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THE ELECTRONIC INTERACTION IN BENZOLOGUES OF PYRENE

E. CLAR, B. A. MCANDREW and J. F. STEPHEN
Department of Chemistry, The University, Glasgow, W.2

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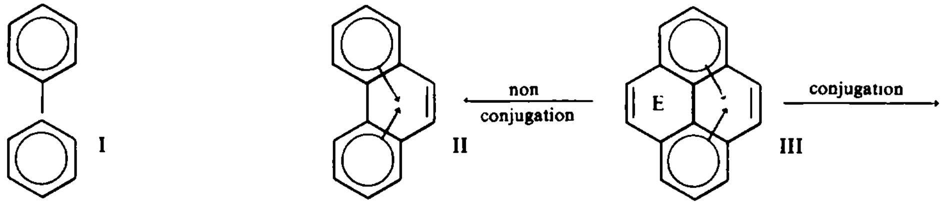
Abstract—6-Methyl-1,2:3,4:9,10-tribenzopyrene (VIII, R = CH_3), 1,2:3,4:6,7:9,10-tetrabenzopyrene (IX), 3,4:9,10-dibenzo-naphtho(2′:3′:6:7)pyrene (X), 3,4:9,10-dibenzo-naphtho(2′:3′,1:2)pyrene (XI), 3,4:6,7:9,10-tribenzo-naphtho(2′:3′.1:2)pyrene (XII), 5:6-benzopicene (XV), naphtho(2′:3′,11.12)picene, 1,2:3,4-dibenzotetracene (XXI) were synthesized. The UV spectra of the benzologues of pyrene can be related to three different types of aromatic conjugation: the picene, pentaphene and 1,2-benzotetraphene type. The first two types may appear together in the same spectrum, indicating that the independent electronic arrangements are stable during the time of light absorption. Annellation can stabilize the predominance of one type.

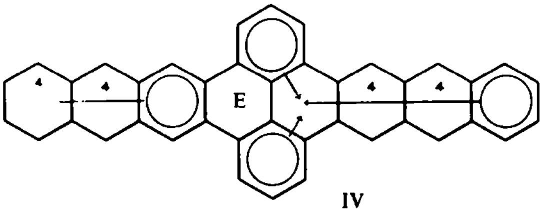
THE formal symmetrical fusion of two ethylene bridges to diphenyl (I) produces two quite different effects in the UV spectra. The formation of the first ring leading to phenanthrene (II) shifts the most intense band of the spectrum, the β-band, 530 Å towards the red, whilst the second annellation giving pyrene (III) causes a shift of only 210 Å.

This asymmetric annellation effect was explained by the formation of an induced sextet when passing from diphenyl to phenanthrene. This induced sextet is composed of 2 pairs of π-electrons (symbolized by arrows) migrating from the highest level of the two inherent sextets (symbolized by circles) and the two π-electrons of the double bond in the central ring. Due to the fact that only two π-electrons can migrate from an inherent sextet to the neighbouring ring, this process cannot be repeated a second time in passing to pyrene (III) and must produce an empty ring "E". This results in the observed electronic asymmetry which must exist during the time of light absorption and which is retained if further rings are annellated as indicated by the arrows in III. Only one annellation direction marked "conjugation" produces aromatic delocalisation and the corresponding shift towards the red, whilst the annellation direction marked "non-conjugation" is ineffective. The latter causes only very small shifts, because of the separation by the empty ring "E".

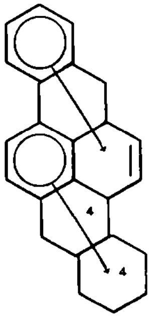
Clear evidence for the existence of empty rings is provided by a comparison of dibenzophenalene and dibenzopyrene as shown by the UV spectra in Fig 1. Although the classical structure of the two hydrocarbons is quite different, the position of the three types of band (α, β and p) is almost the same. Dibenzophenalene has a CH_2 group (proved by the NMR signal at 447 Hz) which must belong to a classical empty ring "E". This being the case an empty ring "E" must also be assumed for dibenzopyrene, because the aromatic conjugation is the same. In both cases this is the phenylphenanthrene complex marked with shadow. The additional ring in dibenzpyrene is ineffective for the conjugation, because only two annellation branches in triphenylene and its lin.benzologues can be in aromatic conjugation.[1]



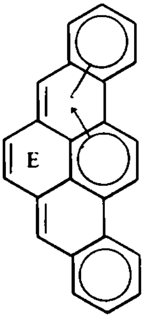
$\lambda_\beta = 1980 \xrightarrow{+530} 2510 \xrightarrow{+210} 2720$ Å



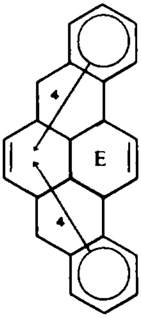
IV



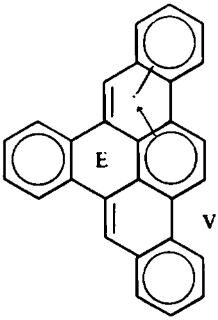
VI



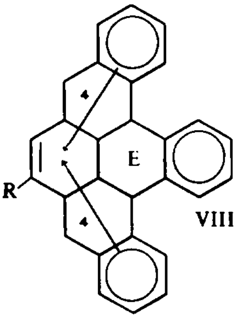
V



Va



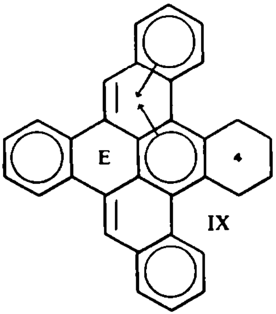
VII



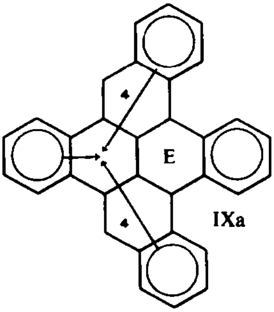
VIII

$\lambda_\beta =$ $3320 \xrightarrow{+55} 3375$ Å

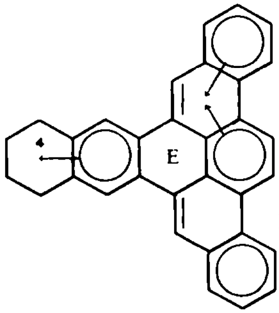
$\lambda_\beta = 2970 \xrightarrow{-5} 2965$



IX



IXa



X

$\lambda_\beta =$

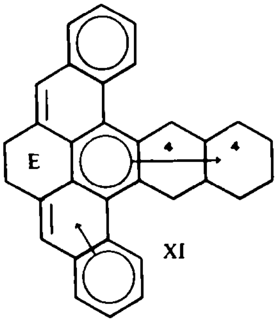
$\lambda_{\beta'} =$ 2920

3360

3470 Å

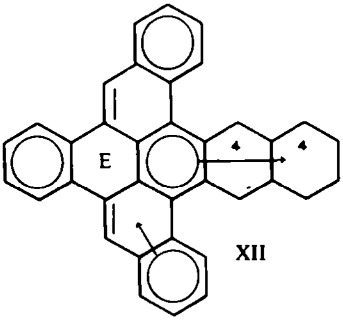
2980 Å

(continued)



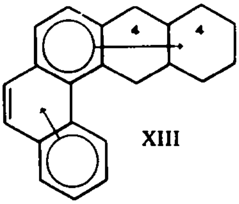
XI

λ_β = 3120



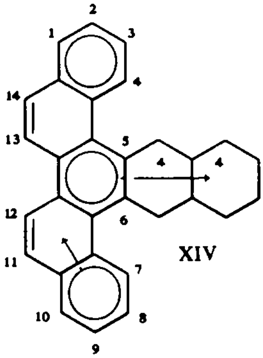
XII

3020

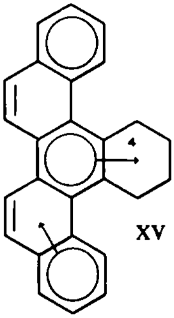


XIII

3080 Å

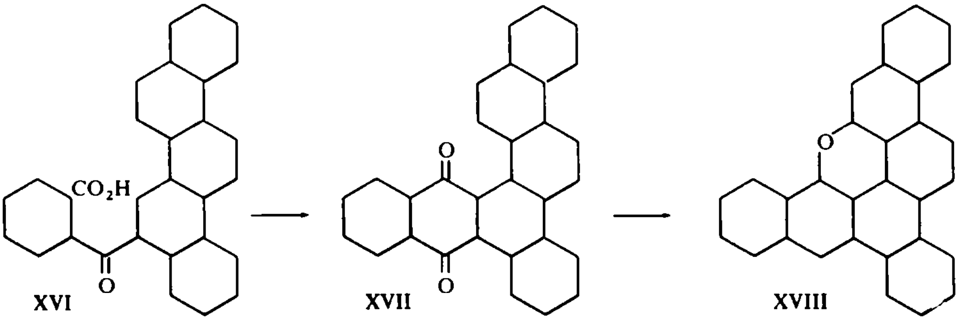


XIV



XV

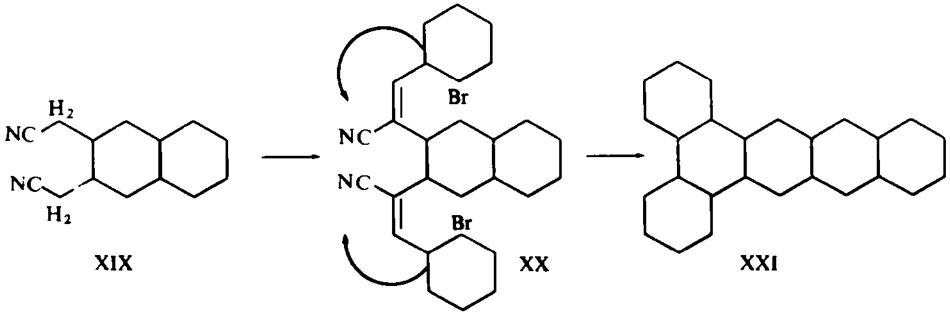
The synthesis of the hydrocarbons



XVI

XVII

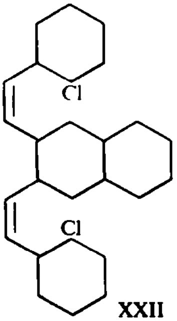
XVIII



XIX

XX

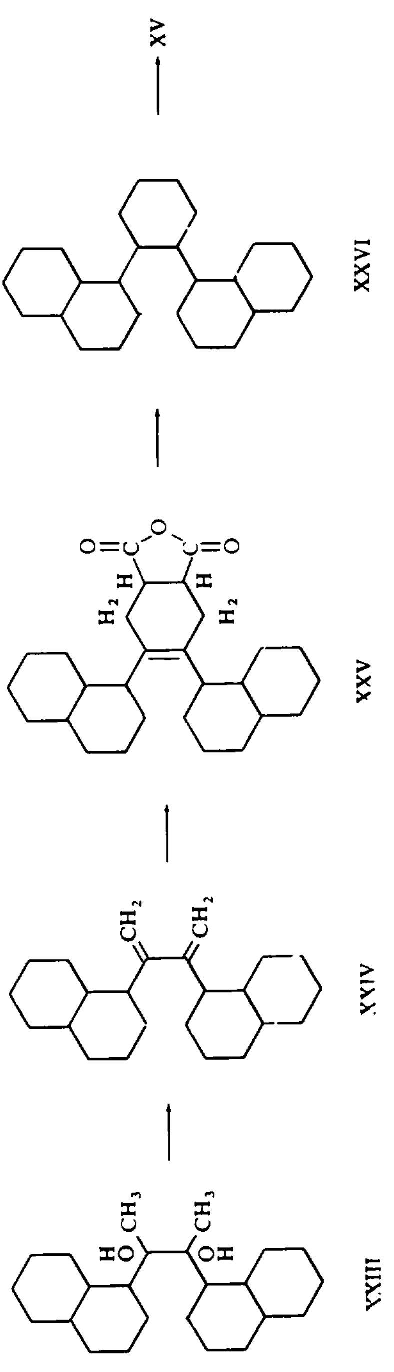
XXI

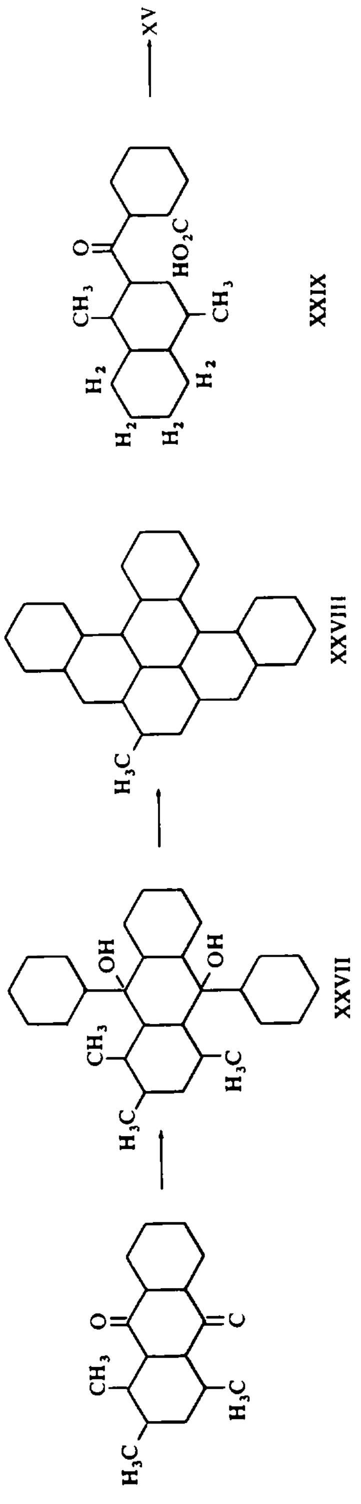


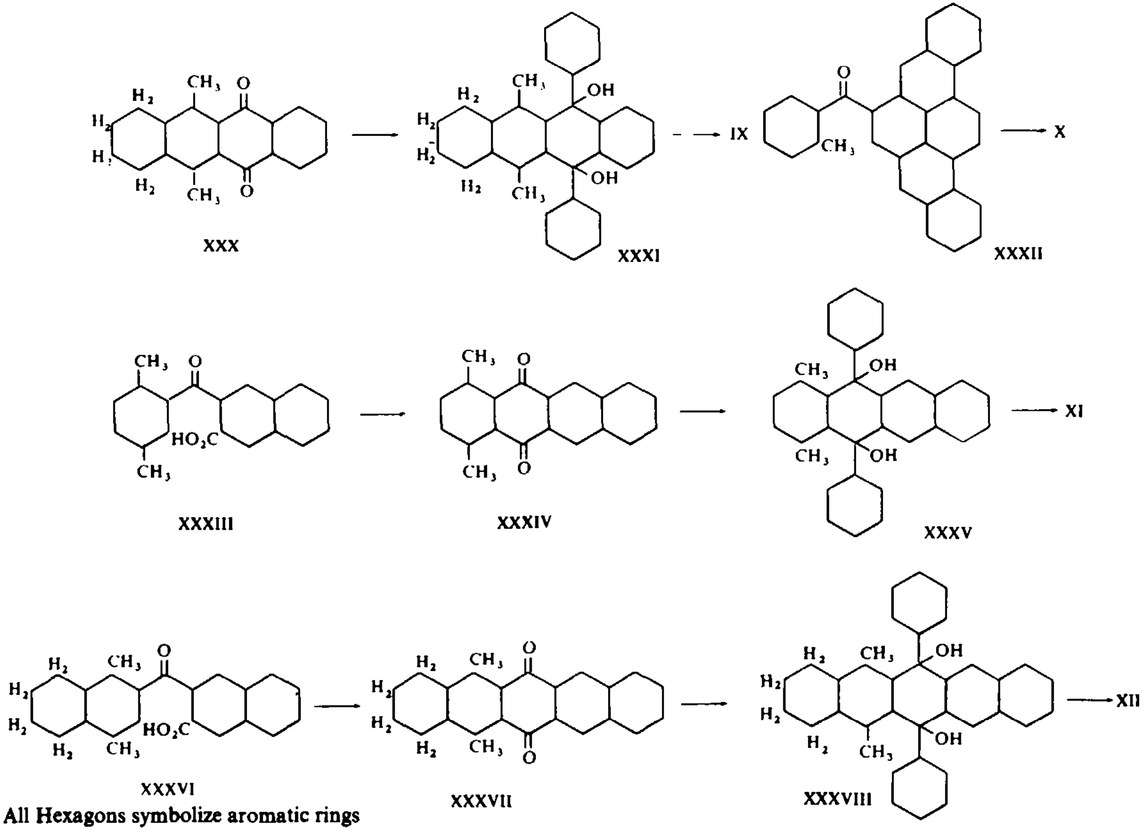
XXII

All Hexagons symbolize aromatic rings

(continued)


XXIII
XXIV
XXV
XXVI
XV


XXVII
XXVIII
XXIX
XV



All Hexagons symbolize aromatic rings

Note for the presentation of the formulae: Robinson's aromatic sextet (the circle) symbolizes strictly 6 π-electrons. An arrow stands for 2 π-electrons which can migrate from the sextet to the neighbouring rings. A double bond means a fixed double bond. Since this double bond fixation has been proved and it has been shown that there is only *one* true double bond in any benzenoid ring (E. Clar, *Tetrahedron* **9**, 202 (1960; E. Clar, A. McCallum and R. A. Robertson, *Ibid.* **18**, 1471 (1962); E. Clar and A. Mullen, *Ibid.* **24**, 6719 (1968); E. Clar, A. Mullen and Ü. Sanigök, *Ibid.* **25**, 5639 (1969); E. Clar and C. C. Mackay, *Tetrahedron Letters* No. 11,871 (1970)) we consider it unjustified and inconsistent to present a benzenoid ring with 3 or 2 double bonds resp. Therefore we are marking a ring with "4" if it contains 4 π-electrons localized within this ring. For the formulation of syntheses the hexagon alone is sufficient to symbolize an aromatic ring.

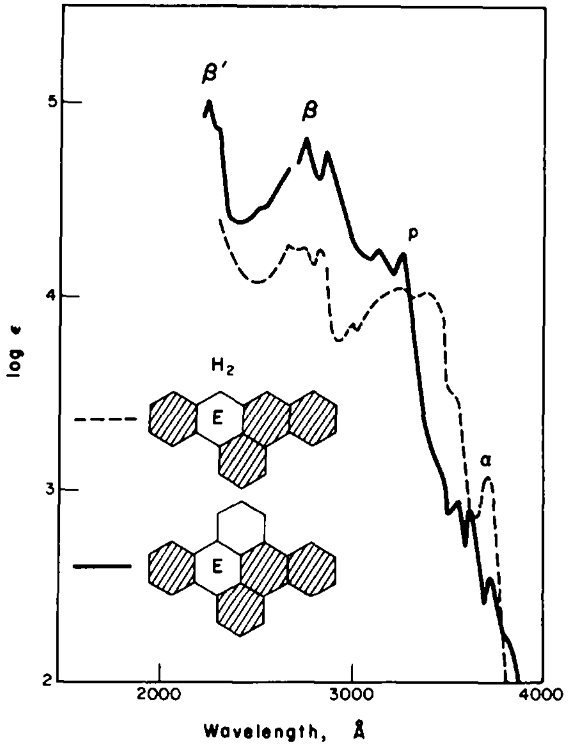


Fig 1. Absorption spectra with max (Å) and log ε in parentheses.

-------- 2,3:7,8-Dibenzophenalene in ethanol: α, 3720 (3·05); *p*, 3390 (4·02), 3270 (4·05), 3020 (3·86); β, 2850 (4·24), 2760 (4·26), 2690 (4·26).

———— 1,2:6,7-Dibenzopyrene in benzene: α, 3720 (2·56); 3620 (2·90), 3550 (2·96); *p*, 3280 (4·24), 3150 (4·26); β, 2880 (4·78), 2780 (4·86), in heptane: β', 2250 (5·04). The common phenyl phenanthrene complex is marked by shadow.

The asymmetry produces drastic deviations from the regular shifts observed in the acene series. For instance the fusion of three rings to each direction in pyrene (III) leads to 7,8:17,18-dibenzoctacene (IV) which is a benzologue of octacene just in name, in fact its UV spectrum brings the orange, very stable hydrocarbon into the tetracene class. As a 1,2:3,4-dibenzotetracene derivative it is connected to the three other rings by single bonds of the ring "E" and has about half the conjugated system of an octacene.[2]

The inherent electronic asymmetry of pyrene must lead to two different conjugations in dibenzopyrene V and Va. The first one, as indicated by the arrows, is derived from picene by fusing an ethylene bridge to it and forming the ring "E". The corresponding shift of the β-bands (2870 → 2970 Å) is 100 Å and accounts only for the formation of the ring "E". It amounts to less than the shift (210 Å) in going from phenanthrene (II) to pyrene (III).

The absorption spectrum (Fig 2) of dibenzpyrene (V) shows also another β-band at 3320 Å. This is derived from pentaphene by fusing an ethylene bridge to it. The small shift (160 Å) in passing from pentaphene (3160 Å) to dibenzpyrene (Va) (3320 Å) is also

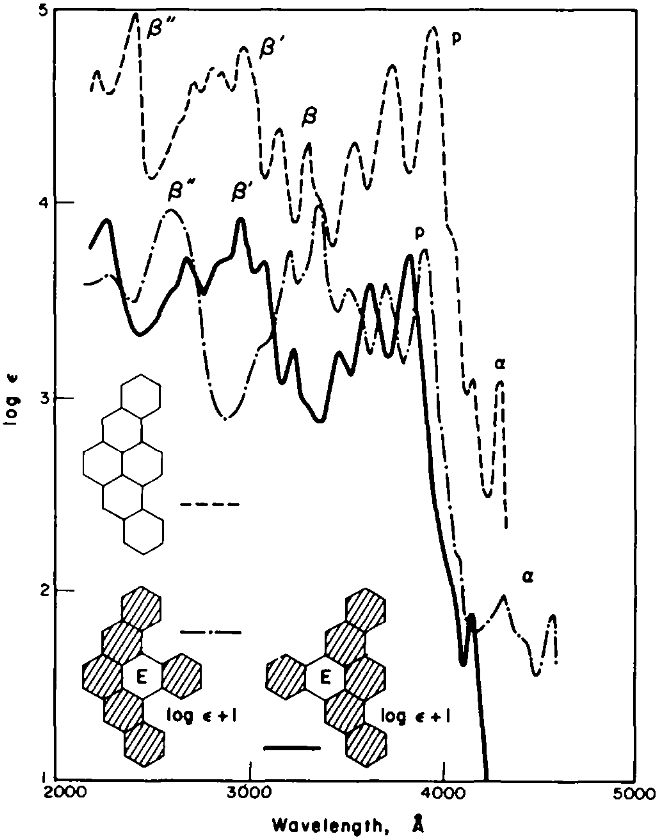


FIG 2. Absorption spectra with max (Å) and log ε in parentheses.

-------- 3,4:9,10-Dibenzopyrene in benzene: α, 4330 (3·10), 4190 (3·10); p, 3970 (4·94), 3750 (4·74), 3565 (4·34); β, 3320 (4·32), 3170 (4·40); β', 2970 (4·84), 2850 (4·70); in ethanol: 2720 (4·63); β'', 2420 (5·00), 2220 (4·70).

———— 1,2:4,5:8,9-Tribenzopyrene in cyclohexane: α, 4180 (2·86); p, 3850 (4·76), 3640 (4·60), 3465 (4·24), 3230 (4·26), 3070 (4·70); β', 2965 (4·94), 2850 (4·70); 2680 (4·73); β'', 2260 (4·92).

—·—·—· 1,2:3,4:9,10-Tribenzopyrene in ethanol: α, 4610 (2·88), 4340 (2·98); p, 3930 (4·78), 3730 (4·58), 3540 (4·56); β, 3375 (5·00), 3220 (4·76); β', 2600 (4·96), 2290 (4·62).

in agreement with the formation of an empty ring "E". In accordance with this there is only one type of conjugation possible in the centrosymmetric dibenzpyrene (VI). In fact only one β-band (3135 Å) is found in the spectrum.[3]

The picene or pentaphene conjugation can become predominant by the fusion of one ring to the fixed double bond in the ring "E" in V or Va. Thus tribenzopyrene (VII) shows in the UV spectrum (Fig. 2) the pure picene type (β'-band at 2965 Å) and tribenzopyrene (VIII) the pentaphene type (β-band at 3375 Å). The difference from the corresponding conjugation in V and Va amounts to − 5 Å and + 55Å resp. Such small differences are only observed if a ring is fused to a fixed double bond.[4] The fixed double bond in (VIII) was proved by the synthesis of the CH_3 derivative of (VIII), $R = CH_3$. The CH_3 NMR signal of this hydrocarbon is a doublet with a separation of 1·1 Hz.

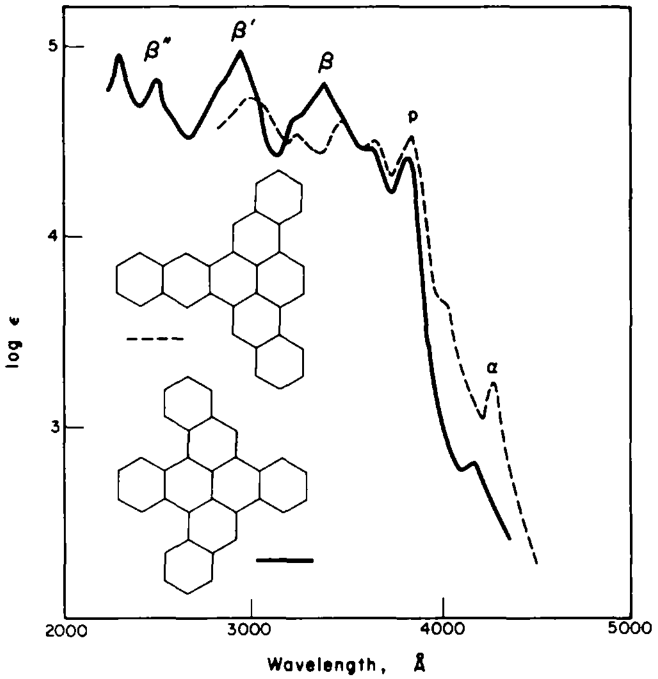


FIG 3 Absorption spectra with max (Å) and log ε in parentheses

———— 1,2:3,4:6,7:9,10-Tetrabenzopyrene in cyclohexane: α, 4140 (2·80); *p*, 3800 (4·40), 3620 (4·46); *β*, 3360 (4·80), 3240 (4·63); *β'*, 2920 (4·96), 2820 (4·80); *β''*, 2480 (4·82); 2280 (4·94).

- - - - - - - - 3,4:9,10-Dibenzo-naphtho(2':3',6:7)pyrene in 1,2,4-trichlorobenzene: α, 4260 (3·24), 4010 (3·66); *p*, 3840 (4·52), 3640 (4·51); *β*, 3470 (4·62), 3220 (4·54); in benzene: *β'*, 2980 (4·74).

It is obvious that the two types of conjugation must re-occur together if the two types of annellations are combined in tetrabenzopyrene (IX and IXa). In fact its spectrum (Fig 3) appears to be a combination of the two spectra in Fig 2 with two β-bands at 3360 and 2920 Å. The p-bands of the above benzologues of pyrene are little affected by the annellations and are situated between 3800 Å and 4000 Å.

The annellation of two rings to the picene type (V) does not alter the spectrum (Fig 3) very much. The β-band of dibenzo-naphtho-pyrene (X) is still at 2980 Å (shift + 10 Å). It may be possible to correlate the band at 3470 Å to the pentaphene type conjugation.

An entirely new type of spectrum is encountered in dibenzo-naphtho-pyrene (XI) and tribenzo-naphtho-pyrene (XII). Neither the broad p-bands nor the β-bands at 3120 and 3020 Å resp. can be related to the picene or pentaphene type (Fig 4). There may be a relation rather with 1,2-benzotetraphene (XIII) which has a similar type of spectrum with a β-band at 3080 Å.[5]

In order to prove this the synthesis of naphtho(2':3',5:6)picene (XIV) was attempted. 5:6-benzopicene (XV) which should have an aromatic conjugation related to tetrabenzopyrene (IX) was synthesized. The β-bands of the two later hydrocarbons are close together, 2920 and 2950 Å resp. (Fig 5).

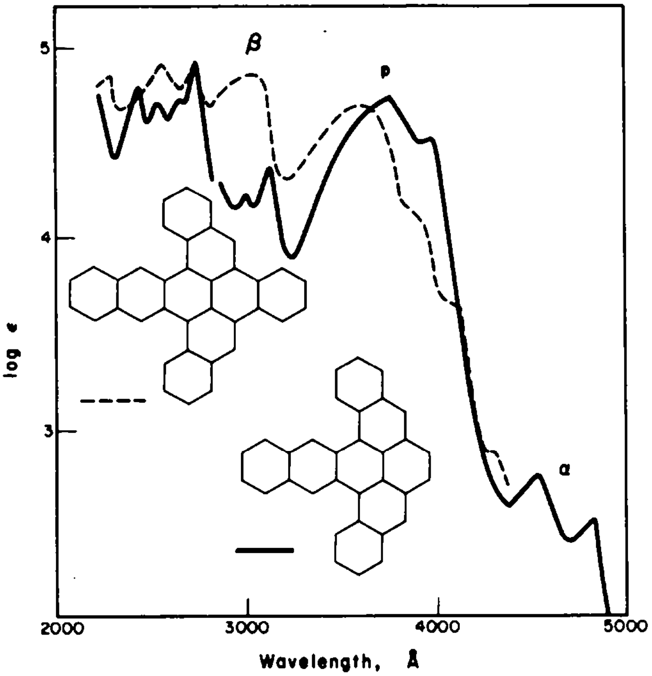


FIG 4. Absorption spectra with max (Å) and log ε in parentheses.

———— 3,4:9,10-Dibenzo-naphtho(2′:3′,1:2)pyrene in benzene: α, 4810 (2·54), 4520 (2·77); 3950 (4·54); p, 3730 (4·74); β, 3120 (4·37), 2990 (4·22); in cyclohexane: β′, 2740 (4·94), 2640 (4·73), 2530 (4·72), 2420 (4·80).

- - - - - 3,4:6,7:9,10-Tribenzo-naphtho(2′:3′,1:2)pyrene in cyclohexane: α, 4300 (2·87), 4080 (3·67), 3880 (4·13); p, 3580 (4·68); β, 3020 (4·85), 2900 (4·78); 2740 (4·92), 2560 (4·91), 2280 (4·83).

Synthesis of the hydrocarbons

Naphtho(2′:3′,11:12)picene (parent hydrocarbon of XVII) was obtained instead of XIV when picene was condensed with phthalic anhydride and aluminium chloride under standard condition. The resulting keto acid could have the structure XVI if the reaction proceeded analogous to the reaction with chrysene[6] or the condensation could take place in 5 position of picene. The course of the reaction gave the answer to this problem.

The acid formed could be cyclised to a quinone which, when submitted to a zinc dust melt, gave the oxido-compound (XVIII). This established the reaction pattern analogous to the condensation with chrysene.[6] Thus the acid must have the structure XVI, the quinone structure XVII and the oxido compound structure XVIII. The parent hydrocarbon naphtho(2′:3′,11:12)picene could be obtained by a reduction with pyridine, zinc dust and acetic acid. Its absorption spectrum s. Fig 5.

5:6-Benzopicene (XV). Naphthalene-2,3-diacetonitrile (XIX) was condensed with *o*-bromobenzaldehyde to give the compound XX. A corresponding chloro compound was obtained with *o*-chlorobenzaldehyde. The cyclisation of XX with KOH followed by a sublimation with soda-lime yielded unexpectedly 1,2:3,4-dibenzotetracene[7] (XXI).

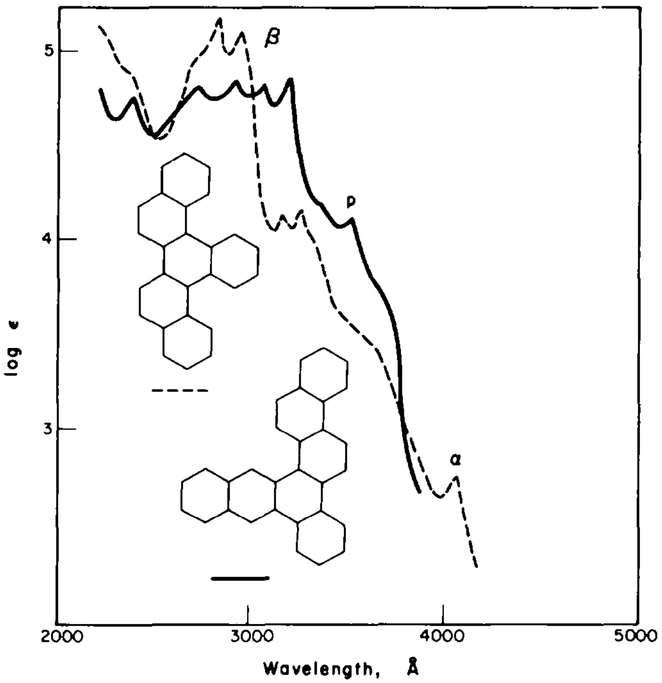


Fig 5. Absorption spectra with max (Å) and log ε in parentheses.

———— Naphtho(2′:3′,11:12)picene in cyclohexane: *p*, 3700 (3·80), 3540 (4·13), 3370 (4·22); *β*, 3200 (4·86), 3060 (4·84), 2930 (4·86), 2530 (4·81), 2400 (4·76).

- - - - - 5:6-Benzopicene in ethanol: *α*, 4030 (2·73); *p*, 3245 (4·16), 3160 (4·09); *β*, 2950 (5·04), 2830 (5·12).

In another attempt, 2,3-bisbromomethylnaphthalene was submitted to a Wittig synthesis with triphenylphosphine. The phosphonium salt was reacted with *o*-chlorobenzaldehyde to give the compound XXII, and with *o*-bromobenzaldehyde to give the corresponding bromo compound. Both halogen compounds could not be cyclised with KOH under different conditions at temperature between 230–290°.

A further synthesis started from 1-acetylnaphthalene which was reduced to the pinacol (XXIII). Dehydration gave XXIV and diene synthesis with maleic anhydride (XXV), followed by dehydrogenation and decarboxylation with lead dioxide yielded dinaphthylbenzene (XXVI). Photocyclisation yielded 5:6-benzopicene (XV). Its picrate and TNB complex crystallized readily but the hydrocarbon could not be obtained in a solid state. Its absorption spectrum is given in Fig 5.

Methyltribenzopyrene (XXVIII) was obtained by heating the diol (XXVII) with copper powder at 400°. The diol was synthesized from 1,2,4-trimethylanthraquinone and phenyl lithium. The synthesis of tetrabenzopyrene (IX) started from 5,8-dimethyltetralin which was condensed with phthalic anhydride to give the keto acid (XXIX). Cyclisation with sulphuric acid yielded the quinone (XXX). Its reaction with phenyl lithium gave the diol (XXXI) and heating with copper powder at 400–440° resulted in the formation of tetrabenzopyrene (IX).

Dibenzpyrene (V) was condensed with *o*-toluyl chloride and aluminium chloride.

The resulting ketone, assumed to have structure XXXII or being a constituent of a mixture of isomeric ketones, was pyrolyzed to dibenzonaphtho-pyrene (X). The isomeric 4- and 8-*o*-toluyl-dibenzpyrenes would decompose under these conditions.

The synthesis of the isomeric dibenzo-naphtho-pyrene (XI) started with a condensation of *p*-xylene and naphthalene-2,3-dicarboxylic anhydride which gave the acid (XXXIII). Cyclisation with sulphuric acid yielded the quinone (XXXIV) and reaction with phenyl lithium gave the diol (XXXV). Cyclisation by heating with copper powder yielded dibenzo-naphtho-pyrene (XI).

In an analogous synthesis *p*-xylene was replaced by 5,8-dimethyltetralin. Via the acid (XXXVI), cyclisation with polyphosphoric acid to the quinone (XXXVII), and the diol (XXXVIII) tribenzo-naphtho-pyrene (XII) was obtained.

EXPERIMENTAL*

11-*o*-*Carboxybenzoylpicene* (XVI). Powdered $AlCl_3$ (10 g) was added to a stirred suspension of finely divided picene (6 g) and phthalic anhydride (3·5 g) in benzene (50 ml). The dark red soln evolved HCl. The mixture was stirred vigorously for 4 hr and an additional portion of $AlCl_3$ (3 g) was added after 2 hr. The red double compound was decomposed with dil HCl, the benzene distilled off with steam and the residue extracted with dil ammonia. Acidification of the filtered extract furnished the keto acid (5·4 g) which was crystallized from AcOH acid and yielded needles, m.p. 270° which dissolved in conc H_2SO_4 to give an intense blue soln. (Found: C,84·3; H,4·4. $C_{30}H_{18}O_3$ requires: C,84·5; H,4·3%).

Naphtho(2′:3′,11:12)picene-1′,4′-quinone (XVII). The above keto acid (5·2 g) was dissolved in boiling benzoyl chloride (20 ml) and conc H_2SO_4 added dropwise until the transient blue colour disappeared. The mixture was refluxed for a further 5 min. On cooling orange-brown needles (440 mg) crystallized. Recrystallization from nitrobenzene gave the quinone as orange needles (350 mg), m.p. 325° dec. The quinone dissolved in conc H_2SO_4 to give an emerald green soln. (Found: C,88·0; H,4·1. $C_{30}H_{16}O_2$ requires: C,88·2; H,4·0%).

Naphtho(2′:3′,11:12)picene (parent hydrocarbon of XVII). The above quinone XVII (180 mg), Zn dust (500 mg) and pyridine (10 ml) were refluxed and AcOH (80%, 4 ml) added during 5 hr. The pyridine soln was poured into dil AcOH and the ppt was heated above its m.p. *in vacuo*. The powdered melt was extracted with benzene, the soln chromatographed on alumina and the eluate concentrated and diluted with light petroleum. The hydrocarbon (20 mg) formed colourless needles, m.p. 239–240°. (Found: 95·7; H,4·9. $C_{30}H_{18}$ requires: 95·2; H, 4·8%).

13,4′-*Oxido-naphtho(2′:3′,11:12)picene* (XVIII). The quinone XVII (150 mg) was ground together with NaCl (150 mg) and Zn dust (150 mg). $ZnCl_2$ (1·5 g) was added and the mixture heated with stirring to 280–310° for 3 min. The cold melt was dissolved in dil AcOH and the residue extracted with xylene. The soln, after treatment with charcoal gave the oxido-compound (30 mg) in clusters of small yellow, sublimable needles, m.p. 322–323° which dissolved in conc H_2SO_4 to give a red soln which changed to brown on standing. (Found: C, 91·6; H, 4·2. $C_{30}H_{16}O$ requires: C, 91·8; H, 4·1%).

–*Di(*o*-bromobenzylidene)naphthalene-2,3-diacetonitrile* (XX). Naphthalene-2,3-diacetonitrile (2·2 g) and *o*-bromobenzaldehyde (5 g) were dissolved in hot EtOH (75 ml). 33% NaOH aq (1 ml) was added and the mixture shaken. The soln became warm, dark red and the condensation product (XX) crystallized from the hot soln. After cooling the ppt was filtered off, washed with EtOH and recrystallized from xylene to give colourless prisms, m.p. 225°. (Found: C, 62·5; H, 3·1. $C_{28}H_{16}Br_2N_2$ requires: C, 62·2; H, 3·0%). The corresponding chloro compound was prepared using *o*-chlorobenzaldehyde, m.p. 197–198°.

1,2:3,4-*Dibenzotetracene* (XXI). The above chloro compound (2 g), quinoline (30 ml) and KOH (4 g) were refluxed for 2 hr, poured into dil HCl, filtered and washed. The ppt (750 mg) was mixed with soda-lime and sublimed 275–300°/0·03 mm. The sublimate was dissolved in benzene and chromatographed on alumina. Concentration of the eluate gave long orange-yellow needles (24 mg) m.p. 260–263° (lit.[7] 265–266°) which dissolved in conc H_2SO_4 forming a red soln. (Found: C, 94·9; H, 5·2. $C_{26}H_{16}$ requires: C, 95·1; H, 4·9%).

2,3-*Di(*o*-chlorostryryl)naphthalene* (XXII). A soln of 2,3-bisbromomethylnaphthalene (50 g) and triphenylphosphine (92 g) in benzene (1 l) was heated under reflux for 3 hr. Colourless crystals (98 g) separated after 5–10 min. After cooling, the ppt, m.p. 254° dec, was filtered off and washed first with benzene and then

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* M.ps are uncorrected and were taken in evacuated capillaries.

with ether. A soln of the phosphonium salt (8 g) and *o*-chlorobenzaldehyde (2·9 g) in abs EtOH (100 ml) was treated with EtOLi prepared from Li chips (270 mg) and EtOH (150 ml). After standing for 30 min the soln was refluxed for 2 hr. The orange-red soln was concentrated under reduced press. Addition of water gave an oil which was extracted with ether. Concentration yielded first phosphonium oxide, m.p. 152–154°. The mother liquor was then evaporated and the resulting oil dissolved in light petroleum 100–120° and chromatographed on alumina. The eluate was evaporated to dryness and the resulting oil crystallized from light petroleum. The condensation product (1·8 g) formed colourless needles, m.p. 70–74°. (Found: C, 78·0; H, 4·8. $C_{26}H_{18}Cl_2$ requires: C, 77·8; H, 4·5%).

2,3-Di(1-*naphthyl*)*butane*-2,3-*diol* (XXIII). Methyl-1-naphthyl ketone (180 g) was dissolved in abs alcohol (750 ml) and dry benzene (750 ml) in a 3-necked flask fitted for reflux with stirring. To this was added freshly scraped Al foil (27 g) and $HgCl_2$ (1 g). On gently warming a vigorous reaction started. After 3 hr the mixture was refluxed for a further 12 hr. The mixture was poured onto dil HCl and extracted with benzene-ether. The extracts were washed with dil HCl, water Na_2CO_3 aq and finally water, and then dried over $MgSO_4$. The solvents were removed *in vacuo*, leaving a yellow-orange oil, to which was added an equal value of ice-cold MeOH. On standing at 0°, the diol crystallized out as colourless needles (65 g). Crystallization from MeOH yielded the diol as dihydrate, needles, m.p. 102–104°. (Found: C, 76·1; H, 6·9. $C_{24}H_{22}O_2 \cdot 2H_2O$ requires: C, 76·2; H, 6·9%).

Crystallization from benzene-light petroleum gave colourless prisms of the anhydrous diol, m.p. 184–186°, which dissolved in conc H_2SO_4 to give an olive-green soln. The IR spectrum showed an OH band at 3558 cm^{-1}.

2,3-Di(1-*naphthyl*)*buta*-1,3-*diene* (XXIV). The above diol (20 g) and freshly dried $NaHSO_4$ (0·5 g) were gently refluxed (200°/1·5 mm) for 30 min. The cool melt was extracted with a small amount of benzene and the soln chromatographed on basic alumina (800 g). Elution with light petroleum (40–60°) gave a colourless soln with a strong blue-violet fluorescence. The solvent was removed and the residue crystallized from EtOH. The hydrocarbon crystallized in colourless platelets, m.p. 174–175° which dissolved in conc H_2SO_4 to form a golden-yellow soln. (Found: C, 93·8; H, 6·1. $C_{24}H_{18}$ requires: C, 94·1; H, 6·0%). The mother liquor contained a compound with a C=O band in its IR spectrum.

1,2-*Di*(1-*naphthyl*)*cyclohex*-1-*ene*-4,5-*dicarboxylic anhydride* (XXV). The diene (1·53 g) and maleic anhydride (0·44 g) were refluxed in dry xylene (10 ml) for 1 hr. After concentration the adduct crystallized and was recrystallized from benzene-Ac_2O. It formed colourless asterisks, m.p. 213° (1·22 g). (Found: C, 83·3; H, 5·2. $C_{28}H_{20}O_3$ requires: C, 83·2; H, 5·0%).

o-*Di*(1-*naphthyl*)*benzene* (XXVI). A finely powdered mixture of the anhydride (1·0g) and lead dioxide (4·0 g) in decalin (20 ml) was refluxed for 5 hr. The evolution of CO_2 was measured by a current of N_2 which was bubbled into BaOH soln. At the end of the reaction xylene was added and the residue repeatedly extracted with xylene. The combined solns were concentrated to a small volume and chromatographed on alumina. Elution with light petroleum (40–60°) yielded a colourless soln with a strong violet fluorescence. Crystallization from benzene-EtOH yielded the hydrocarbon as colourless plates (237 mg), m.p. 155°. (Found: C, 94·2; H, 5·7. $C_{26}H_{18}$ requires: C, 94·5; H, 5·5%).

5,6-*Benzopicene* (XV). The above hydrocarbon (220 mg) and I_2 (22 mg) were irradiated in cyclohexane (500 ml) for 48 hr. Chromatography in benzene or xylene resulted only in the enrichment of the benzopicene. It was therefore transformed into the TNB complex which was obtained in stout orange rods, m.p. 179–180°. (Found: N, 11·30; $C_{26}H_{16} \cdot C_{12}H_6O_{12}N_6$ requires: N, 11·14%). The complex was decomposed by passing it down an alumina column to yield a yellow soln of 5,6-benzopicene which could not be induced to crystallize; mass spectral analysis showed that 5,6-benzopicene had indeed been obtained: M.S. molecular ion $m/e = 328$; calc. M.W. = 328.

A further attempt was made to obtain 5:6-benzopicene as a solid by the formation and decomposition of its picrate, which formed red-orange needles, m.p. 162–163°. (Found: N, 10·62; $C_{26}H_{16} \cdot C_{12}H_6O_{14}N_6$ requires: N, 10·68%).

The decomposition of this picrate yielded also 5:6-benzopicene as an oil which did not crystallize.

9,10-*Diphenyl*-9,10-*dihydroxy*-9,10-*dihydro*-1,2,4-*trimethylanthracene* (XXVII). Bromobenzene (40 g) was added to strips of Li metal (3 g) suspended in dry ether (500 ml) under N_2 and refluxed until the Li had dissolved. The soln was filtered through glass wool into a suspension of 1,2,4-trimethylanthraquinone[8] (14 g) in dry benzene (300 ml). The mixture was refluxed and stirred for 20 min and then decomposed with ice and dil AcOH. After steam distillation an orange-yellow oil was obtained. This was dissolved in ether and the soln extracted with alkaline sodium dithionite, dried over $MgSO_4$ and concentrated. The light yellow ppt was recrystallized from benzene and formed colourless plates (12·5 g), m.p. 278–279°. This diol dissolved in conc H_2SO_4 to give a yellow-brown soln. (Found: C, 85·8; H, 6·6. $C_{29}H_{26}O_2$ requires: C, 85·7; H, 6·5%).

6-Methyl-1,2:3,4:9,10-tribenzopyrene(XXVIII). The above diol (4 g) and Cu powder (30 g) were thoroughly mixed and heated under CO_2 at 400–410° for 3 hr. The mixture was extracted with xylene and the extract chromatographed on alumina. Elution with benzene gave a greenish-yellow soln which after concentration and addition of light petroleum yielded greenish-yellow needles (55 mg), m.p. 212-213°. The hydrocarbon gave an apple green soln with conc H_2SO_4. (Found: C, 94·8; H, 5·3. $C_{29}H_{18}$ requires: C, 95·0; H, 5·0%).

6-o-Carboxybenzoyl-5,8-dimethyltetralin (XXIX). Powdered $AlCl_3$ (49·6 g) was added to a mixture of phthalic anhydride (18·3 g) and 5,8-dimethyltetralin (18 g) in benzene (90 ml). The red mixture was kept at room temp for 40 min and then at 60–70° for 1 hr. After decomposition with ice and dil HCl and steam distillation the yellow residue was extracted with dil ammonia. Acidification of the filtered extract gave the keto acid (32 g) which crystallized from benzene-heptane in colourless prisms, m.p. 154–156°, and dissolved in conc H_2SO_4 to form a red soln. (Found: C, 77·8; H, 6·4. $C_{20}H_{20}O_3$ requires: C, 77·9; H, 6·4%).

1,2,3,4-Tetrahydro-5,12-dimethyltetracene-6,11-quinone (XXX). The above keto acid (20 g) was dissolved in conc H_2SO_4 (100 ml) and the soln heated to 80° for 2 min. After cooling the red soln was poured onto ice and the ppt (15·2 g) filtered off, washed with water and dil ammonia. Crystallization from xylene gave the quinone as large yellow prisms, m.p. 207–208°. (Found: C, 83·0; H, 6·4. $C_{20}H_{18}O_2$ requires: C, 82·7; H, 6·3%).

1,2,3,4,6,11-Hexahydro-6,11-diphenyl-6,11-dihydroxy-5,12-dimethyltetracene (XXXI). The above quinone (10 g) was added as a fine suspension in benzene (200 ml) to an etheral soln (180 ml) of PhLi, prepared from Li chips (1·95 g) and bromobenzene (21·7 g). The ether was distilled off and the mixture refluxed for 15 min. Decomposition with ice and dil AcOH, steam distillation and treatment of the residue with ether yielded the diol (7·6 g) which was recrystallized from THF. It formed colourless prisms, m.p. 235–275° dec and dissolved in conc H_2SO_4 to give a red soln which changed to green on standing. (Found: C, 85·6; H, 6·9. $C_{32}H_{30}O_2$ requires: C, 86·1; H, 6·8%).

1,2:3,4:6,7:9,10-Tetrabenzopyrene (IX). An intimate mixture of the above diol (3 g) and Cu powder was heated under CO_2 at 400–440° for 2 hr. The mixture was extracted with hot xylene and the soln chromatographed on alumina. When eluted with xylene a single yellow band gave a soln yielding yellow needles (200 mg) m.p. 311–312°, which dissolved in conc H_2SO_4 to give a green soln which changed to brown on standing. (Found: C, 95·5; H, 4·2. $C_{32}H_{18}$ requires: C, 95·5; H, 4·5%).

3,4:9,10-Dibenzo-naphtho(2':3',6:7)pyrene (X). 3,4:9,10-Dibenzopyrene[9] (5 g) was finely powdered and suspended in a mixture of *o*-toluyl chloride (2·82 g) and CH_2Cl_2 (30 ml). Powdered $AlCl_3$ (5 g) was added and the mixture stirred for 5 min at room temp and then boiled for a few min. It changed its colour from blue to green. Decomposition with ice and dil HCl followed by steam distillation yielded a brown resin which was dissolved in hot xylene and chromatographed on alumina. Elution gave first unchanged dibenzopyrene and then a fraction which on concentration yielded a yellow oil. This was heated under CO_2 to 420° for 15 min and then briefly to 450°. The pyrolysate (4·5 g) was sublimed *in vacuo*. Two sublimates were obtained, first 3,4:9,10-dibenzopyrene (1 g) and at higher temp a yellow-brown fraction which was dissolved in xylene and chromatographed on alumina. Hot xylene followed by hot trichlorobenzene gave an eluate which on concentration yielded X (12 mg) as golden brown needles, m.p. 404°, which dissolved in conc H_2SO_4 to give a brown soln. (Found: C, 95·6; H, 4·5. $C_{32}H_{18}$ requires: C, 95·5; H, 4·5%).

2-(3'-Carboxy-2'-naphthoyl)-1,4-dimethylbenzene (XXXIII). An intimate mixture of finely powdered naphthalene-2,3-dicarboxylic anhydride (5 g) and $AlCl_3$ (10 g) was added to *p*-xylene (23 g). The initially yellow soln became orange and finally yellow-brown. The vigorous reaction had ceased after 10 min. The mixture was heated at 80° for 1½ hr. Decomposition with ice and HCl followed by steam distillation left a residue which was dissolved in dil ammonia. The filtered soln was acidified with conc HCl. The white ppt (7·4 g) crystallized from xylene in white needles, m.p. 224–225°, which dissolved in conc H_2SO_4 to give a red soln which changed to violet on standing. (Found: C, 79·3; H, 5·2. $C_{20}H_{16}O_3$ requires: C, 79·0; H, 5·3%).

1,4-Dimethyltetracene-5,12-quinone (XXXIV). The powdered keto acid (5 g) was added to conc H_2SO_4 (40 g) and the mixture was heated with stirring at 100–110° for 20 min. The colour of the soln changed from red to violet. The mixture was poured onto ice and the ppt (4·41 g) washed with dil ammonia and water. Crystallization from xylene yielded yellow needles, m.p. 264–265°, which dissolved in conc H_2SO_4 to form a violet soln. (Found: C, 84·0; H, 5·0. $C_{20}H_{14}O_2$ requires: C, 83·9; H, 4·9%).

5,12-Diphenyl-5,12-dihydro-5,12-dihydroxy-1,4-dimethyltetracene (XXXV). The above quinone (5 g) was added to an etheral soln of PhLi, prepared from Li chips (1 g) and bromobenzene (11 g), as a fine suspension in benzene (150 ml). The ether was distilled off and after refluxing for 15 min the complex was decomposed with ice and dil AcOH. The benzene was distilled off with steam and the resulting brown residue was dissolved in ether. After 2 days the diol (3 g) separated as a white crystalline powder. Recrystallization from xylene gave colourless needles, m.p. 260–290° dec, which dissolved in conc H_2SO_4 to form a green soln. (Found: C, 86·8; H, 6·0. $C_{32}H_{26}O_3$ requires: C, 86·9; H, 5·9%).

3,4:9,10-*Dibenzo-naphtho*(2′:3′,1:2)*pyrene* (XI). An intimate mixture of the above diol (2·8 g) and Cu powder was heated under CO_2 at 400° for 1½ hr. The mixture was extracted with hot xylene and the soln chromatographed on alumina. Two fractions were obtained; yellow eluate followed by a red one. The yellow eluate was concentrated to a small volume and light petroleum (60–80°) added. Long yellow needles (259 mg), m.p. 274–276°, crystallized which dissolved in conc H_2SO_4 to give a wine red soln. (Found: C, 95·6; H, 4·7. $C_{32}H_{18}$ requires: C, 95·5; H, 4·5%).

6-(3′-*Carboxy-2′-naphthoyl*)-5,8-*dimethyltetralin* (XXXVI). A finely powdered mixture of naphthalene-2,3-dicarboxylic anhydride (24·5 g) and $AlCl_3$ (49·6 g) was added to a soln of 5,8-dimethyltetralin (18 g) in benzene (90 ml). The mixture was kept at room temp for 1 hr and then at 70° for 1 hr. Decomposition with ice and dil HCl, followed by steam distillation resulted in a resin which was extracted with dil ammonia. Acidification with HCl yielded the keto acid (33 g) which crystallized from benzene-heptane as a white powder, m.p. 204–206°. It dissolved in conc H_2SO_4 to give a red soln which changed to violet on standing. (Found: C, 80·6; H, 6·2. $C_{24}H_{22}O_3$ requires: C, 80·4; H, 6·2%).

1,2,3,4-*Tetrahydro*-5,14-*dimethylpentacene*-6,13-*quinone* (XXXVII). The above acid (30 g) was added to polyphosphoric acid (300 g) at 70° and the mixture heated to 150–170° for 3–4 min. The cold mixture was poured onto ice, the ppt filtered off and washed with dil ammonia and water. Crystallization from xylene gave the quinone (8·55 g) as yellow prisms, m.p. 252°, which dissolved in conc H_2SO_4 to give a violet soln. (Found: C, 84·7; H, 6·0. $C_{24}H_{20}O_2$ requires: C, 84·7; H, 5·9%).

1,2,3,4,6,13-*Hexahydro*-6,13-*diphenyl*-6,13-*dihydroxy*-5,14-*dimethylpentacene* (XXXVIII). The above quinone (7 g) in benzene (200 ml) was reacted with bromobenzene (13 g), Li (1·15 g) and ether (180 ml) as described under XXXV. The diol (4·2 g), m.p. 230–275° dec, dissolved in conc H_2SO_4 to form a green soln which changed to red on standing. (Found: C, 87·7; H, 6·7. $C_{36}H_{28}O_2$ requires: C, 87·1; H, 6·5%).

3,4:6,7:9,10-*Tribenzo-naphtho*(2′:3′,1:2)*pyrene* (XII). The diol (2 g) and Cu powder were condensed at 420° as described for XI. The hydrocarbon formed yellow needles, m.p. 258–260°, and dissolved in conc H_2SO_4 to give a ruby red soln which changed to yellow-brown on standing. (Found: C, 95·2; H, 4·4 $C_{36}H_{20}$ requires: C, 95·5; H, 4·5%).

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