SYNTHESES
OF
POLYCYCLIC AROMATIC HYDROCARBONS

Thesis

presented by

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for the Degree of

DOCTOR OF PHILOSOPHY

of the

UNIVERSITY OF GLASGOW

August 1958

I wish to express my deep gratitude to Dr. E. CLAR, under whose supervision this work was carried out. He has freely given me the benefit of his wide experience in this field of chemistry and his encouragement has been unfailing.

I record my indebtness to the BRITISH COUNCIL (London), which has given me a grant for carrying out this work in Glasgow.

PUBLICATIONS

The following papers have been published by E. CLAR and W. WILLICKS. Reprints are enclosed at the end:

Aromatische Kohlenwasserstoffe LXIX:
7.8;15.16-Dibenzterrylen
Chemische Berichte 88 (1955), 1205-07

Aromatische Kohlenwasserstoffe LXXIX:
1.2,5.6-Dibenzperylen und 2.3, 6.7, 10, 11-Tribenzfluoranthen
Liebigs Ann. Chem. 601 (1956), 193-201

2:3-Benzorubicene, Rubicene and their Derivatives
Journal of the Chemical Society
(1958), 942-946

CONTENTS

SUMMARY

The main body of work described in this Thesis was the synthesis of peri-aryltetracene derivatives, and the cyclisation of these to new condensed hydrocarbons, all of which contained the tetracene ring-system.

Closely related to this work, however, were the syntheses of 1:2-8:9-dibenzanthrene, rubicene, and iso-rubicene.

The Thesis, then, falls mainly into three interrelated parts.

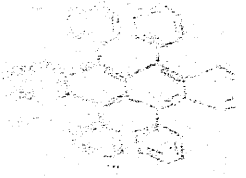
The first deals with the synthesis of 5-naphthyltetracene, and the condensation of this compound to 1:2-5:6-dibenzperylene, and to 1:2-5:6-7:8-tribenzfluoranthene. It was as an integral part of this study that 1:2-8:9-dibenzanthrene was synthesized, and two hydrogenated derivatives of this hydrocarbon were found to constitute the first known example of linear-angular isomerism in tetraphene - 3:4-benzphenanthrene systems.

The second part describes the synthesis of 5:12-dinaphthyl-tetracene, and the condensation of this coumpound to 7:8-15:16-dibenzterrylene.

The remainder of the Thesis began with the synthesis of 5:12-diphenyltetracene and the cyclisation of this to 2:3-benzorubicene, and this in turn led to a full study of the synthesis of rubicene and iso-rubicene (including a new synthesis of rubicene) and several new derivatives of 2:3-benzfluoranthene.

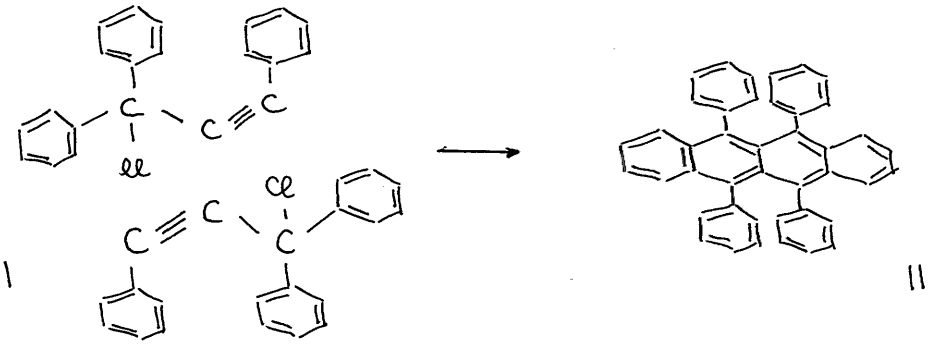
Throughout all these investigations, the absorption spectra of the numerous new compounds were examined, and this, coupled with the formation of maleic anhydride adducts, was used as an important tool in establishing the structures of the new hydrocarbons.

In addition, the Annelation Principle of E. Clar was extended in the series of perylenes and terrylenes.

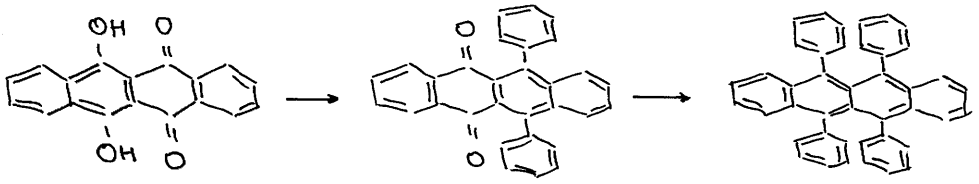


INTRODUCTION

The first aromatic hydrocarbon derived from tetracene was the deep red "rubicene" (II), which was synthesized by MOREU and co-workers (1) by condensation and ring closure of two molecules of isoaethindi-phthalide (I). MOREU, however, was atthis time not



able to establish the structure of II. This was left to DUFRAISSE (2) and ALLEN (3) who were able to show that MOREU's "rubrene" (II) was in fact a tetracene derivative, namely 5:6-11:12-tetraphenyltetracene.



DUFRAISSE synthesis

One very interesting property of rubicene (II) was its deep red colour, both alone and in solution. Tetracene is only orange in colour and the two phenyl-groups of 5:12-diphenyltetracene have only a minor effect on colour, this derivative being still orange. The deep red of 5:6-11:12-tetraphenyltetracene is probably due to

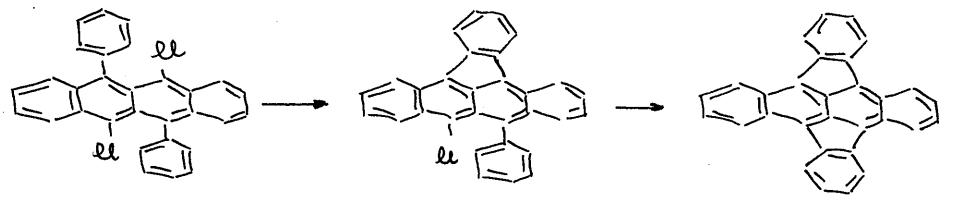
the high electron density of this complex molecule, and later CLAR and MARSHALK (4) gave an explanation of the strong colour shift in peri-tetracene derivatives.

The colour shift towards red, i. e. towards longer wave-length in absorption, is much higher when peri-aryltetracenes are ring closed by various methods to form condensed ring systems with a tetracene skeleton.

CLAR and STEWART (5) synthesized the deep red 2:3-6:7-dibenz-fluoranthene (III) by ring closure of 5-phenyltetracene in an aluminium chloride - sodium chloride melt.

III

DUFRAISSE (6) ring closed 5:11-dichloro-6:12-diphenyltetracene with potassium hydroxide in quinoline and obtained the blue hydrocarbon diphenylenerubene. (IV).



IV

In fig. 1 the absorption spectra of both hydrocarbons III and IV are given in comparison with that of tetracene. The strong shift towards the red can be seen clearly.

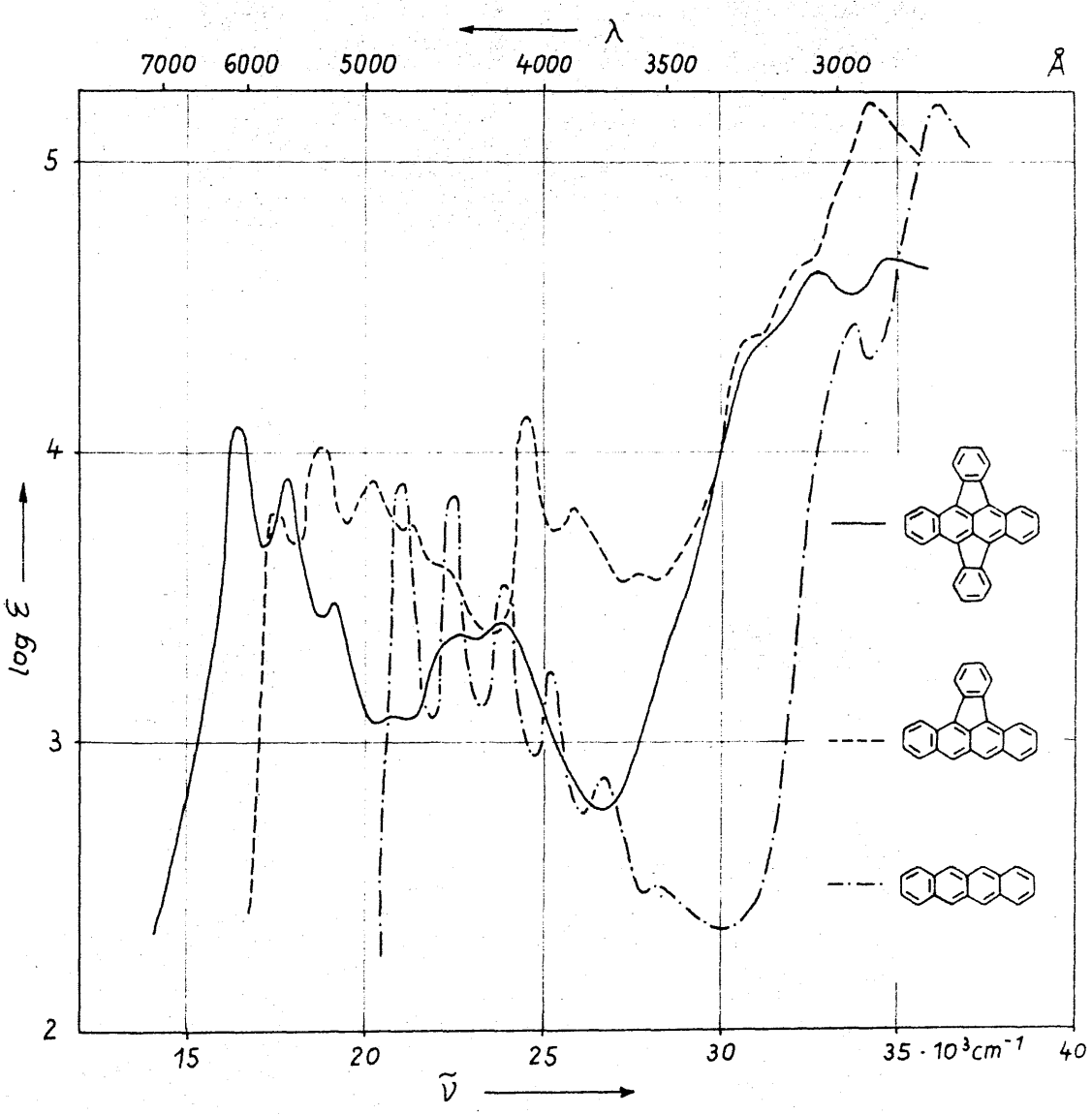
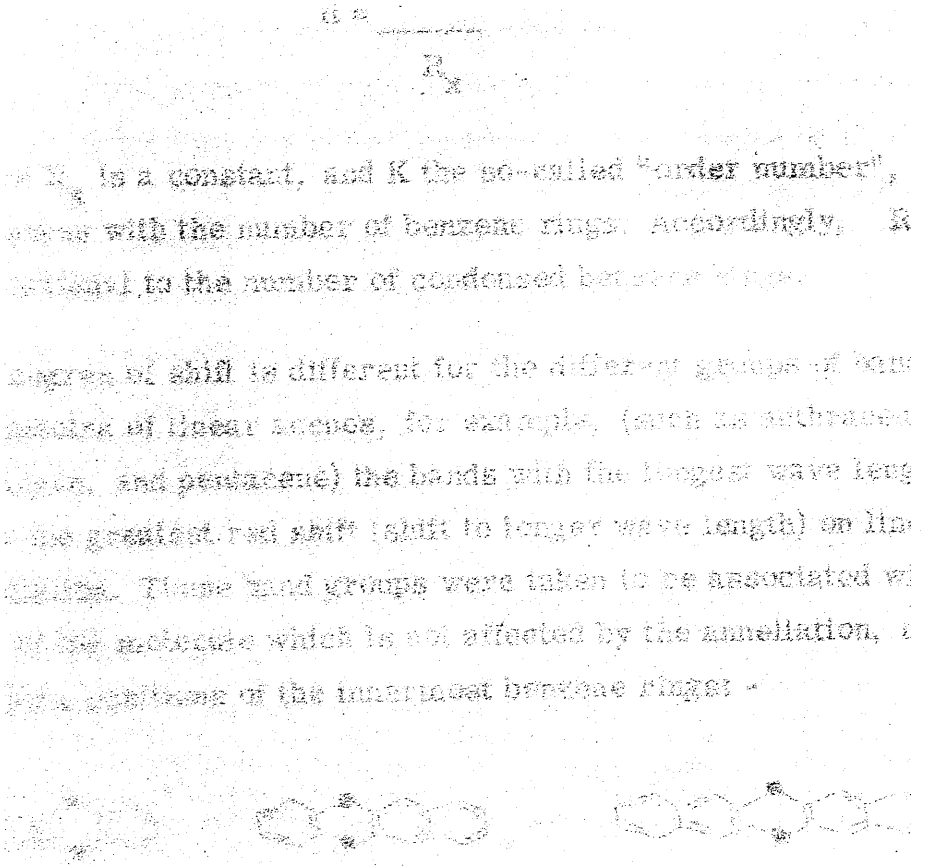

λ
7000
6000
5000
4000
3500
3000
Å
5
4
3
2
log ε
15
20
25
30
35 · 10³cm⁻¹
40
ν̃

Fig. 1

It was proposed, in the work described in this Thesis, to synthesize further hydrocarbons having tetracene as the basic skeleton. This was to some extent governed by the now ready availability of tetracene.

It was intended to prepare new peri-derivatives of tetracene, and to condense these to hydrocarbons with a tetracene skeleton.

Moreover, the absorption spectra of the substances thus synthesized would be examined and possibly fitted into the anellation-principle of E. CLAR (7).



Absorption Spectra of Polycyclic Aromatic Hydrocarbons

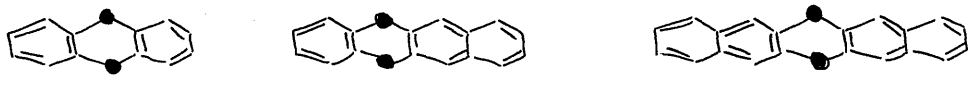
Spectra of polycyclic aromatic hydrocarbons show individual absorption bands with distinct structure, and these bands belong to distinct band groups which bear direct relation to the structure and constitution of the polycyclic system. The positions of the bands shift on the addition of benzene rings to the molecule, in a manner which is characteristic of the method of annellation.

The annellation principle of E. CLAR (7) gives a method of classifying these band shifts. It was found that the maxima of individual bands can be described in the equation

$$R = \frac{K^2}{R_x}$$

where R_x is a constant, and K the so-called "order number", which increases with the number of benzene rings. Accordingly, R is proportional to the number of condensed benzene rings.

The degree of shift is different for the different groups of bands. In the spectra of linear acenes, for example, (such as anthracene, tetracene, and pentacene) the bands with the longest wave lengths show the greatest red shift (shift to longer wave length) on linear annellation. These band groups were taken to be associated with that part of the molecule which is not affected by the annellation, namely the para-positions of the innermost benzene rings: -



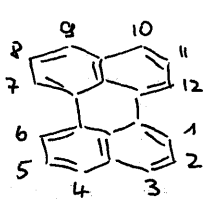
In tab. 1 the positions of the absorption maxima of the bands with the longest-wave lengths (now called para-bands or p-bands) are given in comparison with the values calculated from CLAR's formula:-

Acene	K	K^2/R_p (Å) (calculated)	R (Å) (experimental)
Anthracene	8	3737	3780
Tetracene	9	4729	4735
Pentacene	10	5838	5755

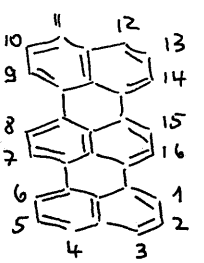
$R_p = 1712800\ cm^{-1}$ for benzene as solvent.

The phenes, condensed systems starting from phenanthrene in angular annellation, have as their characteristic bands the α-bands and β-bands. These band groups do not shift as much as the p-bands on annellation but they also obey the annellation principle of E. CLAR.

Not only the simple aromatic hydrocarbons (the acenes and phenes) can be described by the annellation principle, but condensed systems, such as the perylenes (V) and terrylenes (VI) have definite band structures, which shift in a regular manner with the annellation of benzene rings to the system

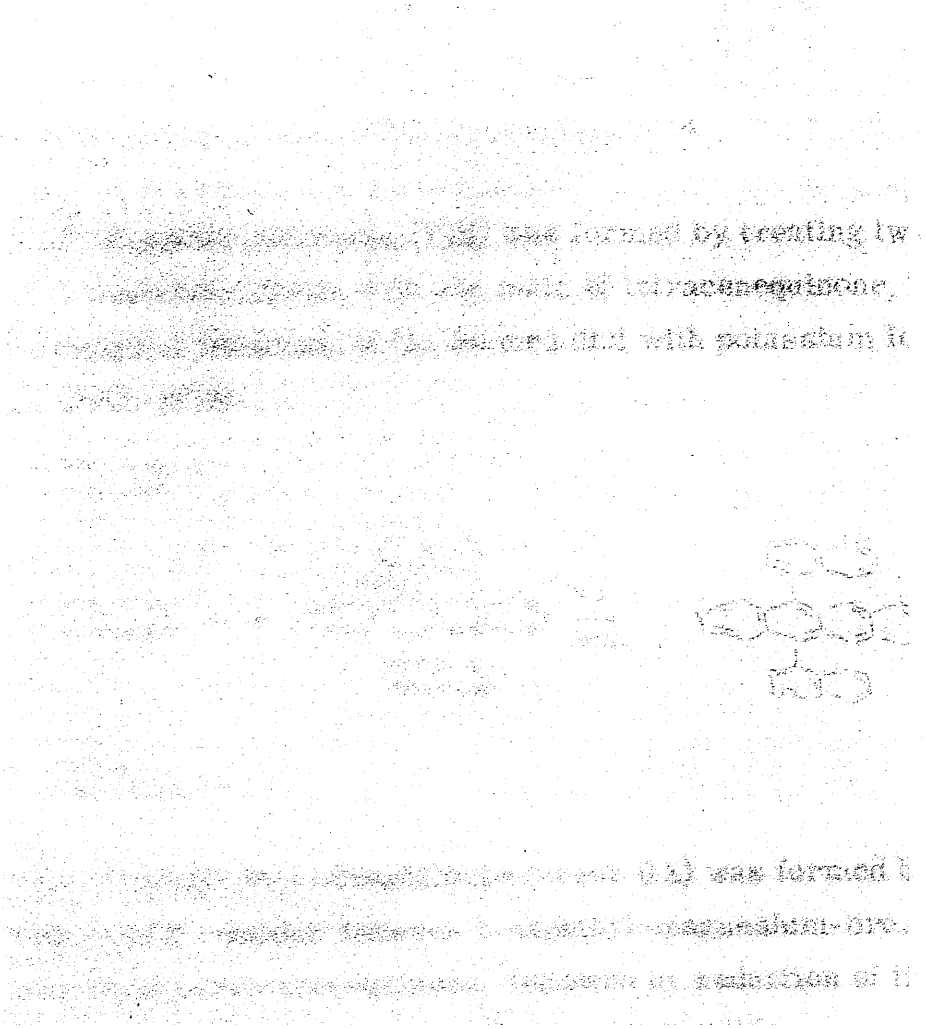


V



VI

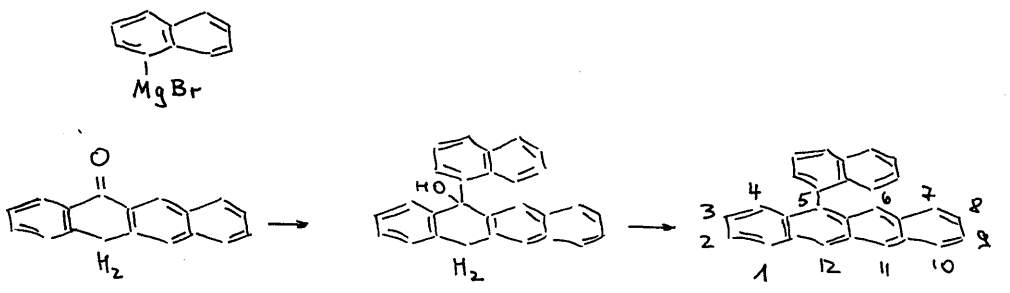
Two of the new hydrocarbons, synthesized in the course of this work, namely a benzohomologue of perylene and a benzohomologue of terrylene, were fitted into the already known series of "perylenes" and "terrylenes" and their positions in these series is discussed. Their unusually high shift, in comparison with other benzologues, gives rise to a new theory of acene-type annellation in condensed systems.



The synthesis of peri-aryltetracene derivatives

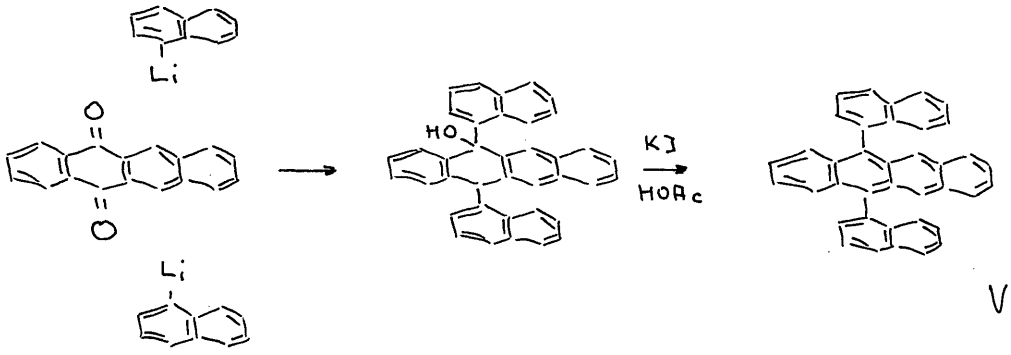
The methods of preparation of peri-aryltetracene derivatives involved the use of the GRIGNARD reaction, or the reaction between aryl lithium and the necessary keto-detivatives of tetracene:-

1.) 5-naphthyltetracene (VII) was formed by the action of 1-naphthyl-magnesium-bromide on tetracenone-5 (8). The alcohol, formed as an intermediate stage, is unstable and splits off water and thus forms the 5-naphthyltetracene (VII) immediately:-



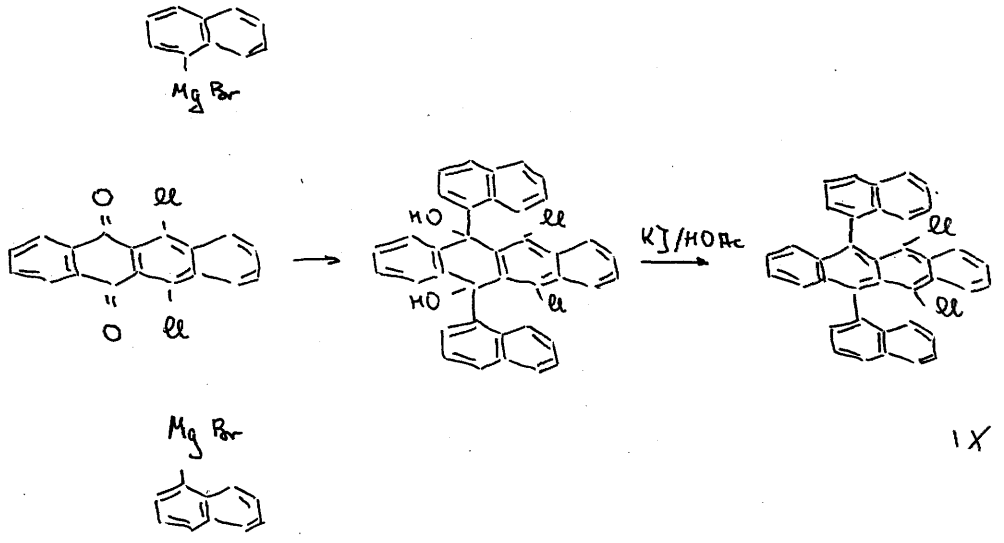
VII

2.) 5:12-dinaphthyltetracene (VIII) was formed by treating two moles of 1-naphthyl-lithium with one mole of tetracenequinone, and subsequent reduction of the formed diol with potassium iodide in acetic acid:-



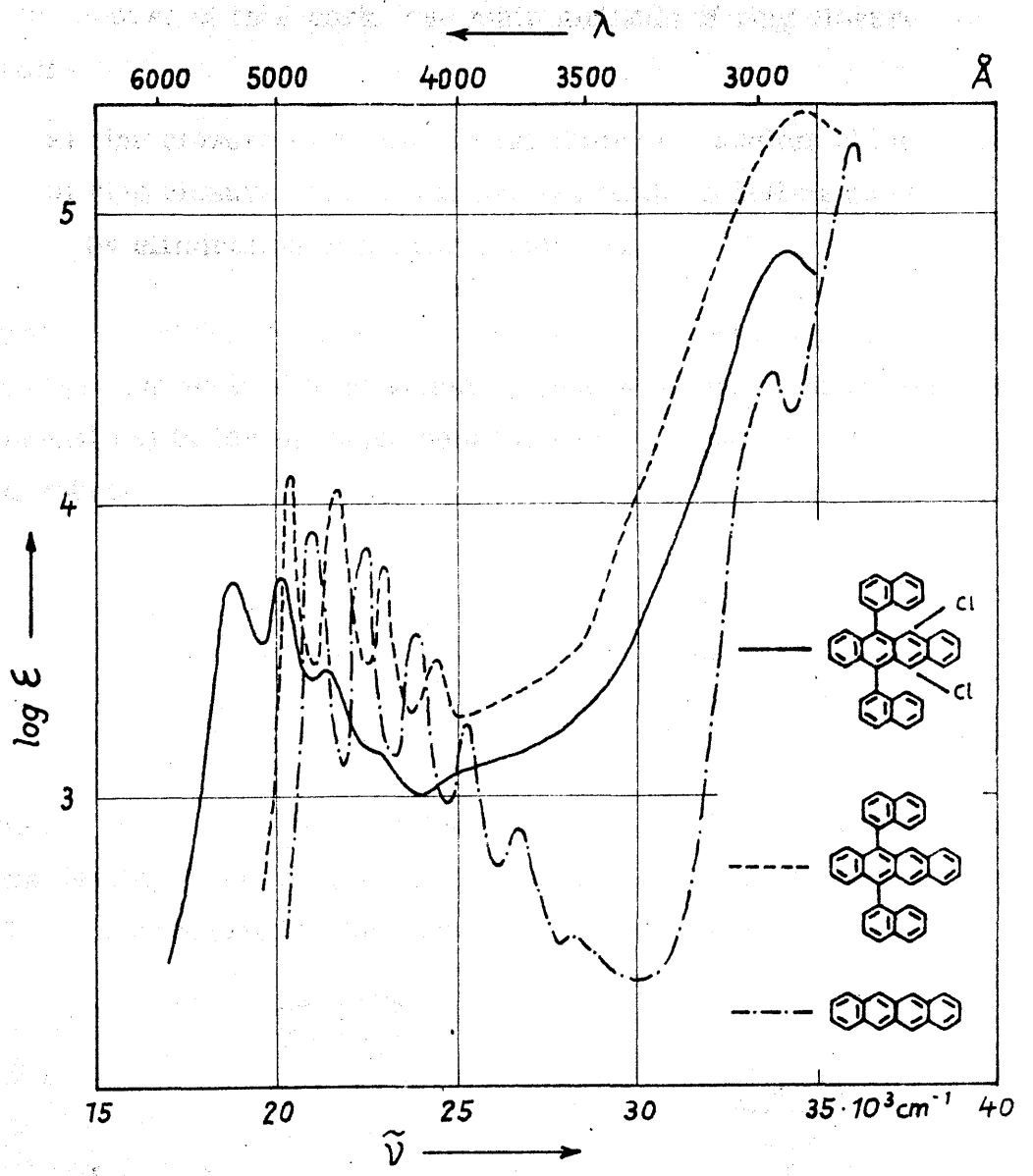
VIII

3.) 5:12-dichloro-6:11-dinaphthyltetracene (IX) was formed by GRIGNARD reaction between 1-naphthyl-magnesium-bromide with dichlorotetracenequinone, followed by reduction of the formed diol with potassium iodide in acetic acid:



IX

The absorption spectra of the two dinaphthyltetracenes are shown in Fig. 2 in comparison with tetracene. The strong shift towards the red in absorption is clearly indicated, and here again the tetra-substituted derivative (dinaphthyldichlorotetracene) gives the strongest shift.


λ
6000
5000
4000
3500
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Å
5
4
3
log ε
Cl
Cl
15
20
25
30
35·10³cm⁻¹
40
ν̃

Fig. 2

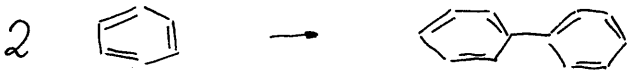
Ring closure of peri-aryltetracene derivatives

Introduction:-

In the course of this work, two main methods of ring closure were used:-

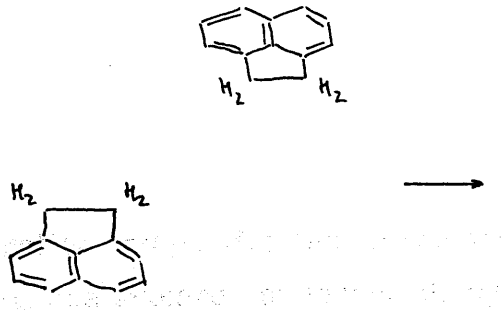
a) ring closure in an aluminium chloride - sodium chloride melt
b) ring closure with potassium hydroxide in boiling quinoline by elimination of hydrogen chloride.

Pyrocondensation of benzene, naphthalene and other hydrocarbons (9) was the first method of condensing smaller aromatic molecules. Thus, diphenyl (X) is formed when benzene vapour is passed through a red hot tube:-



X

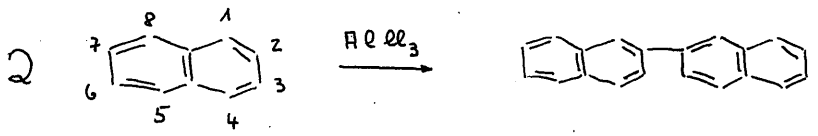
The use of a red hot wire instead of a tube (10) improved this method considerably, and recently the red hydrocarbon 1:2-6:7-dibenztetracene (XI) was synthesized in this manner (11) from acenaphthene.



acenaphthene

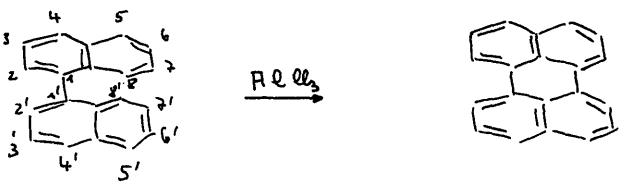
XI

Later it was found that an aluminium chloride melt (temperature ca. 160°) was a good substitute for the red hot tube or wire. Condensation of naphthalene in an aluminium chloride melt gave 2:2'-dinaphthyl (XII) in good yield (12).



XII

If 1:1'-dinaphthyl is treated in an aluminium chloride melt, perylene (XIII) is formed.



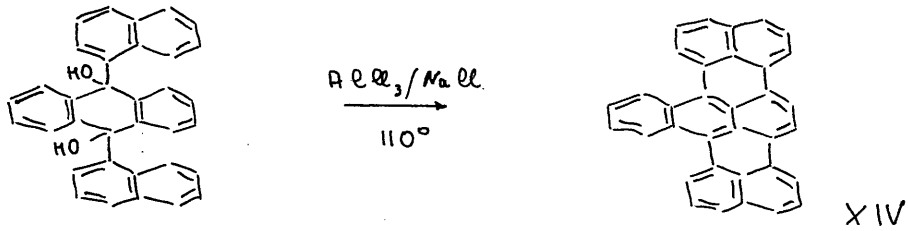
XIII

Further improvement in this ring closure method was brought about by using a mixture of aluminium chloride and sodium chloride (in the proportions five to one) which melts at 110°. Such a melt is of course still very violent, and some side reaction, such as carbonisation, rearrangement, and splitting, always take place. Furthermore, the hydrogen produced during the course of the reaction often reacts with the starting material or the final product, giving rise to difficulties in separation and purification of the produced hydrocarbon. Hydrogenation is sometimes avoided, or lessened, by using oxygen-containing derivatives for the final ring-closure. Thus, alcohols may be used

for the final step instead of hydrocarbons, or oxygen gas may be bubbled through the melt.

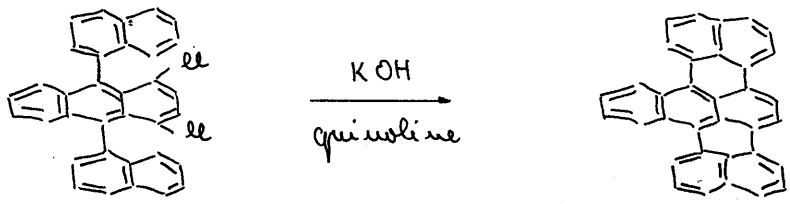
The sodium chloride - aluminium chloride melt is, therefore, when used with due care and precautions, an excellent method for synthesizing new hydrocarbons.

A good example of the method is the synthesis of 7:8-benzterrylene (XIV) (14)

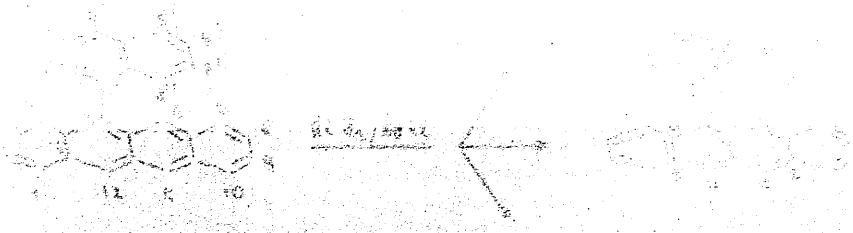


XIV

If an unambiguous method is wanted for finally establishing the structure, the ring-closure method using potassium hydroxide in boiling quinoline is generally preferred. The structure of the above mentioned 7:8-benzterrylene is verified by ring-closing 1:4-dichloro-9:10-di-(1-naphtyl)-anthracene with potassium hydroxide in boiling quinoline (15).



The course of this reaction is not as complicated as an aluminium chloride - sodium chloride melt. In some cases chlorine is split off and ring-closure is thus not complete. The method has however one drawback, namely, the starting material. The corresponding chloroquinones are rarely available and their syntheses are always difficult. In this reason the aluminium chloride - sodium chloride melt is very often preferred in synthesizing new hydrocarbons.

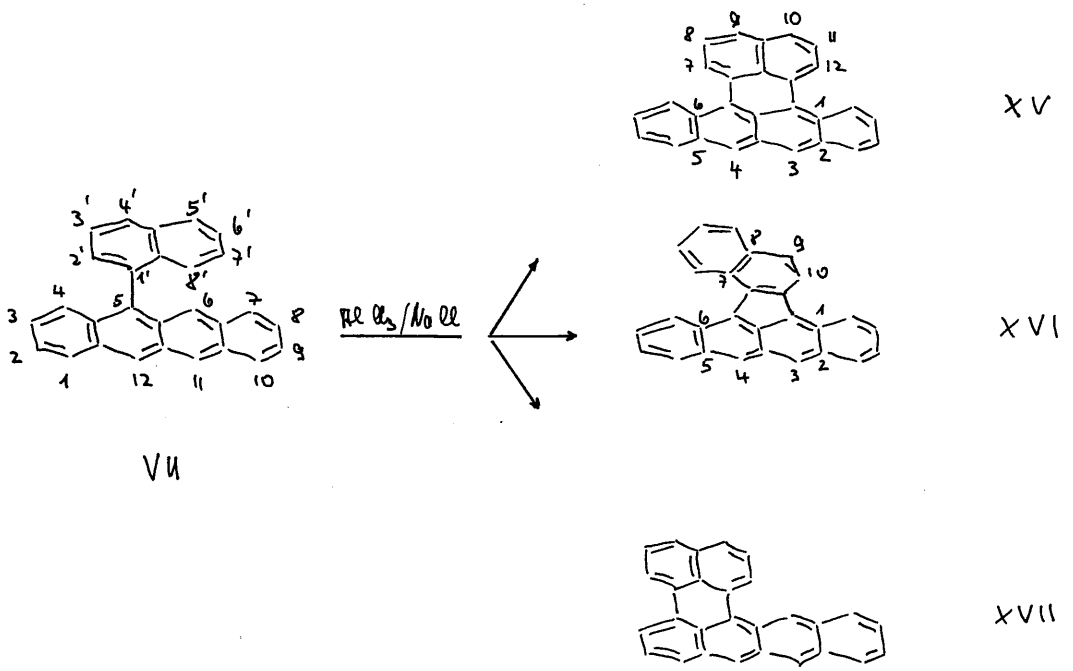


VII

Ring-closure of 5-(1-naphthyl)-tetracene

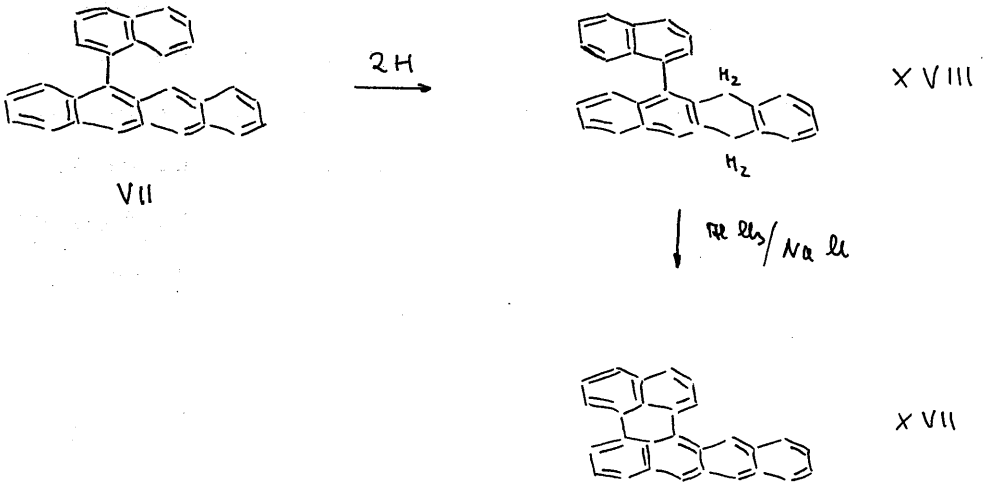
1:2-5:6-dibenzperylene (XV) and 1:2-5:6-7:8-tribenzfluoranthene (XVI).

If 5-(1-naphthyl)-tetracene (VII) is cyclised in an aluminium chloride - sodium chloride melt the possible formation of three different hydrocarbons can be predicted:-



One would expect mainly a ring-closure in the peri-position 6 of the tetracene molecule. In the naphthalene residue, positions 2'- and 8'- are similar in their reactivity. Thus, if ringclosure only takes place in the 6-position of tetracene, either the naphthalene residue ring-closes in the 8'-position (forming the perylene system of XV) or it ring closes in the 2'-position (thus forming the five membered ring system of fluoranthene in XVI).

If ring-closure is to take place in the 4-position of the tetracene molecule, this can only happen if the 6-position is blocked. Hydrogen atoms, split off during the course of the reaction, may form a 6:11-dihydro-derivative (XVIII) of the naphthyltetracene, which is then unable to ring-closure in the 6-position. Ring-closure towards the outer ring takes place, and, by finally splitting off the two hydrogen atoms, 1:2-(2':3'-naphtho)-perylene (XVII) is formed:-

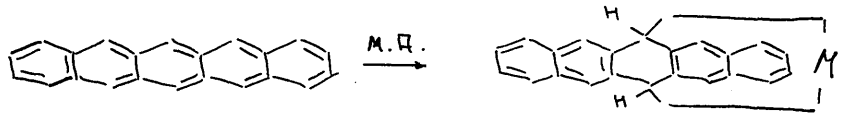


Previous experiments (8) indicated that two hydrocarbons were always formed. Isolation and purification, however, was somewhat troublesome, particularly due to the high photosensitivity of the resulting hydrocarbons.

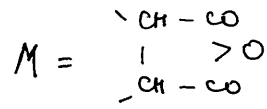
Eventually, both hydrocarbons were prepared in the course of this work. Naphthyltetracene was treated in an aluminium chloride - sodium chloride melt for fifteen minutes at 130° resulting mainly in the violet-blue 1:2-5:6-dibenzperylene (XV). A melt at 110° for seven minutes, however, gave mainly the blue hydrocarbon 1:2-5:6-7:8-tribenzfluoranthene (XVI). In both melts, of course, both hydrocarbons were found to some extent through separation by chromatography.

Formation of maleic anhydride adducts

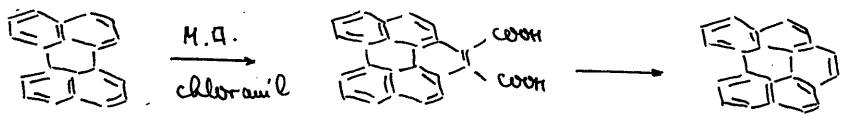
One simple aid to establishing the structure of an aromatic hydrocarbon is by reaction with maleic anhydride (M.A.). CLAR was able to show (16) that such hydrocarbons as anthracene, tetracene and pentacene form adducts with maleic anhydride by boiling the hydrocarbon with the anhydride in xylene for about fifteen minutes. The solution of the hydrocarbon, if coloured, is rapidly decolourized and on cooling, the adduct crystallizes in long needles. The absorption spectrum of the disodio salt of such an adduct is of course entirely different from that of the hydrocarbon. It gives the absorption spectrum of a smaller part of the hydrocarbon, since aromatic resonance over the whole molecule is broken through the formation of the adduct. Pentacene (XIX), for instance, shows after formation of its maleic anhydride adduct (XX) the absorption spectrum of naphthalene.



XX

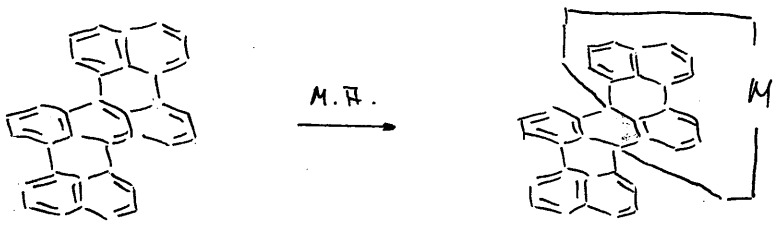


Perylene (XXI) reacts with maleic anhydride in the 1:12-position (17). The reaction is best carried out in a melt of perylene and the anhydride with added chloranil, when the 1:12-benzperylene-dicarboxylic acid (XXII) is formed, which can be decarboxylated to yield 1:12-benzperylene (XXIII).

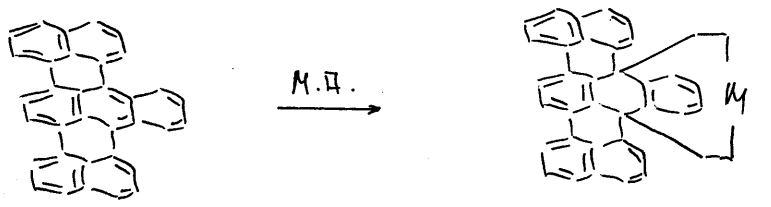


XXI XXII XXIII

The structures of more complex molecules are very often easily established by the formation of maleic anhydride adducts. Recently, CLAR and KELLY (15) synthesized the two di-peri-naphthylene-anthracenes XXIV and XXVI by unambiguous methods, and compared the absorption spectra of their maleic anhydride adducts XXV and XXVII:



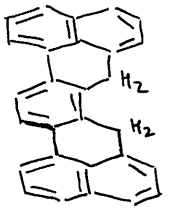
XXIV XXV



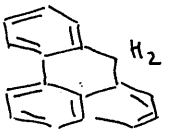
XXVI XXVII

M = CH-CO, CH-CO, >O

Whilst the absorption spectrum of the adduct XXVII shows bands in the visible region thus indicating its more complex resonance system of dibenzterphenyl (as in the dihydro compound XXVIII),



XXVIII

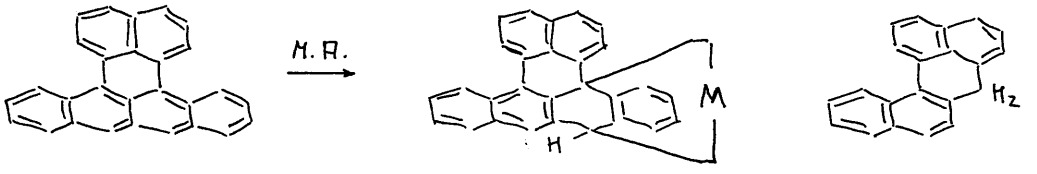


XXIX

the resonance system of the hydrocarbon XXIV is broken into two halves by addition of maleic anhydride, the adduct showing the low absorption of benzanthrene (XXIX).

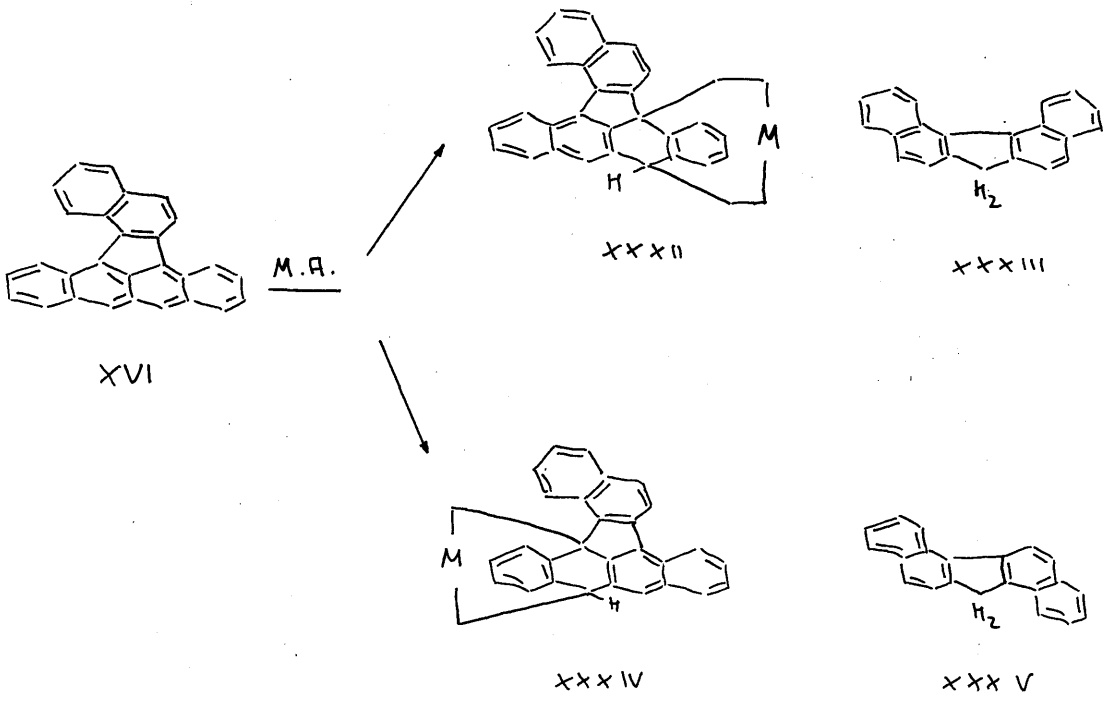
For the postulated hydrocarbons XV, XVI, and XVII we can predict the possible formation of the following adducts:-

i) for 1:12-5:6-dibenzperylene (XV) the adduct XXX with the resonance system of 1:2-8:9-dibenzanthrene XXXI



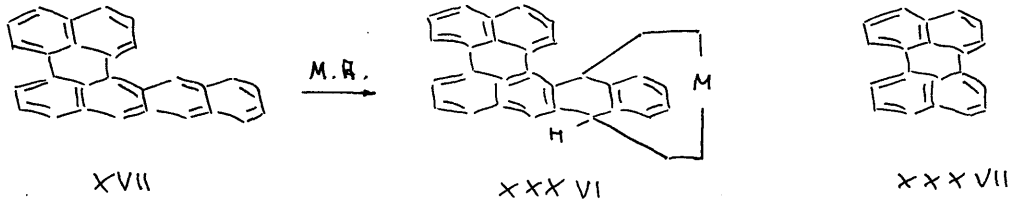
XV XXX XXXI

ii) for 1:2-5:6-7:8-tribenzfluoranthene (XVI) the adducts XXXII or XXXIV, with resonance systems of 3:4-5:6-dibenzfluorene XXIII or 1:2-5:6-dibenzfluorene XXXV respectively:



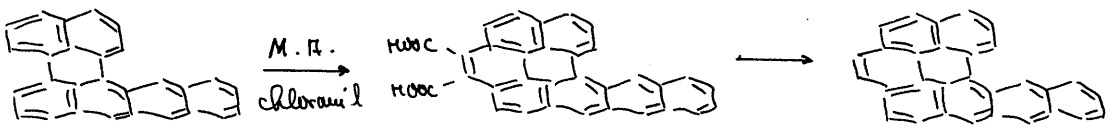
XVI XXXII XXXIII XXXIV XXXV

iii) for 1:2-(2':3'-naphtho)-perylene (XVII) the adduct XXXVI with the resonance system of perylene (XXXVII)



XVII XXXVI XXXVII

This hydrocarbon would probably also react with maleic anhydride in a melt with chloranil, forming the 6:7-benz-1:2-(2':3'-naphtho)-perylenedicarboxylic acid (XXXVIII), which, when formed, could be decarboxylated to the corresponding hydrocarbon XXXIX:-



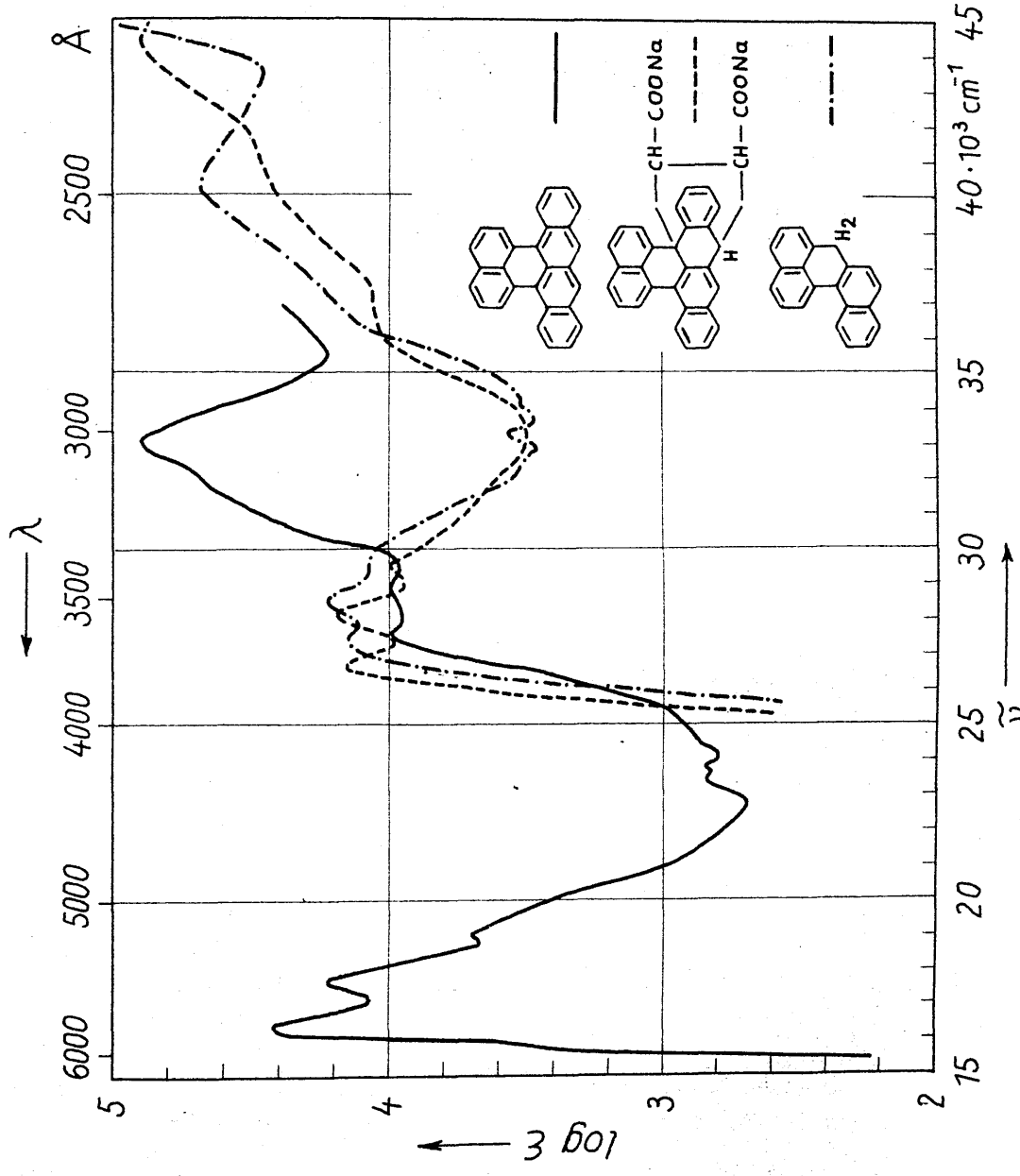
XVII XXX VIII XXXIX

In fact, the violet blue hydrocarbon (XV) mainly formed in the melt at 130° was decolourized by boiling with maleic anhydride for fifteen minutes in xylene. The disodio salt of the formed adduct showed an absorption spectrum similar to that of 1:2-8:9-dibenzanthrene (XXXI) (fig. 3).

The blue hydrocarbon (XVI) formed in the melt at 110° also gave a colourless adduct, which, as a disodio salt, had an absorption spectrum similar to that of either 3:4-5:6-dibenzfluorene XXXIII or 1:2-5:6-dibenzfluorene XXXV.

There seem to be some differences in regard to the latter spectra (18) so that an exact comparison could not be made. Thus, the spectra of 1:2-5:6-7:8-tribenzfluoranthene (XVI) and its maleic anhydride adduct (XXXII or XXXIV) are given in fig. 4, and the spectra of the two fluorenes XXXIII and XXXV are given separately in fig. 5. The very similar shapes of all these spectra show clearly enough the close relationship among the different substances.

No adduct was formed having an absorption spectrum similar to that of perylene. Nor did any of the two hydrocarbons react with maleic anhydride and chloranil in a melt. Thus, the formation of 1:2-(2':3'-naphtho)-perylene can be entirely excluded from the above described aluminium chloride - sodium chloride melt of naphthyl-tetracene.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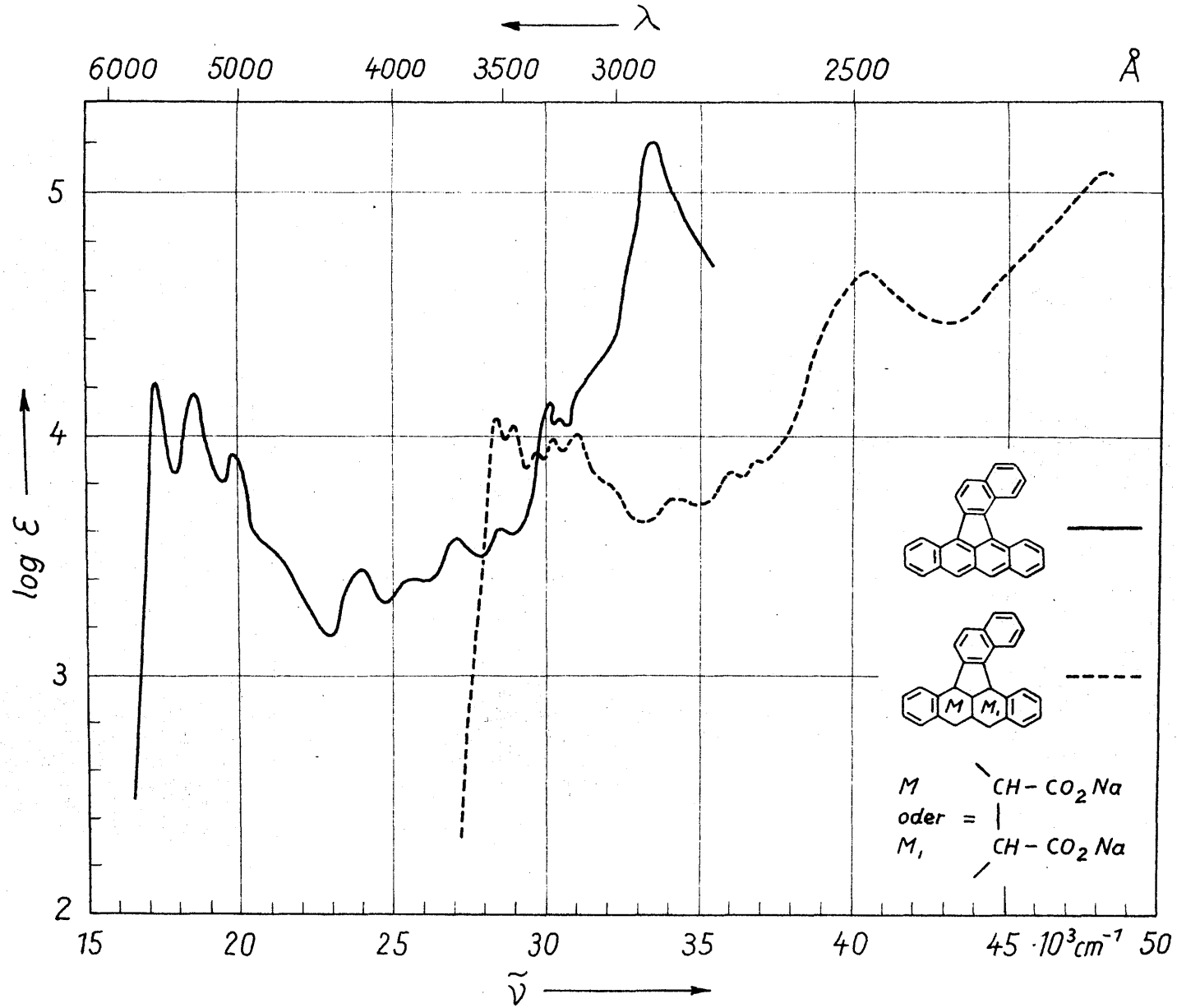
CH—COONa
CH—COONa
H
H₂

Fig. 3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M₁
M CH – CO₂Na
oder =
M₁ CH – CO₂Na

Fig. 4

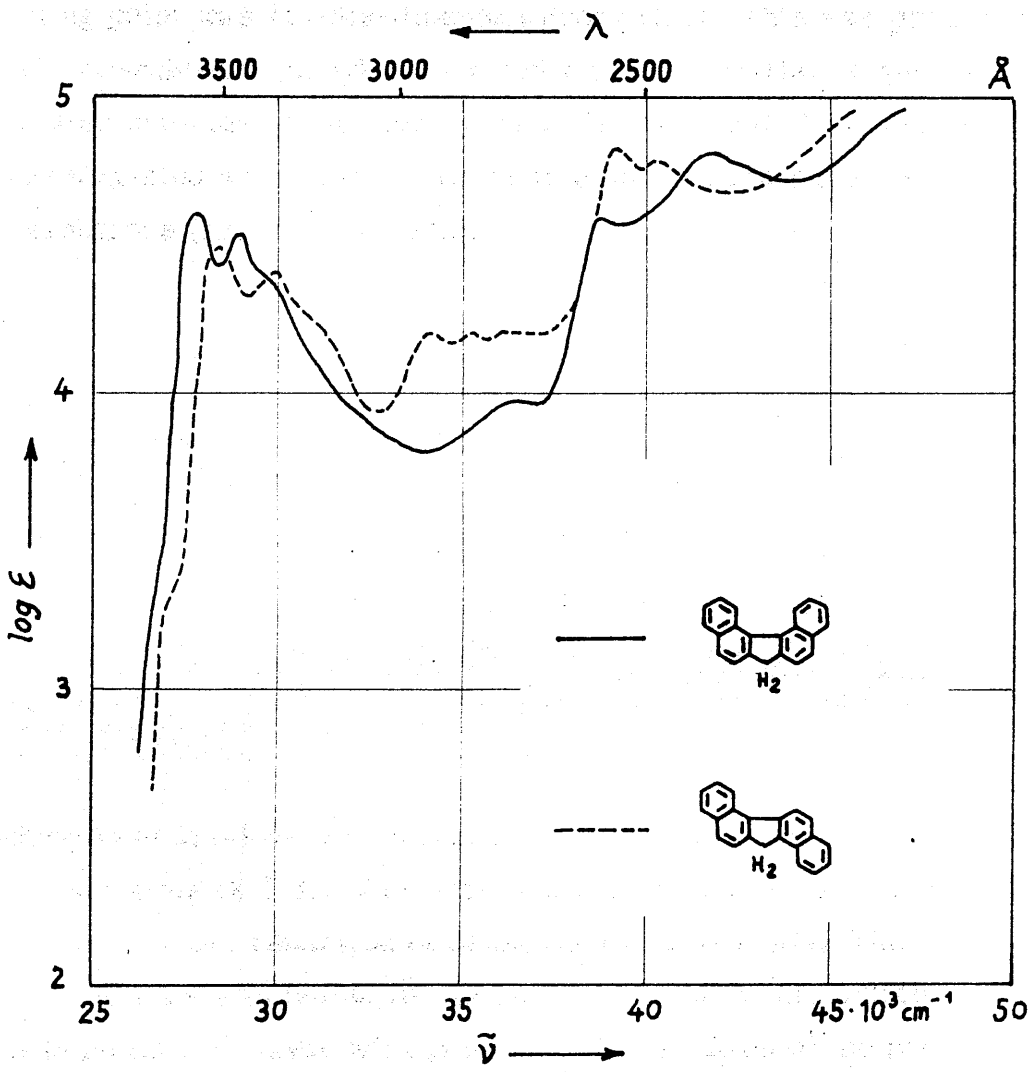
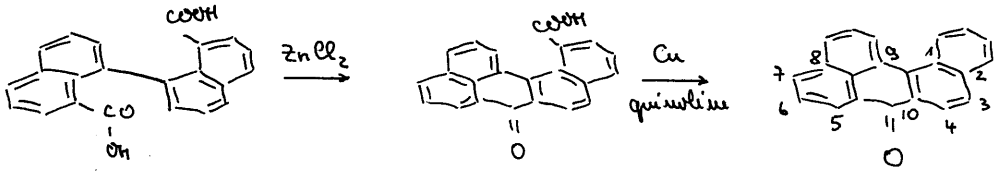


Fig. 5

The synthesis of 1:2-8:9-dibenzanthrene

1:2-8:9-dibenzanthrene had, up till now, not been described in the literature, attempts to prepare it having failed (19). A possible starting point was 1:2-8:9-dibenzanthrone (XL). This was prepared from 1:1'-8:8'-dinaphthyl-dicarboxylic acid by partial ring-closure with zinc chloride to the mono-carboxylic acid (20). This acid was decarboxylated with copper powder in quinoline and gave the benzanthrone (XL) in good yield.



XL

Reduction of 1:2-8:9-dibenzanthrone (XL) gave the corresponding dibenzanthrene (XXXI). The first attempt was made using a method described for the reduction of benzanthrene itself (21). The dibenzanthrone was boiled for 12 hours in an ethanolic solution of potassium hydroxyde with zinc dust. Sublimation of the product thus obtained yielded a trimethylene derivative, which, from its absorption and phosphorescence spectra, was a derivative of tetraphene. A possible structure is 11:12-trimethylenetetraphene (XLI; fig. 6).

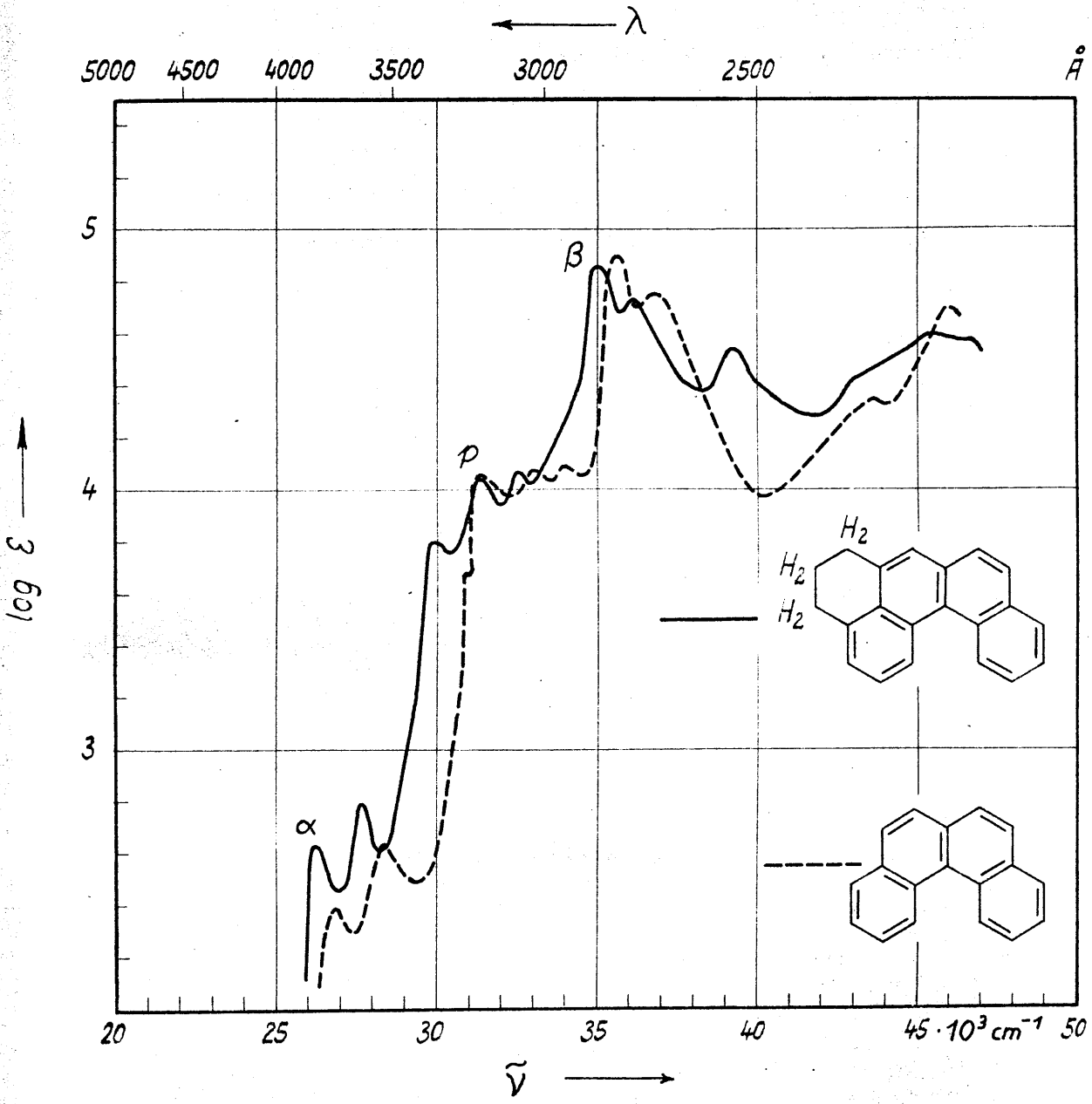

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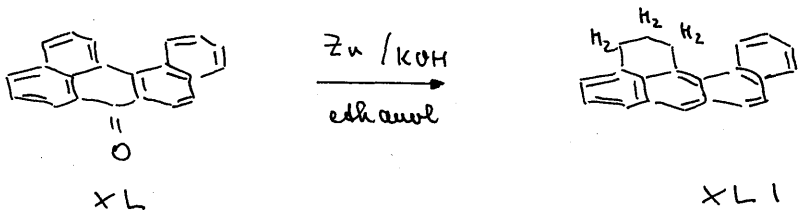
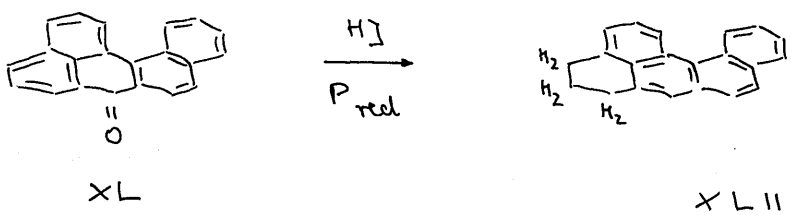
Fig. 6



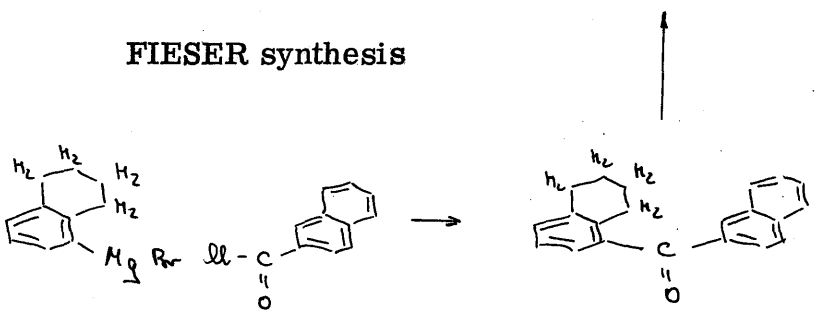
XL XLI

A second attempt was made by treatment of the dibenzanthrone (XL) with hydriodic acid and red phosphorus. The obtained hydrocarbon was again a trimethylene derivative, namely 8:9-trimethylene-3:4-benzphenanthrene (XLII) (shown to be a derivative of 3:4-benzphenanthrene by comparison of the absorption and phosphorescence spectra (fig. 7)). Also, this hydrocarbon proved to be identical with a hydrocarbon prepared by FIESER by the indicated route:-

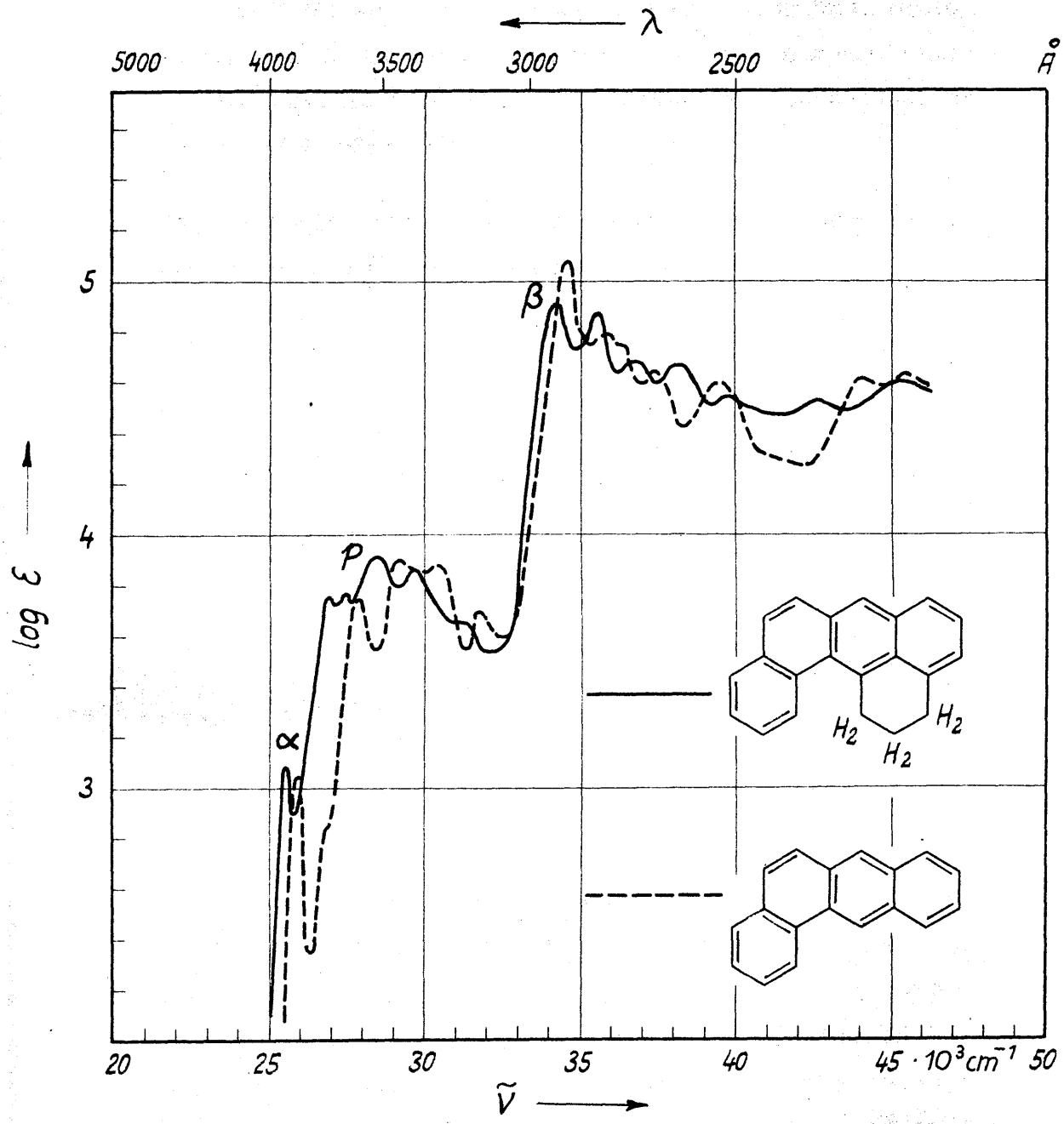


XL XLII

FIESER synthesis



The two synthesized trimethylene derivatives constitute another interesting example of linear-angular isomerism in aromatic chemistry. FIESER believed that, when an aromatic skeleton is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H2
H2
H2
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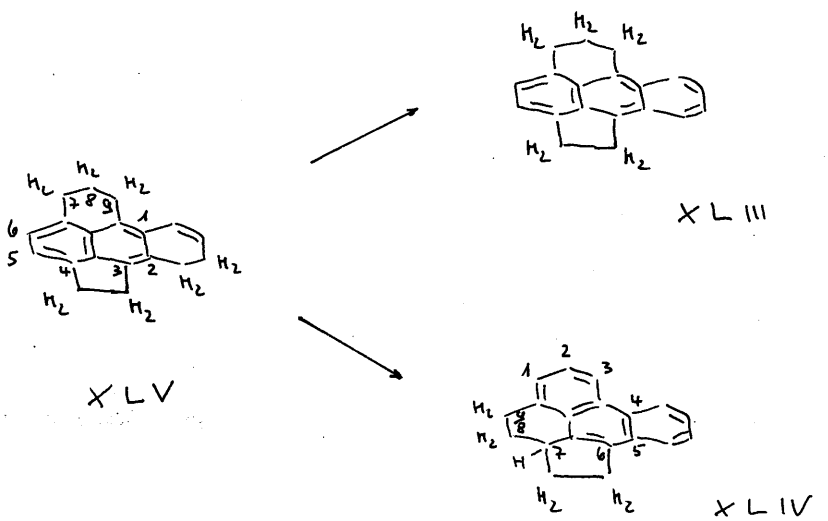
30
35
40
45 · 10³cm⁻¹
50
ν̃

Fig. 7

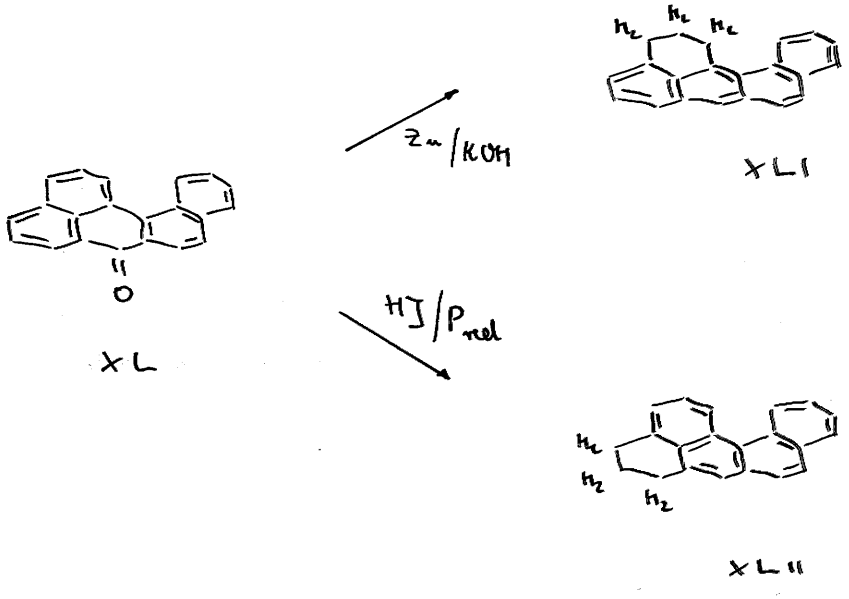
formed by condensation or dehydrogenation, of the two possible forms the angular structure is always favoured to the linear (22). His prediction was that in such a case the linear form would rearrange during the course of the reaction and thus would not be isolated. Recent developments, however, have shown that both forms are stable under certain conditions (23).

The two hydrocarbons 1:2-benz-3:4-ace-peri-naphthane (XLIII) and 4:5-benz-6:7-ace-peri-naphthane (XLIV)



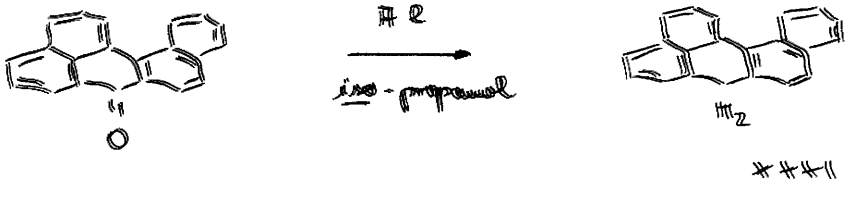
were synthesized from 3':4'-dihydro-1:2-benz-3:4-ace-peri-naphthane (XLV) by varying the conditions of dehydrogenation in temperature and reaction time. Both hydrocarbons were easily isolated by chromatography. Whilst one hydrocarbon (XLIII) has an anthracene skeleton the other (XLIV) has the skeleton of phenanthrene. These two hydrocarbons represent the first example of the so-called linear-angular isomerism of condensed peri-naphthanes.[23]

The same linear-angular isomerism occurs when 1:2-8:9-dibenz-anthrone (XL) is reduced. In one process, only the mainly linear tetraphene skeleton (XLI) is formed; in the other, only the wholly angular 3:4-benzphenanthrene



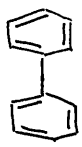
(XLII) skeleton. Both derivatives were formed in a zinc-dust melt (CLAR's "zinc-dust melt") of the benzanthrone (XL) and were separated and isolated by repeated chromatography. The above isomerism (tetraphene, 3:4-benzphenanthrene) has not till now been recorded in the literature. Attempts in this direction only produced the angular derivative (XLII) (24).

A successful synthesis of 1:2-8:9-dibenzanthrene (XXXI) was carried out using aluminium-iso-propoxyde as reducing agent (25). The dibenzanthrene was obtained by this method in good yield:



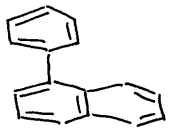
The p-absorption in perylene homologues

The absorption spectrum of perylene can be related to that of biphenyl (XLVI). Though the absorption spectrum of biphenyl is very diffuse, due to distortion of the two benzene rings to ca 25° out of plane, there is obviously interaction between each ring, so that the absorption spectrum is not benzene-like.

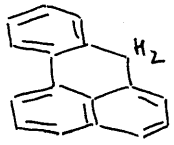


XLVI

Addition of one benzene ring to biphenyl gives the hydrocarbon 1-phenylnaphthalene (XLVII). This hydrocarbon has the absorption spectrum of a naphthalene derivative. This means that electronic flux between the naphthalene and the benzene ring is hindered. If, however, the benzene and naphthalene rings are fixed in plane by a methylene bridge, as it is in benzanthrene (XLVIII), the absorption spectrum shows fine structure, and is entirely different from phenylnaphthalene (XLVII). This indicates that in benzanthrene electron interaction takes place throughout the molecule.

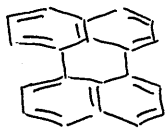


XLVII

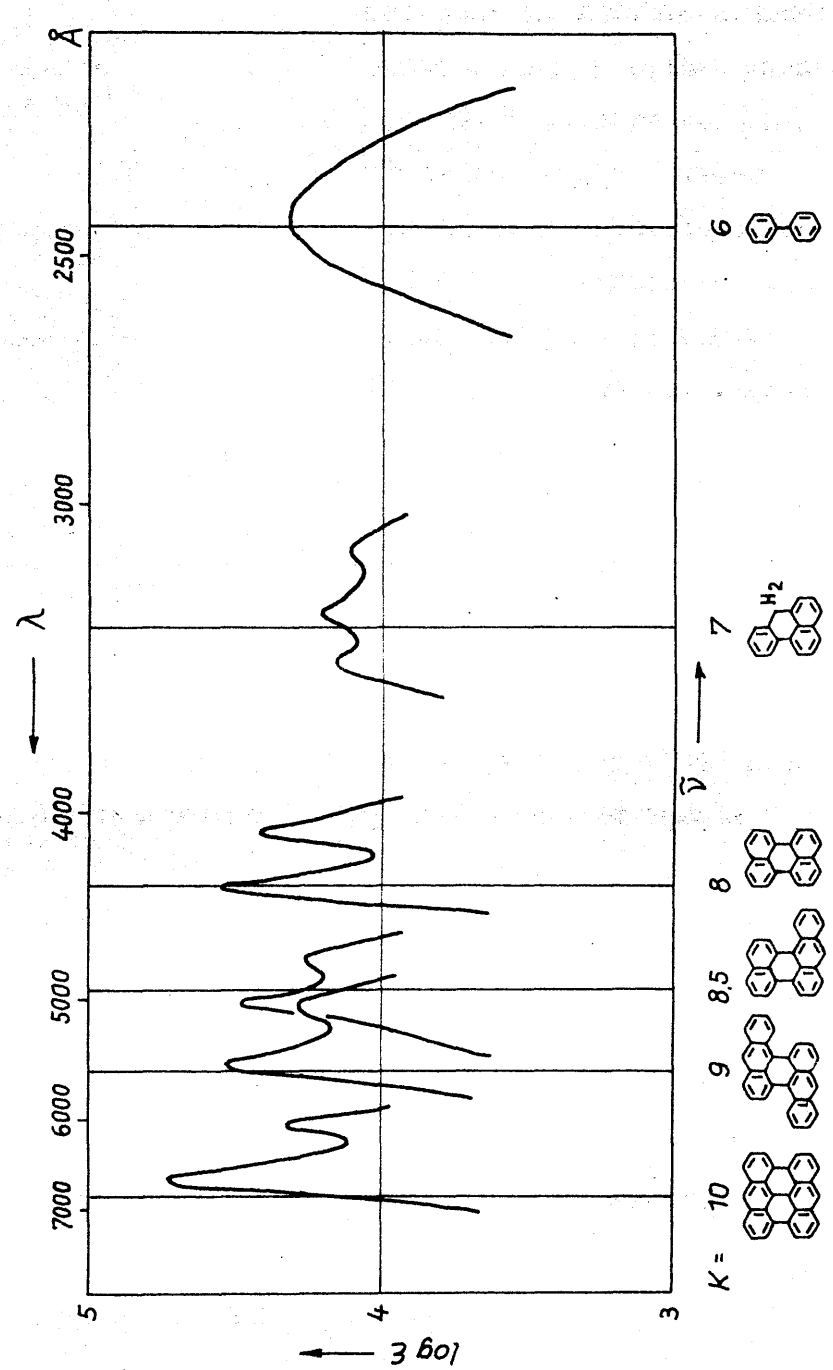


XLVIII

Perylene (IL) can be considered as two condensed biphenyl molecules. It has a very distinct absorption spectrum which indicates that electron interaction takes place



IL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K=
10
9
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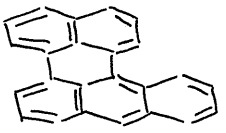
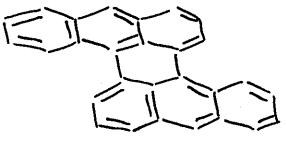
8
7
6
H_2

Fig. 8

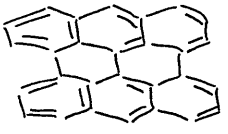
over the whole molecule. Addition of one benzene ring to perylene gives the hydrocarbon 1:2-benzperylene (L); addition of another benzene ring gives the hydrocarbon 1:2-7:8-dibenzperylene (LI). Three biphenyl molecules condensed together form the hydrocarbon bisanthrene (LII) which exhibits very strong absorption in the blue region of the spectrum.



L



L I



L II

The hydrocarbons mentioned above form a series of which the lowest member is biphenyl (XLVI) and the highest member bisanthene (LII). Their para-absorption bands follow CLAR's annellation principle (7) and the equation

$$R = \frac{K^2}{R}$$

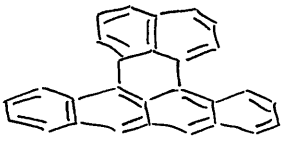
where R = wave length of the highest para absorption band

K = order number (see page 10)

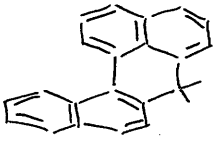
R = constant factor for the perylenes.

In fig. 8 the absorption spectra of the perylenes are compared and the order number K is given.

The newly synthesized hydrocarbon 1:2-5:6-dibenzperylene (XV, page 19) also fits into this series. Moreover, the spectrum of the disodio salt of the maleic anhydride adduct (XXX, page 23) also gives a new member of the perylene-series.



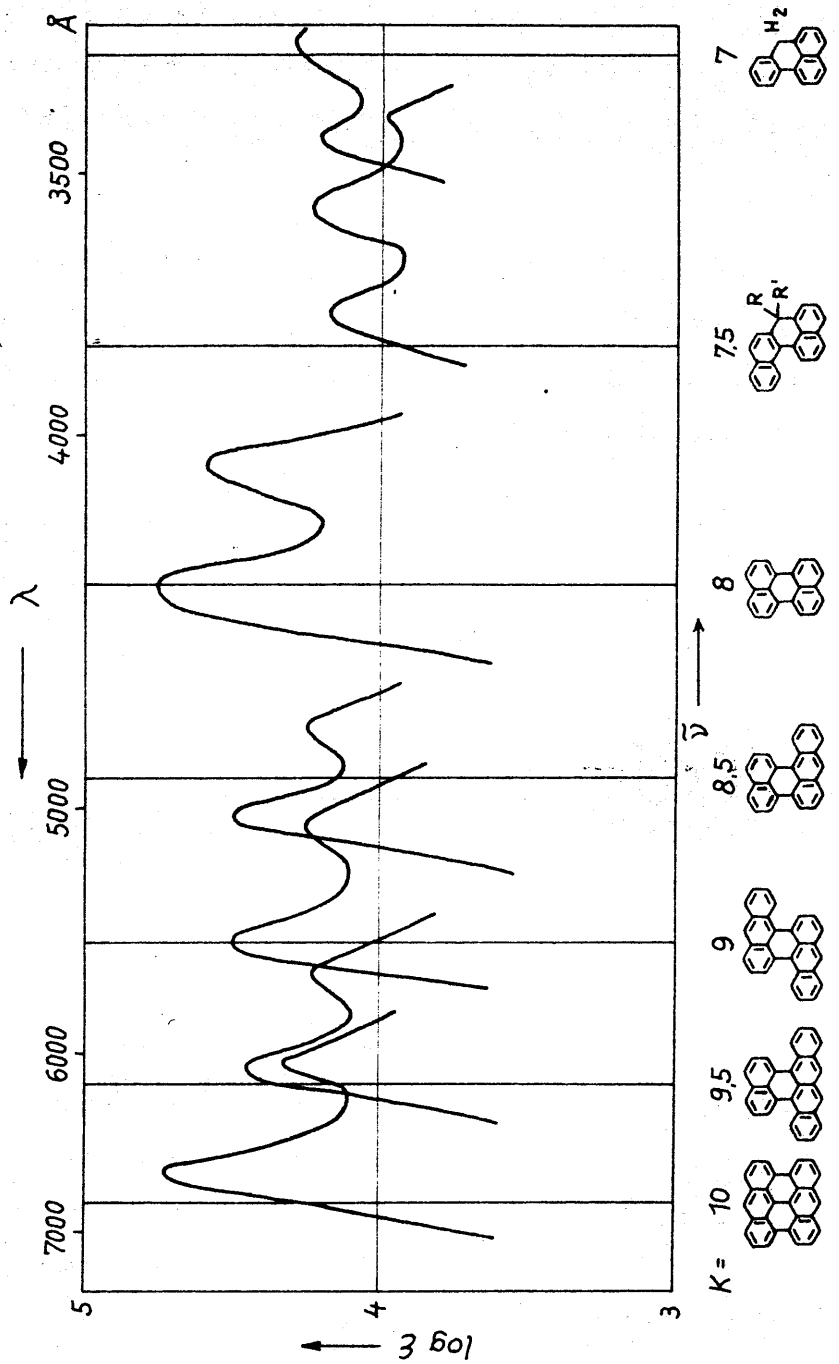
XV



XXX

Noteworthy is the very strong shift exhibited by XV from perylene IL. This shift is stronger than the one in LI from perylene IL. This seems to be surprising, for, in both hydrocarbons XV and LI the two additional benzene rings are the cause of the red shift. Calculation in the perylene gives for each additional benzene ring an increase in order number of 0.5. This is exactly verified in LI which has the order number 9 (see fig. 8). The new hydrocarbon XV has, however, order number 9.5 (see fig. 9), whilst 1:2-benzperylene (L) has order number 8.5 (see fig. 9). Addition of one benzene ring in the linear 5:6-position has thus shifted the absorption spectrum of L by <u>one</u> order number, from 8.5 to 9.5. Such a shift (<u>one</u> order number for each additional benzene ring) is common only in the acene-series. Thus, it seems, that the tetracene system in 1:2-5:6-dibenzperylene (XV) gives rise to <u>acene-like</u> annellation effects.

In fig. 9 the absorption spectra of 1:2-5:6-dibenzperylene and the disodio salt of its maleic anhydride adduct are shown in the perylene-series.


Å
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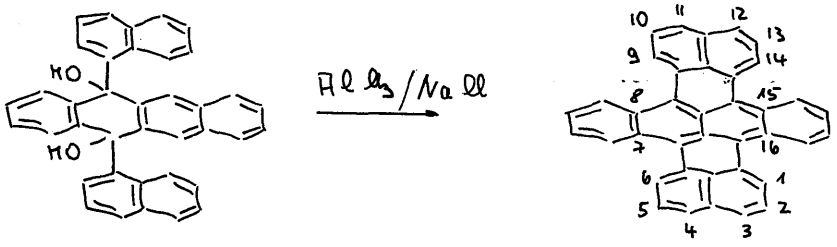
8
7,5
7
R
R'
H2

Fig. 9

7:8-15:16-Dibenzterrylene

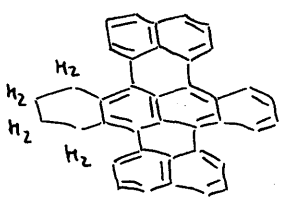
The action of a sodium chloride - aluminium chloride melt on 5:12-dihydro-5:12-di-(1-naphthyl)-tetracene-5:12-diol (LII) gave the green hydrocarbon 7:8-15:16-dibenzterrylene (LIV) as main product.

Unlike the ring-closure of 5-(1-naphthyl)-tetracene, the ring-closure of LIII proceeds only in one direction. This can be compared with the ring-closure of 9:10-di-(1-naphthyl)-9:10-dihydroanthracene-9:10-diol, which also forms only one hydrocarbon, namely 7:8-benzterrylene (see page 17).

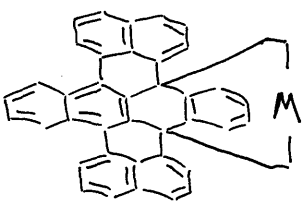


LIII LIV

As a by-product in this synthesis a blue hydrocarbon was found, which showed great similarity in its absorption spectrum to that of 7:8-benzterrylene (XIV) and was, probably 1':2':3':4'-tetrahydro-7:8-15:16-dibenzterrylene LV.



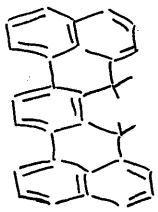
LV



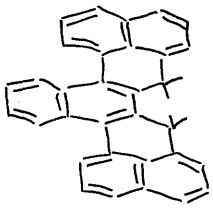
LVI

M = CH - CO / CH - CO

7:8-15:16-dibenzterrylene gave a green solution in xylene, and, on boiling with maleic anhydride, formed a yellow adduct (LVI), (spectrum see fig. 10). The disodio salt of this adduct showed an absorption spectrum similar to that of the disodio-salt of the maleic anhydride adduct XXV of 7:8-benzterrylene XXIV (see p. 22), except that the shift to the red was here much stronger than in the former adduct. Comparison of the aromatic structure of both adducts, XXVIII and LVI, as in XXVIII and LVII showed, that the one additional benzene ring was the cause of the stronger shift in LVI.



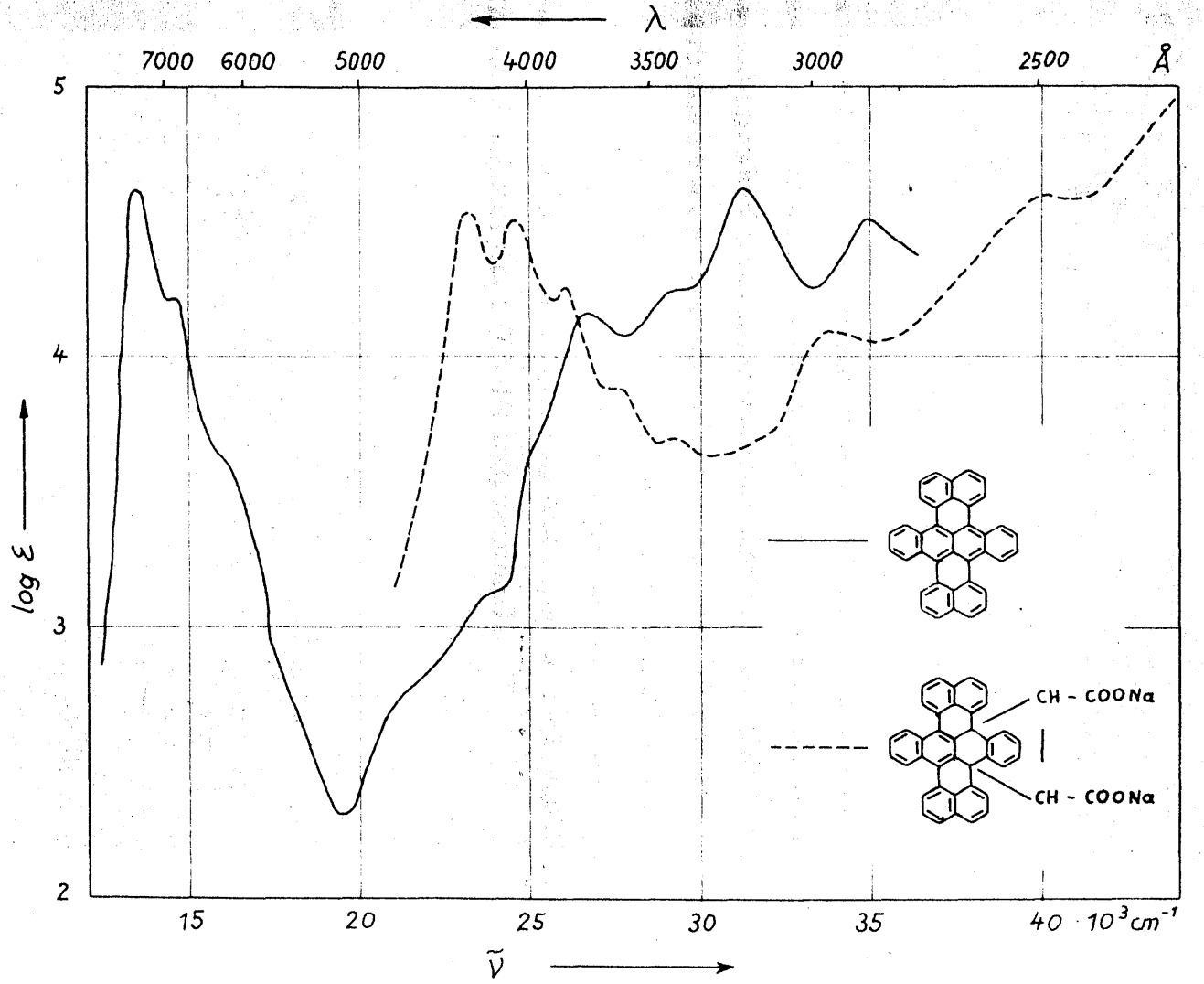
XXVIII



LVII

This observation gave the first confirmation that LIV had the asigned structure. Further confirmation derived from the tetrahydro-derivative LV with its 7:8-benzterrylene-like spectrum.

The final confirmation of the structure of LIV was provided by an unambiguous synthesis. 5:12-dichloro-6:11-di-(1-naphthyl)-tetracene (IX) cyclized smoothly to the same green hydrocarbon, when boiled with potassium hydroxyde in quinoline. After boiling for two hours the green hydrocarbon LIV was isolated in an almost pure state.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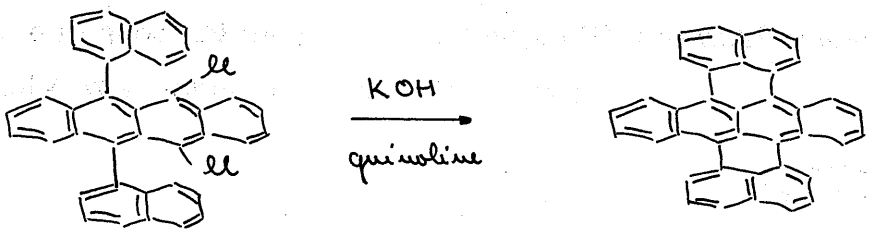
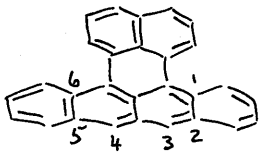
CH - COONa
CH - COONa

Fig. 10

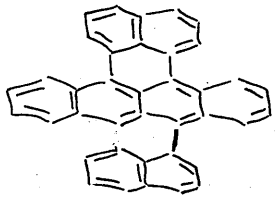


IX LIV

As an interesting by-product in this synthesis, a blue hydrocarbon was isolated from the reaction mixture. This blue hydrocarbon was the main product when dichlorodinaphthyltetracene (IX) was heated in quinoline with potassium hydroxyde for only 20 minutes, instead of two hours. Comparison of its absorption spectrum and the spectrum of 1:2-5:6-dibenzperylene (XV) showed similarities. Therefore, the structure of this hydrocarbon a 3-(1-naphthyl)-1:2-5:6-dibenzperylene (LVIII) was assumed.



XV



LVIII

If this prediction were true, an aluminium chloride - sodium chloride melt of LVIII should yield the green hydrocarbon 7:8-15:16-dibenz-terrylene (LIV). This was in fact the case.

Thus, the course of the reaction could be followed easily by observation of the absorption bands. The first ring-closure took place in about 20 minutes, yielding LVIII; the final ring-closure to LIV was complete in about two hours.

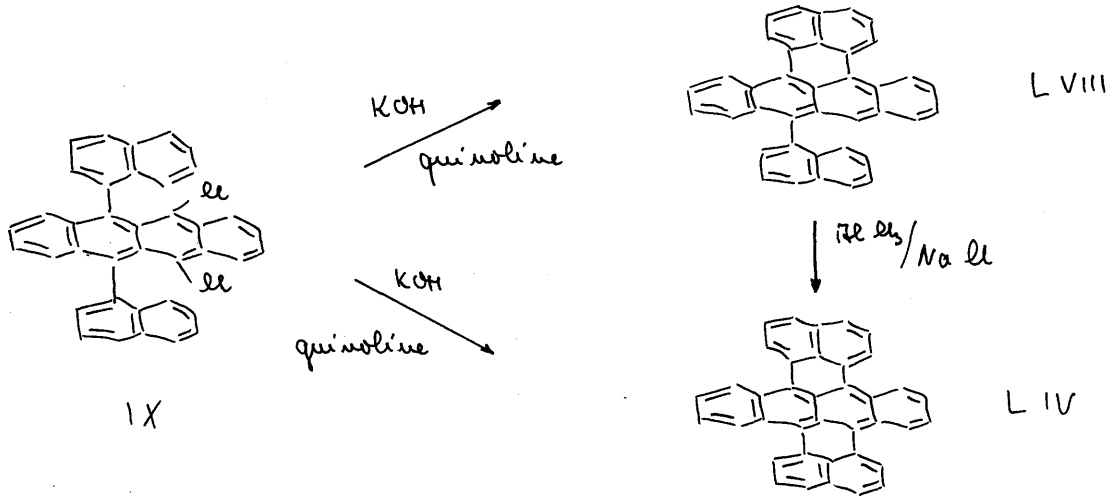


Fig. 11 gives the first p-bands of the starting material (IX) for the synthesis, the intermediate 3-(1-naphthyl)-1:2-5:6-dibenzterrylene (LVIII), and the final product 7:8-15:16-dibenzterrylene (LIV). The p-bands of 1:2-5:6-dibenzperylene (XL) are given for comparison. Recently a paper was published(26) which describes the reaction between 5:12-dihydro-5:5:6:11:12:12-hexachlorotetracene (LIX) and naphthalene in benzene solution, using aluminium chloride as condensation-catalyst. As main products a blue and a green hydrocarbon resulted. The blue hydrocarbon was 1:2-5:6-7:8-tribenzfluoranthene (XVI, page 19), and the green one probably 5:6-11:12-di-(1:2-naphthylene)-tetracene (LX):

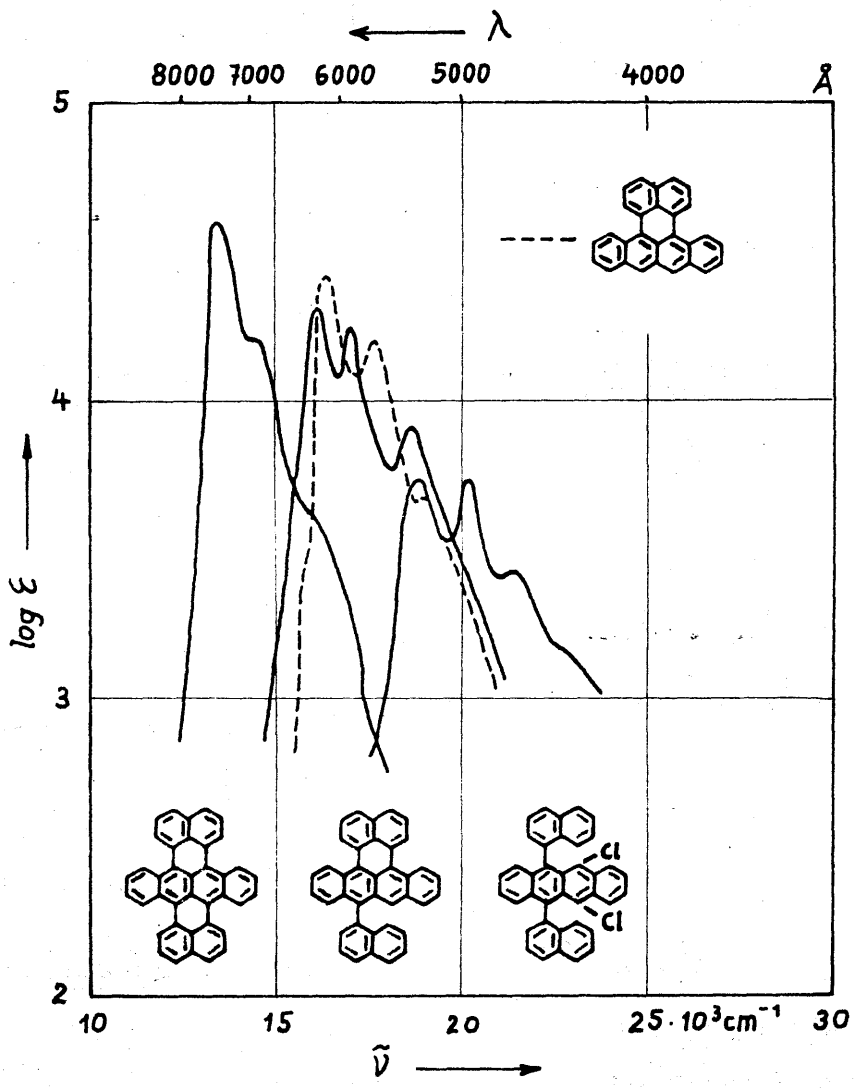
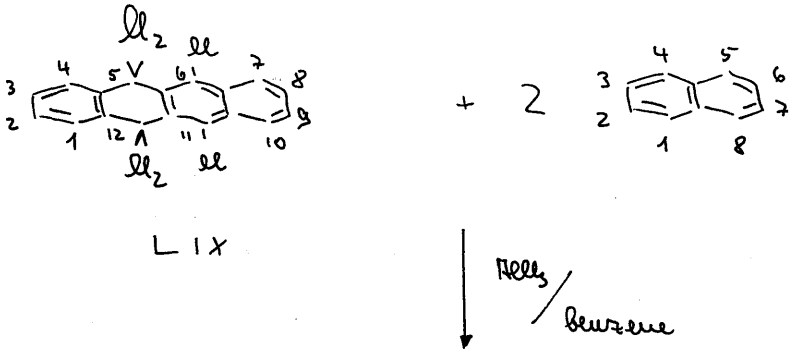

λ
8000 7000 6000 5000 4000 Å
5
4
3
2
log ε
10 15 20 25·10³cm⁻¹ 30
ν̃
Cl
Cl

Fig. 11



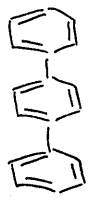
LIX

XVI

LX

The significance of this reaction is that neither 1:2-5:6-dibenzperylene (XV) nor 7:8-15:16-dibenzterrylene (LIV) was found as reaction product. It shows that naphthalene prefers to react in the 1:2-position, and does so in the 1:8-position only when special conditions are provided.

The p-absorption in the "terrylene-series" (fig. 12)



LXI

Terphenyl (LXI), the lowest member of the "terrylenes", has, like diphenyl, a very diffuse absorption spectrum, due to out of plain distortion of the benzene rings. As in the "perylene-series", addition of each benzene ring gives rise to a shift in absorption of 0.5 of an annelletion unit. The maleic

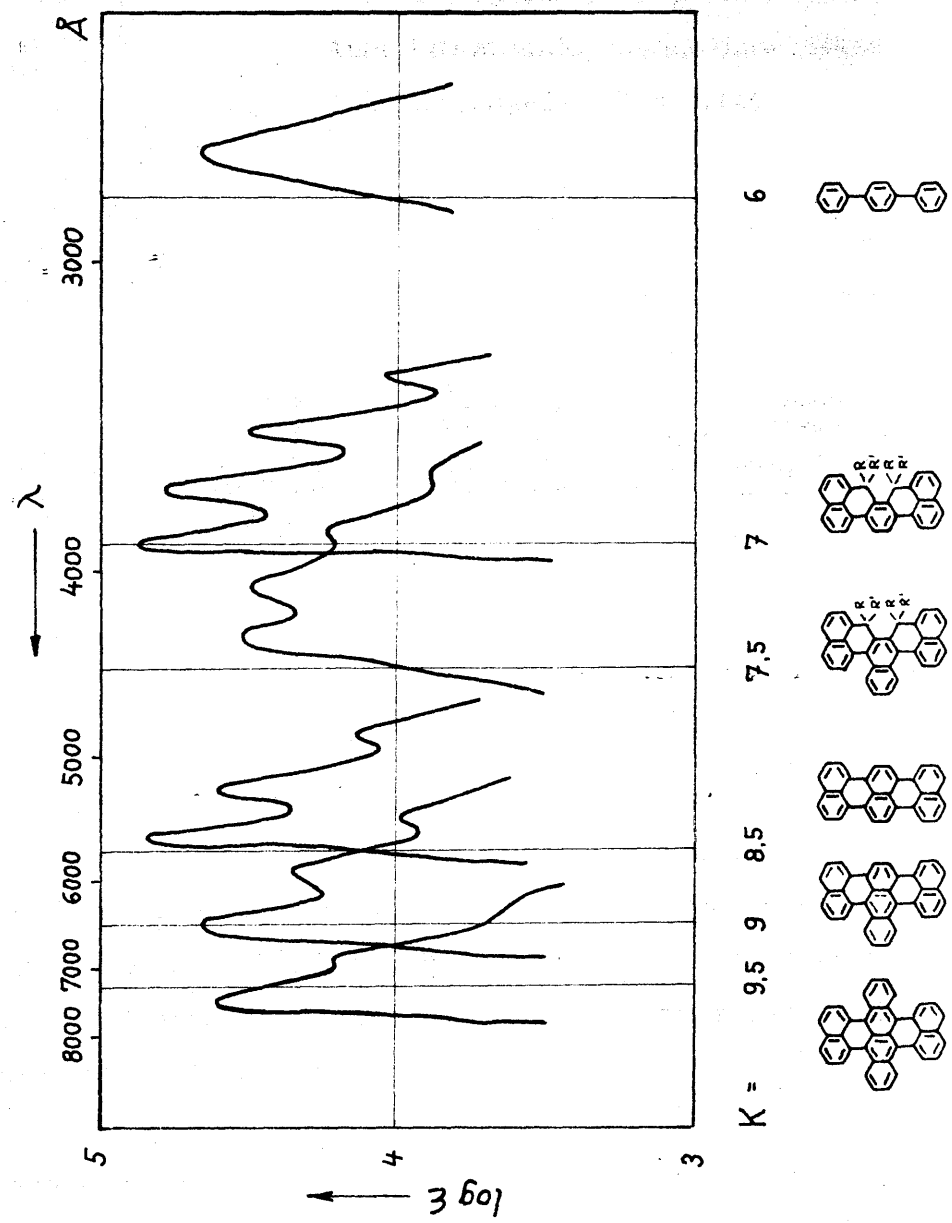
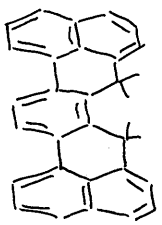


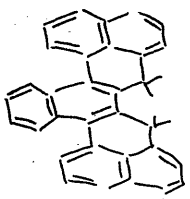
Fig. 12

anhydride adduct of 7:8-benzterrylene (XXVII) has order number 7.0 and is thus to be considered a dibenzterphenyl-derivative.

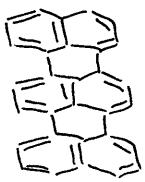


XXVII

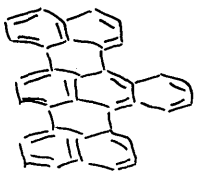
The maleic anhydride adduct of 7:8-15:16-dibenzterrylene LVII gives a shift of 0.5 annellation units, being thus related to a tribenzterphenyl-derivative.



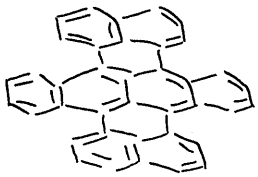
LVII



VI



XIV



LIV

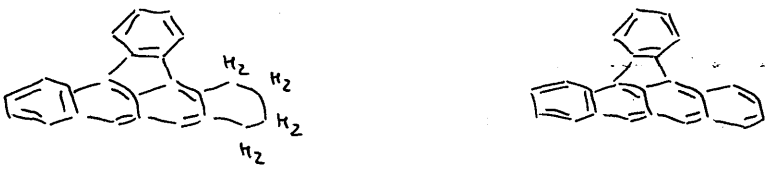
Terrylene (VI) has order number 8.5. Addition of one benzene ring gives order number 9, as verified in XIV. The order number of LIV is higher than expected for two benzene rings - 1.0 annellation unit - which should give 9.5. This could also be the effect of the dominating tetracene system in the molecule, first exhibited in 1:2-5:6-dibenzperylene (page 32).

2:3-Benzorubicene

It was expected that ring-closure of 5:12-dihydro-5:12-diphenyl-tetracene-5:12-diol (LXII) (27) would lead to the known hydrocarbon diphenylenrubene (IV, page 8) (6).

LXII IV

A chromatograph of the crude product (produced by an aluminium chloride - sodium chloride melt of LXII) gave on development the known hydrocarbons tetrahydrodibenzfluoranthene (LXIII) and dibenzfluoranthene (III, page 8).

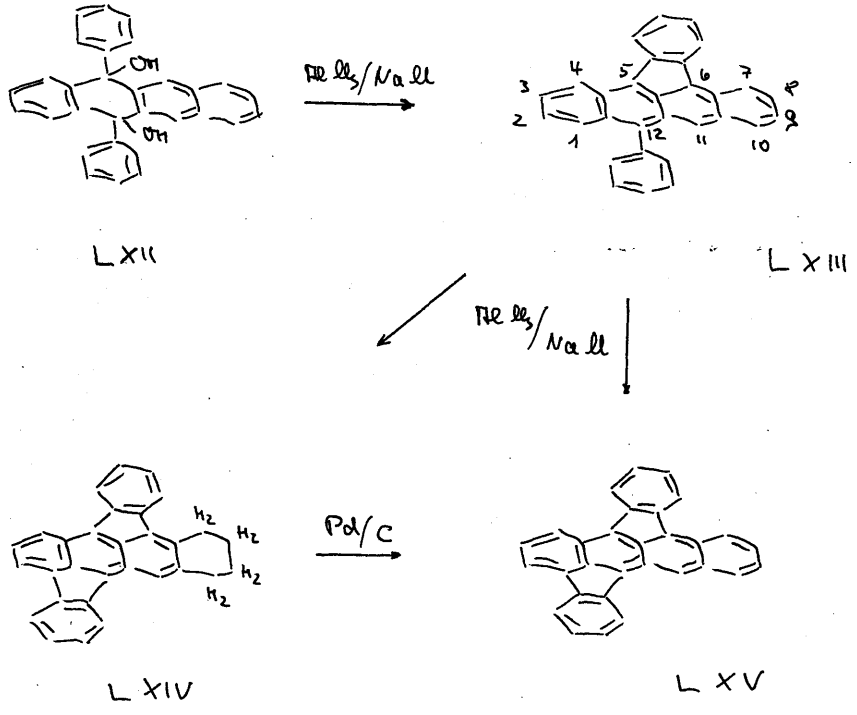


LXIII III

The hydrocarbons occur as the first step in ring-closure. The second phenyl group of LXII has been split off, a not unusual occurance in vigorous melts.

Further development of the chromatogram gave firstly a small amount of red hydrocarbon (LXIV) (with an absorption spectrum not unlike that of rubicene (LXXI on page 42) (28) and secondly a larger amount of blue hydrocarbon (which had an absorption spectrum slightly, but noticeably different from that of diphenylene-

rubene (IV, see fig. 13). The melting point of this new hydrocarbon was, however, 215° lower than the melting point of IV. Since repeated chromatography, recrystallisation and resublimation did not change the absorption spectrum nor the melting point of the new hydrocarbon it seemed that an isomer of IV had been formed. The only feasible possibility was that, after one phenyl group in LXII had ring-closed in the 6-position of tetracene, yielding LXIII as an intermediate product, the other group had ring-closed to the benzene ring of tetracene, not attached by the first ring-closure, that is the 1-position of the tetracene molecule.



The thus formed hydrocarbon was then a benzene homologue of rubicene, namely 2:3-benzorubicene (LXV). The red hydrocarbon was according to analysis a tetrahydroderivative. When it was dehydrogenated over palladium charcoal, 2:3-benzorubicene (LXV)

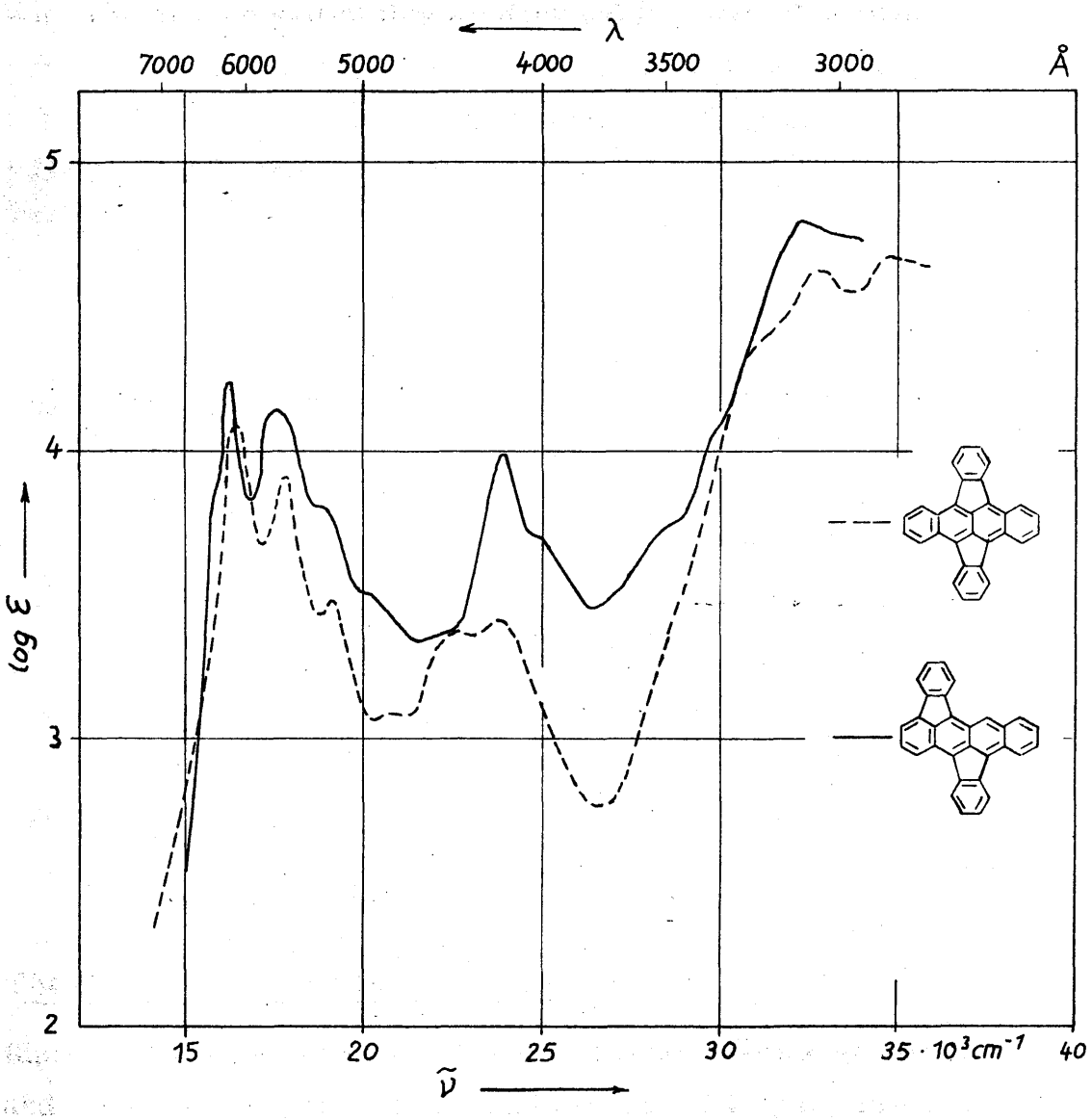
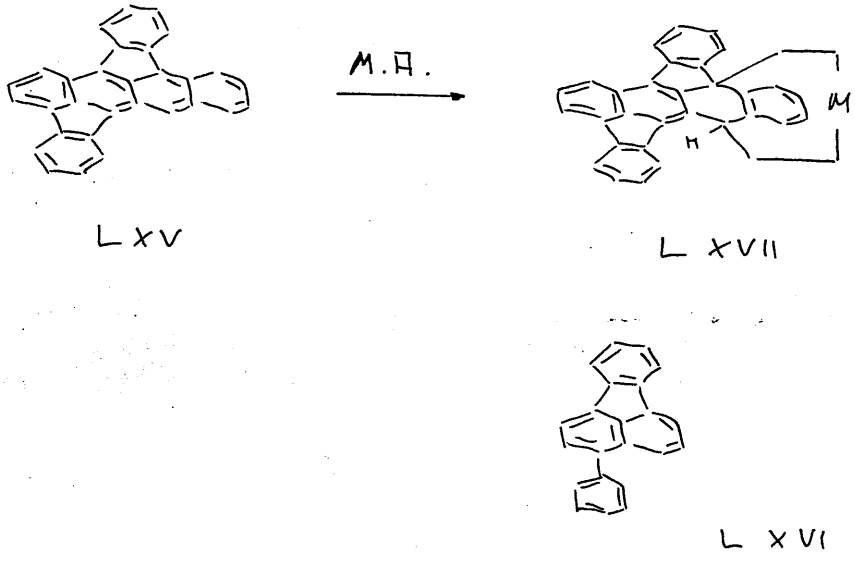

λ
7000
6000
5000
4000
3500
3000
Å
5
4
3
2
log ε
15
20
25
30
35 · 10³cm⁻¹
40
ν̃

Fig. 13

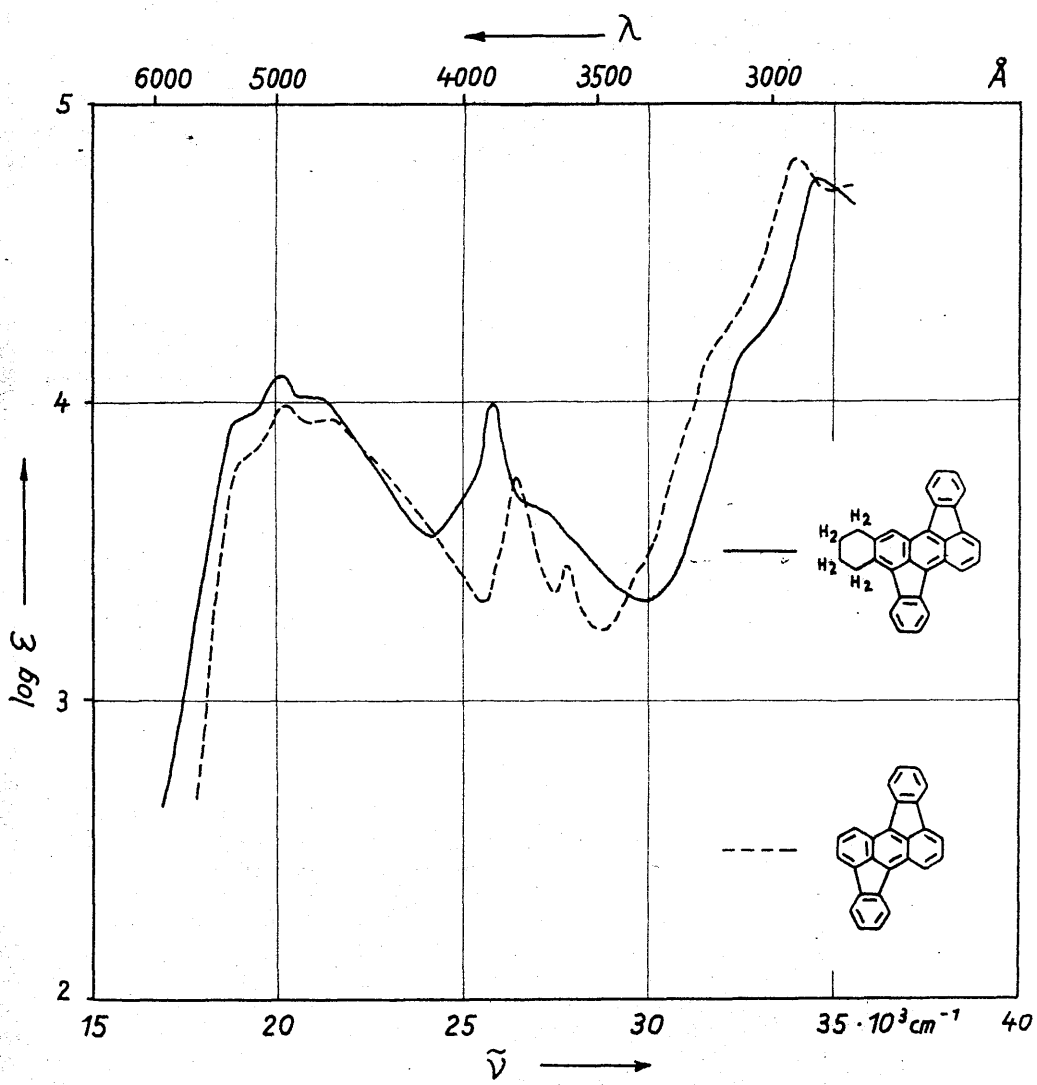
was formed. Thus the rubicene-like spectrum of LXIV supported the view that the blue hydrocarbon was in fact 2:3-benzorubicene(fig. 14).

2:3-Benzorubicene (LXV) added maleic anhydride in boiling xylene, and on cooling and concentration a colourless product crystallised out. The disodio salt of this product had an absorption spectrum very much like 4-phenylfluoranthene (LXVI) (29) with a shift towards the red, due to the more complex structure of the maleic anhydride adduct - LXVII (see fig. 15).



The Synthesis of Rubicene and Iso-rubicene

Since the reported spectrum of iso-rubicene (30) was not complete, and the reported synthesis (31) had as its final step a ring-closure reaction carried out at 300°, which might give rise to rearrangements, new routes were investigated to synthesize iso-rubicene.


λ
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Å
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4
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2
log ε
15
20
25
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35 · 10³cm⁻¹
40
ν̃
H2
H2
H2
H2

Fig. 14

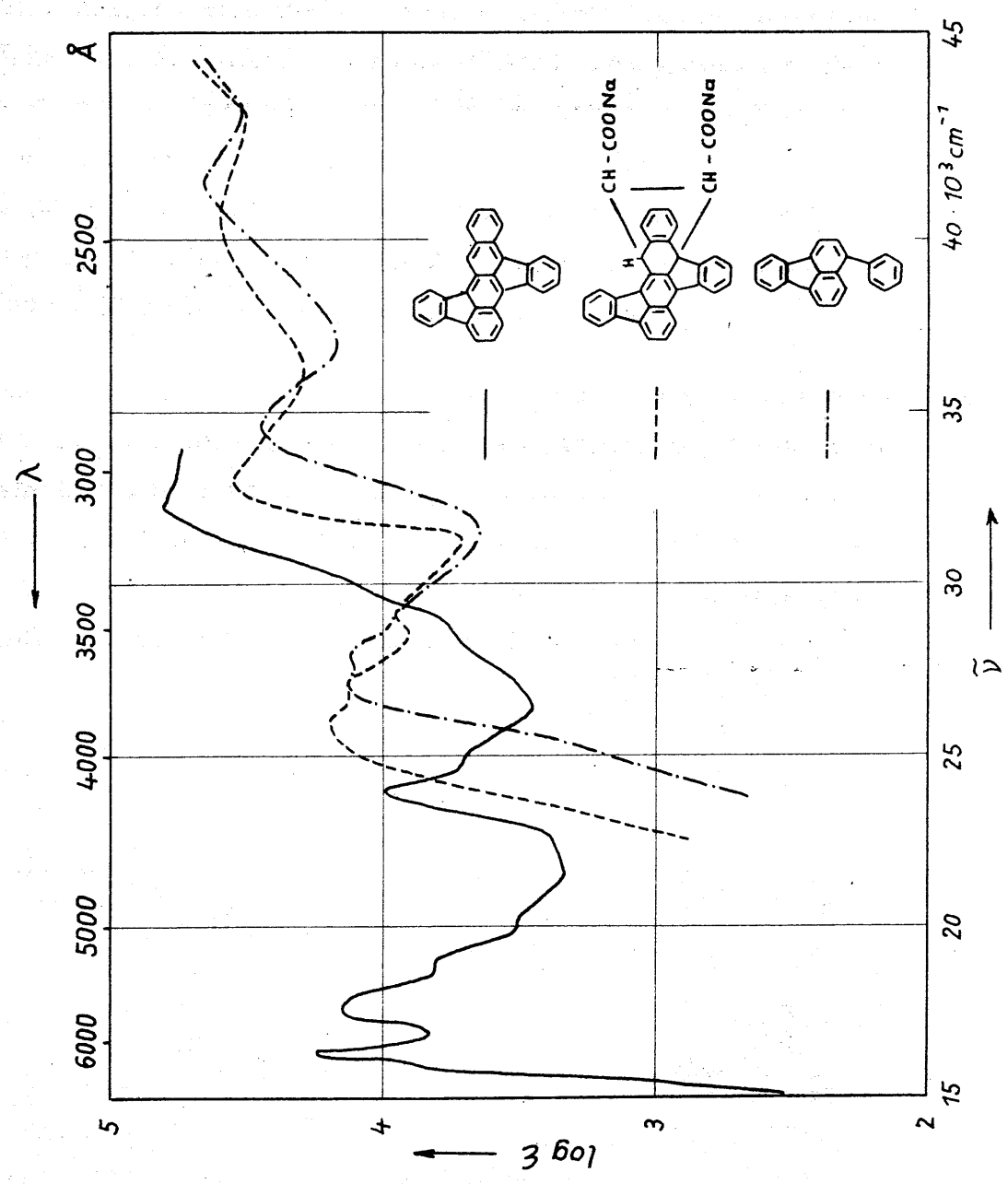
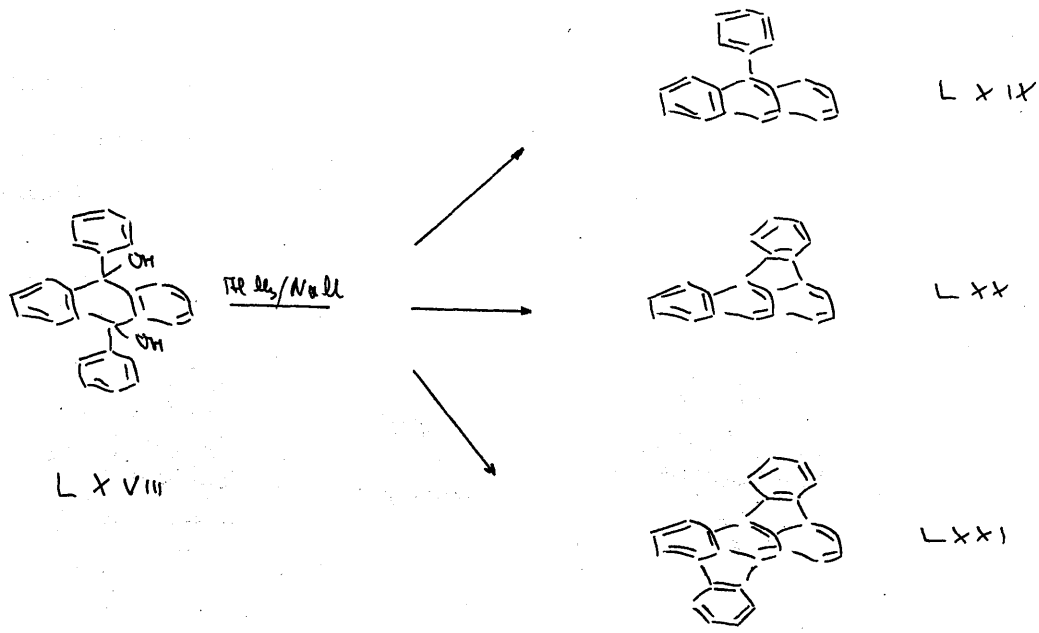

λ
Å
2500
3000
3500
4000
5000
6000
log ε
5
4
3
2
$\tilde{\nu}$
$40 \cdot 10^3 cm^{-1}$
45
35
30
25
20
15
CH-COONa
CH-COONa
H

Fig. 15

1.) Ring-closure of 9:10-dihydro-9:10-diphenylanthracene-9:10-diol and of 4-phenyl-2:3-benzfluoranthene

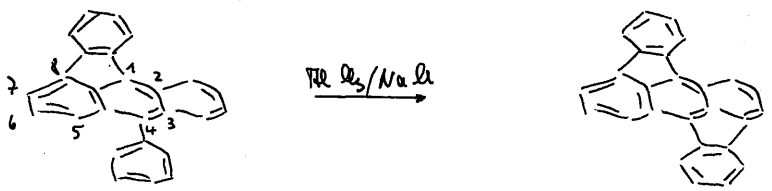
Treatment of anthraquinone with phenyl magnesium bromide gave 9:10-dihydro-9:10-diphenylanthracene-9:10-diol in good yield (32). When this diol LXVIII was ring-closed in an aluminium chloride - sodium chloride melt, several hydrocarbons other than iso-rubicene were formed. As a first reaction product (separated by chromatography) 9-phenylanthracene (LXIX) was found. The second reaction product was 2:3-benzfluoranthene (LXX). These two hydrocarbons originate from LXVIII by splitting off one phenyl group.

As a main product, rubicene (LXXI) was formed. A last product was a very high melting, very insoluble hydrocarbon, the structure of which is still unknown. But, since this hydrocarbon was also formed in an aluminium chloride - sodium chloride melt of rubicene itself, it is expected to be a transformation product, probably by rearrangement and/or further condensation of rubicene.



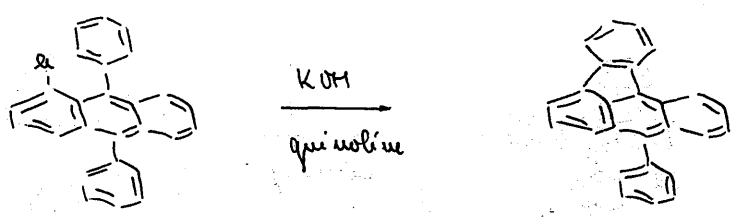
Like 5:12-dihydro-5:12-diphenyltetracene-5:12-diol (LXII on page 40) 9:10-dihydro-9:10-diphenylanthracene-9:10-diol (LXVIII) did not ring-close to the same benzene ring of the anthracene molecule for both stages, but ring-closed in the second stage to the benzene ring of anthracene, not attached by the first ring-closure.

The same observation was made when 4-phenyl-2:3-benzfluoranthene (LXII) was treated in an aluminium chloride - sodium chloride melt. Here too, rubicene (LXXI) and its transformation product were formed in good yields, but no iso - rubicene:



LXX II LXXI

The 4-phenyl-2:3-benzfluoranthene (LXXII), used in the above reaction, was thus far not known. It was synthesized from 1-chloro-9:10-diphenylanthracene (LXXIII) (33) by boiling in quinoline with potassium hydroxide:

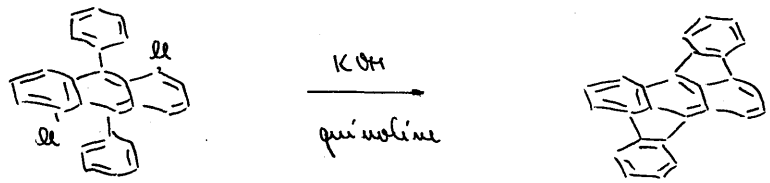


LXX III LXXII

The spectra of 2:3-benzfluoranthene (LXX), 4-phenyl-2:3-benzfluoranthene (LXXII) and of 5-chloro-4-phenyl-2:3-benzfluoranthene (LXXVI, see below) are reported in fig. 16. The close relationship of all three compounds is clearly indicated.

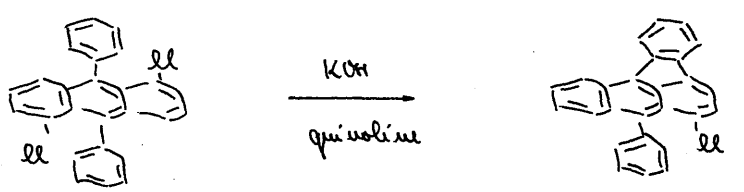
2.) Ring-closure of 1:5-dichloro-9:10-diphenylanthracene and of 1:4-dichloro-9:10-diphenylanthracene

1:5-dichloro-9:10-diphenylanthracene (LXXIV) (33) ring-closed easily with potassium hydroxide in quinoline to form rubicene (LXXI) in good yield:-

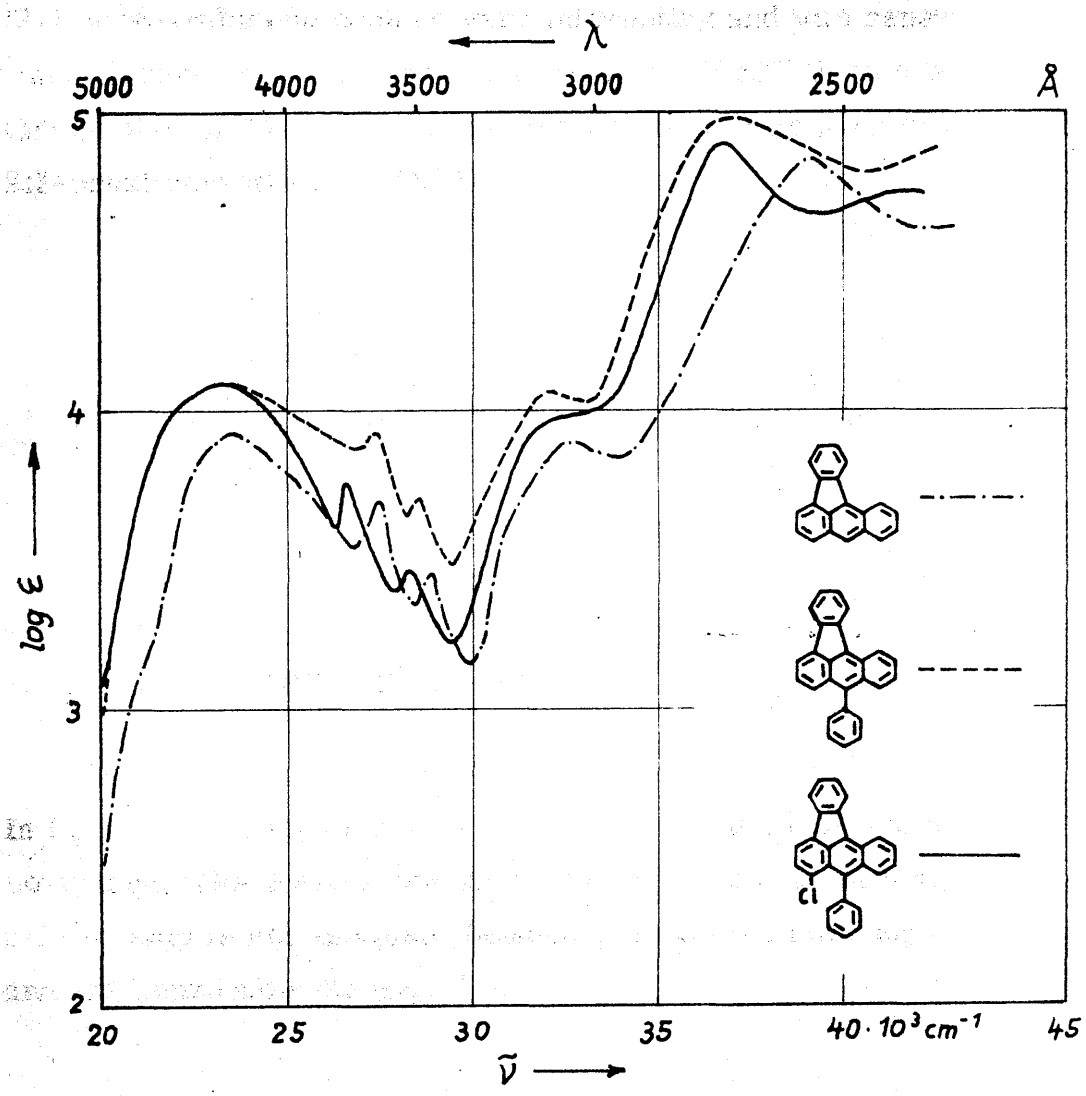


LXXIV LXXI

When, however, 1:4-dichloro-9:10-diphenylanthracene (LXXV) (34) was given the same treatment, firstly 5-chloro-4-phenyl-2:3-benzfluoranthracene (LXXVI) was formed:



LXXV LXXVI


λ
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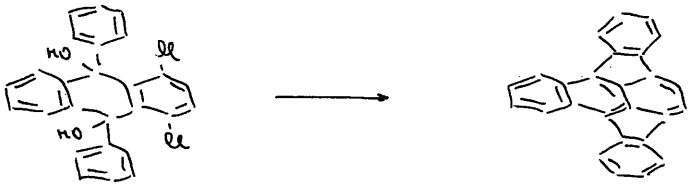
35
40 · 10³ cm⁻¹
45
ν̃
Cl

Fig. 16

Further reaction in potassium hydroxide and boiling quinoline gave only tarry products, which dissolved to give yellow solutions in alkali. No iso-rubicene was formed.

Now, in view of the above experiments, the FEDOROV synthesis (31) of iso-rubicene seemed very interesting and was repeated. In fact, a very small amount of iso-rubicene (LXXVII) was obtained, though also in this synthesis the main product was 5-chloro-4-phenyl-2:3-benzfluoranthene (LXXVI):



LXXVII

FEDOROV synthesis

In fig. 17 the absorption spectra of rubicene and iso-rubicene are compared. There are some similarities in the two spectra, but the relationship is not as close, however, as between diphenylenerubene and 2:3-benzorubicene (fig. 14).

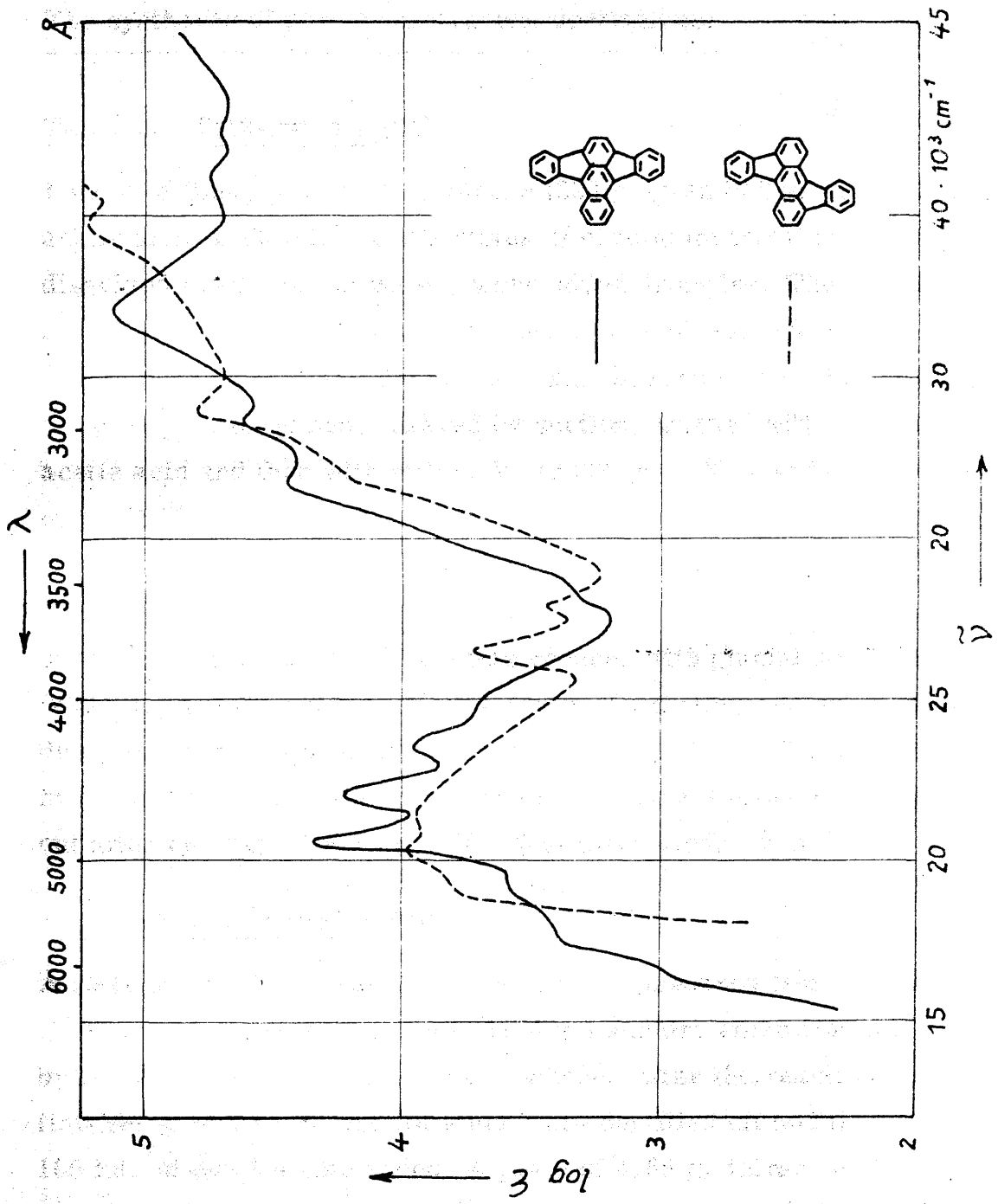

Å
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Fig. 17

Experimental

The syntheses of peri-aryltetracene derivatives:

Tetracene-5:12-quinone (34)

1 mole of finely powdered tetracene (228 g.) was boiled with glacial acetic acid (1000 ml.), and 3 moles of chromium trioxide (300 g.) dissolved in 300 ml. of water, were added dropwise. The solution turned green and the tetracene gradually dissolved. When the reaction was complete, the mixture was allowed to cool down and the precipitated quinone filtered by suction, washed with cold glacial acetic acid and then with water. Yield 230 g. = 90 % of theoretical. m.p. 285°.

Tetracene-5-one (35)

Tetracene-5:12-quinone (9 g.) was reduced with glacial acetic acid (200 ml.) and tin (15 g.). After 2 hours of refluxing the solution was decanted from residues of tin and mixed with 22 ml. of concentrated hydrochloric acid. Pale yellow needles of tetracene-5-one crystallized out after cooling. Yield 7 g. = 82 % of theoretical. m.p. 194°.

5-(1-naphthyl)-tetracene (VII)

A solution of lithium-naphthyl in ether was prepared from lithium (1.08 g.), 1-bromonaphthalene (12.4 g.) and dry ether (150 ml.) by refluxing under a nitrogen atmosphere. After the reaction had finished (2 hours) 100 ml. of ether were destilled off and then 100 ml. of dry benzene added. A paste of 4.88 g. tetracene-5-one in benzene was added slowly with stirring to the benzene/ether solution of lithium-naphthyl. The reaction proceeded with gradually changing

colour from pale brown to red. After refluxing for 1 hour the reaction mixture was decomposed with ice-cold dilute (50 %) acetic acid and steam distilled to remove benzene and ether. The residue (4 g.) was filtered off and dissolved in dry benzene, and chromatographed on alumina. This yielded 2.3 g. of orange-yellow needles which (after recrystallization from benzene) melted at 204°. and dissolved in concentrated sulphuric acid giving a green solution.

Found: C, 94.8; H, 5.4; calculated for $C_{28}H_{18}$: C, 95.0; H, 5.0 %.

5:12-dihydro-5:12-di-(1-naphthyl)-tetracene-5:12-diol

A solution of 1-bromonaphthalene (16.56 g., 4 moles) in 50 ml. of dry ether was added dropwise and with stirring to a suspension of 1.4 g. lithium (2 equivalents) in 100 ml. of dry ether under a nitrogen atmosphere. After 1 1/2 hours the reaction was complete and the ether-solution coloured deep violet. The solution was refluxed for another 1/2 hour, 100 ml. of the ether-solvent was distilled off and then 100 ml. of dry benzene added. To this benzene solution of lithium-naphthyl were added with stirring 5.16 g. (2 moles) of finely powdered tetracene-5:12-quinone in small portions. After each addition the solution refluxed vigorously. The reaction was completed by another 2 hours refluxing and stirring. The now brownish-red coloured solution was decomposed by pouring it into dilute acetic acid and ice (1000 ml.). The whole solution was then filtered and the residue washed several times with hot benzene. The diol remained as a colourless residue. m.p. 236 - 239°. Yield 8 g. = 80 % of theoretical. Crystallization from xylene gave colourless needles, m.p. 242° (decomp.).

Found: C, 88.8; H, 5.4 %. $C_{38}H_{26}O_2$ requires C, 88.7, H, 5.1 %.

The diol gave a deep green solution in concentrated sulphuric acid.

5:12-di-(1-naphthyl)-tetracene (VIII)

The diol prepared above (5.1 g.) was refluxed for 1 hour with potassium iodide (10 g.) and glacial acetic acid (100 ml.). The yellow reaction product crystallized out slowly during the reaction, and on further cooling, 4.3 g. (90 % of theoretical) of the product were obtained, which were filtered off and sublimed in vacuo, then recrystallized from xylene. m.p. 291°.
Found: C, 94.8; H, 5.2. $C_{38}H_{24}$ requires C, 95.0, H, 5.0 %.

5:12-dihydro-5:5:6:11:12:12-hexachlorotetracene (LIX)

Tetracene (23 g.), dichlorobenzene (220 ml.) and sulfuryl chloride (73 g.) were heated together for 5 hours at 100°. The reaction proceeded with evolution of hydrogen chloride and with colour-change from orange to red and later again to colourless. After cooling, the crude product was filtered off and washed with xylene. Yield 35 g. = 80 % of theoretical. m.p. 248 - 249° (decomp.).

6:11-dichlorotetracene-5:12-quinone

Dihydrohexachlorotetracene (20 g.) was added in small portions to concentrated sulphuric acid (100 ml.). The colour of the resulting solution changed from red to deep violet, and hydrogen chloride was evolved. After all the dihydrohexachlorotetracene was added, the mixture was stirred for two hours and then decomposed by pouring into ice. The yellow quinone precipitated out and was recrystallized from xylene. Yellow needles. m.p. 250°.
Yield 9 g. = 60 % of theoretical.

6:11-dichloro-5:12-di-(1-naphthyl)-tetracene (IX)

A solution of naphthyl magnesium bromide in ether was prepared from 1-bromonaphthalene (8 g.), magnesium (1 g.) and ether (50 ml.); the ether was removed by distillation and replaced by 100 ml. of

dry benzene. 6:11-dichlorotetracene-5:12-quinone (3.2 g.) was added in portions. The reaction proceeded with frothing and was completed by a further 3 hours' boiling. The brown-yellow reaction product was decomposed with ice cold dilute acetic acid (250 ml. 1:1), and the precipitate filtered off and washed with hot water. To remove unchanged quinone, the residue was extracted three times with a solution (10 % in water) of sodium hydrosulphite. The remaining crude material (6:11-dichloro-5:12-dihydro-5:12-di-(1-naphthyl)-tetracene-5:12-diol) (3.5 g.) was refluxed for one hour with glacial acetic acid (100 ml.) and potassium iodide (3.5 g.). A red reaction product crystallized out slowly during the reaction and, on cooling the solution, 3 g. of a bright red material were filtered off, washed, dried, and recrystallized from petroleum ether (b.p., 100 - 120°). Red needles. m.p. 200 - 205°. It dissolved in benzene to give a pink solution with green fluorescence, and in concentrated sulphuric acid to give a green solution.

Found: Cl, 13.3. $C_{38}H_{22}Cl_2$ requires 12, 9 % Cl.

The syntheses of 1:2-5:6-dibenzperylene and 1:2-5:6-7:8-tribenzfluoranthene:

1:2-5:6-dibenzperylene (XV)

5-(1-naphthyl)-tetracene (VII) (4.g.) was added to a sodium chloride - aluminium chloride melt (8 g. - 40 g.) at 130°. This temperature was retained, whilst stirring, for 15 minutes. The deep green melt was decomposed by pouring into dilute hydrochloric acid (1:2) and subsequent boiling and filtration. The residue was washed well with water and then with dilute ammonia (5 %). The dried residue was dissolved in benzene and chromatigraphed on alumina, previously activated at 400° for two hours, deactivated with methanol and again activated in vacuo at 300° under carbon dioxide. The chromato-

gram was washed with petroleum ether (b.p. 40 - 60°) and then with benzene. A first colourless solution (blue fluorescence) was discarded, as was a second yellow solution (green fluorescence). The main fraction (a deep violet solution) followed and the last fraction was wine red. The violet solution yielded on concentration reddish-violet crystals (300 mg.) which, after sublimation at 300° and 10^{-4} mm. pressure, and recrystallization from xylene had a melting point of 238°, and dissolved in concentrated sulphuric acid to give a solution at first yellow, then emerald green. The solution in benzene was blue with red fluorescence. The substance was very sensitive to photo-oxidation and the greatest care was taken during the preparation to exclude strong light.
Found: C, 95.0; H, 4.8. $C_{28}H_{16}$ requires C, 95.4; H, 4.6 %.

Maleic anhydride adduct of 1:2-5:6-dibenzperylene (XXX)

The hydrocarbon (50 mg.) and maleic anhydride (50 mg.) were refluxed in xylene (20 ml.) for 15 minutes. The solution became almost colourless and the adduct crystallized, after cooling, in colourless needles, which decomposed above 250° yielding the violet hydrocarbon again, and maleic anhydride.
Found: C, 84.9; H, 4.2. $C_{32}H_{18}O_3$ requires C, 85.3; H, 4.0 %.

1:2-5:6-7:8-tribenzfluoranthene (XVI)

5-(1-naphthyl)-tetracene (VII) (4 g.) was added to a melt of sodium chloride - aluminium chloride (8 g. - 40 g.) at 110°, and the melt held at this temperature for 7 minutes. The melt was decomposed with dilute hydrochloric acid (1:2) and worked up as usual (see above). The main fraction of the chromatogram yielded after concentration long blue needles (450 mg.) of tribenzfluoranthene, which, after sublimation at 10^{-3} mm. pressure and 300° and recrystallization from xylene melted at 298°. It dissolved in concentrated sulphuric

acid to give a yellow solution, changing slowly to deep green. The solution in benzene was red with orange fluorescence and again very sensitive to light.
Found: C, 95.3; H, 4.7. $C_{28}H_{16}$ requires C, 95.4; H, 4.6 %.

Maleic anhydride adduct of 1:2-5:6-7:8-tribenzfluoranthene (XXXII or XXXIV)

Tribenzfluoranthene (50 mg.) and maleic anhydride (50 mg.) were refluxed in xylene (10 ml.) for 15 minutes. The solution decolourized and yielded, after cooling, colourless needles, which decomposed above 250°, yielding the parent hydrocarbon and maleic anhydride again.
Found: C, 84.4; H, 4.3. $C_{32}H_{18}O_3$ requires C, 85.3; H, 4.0 %.

The synthesis of 1:2-8:9-dibenzanthrene:

1:2-8:9-dibenzanthrone-1'-carboxylic acid

1:1'-binaphthyl-8:8'-dicarboxylic acid (5 g.) and zinc chloride (10 g.) were refluxed for 5 hours in glacial acetic acid (150 ml.) The initially yellow solution gradually changed to brown-red. After cooling the solution was filtered and the red residue (anthanthrone) thoroughly washed with warm dilute (15 %) acetic acid. Filtrate and wash-liquors were united and diluted with water till no more acid was precipitated. The yellow dibenzanthrone-carboxylic acid was filtered off, washed with hot water and dried, yielding 3.5 g. of crude material.
m.p. 275 - 278°.

1:2-8:9-dibenzanthrone (XL)

5 g. of the acid prepared above were refluxed with copper-powder (2.5 g.) in quinoline (30 ml.) for 10 hours. After cooling the liquid was poured into dilute hydrochloric acid and the precipitate filtered off, dried and sublimed in vacuo. The dibenzanthrone sublimed in

long yellow needles (4 g.; 86 % of theoretical) which melted at 185° and dissolved in concentrated sulphuric acid to give a brown-red solution.

11:12-trimethylenetetraphene (XLI)

Dibenzanthrone (XL) (3 g.), zinc dust (12 g.), and potassium hydroxide (12 g.) were refluxed for 12 hours in alcohol (25 ml.) and water (75 ml.). The brown solution was filtered while hot into concentrated hydrochloric acid (300 ml.). Yellow flakes precipitated, which were filtered off (500 mg.) and sublimed under 10^{-4} mm. pressure at 350°. A yellow oil was yielded, which, after solution in petroleum-ether (b.p. 60 - 80°) was chromatographed on alumina. A colourless solution with blue fluorescence was obtained, from which silky needles crystallized after concentration (78 mg.). m.p. 136 - 137°. Colour in concentrated sulphuric acid: bright red.
Found: C, 94.1; H, 5.8. $C_{21}H_{16}$ requires C, 94.0; H, 6.0 %.
Mixed melting point with 8:9-trimethylene-3:4-benzphenanthrene: 115 - 120°.

8:9-trimethylene-3:4-benzphenanthrene (XLII)

Dibenzanthrone (XL) (4 g.), red phosphorus (4 g.), hydroiodic acid (40 ml. of 55 % solution), and xylene (50 ml.) were refluxed for 48 hours. After cooling the xylene layer was separated off, washed several times with water, then with dilute sodium carbonate solution (10 % in water) and sodium bisulfite solution (10 % in water), to remove acid and free iodine. Chromatography on aluminia (prepared as above) with petroleum ether (b.p. 60 - 80°) yielded a colourless (blue fluorescent) solution, which, on concentration, gave light yellowish crystalls (2.3 g.; 60 % of theoretical). These, on recrystallization from petroleum ether (b.p. 60 - 80°), were almost colourless and melted at 139°. They gave a yellow solution in concentrated sulphuric acid.

Found: C, 94.1; H, 6.0. Calculated for $C_{21}H_{16}$: C, 94.0; H, 6.0 %.

"Zinc dust melt" of 1:2-8:9-dibenzanthrone

Dibenzanthrone (XL) (2 g.) and zinc dust (4 g.) were mortared thoroughly. A mixture of sodium chloride (4 g.) and zinc chloride (20 g.) was added. The whole mixture was heated to 300° over 15 minutes with stirring. The melt became red and separated into two layers. After further 5 minutes at 300° it was allowed to cool and then decomposed with dilute acetic acid (250 ml.). The residue was washed, dissolved in benzene, the solution dried with calcium chloride, and chromatographed on alumina, using petroleum ether (b.p. 60 - 80°) as eluant. As firstfraction 8:9-trimethylene-3:4-benzphenantrene (XLII) (150 mg.) was obtained, and as second fraction 11:12-trimethylenetetraphene (XLI) (65 mg.).
The trimethylene derivatives could not be dehydrogenated by sublimation through 10 % palladium-charcoal at 300 - 350° and 10^{-2} mm. pressure in a stream of carbon dioxide.

1:2-8:9-dibenzanthrene (XXXI)

A solution of 1:2-8:9-dibenzanthrone (XL) (12 g.) in iso-propanole (200 ml.) containing aluminium-iso-propoxide (5 g.) was refluxed for 24 hours. 150 ml. of the solvent, which contained acetone (generated during the course of the reaction) were then distilled off. Renewed boiling for 24 hours followed, after addition of further 5 g. of aluminium iso-propoxide and 100 ml. of iso-propanol. Finally, the solution was concentrated to 100 ml. and decomposed with dilute sulphuric acid (250 ml. 1:3), yielding a brown, gummy residue, which was washed with hot water, dissolved in benzene, and the benzene solution dried with calcium chloride. Chromatography on alumina with petroleum ether (b.p. 60 - 80°) yielded a colourless solution (with blue fluorescence) from which on concentration

yellowish dibenzanthrene crystallized out (80 % of theoretical, 9 g.) Rechromatography on alumina gave colourless, long plates. m.p. 89.5 - 90.5°. Colour in concentrated sulphuric acid, orange, with pink fluorescence.

Found: C, 94.6; H, 5.3. $C_{21}H_{14}$ requires C, 94.7; H, 5.3 %.

The synthesis of 7:8-15:16-dibenzterrylene:

dibenzterrylene (LIV) by an aluminium chloride - sodium chloride melt of 5:12-dihydro-5:12-di-(1-naphthyl)-tetracene-5:12-diol (LIII)

5 g. of 5:12-dihydro-5:12-di-(1-naphthyl)-tetracene-5:12-diol (preparation, page 47) were added to a melt of sodium chloride (10 g.) and aluminium chloride (50 g.) and heated to 120° with stirring. The initial deep green of the melt changed to deep violet-blue. After 10 minutes the melt was poured into dilute hydrochloric acid (1:3), boiled and filtered. The residue was washed with hot water, then dilute (10 %) ammonia solution, and the resulting deep green substance (2 g.) sublimed at 10^{-4} mm. pressure in a stream of carbon dioxide. This yielded 500 mg. deep green needles, which were dissolved in xylene and chromatographed on alumina. A blue forerun, on concentration, yielded a small amount of blue needles which gave an blue solution in concentrated sulphuric acid (absorption bands at 6480, 5890, and 5500 A). This is presumably 1':2':3':4'-tetrahydro-7:8-15:16-dibenzterrylene (LV), After the forerun the 7:8-15:16-dibenzterrylene came off the chromatogram and, after repeated crystallization from xylene, followed by sublimation, gave 350 mg. of deep green needles, m.p. 460°, which dissolved in xylene to give a green solution with red fluorescence. Dibenzterrylene dissolved in concentrated sulphuric acid to give a blue solution with red fluorescence.

Found: C, 95.5; H, 4.2. $C_{38}H_{20}$ requires: C, 95.8; H, 4.2 %

Dibenzterrylene by ringclosure with potassium hydroxide of 6:11-dichloro-5:12-di-(1-naphthyl)-tetracene (IX)

Dichlorodinaphthyltetracene (IX) (3 g.) was refluxed with potassium hydroxide (3 g.) in 50 ml. of quinoline. The initial deep red colour of the solution changed after 15 minutes to blue, and after a further 30 minutes to green. After 2 hours' boiling, the quinoline layer was poured into 250 ml. of dilute hydrochloric acid (1:1). The precipitated material was filtered off, washed with methanol (500 ml.), then with benzene (200 ml.) till the mother liquor was almost colourless. The remaining green hydrocarbon was recrystallized from trichlorobenzene. It was identical in melting point, absorption spectrum, and colour in concentrated sulphuric acid with the hydrocarbon prepared according to above.

Maleic anhydrice adduct of 7:8-15:16-dibenzterrylene (LVI)

The hydrocarbon (50 mg.) and maleic anhydride (50 mg.) were refluxed in xylene (20 ml.) for 5 minutes. The solution became yellow and the adduct crystallized in yellow needles (decomp. above 200° to the green hydrocarbon and maleic anhydride).
Found: C, 87.9; H, 4.6. $C_{42}H_{22}O_3$ requires C, 87.8; H, 3.8 %.

1:2-5:6-dibenz-3-(1-naphthyl)-perylene (LVIII)

5:12-dichloro-6:11-di-(1-naphthyl)-tetracene (IX) (2 g.), potassium hydroxide (2 g.), and quinoline (30 ml.) were refluxed for 30 minutes and worked up as above. The precipitated material was chromatographed on alumina, using petroleum ether (100 - 110°) as solvent. After a first red fraction (starting material) a blue fraction came out which yielded on concentration blue crystals. m.p. 215 - 220°. Colour in concentrated sulphuric acid, green.
Found: C, 95.1; H, 4.2. $C_{38}H_{22}$ requires: C, 95.5; H, 4.5 %.
An aluminium chloride - sodium chloride melt of this hydrocarbon

yielded 7:8-15:16-dibenzterrylene (LIV), this being proved by comparison of its melting point, colour in concentrated sulphuric acid, and absorption spectrum with those of the original material.

The synthesis of 2:3-benzorubicene:

5:12-dihydro-5:12-diphenyltetracene-5:12-diol (LXII)

A solution of phenyl-lithium in ether was prepared from bromobenzene (25.2 g.), lithium (1.2 g.) and dry ether (50 ml.). The ether was removed by distillation and replaced by 100 ml. of dry benzene. Tetracene-quinone (10.1 g.) was added in portions. The reaction proceeded with frothing, and was completed by a further 3 hours' boiling. The brown reaction product was decomposed with dilute acetic acid, the benzene layer decanted off and dried with calcium chloride. On concentration the diol crystallized out and was purified by repeated crystallization from petrol ether (b.p. 60 - 80°). m.p. 252°; colour in concentrated sulphuric acid, green.

Aluminium chloride melt of 5:12-dihydro-5:12-diphenyltetracene-5:12-diol (LXII)

The diol (5 g.) was added to a melt of 10 g. sodium chloride and 50 g. aluminium chloride at 120° and the melt held at this temperature with stirring for 5 minutes. The deeply coloured melt was decomposed by pouring into dilute hydrochloric acid (500 ml. 1:2), filtered, washed with hot water (500 ml.) and then with dilute ammonia (500 ml., 10 %) and then dried. 4 g. of black condensation product were obtained which were chromatographed on alumina, starting with petroleum ether (b.p. 60 - 80°) as eluant and progressing to benzene. The forerun was discarded and the following main fractions were obtained successively:

1':2':3':4'-tetrahydro-1:2-5:6-dibenzflouranthene (LXIII) (petroleum ether with 10 % benzene as eluant)

A first main fraction was yellow and gave on concentration yellow needles. m.p. 150° after recrystallization. Yield: 120 mg. No depression was observered in a determination of melting point on admixture with an authentic specimen.

1:2-5:6-dibenzfluoranthene (III) (petroleum ether with 25 % benzene as eluant)

Evaporation of a second red fraction yielded red needles, which were purified by recrystallization from xylene. Yield: 25 mg. Its melting point (215°) was not depressed on admixture with an authentic specimen, and its absorption spectrum was identical with that of an authentic specimen.

1':2':3':4'-tetrahydro-2:3-benzorubicene (LXIV) (petroleum ether with 50 % benzene as eluant)

A third red fraction yielded, after the usual purification methods, reddish-brown needles. m.p. 182°. Yield: 85 mg. These dissolved in concentrated sulphuric acid to give an orange solution, changing on standing to green.

Found: C, 95.0; H, 5.1. $C_{30}H_{20}$ requires C, 94.7; H, 5.3 %.

2:3-benzorubicene (LXV) (petroleum ether with 90 % benzene as eluant)

The fourth, main fraction was violet; on concentration blue needles were obtained. m.p. 250°. Yield: 450 mg. Its solution in benzene was blue with a deep red fluorescence, and its solution in concentrated sulphuric acid, deep green.

Found: C, 95.4; H, 4.4. $C_{30}H_{16}$ requires C, 95.7; H, 4.3 %.

Maleic anhydride adduct of 2:3-benzorubicene (LXVII)

Benzorubicene (20 mg.) and maleic anhydride (20 mg.) were refluxed for 30 minutes in 20 ml. of xylene. The solution became yellow and on

concentration the maleic anhydride adduct crystallized out. It decomposed above 300° into the original hydrocarbon and maleic anhydride.

Found: C, 85.2; H, 4.6. $C_{34}H_{18}O_3$ requires C, 86.0; H, 3.8 %.

Syntheses of Rubicene and Isorubicene:

9:10-dihydro-9:10-diphenylanthracene-9:10-diol (LXVIII)

A solution of phenyl magnesium bromide in ether was prepared from bromobenzene (62.8 g.), magnesium (9.6 g.), and dry ether (250 ml.). After the ether was removed by distillation and replaced by 250 ml. of dry benzene 9:10-anthraquinone (20.8 g.) was added in small portions. The reaction proceeded with frothing, and was completed by a further 5 hours' boiling. The yellow reaction product was decomposed with 500 ml. of aque-ous ammonium chloride solution (10 %), steam distilled, and the residue extracted with an aqueous sodium hydrosulfite solution (10 %), till the unchanged anthraquinone was completely removed. The remaining, almost colourless diol was recrystallized from xylene. Colourless needles. m.p. 261°.

Aluminiumchloride melt of 9:10-dihydro-9:10-diphenylanthracene-9:10-diol (LXVIII)

The diol (5 g.) was added to a sodium chloride - aluminium chloride melt (10 g. - 50 g.) at 120° and the melt held at this temperature, with stirring, for 10 minutes. The deep red coloured melt was decomposed by pouring into ice-cold dilute hydrochloric acid (500 ml. 1:2), filtered, and the residue washed with hot water and dried. 3.5 g. of brown condensation product were obtained, which was chromatographed on alumina, starting with petroleum ether (b.p. 60 - 80°) as eluant and progressing to benzene. The forerun was discarded and then-after the following main fractions were obtained successively:

9-phenylanthracene (LXIX) (100 % petroleum ether as eluant)
A first fraction was colourless with blue fluorescence and gave on concentration colourless plates, m.p. 154°. Yield: 75 mg. Its absorption spectrum was identical with the reported spectrum of 9-phenylanthracene.

2:3-benzfluoranthene (LXX) (100 % petroleum ether as eluant)
A second fraction was yellow (green fluorescence) and on concentration, orange yellow needles (15 mg.) were obtained with m.p. 143 - 145°, which dissolved to give a violet solution in concentrated sulphuric acid. The absorption spectrum was identical with that of an authentic specimen of 2:3-benzfluoranthene.

Rubicene (LXXI) (petroleum ether with 20 % benzene as eluant)
A third orange fraction yielded on concentration long bright red needles (50 mg.), m.p. 303°, which dissolved to give a reddish-brown solution in hot concentrated sulphuric acid. There was no depression observed in melting point on admixture with an authentic specimen of rubicene.
Found: C, 95.5; H, 4.5. Calculated for $C_{26}H_{14}$ C, 95.7; H, 4.3 %.

Transformation product of rubicene

When the alumina of the above chromatigram was extracted with trichlorobenzene, a deep violet, almost black hydrocarbon was obtained (60 mg.) on concentration, which did not melt below 450°. Its solution in trichlorobenzene was deep violet. It did not dissolve in cold concentrated sulphuric acid, in warm acid a reddish colour was observed. No addition product was formed on fusion with maleic anhydride.
Found: C, 95.7; H, 4.0. $C_{26}H_{14}$ requires C, 95.7; H, 4.3 %.

9:10-diphenyl-9:10-dihydro-1-chloro-anthracene-9:10-diol

A Grignard solution was prepared from 31.4 g. of bromobenzene and 4.8 g. of magnesium in 100 ml. of dry ether. The ether was distilled

off and replaced by benzene (200 ml.). 1-chloroanthraquinone (12.1 g.) was added to this solution in small portions. After the initial reaction had subsided the solution was boiled for a further 3 hours and worked up as usual. The unchanged starting material was removed by extracting with aqueous sodiumhydrosulphit solution (10 %). The crude diol was recrystallized twice from alcohol. Colourless needles were obtained, m.p. 134°, which gave a yellow solution in concentrated sulphuric acid.

9:10-diphenyl-1-chloroanthracene

6 g. of the above prepared diol, 6 g. of hydroiodic acid (55 %) and 100 ml. of glacial acetic acid were boiled together for 30 minutes. On concentration faintly yellow needles crystallized out, which melted at 182° and dissolved green in concentrated sulphuric acid. Found: Cl, 9.7. $C_{26}H_{17}Cl$ requires Cl, 9.7 %.

4-phenyl-2:3-benzofluoranthene (LXXII)

9:10-diphenyl-1-chloroanthracene (3 g.), potassium hydroxide (3 g.), and quinoline (20 ml.) were boiled together for 30 minutes. After cooling the quinoline layer was decomposed by pouring into dilute hydrochloric acid (100 ml., 1:1). The precipitate was filtered off, washed with hot water and dried. On recrystallization from alcohol yellow leaflets were obtained, m.p. 185 - 186°, which gave a green solution in concentrated sulphuric acid. Yield: 2.2 g.
Found: C, 94.8; H, 5.1. $C_{26}H_{16}$ requires C, 95.1; H, 4.8 %.

Aluminium chloride - sodium chloride melt of 4-phenyl-2:3-benzfluoranthene (LXXII)

The hydrocarbon (5 g.) was added to a sodium chloride - aluminium chloride melt (10 g. - 50 g.) at 120° and the melt held at this temperature, with stirring, for 10 minutes. The melt was decomposed and worked up as usual, and the dried condensation product (4 g.)

was chromatographed on alumina, starting with petroleum ether (b.p. 60 - 80°) as eluant and progressing to benzene.
The following main fractions were obtained successively:

2:3-benzofluoranthene (LXX) (100 % petroleum ether as eluant)
A first fraction was yellow and on concentration orange yellow needles were obtained, m.p. 143 - 145°. Yield: 55 mg.

Rubicene (LXXI) (petroleum ether with 20 % benzene as eluant)
A second fraction yielded on concentration bright red needles, m.p. 303°. Yield: 105 mg.

Transformation product of rubicene

On extraction of the alumina of the above chromatogram with trichlorobenzene the deep violet hydrocarbon was obtained. Yield: 25 g.

Aluminium chloride melt of rubicene (transformation product)

Rubicene (1 g.) was added to a melt of aluminium chloride and sodium chloride (10 g. - 2 g.) at 130° and kept there with stirring for 15 minutes. The melt was then-after decomposed with ice-cold dilute (1:3) hydrochloric acid, filtered, and the residue washed and dried. The residue (600 mg.) was dissolved in trichlorobenzene and on cooling almost black needles (see pages 59 and 61) were obtained.

1:5-dichloro-9:10-dihydro-9:10-diphenylanthracene-9:10-diol

6 g. of 1:5-dichloroanthraquinone were refluxed for 3 hours with a Grignard compound from 2 g. of magnesium, 8.5 g. of bromobenzene, and 100 ml. of dry ether, the ether removed by distillation and replaced by 100 ml. of dry toluene. The reaction product was worked up as usual and 3.5 g. of the diol, m.p. 318°, were received.

1:5-dichloro-9:10-diphenylanthracene (LXXIV)

The diol (3 g.), hydroiodic acid (6 g. of 55 % solution), and glacial acetic acid (20 ml.) were refluxed for 30 minutes. On cooling the chloro-derivative crystallized out, m.p. 233°. Yield: 2 g.

Rubicene (LXXI)

2 g. of 1:5-dichloro-9:10-diphenylanthracene were refluxed in quinoline (50 ml.) with potassium hydroxide (2 g.). After 10 minutes the colour changed to deep yellow, after 30 minutes to deep red. The reaction was interrupted after 60 minutes' boiling by pouring the quinoline into dilute hydrochloric acid (1:3). The remaining residue was recrystallized from xylene, yielding 1.2 g. of long, bright red needles, m.p. 304°, which gave no depression with rubicene, prepared as on page 59.

1-oxy-4-chloro-9:10-anthraquinone

A mixture of phthalic anhydride (15 g.) and chlorophenol (13 g.) was added to a melt of aluminium chloride (125 g.) and sodium chloride (25 g.) at 220° and kept there with occasional stirring for 3 hours. Then-after the melt was decomposed by pouring into ice (1.000 g.) and concentrated hydrochloric acid (2.000 g.). After filtration and thorough washing with dilute hydrochloric acid (1:3) and later with water, the remaining residue was recrystallized from glacial acetic acid; slightly yellow needles, m.p. 192 - 193°. Yield: 70 % of theoretical.

1:4-dichloro-9:10-anthraquinone

20 g. of the above prepared 1-oxy-4-chloro-9:10-anthraquinone and 20 g. of phosphorus pentachloride were heated together in a distillation flask with attached condensor for 4 hours at 160° with an oil bath. The phosphorus oxychloride, generated during the

reaction, distilled off and in the flask a yellow mass of 1:4-dichloro-9:10-anthraquinone remained. After recrystallization from glacial acetic acid 16 g. of the quinone, m.p. 185°, were obtained.

1:4-dichloro-9:10-dihydro-9:10-diphenylanthracene-9:10-diol

6 g. of 1:4-dichloroanthraquinone were refluxed for 3 hours with a Grignard compound from 2 g. of magnesium, 8.5 g. of bromobenzene, and 100 ml. of dry ether, the ether then removed by distillation and replaced by toluene. The reaction product was decomposed in dilute acetic acid (50 %, 150 ml.), filtered, washed and dried. On recrystallization with ethanol, 3 g. of the diol, m.p. 216° (decomp.) were obtained.

1:4-dichloro-9:10-diphenylanthracene (LXXV)

The above prepared diol (2 g.), hydroiodic acid (6 g. of 55 % solution), and glacial acetic acid (20 ml.) were refluxed for 30 minutes. On cooling down, the hydrocarbon crystallized out, m.p. 176 - 177 °. Yield: 1.2 g.

5-chloro-4-phenyl-2:3-benzfluoranthene (LXXVI)

2 g. of the above prepared hydrocarbon were refluxed in quinoline (20 ml.) with potassium hydroxide (2 g.). The colour changed after 10 minutes to deep yellow. The reaction was interrupted after 15 minutes and the quinoline poured into dilute hydrochloric acid (1:3). When the received brown residue was recrystallized from petroleum ether (b.p. 60 - 80°), yellow needles were received, m.p. 215°. Found: Cl, 9.9. $C_{26}H_{15}Cl$ requires Cl, 9.8 %.

Isorubicene (FEDOROV-Synthesis)

1 g. of 1:4-dichloro-9:10-dihydro-9:10-diphenylanthracene-9:10-diol (preparation as above), 12 g. of dry oxalic acid, 3 g. of sodium

acetate, 0.3 g. of copper bronze, 0.3 g. of powdered aluminium were heated in a distillation flask for 30 minutes to 300° at 30 mm. vacuum, then for 1 hour at 360°. After cooling down, the product was treated with hot water, then extracted with benzene (50 ml.) and chromatographed on alumina, starting with petroleum ether (b.p. 40 - 60°) and progressing to benzene. The following three fractions were received:

1:4-dichloro-9:10-diphenylanthracene (100 % petroleum ether as eluant)
Almost colourless prisms were yielded on concentration of the first fraction. m.p. 178°, yield: 50 mg. Mixed melting point with a sample prepared according to page 63 gave no depression.

5-chloro-4-phenyl-2:3-benzfluoranthene (LXXVI) (100 % petroleum ether as eluant)
A second yellow fraction yielded on concentration yellow needles, m.p. 214°, yield: 200 mg. This compound was identical in melting point and absorption spectrum with the compound, prepared as above.

Isorubicene (LXXVII) (100 % benzene as eluant)
The last fraction was red and yielded on concentration reddish-brown needles, m.p. 279°, in a yield of 10 mg. It gave no addition product with maleic anhydride in boiling xylene or a melt of the anhydride.

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