Tetrahedron, 1963, Vol. 19, pp. 2185 to 2197. Pergamon Press Ltd. Printed in Northern Ireland

ANNELLATION EFFECTS IN THE PYRENE SERIES AND THE CLASSIFICATION OF ABSORPTION SPECTRA

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(*Received* 6 *May* 1963)

Abstract—The classification of absorption bands in the acene series (α, p, β-bands) was first based on the annellation effect and later on the polarization of the bands with regard to the molecular axes (L_b, L_a, B_b, B_a-bands). Both give the same result since annellation axes and molecular axes coincide. This is not so in the pyrene series. Annellation axes and molecular axes are different and it is shown that the classification of bands can be based only on the annellation effects. Moreover, the electronic asymmetry of the pyrene system is demonstrated by a striking asymmetric annellation effect. A number of higher annellated pyrenes have been synthesized:

1·2-benzonaphtho-(2″·3″:6·7)-pyrene, dinaphtho-(2′·3′:1·2)-(2″·3″:6·7)-pyrene, 1·14,4·5-dibenzopentacene, 5·6,15·16-dibenzohexacene, 6·7,16·17-dibenzoheptacene, 1·16,4·5-dibenzohexacene and 7·8,17·18-dibenzo-octacene.

THE classification of absorption bands based on the annellation effects was first described in 1936.[1] Later, in 1949, a similar classification was given based on the molecular axes. Thus the p-bands which show a maximum red shift with linear annellation are polarized across the width of the acenes and are termed L_a-bands. The α- and β-bands are polarized along the length of the molecule and are called L_b- and B_b-bands respectively (I).[2] Since the long axis of the acenes is identical with the annellation axis there is no difference between the classification of the p-bands and L_a-bands except in name.

However, this is not so in angular and condensed hydrocarbons where considerable deviations in the polarization of the absorption and fluorescence bands are observed.[3]

These are so strong in perylene (II) that the prediction of the polarization differs by 90° between the classification based on the molecular axes and the annellation axes, the latter giving the correct answer.[4]

There are significant differences in the classification of bands in the pyrene series. Polarization along the molecular axes would correlate the L_b and B_b bands to the long axis and the L_a and B_a bands to the short axis (III).[5] However, quite different results must be expected from a correlation to the annellation axes. There are four annellation axes (a, b, c, d) which are equal in pyrene but unequal in the benzologues of pyrene (IV). Annellation in the directions a, d or b, c produces strong equal shifts of the p-bands towards the red. These bands must be polarized therefore perpendicular to these axes (a and d or b and c). In fact, polarization measurements have given the same fluorescence polarization for the L_b, L_a and B_b bands.[6]

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[1] E. Clar, *Ber. Dscht. Chem. Ges.* **69**, 607, 1677 (1936); *Spectrochimica Acta* **4**, 116 (1950); *Chem. Ber.* **82**, 495 (1949); *J. Chem. Phys.* **17**, 741 (1949).

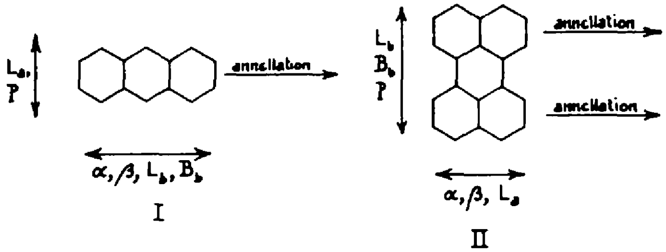
[2] H. B. Klevens and J. R. Platt, *J. Chem. Phys.* **17**, 470 (1949); J. R. Platt, *Ibid.* **17**, 484 (1949); W. Moffit, *Ibid.* **22**, 320 (1954); N. S. Ham and K. Ruedenberg, *Ibid.* **25**, 1, 13 (1936).

[3] H. Zimmermann and N. Joop, *Zeitschr. für Elektrochem.* **65**, 66, 138 (1961).

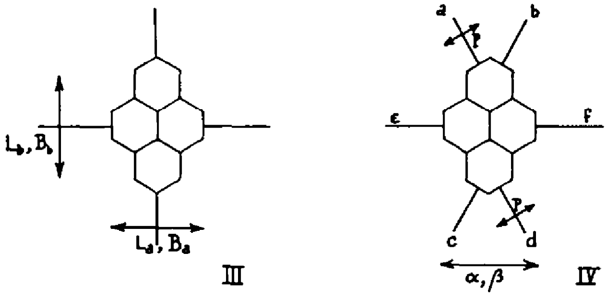
[4] H. Zimmermann and N. Joop, *Zeitschr. für Elektrochem.* **65**, 142 (1961).

[5] N. S. Ham and K. Ruedenberg, *J. Chem. Phys.* **25**, 1, 13 (1956).

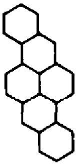
[6] R. Williams, *J. Chem. Phys.* **26**, 1186 (1957).



Polarization of absorption bands and annellation in acenes and perylenes.



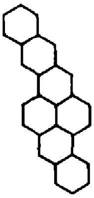
Polarization of absorption bands and annellation in pyrenes.



VII

λ_p = 4510 (B)

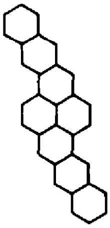
λ_β 3135 (B)



VIII

5160 (B)

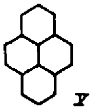
3260 (B)



IX

5760 (B)

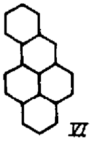
3530 (M)



V

λ_p = 3335 (A)

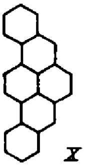
λ_β = 2720 (A)



VI

3845 (A)

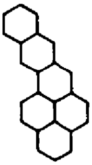
{2965 (A)
2655 (A)



X

λ_p = 3970 (B)

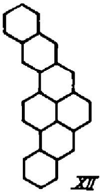
λ_β = {3320 (B)
2970 (B)



XI

4580 (B)

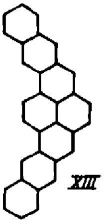
{3360 (B)
2970 (B)



XII

4380 (B)

{3620 (B)
3450 (B)
3280 (B)



XIII

4620 (B)

{4000 (B)
3640 (B)

Solvents in parenthesis : A = alcohol ; B = benzene ; M = methylnaphthalene.
Double bonds and aromatic sextets are used only if they have strict significance.

Symmetric annellation of 2 or 4 rings in the direction a and c (X and XIII) causes only half the red shift of the p-bands as that in the direction a and d.[7] This cannot be explained by a deviation of the annellation axes from the molecular axes which is the same for a, b, c and d. If an unequal number of rings is fused in the direction a and c, as in VI, XI and XII, then essentially the longest branch is responsible for the red shift of the p-bands, whilst the other rings produce minor effects as is the case in the phene series.[7] This is not so in the annellation direction a and d where each ring produces the same red shift (in $\sqrt{\text{Å}}$) of the p-bands (VI, VII, VIII and IX). It must be concluded therefore that the p-bands are polarized perpendicular to the annellation axes a and d in III and IV.

The β-bands show a regular shift towards the red which is a function of the number of rings. The symmetry has an influence on the structure of the β-bands. It is simple in the case of the centrosymmetric hydrocarbons (V, VII and IX). In the less symmetrical hydrocarbons (VI, X, XI, XII and XIII) consists of two sets of bands which follow each other closely.

The annellation axes e and f in IV are formally symmetric and should correspond to the polarization of the α- and β-bands or L_b- and B_b-bands along the long axis in III. This is also incorrect as shown by the following comparison:

In passing from pyrene (XIV) to 1·2-benzopyrene (XV) a red shift of the β-bands of +170 Å is recorded. A derivation of this β-band from the β'-band of pyrene at 2410 Å is excluded, because the difference of 480 Å would be bigger than the annellation effect in the acene or phene series which is impossible. The next shift to 1·2,6·7-dibenzopyrene (XVI) is a small violet shift of −30 Å which corresponds to an annellation to a fixed double bond.[7] The further red shift in going to naphthopyrene (XVII) (+320 Å) is about the same as for one ring in the acene or phene series. However, a violet shift (−20 Å) and no red shift is observed in passing to benzonaphthopyrene (XVIII) and further to dinaphthopyrene (XIX). Thus a strong asymmetric annellation effect[8] is recorded which cannot be explained except by the asymmetric interaction of the aromatic sextets, as indicated by the arrows.

The shifts of the α-bands (+45, −40, +355, −115, −120) follow the trend of the β-bands between XIV, XV, XVI, XVII, XVIII and XIX. The p-bands show violet shifts of −20 and −25 Å respectively between pyrene (XIV), benzopyrene (XV) and dibenzopyrene (XVI) respectively. There is a red shift of +160 Å in proceeding to naphthopyrene (XVII). This is accompanied by a change in the localization on the π-electrons in different positions as indicated by the points in XVI and XVII respectively. If this were not so the shift would be much bigger like the difference between the p-bands of triphenylene and 1·2,3·4-dibenzoanthracene which is 650 Å. It is obvious that a corresponding change must also take place in the polarization of the p-bands. The further shifts of the p-bands in passing from naphthopyrene (XVII) to benzonaphthopyrene (XVIII) and dinaphthopyrene (XIX) are small shifts, showing the asymmetric annellation effects. The complete spectra of this series are recorded in Fig. 1.

These become even more drastic in the next series. There is a shift toward the red

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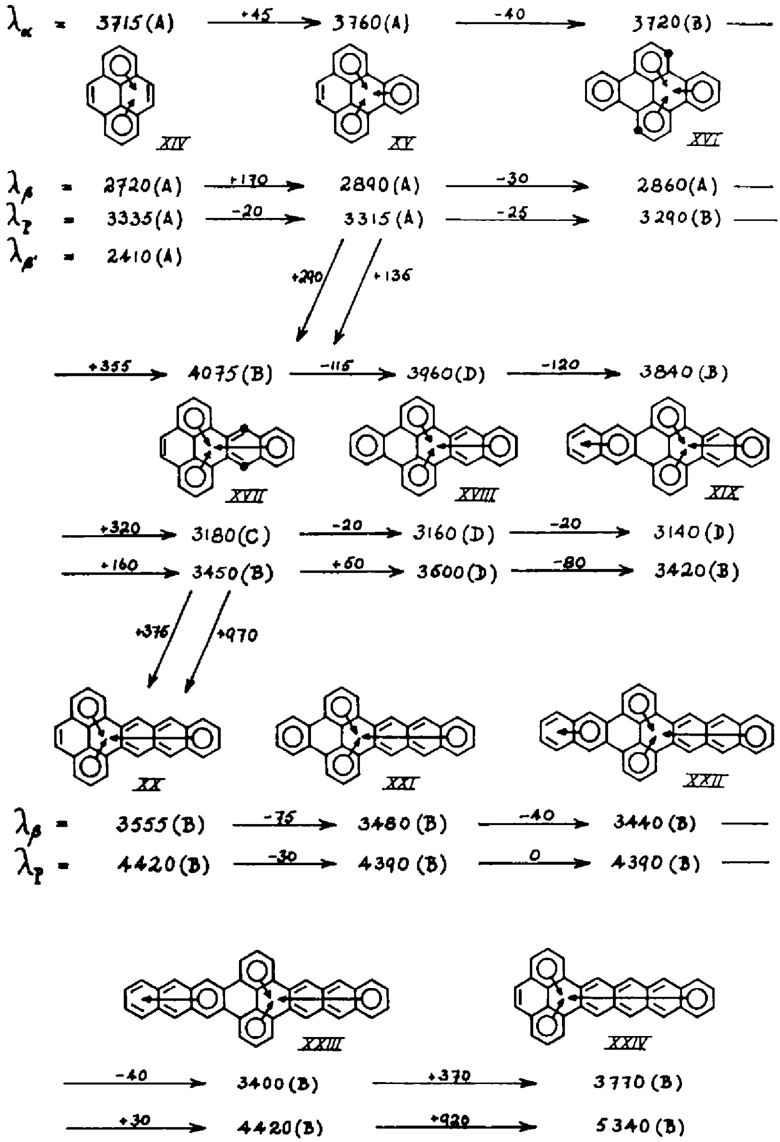
[7] E. Clar, *J. Chem. Soc.* 2013 (1949); E. Clar and M. Zander, *Tetrahedron* **19**, 521 (1963).

[8] E. Clar, *Tetrahedron* **5**, 98 (1959); **6**, 355 (1959); *Ibid.* E. Clar, C. T. Ironside and M. Zander, **6**, 358 (1959); E. Clar, *Ibid.* **9**, 202 (1960); **16**, 113 (1961); E. Clar, A. McCallum and R. A. Robertson, *Ibid.* **18**, 1471 (1962).



Solvents in parenthesis : A = alcohol ; B = benzene ; D = dioxan ;
C = cyclohexane.

of 375 Å in going from naphthopyrene (XVII) to dibenzopentacene (XX). However the annellation of one, two, or three rings in passing to the hydrocarbons (XXI, XXII and XXIII) produces small violet shifts of −75, −40 and −40 Å respectively. This demonstrates again the asymmetry of the annellation. The same applies to the shifts of the p-bands which are +970 Å between naphthopyrene (XVII) and dibenzopentacene (XX) and then only −30, 0 and +30 Å in going to XXI, XXII and XIII. The complete spectra of this series are shown in Figs. 2 and 3.

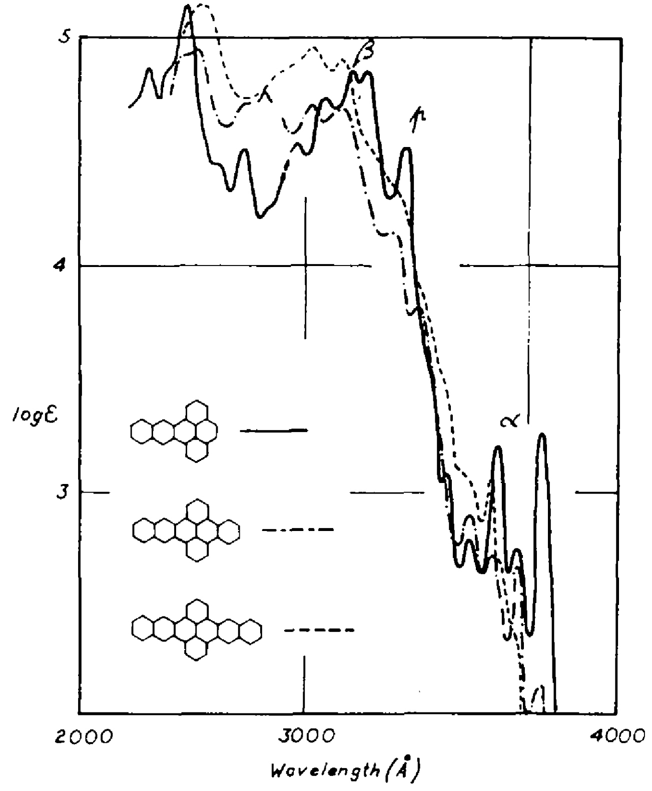


FIG. 1. Absorption max (Å) and log ε (in parentheses). Naphtho-(2′·3′:1·2)-pyrene in benzene, α: 4075 (3·24), 3960 (2·76), 3860 (3·21), 3750 (2·78), 3670 (3·09); p: 3450 (4·50) 3280 (4·80); in cyclohexane, β: 3180 (4·77), 3060 (4·64), β′: 2730 (4·44); β″: 2470 (5·06), 2300 (4·80).

1·2-Benzo-naphtho-(2″·3″:6·7)-pyrene in dioxane, α: 3960 (2·70), 3845 (2·74), 3750 (2·92); p: 3500 (3·81), 3400 (4·14); β: 3160 (4·71), 3020 (4·72); β′: 2820 (4·77), 2740 (4·72); β″: 2520 (4·96), 2460 (4·93).

Dinaphtho-(2′·3′:1·2); (2″·3″:6·7)-pyrene in benzene, α: 3840 (3·04); p: 3420 (4·30); β: 3160 (4·90), 3030 (4·96); in dioxane β: 3140 (4·90), 3010 (4·96); β′, 2530 (5·14).

A big shift of the acene type is also recorded in passing from dibenzopentacene (XX) to dibenzohexacene (XXIV) and it amounts to +920 Å for the p-bands and to 215 Å for the β-bands. It can be safely predicted that the linear annellation of one, two, three or four rings to dibenzohexacene (XXIV) will cause only minor shifts in comparison with the preceding ones. The absorption spectrum of dibenzohexacene given in Fig. 4.

These results show the impossibility of relating the absorption bands to the molecular axes and deriving a classification of bands in this way. The only reliable classification must be based on the annellation effects.

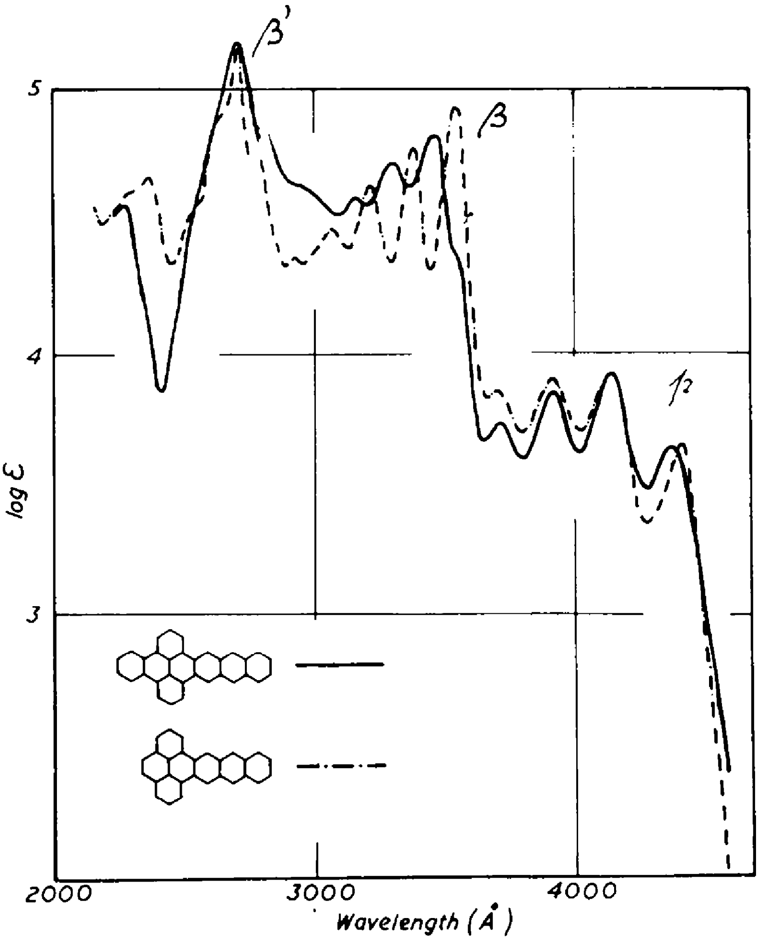
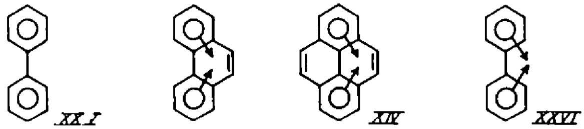


Fig. 2. Absorption max (Å) and log ε (in parentheses). 1·14, 4·5-Dibenzopentacene in benzene, p: 4420 (3·68), 4150 (3·94), 3930 (3·92), 3720 (3·83); β: 3555 (4·96), 3390 (4·80), 3225 (4·65), 3080 (4·48), 2950 (4·38); in cyclohexane, β': 2715 (5·19); 2380 (4·68). 5·6,15·16-Dibenzohexacene in benzene, p: 4390 (3·64), 4150 (3·91), 3930 (4·84), 3720 (3·72); β: 3480 (4·82), 3320 (4·71), 3170 (4·59); in cyclohexane, β': 2720 (5118), 2280 (4·57).

The electronic asymmetry is already inherent in the pyrene system. This can be shown if pyrene is derived in the following way from diphenyl (XXV):

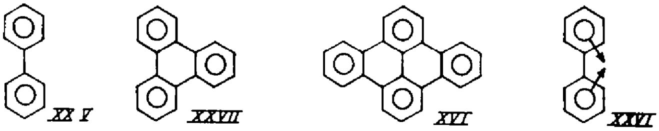
A strong asymmetric annellation effect is thus observed and the shift subtraction rule[8] gives the same imaginary diphenyl (XXVI) with an external quartet[9] independent of whether ethylene bridges or *o*-phenylene groups are fused to diphenyl.

[8] E. Clar, *Tetrahedron* **16**, 113 (1961).



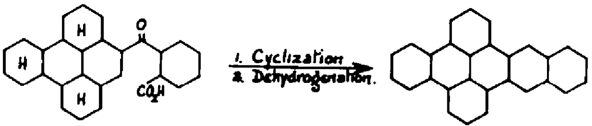
$$\lambda_\beta = 1980 \xrightarrow{+530} 2510 \xrightarrow{+210} 2720 \xrightarrow{-411} 2309\ \text{Å}$$

$$\sqrt{\lambda_\beta} = 44.50 \xrightarrow{+5\,60} 50.10 \xrightarrow{+2.06} 52.15 \xrightarrow{-4\,10} 48.05\ \sqrt{\text{Å}}$$

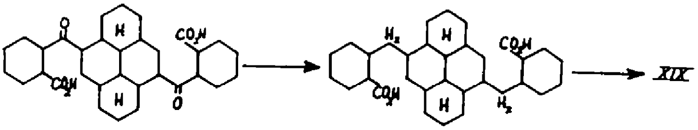


$$\lambda_\beta = 1980 \xrightarrow{+690} 2570 \xrightarrow{+280} 2850 \xrightarrow{-544} 2306\ \text{Å}$$

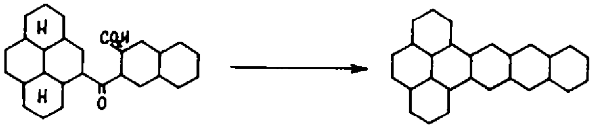
$$\sqrt{\lambda_\beta} = 44.50 \xrightarrow{+6\,20} 50.70 \xrightarrow{+2\,68} 53.38 \xrightarrow{-5\,36} 48.02\sqrt{\text{Å}}$$



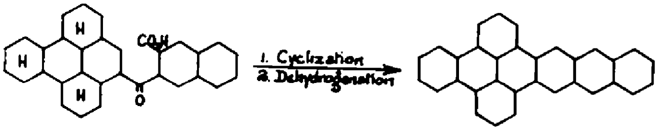
XXVIII XVIII



XXIX XXX



XXXI XX



XXXII XXI

The syntheses of the hydrocarbons

The dibenzopyrenes (VII, X[10] and XVI[11]), as well as the naphthopyrenes (XI[10] and XVII[12]) and the benzonaphthopyrenes (VIII,[13] XII and XVIII[14]) and the naphthopyrenes (IX and XIII),[15] have been described before.

A new synthesis of 1·2-benzonaphtho-(2″·3″ : 6·7)-pyrene (XVIII) was carried out starting from decahydro-1·2-benzpyrene which reacted with phthalic anhydride and aluminium chloride to form the keto acid (XXVIII). This was cyclized and dehydrated in a melt of sodium chloride and zinc chloride and the resulting hydrocarbon dehydrogenated with copper powder to benzonaphthopyrene (XVIII).

Hexahydropyrene condensed twofold with excess phthalic anhydride and aluminium chloride in tetrachloroethane to give the acid (XXIX). Reduction with sodium hydroxide and zinc dust yields the acid (XXX), which cyclized in a sodium chloride zinc chloride melt to dinaphthopyrene (XIX).

A condensation of hexahydropyrene with naphthalene-2·3-dicarboxylic anhydride gave the acid (XXXI) which in a melt of sodium chloride and zinc chloride yielded dibenzopentacene (XX).

Decahydro-1·2-benzpyrene reacts with naphthalene-2·3-dicarboxylic anhydride and aluminium chloride to give the acid (XXXII). Cyclization followed by dehydrogenation with copper powder leads to dibenzohexacene (XXI).

The keto acid (XXXI) was reduced to the lactone (XXXIII) with zinc dust in sodium hydroxide solution. The condensation with phthalic anhydride and aluminium chloride gave the acid (XXXIV) which was reduced to the dicarboxylic acid (XXXV). Its cyclization in a melt of sodium chloride in zinc chloride yielded dibenzoheptacene (XXII).

Prolonged reduction of the keto acid (XXXI) with zinc dust in sodium hydroxide solution gave the acid (XXXVI). This reacted again with naphthalene-2·3-dicarboxylic anhydride and aluminium chloride to form the acid (XXXVII). Another reduction of the carbonyl to a methylene group followed by a cyclization in a sodium chloride–zinc chloride melt yielded dibenzooctacene (XXIII).

A condensation of hexahydropyrene with benzophenone-tricarboxylic acid anhydride and aluminium chloride gave the isophthalic acid (XXXVIII) or the corresponding terephthalic acid. This was reduced to a lactone-acid which cyclised in a melt of sodium chloride, zinc chloride and zinc dust to dibenzohexacene (XXIV).

EXPERIMENTAL*

6-(o-*Carboxybenzoyl*)-*decahydro*-1,2-*benzopyrene* (XXVIII). Decahydro-1,2-benzopyrene† (4·4 g) and phthalic anhydride (2·2 g) were dissolved in benzene (60 ml) and aluminium chloride (16 g) added. The colour of the mixture was deep claret. After agitation for 1 hr at 40°, the mixture was decomposed with dil hydrochloric acid. The solid material was filtered from the benzene and aqueous

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* All m.p. are uncorrected and were taken in evacuated capillaries.

† Prepared from ketodecahydrobenzopyrene (G. W. Coolz and C. L. Hewett, *J. Chem. Soc.* 401 (1933) by Chemmenion reduction formed colourless rods, m.p. 196–197°. (Found: C, 91·4; H, 8·8. $C_{20}H_{22}$ requires: C, 91·6; H, 8·45%).

[10] E. Clar, *Ber. Dscht. Chem. Ges.* **69**, 1671 (1936).

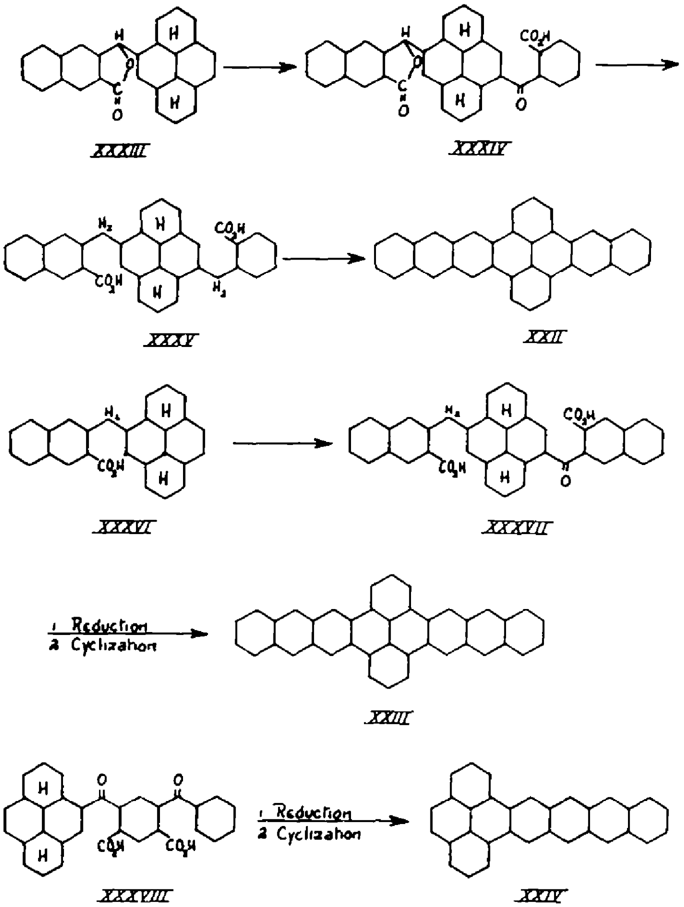
[11] E. Clar, *Ber. Dscht. Chem. Ges.* **76**, 609 (1943).

[12] E. Clar, *J. Chem. Soc.* 2168 (1949).

[13] J. F. Grove, *J. Chem. Soc.* 483 (1953).

[14] E. Clar and M. Zander, *Tetrahedron* **19**, 521 (1963).

[15] E. Clar, *J. Chem. Soc.* 2013 (1949).



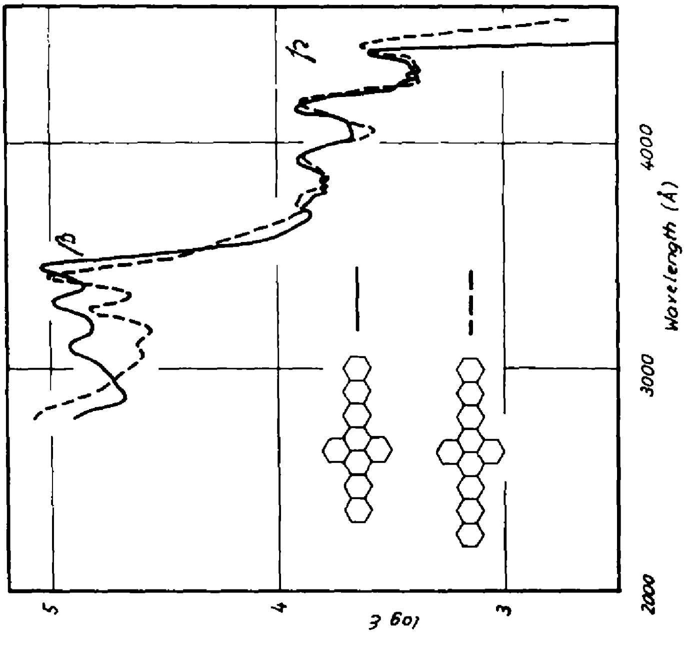


FIG. 3. Absorption max (Å) and log ε (in parentheses). 6·7,16·17-Dibenzoheptacene in benzene, p: 4390 (3·60), 4150 (3·92), 3920 (3·91), 3710 (3·88); β: 3440 (5·05), 3290 (5·00), 3090 (4·92), 7·8,17·18-Dibenzooctacene in benzene, p: 4420 (3·63), 4280 (3·42), 4160 (3·90), 3920 (3·88), 3720 (3·91); β: 3400 (5·00), 3260 (4·82), 3110 (4·62); in dioxane, β′: 2780 (5·30).

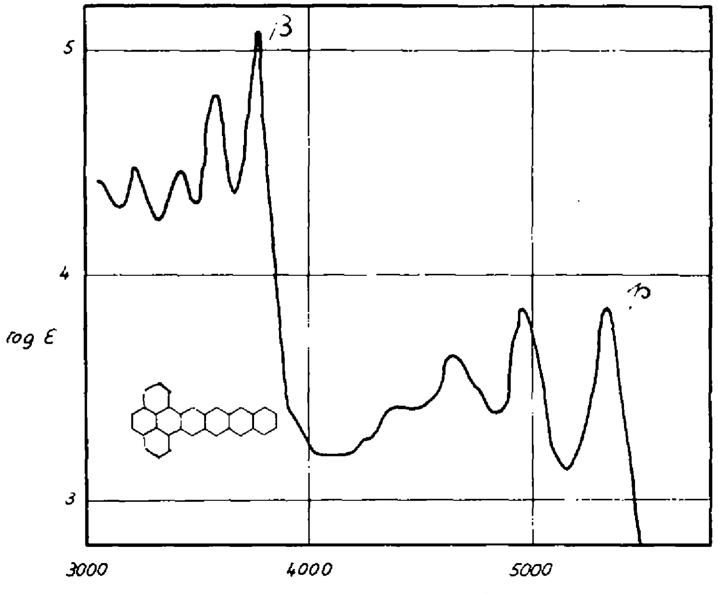


FIG. 4. Absorption max (Å) and log ε (in parentheses). 1·16,4·5-Dibenzohexacene in benzene, p: 5340 (3·85), 4960 (3·85), 4650 (3·65), 4400 (3·42)-4240 (3·27); β: 3770 (5·08), 3580 (4·60), 3430 (4·46); 3220 (4·48); in cyclo, hexane, β′: 2900 (5·44), 2610 (4·72), 2540 (4·78), 2500 (4·56).

layers, dissolved in dilute ammonia, filtered and the hot solution precipitated with hydrochloric acid. The precipitate (4·1 g) was recrystallized from benzene and formed small yellow blades, m.p. 237–238° which dissolved in conc sulphuric acid to give a red-violet solution which changed to red brown on standing (Found: C, 82·1; H, 6·5. $C_{28}H_{26}O_3$ requires: C, 81·9; H, 6·4%).

1·2-*Benzonaphtho*-(2″·3″:6·7)-*pyrene* (XVIII). The above keto acid (1 g) was ground with sodium chloride (1 g) and zinc chloride (5 g) and heated at 310° for 2 min. The dark mixture was decomposed with water and hydrochloric acid, filtered and washed with water and then with ammonia. The residue was sublimed at 350° and 10^{-2} mm. The oily sublimate was dissolved in benzene and the solution extracted quickly and repeatedly with conc sulphuric acid in order to remove impurities. The solution was then washed with water and with ammonia and concentrated. The hydrocarbon crystallized in long colourless needles (27 mg), m.p. 316–317° which do not dissolve in conc sulphuric acid. It is identical with the benzonaphthopyrene obtained by another synthesis[16] (Found: C, 95·1; H, 4·5. $C_{28}H_{16}$ requires: C, 95·4; H, 4·6%).

1·6-*Di*(o-*carboxybenzoyl*)-3·4·5·8·9·10-*hexahydropyrene* (XXIX). Hexahydropyrene (11 g) was added to a mixture of phthalic anhydride (62 g), and aluminium chloride (140 g) in tetrachloroethane (150 ml) at 60°. The bright violet mixture was shaken for 30 min at this temp. The decomposition with hydrochloric acid was followed by a steam distillation and the residue extracted with warm ammonia. The acid was fractionally precipitated from the hot solution first with acetic acid then with hydrochloric acid, the later fraction giving the purer compound. Crystallization from acetic acid yielded needles, m.p. 292°, which dissolved in conc sulphuric acid to give a green solution which turned to blue on standing (Found: C, 76·3; H, 5·3. $C_{32}H_{24}O_6$ requires: C, 76·2; H, 4·8%).

1·6-*Di*(o-*carboxybenzyl*)-3·4·5·8·9·10-*hexahydropyrene* (XXX). The above acid (1·5 g) in 5% sodium hydroxide solution was boiled with excess zinc dust and a trace of copper sulphate for 3 days. After filtration the solution was acidified with hydrochloric acid. The precipitate which was very sparingly soluble in organic solvents was purified with charcoal in alkaline solution and reprecipitated. It formed a white powder, m.p. 303–305°, which dissolved in conc sulphuric acid violet changing to red on standing (Found: C, 80·2; H, 6·0. $C_{32}H_{28}O_4$ requires: C, 80·6; H, 5·9%).

Dinaphtho-(2′·3′:1·2); (2″·3″:6·7)-*pyrene* (XIX). The acid (XXX; 1 g), zinc chloride (9 g) and sodium chloride (1·8 g) were heated under stirring to 310°. The hydrocarbon separated from the inorganic layer. The melt was dissolved in dil hydrochloric acid and the powdered residue washed with water and ammonia. The residue was sublimed in a vacuum and recrystallized from 1-methylnaphthalene. It formed long pale yellow needles which became colourless when chromatographed in trichlorobenzene. The hydrocarbon melts at 428–429° and does not dissolve in conc sulphuric acid (Found: C, 95·3; H, 4·8. $C_{32}H_{18}$ requires: C, 95·5; H, 4·5%).

1-(3-*Carboxy-2′-naphthoyl*)-3·4·5·8·9·10-*hexahydropyrene* (XXXI). A powdered mixture of naphthalene-2·3-carboxylic anhydride (17·6 g) and aluminium chloride (36 g) was added to a suspension of hexahydropyrene (20 g) in tetrachloroethane (80 ml). The violet mixture was shaken and the temp. rose to 30°. The reaction was completed by a short heating on a water bath at 40° for 15 min. The mixture was decomposed with dil hydrochloric acid, the organic layer washed with hot water and then with dil ammonia. The main portion of the acid (XXXI) crystallized as ammonium salt and only a smaller portion was in the alkaline solution from which it can be precipitated with hydrochloric acid. The insoluble ammonium salt was treated with strong sodium hydroxide solution and then diluted and filtered. The acid was precipitated with hydrochloric acid, yield 28·5 g. Crystallization from xylene gave colourless needles, m.p. 267°, which dissolved in conc sulphuric acid to give a yellow brown solution which changed through violet, black and turquoise to blue (Found: C, 82·9; H, 5·7. $C_{28}H_{22}O_3$ requires: C 82·9; H, 5·5%).

1·14,4·5-*Dibenzopentacene* (XX). The above keto-acid (1 g), zinc chloride (5 g) and sodium chloride (1 g) were heated to 320° for 2 min. The melt was dissolved in water and dil acetic acid and the residue washed with dil ammonia. Extraction with xylene and concentration of the extract gave the hydrocarbon (275 mg) which was sublimed with copper powder at 300° in vacuum under a current of CO_2. Recrystallization from benzene yielded golden yellow plates, m.p. 285°, which dissolved in conc sulphuric acid to give a violet solution which changed through red to olive green (Found: C, 95·6; H, 4·6. $C_{28}H_{16}$ requires: C, 95·4; H, 4·6%).

6-(3′-*carboxy-2′-naphthoyl*)-*decahydro-*1·2-*benzopyrene* (XXXII). Decahydro-1·2-benzopyrene (3·9 g) and naphthalene-2·3-dicarboxylic anhydride (3 g) were suspended in benzene and aluminium chloride (12 g) added. The violet red mixture was stirred at 70° for 1½ hr and then decomposed with dil hydrochloric acid and the benzene distilled off. The remaining yellow resin was dissolved in dil ammonia, the solution filtered and then acidified with hydrochloric acid. The precipitate (4·5 g) crystallized from acetic acid as small yellow leaflets, m.p. 240–242°, and dissolved in conc sulphuric acid to give a violet red solution. (Found: C, 84·2; H, 6·2. $C_{32}H_{28}O_3$ requires: C, 83·5; H, 6·1%).

5·6, 15·16-*Dibenzohexacene* (XXI). The above keto-acid (1 g) was ground with sodium chloride (1 g) and zinc chloride (5 g) and heated at 320° for 3 min, the colour of the melt becoming yellow brown. The mixture was decomposed with dil acetic acid and the resulting dark brown solid ground with copper powder and sublimed at 350° and 10^{-3} mm. The yellow sublimate (0·4 g) crystallized from trichlorobenzene in orange yellow needles, m.p. 372–373°, which dissolved slowly in conc sulphuric acid to give a brown solution which changed to green on standing (Found: C, 95·6; H, 4·4. $C_{32}H_{18}$ requires: C, 95·5; H, 4·5%).

1-(3′-*Carboxy-2′-naphthylhydroxymethyl*)-3·4·5·8·9·10-*hexahydropyrene* (XXXIII). The keto-acid (XXXI; 21·5 g), zinc dust (20 g), a trace of copper sulphate, sodium hydroxide (20 g) and water (2 l) were refluxed for 24 hr. Then zinc dust (20 g), water (500 ml) and a trace of copper sulphate were added and refluxed for another 4 days. A further portion of zinc dust (5 g) and water (500 ml) was added and boiled one day. A precipitate was formed during the reduction which did not dissolve again. This was filtered off together with zinc and zinc hydroxide, washed and treated with hydrochloric acid. The insoluble product (13·5 g) was recrystallized from acetic acid and then from xylene. The lactone formed colourless crystals, m.p. 258–261°, which are sublimable and dissolved in conc sulphuric acid to give a dark red solution (Found: C, 86·1; H, 5·9. $C_{28}H_{24}O_2$ requires: C, 86·1; H, 5·7%).

1-(o-*Carboxybenzoyl*)-6-(3′-*carboxy-2′-naphthylhydroxymethyl*)-3·4·5·8·9·10-*hexahydropyrene* (XXXIV). A powdered mixture of phthalic anhydride (1·9 g) and aluminium chloride (7·5 g) was added to a suspension of the above lactone (5·0 g) and tetrachloroethane (20 ml). The temp rose to 30° and the green mixture was shaken for 15 min. When the temperature had fallen to 20° the mixture was decomposed with dil hydrochloric acid, more tetrachloroethane added and the organic layer separated and washed with water and then extracted with ammonia. The separated alkaline layer was acidified hot with hydrochloric acid. The resulting acid (2·5 g) was recrystallized from nitrobenzene and then reprecipitated from ammonia. It had m.p. 305–315° (dec), and dissolved in conc sulphuric acid, red violet turning soon to dark green (Found: C, 79·8; H, 5·6. $C_{36}H_{26}O_5$ requires: C, 80·3; H, 4·9%).

1-(o-*Carboxybenzyl*)-6-(3′-*carboxy*-2′-*naphthylmethyl*)-3·4·5·8·9·10-*pyrene* (XXXV). The above lactone-acid (1·5 g) was reduced with copper activated zinc dust (5 g), sodium hydroxide (5 g) and water (150 ml) by boiling under reflux for 24 hr. Then zinc dust (5 g), sodium hydroxide (5 g) and water (50 ml) were added and refluxed for 4 days. The alkaline solution was filtered off and acidified with hydrochloric acid. The acid (1·5 g) was reprecipitated from ammonia and then extracted with acetic acid. This procedure was repeated with the insoluble part. The acid, m.p. 320–330° (dec), dissolved in conc sulphuric slowly with a brown red colour (Found: C, 81·9; H, 5·8. $C_{36}H_{30}O_4$ requires: C, 82·1; H. 5·7%).

6·7,16·17-*Dibenzoheptacene* (XXII). The above acid (1 g), zinc dust (1 g), sodium chloride (2 g) and zinc chloride (10 g) were melted and stirred together at 308–320° for 3 min. The brown melt was dissolved in dil acetic acid, then with hydrochloric acid, and the residue washed with water and ammonia. Sublimation in a vacuum yielded orange needles, which were washed with hot xylene and then crystallized from trichlorobenzene and finally resublimed in vacuum. They had m.p. 407° and dissolved in conc sulphuric acid, first violet, then becoming brown on standing (Found: C, 95·4; H, 4·5. $C_{36}H_{25}$ requires: C, 95·6; H, 4·5%).

1-(2′-*Carboxy*-3′-*naphthylmethyl*)-3·4·5·8·9·10-*hexa-hydropyrene* (XXXVI). The keto-acid (14 g), copper activated zinc dust (20 g), sodium hydroxide (20 g) and water (2000 ml) were refluxed for 24 hr. Then zinc dust (20 g), sodium hydroxide (5 g) and water (200 ml) were added and boiled for another 24 hr and zinc dust (10 g) added. After another 2 days refluxing the alkaline solution was filtered and acidified with hydrochloric acid. The crude acid was 3 times recrystallized from acetic acid and sublimed in a vacuum. The colourless needles, m.p. 272–274°, dissolved in conc sulphuric acid slowly with a pink colour (Found: C, 85·5; H, 6·4. $C_{28}H_{24}O_2$ requires: C, 85·7; H, 6·2%).

1-(2′-*Carboxy*-3′-*naphthyl*)-6-(2″-*carboxy*-2″-*naphthyl*-*methyl*)-3·4·5·8·9·10-*hexahydropyrene* (XXXVII). The acid (XXXVI; 5 g) was suspended in tetrachloroethane (20 ml) and a powdered mixture of 2·3-naphthalenedicarboxylic anhydride (2·5 g) and aluminium chloride (8·5 g) added. The dark red brown mixture was shaken for 15 min. The temp rose to 30°. The mixture was decomposed with dil hydrochloric acid and chloroform (1800 ml) added. The precipitate (2 g) was filtered off and washed with water. It was purified by extraction with acetic acid and reprecipitated from the solution in ammonia. The colourless product had m.p. 325° (dec) and dissolved in conc sulphuric acid with a red colour which changed to greenish brown on standing (Found: C, 80·8; H, 5·5. $C_{40}H_{30}O_5$ requires: C, 81·3; H, 5·1%).

1·6-*Di*-(3′-*carboxy*-2′-*naphthylmethyl*)-3·4·5·8·9·10-*hexahydropyrene*. The above acid (2 g) was reduced with activated zinc dust (4 g), sodium hydroxide (2 g) and water (200 ml), further portions of zinc dust (2 g) and sodium hydroxide (2 g) and water (200 ml) being added after 24 hr. After refluxing for 4 days, filtering the alkaline solution and acidification with hydrochloric acid, the crude acid (2 g) was purified by reprecipitation from the ammonium salt. It melted at 355° (dec) and dissolved in conc sulphuric acid slowly to give a brown red solution (Found: C, 83·9; H, 5·9. $C_{30}H_{32}O_4$ requires: C, 83·3; H, 5·6%).

7·8,17·18-*Dibenzo-octacene* (XXIII). The above acid (1 g), sodium chloride (2 g), zinc dust (1 g) and zinc chloride (10 g) were powdered together and heated under stirring to 310–320° for 3 min. The red melt was dissolved first in acetic acid and then in hydrochloric acid. The residue, after washing with water and ammonia, was sublimed in a vacuum. The orange sublimate yielded orange needles, m.p. 560°, from trichlorobenzene which were resublimed. These became green in conc sulphuric acid and dissolved slowly with a brown colour (Found: C, 95·6; H, 4·5. $C_{40}H_{20}$ requires: C, 95·6; H, 4·4%).

6-(*Hexahydro*-1′-*pyrenoyl*)-4-*benzoyl-isophthalic acid* (XXXVIII). A powdered mixture of benzophenone-tricarboxylic-acid-anhydride (50 g) and aluminium chloride (135 g) was added to a suspension of hexahydropyrene (40 g) in tetrachloroethane (200 ml). The mixture was heated to 80°, became violet and hydrochloric acid was evolved. The temp was reduced to 40° within 25 min. The decomposition with hydrochloric acid gave an organic layer which was washed with water and then extracted with dil ammonia. The acidification of the alkaline solution yielded the crude acid (43 g). This was crystallized from acetic acid and formed colourless crystals, m.p. 322–324° (dec) which dissolved in conc sulphuric acid with a blue-violet colour which soon changed to dark red on standing (Found: C, 75·7; H, 4·8. $C_{32}H_{24}O_6$ requires: C, 76·2; H, 4·8%).

6-*(Hexahydro-1′-pyrenylhydroxymethyl)-4-benzylisophthalic* acid lactone. The reduction of the above acid (10 g) was carried out by refluxing it with zinc dust (20 g), sodium hydroxide (20 g) and water (370 ml) for 4 days. The zinc dust and sodium hydroxide were added in portions. The alkaline solution was filtered and acidified with hydrochloric acid. The crystallization of the crude product (9·5 g) gave colourless crystals, m.p. 275° (dec) which dissolved in conc sulphuric acid slowly with a green colour (Found: C, 81·0; H, 5·4. $C_{32}H_{26}O_4$ requires: C, 81·0; H, 5·5%).

1·16,4·5-*Dibenzohexacene* (XXIV). The above acid (15 g), zinc dust (15 g), sodium chloride (15 g) and zinc chloride (75 g) were powdered together and under stirring heated to 310–320° for 4 min. The melt was dissolved in dil acetic acid and then in hydrochloric acid. The product was washed with water and ammonia and sublimed in vacuum under CO_2. The sublimate was dissolved in boiling xylene, the solution concentrated and the crystallized hydrocarbon sublimed with copper powder in vacuum. All operations must be carried out under CO_2 or in vacuum. The violet needles, m.p. 344–345° (dec) dissolved in conc sulphuric acid first with a green colour changing to violet and then brown on standing (Found: C, 95·3; H, 4·5. $C_{32}H_{16}$ requires: C, 95·5; H, 4·5%).

Acknowledgment—One of us (J. F. G-V.) wishes to express his gratitude for a Ciba Scholarship.