Tetrahedron, 1964, Vol. 20, pp. 2107 to 2117. Pergamon Press Ltd. Printed in Northern Ireland

HIGHER ANNELLATED 1:2,7:8-DIBENZOCHRYSENES

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(*Received* 12 *May* 1964)

Abstract—Oxidation and the annellation effect point to a fixed double bond in 1:2,7:8-dibenzochrysene (II). This is not so in the higher benzologues (V and VII) which are closely related to the hydrocarbons (IV and VI). Regular annellation effects are obtained in passing from dibenzochrysene to the pyrene benzologues (VIII and IX). The hydrocarbon (VIII) was prepared by zinc dust melt of a mixture of fluorenone and the ketomethylenephenanthrene (XII) and the hydrocarbon (IX) from the ketone (XII) alone. Dibenzochrysene (II) was also prepared in good yield by zinc dust melt from fluorenone. The syntheses of tetraphenotetraphene (V), naphtho-(2′,1′:1,2)-tetracene (VI), benzophenanthrenotetracene (VII), phenanthrenopyrene (VIII), pyrenopyrene (IX), dibenzo-*o*-phenyleneperylene (XVII) are described.

1:2,7:8-Dibenzochrysene (II) is so far the only polycyclic hydrocarbon in which a double bond between two rings is attacked by oxidation to form a diketone (III). This indicates that contrary to naphthalene a double bond is fixed between the two rings. This being the case there ought to be an asymmetric annellation effect as observed in the pyrene series.[1] If this bond fixation were preserved in the benzologues of dibenzochrysene, then a red shift ought to be observed only on annellation to one of the two phenanthrene complexes forming dibenzochrysene (II).

In passing from chrysene (I) to 1:2,7:8-dibenzochrysene (II) a rather big red shift of both β- and p-bands (+340 and +320 Å respectively) is recorded (Fig. 1). This shift could consist of two components, namely the shift associated with the formation of overcrowded positions (marked *)[2] and the shift due to the fixation of the central double bond.

Much smaller red shifts (150 and 140 Å respectively) are observed in going from anthracenoanthracene (IV) to tetraphenotetraphene (V; Fig. 2) and from naphthotetracene (VI) to benzophenanthrenotetracene (VII; Fig. 3). These shifts probably account for the formation of overcrowded positions in V and VII. The same difference of 140 Å of the β-bands is recorded between chrysene and 3:4-benzophenanthrene and is due to overcrowding.[3] It must therefore be assumed that no fixation of a double bond has taken place in V and VII. This view is supported by the fact that the β-bands of IV and VI and of V and VII show almost the same difference (70 and 80 Å respectively).

Regular shifts are recorded in passing from dibenzochrysene (II) to phenanthrenopyrene (VIII) and pyrenopyrene (IX): 130 and 120 Å for the β-bands and 230 and 260 Å for the p-bands (Fig. 4). Since the degree of overcrowding remains constant in this series, these shifts must be considered pure annellation effects.

1:2,7:8-Dibenzochrysene (II) can be obtained easily from fluorenone (X) in a zinc dust melt. Large amounts of the ketone (XI) are also formed, which can be

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[1] E. Clar, J. F. Guye-Vuillème, A. McCallum and I. A. Macpherson, *Tetrahedron* **19**, 2185 (1963).

[2] E. Clar and D. G. Stewart, *J. Amer. Chem. Soc.* **74**, 6235 (1952).

[3] F. H. Herbstein and G. M. F. Schmidt, *J. Chem. Soc.* 3302 (1954).

reduced to dibenzochrysene in a second zinc dust melt. Ketomethylenephenanthrene (XII)[4] gives only pyrenopyrene (IX) in a zinc dust melt. Phenanthrenopyrene (VIII) was obtained by the same method from a mixture of fluorenone and ketomethylenephenanthrene (XII).

The dicarboxylic acid (XIII) which can be prepared in 4 stages from chrysene[5] was cyclized in sulphuric acid to the compound XIV. This was rather sensitive to aerial oxidation and was immediately reduced to the hydrocarbon (V) with zinc dust, pyridine and acetic acid. Oxidation of the hydrocarbon with chromic acid in acetic acid gave the diquinone (XV) which can be obtained also from the diketone (XIV). This shows that tetraphenotetraphene (V) has no fixed double bond in the centre of the molecule like dibenzochrysene (II). Benzophenanthrenotetracene (VII) is formed together with two other hydrocarbons by pyrolysis of the ketone XVI. This was obtained from toluyl chloride, dibenzochrysene (II) and aluminium chloride. Its constitution (XVI) appears to be supported by the formation of another hydrocarbon which according to its spectrum (Fig. 5) and its analyses has probably the structure XVII. For a third red hydrocarbon formula (XVIII) might be considered possible (Absorption spectrum, Fig. 5). The main product of the pyrolysis, the hydrocarbon (VII) was also synthesized from dibenzochrysene (II), phthalic anhydride and aluminium chloride. The resulting keto acid (XIX) was reduced and cyclized in a zinc dust melt to the hydrocarbon VII.

The latter gives the compound XX when oxidized with chromic anhydride in acetic acid. Since this is probably preceded by the formation of the quinone it does not prove any fixation of the double bond in the central region.

Toluyl chloride, pyrenopyrene (IX) and aluminium chloride give a uniform ketone (XXI) from which, by pyrolysis, only one hydrocarbon, probably XXII, is obtained. Its absorption spectrum (Fig. 6) shows two groups of p-bands. The comparison with pyrenopyrene shows that the short wavelength group of p-bands (p′) can be related to the non-annellated pyrene complex and the long wavelength group (p) to the naphthopyrene complex in XXII.

The condensation of toluyl chloride with chrysene and aluminium chloride in tetrachloroethane gives a mixture of ketones which contains the ketone XXIII. The pyrolysis of this mixture gave 2:3-benzopicene and an oxido compound as described before.[6] We have now succeeded in isolating also naphthotetracene (VI) from the mixture by means of its adduct with maleic anhydride.

When this manuscript was written we received knowledge of a paper by Martin, *et al.*[7] in which the hydrocarbon V is mentioned and a future paper describing its synthesis is referred to. This synthesis appears different from ours and the m.ps given indicate that the hydrocarbons are identical.

EXPERIMENTAL*

10,10-Biphenylene-9-phenanthrone (XI). Fluorenone (X; 20 g) was ground together with Zn dust (20 g) and NaCl (20 g). Zinc chloride (100 g) was added and the mixture was melted, the temp

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

[4] O. Kruber and A. Marx, *Ber. Dscht. Chem. Ges.* 71, 2478 (1938).

[5] K. F. Lang and M. Zander, *Chem. Ber.* in press.

[6] E. Clar and W. Kelly, *J. Chem. Soc.* 4163 (1957).

[7] R. H. Martin, N. Defay, F. Geerts-Evrard and S. Delavarenne, *Bull. Soc. Chim., Belg.* 73, 189 (1964).

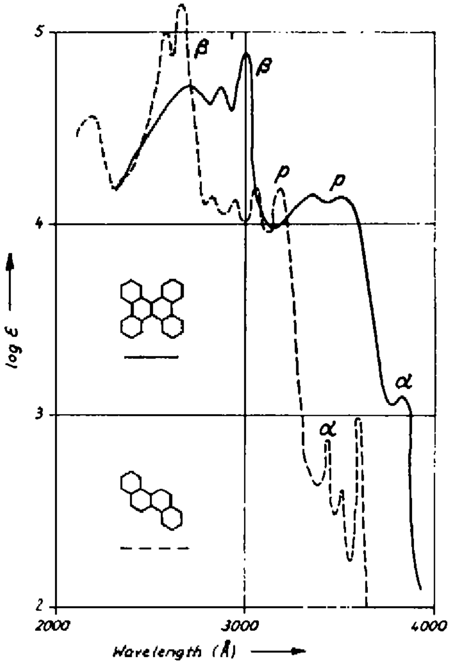


FIG. 1. Absorption max (Å) and log ε (in parentheses). Chrysene in alcohol, α: 3600 (3·00), 3510 (2·62), 3435 (2·88); p: 3190 (4·19), 3060 (4·19), 2950 (4·13), 2830 (4·14); β: 2670 (5·20), 2590 (5·00); β′: 2410 (4·36), 2200 (4·56). 1:2,7:8-Dibenzochrysene (II) in alcohol, α: 3830 (3·10); p: 3510 (4·14), 3360 (4·16); β: 3010 (4·90), 2880 (4·72); β′: 2700 (4·72).

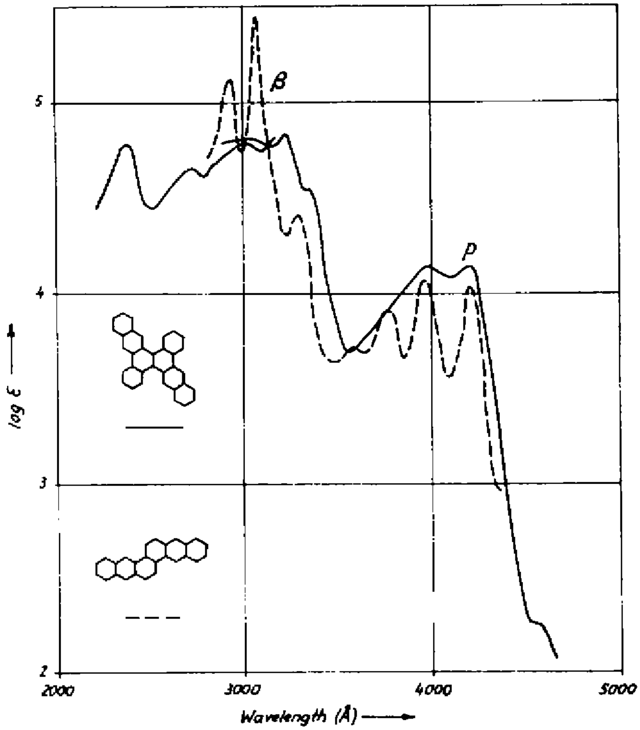


FIG. 2. Absorption max (Å) and log ε (in parentheses). Anthraceno-(2′,1′:1,2)-anthracene (IV) in benzene, p: 4200 (4·03), 3960 (4·06), 3770 (3·90), 3580 (3·71); 3290 (4·40); β: 3070 (5·44), 2940 (5·11). Tetrapheno-(6′,5′:5,6)-tetraphene (V) in benzene, p: 4200 (4·14), 4000 (4·14); 3360 (4·54); β: 3220 (4·84), 3040 (4·81); in cyclohexane, 2720 (4·65); β′: 2400 (4·80).

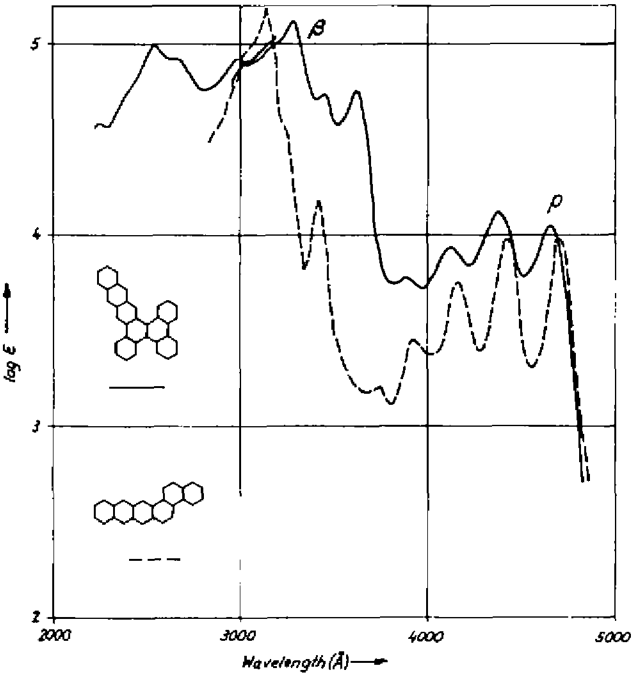


FIG. 3. Absorption max (Å) and log ε (in parentheses). Naphtho-(2′,1′:1,2)-tetracene (VI) in benzene, p: 4720 (3·98), 4420 (3·98), 4160 (3·76), 3930 (3·46), 3760 (3·21); 3420 (4·20); β: 3140 (5·20) 3040 (4·98). 1:2-Benzophenanthreno-(9′,10′:3,4)-tetracene (VII) in benzene, p: 4660 (4·04), 4380 (4·12), 4120 (3·94), 3880 (3·78); 3620 (4·76), 3450 (4·74); β: 3280 (5·12), 3040 (4·92); in cyclohexane, 2680 (4·91), 2540 (5·00).

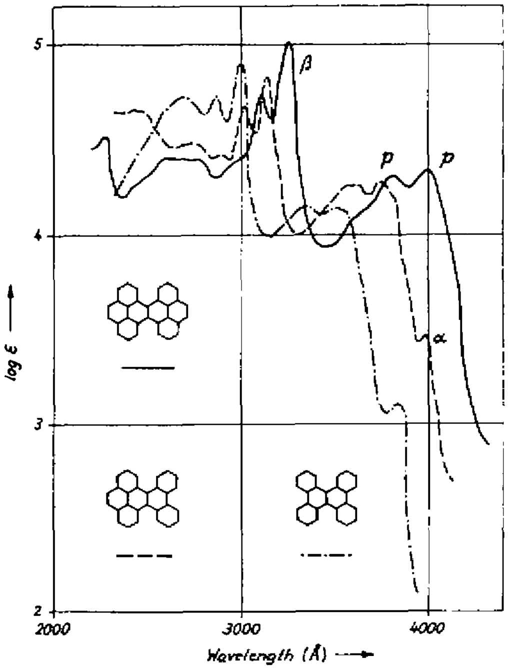


FIG. 4. Absorption max (Å) and log ε (in parentheses). Pyreno-(1′,2′:1,2)-pyrene (IX) in cyclohexane, p: 4000 (4·34), 3800 (4·32); β: 3260 (5·01), 3110 (4·75); 2700 (4·40); 2260 (4·52). Phenanthreno-(9′,10′:1,2)-pyrene (VIII) in cyclohexane, α: 3980 (3·45); p: 3740 (4·28), 3600 (4·26); β: 3140 (4·83), 3010 (4·68), 2900 (4·42); 2750 (4·48); 2480 (4·65), 2400 (4·65). 1:2,7:8-Dibenzochrysene as in Fig. 1.

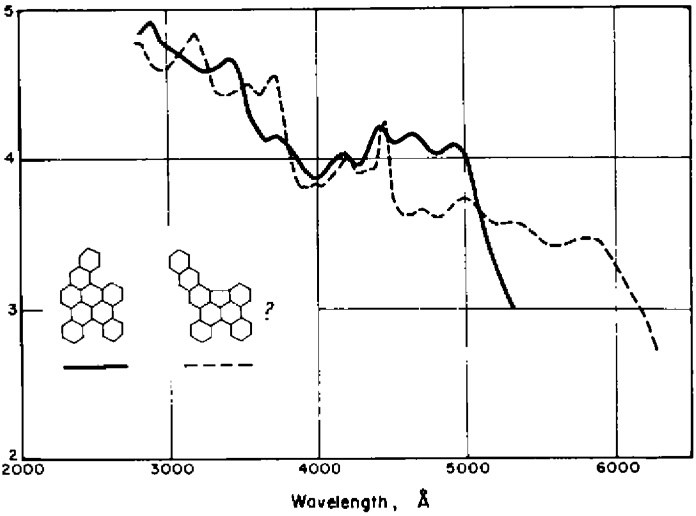


FIG. 5. Absorption max (Å) and log ε (in parentheses). 2:3,7:8-Dibenzo-1,12-(*o*-phenylene)-perylene (XVII) in benzene, 4900 (4·10), 4620 (4·18), 4410 (4·24), 4160 (4·06), 3720 (4·18); 3400 (4·69); 2890 (4·94). 5:6-Benzo-7,10-(*o*-phenylene)-naphtho-2‴, 3‴:2,3)-fluoranthene (XVIII) in benzene, 5840 (3·46), 5240 (3·57), 4980 (3·74), 4680 (3·66), 4460 (4·24), 4360 (3·94), 4200 (4·02), 4000 (3·84), 3940 (3·82), 3610 (4·56), 3540 (4·50), 3180 (4·84).

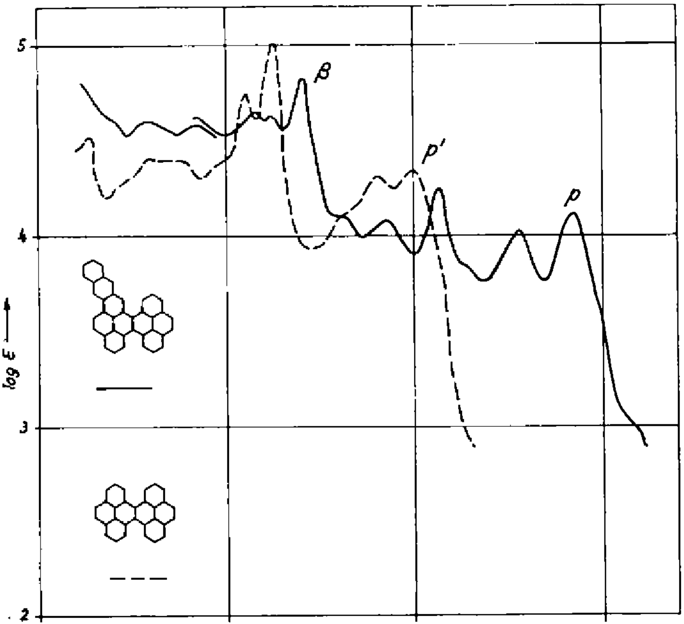
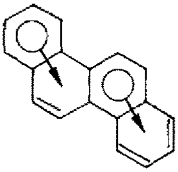
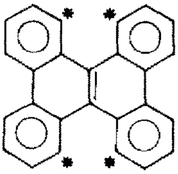
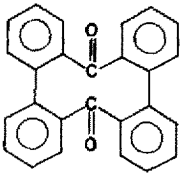


FIG. 6. Absorption max (Å) and log ε (in parentheses). Naphtho-(2″,3″:4,5)-pyreno-(1′,2′:1,2)-pyrene (XXII) in benzene, p: 4850 (4·10), 4560 (4·02); p′: 4140 (4·24), 3850 (4·08), 3630 (4·10); β: 3420 (4·82), 3260 (4·63), 3170 (4·66); in cyclohexane, 2830 (4·60), 2570 (4·60). Pyreno-(1′,2′:1,2)-pyrene as in Fig. 4.

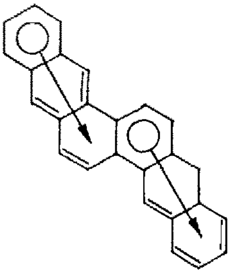

I

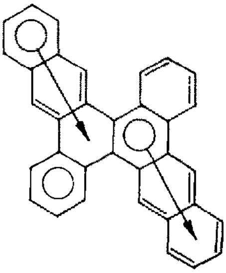

II


III

λ_β = 2670 (A) $\xrightarrow{+340}$ 3010 (A)

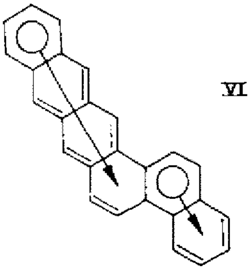
λ_p = 3190 (A) $\xrightarrow{+320}$ 3510 (A)

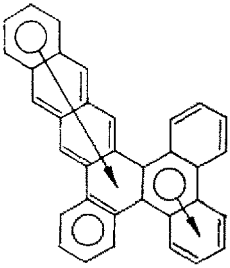

IV


V

λ_β = 3070 (B) $\xrightarrow{+150}$ 3220 (B)

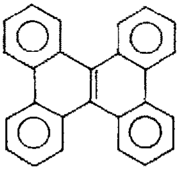
λ_p = 4200 (B) $\xrightarrow{0}$ 4200 (B)

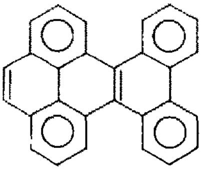

VI

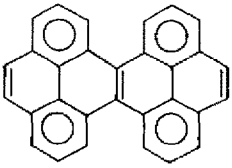

VII

λ_β = 3140 (B) $\xrightarrow{+140}$ 3280 (B)

λ_p = 4720 (B) $\xrightarrow{-60}$ 4660 (B)


II

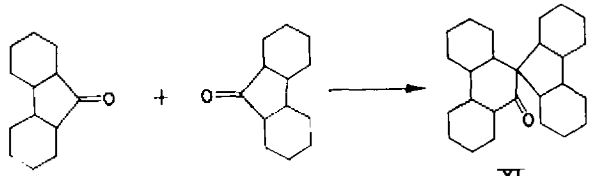

VIII


IX

λ_β = 3010 (A) $\xrightarrow{+130}$ 3140 (C) $\xrightarrow{+120}$ 2260 (C)

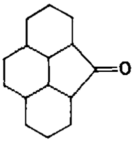
λ_p = 3510 (A) $\xrightarrow{+230}$ 3740 (C) $\xrightarrow{+260}$ 4000 (C)

Solvent: A = Alcohol, B = Benzene, C = Cyclohexane

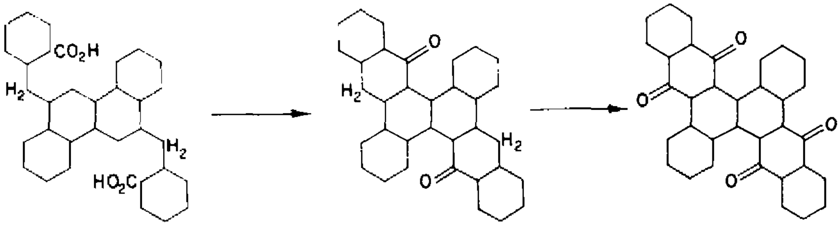


X

XI



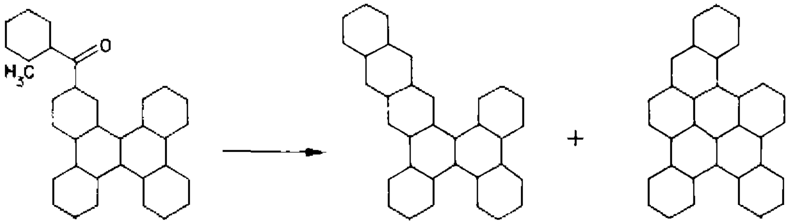
XII



XIII

XIV

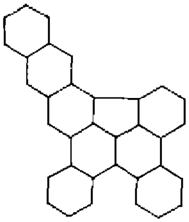
XV



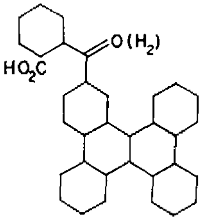
XVI

VII

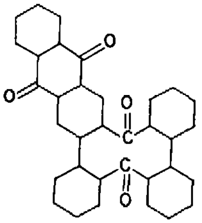
XVII



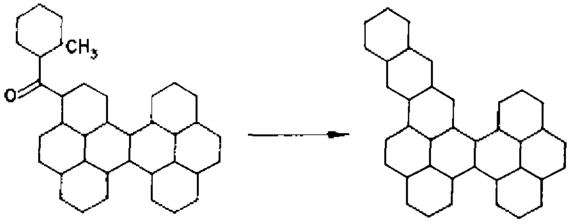
XVIII



XIX

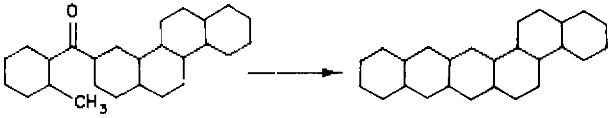


XX



XXI

XXII



XXIII

VI

being raised, with constant stirring, to 320–330° for 4 min. The initial colour of the melt was green and this became bright red and dark red in turn, the dark red organic phase separating from the molten $ZnCl_2$. The cold melt was decomposed with dil. acetic acid, and the residue was extracted with benzene. When the dark red extract was concentrated XI (7·3 g) crystallized from solution. The benzene mother liquor was chromatographed on alumina grade I. Eluting with petroleum ether 100–120° gave a yellow eluate which yielded on concentration an additional 1·8 g of XI. Eluting with benzene gave a red eluate which on concentration yielded a red resin. Compound XI crystallized from benzene in colourless prisms, m.p. 268–270° [lit. 258°].[8] The ketone dissolves in conc. H_2SO_4 to give an orange yellow solution. (Found: C, 90·3; H, 4·8. $C_{26}H_{16}O$ requires: C, 90·7; H, 4·7%).

1:2,7:8-*Dibenzochrysene* (II). The above ketone (XI; 2·5 g) was ground together with Zn dust (2·5 g), NaCl (2·5 g) and moist $ZnCl_2$ (12·5 g) were added. The mixture was melted and the temp raised over 15 min to 320–330°. After the usual decomposition the grey residue was extracted with benzene and the extract chromatographed on alumina. Eluting with benzene gave two colourless fractions, the first having a strong blue fluorescence. Evaporation of the benzene from the first fraction and crystallization of the white solid thus obtained from acetic acid gave 1:2,7:8-dibenzochrysene (II; 200 mg) as long colourless needles, m.p. 218–220° [lit. 218].[8] Compound II dissolves slowly in conc. H_2SO_4 to give a colourless solution with a blue fluorescence. (Found: C, 95·1; H, 5·0. $C_{26}H_{16}$ requires: C, 95·1; H, 5·0%).

Concentration of the second fraction gave unchanged 10:10-biphenylene-9-phenanthrone (1·2 g).

Pyreno-(1′,2′:1,2)-*pyrene* (IX). Sodium chloride (10 g) and $ZnCl_2$ (50 g) were added to an intimate mixture of 4:5-carbonylphenanthrene (XII; 10 g) and Zn dust (10 g). The mixture was melted and the temp raised, with stirring, to 320–330° for 4 min. The melt initially green in colour became red brown. After decomposition of the cold melt with dil. acetic acid the residue was extracted with ethanol. Evaporation of the ethanol and crystallization of the residue from aqueous ethanol furnished 4:5-methylenephenanthrene (500 mg) as leaflets, m.p. 114–116° undepressed on admixture with an authentic sample of 4:5-methylenephenanthrene. The ethanol insoluble residue was dissolved in xylene and chromatographed over alumina. Eluting with hot xylene gave a yellow eluate with a violet blue fluorescence which, on concentration, gave pyreno-(1′,2′:1,2)-pyrene (IX; 2·7 g) as yellow leaflets, m.p. 302–304°. When allowed to crystallize slowly from xylene or benzene, IX crystallizes in large thick yellow needles, m.p. 305–307°. Compound IX dissolves in conc. H_2SO_4 slowly, the surface of the crystals becomes dark green and the solution yellow green, the solution becoming dark green as the hydrocarbon dissolves. (Found: C, 95·8; H, 4·2. $C_{30}H_{14}$ requires: C, 95·7; H, 4·3%).

Phenanthreno-(9′,10′:1,2)-*pyrene* (VIII). A mixture of 4:5-carbonylphenanthrene (XII; 10 g) and fluorenone (X; 12 g) was ground together with Zn dust (22 g), NaCl (22 g) and $ZnCl_2$ (110 g). The mixture was melted and kept at 320–330° for 4 min, with constant stirring. The colour changed from green to red brown and the red brown organic phase separated from the $ZnCl_2$. After the usual decomposition with dil. acetic acid the residue was extracted with benzene and chromatographed over alumina grade I. Eluting with pet. ether 100–120° and then with a 1:1 mixture of pet. ether 100–120° and benzene gave a yellow brown eluate with a strong violet fluorescence followed by a colourless eluate from which 10:10-biphenylene-9-phenanthrone (230 mg) was obtained on concentration. The combined pet. ether and pet. ether–benzene fractions were concentrated and rechromatographed on alumina with pet. ether 100–120° as solvent. The UV spectra of even the earliest fractions showed that pyreno-pyrene and phenanthreno-(9′,10′:1,2)-pyrene were being eluted simultaneously. This chromatogram therefore merely served to purify the mixture. The combined fractions from the second chromatogram were concentrated and the orange yellow leaflets which crystallized from solution were dissolved in benzene. On standing pyreno-(1′,2′:1,2)-pyrene (420 mg) crystallized out. The benzene mother liquor was concentrated when phenanthreno-(9′,10′:1,2)-pyrene (VIII; 720 mg) m.p. 258–260° crystallized. After several crystallizations from benzene VIII crystallized as large very pale orange prisms, m.p. 259–261°. Compound VIII dissolves slowly in conc. H_2SO_4 to give a yellow green changing to brown red solution. (Found: C, 95·5; H, 4·7. $C_{28}H_{16}$ requires: C, 95·45; H, 4·55%).

Tetrapheno-(6′,5′:5,6)-*tetraphene* (V). 2,8-Di-(*o*-carboxybenzyl)-chrysene (XIII; 5 g) was dissolved

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[8] H. Klinger and C. Lonnes, *Ber. Dtsch. Chem. Ges.* **29**, 2156 (1896); J. Suszko and R. Schillak, *Rocz. Chem.* **14**, 1216 (1934); E. Bergmann and S. Fujise, *Liebigs Ann.* **483**, 65 (1930); K. F. Lang, H. Buffleb and J. Kalowy, *Chem. Ber.* **94**, 523 (1961).

in conc. H_2SO_4 (70 ml). The acid, insoluble in the first instance, dissolves to give a red brown changing to red solution. The mixture was allowed to stand at room temp for 10 min when the red solution was poured onto ice and the precipitated bright yellow cyclization product filtered off and washed with warm water. The moist diketone (XIV) was dissolved in hot pyridine (100 ml), Zn dust (10 g) and glacial acetic acid (10 ml) were added and the mixture heated under reflux for 3½ hr. The solution, initially orange-yellow, became yellow and after about 1 hr small yellow prisms of hydrocarbon crystallized from solution. Two additional portions of acetic acid (10 ml and 5 ml) were added at intervals of 1 hr. The cold pyridine mother liquor was filtered from excess Zn and crystallized hydrocarbon into dil. HCl and the precipitated yellow solid filtered off and washed with ammonia and water. Excess Zn was destroyed with conc. HCl acid and the crystallized hydrocarbon was combined with the yellow complex. The complex was decomposed by sublimation *in vacuo*. The sublimate, a yellow red oil was dissolved in xylene and chromatographed on alumina grade I. Development of the chromatogram with xylene gave a single yellow band which was eluted with xylene. Concentration of the yellow eluate gave tetrapheno-(6′,5′:5,6)-tetraphene (V; 420 mg) as clusters of small bright yellow needles, m.p. 320–326°. Compound V was dissolved in xylene and rechromatographed on alumina. The chromatogram was eluted with hot xylene and concentration of the first fractions gave pure V as yellow needles, m.p. 339–340°. The hydrocarbon dissolves slowly in conc. H_2SO_4 to give a yellow brown solution. (Found: C, 95·2; H, 4·7. $C_{34}H_{20}$ requires: C, 95·3; H, 4·7%).

Tetrapheno-(6′,5′:5,6)*-tetraphene-*7′,12′:7,12*-diquinone* (XV). Tetrapheno-(6′,5′:5,6)-tetraphene (V; 100 mg) was suspended in glacial acetic acid (10 ml) and CrO_3 (150 mg) in water (1 ml) was added. The mixture was refluxed for 2 hr and the brown red oxidation product which had precipitated from solution was filtered off and extracted with dil. NH_4OH leaving a brown red powder (80 mg). Repeated crystallization from nitrobenzene gave the diquinone (XV) as violet red needles, m.p. 374°(dec). Compound XV dissolves slowly in conc. H_2SO_4 to give a blue green solution which changes to violet on standing. (Found: C, 83·4; H, 3·2. $C_{34}H_{16}O_4$ requires: C, 83·6; H, 3·3%).

The diquinone (XV) *from the diketone* (XIV). Moist diketone (XIV) from 2,8-di-(*o*-carboxybenzyl)-chrysene (1 g) and conc. H_2SO_4 (14 ml) was dissolved in glacial acetic acid (30 ml). Chromium trioxide (800 mg) in water (2 ml) was added and the mixture refluxed for 15 min. The precipitated brown red solid (230 mg) was filtered off, extracted with hot dil. NH_4OH and crystallized from nitrobenzene. The diquinone (XV) crystallized as violet red needles, m.p. and mixed m.p. with a sample obtained by direct oxidation of V 374°(dec). (Found: C, 83·5; H, 3·4. $C_{34}H_{16}O_4$ requires: C, 83·6; H, 3·3%).

5-(o-*Toluyl*)-1:2,7:8*-dibenzochrysene* (XVI). Finely ground $AlCl_3$ (9·2 g) was added to a mixture of powdered 1:2,7:8-dibenzochrysene (II) (10 g) and *o*-toluyl-chloride (4·75 g) in benzene (40 ml), the colour immediately becoming deep red and HCl being evolved. The mixture was permitted to stand at room temp for 8 min when the double compound was decomposed with dil. HCl and the benzene removed by steam distillation. The yellow brown residue was powdered and extracted with dil. NH_4OH leaving the crude ketone (12 g). A portion of the ketone was crystallized from acetic acid. A second crystallization from benzene gave XVI as white prisms, m.p. 214–215°. The ketone dissolves in H_2SO_4 to give a violet changing to red solution. (Found: C, 91·35; H, 4·9. $C_{34}H_{22}O$ requires: C, 91·4; H, 5·0%).

Pyrolysis of 5-(o-*toluyl*)-1:2,7:8*-dibenzochrysene*. Crude 5-(*o*-toluyl)-1:2,7:8-dibenzochrysene (15 g) was dissolved in xylene and the xylene solution filtered. The xylene was removed by distillation and the residue was pyrolysed at 420–430° for 10 min under CO_2. The pyrolysate (10 g) was dissolved in xylene and the xylene solution concentrated to small volume. On standing a violet red compound A (440 mg) crystallized from solution. The xylene mother liquor was chromatographed on alumina grade I. Two fractions were eluted with xylene. Concentration of the first gave thick orange yellow needles of B (1·5 g) m.p. 240–244° and concentration of the second fraction gave fibrous orange yellow needles of C (100 mg) m.p. 280–282°. Eluting with xylene ether mixture gave a further 20 mg of A.

A crystallized from a large volume of xylene in small red sublimable needles of 5:6-benzonaphtho(2″,3″:2,3)-7,10-(*o*-phenylene)-fluoranthene (XVIII) m.p. 348–350°. XVIII dissolves in conc. H_2SO_4 to give a violet solution which changes to brown on standing. (Found: C, 95·85; H, 4·5. $C_{34}H_{18}$ requires: C, 95·7; H, 4·3%).

Repeated crystallization of B gave orange yellow needles of 1:2-benzophenanthreno-(9′,10′:3,4)-tetracene (VII) m.p. 247–248°. In conc. H_2SO_4 the crystal surface becomes very dark and VII dissolves to give a green brown solution. (Found: C, 95·4; H, 4·6. $C_{34}H_{20}$ requires: C, 95·3; H, 4·7%).

Crystallization of C from xylene gave 2:3,7:8-dibenzo-1,12-(*o*-phenylene)-perylene (XVII) as fibrous orange yellow needles m.p. 282°. XVII dissolves in conc. H_2SO_4 to give an emerald green solution which becomes intense dark green on standing. (Found: C, 95·8; H, 4·2. $C_{34}H_{18}$ requires: C, 95·7; H, 4·3%).

5-(o-*Carboxybenzoyl*)-1:2,7:8-*dibenzochrysene* (XIX). An intimate mixture of finely divided phthalic anhydride (2·70 g) and $AlCl_3$ (7·4 g) was added in portions to a suspension of 1:2,7:8-dibenzochrysene (6 g) in benzene (40 ml). A dark red complex formed immediately and after the evolution of HCl had ceased (12 min) the double compound was decomposed with dil. HCl, the benzene steam distilled off and the pale yellow residue extracted with dil. NH_4OH. Acidification of the filtered alkali extract furnished 5-(*o*-carboxybenzoyl)-1:2,7:8-dibenzochrysene (6·0 g) which crystallized from xylene or anisole in pale yellow prisms m.p. 178–180°. (Found: C, 85·2; H, 4·6. $C_{34}H_{20}O_3$ requires: C, 85·7; H, 4·2%).

5-(o-*Carboxybenzyl*)-1:2,7:8-*dibenzochrysene*. 5-(*o*-Carboxybenzoyl)-1:2,7:8-dibenzochrysene (13 g) was dissolved in acetic acid (260 ml) and Zn dust (39 g) added in portions to the boiling solution. The yellow colour of the solution was discharged rapidly and after refluxing for 12 hr the colourless acetic acid mother liquor was poured into water and the precipitated white solid (8·5 g) filtered off, boiled with conc. HCl, washed with water and extracted with dil. Na_2CO_3 aq. The carbonate insoluble material (5·0 g) was filtered off and acidification of the milky white carbonate extract gave 5-(*o*-carboxybenzyl)-1:2,7:8-dibenzochrysene (2·4 g). The acid was very soluble and could not be obtained in a crystalline state.

1:2-*Benzophenanthreno*-(9′,10′:3,4)-*tetracene*(VII). 5-(*o*-Carboxybenzyl)-1:2,7:8-dibenzochrysene (500 mg) was ground together with NaCl (500 mg) and Zn dust (500 mg). Zinc chloride (2·5 g) was added and the mixture melted, the temp being raised to 320–330° for 4 min with constant stirring. After the usual decomposition with dil. acetic acid the residue was extracted with xylene and chromatographed over alumina. Concentration of the orange yellow eluate gave 1:2-benzophenanthreno-(9′,10′:3,4)-tetracene (40 mg) as needles, m.p. and mixed m.p. with a sample from the pyrolysis of 5-(*o*-toluyl)-1:2,7:8-dibenzochrysene, 247–248°.

2:3,4:5,7:8-*Tribenzoanthraquinono*-(2″,3″:9,10)-*cyclodecan*-1,6-*dione* (XX). Finely powdered hydrocarbon (VII; 250 mg) was suspended in glacial acetic acid (15 ml). Chromium trioxide (260 mg) in water (2 ml) was added and the mixture refluxed for 3 hr. The cold mixture was poured into water and the precipitated oxidation product (290 mg) was filtered off. Crystallization from xylene furnished XX as small white leaflets m.p. 300°. Compound XX dissolves in conc. H_2SO_4, orange changing to yellow on standing. (Found: C, 83·51; H, 3·91. $C_{34}H_{18}O_4$ requires: C, 83·3; H, 3·7%).

5-(o-*Toluyl*)-*pyreno*-(1′,2′:1,2)-*pyrene* (XXI). Finely powdered pyreno-(1′,2′:1,2)-pyrene (IX; 3 g) was suspended in a solution of *o*-toluyl chloride (1·35 g) in benzene (25 ml). Aluminium chloride (1·35 g) was added—an intense blue coloured complex formed immediately and HCl was evolved. The mixture was heated on a water bath at 50° for 8 min and then at 60° for a further period of 15 min. The complex was decomposed with dil. HCl aq and the benzene removed by steam distillation. The residue, after extraction with hot dil. NH_4OH was in the form of a yellow brown resin (3·85 g) which on treatment with ether gave a bright yellow amorphous powder. This was dissolved in benzene and chromatographed on alumina grade "O". Eluting with benzene gave a pale yellow eluate with a blue fluorescence (unchanged pyrenopyrene) followed by a yellow solution with a strong green fluorescence. The latter solution was concentrated to small volume and pet. ether, 100–120°, added. On standing clusters of small yellow needles of 5-(*o*-toluyl)-pyreno-(1′,2′:1,2)-pyrene (XXI) crystallized from solution, m.p. 244–247°. Compound XXI was dissolved in benzene and rechromatographed on alumina grade "O". Concentration of the benzene eluate and addition of pet. ether, 100–120°, gave the ketone as small yellow needles, m.p. 253–254°. The ketone dissolves in conc. H_2SO_4 to give a blue green solution which rapidly changes to claret red. (Found: C, 92·15; H, 4·5. $C_{38}H_{22}O$ requires: C, 92·3; H, 4·5%).

Naphtho-(2″,3″:4,5)-*pyreno*-(1′,2′:1,2)-*pyrene*(XXII). Crude ketone (XXI) was dissolved in xylene, the solution filtered, the xylene distilled off and the residue heated at 430–440° under CO_2. After about 10 min, the elimination of water was complete and the pyrolysate (3·02 g) was extracted with xylene and the xylene solution chromatographed on alumina grade 1. Eluting with xylene gave firstly a yellow solution with a strong blue fluorescence which, on concentration, yielded leaflets of pyreno-(1′,2′:1,2)-pyrene (200 mg), m.p. and mixed m.p. 302–304°. Secondly an orange red eluate with a green fluorescence which afforded, on concentration, orange red needles of naphtho-(2″,3″:4,5)-pyreno-(1′,2′:1,2)-pyrene (170 mg). The hydrocarbon was crystallized in rosettes of orange red needles, m.p. 309–310°. It dissolves in conc. H_2SO_4 to give a violet solution which changes to green.

Naphtho-(2′,1′:1,2)-*tetracene* (VI). The mixture of ketones obtained from the condensation of chrysene with *o*-toluyl chloride and $AlCl_3$ in tetrachloroethane[6] was pyrolysed at 400–420° for 15 min. This product (43 g) was dissolved in xylene and chromatographed on 400 g alumina Grade 1. First cold, then hot xylene was used for eluation. Only fractions which showed the absorption band at 4720 Å were concentrated. The crystallizate (3 g) was dissolved in 1 l. of xylene. Maleic anhydride (450 mg) in xylene (100 ml) was added to the boiling solution and refluxed for 20 min. Xylene (600 ml) was distilled off during 15 min. The solution was extracted with dil. NaOH aq and the adduct precipitated with HCl. It was decomposed by sublimation in a vacuum in a CO_2 current and the sublimed hydrocarbon recrystallized from xylene. Naphthotetracene formed orange leaflets, m.p. 370°, which dissolved in conc. H_2SO_4, mauve changing to brown-violet, and finally to green. (Found: C, 94·9; H, 5·1. $C_{26}H_{16}$ requires: C, 95·1; H, 4·9%).