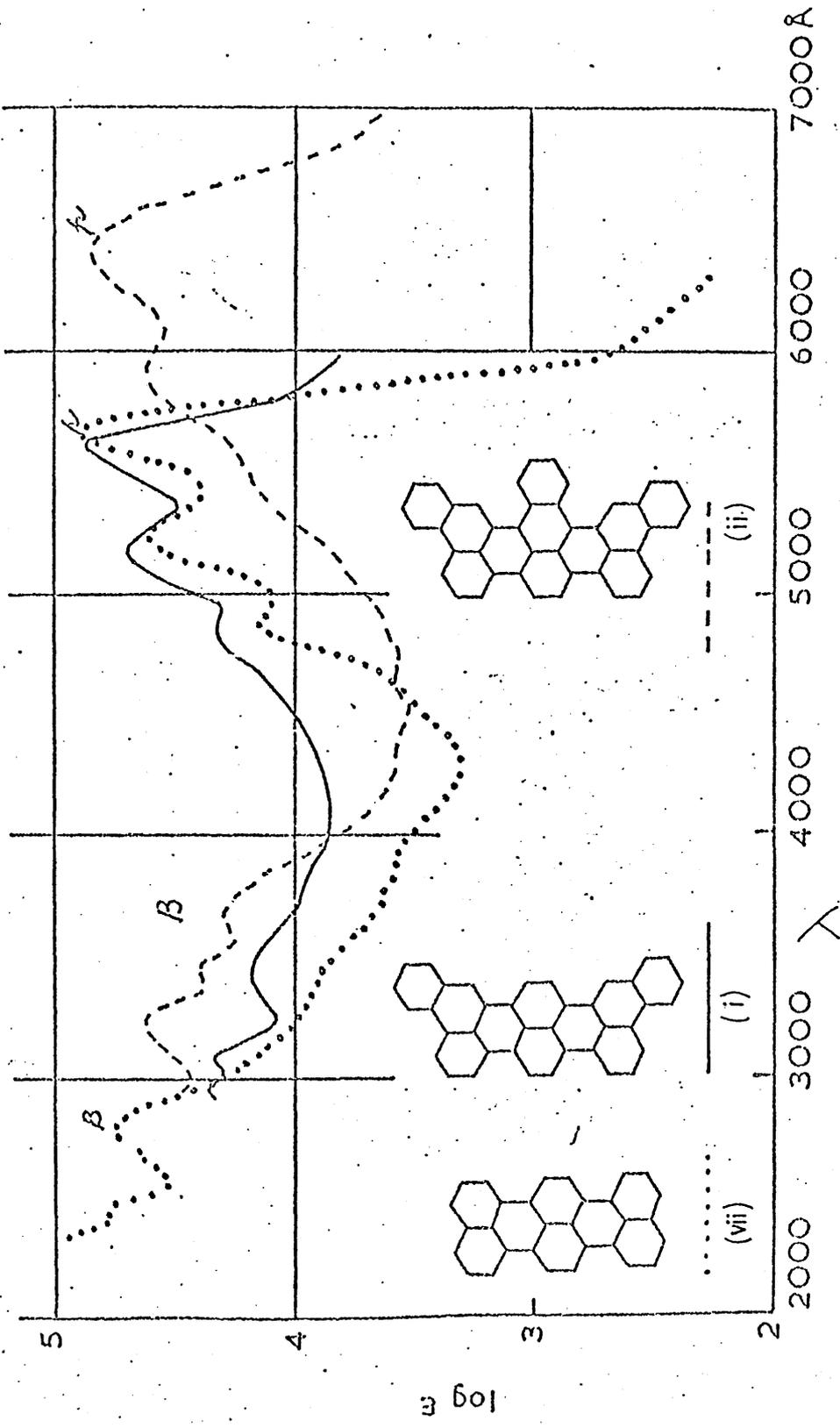
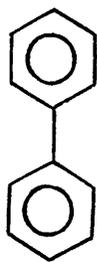
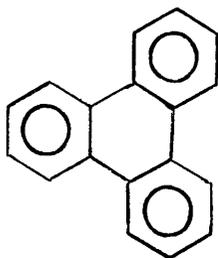


Fig. 1. Absorption spectra with max. ( $\lambda$ ) and  $\log \epsilon$  in parentheses:

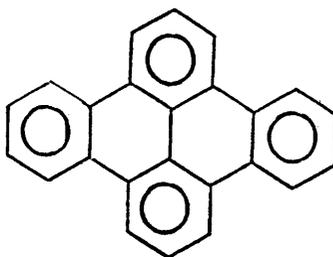
- ..... Terrylene in benzene:  $\beta$ , 5600(4.90), 5190(4.60), 4830(4.14);  $\beta$ , 2770(4.74), in dioxane:  $\beta'$ , 2440(4.74).
- 2,3:12,13-Dibenzoterrylene in xylene:  $\beta$ , 5600(4.87), 5170(4.69), 4850(4.32);  $\beta$ , 3450(4.17); in benzene: 3080(4.33).
- 2,3:12,13:15,16-Tribenzoterrylene in xylene:  $\beta$ , 6420(4.86), 5900(4.63);  $\beta$ , 3680(4.31), 3460(4.40), 3220(4.62).



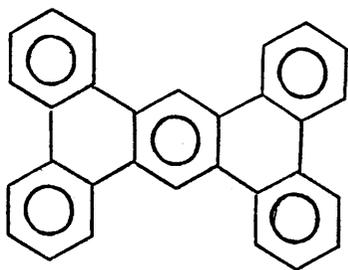
(ix)



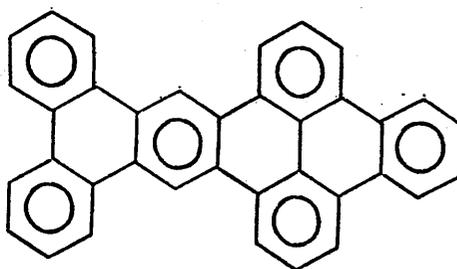
(xxv)



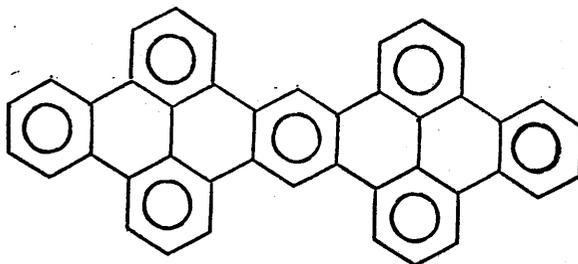
(xxvi)



(xxvii)



(xxviii)



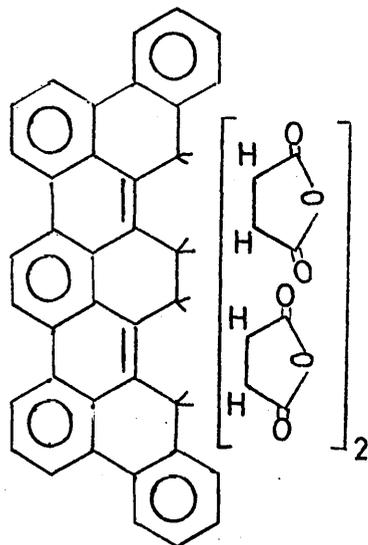
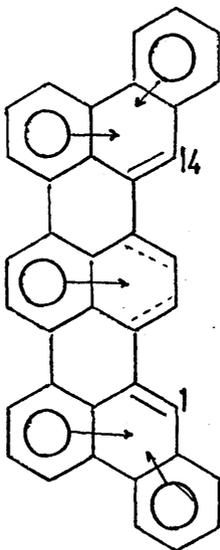
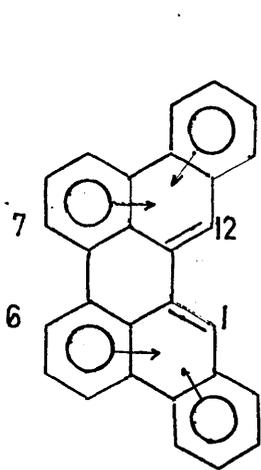
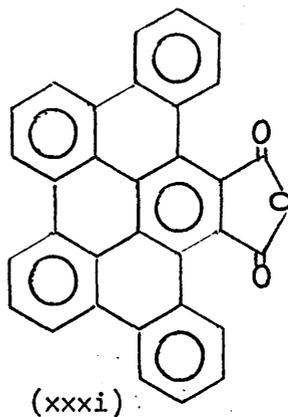
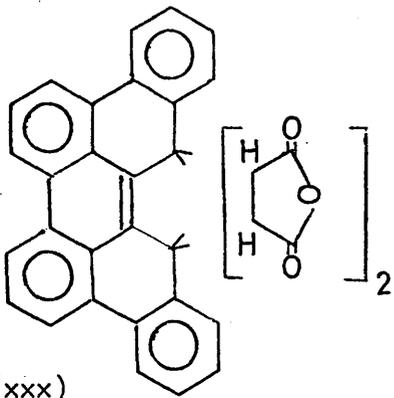
(xxix)

shift is obtained<sup>18</sup>, in keeping with the previous findings outlined above. The red shift due to the addition of 4 $\pi$  electrons per. ring is compensated by the violet shift due to the formation of an aromatic sextet<sup>19</sup>.

Tribenzoperylene<sup>18</sup> (xxiv), is almost colourless and like the rest of the aromatic hydrocarbons which can be written with sextets only it is regarded as being a condensed polyphenyl<sup>2</sup>. Hydrocarbons of this class are highly unreactive, do not dissolve in conc. H<sub>2</sub>SO<sub>4</sub> and have a phosphorescence of long life in solid solution<sup>18</sup>.

The isomer of a polycyclic hydrocarbon which consists purely of aromatic sextets<sup>2</sup> is the most stable form and is highly unreactive. Its u.v. absorption bands are the most strongly shifted to the violet among the spectra of the isomeric aromatic hydrocarbons<sup>18</sup>. Examples of this class<sup>2</sup> are shown on the opposite page (ix-xxix).

The absorption spectrum of the deep violet red 2,3:12,13-dibenzoterrylene (i) is shown in fig. 1 next to the spectrum of terrylene (vii). The  $\rho$  bands of dibenzoterrylene (i) shift slightly towards the violet (-50Å) whereas the  $\beta$  bands show a strong shift towards the red (+320Å). This annellation effect<sup>12</sup> is analogous to that found between perylene<sup>5</sup> (vi) and dibenzoperylene<sup>11</sup> (xiv).



Dibenzoperylene<sup>11</sup> (xiv) forms a di-adduct<sup>18</sup> (xxx) with maleic anhydride using mild dehydrogenating conditions, stronger conditions, using chloranil as reagent yield the mono adduct<sup>18</sup> (xxxi).

The reactive sites for the maleic anhydride diene reaction<sup>11</sup> can be readily anticipated by strict application of Robinson's aromatic sextet<sup>2</sup> and, the fixed double bond concept<sup>13</sup>.

If the structure of dibenzoperylene (xiv) is derived by using sextets<sup>2</sup>, the double bonds are localised as shown opposite (xiv') and the reaction with maleic anhydride therefore must take place at positions 1 & 12.

Attack at the 6,7 positions would be unsuccessful due to the fact that the two sextets<sup>2</sup> would not take part in this energetically unfavourable reaction. A further factor is that attack at the 1,12 positions results in the formation of a new aromatic sextet<sup>2</sup> which would give the molecule enhanced stability<sup>2</sup>. No new sextet<sup>2</sup> would be formed if the attack were at the 6,7 positions.

As suspected dibenzoterrylene (i') reacts in a similar fashion to dibenzoperylene<sup>18</sup> (xiv). With maleic anhydride and a mild dehydrogenating reagent such as iodine, the tetra-adduct (xxxii) is formed, comparable to the diadduct (xxx) obtained with dibenzoperylene<sup>18</sup> (xiv).

Using a stronger dehydrogenating reagent such as chloranil<sup>9</sup>, the

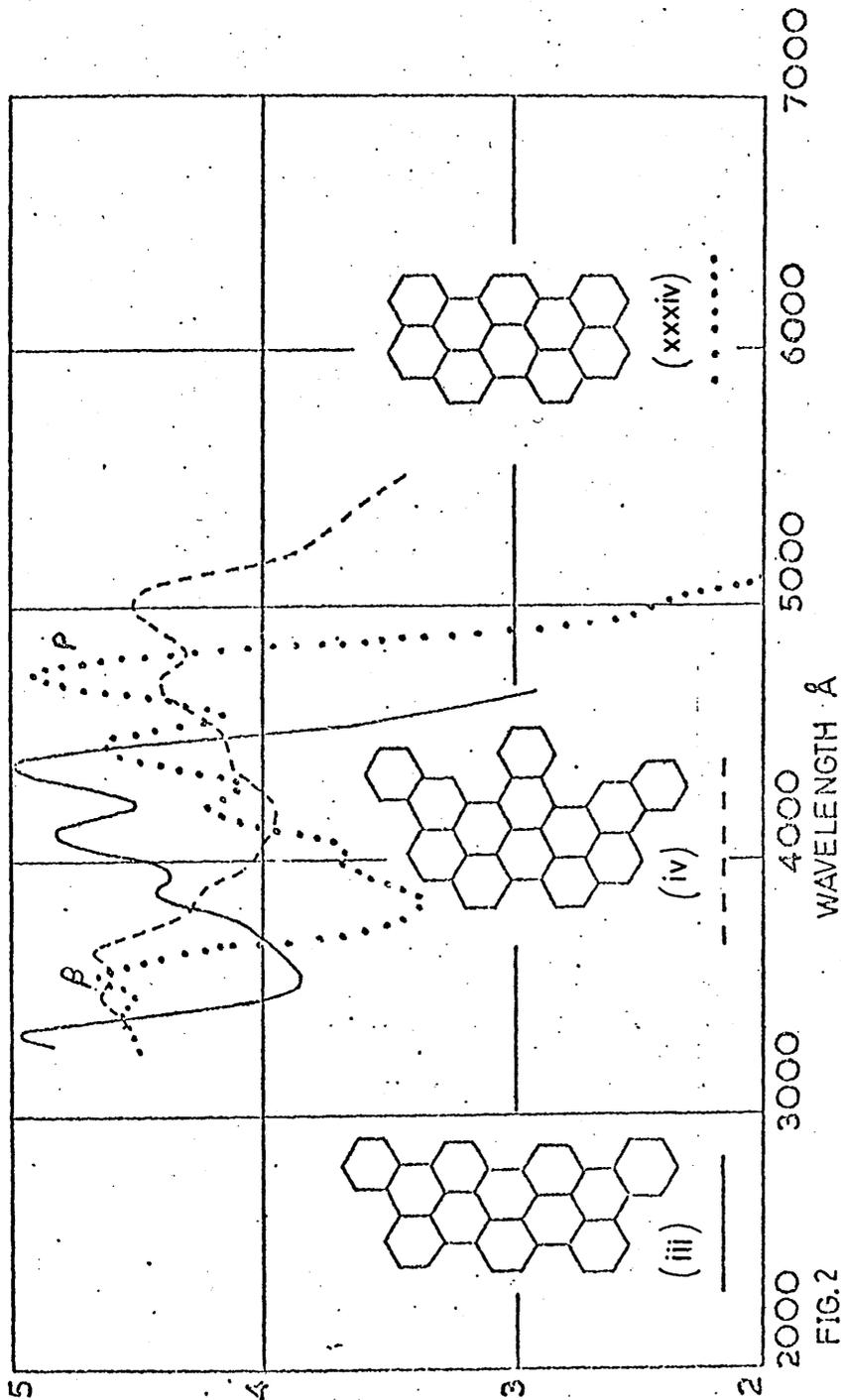
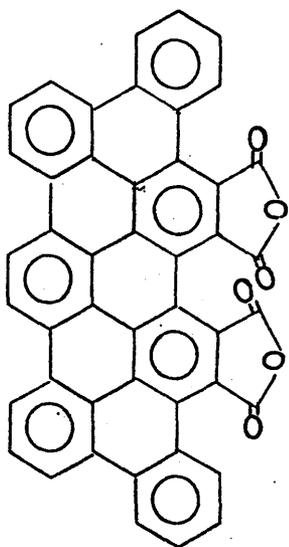


FIG. 2

—  $\alpha$  1,16:2,3:12,13:14,15-Tetrabenzoterrylene in 1,2,4-trichlorobenzene:  $\alpha$ , 4350(4.99), 4090(4.82), 3870(4.41);  $\beta$ , 3310(4.95).

.....  $\beta$  6,7:8,9-Dibenzoterrylene in 1,2,4-trichlorobenzene:  $\beta$ , 4460(4.89), 4200(4.60), 3950(4.23), 3750(3.70);  $\beta$ , 3310(4.65).

- - -  $\gamma$  2,3:6,7:8,9:12,13:15,16-Pentabenzoterrylene in xylene:  $\gamma$ , 5010(4.51), 4695(4.41);  $\beta$ , 3645(4.67), 3470(4.64).



(xxxiii)

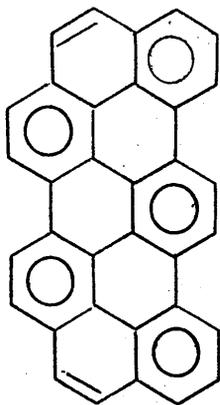
diadduct (xxxiii) is obtained. Strict application of the aromatic sextet<sup>2</sup> - 'fixed double bond'<sup>13</sup> concepts would result in dibenzoterrylene (i') being represented with two fixed double bonds at the 1 and 14 positions which would react readily with the maleic anhydride dienophile. This once again illustrates the usefulness of Clar's aromatic sextet<sup>2</sup> and fixed double bond<sup>13</sup> concepts, which allow one to predict the reactive sites of a hitherto unknown aromatic hydrocarbon.

A further driving force for this reaction is the fact that two new sextets<sup>2</sup> are formed, which would not be the case were the attack to be at the 6,7 and 8,9 positions.

The diadduct (xxxiii) was also obtained by thermal decomposition of the tetra-adduct (xxxii).

Decarboxylation of the adducts yielded 1,16:2,3:12,13:14,15-tetrabenzoterrylene (iii). This yellow hydrocarbon belongs to the class of completely benzenoid hydrocarbons<sup>18</sup>, already discussed earlier.

The increase from five sextets<sup>2</sup> in 2,3:12,13-dibenzoterrylene (i') to seven sextets<sup>2</sup> in 1,16:2,3:12,13:14,15-tetrabenzoterrylene (iii) results in a drastic hypsochromic shift of the  $\rho$  bands (1250 $\text{\AA}$ ) and in a small bathochromic shift (230 $\text{\AA}$ ) of the  $\beta$  bands (see fig. 2).



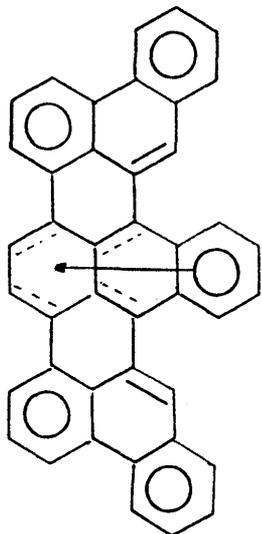
(xxxiv)

This is completely analogous to the shift between dibenzoperylene (xiv) and tribenzoperylene (xxiv) where an increase of four sextets<sup>2</sup> to five takes place.

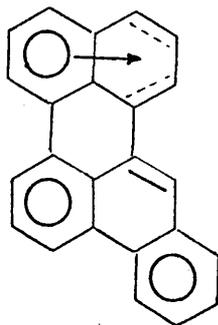
Tetrabenzoterrylene (iii) like other fully benzenoid hydrocarbons<sup>18</sup> is insoluble in conc. sulphuric acid and shows an orange yellow phosphorescence of very long life in solid solution. It is extremely stable and can be sublimed above 500<sup>0</sup> without decomposition. It also does not melt below 540<sup>0</sup>.

Fig. 2 shows the spectrum of tetrabenzoterrylene (iii) in addition to that of 6,7:8,9-dibenzoterrylene<sup>20</sup> (xxxiv), (3,4:5,6:7,8-tribenzoperopyrene). The latter hydrocarbon has two fixed double bonds<sup>13</sup> if written with five aromatic sextets<sup>2</sup> as opposite. Comparison with tetrabenzoterrylene (iii), confirms the rule that no red shift is recorded if the rings are annellated to fixed double bonds, instead small hypsochromic shifts are often found<sup>16</sup>. This is explained by the fact that only two branches of any linear benzologue of triphenylene can be in aromatic conjugation at any one time (see chapter I).

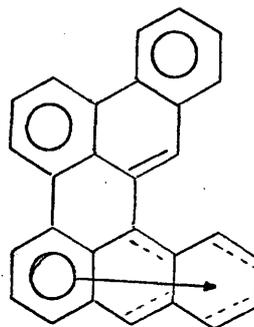
This also has a analogy in the perylene series in the comparison between 1,12-benzoperylene<sup>11</sup> (xv) and tribenzoperylene<sup>18</sup> (xxiv), discussed earlier in this chapter, where a similar hypsochromic effect was found.



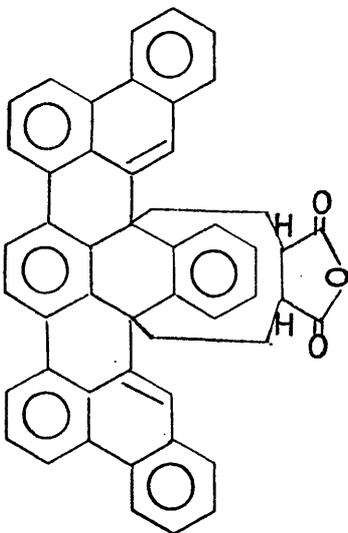
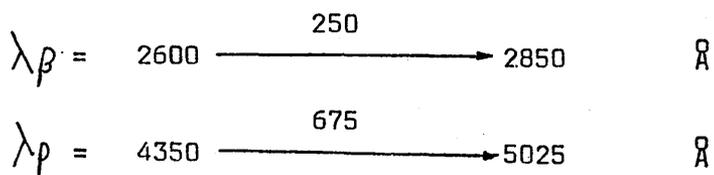
(ii')



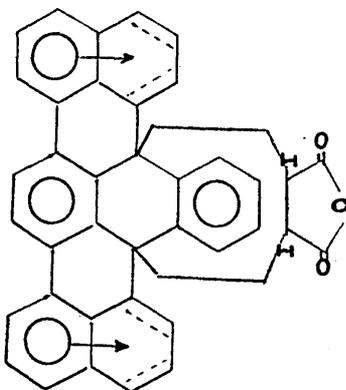
(xxxv)



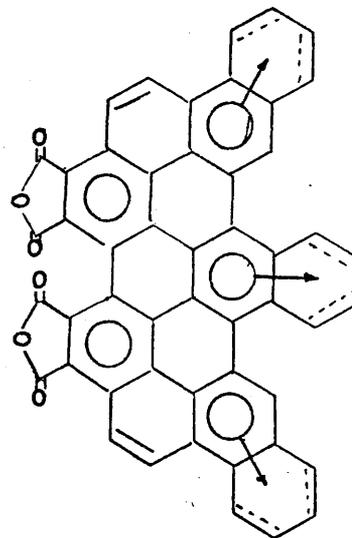
(xxxvi)



(xx)



(xxa)



(xxxvii)

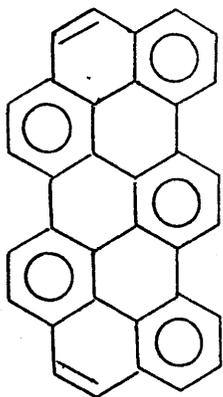


2,3:12,13:15,16-Tribenzoterrylene (ii') in comparison with 2,3:12,13-dibenzoterrylene (i') shows a strong bathochromic shift (Fig. 1) as would be expected from an annellation which produces no new aromatic sextet<sup>2</sup> but a normal extension of conjugation as between linear benzo-  
logues in the lower acene series<sup>12</sup>.

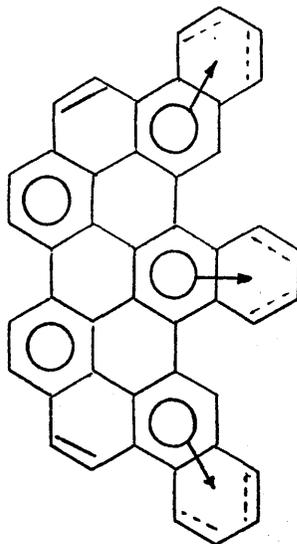
A similar red shift is also found between 2,3-benzoperylene<sup>23</sup> (xxxv) and 1,2:10,11-dibenzoperylene<sup>9</sup> (xxxvi). This illustrates yet again the close relationship between the perylenes and terrylenes, which is readily predictable using Clar's aromatic sextet concepts<sup>2</sup>.

Tribenzoterrylene (ii') with boiling maleic anhydride forms a colourless adduct (xx) Its absorption spectrum is very similar to the maleic anhydride adduct of 7,8-dibenzoterrylene<sup>21</sup> (xxa) (Fig. 3), just as the  $\rho$  bands of naphthalene and phenanthrene are at very similar positions ( 2850 and 2925 Å resp.) However, there is less certainty about the relationship of the rather broad  $\beta$  bands.

A more energetic diene synthesis with maleic anhydride and a dehydrogenating agent produces the dianhydride (xxxvii) which after decarboxylation with soda lime yields the red 2,3:6,7:8,9:12,13:15,16-pentabenzoterrylene (iv). The spectrum is recorded in fig. 2.



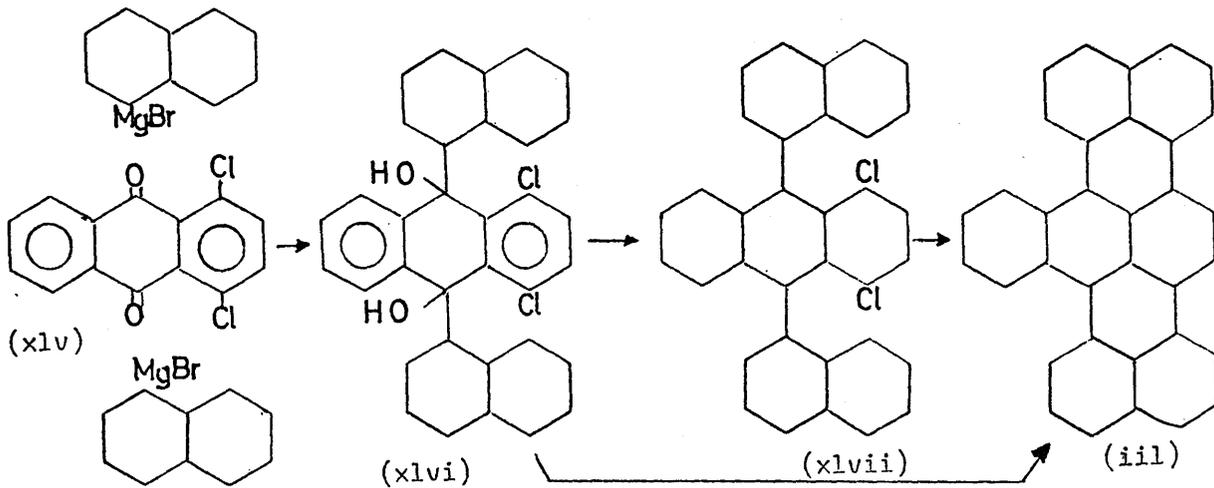
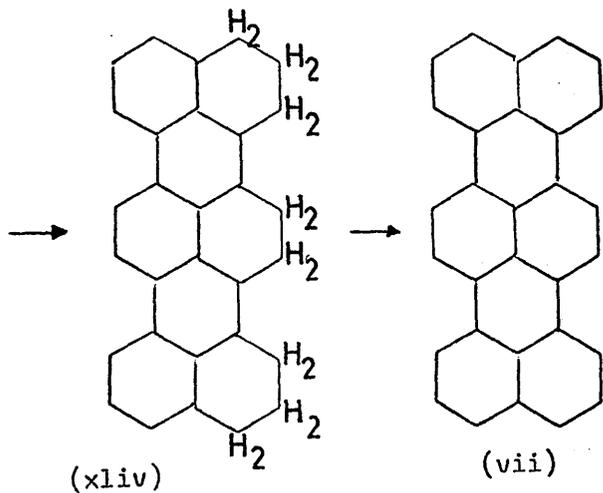
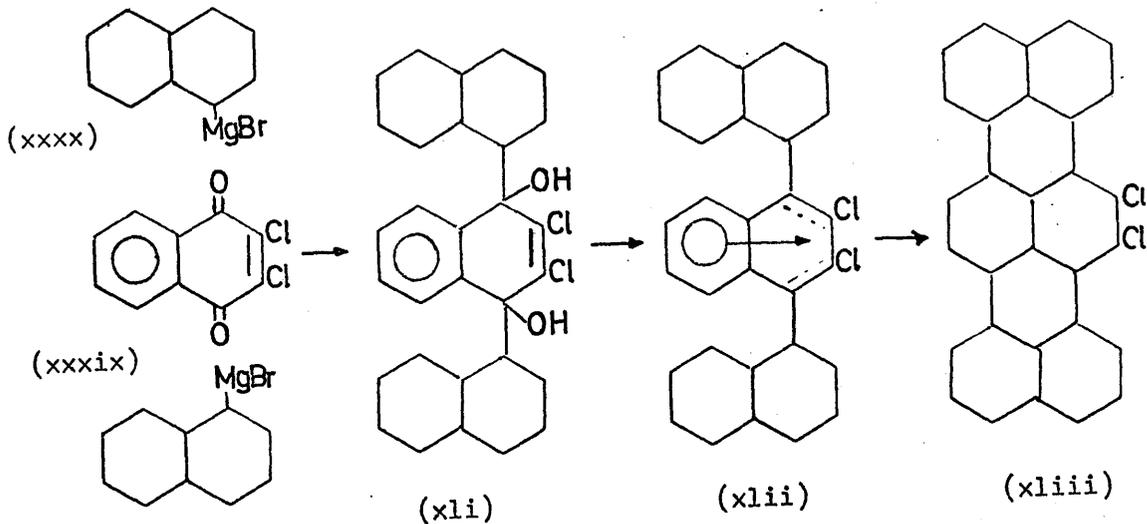
(xxxiv)



(iv')

$$\lambda_{\beta} = 3310 \xrightarrow{335} 3645 \quad \text{R}$$

$$\lambda_{\rho} = 4460 \xrightarrow{550} 5010 \quad \text{R}$$



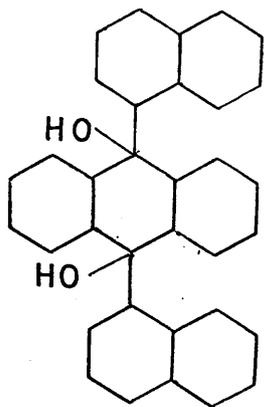
Comparison with 6,7:8,9-dibenzoterrylene<sup>20</sup> (xxxiv) shows that there can be no increase in the number of sextets<sup>2</sup> in passing from (xxxiv) to (iv!). The result is a large bathochromic shift of the  $\rho$  and  $\beta$  bands amounting to 550 & 335Å resp.

The above comparisons fully justify the presentation of the formulae with Robinson's aromatic sextet<sup>2</sup> which gives a clear insight into the electronic fine structure and the colour, reactivity and stability, only if applied in the strictest sense. It is also remarkable that the perylenes and terrylenes follow one another so closely in behaviour, which frequently can be predicted using Clar's aromatic sextet<sup>2</sup> and fixed double bond concepts<sup>13</sup>.

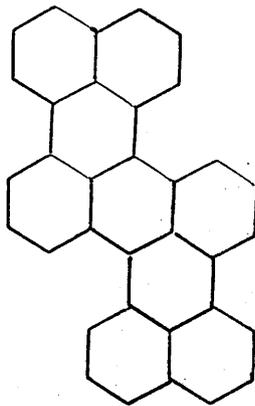
#### Experimental Discussion:

An examination of the various synthetic routes used in the syntheses of terrylene<sup>1</sup> (vii) and its known benzologues was undertaken. The general method used was sound and an analogous reaction sequence was employed to prepare dibenzoterrylene (i) and tribenzoterrylene (ii).

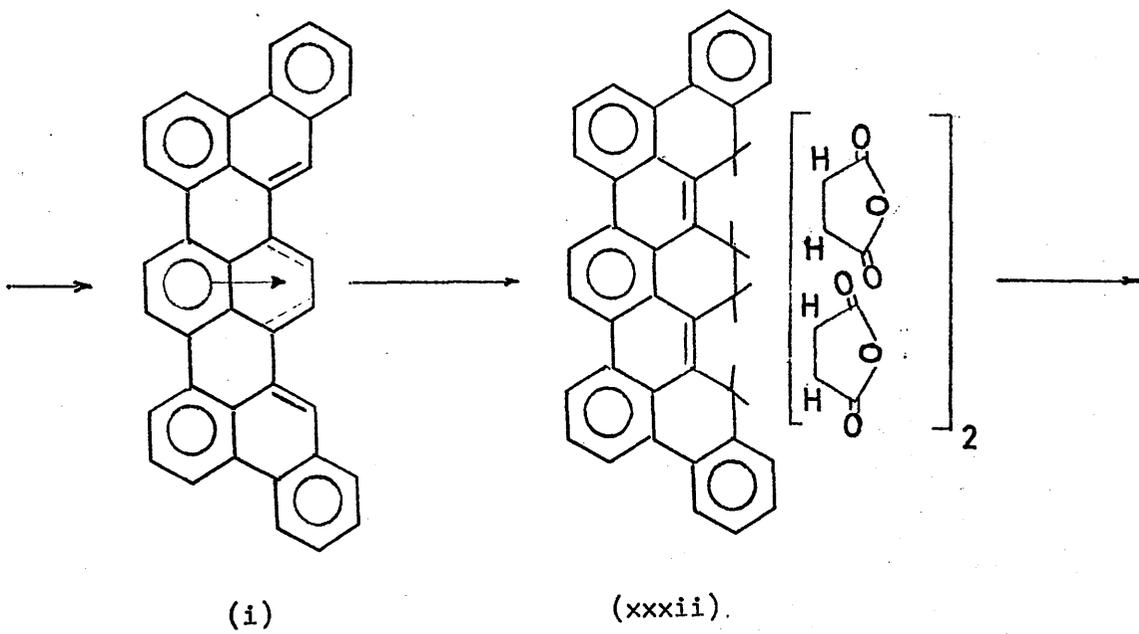
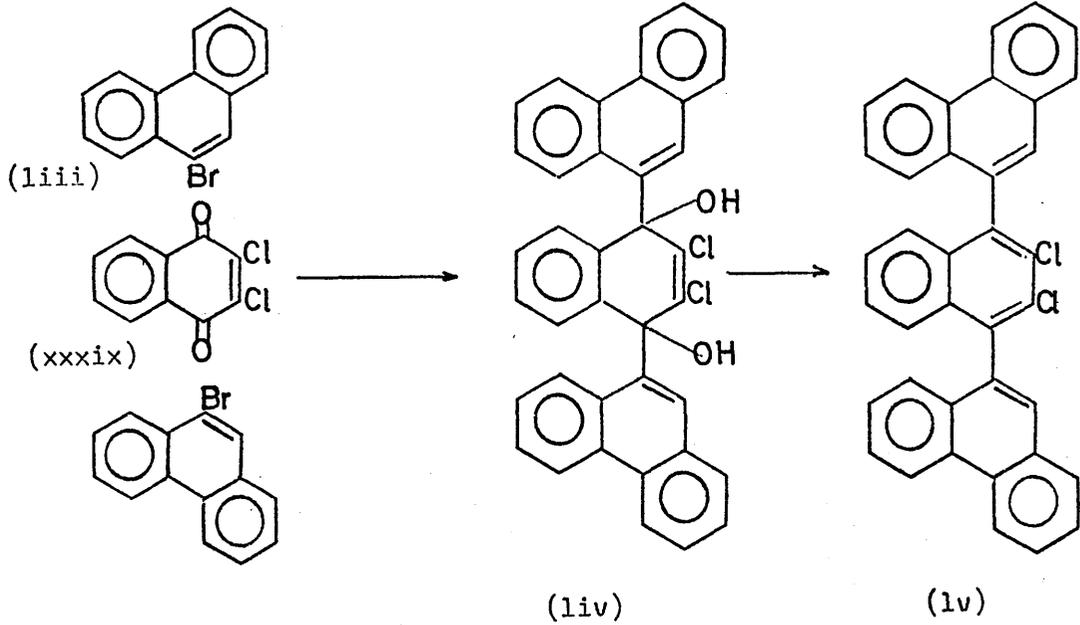
As shown opposite, both terrylene<sup>1</sup> (vii) and 7,8-benzoterrylene<sup>21</sup> (iil)



(1)



(1i)



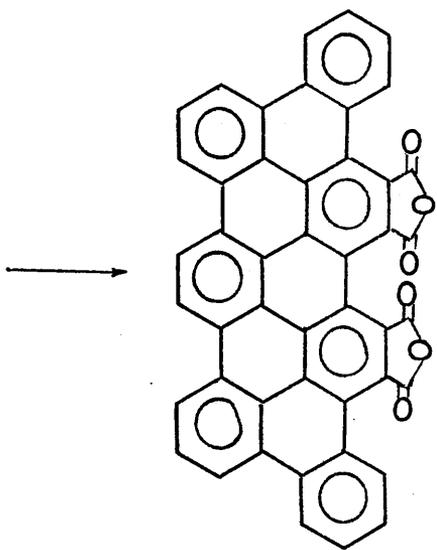
could be synthesised using the same general procedure i.e. initially a Grignard reaction involving a quinone with two 1-bromonaphthalene molecules.

The resultant diols (xli and xlvi) were then reduced to the dichloro compounds (xlii and xlvi resp.) with acetic acid and hydriodic acid<sup>23</sup>. Cyclisation of the dichloro compounds (xlii and xlvi) to terrylene<sup>1</sup> (vii) and benzoterrylene<sup>21</sup> (iil) was achieved by the use of a sodium chloride/aluminium chloride melt<sup>21</sup>.

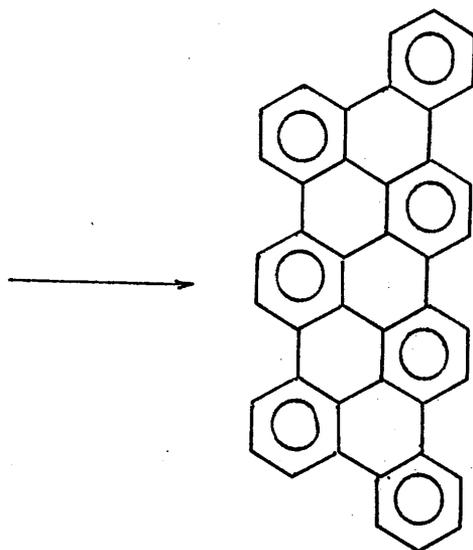
Benzoterrylene<sup>21</sup> (iil) could also be synthesised by starting from anthraquinone and 1-bromonaphthalene which yielded the diol (1). Cyclisation by a sodium chloride/aluminium chloride melt<sup>21</sup> yielded 7,8 - benzoterrylene (iil). No trace of the isomer 1,9:5,10-diperinaphthalene-anthracene<sup>21</sup> (li) was found.

It thus seemed promising to use a variation of these proved reaction routes outlined above for the preparation of dibenzoterrylene (i), tribenzoterrylene (ii) and their benzologues (iii and iv).

To this end, 2,3-dichloro-1,4-naphthoquinone (xxxix) was reacted with 9-bromophenanthrene (liii). The Grignard reaction gave a good yield of the dichloro-diol (liv). The diol (liv) was reduced, as were the



(xxxiii)

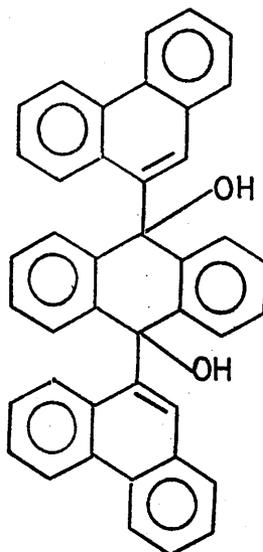
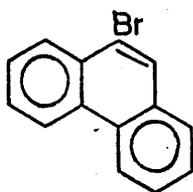
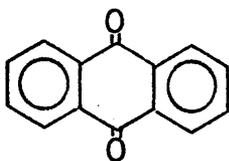


(iii)

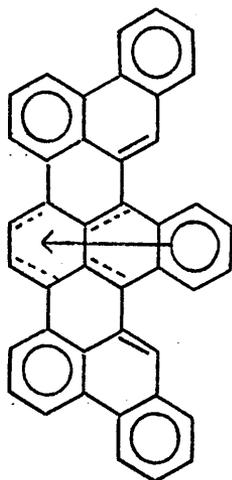
(liii)



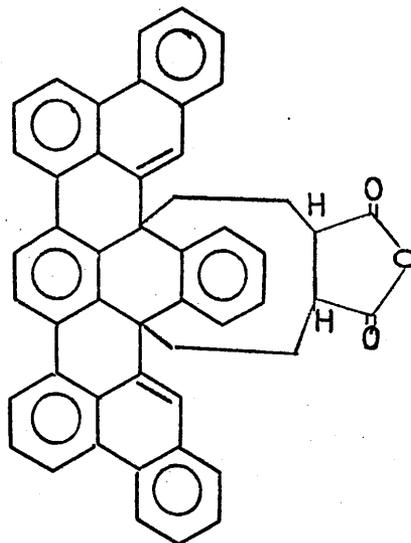
(xlv)



(lvii)



(ii)



(xx)

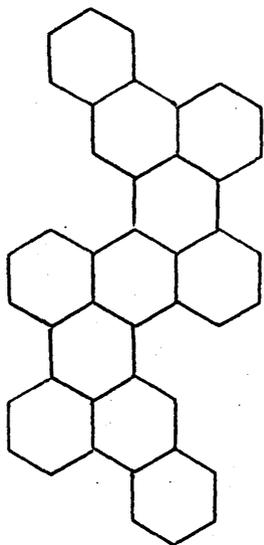
analogues (xliiii and xlvi) in the previous syntheses, with acetic acid and hydriodic acid<sup>22</sup>.

The dichloro compound (lv) was subjected to a melt of aluminium chloride/sodium chloride and zinc, the latter being added to help reduce the dichloroterrylene derivative to the hydrocarbon.

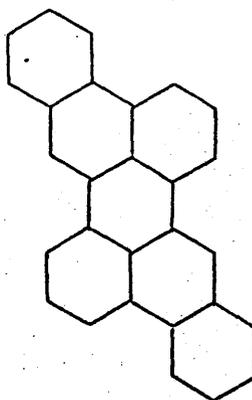
It was found that the best yield was obtained with a very short melt (1 min.). (In the terrylene<sup>1</sup> (vii) synthesis a melt of 5 min. duration was employed). During chromatographic elution, the expected cleavage product 2,3-benzoperylene<sup>23</sup> (xxxv) was characterised by its u.v. spectrum and m.pt. Further development of the column yielded dibenzoterrylene (i) which was identified by its u.v. spectrum and microanalysis.

The maleic anhydride reactions have already been discussed in the theoretical section and it is suffice to mention that the tetra-adduct when heated with soda lime yielded tetrabenzoterrylene (iii), which belongs to the condensed polyphenyl class<sup>18</sup> of hydrocarbons.

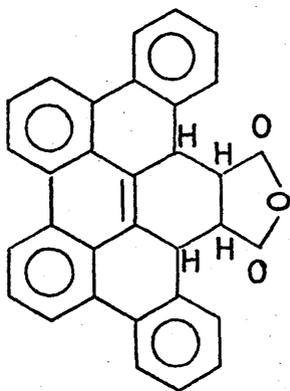
Tribenzoterrylene (.ii) was synthesised starting from anthraquinone (xlv) and 9-bromophenanthrene. The Grignard reaction gave a better yield of the diol (lvii) when the anthraquinone was thoroughly milled and the Grignard solution shaken for several days at room temp. The



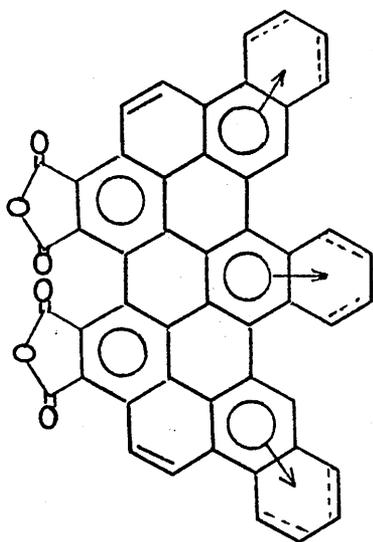
(lviii)



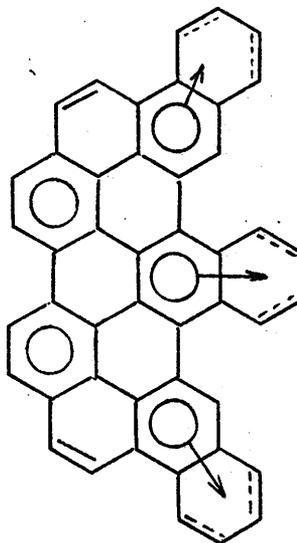
(lx)



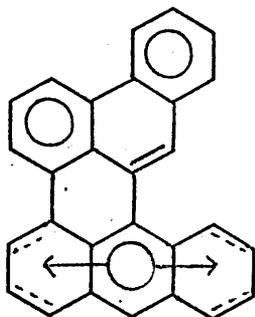
(lix)



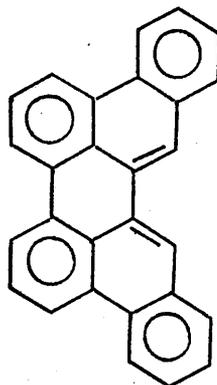
(xxxvii)



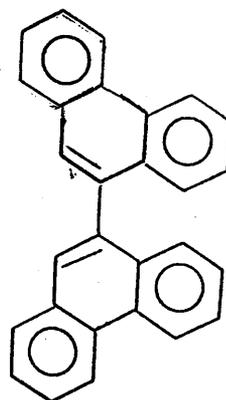
(iv)



(xxxvi)



(xiv)



(lxi)

resultant diol (lvii) was cyclised in a sodium chloride / aluminium chloride melt, yielding the hydrocarbon (ii). No trace of the isomer (lviii) was found, in agreement with the specificity also found in the benzoterrylene<sup>21</sup> cyclisation reaction.

Once again, discussion of the adducts has already been fully dealt with in the previous section. The di-adduct was decarboxylated using soda lime, yielding pentabenzoterrylene (iv). The expected cleavage product 1,2:10,11-dibenzoperylene<sup>9</sup> (xxxvi) was found during chromatographic purification of the product from the melt. It was readily identified by its u.v. spectrum and m.pt. When zinc dust was added to the melt the main cleavage product was 2,3:10,11-dibenzoperylene (xiv), which was also identified by its u.v., m.pt. and immediate reaction with maleic anhydride forming the relatively stable mono adduct<sup>18</sup> (lix), which breaks down on heating in high boiling solvents<sup>18</sup>.

It is noteworthy that dibenzoperylene (xiv) is not formed when phenanthrene is heated with aluminium chloride in benzene, but the other isomer 2,3:8,9-dibenzoperylene (lx) is obtained. Dibenzoterrylene (xiv)<sup>11</sup> is formed when 9,9'-diphenanthryl (lxi) is added to an aluminium / sodium chloride melt. This suggests that the mechanism must involve two mono phenanthryl radicals which form 9,9'-diphenanthryl (lxi) and then are cyclised, yielding 2,3:10,11-dibenzoperylene (xiv).

EXPERIMENTAL1,4-Di-(9'-phenanthryl)-1,4-dihydroxy-1,4-dihydro-2,3-dichloro-naphthalene (liv)

To a Grignard solution prepared from magnesium (35.5g), 9-bromophenanthrene (liii) (350g) and ether (500ml.), a suspension of 2,3-dichloro-1,4-naphthoquinone (xxxix) (54.6g) in benzene (150ml.) was gradually added. The mixture, which became green and eventually dark yellow, was refluxed for 4 hours. On decomposing the mixture with ice and acetic acid a precipitate was formed in the organic layer. This was filtered off and washed with water, ethanol and ether.

Yield 52g. Concentration of the organic layer yielded a further 15g of product and steam distillation of the mother liquor produced a residue of low m.pt., the u.v. spectrum of which closely resembled phenanthrene<sup>24</sup> (3450, 3380, 3290, 3230, 3150, 2950 Å)

The product was three times crystallised from xylene and dried at 120° for 48 hours. The almost colourless needles, m.pt. 335-38° decomp., dissolved in conc. sulphuric acid to give a dark yellow brown solution.

Found: C, 77.92 ; H, 4.30%

$C_{38}H_{24}O_2Cl_2$  requires C, 78.20 ; H, 4.14%

1,4-Di-(9'-phenanthryl)-2,3-dichloronaphthalene (lv)

A suspension of the diol (lv) (25g) in acetic acid (312ml.) was refluxed and stirred. Hydriodic acid (31.25ml., 55%) was introduced dropwise over a 20 min. period and the mixture refluxed for one hour. After cooling, the light brown precipitate was filtered off and washed with acetic acid, benzene and ether. Yield 18.4g. Recryst. from first nitrobenzene and then twice from xylene gave almost colourless prismatic crystals, m.pt.  $420^{\circ}$  decomp., which dissolved slowly in conc. sulphuric acid with a yellowish tinge.

Found: C, 82.9 ; H, 4.19%

$C_{38}H_{22}Cl_2$  requires C, 83.05 ; H, 4.03%

2,3:12,13-Dibenzoterrylene (i)

The dichloro compound (lv)(2g) and sodium chloride (1g) were powdered together and added to a melt of sodium chloride (3g), aluminium chloride(15g) and zinc dust (0.5g) at  $110^{\circ}$ . After stirring for one min. the mixture was decomposed with dilute hydrochloric acid. The precipitate was filtered off and washed with water. The zinc dust was dissolved in conc. hydrochloric acid and the reddish violet precipitate (1.9g) filtered off, washed with dilute hydrochloric acid

water and then ammonia. The product from 7 melts was dissolved in hot xylene and chromatographed on highly active alumina (600g). The column was eluted at 60° with hot xylene, and the first col. fraction contained 2,3-benzoperylene (xxxv), which was identified by its u.v. spectrum, m.pt. and colour in sulphuric acid<sup>25</sup>. The column was heated to 110° and concentration of the violet red eluate gave brownish red needles m.pt. 450°. In conc. sulphuric acid the hydrocarbon (i) dissolved to give a greenish blue solution which became blue on heating. The hydrocarbon (i) can be sublimed in vacuum.

Found: C, 95.81 ; H, 4.15%

$C_{38}H_{20}$  requires C, 95.80 ; H, 4.23%

#### Tetra-adduct with maleic anhydride (xxxii)

Dibenzoterrylene (i) (10mg) was powdered and added to refluxing maleic anhydride (300mg). Small portions of iodine were gradually introduced to the deep violet solution which turned brown. The mixture was refluxed for 2 hours always ensuring that the vapour contained excess iodine. The iodine and some maleic anhydride were distilled off, and on cooling acetone was added. The precipitate was filtered off and washed with acetone. Yield 9mg. The

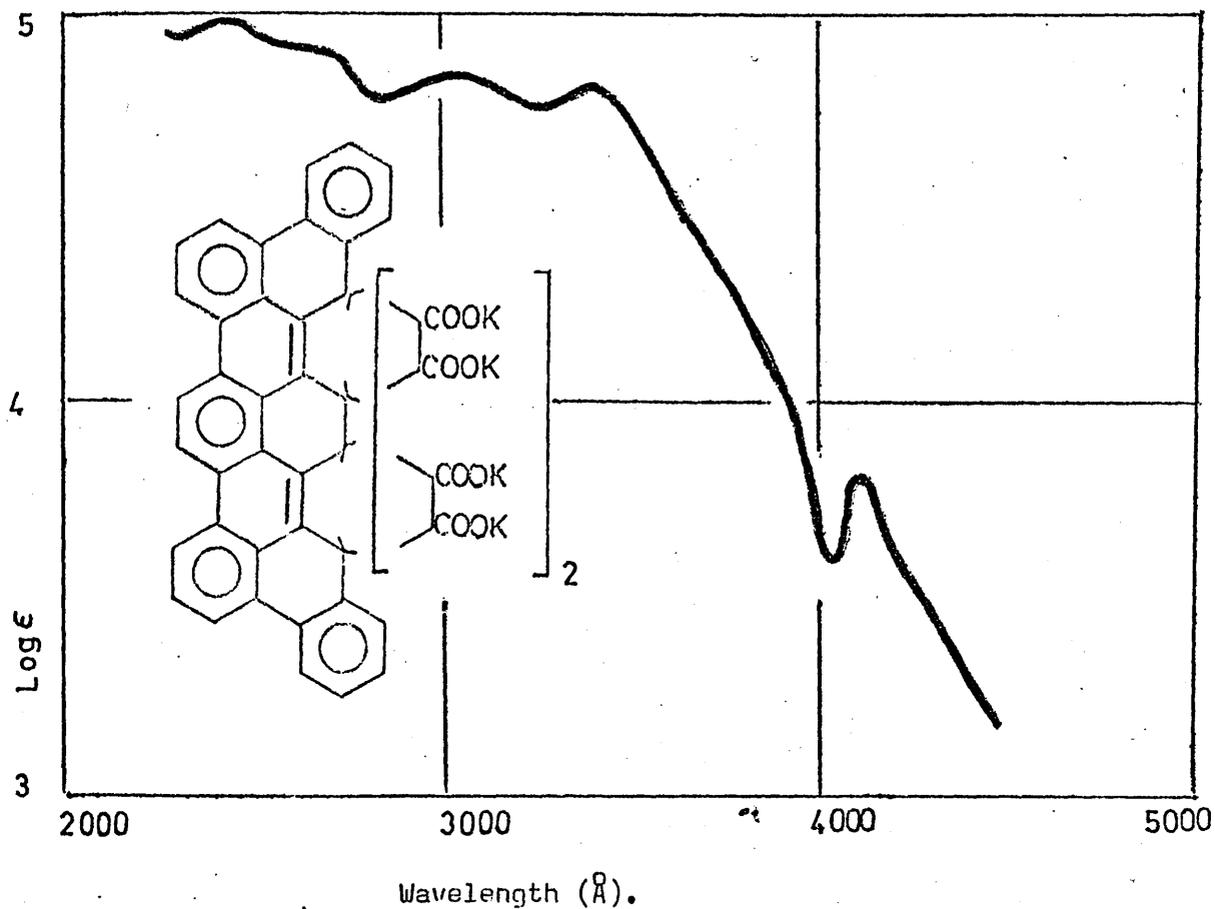


Fig. 4. Absorption maxima ( $\text{\AA}$ ) and log (in parentheses).

Tetra-adduct (xxxii) of dibenzoterrylene (i) in dil. KOH :  $\infty$ , 4100 (3.82) ; p, 3380 (4.82), 3080 (4.85) ;  $\beta$ , 2450 (4.99).

yellowish brown crystals, m.pt.420<sup>o</sup> decomp., dissolved in conc. sulphuric acid to give a colourless solution.

The spectrum is recorded in fig. 4.

Found: C, 74.37 ; H, 2.78%

$C_{52}H_{24}O_{12}$  requires C, 74.27 ; H, 2.87%

1,16:2,3:12,13:14,15-Tetrabenzoterrylene-1<sup>''</sup>,2<sup>''</sup>,1<sup>'''</sup>,2<sup>'''</sup>-tetracarboxylic-dianhydride (xxxiii).

The tetra-adduct (xxxii) was sublimed at 450<sup>o</sup>/4x10<sup>-4</sup> mm. An orange brown sublimate was obtained and refluxed in xylene for purification. It did not melt below 540<sup>o</sup>. The same dianhydride was also obtained by refluxing dibenzoterrylene (i), maleic anhydride and chloranil together for 3 hours. Although the spectrum in NaOH showed that the main constituent was the tetra acid derived from (iii), it was difficult to obtain an exact C,H analysis. From many experiments, it became obvious that there must be other acidic compounds present which influence the analytical data. However the spectrum showed only one aromatic complex, the same as is present in the parent hydrocarbon (ii).

Found: C, 83.80 ; H, 3.11%

$C_{46}H_{16}O_6$  requires C, 83.21 ; H, 2.42%

1,16:2,3:12,13:14,15-Tetrabenzoterrylene (iii)

The tetra adduct (xxxii) was powdered with soda lime and a drop of alcohol to ensure intimate contact of the particles. The mixt. was then heated to  $350^{\circ}$  under nitrogen for 1 hour, to remove alcohol and moisture. The sublimation was carried out at  $450-500^{\circ}/2 \times 10^{-4}$  mm and the orange yellow sublimate resublimed. Yield 15.1mg. The hydrocarbon (iii) does not melt below  $540^{\circ}$ , is insoluble in conc. sulphuric acid and almost insoluble in organic solvents. However, it can be recrystallised from boiling pyrene under nitrogen. When cooled slowly large yellow plates were obtained, which were filtered off after 1-methylnaphthalene was added in order to keep the pyrene in solution. The crystals were washed with hot xylene. In solid solution the hydrocarbon (iii) showed a yellow phosphorescence of very long life time.

Found: C, 96.23 ; H, 3.86%

$C_{42}H_{20}$  requires C, 96.12 ; H, 3.93%

9,10-Di-(9'-phenanthryl)-9,10-dihydroanthracene (lvii).

A very finely divided suspension of anthraquinone (39.6g) in benzene (150ml.) was prepared by shaking the mixture with glass balls

for 2 days. A Grignard solution obtained from 9-bromophenanthrene (liii) (200g) and magnesium (19.6g) was added to the above suspension, the mixture which changed from dark brown to light yellowish green was stirred and refluxed for 6 hours. Decomposition with acetic acid and ice yielded a precipitate from the organic layer which was filtered off and washed with acetic acid, water, ethanol and ether. The wet product was thoroughly treated with a sodium hydroxide/sodium hydrosulphite solution in order to remove the unreacted anthraquinone<sup>26</sup>. After five extractions, the filtrate was no longer red and the product showed no C=O absorption in the i.r. Yield 17.4g. When the conditions were changed by milling the Grignard solution with the anthraquinone for 3 days, the yield increased to 37.2g. The diol (lvii) was three times crystallised from xylene. It formed prisms, m.pt 420<sup>o</sup> decomp., which dissolved in conc. sulphuric acid to give a dark leaf green solution which became golden brown on heating.

Found: C, 89.6 ; H, 4.6%

$C_{42}H_{28}O_2$  requires C, 89.3 ; H, 5.0%

2,3:12,13:15,16-Tribenzoterrylene ( ii )

The diol (lvii) (3g) was powdered with sodium chloride (3g) and

added to a melt of sodium chloride (3g), aluminium chloride (24g) and two drops of pyridine<sup>27</sup>. The temperature was kept just below 110°. After stirring the melt for 1 min., it was decomposed with dilute hydrochloric acid, boiled, filtered and washed with water. The crude yield from four batches was 11.8g.

The crude dark blue hydrocarbon was added to boiling xylene, the solution boiled to remove moisture and chromatographed on highly active alumina (400g). The first coloured fraction contained 1,2:10,11-dibenzoperylene (xxxvi), which was formed as a cleavage product. It was obtained in a crystalline state and identified by its abs. spectrum, m.pt. etc. The column was heated to 110° and eluted with hot xylene. The blue solution yielded the hydrocarbon (ii) (2.19g) on concentration. Recrystallisation gave dark blue needles m.pt. 310°, which dissolved in conc. sulphuric acid to form a blue solution.

When zinc dust (0.5g) is added to the melt, the main cleavage product is 2,3:10,11-dibenzoperylene (xiv). It readily reacted with maleic anhydride to form the tetrahydro mono-adduct, which was identified by its u.v. absorption spectrum<sup>18</sup>.

The blue hydrocarbon can be sublimed in vacuum.

Found: C, 95.9 ; H, 4.2%

$C_{42}H_{22}$  requires C, 95.8 ; H, 4.2%

Endocyclic addition product with maleic anhydride (xxxv)

The hydrocarbon (.ii) (6mg) was added to refluxing maleic anhydride (200mg). The deep blue solution rapidly bleached and light yellow crystals began to separate. After refluxing for 1 min., acetic acid (10ml.) was introduced and the crystals filtered off, washed with acetic acid and acetone. Yield 2.2mg. Since the adduct tends to decay into its components, the crude product cannot be recryst. It was boiled with acetic acid in order to further purify. The prismatic crystals dissolved without colour in conc. sulphuric acid, which became light blue on standing, m.pt.  $240^{\circ}$  decomp.

Found: C, 86.78 ; H, 3.92%

$C_{46}H_{24}O_3$  requires C, 88.43 ; H, 3.87%

2,3:6,7:8,9:12,13:15,16-Pentabenzoterrylene-1".2",1'"'.2'"'-tetra-carboxylic-dianhydride (xxxvii)

Tribenzoterrylene (.ii) (560mg) was powdered with maleic anhydride (12g) and small crystals of iodine were added to the refluxing solution. It was refluxed for 1 hour, always ensuring an excess of iodine was visible in the vapour. Some maleic anhydride and the excess iodine were distilled off, the mixture cooled and acetic acid (20ml.) introduced. The precipitate was filtered off and washed

with acetic acid and acetone. Yield 536mg. The dark brown prisms m.pt.  $380^{\circ}$  decomp., dissolved in conc. sulphuric acid to form a green solution which became brown on heating.

Found: C, 83.86 ; H, 2.76%

$C_{50}H_{18}O_6$  requires C, 84.03 ; H, 2.53%

2,3:6,7:8,9:12,13:15,16-Pentabenzoterrylene (iv).

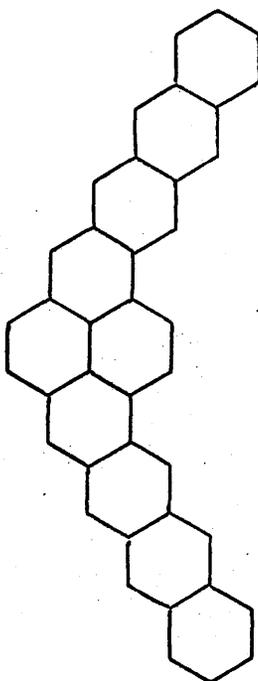
The dianhydride (xxxvii) (250mg) was powdered thoroughly with soda lime (1.3g) and two drops of ethanol added to aid contact of the particles. The mixture was therefore heated to  $350^{\circ}$  under nitrogen for 2 hours to remove humidity. Sublimation in vacuum gave a product which still contained some dianhydride (xxxvii). The mixture was thus powdered with KOH, a drop of ethanol added, and transferred to a boat. The mixture was covered with soda lime and sublimed at  $350^{\circ}/1 \times 10^{-4}$  mm. Dark reddish brown needles, m.pt.  $330^{\circ}$  were obtained which dissolved in conc. sulphuric acid with a slight violet colour only after standing for a few days.

Found: C, 96.0 ; H, 3.9%

$C_{46}H_{22}$  requires C, 96.1 ; H, 3.9%

CHAPTER III

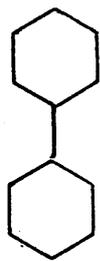
The synthesis and study of  
dianthraceno(2':3',3:4);(2":3",9:10)-  
pyrene.



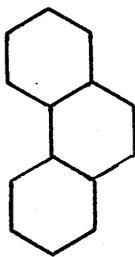
(i)

Introduction:

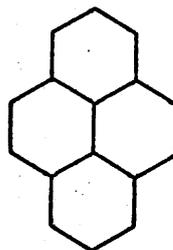
Dianthracenopyrene (i) was synthesised in order to study whether the the duality of conjugation<sup>1</sup> present in both 3,4:9,10-dibenzopyrene<sup>8</sup>(v)



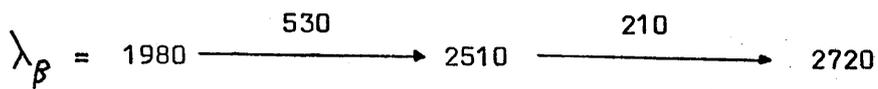
(ii)



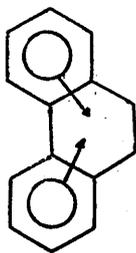
(iii)



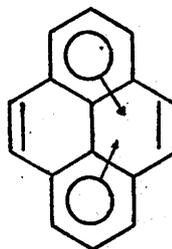
(iv)



A



(iii')



(iv')

and dinaphtho(2':3',3:4);(2":3",9:10)pyrene<sup>13</sup> (xi), was also evident in this higher benzologue.

### Discussion:

Pyrene (iv), which although a formally symmetric compound, exhibits electronic asymmetry<sup>2</sup>. This asymmetry can be readily demonstrated if pyrene (iv) is built up from diphenyl (ii) by the fusion of ethylenic bridges. The series is shown opposite ( ii - iv )

With the formation of phenanthrene (iii), there is a large bathochromic shift (530Å) and a much smaller red shift is observed in proceeding to pyrene (iv) (210Å). This asymmetric annellation effect<sup>3</sup> is not altogether surprising if the electronic structure of pyrene (iv) is more closely examined with regard to Clar's theories<sup>4</sup> involving Robinson's aromatic sextet<sup>6</sup>.

Pyrene has two inherent aromatic sextets<sup>5</sup>, with two pairs of mobile  $\pi$  electrons available for delocalisation and the formation of one induced sextet<sup>5</sup>. In phenanthrene (iii'), there are already two inherent sextets and one induced sextet<sup>16</sup>. The fusing of a second ethylenic bridge in going to pyrene (iv') does not result in the formation of either another sextet<sup>6</sup> or another induced benzenoid ring<sup>5</sup> and thus

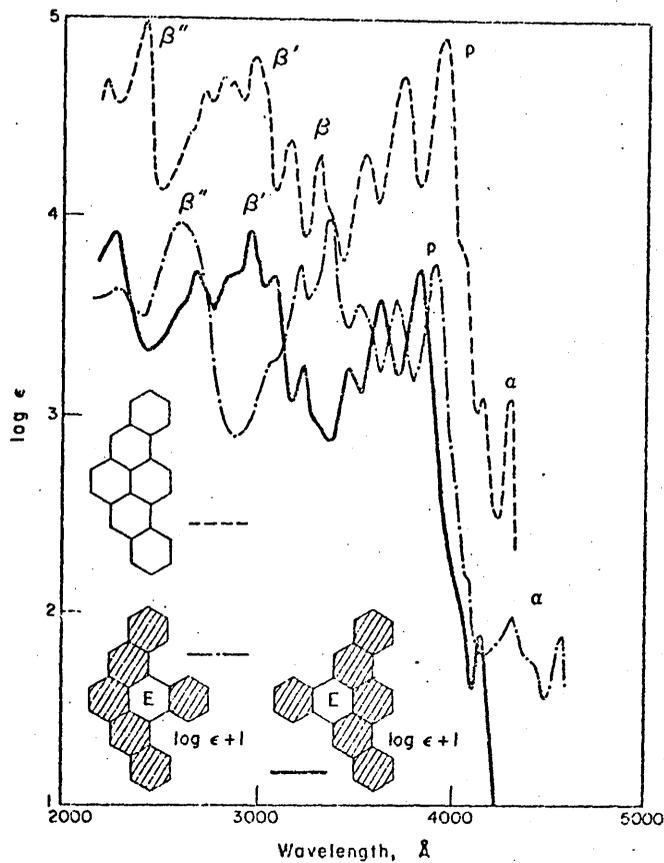
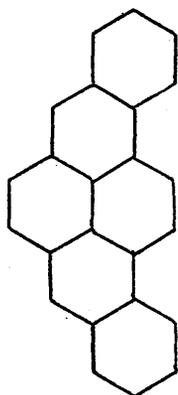


FIG. 1. Absorption spectra with max ( $\text{\AA}$ ) and  $\log \epsilon$  in parentheses.

----- 3,4:9,10-Dibenzopyrene in benzene:  $\alpha$ , 4330 (3.10), 4190 (3.10);  $p$ , 3970 (4.94), 3750 (4.74), 3565 (4.34);  $\beta$ , 3320 (4.32), 3170 (4.40);  $\beta'$ , 2970 (4.84), 2850 (4.70); in ethanol: 2720 (4.63);  $\beta''$ , 2420 (5.00), 2220 (4.70).

————— 1,2:4,5:8,9-Tribenzopyrene in cyclohexane:  $\alpha$ , 4180 (2.86);  $p$ , 3850 (4.76), 3640 (4.60), 3465 (4.24), 3230 (4.26), 3070 (4.70);  $\beta'$ , 2965 (4.94), 2850 (4.70); 2680 (4.73);  $\beta''$ , 2260 (4.92).

----- 1,2:3,4:9,10-Tribenzopyrene in ethanol:  $\alpha$ , 4610 (2.88), 4340 (2.98);  $p$ , 3930 (4.78), 3730 (4.58), 3540 (4.56);  $\beta$ , 3375 (5.00), 3220 (4.76);  $\beta'$ , 2600 (4.96), 2290 (4.62).

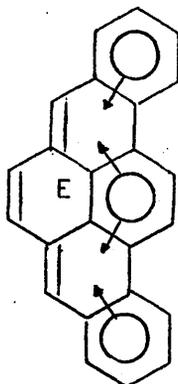


(v)

$$\lambda_{\beta} = 3320$$

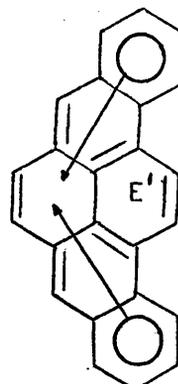
$$\lambda_{\beta'} = 2970$$

0  
A  
A



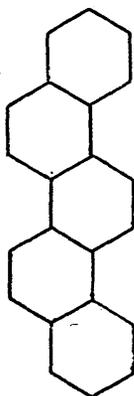
(va)

' Picene '



(vb)

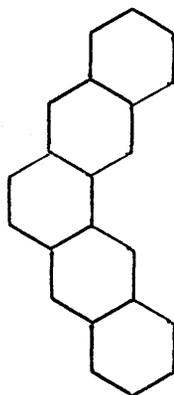
' Phene '



(vi)

$$\lambda_{\beta} = 2870$$

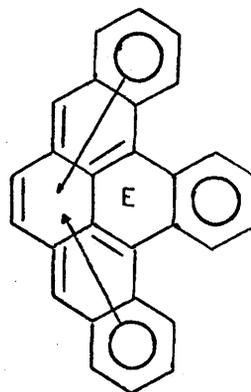
Picene



(vii)

3160

Pentaphene



(viii)

3375

A

affects the conjugation to a much lesser extent as is demonstrated by the u.v. absorption values.

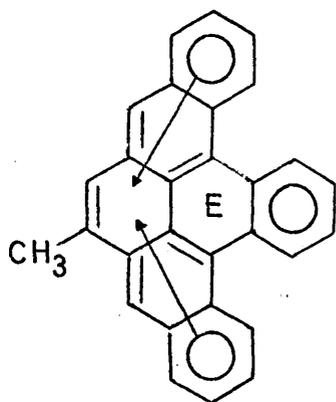
That this asymmetry is an inherent property of pyrene (iv) is readily confirmed by examining its benzologues<sup>7</sup>. Dibenzopyrene<sup>8</sup> (v) might be expected to have two types of conjugation (va) and (vb) corresponding to a picene and phenanthrene type electronic arrangement resp.

The  $\beta$  band of picene<sup>10</sup> (vi) (2870Å) is very close to the  $\beta'$  band of dibenzopyrene<sup>8</sup> (v) (2970Å), the difference of 100Å can be readily attributed to the formation of the 'empty' ring E<sup>7</sup>.

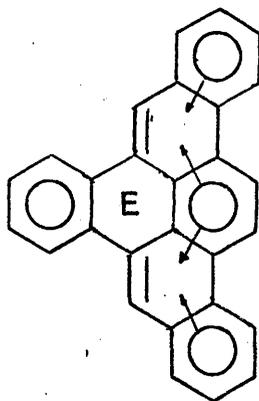
The  $\beta$  band of pentaphene<sup>9</sup> (vii) (3160Å) is comparable with the  $\beta$  band of dibenzopyrene<sup>8</sup> (v) (3320Å), the difference (160Å) once again can be accounted for by the formation of an 'empty' ring E<sup>7</sup>.

By the fusing of rings at the 1,2 or 6,7 positions in dibenzopyrene<sup>8</sup> (v), either the pentaphene<sup>9</sup> or picene<sup>10</sup> moieties can be made to dominate the spectra<sup>7</sup> (see fig. 1)

With 1,2:3,4:9,10-tribenzopyrene<sup>11</sup> (viii), the ring fused at the 1,2 positions results in another sextet<sup>6</sup> being formed as well as an 'empty' ring E, which cuts off conjugation with the third sextet<sup>7</sup>. The  $\beta$  band

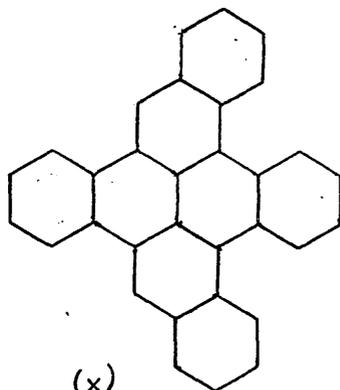


(viiiia)



(ix)

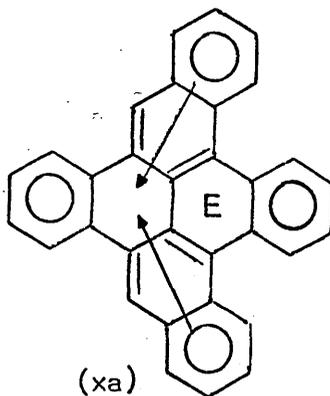
$$\lambda_{\beta} = 2965 \text{ \AA}$$



(x)

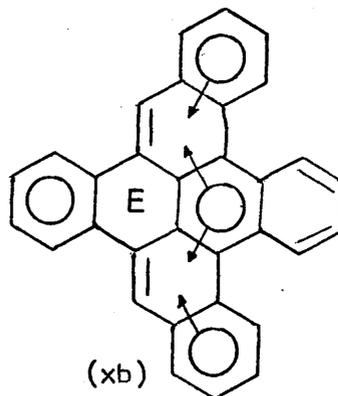
$$\lambda_{\beta} = 3360$$

$$\lambda_{\beta'} = 2920$$



(xa)

$$3360$$

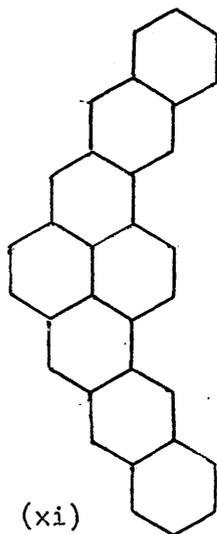


(xb)

$$2920$$

\AA

\AA



(xi)

$$\lambda_{\beta} = 4030 \text{ \AA}$$

$$\lambda_{\beta'} = 3655 \text{ \AA}$$

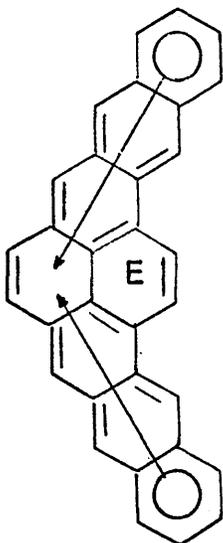
is at  $3375\text{\AA}$  and there is no trace of a  $\beta$  band in the  $2900\text{\AA}$  region, the spectra is thus that of a 'pure' pentaphene type<sup>9</sup>. The N.M.R. spectrum of 6-methyl-tribenzopyrene<sup>7</sup>(viii) shows a methyl doublet of 1.1Hz. in accordance with the fixed double bond at that position in the phenes.

Conversly, when tribenzopyrene<sup>12</sup>(ix) was examined, it was found to have a  $\beta$  band at  $2965\text{\AA}$  corresponding to a 'pure' picene type electronic arrangement, and no  $\beta$  band at longer wavelength related to a phene type conjugation<sup>7</sup>.

Thus one electronic arrangement can be made to dominate by the fusing of a ring to the fixed double bond of the 'empty' ring 'E' as in (viii) or (ix). (See fig. 1)

When 1,2:3,4:6,7:9,10-tetrabenzopyrene<sup>7</sup>(x) was studied, it had the duality character<sup>1</sup> once again as had been exhibited by dibenzopyrene<sup>8</sup>(v). The  $\beta$  band of tetrabenzopyrene<sup>7</sup>(x) was at  $3360\text{\AA}$  and the  $\beta'$  band at  $2920\text{\AA}$  corresponding to the  $\pi$  electronic distribution of the phene (xa) and picene (xb) type.

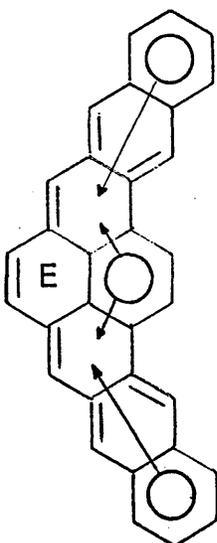
In dinaphthopyrene<sup>13</sup>(xi), the duality character<sup>1</sup> was found to be present. Dinaphthopyrene<sup>13</sup>(xi) could be expected to have two main



(xia)

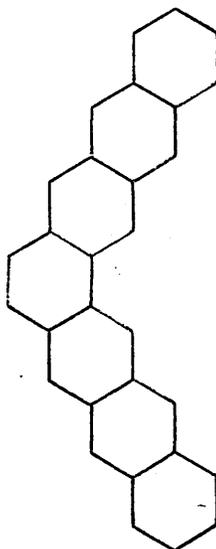
$\lambda_{\beta} = 4030$

$\lambda_{\beta'} =$



(xib)

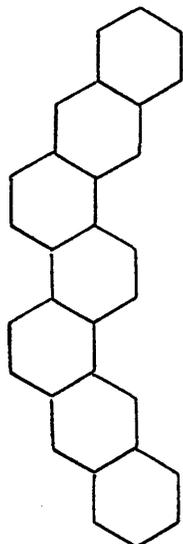
3655



(xii)

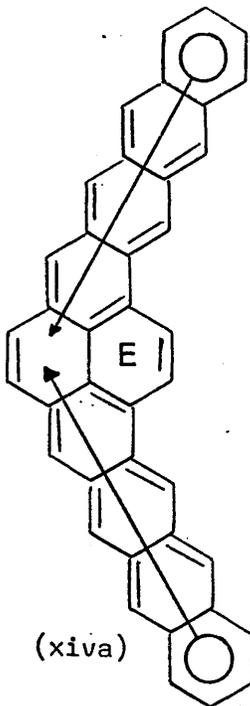
3910

Å  
Å

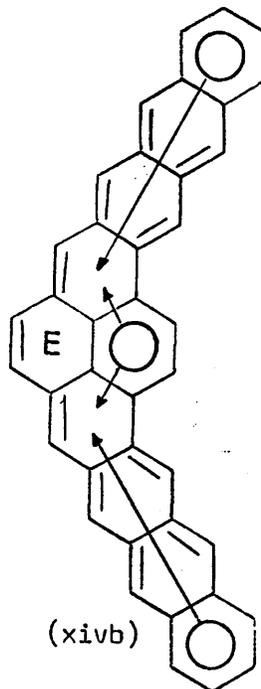


(xiii)

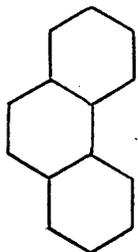
$\lambda_{\beta} = 3450 \text{ Å}$



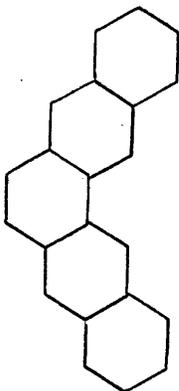
(xiva)



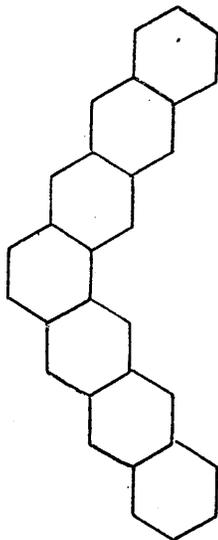
(xivb)



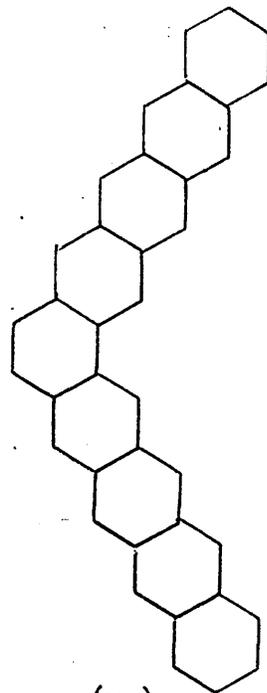
(iii)



(vii)



(xii)

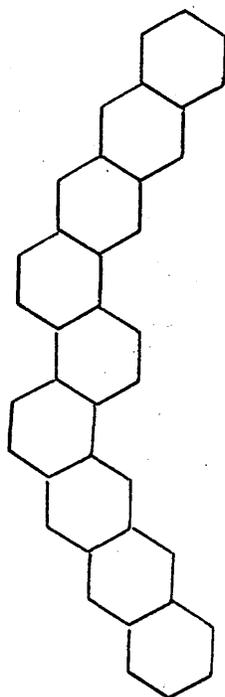


(xv)

$$\lambda_{\beta} = 2510 \xrightarrow{635} 3145 \xrightarrow{765} 3910$$

calc. 4719 Å

$$\sqrt{\lambda_{\beta}} = 50.10 \xrightarrow{6.02} 56.12 \xrightarrow{6.41} 62.53 \text{ \AA}$$



(xvi)

(xivb)

types of conjugation related to a phene and picene type electronic distribution, (xia) and (xib) resp. The  $\beta$  bands of the corresponding heptaphene<sup>14</sup>(xii) and 2,3:8,9-dibenzopicene<sup>14</sup>(xiii) are 3910Å and 3450Å resp., the values found for the  $\beta$  band (4030Å) and  $\beta'$  band (3655Å) of dinaphthopyrene<sup>13</sup>(xi) are in very close proximity to the 'pure' conj. values of each type. The deviations are readily accountable for by the fusing of two single bonds of the ethylenic bridge to form the pyrene parent compound.

Dianthracenopyrene(i) was synthesised in order to study whether this duality<sup>1</sup> of conjugation would be present in a higher benzologue of pyrene. If this duality<sup>1</sup> were present, then  $\beta$  bands related to the phene (xiva) and the picene (xivb) type would be expected.

As neither of the parent compounds, nonaphene (xv) and dinaphtho(2':3',2:3);(2":3",8:9)picene (xvi) have been synthesised, the approximate wavelength of their  $\beta$  bands is obtained using the Annellation Principle<sup>15</sup>.

In the first example the phene series is examined (iii-xii). The average difference is  $6.2\sqrt{\text{Å}}$  between the members of the series and thus the wavelength of nonaphene(xv) would be expected to be  $68.73\sqrt{\text{Å}}$  or 4719Å.

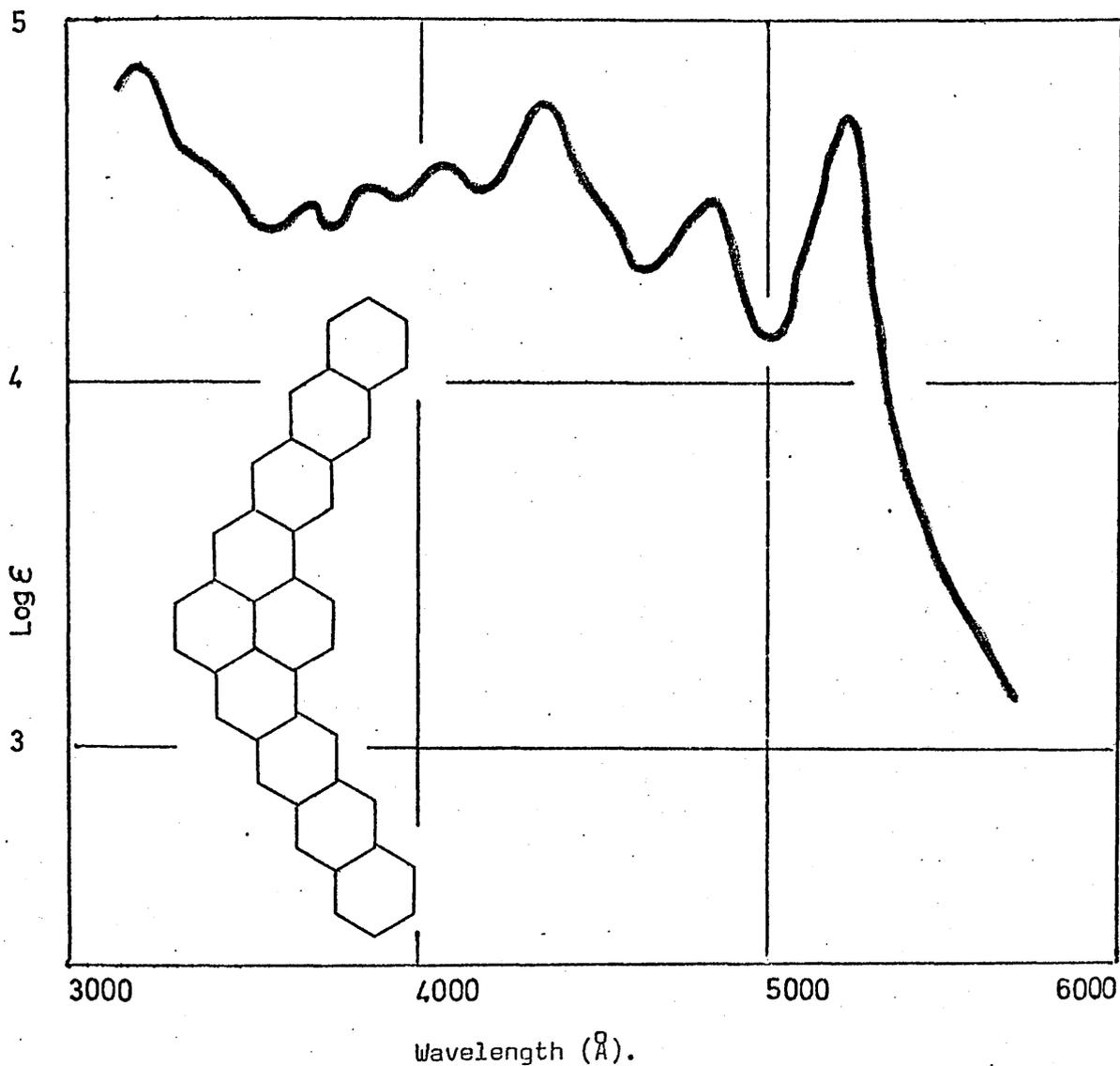
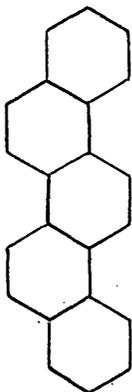
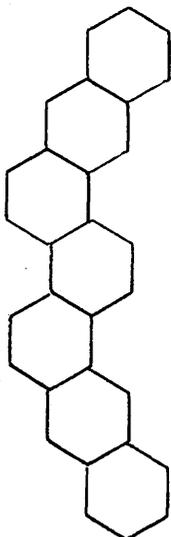


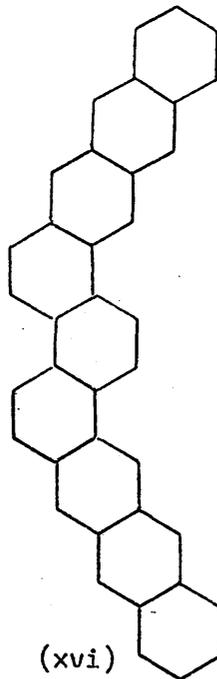
Fig. 2. Absorption maxima ( $\text{\AA}$ ) and  $\log \epsilon$  ( in parentheses ).  
 Dianthraceno(2':3',3:4);(2'':3'',9:10)pyrene (i) in trichlorobenzene:  
 p, 5230 (4.74), 4830 (4.51) ;  $\beta$ , 4350 (4.78), 4060 (4.6), 3860 (4.53),  
 3680 (4.49).



(vi)



(xiii)

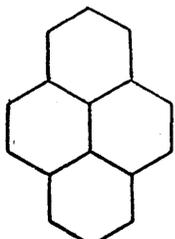


(xvi)

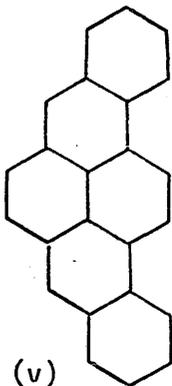
$$\lambda_{\beta} = 2870 \xrightarrow{580} 3450$$

$$\sqrt{\lambda_{\beta}} = 53.57 \xrightarrow{5.17} 58.74/\text{\AA}$$

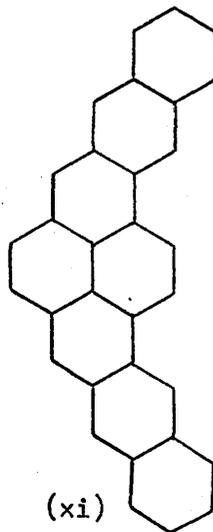
calc. 4085 \text{\AA}



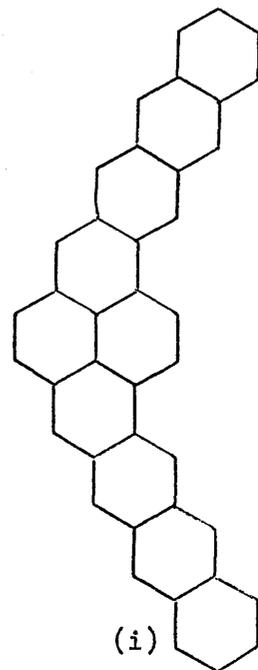
(iv)



(v)



(xi)



(i)

$$\lambda_{\beta} = 2720 \xrightarrow{5.47} 3320 \xrightarrow{5.86} 4030 \text{\AA}$$

$$\sqrt{\lambda_{\beta}} = 52.15 \xrightarrow{5.47} 57.62 \xrightarrow{5.86} 63.48 \sqrt{\text{\AA}}$$

$$\lambda_{\beta'} = 2410 \xrightarrow{5.41} 2970 \xrightarrow{5.17} 3655 \text{\AA}$$

$$\sqrt{\lambda_{\beta'}} = 49.09 \xrightarrow{5.41} 54.50 \xrightarrow{5.17} 59.67 \sqrt{\text{\AA}}$$

calc.  $\beta$  = 4779 \text{\AA}

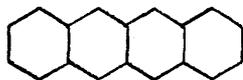
calc.  $\beta'$  = 4219 \text{\AA}

For the picene series (vi-xvi), the expected wavelength of a dinaphthopicene (xvi) would be  $63.91\sqrt{\text{\AA}}$  or  $4085\text{\AA}$ . However obviously the system is neither a pure picene nor phene type as an ethylenic bridge is present which must affect the conjugation, as in dibenzopyrene<sup>8</sup>(v) and dinaphthopyrene<sup>13</sup>(xi), shifting the  $\beta$  bands of dianthracenopyrene bathochromically. The values obtained serve as a good guide to the expected values if dianthracenopyrene (i) were to possess this duality character<sup>1</sup>.

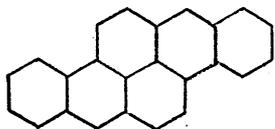
The annellation effect<sup>15</sup> was also examined with regard to the pyrene series as shown (iv-i). For the phene type conjugation (xiva), a  $\beta$  band at  $69.14\sqrt{\text{\AA}}$  or  $4779\text{\AA}$  would be expected, and for the picene type (xivb) a  $\beta$  band at  $64.96\sqrt{\text{\AA}}$  or  $4219\text{\AA}$ . Once again, this is a legitimate use of the annellation principle<sup>15</sup>, as the annellation does not produce any new sextets<sup>6</sup> and thus must extend the conjugation in a regular manner.

Dianthracenopyrene (i) was found to have only one  $\beta$  band - at  $4350\text{\AA}$  (in tcb) in close proximity to the expected value for the picene type arrangement (xivb) ( $4219\text{\AA}$ ). There is no  $\beta$  band present at greater wavelength than  $4350\text{\AA}$ . (See fig. 2)

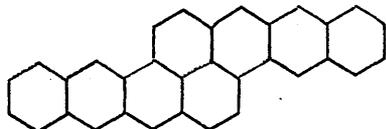
Thus in this case the picene type conjugation dominates. The picene



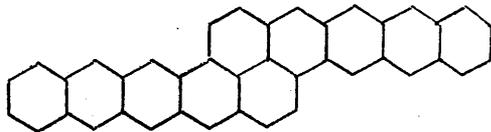
(xvii)



(xviii)



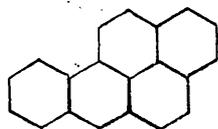
(xix)



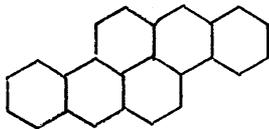
(xx)

$\lambda_{\beta} =$	3135			3530
$\sqrt{\lambda_{\beta}} =$	55.99	— 3.42 —>		59.41
$\lambda_{\rho'} =$	4510			5820
$\sqrt{\lambda_{\rho'}} =$	67.16	— 9.13 —>		76.29
$\lambda_{\rho''} =$	4240			5390
$\sqrt{\lambda_{\rho''}} =$	65.12	— 8.30 —>		73.42
$\lambda_{\rho'''} =$	4010			4990
$\sqrt{\lambda_{\rho'''}} =$	63.32	— 7.32 —>		70.64
$\lambda_{\rho''''} =$	3790			4660
$\sqrt{\lambda_{\rho''''}} =$	61.56	— 6.70 —>		68.26

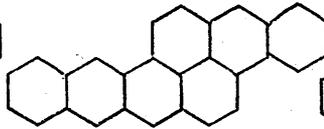
calc.	3949 Å
calc.	62.83√Å
calc.	7298 Å
calc.	85.42√Å
calc.	6676 Å
calc.	81.72√Å
calc.	6078 Å
calc.	77.96√Å
calc.	5620 Å
calc.	74.96√Å



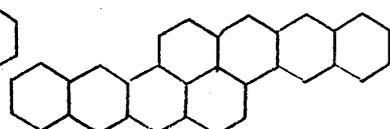
(xxi)



(xviii)



(xxiii)



(xix)

$\lambda_{\rho'} =$	3845		4510		5160		5760	Å
$\sqrt{\lambda_{\rho'}} =$	62.01	— 5.15 —>	67.16	— 4.67 —>	71.83	— 4.07 —>	75.90	√Å

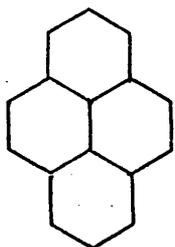
Wavelength of the first  $\rho$  band.

electronic distribution has three inherent aromatic sextets<sup>6</sup>, whilst the phene arrangement has only two sextets<sup>6</sup> and thus less stable.<sup>16</sup>

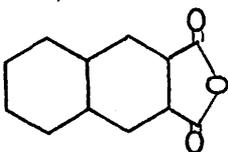
In nonaphene (xv), the sextets<sup>6</sup> are considerably diluted, giving the molecule a reactive character similar to a higher acene such as tetracene<sup>17</sup>(xvii). In sharp contrast to this, the sextets<sup>6</sup> in dinaphthopicene (xvi) are much less diluted, giving the molecule a less reactive electronic distribution.

Thus the picene arrangement(xivb) dominates in order to lower the reactivity of the molecule and thus the duality<sup>1</sup> character present in both dibenzopyrene<sup>8</sup>(v) and dinaphthopyrene<sup>13</sup>(xi) is no longer evident in this higher benzologue.

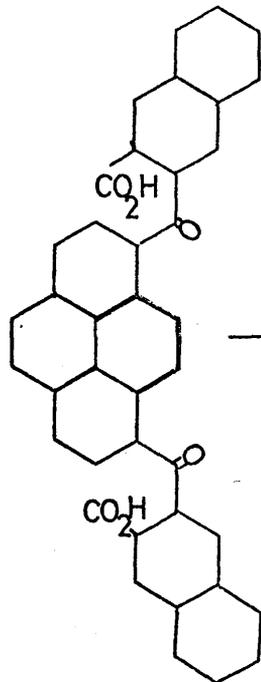
For the centrosymmetric isomer (xx), the expected wavelengths of the  $\beta$  and  $\rho$  bands were calculated using the Annellation Principle<sup>15</sup>, as shown opposite (xviii-xx). As the difference between each member of the series(xxi-xix) is actually decreasing<sup>23</sup>, the values obtained would be slightly greater than the actual values. This information regarding the expected wavelength of the centrosymmetric isomer was to prove invaluable in the final stages of purification of (i).



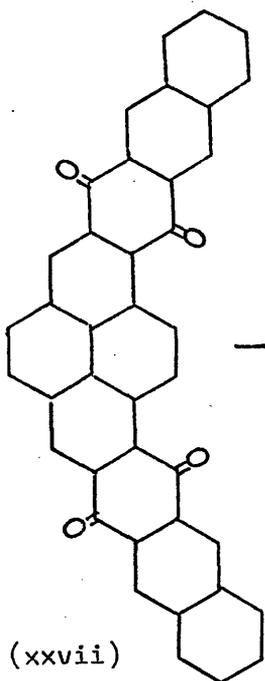
(iv)



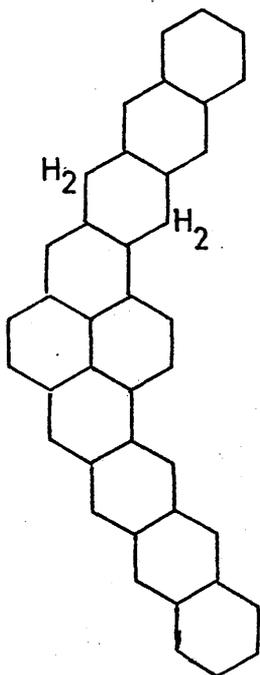
(xxv)



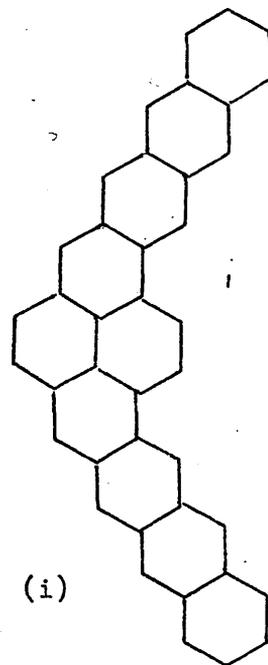
(xxvi)



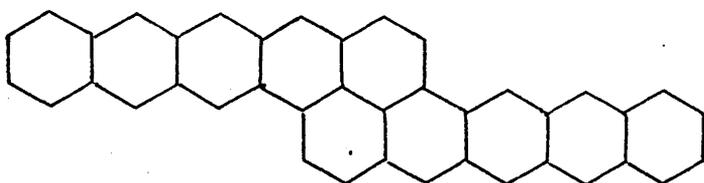
(xxvii)



(xxviii)



(i)



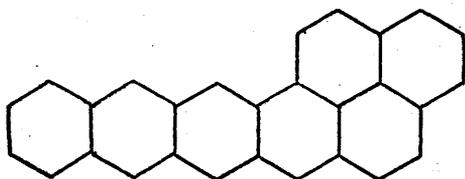
(xx)

### Experimental Discussion:

The reactions of pyrene(iv) with anhydrides and aluminium chloride have been studied closely by various workers<sup>13,18,19,20</sup>. Vollmann et al<sup>18</sup> found that pyrene condensed with phthalic anhydride in a melt of aluminium chloride / sodium chloride at 150-60<sup>o</sup>. A small yield of the diphthaloyl isomers was obtained. Scholl, Meyer and Donat<sup>20</sup> found that when the carbon disulphide solvent of previous condensation reactions<sup>21</sup>, involving pyrene and benzoyl chloride, was replaced with benzene, toluene, chlorobenzene or sym. tetrachloroethane good yields of the dibenzoyl isomers were obtained. No trace of a tribenzoyl isomer, reported with carbon disulphide<sup>21</sup>, was found with these other solvents<sup>20</sup>.

It was decided to synthesise dianthracenopyrene (i) by condensing pyrene with two molecules of 2,3-naphthalene dicarboxylic acid anhydride (xxv) in the presence of aluminium chloride. The reaction proceeded smoothly using sym. tetrachloroethane as solvent.

A mixture of the two isomers was obtained, the 3,10 and the 3,8. In the diagram outlining the reaction route only the 3,10 isomer will be shown (xxvi). The 3,10 dicarboxylic acid (xxvi) was refluxed in



(xxviiiia)

benzoyl chloride with a few drops of conc. sulphuric acid present. This cyclisation technique has been employed in similar cyclisation reactions with aroyl acids<sup>13</sup>. The i.r. spectrum showed only one carbonyl absorption band at  $1665\text{cm}^{-1}$ , the acid carbonyl band at  $1690\text{cm}^{-1}$  being no longer present in the reaction product.

The diquinone (xxvii) was reduced using pyridine / acetic acid and zinc dust, a mild technique which has proved to be extremely useful in reducing quinones<sup>22</sup>. The absorption spectrum of the reduced quinone (xxviii) in xylene (1- 3235, 2- 3450, 4- 3600, 3- 3795, 8- 4400, 9- 4695, 6- 5030, 5- 5400 $\text{\AA}$ ) has a very close relationship to that of naphtho(1':7',2:14)pentacene<sup>23</sup> (xxviiiia) in benzene (3250/5.15, 3440/4.06, 3630/4.33, 3820/4.65, 4430/3.25, 4720/3.65, 5040/4.60, 5410 $\text{\AA}$  4.15). The absorption value is given after the wavelength as a  $\log \epsilon$  value. The analytical data indicated that the reduced quinone was a dihydro derivative of (i) confirming the spectral results.

The 1',4'-dihydro-dianthraceno(2':3',3:4);(2":3",9:10)pyrene (xxviii) was sublimed over copper powder at  $400^{\circ}$ . The spectrum of the dark reddish brown prismatic sublimate indicated that there were traces of the centrosymmetrical isomer (xx) present-- from the bands at 6650, 6035 and 5530 $\text{\AA}$  (see theoretical discussion). There was no indication

in the u.v. absorption spectrum that the dihydro compound was also present (xxviii). As the centrosymmetric pyrenes are known to have acene character<sup>23</sup> and thus react fairly readily with maleic anhydride, it was decided to purify dianthracenopyrene by making use of this property.

The hydrocarbon was crystallised repeatedly from diphenyl / diphenylene oxide and traces of maleic anhydride. The crystals formed were extracted with alkali, yielding a pure sample of dianthracenopyrene (i), the spectrum of which is recorded in fig. 2.

EXPERIMENTAL

3,10-Di(3'-carboxy-2'-naphthoyl)pyrene (xxvi) and 3,8-di(3'-carboxy-2'-naphthoyl)pyrene.

Pyrene (iv) (15g) and naphthalene-2:3-dicarboxylic anhydride (xxv) (35g) were melted together and after cooling slightly, tetrachloroethane (50ml.) added. Then aluminium chloride was introduced portionwise to the mixture at 50°, a total of 34g was used. The mixture was heated with stirring for one hour at 80°.

The dark brown mixture was decomposed with dilute hydrochloric acid, the tetrachloroethane steam distilled and the resinous brown product extracted with glacial acetic acid. The hot solution deposited yellowish orange crystals which were filtered hot and washed with acetic acid and ether. Yield 14.6g. A small quantity was recryst. twice from nitrobenzene, once from acetic acid and dried at 200° for 48 hours, m.pt. 315°. In conc. sulphuric acid, it formed a brown solution becoming bluish green on heating.  $\nu$  <sup>KBr</sup> = 1690cm.<sup>-1</sup> (C=O acid), 1660cm.<sup>-1</sup> (C=O diaryl ketone).

Found: C, 80.3 ; H, 3.7%

C<sub>40</sub>H<sub>22</sub>O<sub>6</sub> requires C, 80.6 ; H, 3.4%

Dianthraceno(2':3',3:4);(2":3",9:10)pyrene(1':4',1":4")diquinone (xxvii)  
and dianthraceno(2':3',3:4);(2":3",8:9)pyrene(1':4',1":4")diquinone.

The diacid (xxvi) (7.5g) was refluxed in benzoyl chloride (70ml.) then 7 drops of conc. sulphuric acid were added and the mixture refluxed for 20 min. The colour changed from light green to dark green during the reaction. Whilst still hot, yellowish coloured crystals were deposited, which were filtered off and washed with hot nitrobenzene and ether. Yield 1.5g, a further 3g were obtained on cooling.

The product was extracted with dilute sodium hydroxide solution and recrystallised from nitrobenzene. A small amount was sublimed, recrystallised from nitrobenzene, acetic acid and dried at 160<sup>o</sup> for 48 hours, m.pt 280-3<sup>o</sup>. In conc. sulphuric acid it formed a dark leaf green solution which became bluish green on heating.

In sodium hydroxide / sodium dithionite solution a dark wine coloured vat was formed.  $\nu_{\text{max}}^{\text{KBr}} = 1665\text{cm}^{-1}$  (C=O diaryl ketone)

Found: C, 85.1 ; H, 3.34%

$\text{C}_{40}\text{H}_{18}\text{O}_4$  requires C, 85.4 ; H, 3.23%

1',4'-Dihydro-dianthraceno(2':3',3:4);(2'':3'',9:10)pyrene (xxviii)

and 1',4'-dihydro-dianthraceno(2':3',3:4);(2'':3'',8:9)pyrene.

The diquinone (2.5g), zinc dust (6.5g) and pyridine (60ml.) were refluxed together for 5 hours. During this period acetic acid (25ml., 80%) was introduced dropwise. The colour of the mixture changed from dark reddish brown to cherry red.

The mixture was filtered hot, the residue washed with hot pyridine and treated with conc. hydrochloric acid to decompose the zinc dust. It was filtered, the residue washed with water and dil. ammonia (to remove any zinc chloride present which could destroy the hydrocarbon during sublimation). Yield 1g. The dihydro compound was sublimed at  $2 \times 10^{-3}$  mm /  $450^{\circ}$ , m.pt.  $420^{\circ}$ . In conc. sulphuric acid it formed a yellowish brown solution becoming brownish violet on heating. There was no carbonyl absorption in the i.r. at  $1660\text{cm.}^{-1}$ . The u.v. spectrum in xylene had bands at 1)-3230, 2)-3450, 3)-3795, 4)-4050, 7)-4685, 6)-5030, 5)-5405 Å.

Found: C, 95.01 ; H, 4.84%

$\text{C}_{40}\text{H}_{24}$  requires C, 95.2 ; H, 4.79%

Dianthraceno(2':3',3:4);(2'':3'',9:10)pyrene (i)

The dihydro compound (1g) was powdered with copper powder (2g) and heated for 2 hours at 450° under nitrogen. The mixture was sublimed, and at 400° /  $4 \times 10^{-3}$  mm yielded a reddish brown prismatic sublimate. It was extracted with boiling xylene, yield 500mg. The u.v spectrum in methylnaphthalene showed the presence of the centrosymmetric isomer dianthraceno(2':3',3:4);(2'':3'',8:9)pyrene (xx) by the bands at 5530, 6035 and 6650 Å. There was no trace of the dihydro compound in the u.v. spectrum.

The hydrocarbon was crystallised from  $\alpha$ -methylnaphthalene, filtering off the deposited crystals whilst the solvent was still hot. Yield 400mg. The u.v. spectrum indicated that the other isomer (xx) was still present, and to ensure removal of the centrosymmetric isomer (xx), the hydrocarbon was twice recrystallised from a mixture of diphenyl, diphenylene oxide and traces of maleic anhydride. The isomer (xx) would react more readily with maleic anhydride<sup>23</sup> and could thus be separated by extraction with alkali.

After the crystals had been deposited, xylene (20ml.) was added, the hot mixture filtered and the residue washed with xylene, benzene and ether. After a further crystallisation the substance was

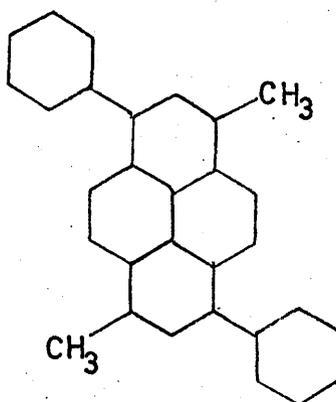
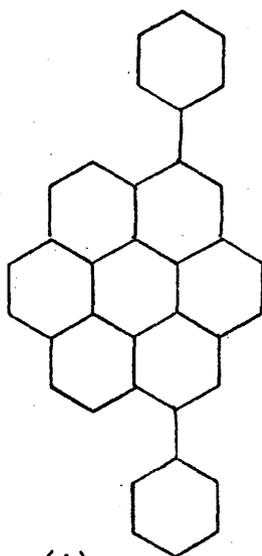
refluxed for 4 hours in a KOH / digol solution, m.pt.  $530^{\circ}$ . The u.v. spectrum indicated that the isomer (xx) was no longer present. In conc. sulphuric acid, (i) formed a brownish yellow solution which became brownish violet on heating. The spectrum of dianthracenopyrene (i) is shown in fig. 2.

Found: C, 95.34 ; H, 4.48%

$C_{40}H_{22}$  requires C, 95.59 ; H, 4.41%

C H A P T E R I V

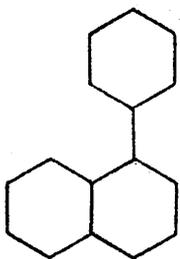
The Synthesis of phenyl substituted Polycyclic Hydrocarbons



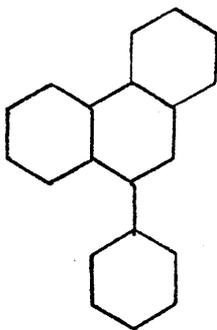
Introduction:

2,9-Diphenyl-coronene (i) was synthesised and its u.v. absorption spectrum was compared with coronene<sup>1</sup>(xxxviii) which showed that there was no appreciable bathochromic shift as was obtained with  $\beta$  substituted phenyl acenes<sup>4</sup>.

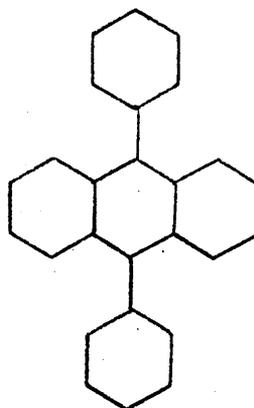
The synthesis of 3,8-diphenyl-5,10-dimethylpyrene(ii) was attempted in order to study the effect of the phenyl group on double bond local-



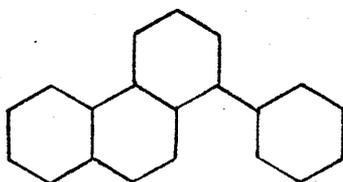
(iii a)



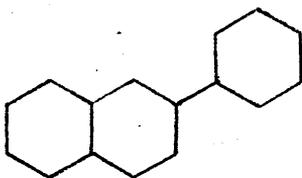
(iii b)



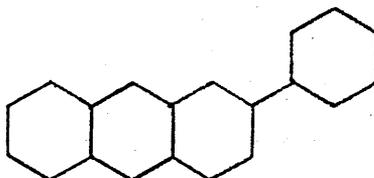
(iii c)



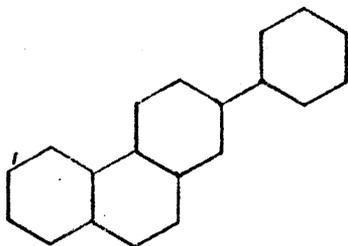
(iii d)



(v)



(vi)



(vii)

isation in the 3,4,5 and 8,9,10 position in pyrene.

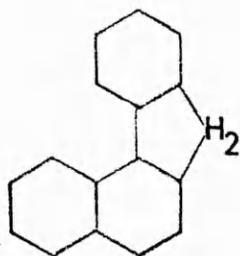
### Discussion:

The effect of phenyl substitution on a polycyclic aromatic hydrocarbon is not greatly understood as can be readily ascertained from the different theories proposed by various workers<sup>2</sup>.

Generally, substituted phenyl groups in  $\alpha$  and meso positions in acenes and attached to the central ring in phenes and positions  $\alpha$  to it, do not cause an extension of conjugation<sup>3</sup>. Examples of these compounds are shown opposite<sup>5</sup> (iia-iid). The only difference between the u.v. absorption of the parent hydrocarbon and the  $\alpha$  phenyl substituted (iia-iid) is that there is a small bathochromic shift and increased fine structure. The intensities of the maxima are not greatly affected by phenyl substitution<sup>4</sup>.

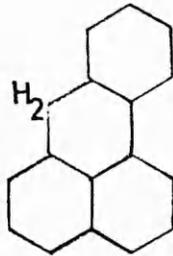
However extensive conjugation does take place in  $\beta$  substituted<sup>t</sup> acenes<sup>6</sup> as well as in 2-phenylphenanthrene<sup>7</sup>(v-vii).

The fact that appreciable conjugation did not take place in the former cases (iia-iid) was thought to be due to the non co-planarity of the  $\alpha$ -phenyl substituent and the hydrocarbon itself<sup>8</sup>. This was said to



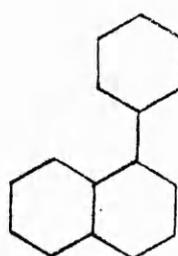
(iix)

$$\lambda_{\beta} = 2280$$



(ix)

$$2310$$

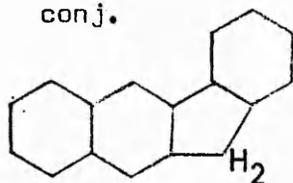


(iiia)

$$2260$$

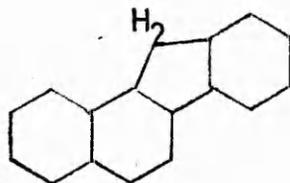
Å

Forcing the  $\alpha$ -phenyl substituent into coplanarity does not result in incr. conj.



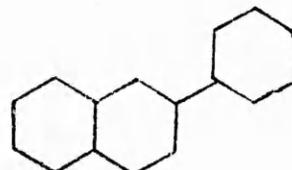
(x)

$$\lambda_{\beta} = 2630$$



(xi)

$$2620$$



(v)

$$2500$$

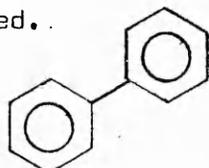
Å

The introduction of a methylene group in the above case (x - v) results in a small bathochromic shift, as all conj. has already occurred.



(xii)

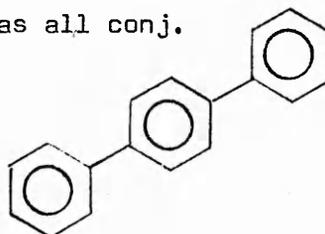
$$\lambda_{\beta} = 1835$$



(xiii)

$$145$$

$$1980$$

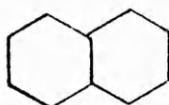


(xiv)

$$85$$

$$2065$$

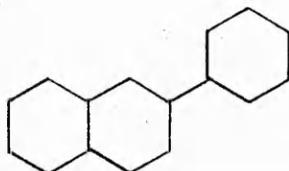
Å



(xv)

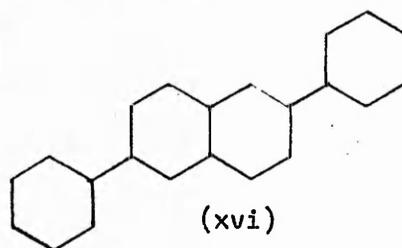
$$\lambda_{\beta} = 2210$$

$$290$$



(v)

$$2500$$

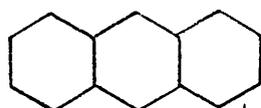


(xvi)

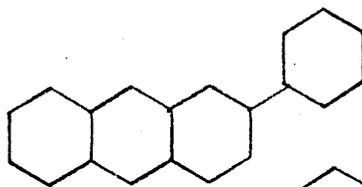
$$130$$

$$2630$$

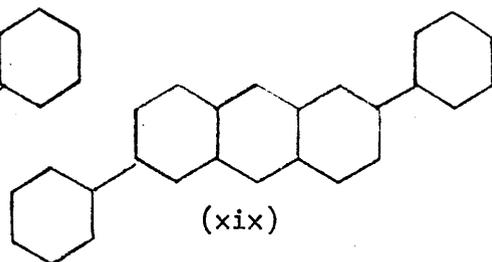
Å



(xvii)



(xviii)



(xix)

280

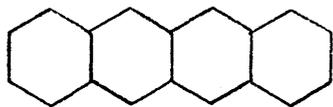
130

$\lambda_{\beta} = 2540$

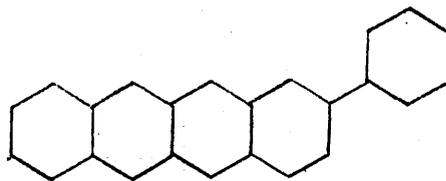
2820

2950

R



(xx)



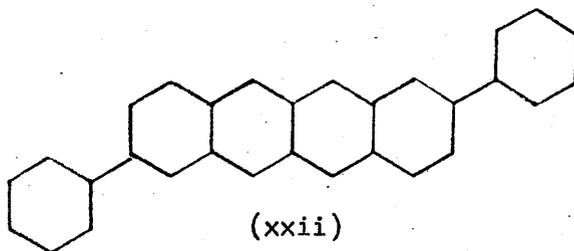
(xxi)

170

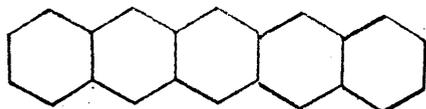
$\lambda_{\beta} = 2740$

2910

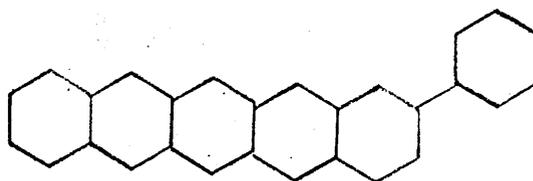
R



(xxii)



(xxiii)



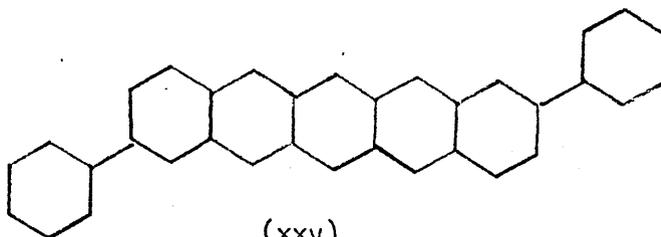
(xxiv)

170

$\lambda_{\beta} = 3030$

3200

R



(xxv)

80

3280

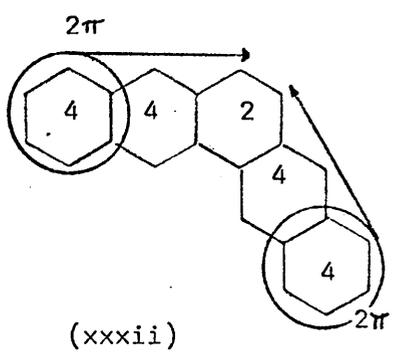
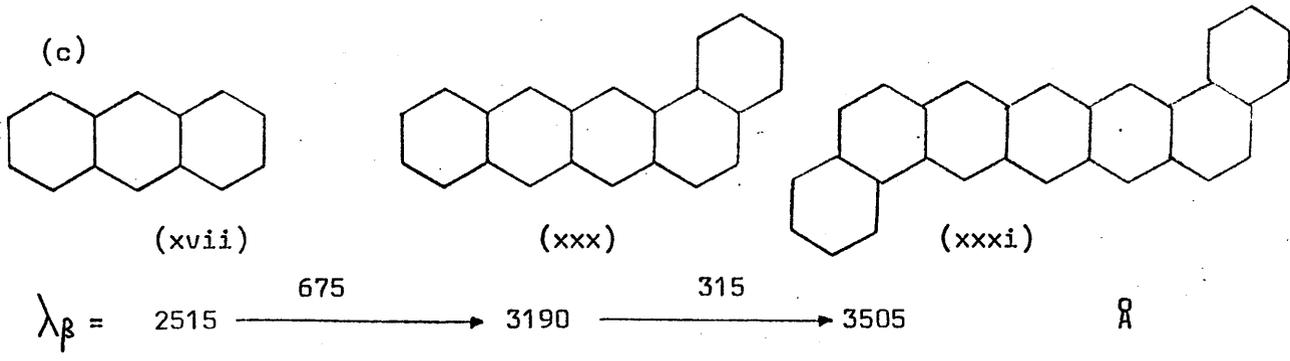
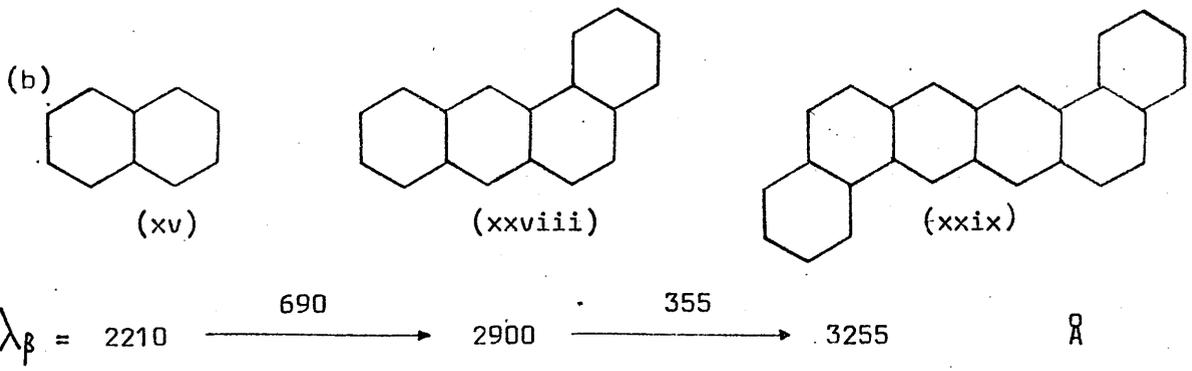
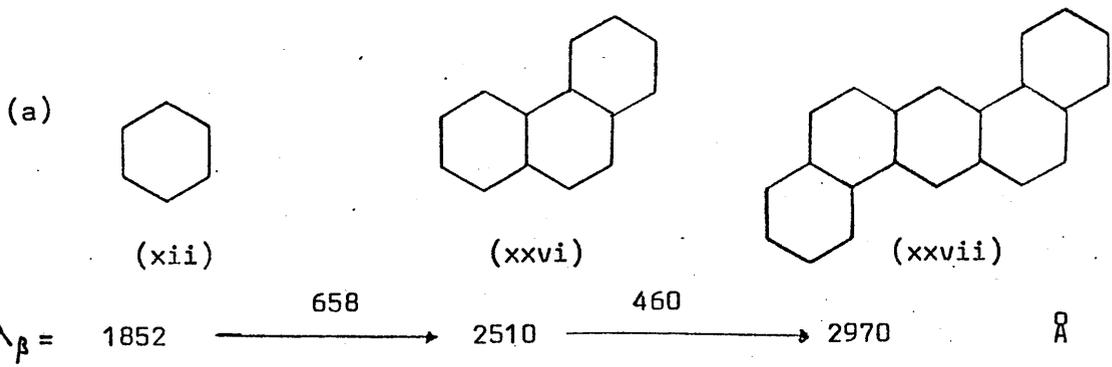
R

be due to interaction of the peri hydrogens with the neighbouring ortho hydrogens of the phenyl group<sup>4</sup>. This steric factor was thought to account completely for the non conjugation<sup>9</sup>.

Clar<sup>10</sup> undermined the above concept by examining the u.v. absorption spectra of (iix) and (ix) in which the methylene group forces the  $\alpha$ -phenyl substituent into co-planarity with the rest of the molecule. The bathochromic shifts found were too small to be considered as a real extension to the conjugation of the system. Thus, even when the steric factors were eliminated, conjugation did not ensue. The reason for the non co-planarity of any  $\alpha$ -substituent must be considered to be due to the fact that no energy would be gained by conjugation if it were co-planar<sup>2</sup>.

When various  $\beta, \beta'$  diphenyl acenes were examined, a definite trend was seen in their bathochromic u.v. shifts (xii-xxv)<sup>7</sup>. [ The series diphenyl, terphenyl (xii-xiv) was thought to be a special case by Clar<sup>2</sup>, as sextets were being connected together. ]

The first shift in these  $\beta$  phenyl-acenes is approximately double the second shift. It is comparable with the shift obtained when annellating one ring in the normal acene series<sup>11</sup> (+300Å) and the second shift is



similar to that between diphenyl and terphenyl<sup>2</sup>.

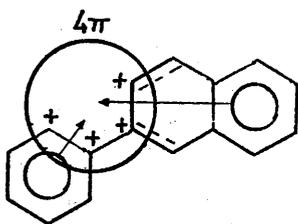
This asymmetric annellation effect<sup>12</sup> has already been found in the acene series by the fusing of styryl complexes to each end of an acene as shown opposite (xii-xxxi).

When the Shift Difference Rule<sup>13</sup> is applied to the series (a), (b) and (c) it is found that in case (a) the conjugation is extended to naphthalene, (b) to anthracene and (c) to tetracene<sup>12</sup>.

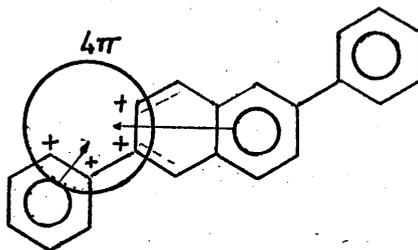
The asymmetric annellation effect<sup>12</sup> can be accounted for if the electronic distribution is considered in more detail.

As mentioned in chapter (1), phenes can be represented by (xxxii), where there are two freely mobile  $\pi$  electron pairs migrating over each branch of the system, sharing the two sextets between five rings and therefore giving the whole molecule aromatic character.

Dibenzacenes can be explained on a similar basis. They can be represented in three ways as shown on the next page:

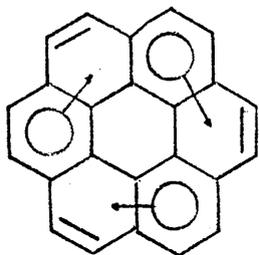


(xxxvi)

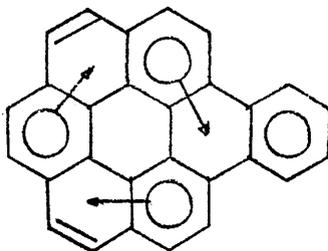


(xxxvii)

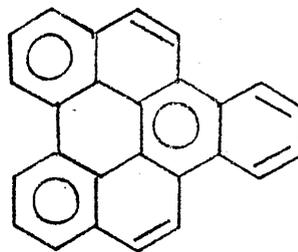




(xxxviii)



(XII)



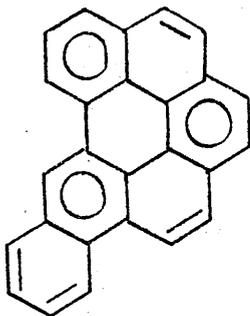
(XL)

$\lambda_{\beta} = 3050$

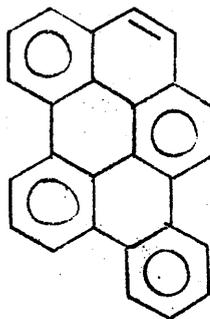
3200

3105

Å



(XLI)



(XLII)

$\lambda_{\beta} = 3330$

3090

Å

In the acenes there is only one pair of  $\pi$  electrons free to migrate<sup>11</sup>, which would account for the asymmetric annellation effect<sup>12</sup> in going to 2,6-diphenylnaphthalene<sup>2</sup>.(xxxvii).

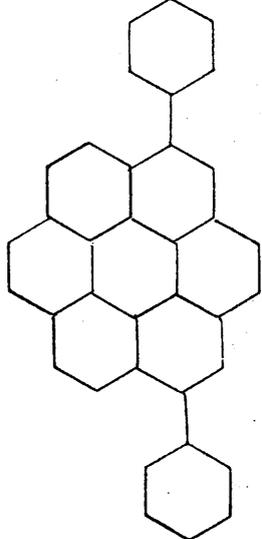
The transfer of a pair of  $\pi$  electrons from a phenyl group to form a quartet is only possible in  $\beta$  positions in acenes<sup>2</sup>.

When the N.M.R. of coronene (xxxviii) was examined<sup>14</sup> it was found to consist of a singlet at  $\tau$  1.28 with no indication of splitting. Thus, the protons must be equivalent and the electronic arrangement in each ring must be equal. This is unlike pyrene, phenanthrene, perylene, etc. where a much more complex pattern is seen in the N.M.R.<sup>15</sup>.

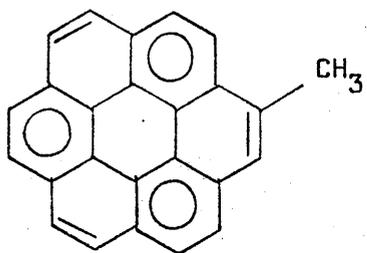
This would suggest that coronene (xxxviii) consists of three fused naphthalene complexes (xxxviii) with the electron pairs strongly delocalised and constantly migrating to give coronene (xxxviii) its "superaromaticity"<sup>16</sup>.

This superaromaticity<sup>16</sup> is also exemplified by its high m.pt., resistance to oxidation, insolubility in cold  $H_2SO_4$ , weak colour and its low reactivity<sup>17</sup>. Coronene (xxxviii) will also only condense with one molecule in a Friedel Crafts reaction<sup>18</sup>.

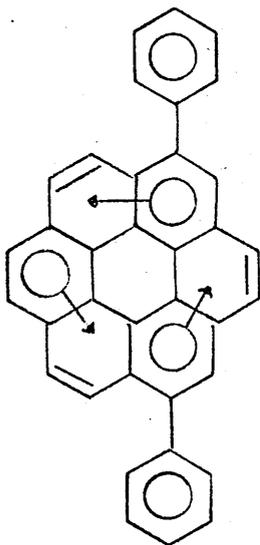
The  $\beta$  band of 1,2-benzocoronene<sup>18</sup> (XII) lies between that of (XL), (XLI)



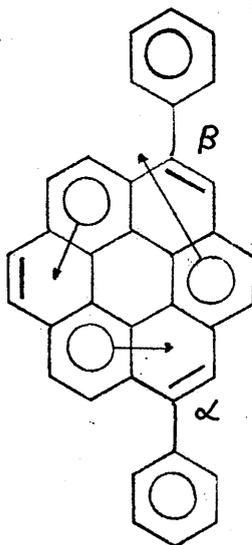
(i)



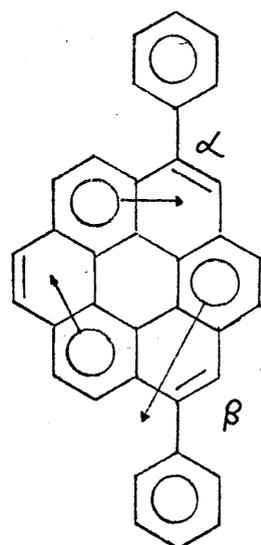
(XLIII)



(i')



(XLVa)



(XLVb)

(XLII) suggesting that the annellation effect<sup>11</sup> results from the combination of annellating to a sextet<sup>20</sup> as in (XL), (XLI) and to a double bond as in (XLII)<sup>16</sup>.

In methylcoronene (XLIII), the methyl signal at  $\tau$  6.76 in the N.M.R.<sup>19</sup> is split by 0.9c/s. which is comparable to the splitting of the methyl signal in 9-methylphenanthrene in which a double bond was assigned<sup>19</sup>. There must be a high degree of double bond character in the bond attached to the methyl group, in methylcoronene (XLIII).

Methyl substitution has a very powerful effect in altering the electronic arrangement in coronene. Strict application of Robinson's aromatic sextet<sup>20</sup> explains the N.M.R. result. There must be strong localisation of double bonds and sextets<sup>20</sup> in methylcoronene compared with the arrangement in coronene<sup>19</sup> (xxxviii).

In order to study the effect of the substitution of phenyl groups, 2,9-diphenylcoronene (i) was synthesised. If (i) retains the superaromaticity of coronene<sup>16</sup> (xxxviii), then there will be no conjugation between the phenyl groups and coronene. However if coronene (xxxviii) behaves as three fused naphthalene complexes when substituted, then one phenyl group is always in the  $\beta$  position in a naphthalene (xv) unit, whilst the other is always in an

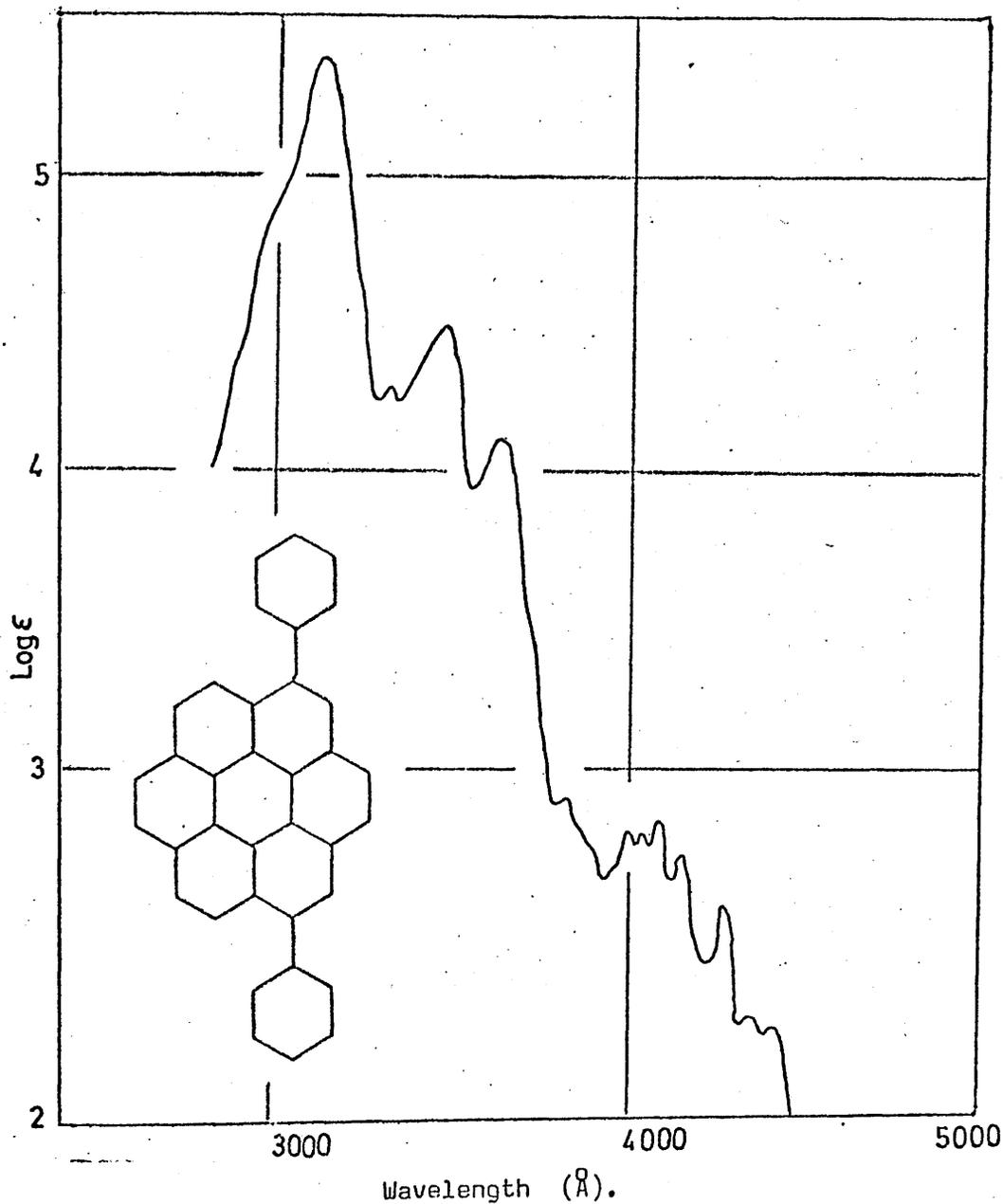
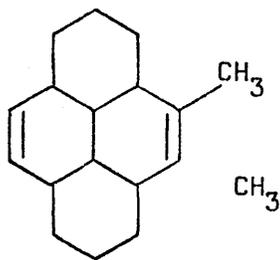
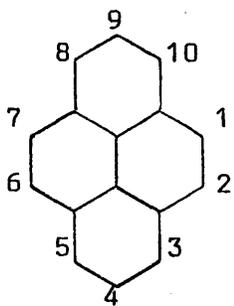
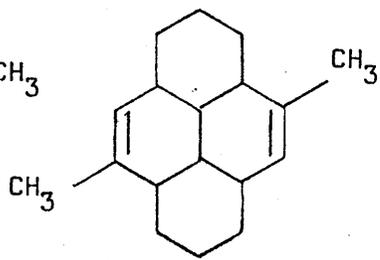


Fig. 1. Absorption maxima ( $\text{\AA}$ ) and  $\log \epsilon$  ( in parentheses ).  
 2,9-Diphenylcoronene (i) in cyclohexane :  $\alpha$  , 4410 (2.10), 4360 (2.13),  
 4360 (2.13), 4270 (2.52), 4150 (2.70), 4080 (2.80), 4040 (2.75), 3990  
 (2.78), 3820 (2.90) ;  $\rho$ , 3610 (4.13), 3460 (4.47), 3310 (4.26);  $\beta$  ,  
 3110 (5.41), 3000 (4.90).



(XLVI)



(XLVII)

$\alpha$  position (XLVa & XLVb).

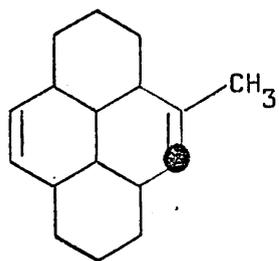
Conjugation as in  $\beta$ -phenyl naphthalene<sup>4</sup> might then be expected, if the superaromaticity<sup>16</sup> of coronene (xxxviii) were interrupted by phenyl substitution.

From the u.v. absorption spectra a small bathochromic shift (60Å) was recorded in going from coronene (xxxviii) to 2,9-diphenyl-coronene (i). There is thus no extension of conjugation comparable to that found in  $\beta$ -substituted acenes<sup>4</sup>. (See fig. 1)

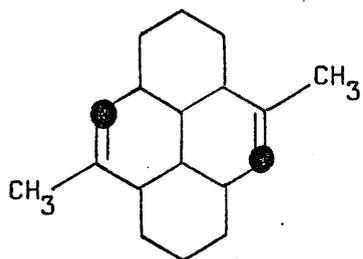
Although substitution must affect the electronic distribution in coronene (xxxviii), it does not result in a full extension of conjugation to the phenyl substituents. The role of steric effects must also be considered but it is unlikely that they would be the sole determining factor.

The tendency for coronene (xxxviii) to retain its superaromatic character<sup>16</sup>, although disturbed by substitution, must at least partially account for the non conjugation of the phenyl groups.

Recently, many N.M.R. studies have been conducted on methyl substituted pyrenes<sup>19,21</sup>. Double bond character was identified in the 1,2 and 6,7 positions by studies on 1-methylpyrene (XLV1) and 1,6-dimethylpyrene (XLV11)<sup>21</sup>.

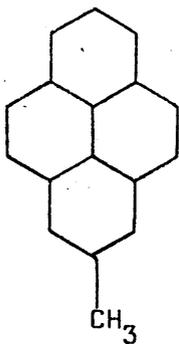


(XLVI')

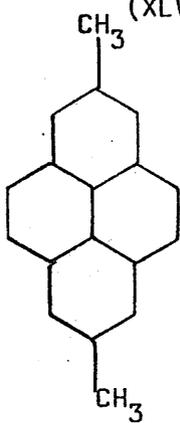


● = irradiating

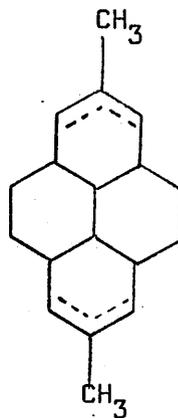
(XLVII')



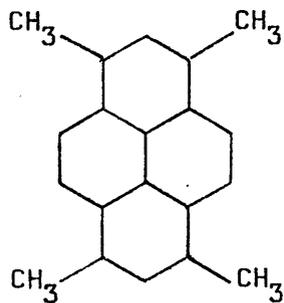
(IIL)



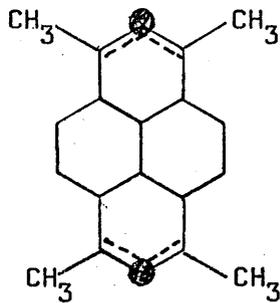
(IL)



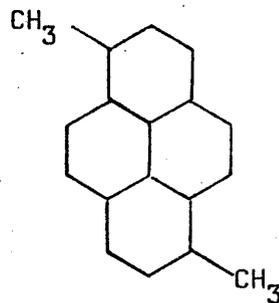
(L)



(LI)



(LII)



(LIII)

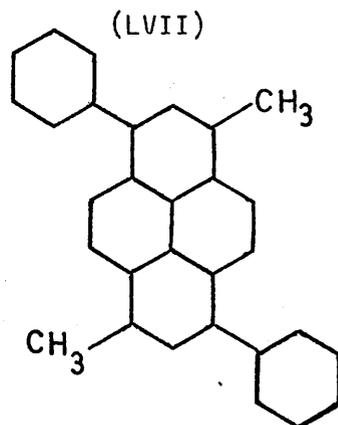
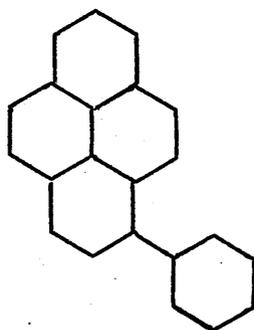
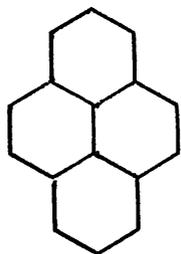
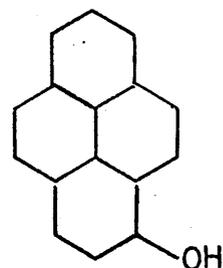
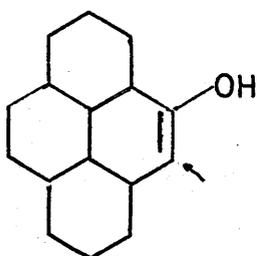
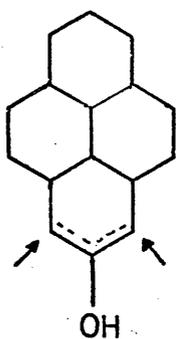
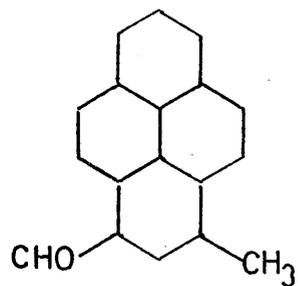
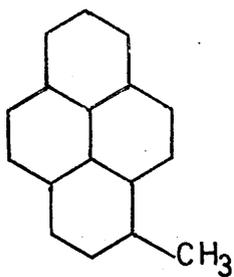
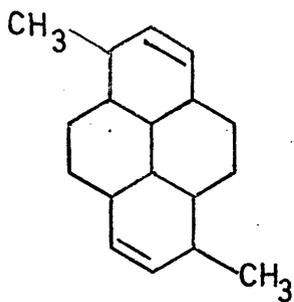
Very strong splitting of the methyl signals were seen (1c/s.), which disappeared on irradiating the neighbouring protons as shown (XLVI' and XLVII')<sup>21</sup>.

Ambiguities were found when when methyl substituents were studied in the other rings. Both 4-methyl and 4,9-dimethylpyrene, (IIL and IL resp.), had a methyl signal which was split into a triplet with a separation of 0.55c/s.<sup>21</sup>

This would suggest that the adjacent bonds have 'true double bond' character<sup>21</sup> and that a three centred  $\pi$  bond was present to account for the splittings<sup>21</sup>.

On examining the N.M.R. of 3,5,8,10-tetramethylpyrene (LI), the methyl signal was found to be split into a doublet with a separation (0.5c/s.) which disappeared on irradiat. protons 4 and 9<sup>21</sup> (LII). This strengthens the concept of a three centred  $\pi$  bond being present.

An unexpected result was recorded when the N.M.R. of 3,8-dimethylpyrene (LIII) was examined. A sharp methyl singlet, which showed no indication of any splitting was obtained. In this instance, there must be no appreciable double bond character immediately adjacent to the methyl groups.



(ii)

$$\lambda_R = 2720 \xrightarrow{40} 2760 \text{ \AA}$$

Due to the fact that 3-methylpyrene (LIVa) gives 3-methylpyrene-5-aldehyde (LIVb) when submitted to the Vilsmeier synthesis<sup>22</sup>, and not substitution in the 8 or 10 position, Clar suggested that (LIV) was the probable structure<sup>21</sup>.

An experimental analogy was also found in the diazo coupling reaction with hydroxypyrenes<sup>23</sup>. 4-Hydroxypyrene (LV) couples readily with diazo compounds in the ortho positions. 1-Hydroxypyrene (LVI), also couples readily in the 2 position, this is in complete agreement with the N.M.R. double bond fixation ideas.

With 3-hydroxypyrene (LVII), there is no diazo coupling reaction and thus no double bond at the 3 position, once again in complete agreement with the N.M.R. findings.

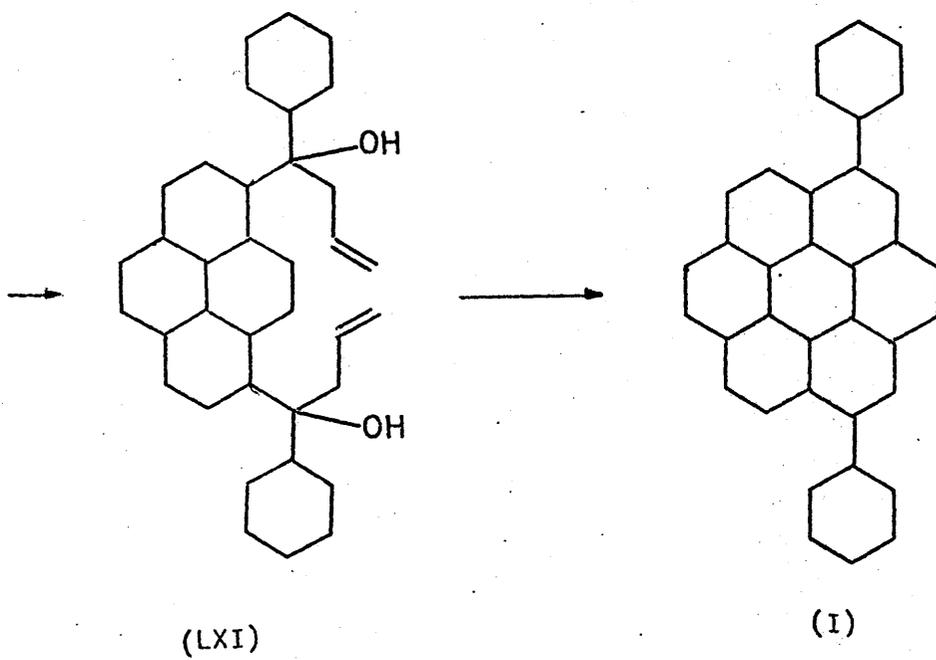
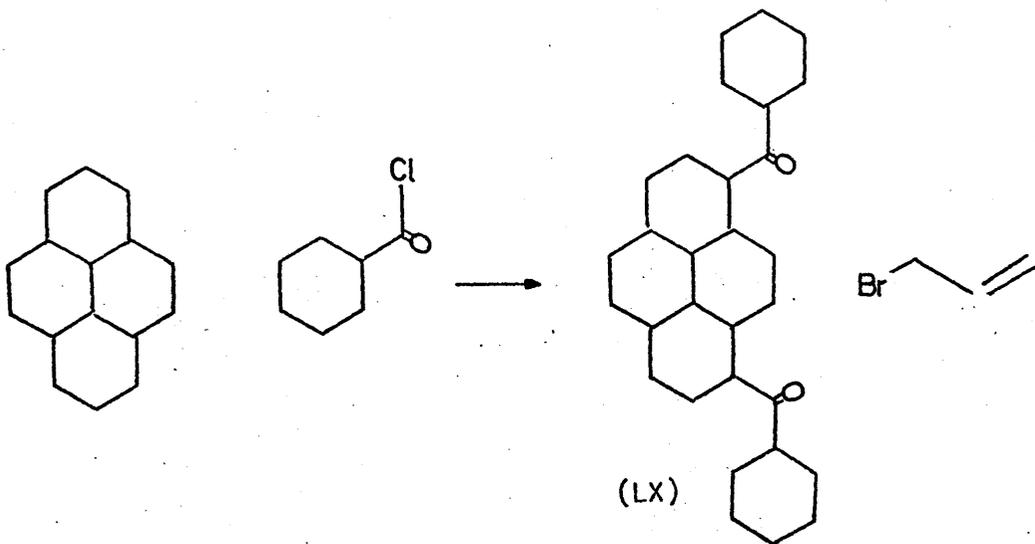
3-Phenylpyrene (LIX), showed no appreciable increase in conjugation relative to pyrene (LVIII), only a slight bathochromic shift<sup>24</sup> (40Å) similar to that between naphthalene (xv) and 1-phenylnaphthalene<sup>4</sup> (iiia).

In order to study the effect of a phenyl group on the double bond position, the synthesis of 3,8-diphenyl-5,10-dimethylpyrene (ii) was attempted.

If the phenyl group behaved as a normal non-conjugated substituent, one

would expect to find some form of splitting of the methyl signal in the N.M.R., the degree of splitting being proportional to the amount of double bond character in the 4,5 and 9,10 bonds<sup>21</sup>. Whether a three centred  $\Pi$  bond would be produced as in 3,5,8,10-tetramethylpyrene (LI), or if actual localisation of the double bond took place could only be determined by an examination of the N.M.R. of diphenyldimethylpyrene (ii), with special emphasis on the methyl signal.

Unfortunately, it was not possible due to separation difficulties to obtain a pure sample of the hydrocarbon.



Experimental Discussion:

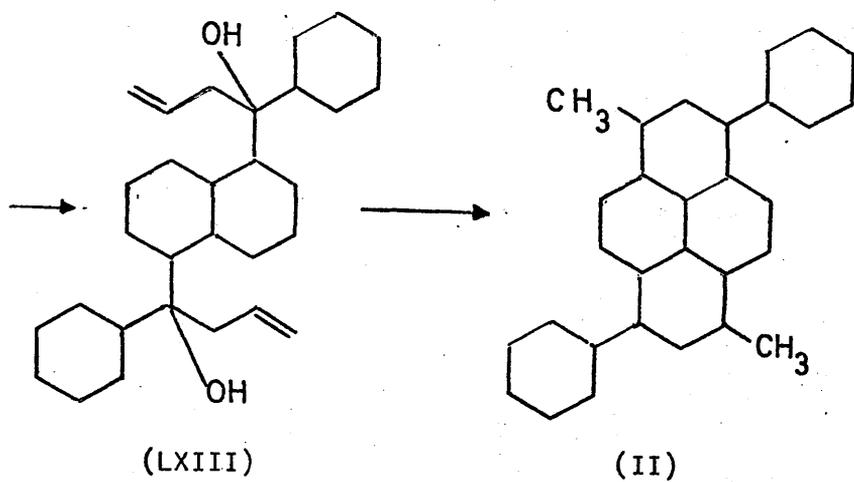
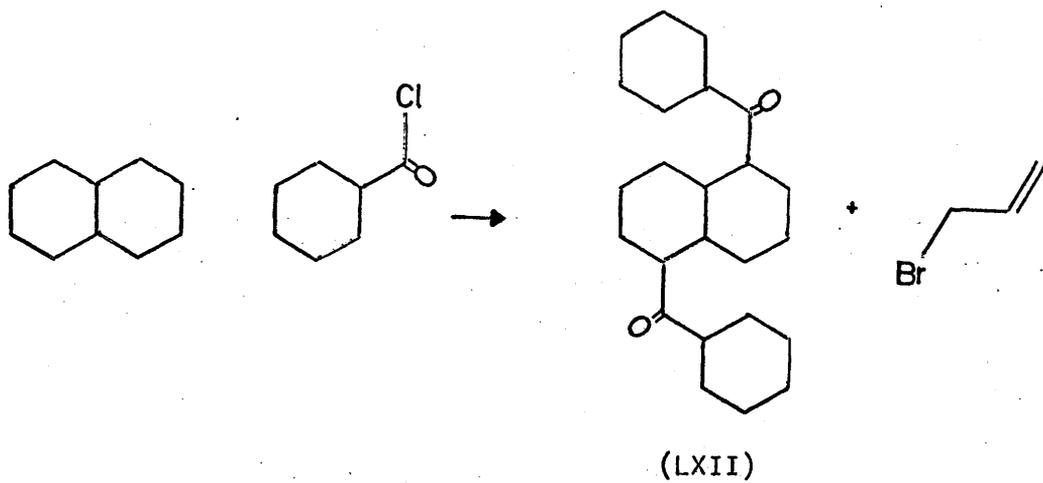
Coronene<sup>1</sup> (xxxviii) is an unreactive compound, condensing with only one molecule of acid chloride or anhydride in a Friedel Craft's reaction<sup>18</sup>. It is also very resistant to oxidation<sup>17</sup>. With bromine, depending on the conditions it forms either the tetrabromo or dibromo derivative<sup>25</sup>. The actual substitution pattern of the bromo compound is not known.

Many phenyl substituted acenes have been synthesised using diphenyl as starting material and condensing with appropriate anhydrides<sup>7</sup>.

The reaction of allyl bromide with ketones, discussed by Houben<sup>26</sup>, was thought to be a possible synthetic route to 2,9-diphenylcoronene (i).

If allyl bromide and magnesium were reacted with 3,10-dibenzoylpyrene (LX) a ditertiary alcohol (LX1) would be formed which could be aromatised by heating with copper powder at 400<sup>o</sup>. The 3,10-dibenzoylpyrene (LX) was prepared using a modification of Vollman's method<sup>23</sup>, making use of the greater solubility of the 3,10 isomers of pyrene relative to the 3,8.<sup>23</sup> Instead of purifying by repeated crystallisations, the isomers were separated by chromatography resulting in a higher yield.

The method outlined by Houben<sup>26</sup> for allyl bromide reactions was followed and the diol (LX1) was obtained in good yield.



To cyclise and aromatise the diol with Cu powder, temperatures above 420° were required. Reactions conducted below 420° resulted in very little 2,9-diphenylcoronene (i) being formed.

Purification of the hydrocarbon was by column chromatography. The latter resulted in pure 2,9-diphenylcoronone (i) being obtained which was identified by a mixed melting point determination with an authentic sample (prepared in this laboratory by a different method).

Due to the success of this allyl bromide/aryl ketone method it was decided to synthesise 3,8-diphenyl-5,10-dimethylpyrene (ii) using a similar reaction sequence.

1,5-Dibenzoylnaphthalene (LX11) was synthesised using the method described in the I.G. Farben Ind. A.G. British Patent<sup>27</sup>.

Following the technique outlined by Houben<sup>26</sup>, the diketone (LX11) was reacted with allyl bromide and magnesium yielding the diol (LX111).

As in the previous synthesis, the diol was heated at 400° with Cu powder for several hours. Concentration of the benzene extracts followed by column chromatography gave partial separation of the required compound (u.v. absorption bands at 3500, 2830Å) which to further purify was run several times on a t.l.c. plate using very weakly polar solvent mixtures.

The resultant oil, which was obtained on concentrating the eluate of the required t.l.c. band (from u.v. absorption measurements) formed a crystalline picrate, which analysed correctly for the picrate of the hydrocarbon (ii). On decomposition of the picrate, the resultant oil could not be induced to crystallise despite the use of a wide variety of solvents.

EXPERIMENTAL3,10-Dibenzoylpyrene (1x).

A variation of the procedure used by Vollmann et al<sup>23</sup> was used. The crude product (402g) from the Friedel Crafts reaction was extracted with boiling acetic acid (4l), leaving 3,8-dibenzoylpyrene (140g) (lit. 97g)<sup>23</sup> of m.pt. 236° (lit. 239°)<sup>23</sup>.

Concentration of the acetic acid mother liquor yielded 3,10-dibenzoylpyrene (1x), which after two recrystallisations had m.pt. 172° (lit. 165°)<sup>23</sup>. In order to further purify the 3,10 isomer, a concentrated xylene solution was chromatographed on neutral alumina (700g) using hot xylene as eluant. Long yellow needles (160g) (lit. 140g) of 3,10-dibenzoylpyrene (1x) were obtained which dissolved in conc. sulphuric acid to form a red solution; m.pt. 164-5° (lit. 165°)<sup>23</sup>.  $\nu_{\text{max}}^{\text{KBr}} = 1665\text{cm}^{-1}$  (C=O diaryl ketone).

3,10-Dibenzyl- $\alpha,\alpha'$ -dihydroxy- $\alpha,\alpha'$ -diallyl-pyrene (1xi).

Freshly distilled allyl bromide (11.3ml.) in dry ether (30ml.) was introduced dropwise to iodine activated magnesium (3.65g), causing immediate reaction to take place. After the addition

of the first few drops of allyl bromide, dibenzolopyrene (1x) (5g) in dry benzene (20ml.) was introduced dropwise into the reaction vessel. After 40 min. both reagents had been added and the mixture was refluxed for 3 hours. It was then decomposed with dilute acetic acid and washed thoroughly with water. Concentration yielded no crystalline product.

The solvents were driven off and the resultant oil induced to cryst. by the addition of a few drops of methanol and stirring. The crude product (4.3g), which had no carbonyl absorption in the i.r., was reprecipitated from acetic acid and crystallised twice from methanol. It was further purified by using prep. t.l.c. with 10% ethyl acetate / 90% benzene as eluant. The band with  $R_f = 0.2$  was extracted and the material obtained crystallised from methanol, m.pt.  $265-70^{\circ}$  decomp. In conc. sulphuric acid the solution was bluish green becoming brownish violet on heating.

Found: C, 87.52 ; H, 5.66%

$C_{36}H_{28}O_2$  requires C, 87.78 ; H, 5.73%

### 2,9-Diphenylcoronene (i)

The diol (1xi) (1g) was ground with copper powder (2g) and the

mixture heated for 2 hours under  $\text{CO}_2$ . Very little product was formed when temperatures below  $420^\circ$  were used.

The mixture was extracted with pet. ether ( $60-80^\circ$ ) to remove the pyrene formed during the reaction, and the residue thoroughly extracted with boiling benzene. The benzene concentrate was chromatographed on highly active neutral alumina (40g), using 10% benzene/90% light pet. ether as eluant. The fractions were monitored by u.v. spectroscopy, initially they contained mainly pyrene and the later fractions 2,9-diphenylcoronene (i) (on increasing the polarity of the eluant). On concentrating the diphenylcoronene fractions an oil was obtained.

The oil (70mg) was run on a 1mm prep. t.l.c. plate using 25% benzene / 75% pet. ether as eluant. The yellowish band with  $R_f = 0.26$  contained the required compound (i) and it was extracted and rerun four times on a fresh 1mm prep. t.l.c. plate using 10% benzene / 90% pet. ether as eluant in order to separate out any impurities present. The yellowish band  $R_f = 0.22$  was extracted and on concentrating, the benzene extract yielded light yellow crystals of diphenylcoronene (i). It was identified by a mixed m.pt. with an authentic sample, which showed no depression, m.pt.  $304-306^\circ$  (lit.  $305-307^\circ$ )<sup>28</sup>. In sulphuric acid the colour was brownish yellow

which became mid green on heating.

1,5-Dibenzoylnaphthalene (lxii)

The technique described in the I.G. Farben Ind. A.G. British patent<sup>27</sup> was followed. Powdered aluminium chloride (200g) was added slowly to a melt of naphthalene (128g) and benzoyl chloride (210g). The reaction was violent at room temperature, and after cooling in ice, benzoyl chloride (210g) and powdered aluminium chloride (200g) added.

The reaction mixture was heated to 100° and maintained at this temperature for 30 min. The dark red mixture was decomposed with dilute hydrochloric acid and washed thoroughly with water. Xylene (500ml.) was added to the product, and the mixture boiled to remove water. Its volume was reduced to give on crystallisation 49g of grey diketone (lxii) m.pt. 188° (lit. 188°).<sup>27</sup>

1,5-Dibenzyl- $\alpha,\alpha'$ -dihydroxy- $\alpha,\alpha'$ -diallyl-naphthalene (lxiii)

Freshly distilled allyl bromide (13g) in dry ether (80ml.) was added dropwise to activated magnesium (2.62g). The addition of 1,5-dibenzoylnaphthalene (lxii) (9g) in dry benzene (120ml.) was commenced

almost simultaneously. After the final addition of reagents, the mixture was refluxed for 2 hours, then decomposed with dilute acetic acid and the organic material which precipitated out washed thoroughly with acetic acid, water and ethanol. Yield 1g, m.pt  $202^{\circ}$ . The organic layer was concentrated and the resultant oil induced to crystallise using methanol. Yield 6g in total.

The precipitated product (70mg) was further purified by running on a prep. t.l.c. plate (1mm) using benzene as eluant. The colourless, weakly fluorescent band with  $R_f = 0.3$  was extracted and the product twice crystallised from benzene, yielding almost colourless needles m.pt  $216^{\circ}$  decomp. There was no trace of a carbonyl absorption band in the i.r. only  $\nu_{\max}^{\text{KBr}} = 1650\text{cm}^{-1}$  (C=C stretch). In conc. sulphuric acid the colour was violet brown becoming dark brown on heating.

Found: C, 85.4 ; H, 6.8%

$\text{C}_{30}\text{H}_{28}\text{O}_2$  requires C, 85.7 ; H, 6.7%

### 3,8-Diphenyl-5,10-dimethylpyrene (ii)

The diol (lxiii) (3g) was ground with copper powder (3g) and heated at  $400^{\circ}$  for 3 hours. The mixture was extracted with boiling benzene

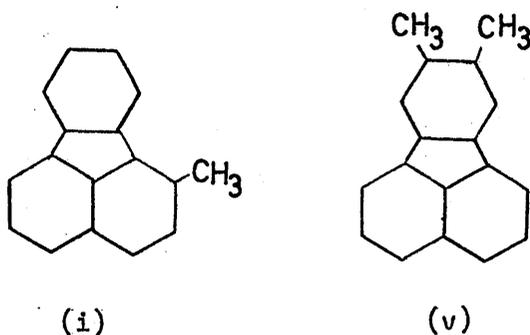
and the concentrate chromatographed on highly active neutral alumina (30g) using 10% benzene/90% pet. ether mixture as eluant. The fractions were followed spectroscopically and concentrated separately, yielding oils which could not be induced to crystallise. The fractions with u.v. absorption bands at 2830 and 3500 Å (similar to 3,8-diphenyl pyrene )<sup>24</sup> were run on a 1mm prep. t.l.c. plate using 5% benzene/95% pet. ether mixture as eluant. (Later fractions from the column indicated that 2,3-o-phenylenepyrene<sup>24</sup> was also present by the u.v. absorption bands at 3040, 3160, 3610, 3870. 4080, 4340 and 4620 Å in hexane). The prep. plate was run four times to aid separation, and the light yellow band, Rf. = 0.42 extracted and on concentration yielded an oil. A picrate was made from the oil, which was three times crystallised from methanol, m.pt. 145° decomp. On recovering the material from the picrate an oil was obtained, which despite treatment with numerous solvents, including light pet. ether, cyclohexane, benzene, methanol and acetic acid, could not be induced to crystallise.

Found: C, 70.7; H, 4.0; N, 6.9%

$C_{36}H_{25}O_7H_3$  required C, 70.7; H, 4.1; N, 6.9%

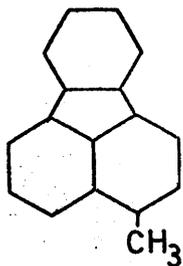
C H A P T E R V

The location of double bonds in fluoranthene and the  
annellation effect in benzologues of fluoranthene.

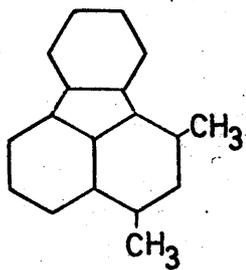


Introduction:

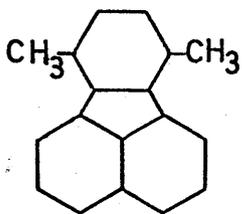
The hydrocarbons 1-methylfluoranthene (i) and 8,9-dimethylfluoranthene (v) have been synthesised. Their N.M.R. spectra were compared with those of 3-methylfluoranthene (ii), 1,3-dimethylfluoranthene (iii), 7,10-dimethylfluoranthene (iv) and 8-methylfluoranthene (vi). The results obtained give a new insight into the electronic arrangement in fluoranthene (ix) and the positions of fixed double bonds in fluoranthene (ix).



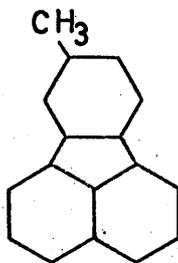
(ii)



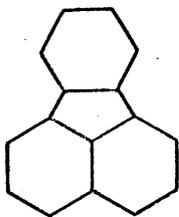
(iii)



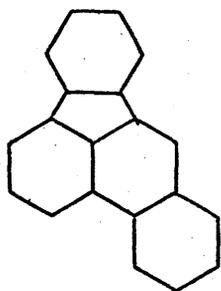
(iv)



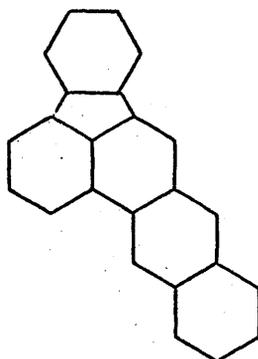
(vi)



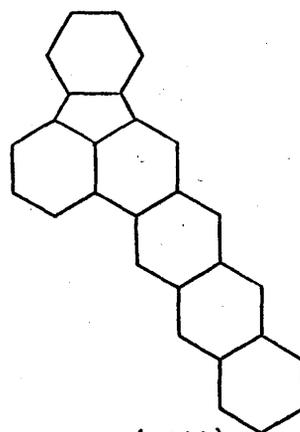
(ix)



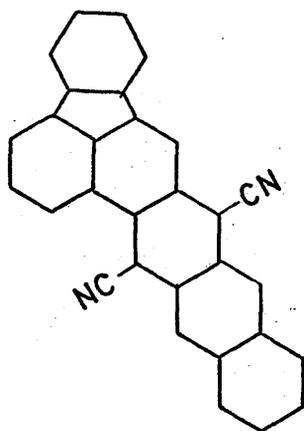
(x)



(vii)



(viii)



(xi)

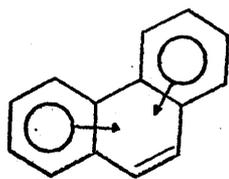
Naphtho (2':3',2:3) fluoranthene (vii), was synthesised and its. u.v. spectrum compared with fluoranthene (ix) and 2,3-benzofluoranthene (x).

The attempted synthesis of anthraceno (2':3',2:3)fluoranthene (viii) failed due to the decomposition of the hydrolysed 1',4'-dicyano-anthraceno (2':3',2:3)fluoranthene (xi) during attempted decarboxylation.

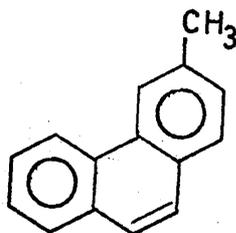
### Discussion:

Recent work executed by Clar et al<sup>1,2</sup> has shown the usefulness of N.M.R. studies of methyl derivatives of polycyclic hydrocarbons for pinpointing double bond localisation<sup>3</sup> in the molecule.

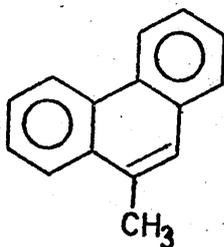
Clar has long purported the existence of 'fixed double bonds'<sup>3</sup> and inherent aromatic sextets<sup>4,5</sup> in polycyclic hydrocarbons. N.M.R. spin-spin coupling studies are proving to be an excellent tool for looking at these electronic concepts in more detail than was previously possible.



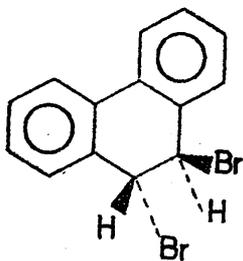
(xii)



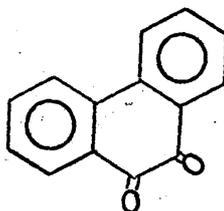
(xiii)



(xiv)



(xv)



(xvi)

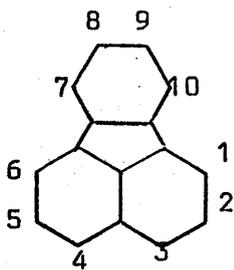
According to Clar's sextet theory<sup>5</sup>, phenanthrene (xii), should be written with two inherent sextets<sup>5</sup> and one induced sextet<sup>5</sup> (xii). If this localised double bond<sup>3</sup> in the central ring has any real degree of fixation, one would expect it to exhibit chemical reactivity and the properties associated with a double bond using physical measurements.

To this end various methyl derivatives of phenanthrene were examined<sup>1</sup>. It was found that a methyl group attached to a sextet<sup>5</sup>, as in 3-methylphenanthrene (xiii) had a singlet resonance signal at  $\tau$  7.5<sup>1</sup>, or as in the case of mesitylene and 2,3,4,5-tetrachlorotoluene, a very small degree of splitting (0.6c/s.)<sup>1</sup> was found. However, in the case of 9-methylphenanthrene (xiv) a doublet resonance signal at  $\tau$  7.45 with a splitting of 1.1c/s. was obtained. This splitting is much greater than that found for the substituted benzenes mentioned above, and is approaching that obtained in the propenes (  $\underline{\text{CH}_3}\text{-C=CH-}\underline{\text{H}}$  ) where a splitting of 1.7 - 1.8c/s. is recorded<sup>6</sup>.

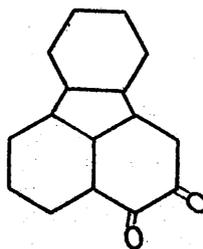
The 9,10 position in phenanthrene (xii) is chemically reactive and behaves like a double bond<sup>7</sup>. Bromine readily forms phenanthrene-9,10-dibromide (xv) with phenanthrene, and the corresponding dichloride with chlorine.<sup>8,9</sup>

With chromic acid in glacial acetic acid, phenanthrene (xii) yields 9,10-phenanthrenequinone (xvi)<sup>9</sup>.

It was thus concluded, that the 9,10 bond in phenanthrene (xii), from



(ix)



(xvii)

chemical evidence and the sextet concept<sup>5</sup> has a high degree of double bond character.

This was neatly confirmed by an N.M.R. study of the methyl derivatives of phenanthrene<sup>1</sup> (xii), with special emphasis being placed on an examination of the splitting of the methyl resonance signal<sup>1</sup>.

The methyl resonance signal is at much higher field ( $\tau$  7.5), than the aromatic proton region ( $\tau$  2.5). The methyl resonance signal can be thus clearly and unambiguously seen as it is not superimposed by other signals. (This is very frequently the case when the aromatic proton signals are examined). The splitting of the methyl signal, if any, can be thus easily measured, due to the non interference of the other resonance signals.

It was decided to study the electronic arrangement in fluoranthene (ix) using methyl derivatives and to examine their splitting pattern due to the obvious success of this technique in the previous case with phenanthrene<sup>1</sup>.

Fluoranthene (ix), when oxidised yielded fluoranthenequinone<sup>10</sup> (xvii) indicating the reactive nature of the 2,3 position.

The N.M.R. of fluoranthene (ix) has previously been recorded by Hefferman et al<sup>11</sup>. It consisted of an AA'BB' system superimposed on an ABC system

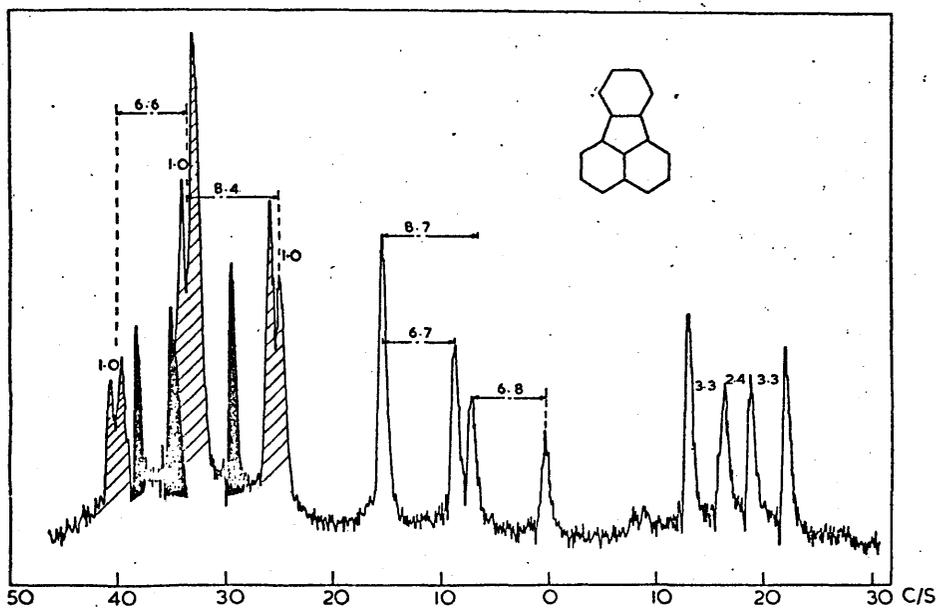


Fig. 1.

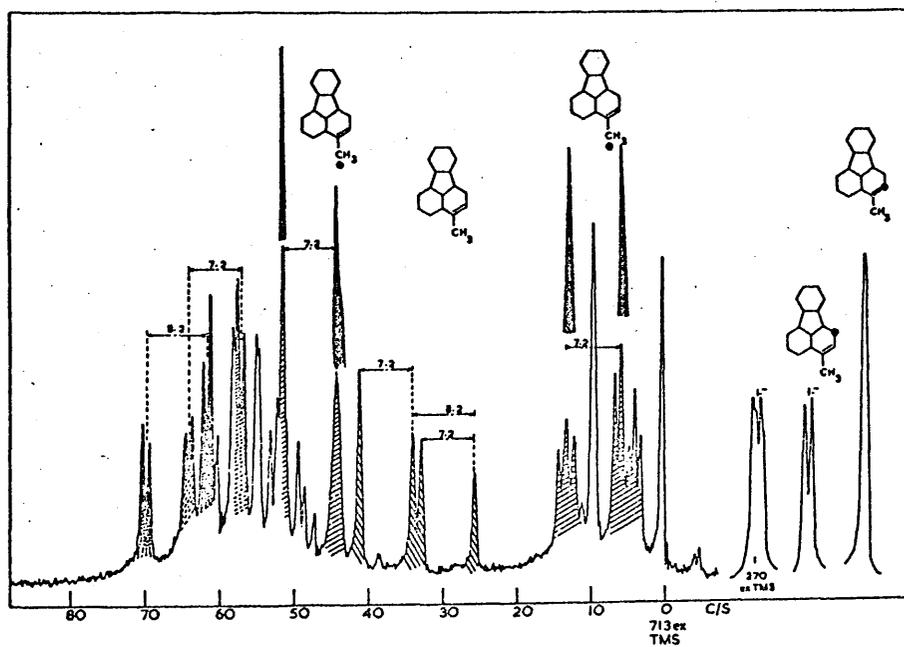


Fig. 2

with the three quartets of the ABC system being clearly seen<sup>11</sup>.

The high degree of coupling,  $J_{2,3} = 8.2 \text{ c/s}$  (in carbon tetrachloride) indicated a high degree of double bond character at the 2,3 position. Our own measurements of fluoranthene (ix) in  $\text{CS}_2$  (see fig. 1) agree well with those found by Hefferman et al<sup>11</sup>. The small variations are readily accounted for by change of solvent ( $J_{2,3} = 8.5$ ;  $J_{1,3} = 1.0$ ;  $J_{1,2} = 6.7 \text{ c/s}$ ).

Clar's concept of examining the methyl resonance signals for splitting in substituted hydrocarbons<sup>1,2</sup> and gaining information about the 'fixed double bond'<sup>3</sup> character of the molecule was employed.

The high degree of double bond character in the 2,3 position was confirmed by the N.M.R. spectrum of 3-methylfluoranthene (ii) (fig. 2). The methyl resonance signal (3rd band from R.H.S.) is split into a doublet of separation 1 c/s., which is very close to that found in 9-methylphenanthrene (xiv) (1.1 c/s)<sup>1</sup>. Obviously, if a double bond is present in the 9,10 position in phenanthrene (xii) then it must also be assumed be present in the 2,3 position of fluoranthene (ix).

The doublet sharpens if the  $\text{H}_1$  proton is radiated<sup>12</sup> (2nd. band from R.H.S. fig. 2) and collapses into a sharp singlet (first band from R.H.S. fig 2), if the  $\text{H}_2$  proton is decoupled<sup>12</sup>. The high field doublet of the

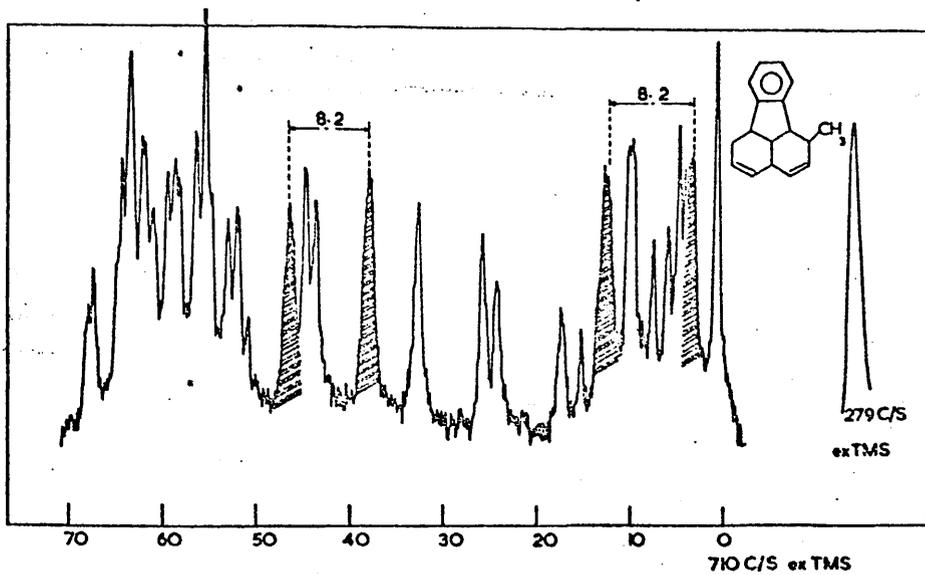


Fig. 3

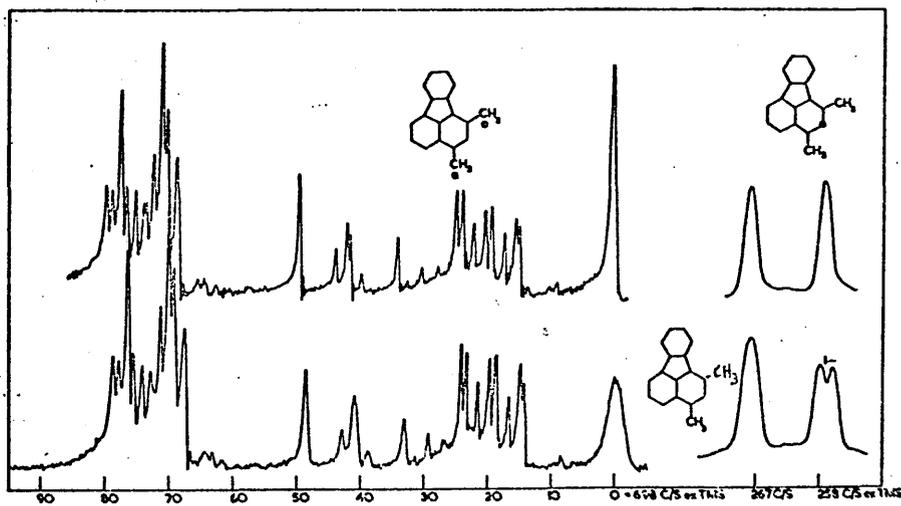


Fig. 4

quartet produced by  $H_2$  and  $H_1$  is split into a multiplet, partly by superimposition with the  $H_8$  and  $H_9$  protons and by coupling with the methyl protons.

If the methyl protons are decoupled<sup>12</sup> a sharp doublet, marked black is obtained. Only minor changes in the low field doublet are observed using the same procedure.

The methyl resonance signal in 1-methylfluoranthene (i) forms a sharp singlet (first band from R.H.S. fig 3). The quartet originating from  $H_2$  and  $H_3$  (marked in shadows) is quite clear despite some superimposition from  $H_8$  and  $H_9$ . Decoupling<sup>12</sup> of the methyl protons resulted in little sharpening of the  $H_2$  and  $H_3$  signals and a similar decoupling<sup>12</sup> of the  $H_2$ ,  $H_3$  protons had a negligible effect on the sharpening of the methyl signal.

Thus the double bond is not freely mobile between the 2,3 and 1,2 positions but fixed in the 2,3 position.

Confirmation of this was obtained when the N.M.R. spectrum of 1,3-dimethyl fluoranthene (iii) (fig. 4) examined. There are two methyl resonance signals, a singlet at 267 c/s. and a doublet at 258 c/s. (first and second band from R.H.S. fig. 4).

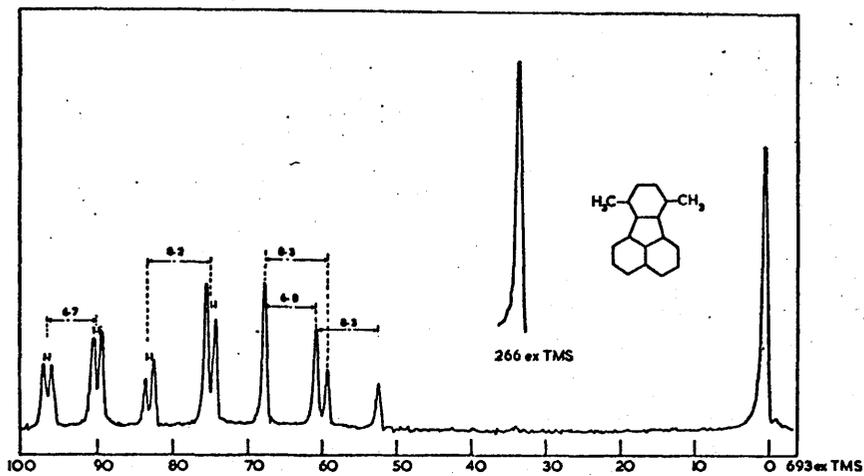


Fig. 5

The 258 c/s. doublet signal collapses into a singlet if  $H_2$  is radiated<sup>12</sup>, whilst the singlet at 267 c/s is only slightly sharpened. Both singlets have then the same height (the upper first two bands on the R.H.S. fig. 4).

The aromatic singlet at 698 c/s due to  $H_2$  is rather broad due to coupling with the methyl protons in the 3 position. Decoupling<sup>12</sup> produces a sharpening as shown in the upper curve. This spectrum also confirms the concept of a fixed double bond<sup>3</sup> in the 2,3 position.

The spectrum of 1,3,6-trimethylfluoranthene (xviii) has two methyl resonance singlets at 274 and 279.4 c/s. as well as a doublet at 266.3 c/s. with a separation of 1.0 c/s.<sup>13</sup>. This suggests that the fixed double bond concept<sup>3</sup> applies equally to both rings.

Attention was now focused on the o-phenylene ring in fluoranthene (ix) The methyl signal at 266 c/s of 7,10-dimethylfluoranthene (iv) (fig. 5) is a very sharp singlet only 50% broader than TMS. The singlet of the aromatic protons  $H_8$  and  $H_9$  at 693 c/s. is also very sharp. Decoupling<sup>12</sup> has very little effect, thus excluding any appreciable double bond character between the 7,8 and 9,10 positions. The other part of the spectrum shows a very clear twelve line pattern originating from the ABC system.

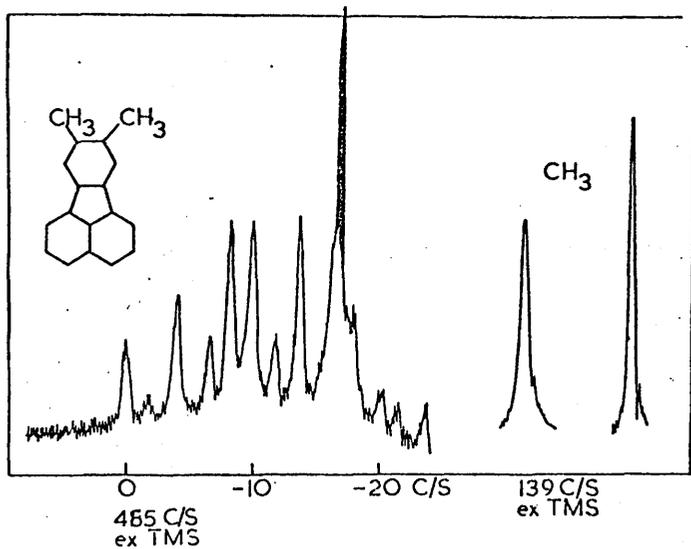


Fig. 6

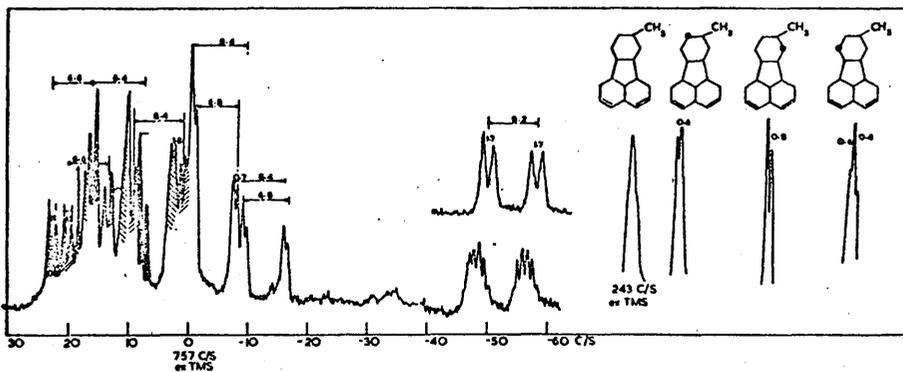
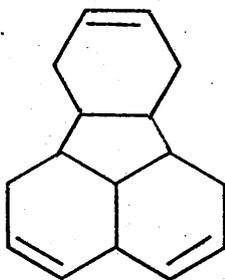


Fig. 7

A methyl singlet (139 c/s. at 60 Mc/s.) is also observed in 8,9-dimethylfluoranthene (v) (second band from R.H.S. fig. 6) Decoupling<sup>12</sup> of the 7,10-protons causes some sharpening. This also the case of the methyl protons are decoupled<sup>12</sup>, the aromatic singlet sharpens as indicated by the black area. However this is not at all comparable with the doublet into singlet transformation as observed in the 1-methyl derivatives, and thus no double bond character can be deduced from it.

From the above two spectra, a fixed double bond<sup>3</sup> could only be present in the 8,9 position or located between the upper ring and the five membered ring. The reactivity of fluoranthene (ix) in the 8,9 position<sup>14</sup> rather points to the former case.

The methyl signal (4th from R.H.S.) of 8-methylfluoranthene (vi) is shown in fig. 7. It is rather broad and splits into a doublet if H<sub>7</sub> is decoupled<sup>12</sup> (2nd band from R.H.S. fig. 7). The separation is 0.8 c/s. indicating a high degree of double bond character in line with the preceding observations. However decoupling<sup>12</sup> of H<sub>9</sub> also produces a doublet with a smaller separation 0.6 c/s. (3rd band from R.H.S. fig. 7). Decoupling<sup>12</sup> of H<sub>10</sub> causes the appearance of an apparently asymmetric triplet which is formed by the superimposition of two doublets (first band from R.H.S.) The two multiplets between 700 and 720 c/s. originate from the superimposition of coupling of the proton H<sub>9</sub> with the methyl



(xix)

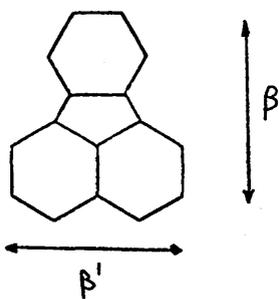
group and meta coupling with  $H_7$ . The latter appears clearly after decoupling<sup>12</sup> of the methyl (upper curve fig. 7). This substantiates the high double bond character<sup>3</sup> between positions 8 and 9. It is remarkable that the rather distant methyl group causes the ABC system to appear doubly as marked.

The N.M.R. spectrum of 8-methylfluoranthene (vi), like the preceding spectra, shows that the coupling of the methyl protons with the proton in the ortho position (benzylic coupling) can be used for the location of double bond character in polycyclic systems.

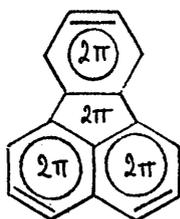
The small double bond character between  $H_7$  and position 8 found in 8-methylfluoranthene (vi), which was not found in other methyl derivatives, suggests that caution should be exercised in the concept, that the basic  $\pi$  electron structure is the same in the parent hydrocarbon and its methyl derivatives. This must be considered before any conclusions are drawn.

The methylfluoranthenes thus show a fixation of double bonds in the 2,3 4,5 and 8,9 positions, and fluoranthene (ix) could perhaps be better formulated as in (xix) where the fixed double bonds are shown.

The u.v. spectrum of fluoranthene (ix) consists of a  $\beta$  and a  $\beta'$  band at

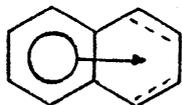


(ixa)

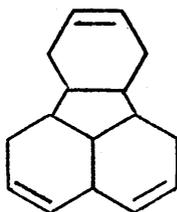


(xixa)

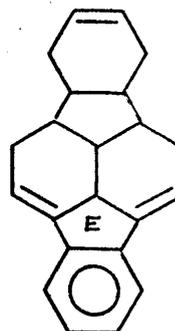
There are also  $2\pi$  electrons free to migrate over the whole system.



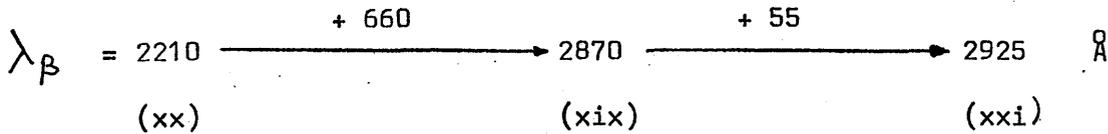
(xx)



(xix)



(xxi)



2870 and 2360 Å respectively<sup>15</sup>. The  $\beta$  is polarised perp. to the  $\beta'$  as is shown opposite<sup>15</sup> (ixa).

The  $\beta'$  is comparable to the  $\beta$  band of naphthalene at 2210 Å, which is due to polarisation along the length of the acene<sup>16</sup>.

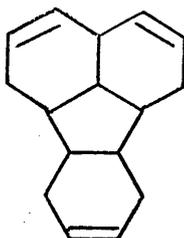
The distribution of double bonds in fluoranthene (ix) [shown opposite (xixa)] is supported by the very asymmetric annellation effect<sup>17</sup> observed in the u.v. spectra of the series naphthalene (xx), fluoranthene (xix) and 3,4-o-phenylene-fluoranthene (xxi) which is shown opposite<sup>15</sup> (xx - xxi).

The large bathochromic shift (660 Å) in going from naphthalene (xx) to fluoranthene (xix) is much greater than that between fluoranthene (xix) and 3,4-o-phenylene-fluoranthene (xxi) (55 Å). This asymmetric annellation effect<sup>17</sup> is readily accounted for by the fact that there are only  $2\pi$  electrons available to migrate over the whole system. If the empty ring (E) in o-phenylene-fluoranthene (xxi) were to have these two mobile  $\pi$  electrons, there would be no electrons available to migrate and form aromatic sextets<sup>5</sup>. Obviously this cannot take place and in 3,4-o-phenylene-fluoranthene (xxi) one of the five membered rings must be empty (E) as shown.

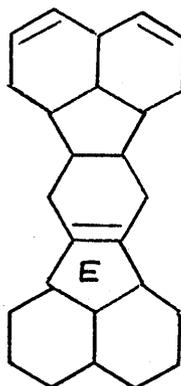
Thus the second annellation (xix - xxi) is one without aromatic conjugation due to the fixed double bonds, and the small red shift is due to the two



(xxii)



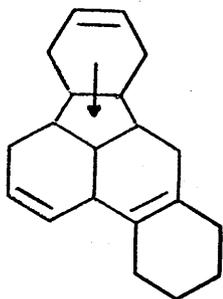
(xix)



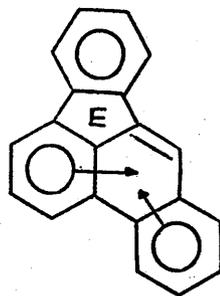
(xxiii)



Å



(xa)



(xb)

single bonds in the ring 'E'.

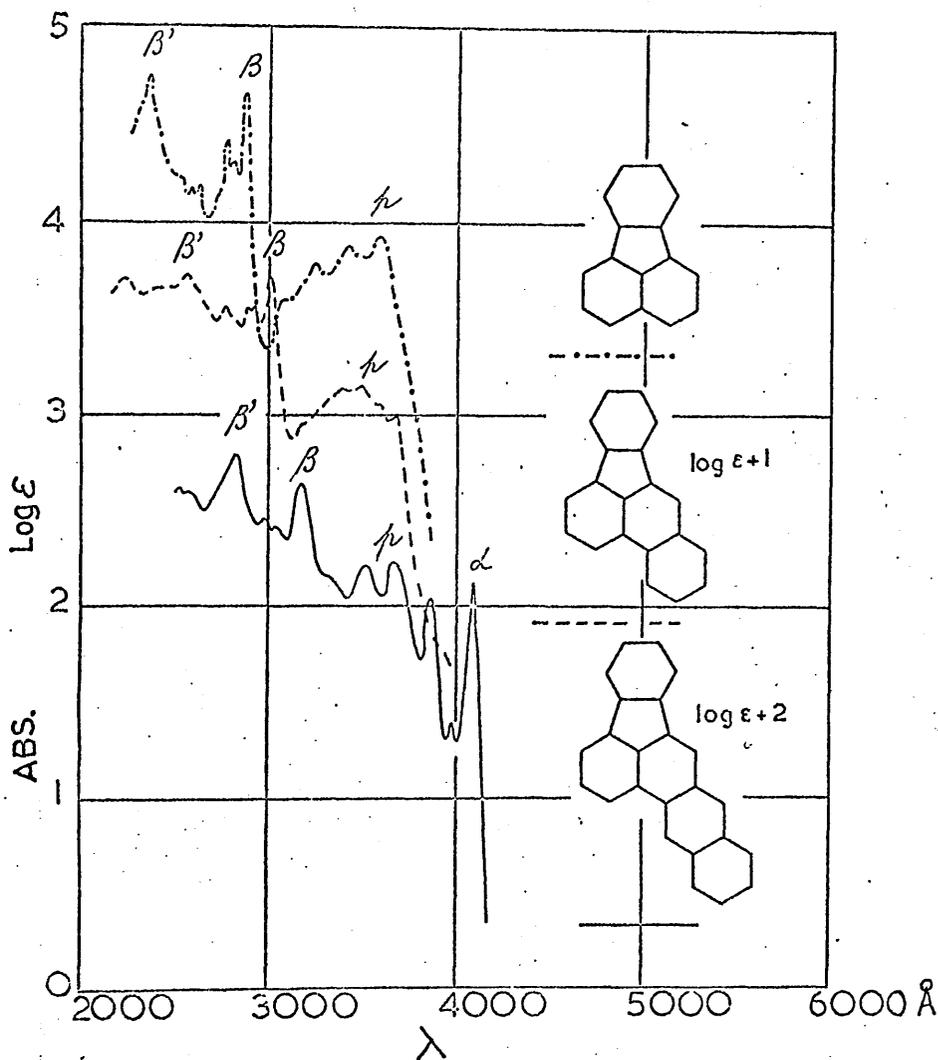
The fixed double bond<sup>3</sup> in the phenylene ring of fluoranthene (xix) also causes an asymmetric annellation effect<sup>17</sup> in going from benzene (xxii) to fluoranthene (xix) (+1035Å) to 8,9-peri-naphthylenefluoranthene (xxiii) (+350Å). The double bond in peri-naphthylenefluoranthene (xxiii) must cut off conjugation from the peri-naphthalene system as in the starphene series (see chapter I).

This asymmetry is thus in ready agreement with the N.M.R. findings and the localisation of double bonds<sup>3</sup> in fluoranthene (ix).

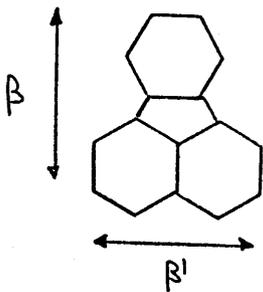
A fusing of rings at the 2,3 position in fluoranthene (xix) can lead to two possible electronic arrangements.

Either the double bond arrangement is retained as in fluoranthene (xix) and cuts off any conjugation (xa) or the five membered ring is 'empty' and the double bond moves to the 1,2 position giving a phene type conjugation and phene character (xb) as opposed to fluoranthene character in the former case.

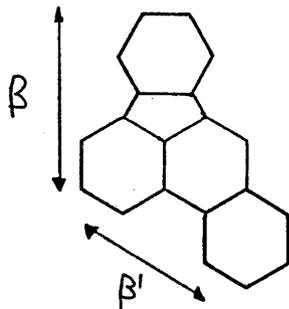
If both conjugations take place, two  $\beta$  bands would be expected - a  $\beta$  and a  $\beta'$  perpendicularly polarised and actually found in fluoranthene (ixa).



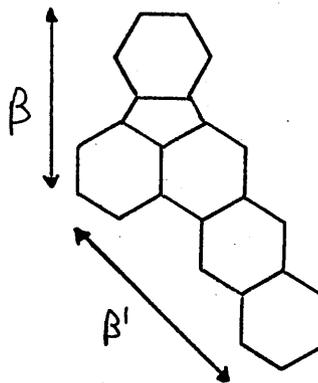
**Fig. 6** Absorption spectra in cyclohexane with max ( $\text{\AA}$ ) and  $\log \epsilon$  in parentheses.  
 - - - Fluoranthene:  $\rho$ , 3580 (3.93), 3410 (3.90), 3240 (3.79), 3090 (3.61);  $\beta$ , 2870 (4.66), 2770 (4.42), 2630 (4.19), 2530 (4.22);  $\rho$ ; 2360 (4.74).  
 - · - · 2,3-Benzofluoranthene:  $\rho$ , 3690 (3.99), 3500 (4.16), 3420 (4.14);  $\beta$ , 3020 (4.72), 2930 (4.57), 2890 (4.57), 2770 (4.57);  $\beta$ ; 2570 (4.74), 2460 (4.67), 2400 (4.66), 2230 (4.71).  
 — Naphtho[2':3', 2:3]fluoranthene:  $\alpha$ , 4100 (4.13), 3880 (4.06);  $\rho$ , 3680 (4.24), 3520 (4.22);  $\beta$ , 3180 (4.65), 3040 (4.43), 2970 (4.36);  $\beta$ ; 2830 (4.80), 2540 (4.62).



(ixa)



(x)



(vii)

$$\begin{array}{rclcl}
 \lambda_{\beta} = 2870 & \xrightarrow{+ 150} & 3020 & \xrightarrow{+ 160} & 3180 \\
 \lambda_{\beta'} = 2360 & \xrightarrow{+ 210} & 2570 & \xrightarrow{+ 260} & 2830
 \end{array}$$

R  
R

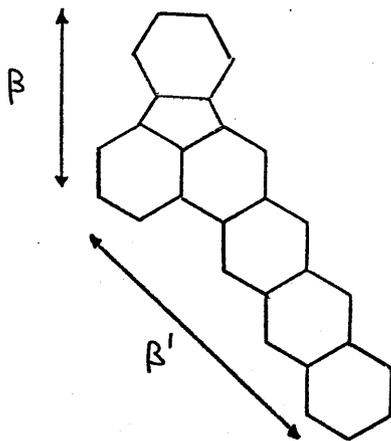
Difference

510

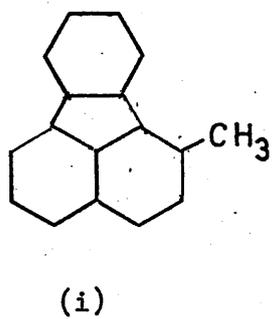
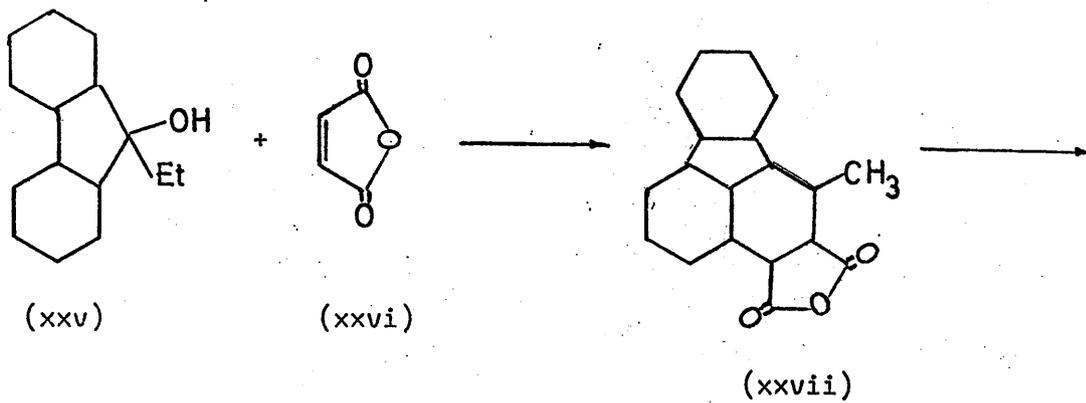
450

350

R



(xxiv)



As shown in fig. 8 and opposite (ixa,x,vii) both conjugations are found in the benzologues and there is a steady movement of the  $\beta'$  band towards the  $\beta$ , the latter moves more weakly to the red than the  $\beta'$ . The difference between the two bands decreases from 510Å to 350Å (ixa,x,vii) as the series is progressed.

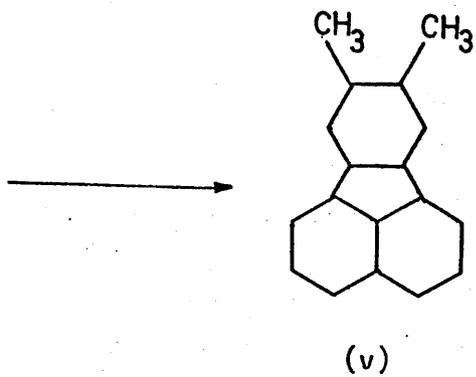
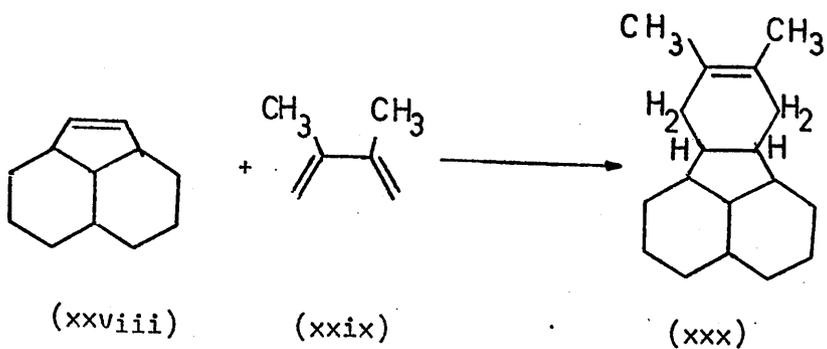
As shown opposite (ixa,x,vii), the inclination of the polarisation axes decreases and in anthracenofluoranthene (viii) an even further decrease ought to be observed (xxiv).

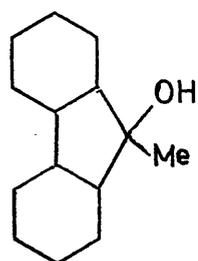
Unfortunately the attempt to synthesise this hydrocarbon failed and an examination of its u.v. spectrum relative to the other members of the series was not possible.

However the  $\beta'$  and  $\beta$  bands are obviously moving such that in higher benzologues they would be very close together and the molecule would probably behave as a substituted phenol.

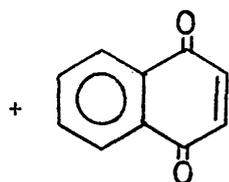
#### Experimental Discussion:

1-Methylfluoranthene (i) was prepared using a variation of Campbell and Wang's<sup>18</sup> method, which is outlined opposite (xxv - i).

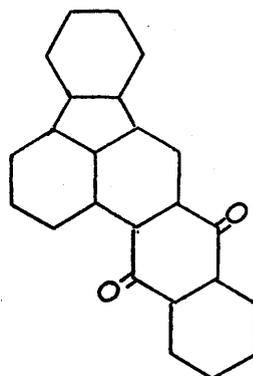




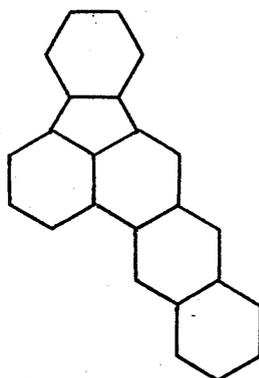
(xxxi)



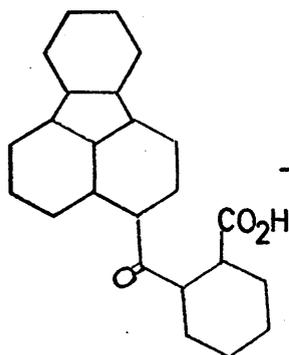
(xxxii)



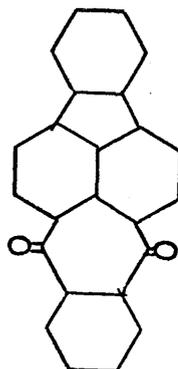
(xxxiii)



(vii)



(xxxiv)



(xxxv)

8,9-Dimethylfluoranthene (v) was prepared via 8,9-dimethyltetrahydrofluoranthene (xxx) which was synthesised according to Kloetzel and Mertel's<sup>19</sup> method.

Dehydrogenation to 8,9-dimethylfluoranthene (v) was accomplished using chloranil as dehydrogenating agent<sup>21</sup>. The synthetic route is shown opposite.

Naphtho (2':3',2:3)fluoranthene (vii) was synthesised by reducing naphtho (2':3',2:3)fluoranthene-1':4'-quinone (xxxiii) which had been prepared according to Campbell and Wang's method<sup>18</sup>. The reduction proceeded smoothly using zinc dust/acetic acid and pyridine which had proved to be a successful technique in many analogous cases<sup>20</sup>.

Cyclisation of 3-o-carboxybenzoylfluoranthene (xxxiv) is reported by Campbell<sup>18</sup> to lead not to the expected naphtho (2':3',2:3)fluoranthene-1':4'-quinone (xxxiii) but to the 3,4-phthaloylfluoranthene (xxxv).

Campbell's synthetic method<sup>18</sup> thus provides a neat alternative reaction sequence for circumventing the usual type of aryl acid anhydride Friedel Craft's reaction followed by ring closure and reduction to the hydrocarbon, which obviously does not work in this case.

In view of this difficulty it was decided to synthesise anthraceno(2':3',2:3)

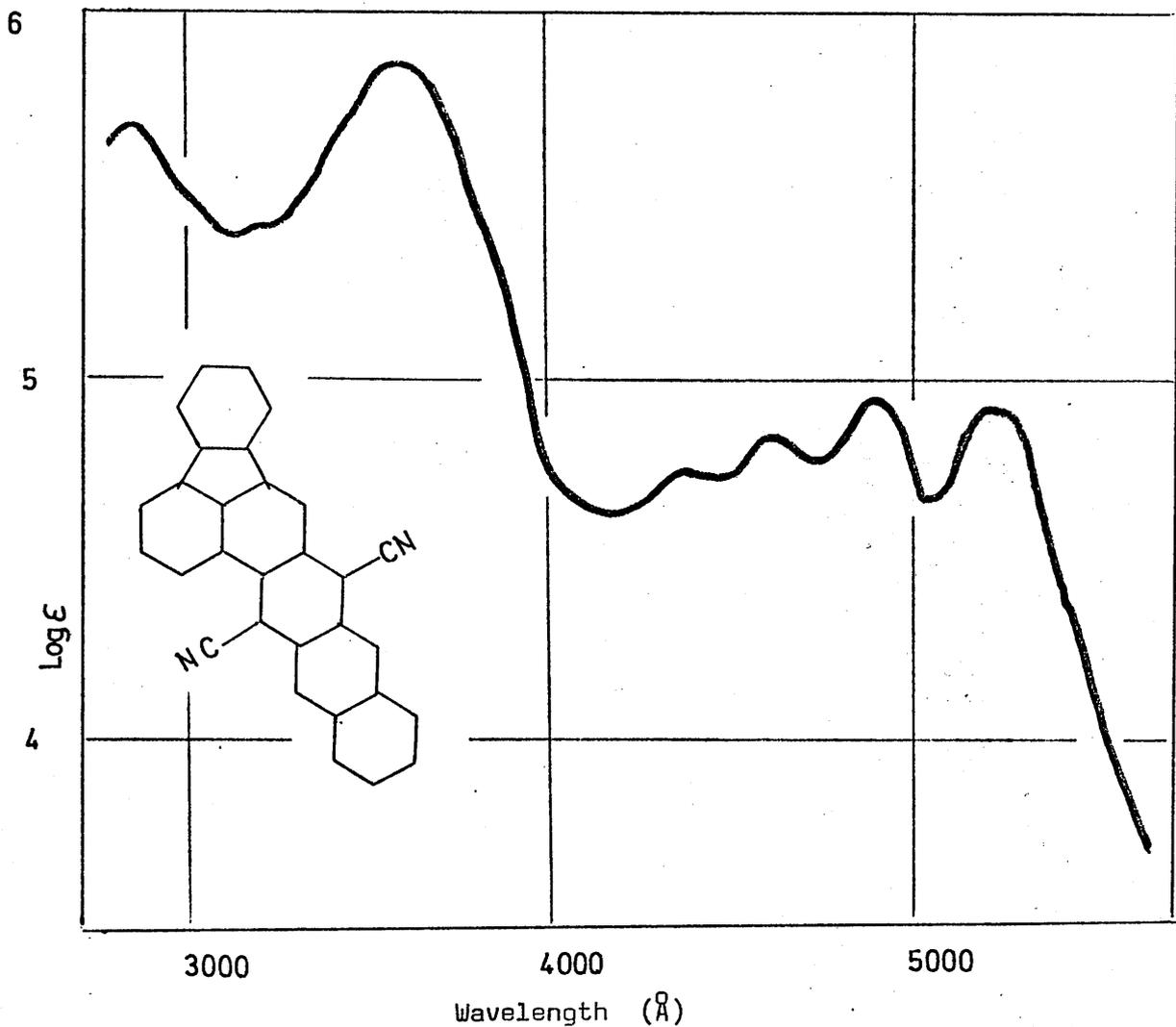
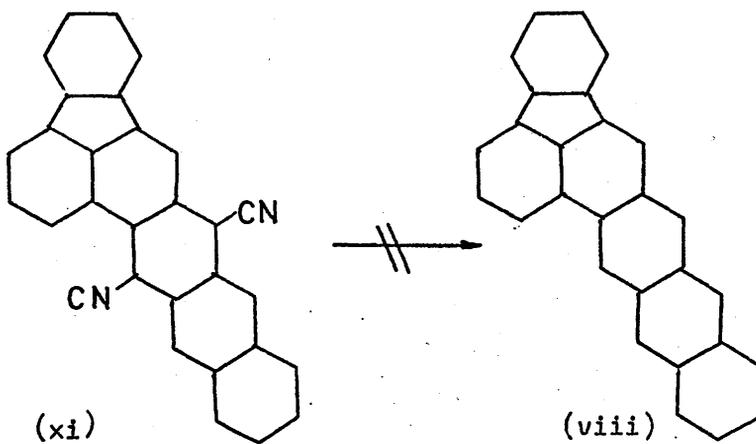
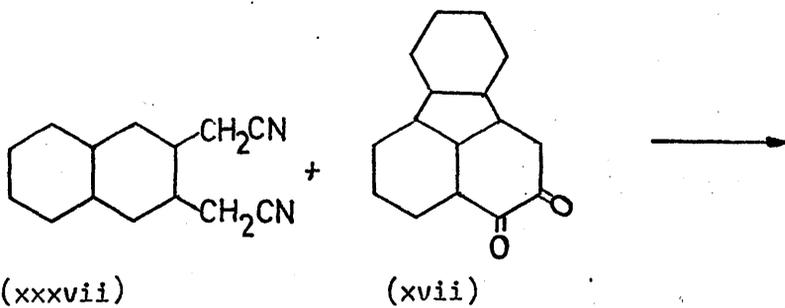


Fig. 9 Absorption maxima ( $\text{\AA}$ ) and  $\log \epsilon$  ( in parentheses ).

1',4'-Dicyano-anthraceno(2':3',2:3)fluoranthene in benzene :  $\alpha$ , 5220 (4.92), 4860 (4.93), 4580 (4.84);  $\beta$ , 3620 (5.84), 3540 (5.87) ; 2850 (5.69).



fluoranthene (viii) by condensing fluoranthene-quinone<sup>10</sup> (xvii) with 2,3-bis-cyanomethyl-naphthalene<sup>21</sup> (xxxvii), this type of condensation had proved to be successful in similar cases<sup>15, 22</sup>.

This gave 1',4'-dicyano-anthraceno (2':3',2:3)fluoranthene (xi) in good yield. Sublimation of the hydrolysed dicyano compound (xi) with soda lime resulted in decomposition although a successful decarboxylation was achieved in similar cases<sup>15</sup>.

Acknowledgement:

3-Methylfluoranthene (ii), 8-methylfluoranthene (vi) and 7,10-dimethylfluoranthene (iv) were prepared by Dr. Ü. Sanigök. 1,3-Dimethylfluoranthene was provided by Dr. H.S. Tucker. Their contribution meant that a complete study of the methyl derivatives could be undertaken.

EXPERIMENTAL1-Methylfluoranthene-2;3-dicarboxylic-anhydride (xxvii).

A variation of the method of Campbell and Wang<sup>18</sup> was used. 9-Hydroxy-9-ethylfluorene (xxv) (11g) was dissolved in nitrobenzene (200ml.) and maleic anhydride (20g), as well as a few crystals of iodine, added to the solution. The solution was refluxed for 1½ hours with frequent changes of air condensers to remove the water formed during the reaction. Acetic acid (50ml.) was added to the solution, which on cooling deposited crystals of (xxvii), which were washed with acetic acid and ether. Yield 6g, m.pt. 274-8° (lit. 275-80°)<sup>18</sup>. Campbell and Wang's method<sup>18</sup> yielded 0.28g from 0.5g which was better than the yield obtained here.

1-Methylfluoranthene (v)

(xxvii) (2g) was powdered with soda lime (6g), a few drops of alcohol being added to aid intimate contact of the particles. The mixture was then strongly heated under reduced pressure ( $2 \times 10^{-2}$  mm) and the yellow product dissolved in pet. ether (60-80°). It was concentrated and chromatographed on neutral alumina (60g) using pet. ether as eluant. The 1-methylfluoranthene (v) (0.4g) obtained

was recrystallised from pet. ether as pale yellow needles, m.pt. 72-73° (lit. 72-73°)<sup>18</sup>. A better yield was obtained by Campbell and Wang<sup>18</sup> who used a sublimation technique instead of a vacuum distillation method as was used here.

Found: C, 94.28 ; H, 5.59%

C<sub>17</sub>H<sub>12</sub> requires C, 94.41 ; H, 5.59%

8,9-Dimethyltetrahydrofluoranthene (xxx).

The method of Kloetzel and Mertel<sup>19</sup> was used to prepare (xxx) A mixture of acenaphthalene (5g), 2,3-dimethyl-1,3-butadiene (30g) and hydroquinone (0.5g) was heated in a sealed tube for 36 hours at 150°. It was then diluted with benzene (20ml.) and extracted with dilute NaOH, and the solvents were removed under reduced pressure. The residue was thoroughly extracted with hot methanol and the solution concentrated, then distilled at 0.2mm. At 70° a yellow oil was obtained, and at 110° a second fraction collected which quickly solidified. The brownish yellow solidified product was crystallised from ethanol as colourless needles of (xxx) of m.pt. 69-70° (lit. 70°)<sup>19</sup>. Yield, from three tubes 6.1g (lit. 5.7g)<sup>19</sup>

8,9-Dimethylfluoranthene (v)

8,9-Dimethyltetrahydrofluoranthene (xxx) (6.1g) was dissolved in xylene (100ml.), chloranil (10g) added and the mixture refluxed for 5 hours. It was then added to dilute NaOH (300ml., 5%) and refluxed with stirring for 4 hours. At this point the mixture was filtered and the organic layer separated and concentrated to a small volume, diluted with light petroleum ether (100-20<sup>o</sup>) and chromatographed on alumina (120g). The hydrocarbon (v), after three crystallisations from ethanol formed long yellowish needles (4g) m.pt. 144-5<sup>o</sup> (lit. 145<sup>o</sup>)<sup>19</sup>

Found: C, 93.7 ; H, 6.3%

Calc. for C<sub>18</sub>H<sub>14</sub> C, 93.9 ; H, 6.1%

Naphtho(2':3',2:3)fluoranthene-1':4'-quinone (xxxiii)

(xxxiii) was synthesised following the description of Campbell and Wang<sup>18</sup>. 9-Hydroxy-9-methylfluorene (10g),  $\alpha$ -naphthaquinone (40g) and acetic anhydride (150ml.) were refluxed together for 4 hours. The solution was allowed to stand for 24 hours, depositing red needle crystals (17.4g) which were filtered off and washed with ethanol. The crude naphtho(2':3',2:3)fluoranthene-1':4'-quinone (xxxiii) had m.pt. 240-44<sup>o</sup> (lit. 248-51<sup>o</sup>)<sup>18</sup>.

Naphtho(2':3',2:3)fluoranthene (vii)

The crude quinone (xxxiii) (17.4g) was dissolved in pyridine (200ml.) and filtered from a white residue, which was washed with pyridine (50ml.). The combined solution was refluxed with zinc dust (50g) and acetic acid (50ml., 80%) introduced dropwise over a 3 hour period. After 5 hours, the solution was decanted from the zinc, and acidified with acetic acid. The precipitate (2.5g) was filtered off and washed with water. More precipitate appeared after prolonged standing. The first portion (2.5g) was dissolved in hot xylene (500ml.), concentrated to remove water and chromatographed on alumina (100g). Concentration of the eluate indicated that the crystals were not uniform. Thus, picrates were prepared from the different fractions and orange needles of the pure picrate (0.22g) obtained. Decomposition with dilute ammonia gave naphtho(2':3',2:3)fluoranthene (vii) which was recrystallised from xylene as pale yellow crystals m.pt. 228-9<sup>o</sup> (lit. 228-9<sup>o</sup>)<sup>23</sup>.

2,3-Bis-cyanomethyl-naphthalene (xxxvii)

A modification of the method of Ried and Bodem<sup>21</sup> was employed which gave a higher yield. Potassium cyanide (10g) was dissolved in a minimum amount of water and refluxed with ethanol (150ml.)

2,3-Bisbromomethyl-naphthalene (10g) was introduced in portions and the mixture refluxed for 2 hours. After cooling, the mixture was poured into water and the precipitate filtered off. Recryst. from benzene/light pet. ether (100-20<sup>o</sup>) gave needles (5.7g) (lit. 4.7g)<sup>21</sup> m.pt 155-7<sup>o</sup> (lit. m.pt. 157<sup>o</sup>).

Fluoranthenequinone (xvii)

A method similar to that of Fittig and Gebhard was used<sup>10</sup>. Fluoranthene (30g) was dissolved in acetic acid (300ml.) and the solution refluxed. Chromic anhydride (35g) in a little water was added portionwise to the refluxing solution. After the vigorous reaction had ceased (3 min.), the solution was boiled for a further 10 min. with stirring. Water was introduced and the mixture allowed to settle. The product was extracted with pet. ether (100-20<sup>o</sup>) and the conc. solution chromatographed on neutral alumina (400g) using benzene as eluant. The crude quinone was crystallised from ethanol as red needles (0.5g) m.pt. 187-88<sup>o</sup> (lit. m.pt. 188<sup>o</sup>).

1',4'-Dicyano-anthraceno(2':3',2:3)fluoranthene (xi)

2,3-Bis-cyanomethyl-naphthalene (xxxvii) (0.2g) was dissolved

in dry ethanol (20ml.) and added to a solution of fluoranthenequinone (xvii) (0.23g) in dry ethanol. The solution was boiled and potass. hydroxide in ethanol (0.05g in 3ml.) introduced. The mixture which became immediately dark and precipitated red needles was cooled and filtered after 2 hours. The needles (0.1g) were recrystallised from dry benzene and sublimed at  $300^{\circ}/4 \times 10^{-2}$  mm., m.pt.  $360^{\circ}$ . In benzene the following bands were found:  $\lambda$  in  $\text{\AA}$ , abs. as  $\log \epsilon$ . p, 5220 (4.92), 4860 (4.93), 4580 (4.84), 4350 (4.73); 3620 (5.84), 3540 (5.87); 2850 (5.69). See diagram 9.

Found: C, 89.72 ; H, 3.62 ; N, 6.73%

$C_{30}H_{14}N_2$  requires C, 89.54 ; H, 3.51 ; N, 6.96%

Molec. wt. Found: m/e = 402

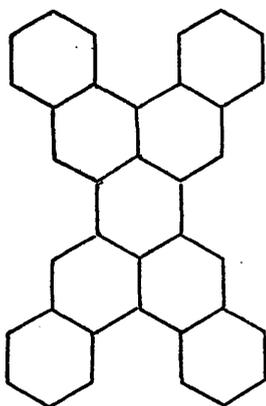
Calc.: m/e = 402.

#### Anthraceno(2':3',2:3)fluoranthene (viii)

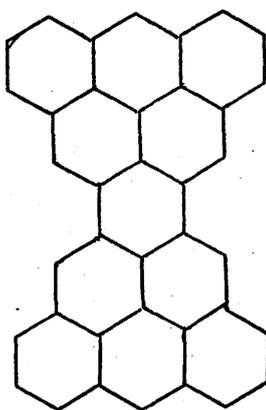
1',4'-Dicyano-anthraceno(2':3',2:3)fluoranthene (0.75g) was powdered intimately with soda lime (3g) then a thick paste was made with sat. aqueous potassium hydroxide. The mixture was heated to  $350^{\circ}$  for one hour under nitrogen to ensure removal of moisture and alcohol.

The pressure was reduced to  $4 \times 10^{-4}$  mm. and although the temperature was raised as high as  $500^{\circ}$ , no sublimation took place.

The contents of the sublimation boat were brownish black in colour and extraction with trichlorobenzene showed no trace (in the u.v. abs. spectrum) of either starting material or product, indicating that decarboxylation had been unsuccessful and had resulted in decomposition.

CHAPTER VIAttempted syntheses of perylene benzologues based on 3,6-dibenzoyl-  
durene.

(i)

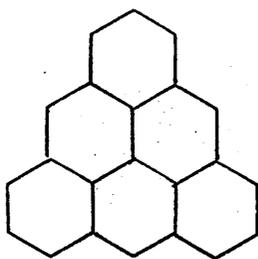


(ii)

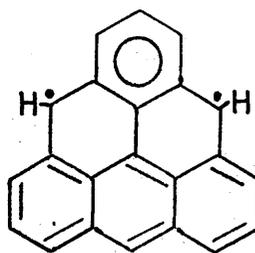
Introduction:

Syntheses of the hitherto known 2,3:4,5:8,9:10,11-tetrabenzoperylene<sup>1</sup>

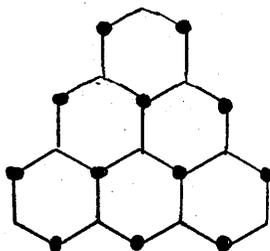
(i) and dianthraceno(1':8',8:11);(1":8",2:5)perylene (ii) were attempted.



(iii)



(iv)



(v)

$$C^{\bullet} = 12$$

$$\underline{C = 10}$$

$$\underline{\underline{\text{Difference } 2}}$$

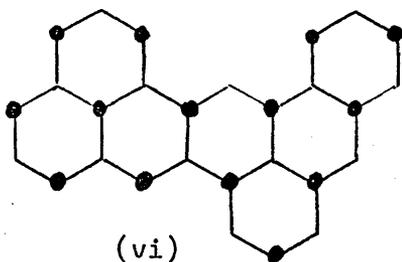
Discussion:

Tetrabenzoperylene<sup>1</sup> (i) has already been synthesised by McAndrew, using a reaction sequence which resulted in a poor yield of product. A new synthetic route was devised starting from 3,6-dibenzoyldurene (xii). The difficulties encountered are discussed in the experimental section.

The second half of this chapter deals with the attempted synthesis of dianthracenoperylene (ii). Triangulene (iii), has been the subject of many synthetic attempts by Clar et al<sup>2</sup>. The results of which led to the conclusion that the structure was, as suspected, a diradical which immediately polymerised on being formed<sup>3</sup>.

Triangulene (iii) cannot be represented using Kekulé structures without there being two unpaired electrons (iv). The alternant marking principle<sup>4,5</sup> shows that there are two more marked than unmarked carbon atoms (v). If the marking is equated with equal spins of  $\pi$ electrons<sup>6</sup>, then it is obvious that there must be two unpaired electrons resulting in the molecule being a diradical<sup>4</sup>.

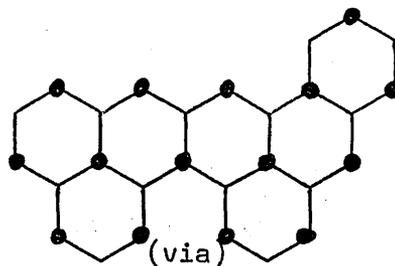
Examples of the wide application of the alternant marking principle and its complete agreement with experimentally found facts are discussed below (vi-viia). (The impossibility of a bond between meta C atoms is inherent



$$C^{\bullet} = 14$$

$$C = 14$$

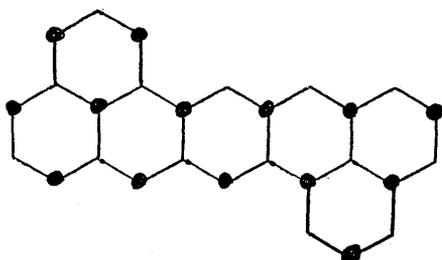
Difference 0



$$C^{\bullet} = 15$$

$$C = 13$$

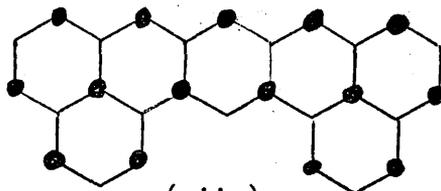
Difference 2



$$C^{\bullet} = 14$$

$$C = 14$$

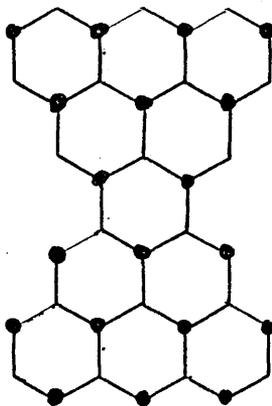
Difference 0



$$C^{\bullet} = 15$$

$$C = 13$$

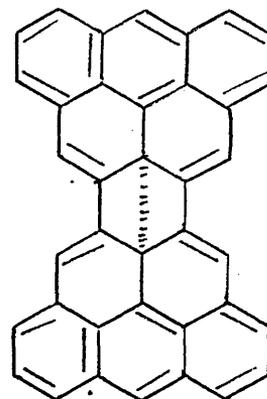
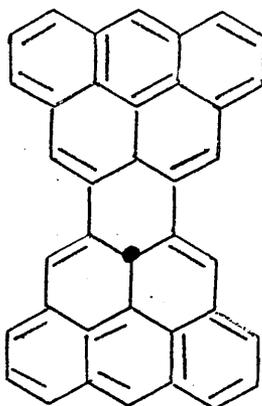
Difference 2



$$C^{\bullet} = 19$$

$$C = 19$$

Difference 0



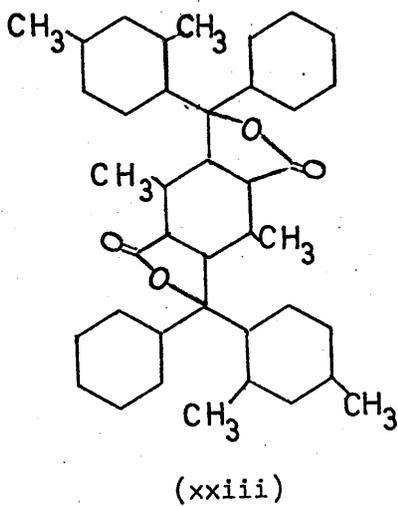
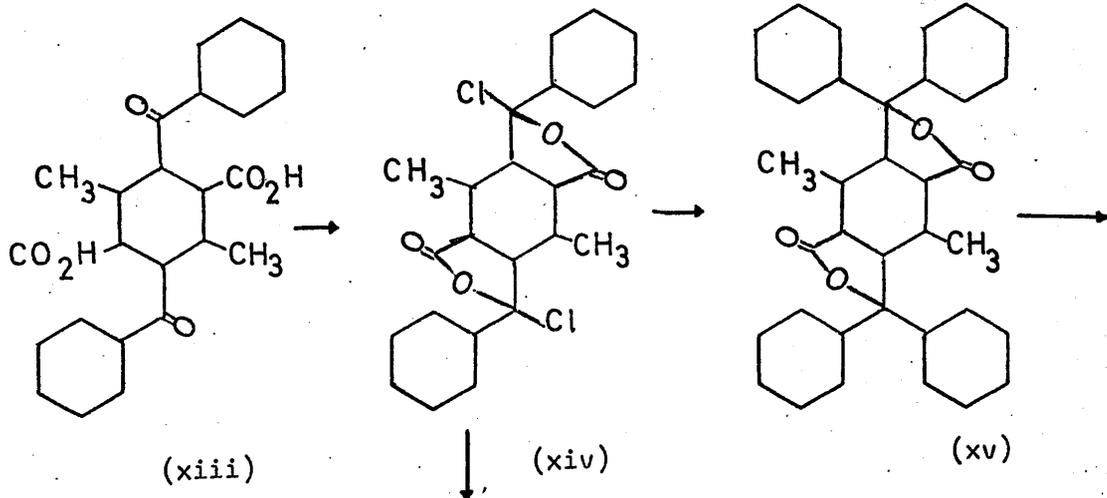
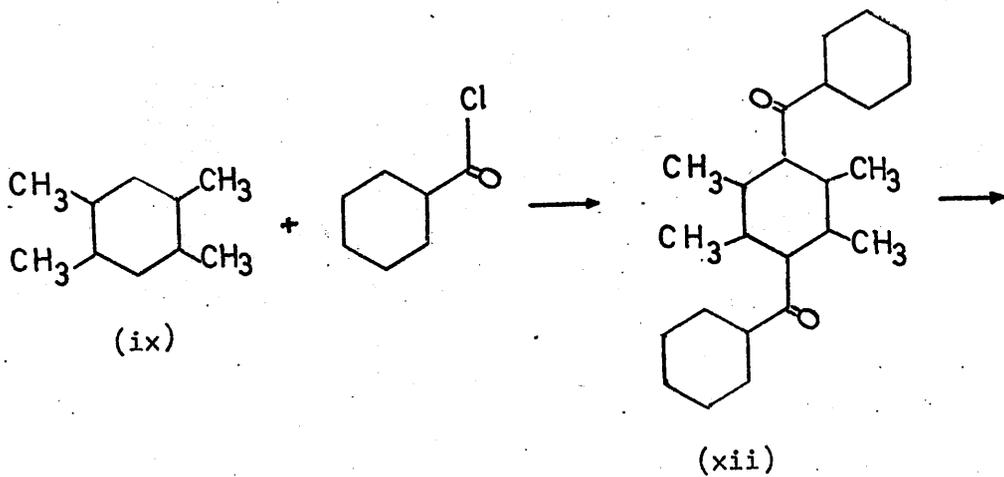
in the alternant marking principle as it would involve a bond with  $\pi$  electrons of the same spin).

5,6-Benzozanthrene (vi) has the same number of marked and unmarked carbon atoms i.e. all electrons are paired and thus the compound should be stable. Its isomer (via) however, has two more marked carbon atoms and thus would be expected to be an unstable diradical. These predictions were confirmed experimentally<sup>4</sup>.

Heptazanthrene (vii) with an equal number of marked and unmarked carbon atoms is a known stable substance. Its isomer 1,14:11,12-dibenzopen-  
tacene with a difference of two, between the number of marked and un-  
marked carbon atoms, is a diradical, which polymerised immediately on  
being formed<sup>7</sup>.

Both benzozanthrene (vi) and heptazanthrene (vii) can be written with Kekulé structures where-as their respective isomers (via) and (viia) cannot

Dianthracenoperylene (ii), is of interest as it has an equal number of marked and unmarked carbon atoms as shown (viii), but cannot be represented with a Kekulé structure (viia). If double bonds are represented by connecting the neighbouring marked and unmarked carbon atoms, then there remains two unpaired  $\pi$  electrons of opposite spin (viia).



For dianthracenoperylene to be stable, these electrons must form a bond, which would of necessity be a  $\pi$  Dewar bond (viiiib). It was thus of considerable interest to attempt to synthesise this compound and study its stability or lack of stability.

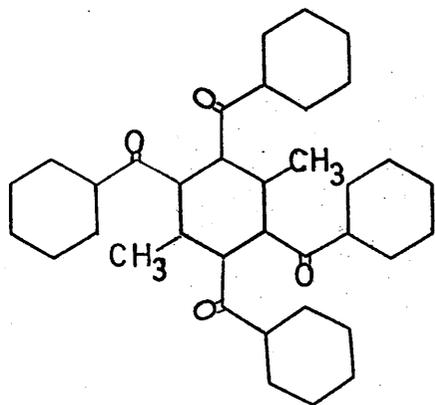
Unfortunately, due to synthetic difficulties encountered, lack of time prevented a satisfactory completion of the project.

#### Experimental Discussion:

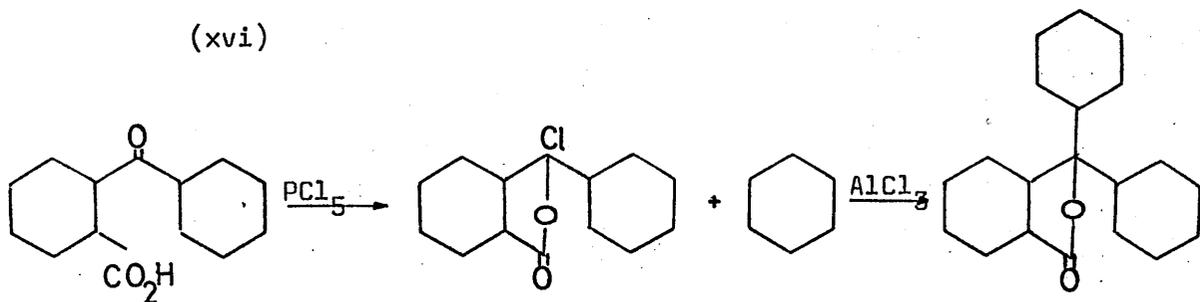
To synthesise both tetrabenzoperylene (i) and dianthracenoperylene (ii) similar syntheses based on 3,6-dibenzoyldurene<sup>8</sup> (xii) were attempted.

An outline of the intended route to tetrabenzoperylene (i) is shown opposite (ix-i). The formation of 3,6-dibenzoyldurene (xii) has already been reported by Friedel and Crafts<sup>8</sup> and a modification of their procedure was employed.

The oxidation of durene by refluxing in dilute nitric acid has been reported by various workers<sup>9,10,11</sup>. The products of the oxidation were two dicarboxylic acids, the 1,4 (x) and the 1,5 (xi) the latter being very soluble in hot water and thus readily separable<sup>9</sup>. Dibenzoyldurene (xii)

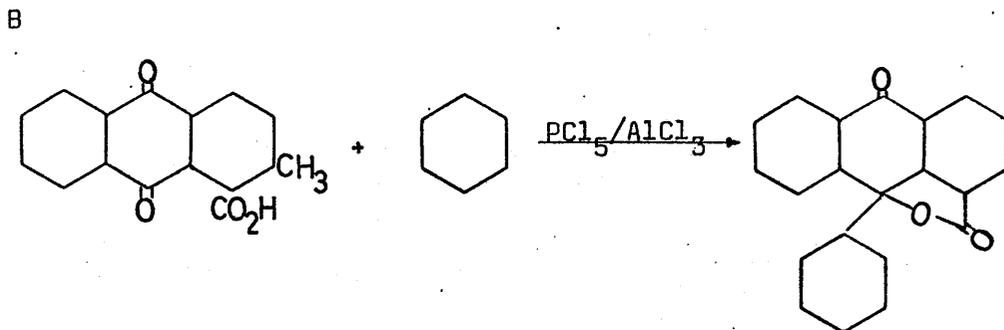
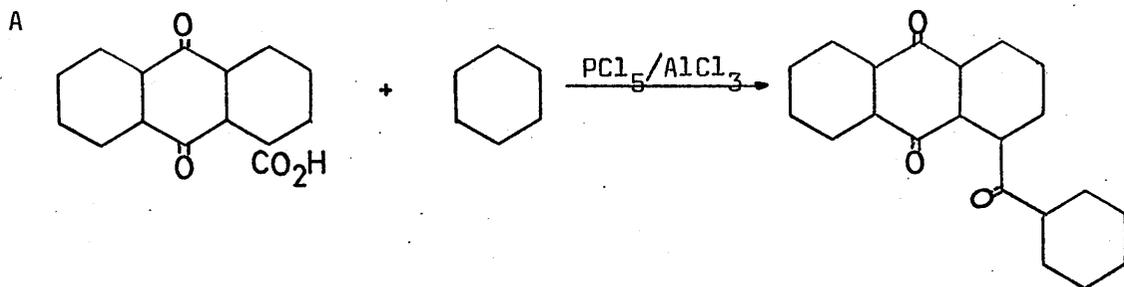


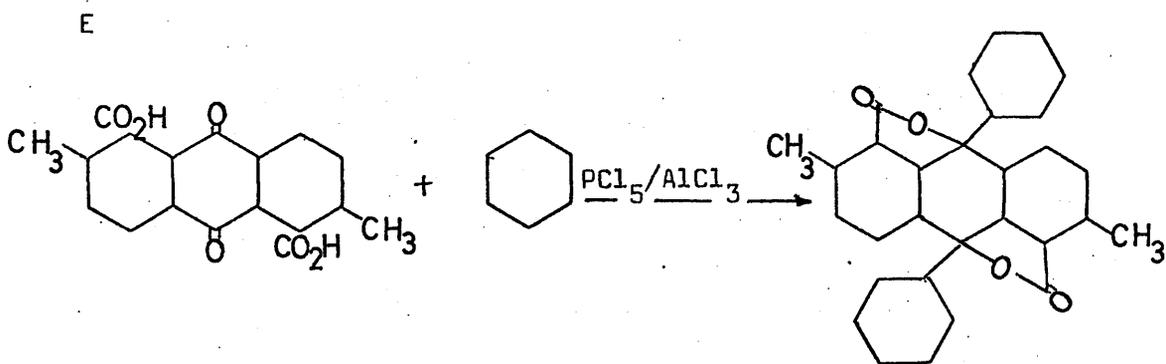
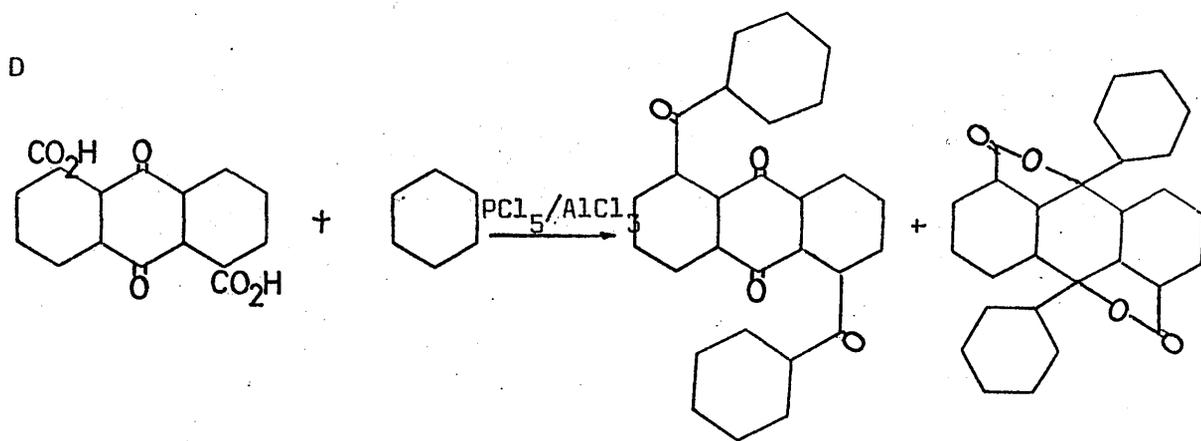
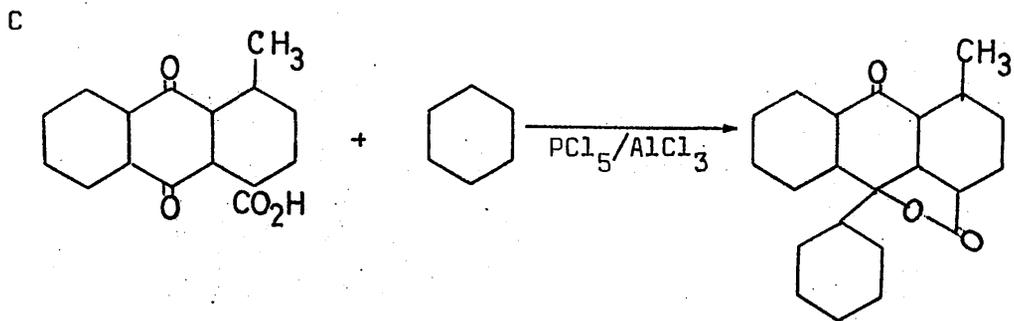
(xvi)



(xvii)

(xviii)





on being oxidised with dilute nitric acid gave a good yield of the 1,4 dicarboxylic acid (xiii), most of the 1,5 remaining in solution. The i.r. had absorption bands at  $1760\text{cm}^{-1}$  (C=O acid) and  $1716\text{cm}^{-1}$  (C=O).

The acid was refluxed with thionyl chloride, yielding a product which had only one i.r. carbonyl absorption at  $1775\text{cm}^{-1}$ . This suggested that the structure was of a lactone type (xiv). Subsequent condensing of the chloride with benzene in the presence of aluminium chloride gave the lactone (xv), which had an i.r. absorption band at  $1760\text{cm}^{-1}$  (C=O for a five membered  $\alpha,\beta$  unsaturated lactone).

The i.r. showed no trace of the other isomer (xvi) that might have been expected to have been formed. Due to energetically unfavourable steric factors, its formation would not be encouraged, especially when compared with the more rigid molecular framework of the lactone.

The formation of a similar type of intermediate lactone (xvii) was suggested by Haller and Guyot<sup>12</sup> in the synthesis of diphenylphthalide (xviii). Scholl et al<sup>13,14</sup>, conducted a great deal of work on substituted anthraquinone carboxylic acids and their results are summarised (A-E).

In all cases the presence of a methyl group ortho or para to the carboxylic acid induced formation of the lactone. This is probably due to the

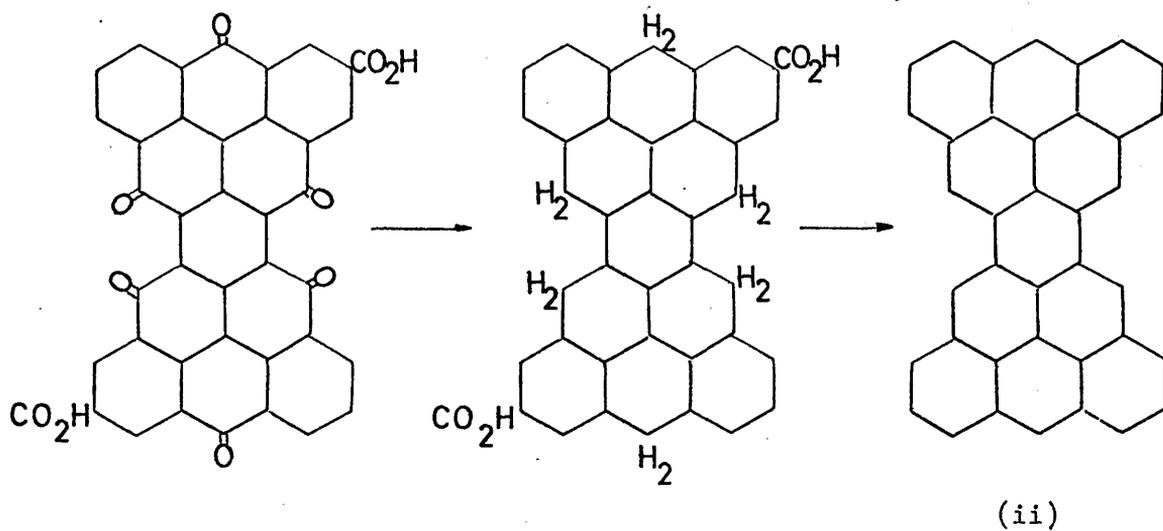
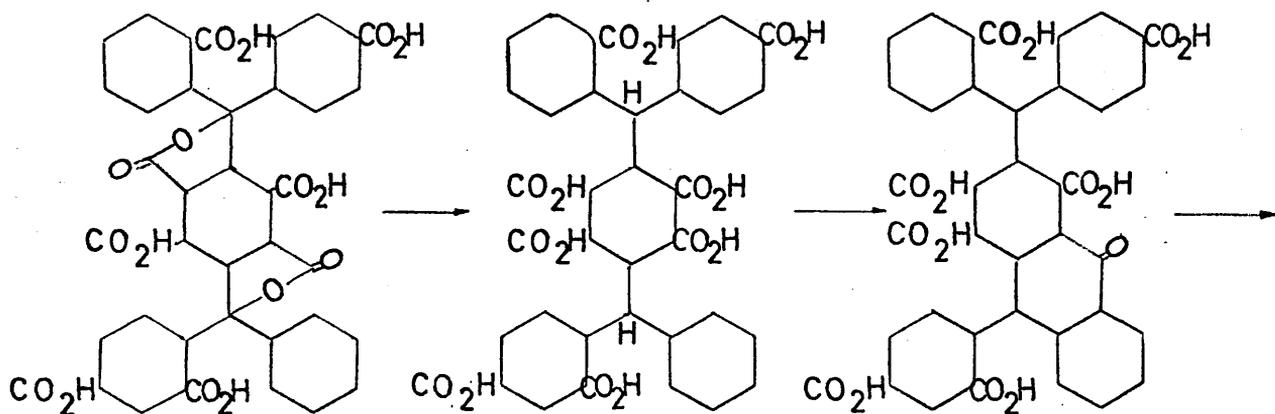
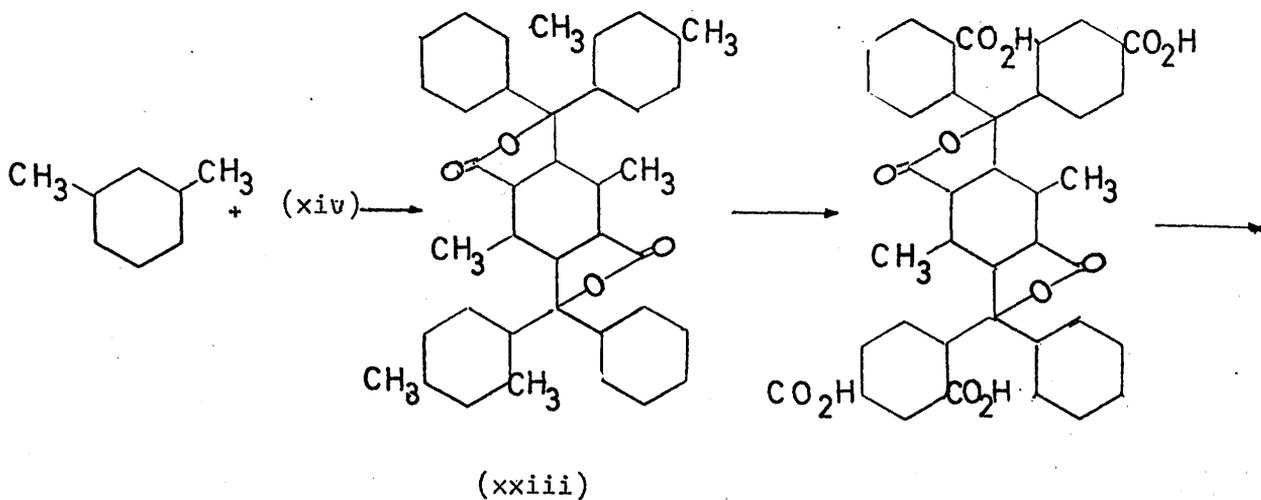
hyperconjugation effect of the methyl group on the acid during the chloride formation. Scholl<sup>14</sup> mentions that lactone formation takes place exclusively when the methyl group is in a para position to the carboxy function. The effect of the methyl group is thus not steric<sup>14</sup> and it must be involved in the electronic arrangement of the molecule.

The lactone (xv) proved to be very unreactive and could not be oxidised to the corresponding diacid with potassium permanganate in alkaline solution, as had been achieved in Scholl's analogous reaction<sup>16</sup>. Despite the use of a wide range of alkalis, the lactone could not be induced to go into solution.

A sealed tube reaction with the lactone (xv) and nitric acid yielded an acidic product, which was also nitrated as was indicated by the i.r. absorption bands at 1530, 1350 $\text{cm}^{-1}$  (N=O stretch) and the micro analytical data. I.R. absorption bands were also present at 1785 $\text{cm}^{-1}$  and 1745 $\text{cm}^{-1}$  (C=O stretch of lactone and acid respectively).

Direct oxidation of the lactone (xv) with potassium permanganate and acetone was without success, the product having the same m.pt. and i.r. as the lactone (xv). A zinc dust melt<sup>15</sup> was also found, as suspected, to be ineffective with this type of compound.

When the lactone (xv), zinc dust and a few drops of water were heated in



a sealed tube for 48 hr. (at  $300^{\circ}$ ), a small amount of oily product was obtained (after chromatography). It showed u.v. absorption bands at 3259, 3425, 3600,  $3780\text{\AA}$  (in benzene), and had possibly an anthraceno type structure.

With copper powder at  $400^{\circ}$ , the lactone (xv) reacted to give traces of oily products (obtained after chromatography) with u.v. absorption bands at 3240, 2400, 3570,  $3580\text{\AA}$  and 3300, 3490, 3685, 3870,  $4120\text{\AA}$  (in benzene).

Due to the lack of any encouraging results, the above reaction sequence was discontinued.

The dianthracenoperylene (ii) synthetic scheme is outlined opposite.

The lactone (xxiii) was readily obtained using meta xylene in the Friedel Crafts reaction instead of benzene as in the last synthesis. As in the previous case (xv), the lactone could not be induced, despite using a wide range of alkalis, to go into solution.

The lactone was oxidised by refluxing with dilute nitric acid for 48 hr. To complete the oxidation of the methyl groups and alkaline solution was treated with potassium permanganate. The lactone was then reduced using KOH/Zn.

The main carbonyl absorption in the i.r. was at  $1710\text{ cm.}^{-1}$  and the crude.

octa acid still had a weak band at  $1760\text{cm}^{-1}$ , arising from traces of lactone.

Cyclisation with  $\text{H}_2\text{SO}_4$  resulted in a great deal of sulphonation taking place. The crude octa acid was therefore powdered with pyrophosphoric acid, phosphorus pentoxide and heated at  $320^\circ$  for several hours<sup>16</sup>.

The product was taken directly and reduced using P/HI in a sealed tube. The u.v. spectrum of the product showed absorption at 4660, 4380, 3960, 3540, 3180 Å.

Due to the time factor involved and the very low yields from any slightly promising reactions the work was discontinued on this reaction scheme.

EXPERIMENTAL3,6-Dibenzoyldurene (xii)

3,6-Dibenzoyldurene (xii) was prepared by a modification of the Friedel and Crafts method<sup>8</sup>. From 160g of durene (ix), 202g of dibenzoyldurene were obtained using tetrachloroethane as solvent.

$\nu_{\text{max}}^{\text{KBr}} = 1662\text{cm}^{-1}$  (C=O absorption). In sulphuric acid, (xii)

formed a light yellow solution which became brownish violet on heating; m.pt.  $268-9^{\circ}$  (lit.  $269-70^{\circ}$ )<sup>8</sup>.

p-Xylene-2,5-dibenzoyl-3,6-dicarboxylic acid (xiii)

A paste of dibenzoyldurene (xii) (90g) in nitrobenzene (100ml.) was added to nitric acid (1500ml., 35%) and the mixture refluxed for 3 days. Initially, there was a brisk evolution of nitrogen dioxide which slackened off after a day or so. After cooling, the mixture was filtered and the product, which was no longer floating on the surface, filtered. It was washed with nitrobenzene and ether.

Yield 42g. It was crystallised twice from nitrobenzene; m.pt.

$320^{\circ}$ .  $\nu_{\text{max}}^{\text{KBr}} = 1760\text{cm}^{-1}$  (acid C=O) and  $1716\text{cm}^{-1}$  (diaryl C=O).

The needles dissolved in conc. sulphuric acid to give a pale yellow solution which became golden brown on heating.

Found: C, 71.56 ; H, 4.48%

$C_{24}H_{18}O_6$  requires C, 71.63 ; H, 4.51%

3,6-Dimethyl-7,9-tetraphenyl-pyromellitide (xv).

The powdered acid (xiii) (15g), thionyl chloride (350ml.) and pyridine (3 drops) were refluxed together for 3 hours. The thionyl chloride was distilled over under reduced pressure, then dry benzene (2x100ml.) added and distilled over - in order to remove all traces of thionyl chloride. The i.r. of the crude product indicated only one carbonyl absorption band at  $1775\text{cm}^{-1}$  which helped to confirm the structure (xiv).

Powdered aluminium chloride (30g) was added to a suspension of the chloride in benzene (80ml.). The mixture was heated and stirred for 3 hours at  $55^{\circ}$ , then decomposed using aqueous hydrochloric acid. The light brown precipitate was filtered and washed with dilute hydrochloric acid, water, ethanol, benzene and ether. Yield 6g. Concentration of the mother liquor gave a further 7g of crystalline product. The combined product was extracted with dilute NaOH, to remove any unreacted acid (xiii). After three crystallisations from HOAc, the almost colourless needle crystals were sublimed in vacuum

m.pt. 327-30<sup>o</sup>. In sulphuric acid the initial light yellow solution became brown on standing.  $\nu_{\text{max}}^{\text{KBr}} = 1760\text{cm.}^{-1}$  (C=O absorption of five membered  $\alpha, \beta$  unsat. lactone).

Found: C, 82.5 ; H, 5.0%

$\text{C}_{36}\text{H}_{26}\text{O}_4$  requires C, 82.7 ; H, 5.0%

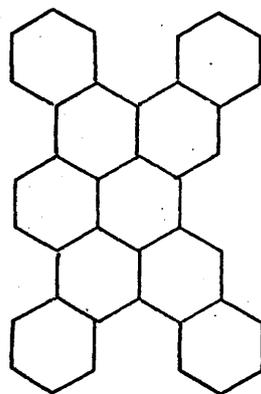
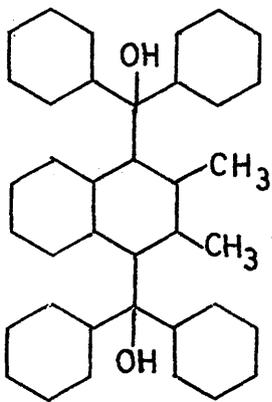
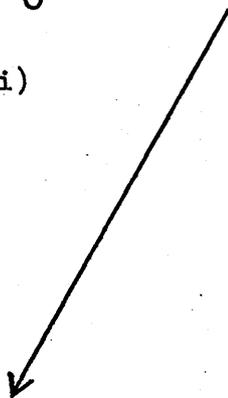
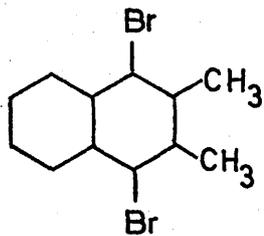
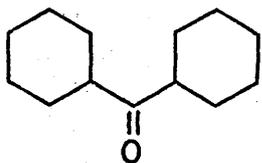
3,6-Dimethyl-7,9-di-(phenyl-6'-m-xylyl)-pyromellitide (xxiii)

The chloride (xiv) was prepared from the acid (xiii) (15g) and m-xylene (2x100ml.) distilled over in order to remove all traces of thionyl chloride. Aluminium chloride (30g) was added portionwise to a suspension of the chloride in m-xylene (80ml.). The mixt. was stirred and heated at 70<sup>o</sup> for 3 hours.

On decomposition with dilute hydrochloric acid, light brown material precipitated out (1.5g). On concentration of the mother liquor a further 13g of crystalline product was obtained. After three cryst. from acetic acid, yielded colourless needles, m.pt. 325-7<sup>o</sup> which were sublimed. In conc. sulphuric acid the needles dissolved slowly becoming brown on standing.  $\nu_{\text{max}}^{\text{KBr}} = 1750\text{cm.}^{-1}$  (C=O of five membered lactone  $\alpha, \beta$  unsat. lactone ).

Found: C, 83.2 ; H, 6.0%

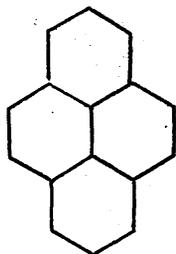
$\text{C}_{38}\text{H}_{30}\text{O}_4$  requires C, 83.0 ; H, 6.0%



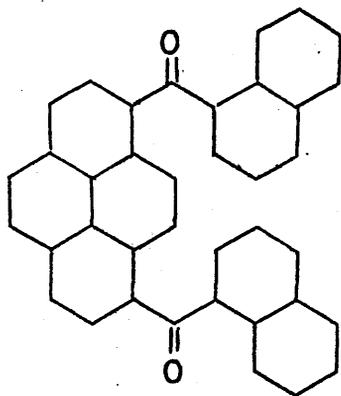
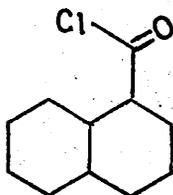
APPENDIXAttempted synthesis of 1,4-di(diphenyl-hydroxymethyl)-2,3-dimethylnaphthalene (iii)

The product (iii) of this reaction was to be used as an intermediate in the synthesis of 2,3:4,5:6,7:8,9:10,11-pentabenzoperylene (iv). Butyl bromide<sup>2</sup> (130g) in ether (200ml.) was introduced dropwise to lithium<sup>2</sup> (16g) in ether (100ml.) under nitrogen. The mixture was cooled using a dry cold/acetone bath and the addition completed after one hour. It was stirred for a further hour at 10<sup>0</sup>. 1,4-Dibromo-2,3-dimethylnaphthalene (ii) (110g) in benzene (150ml.) was added dropwise to the reaction mixture and refluxed for one hour. The addition of benzophenone (200g) in benzene (120ml.) caused an exothermic reaction and shortly after all the reagent had been added the surface of the mixture became blue - due to ketyl<sup>1</sup> formation between the lithium and the benzophenone (i)

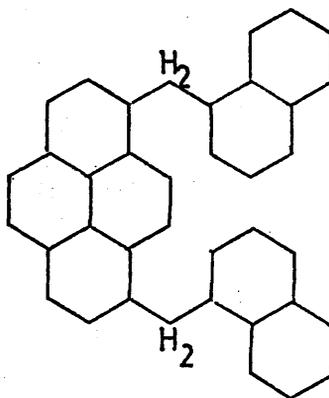
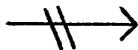
The reaction was stopped and the mixture, filtered free from lithium, decomposed with dilute acetic acid. The ether was boiled off and the benzene solution concentrated, yielding light brown prismatic crystals (78g) m.pt. 132<sup>0</sup>. Further recrystallisation resulted in the m.pt. increasing to 142<sup>0</sup>. The light brown needles



+



(v)



(vi)

gave a +ve Beilstein test for halogen and the i.r. spectrum indicated that there was a C=O absorption band at  $1690\text{cm}^{-1}$ . Dibromo-dimethylnaphthalene (ii) has a m.pt.  $160-1^{\circ}$  and benzophenone  $48^{\circ}$ . The latter (i) also has a carbonyl absorption band in the i.r. at  $1690\text{cm}^{-1}$ .

The reaction was repeated without using butyl bromide and the product (85g), which crystallised from the benzene mother liquor was partially distilled under reduced pressure to remove the low melting benzophenone (i). The residue was crystallised twice from xylene. It gave a +ve Beilstein test for halogen, m.pt.  $157-9^{\circ}$ . Analysis confirmed that it was the unreacted dibromo-dimethylnaphthalene (ii).

Found: C, 45.65 ; H, 3.07%

$\text{C}_{12}\text{H}_{10}\text{Br}_2$  requires C, 45.90 ; H, 3.18%

#### Attempted reduction of 3,10-di- $\alpha$ -naphthoyl-pyrene ( v )

#### 3,10-Di- $\alpha$ -naphthoyl-pyrene ( v )

A variation of the method employed by Scholl and Seer<sup>3</sup> was used. Pyrene (40g), carbon disulphide (600ml.), powdered aluminium chloride (60g) and naphthoyl chloride (80g) were stirred together for 2 hours before being refluxed for 8 hours. The mixture was then decomposed with dilute hydrochloric acid and ice, followed by steam distillation

of the carbon disulphide.

The yellowish green product was extracted with dilute alkali. Yield 110g. The product was extracted with acetic acid (21), leaving a residue (45g), which was mainly the 3,8 isomer, m.pt.  $240^{\circ}$  (lit.  $271^{\circ}$ )<sup>3</sup>. The 3,8 isomer could be further purified by cryst. from nitrobenzene, The acetic acid mother liquor was concentrated and on cooling deposited the crude 3,10 isomer m.pt.  $195^{\circ}$  (lit.  $219-20^{\circ}$ ). As the 3,10 isomer is much more soluble in xylene than the 3,8 it was decided to purify the 3,10 isomer by chromatography. Hot xylene was used as eluant. (Scholl and Seer had purified the isomer by repeated crystallisation). Yield 28g (lit. 18g), m.pt.  $219-221^{\circ}$  (lit.  $219-20^{\circ}$ )<sup>3</sup>.  $\nu_{\text{max}}^{\text{KBr}} = 1690\text{cm}^{-1}$  (C=O absorption). The use of column chromatography greatly improved the yield of an otherwise effective method.

### 3,10-Di- $\alpha$ -naphthylmethyl-pyrene (vi)

Dinaphthoypyrene (v) (20g) was added to ethylene glycol (200g) and hydrazine hydrate (5g, 100%). The mixture was heated gradually to  $200-10^{\circ}$ . Only traces of moisture were seen on the air condenser which was changed several times. It was allowed to cool to  $100-10^{\circ}$  and KOH pellets (2.28g) added. No vigorous reaction took place and the mixture was heated for 40 min. and then allowed to cool.

At 100<sup>o</sup>, water (150ml.) was added and the mixture filtered. Yield 18g, m.pt. 210<sup>o</sup>, the i.r. indicated strong carbonyl absorption at 1690cm.<sup>-1</sup> The u.v. spectrum was also identical with that of dinaphthoylpyrene (v). ( 1 - 2220, 2 - 2475, 3 - 2895, 6 - 3320, 4 - 3705, 5 - 3930 Å) (in hexane)

Scholl and Seer<sup>3</sup> had also attempted to form the hydrazone using phenylhydrazine with (v) without success, suggesting that steric factors made the reaction unfavourable.

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