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BENZOLOGUES OF PERYLENE, CORONENE AND ANTHANTHRENE

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Abstract—1,12-*o*-Phenylene-2,3:10,11-dibenzoperylene (IV) was synthesized from octahydrophenanthrene and phthalic anhydride via the stages I, II and III. The synthesis of 1,2:3,4:5,6-tribenzocoronene (VIII) was carried out from the quinone (V) via the diol (VI). 1,12:2,3:6,7:8,9-Tetrabenzanthanthrene (XII) was obtained from the ketone (IX) via the compounds X and XI.

THE known octahydro-1,2:3,4-dibenzanthraquinone (I)[1] was prepared from octahydrophenanthrene, phthalic anhydride and aluminium chloride followed by a cyclization with anhydrous hydrogen fluoride. It reacted with phenyl lithium to give the diol (II). This can be dehydrated with hydrochloric acid in acetic acid to the 1,4-anthraquinone-dimethide derivative (III). This is so reactive that during its preparation some cyclization to IV takes place. This cyclization is best carried out by heating III with copper powder to 400°.

The absorption spectrum of the hydrocarbon (IV) is shown in Fig. 1 together with 1,12:2,3:10,11-tribenzoperylene.[2] Whilst the latter can be represented with aromatic sextets only, the hydrocarbon (IV) has one ring more but has also only five aromatic sextets. This causes the normal red shift of the absorption curve. In spite of this, the hydrocarbon IV (like tribenzoperylene) does not react with boiling maleic anhydride and chloranil. Neither hydrocarbon shows any perylene character, since no butadiene system can be localized in positions 6 and 7 without sacrificing two sextets.

The quinone (V) was synthesized from phthalic anhydride, hexahydropyrene and aluminium chloride. The resulting keto-acid[3] was cyclized with anhydrous hydrogen fluoride.

The reaction of the quinone (V) with phenyl lithium yielded the diol (VI). Spontaneous dehydration gave the tetracenequinone-dimethide derivative (VII) and cyclization with copper powder at 420°, the tribenzococonene (VIII). The absorption spectra of both these hydrocarbons are given in Fig. 2. The spectrum of tribenzocoronene (VIII) is closely related to other benzologues of coronene. The spectrum of the hydrocarbon (VII) is of a remarkable simplicity showing no relation to tetracene, because of interrupted aromatic conjugation caused by the methylene groups.

The preparation of the known ketone (IX)[4] was modified and improved. When reduced with amalgamated aluminium it formed the diol (X), which was dehydrated to the hydrocarbon (XI). This latter cyclized to tetrabenzanthanthrene (XII) on heating with copper powder. Figure 3 shows the absorption spectra of tetrabenzanthanthrene (XII) and 1,12:2,3:10,11-tribenzoperylene.[2] Both hydrocarbons can

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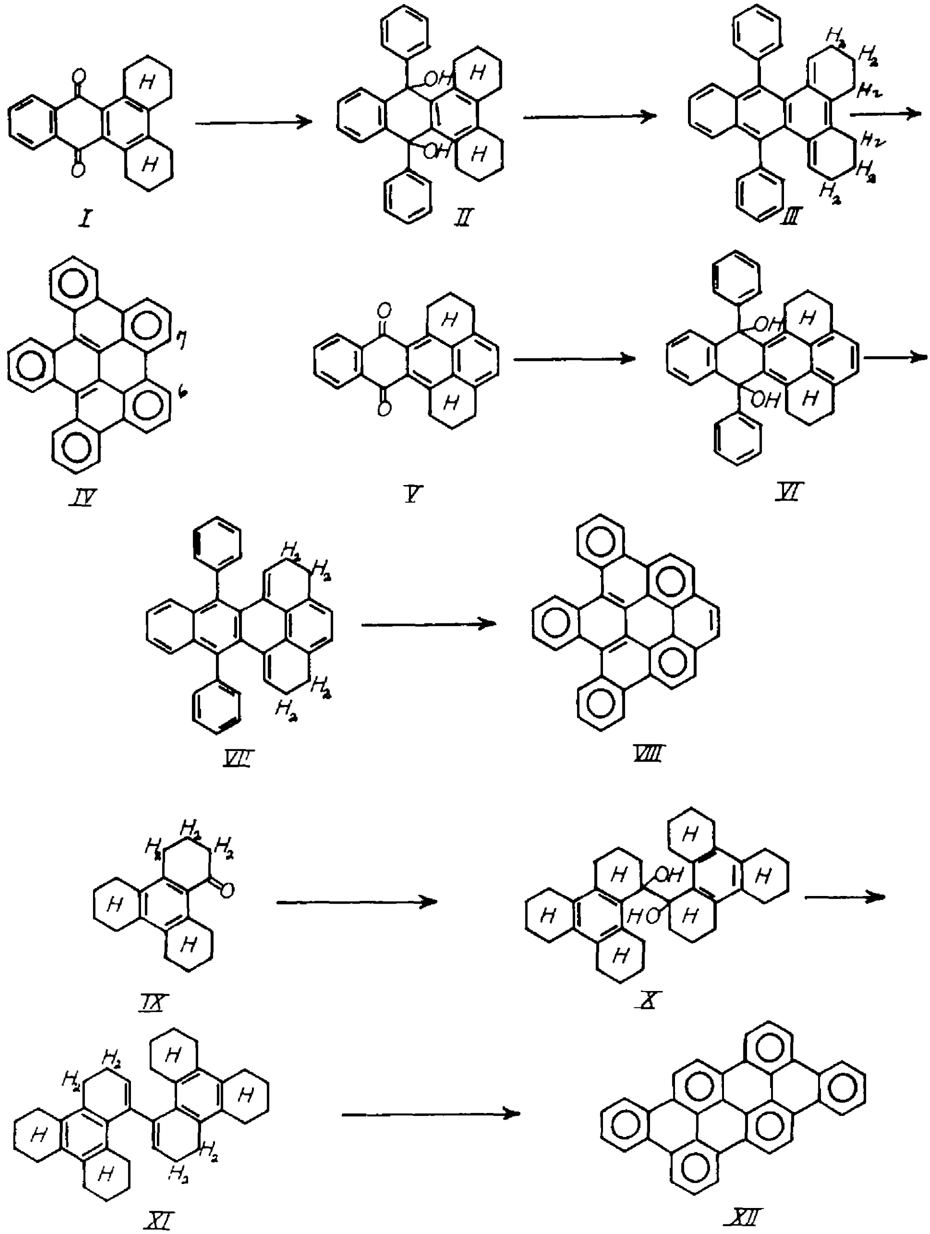
[1] E. de Barry–Barnett, N. F. Goodway and C. A. Lawrence, *J. Chem. Soc.* 1684 (1935); C. Weizmann, E. Bergmann and T. Berlin, *J. Amer. Chem. Soc.* **60**, 1331 (1938); F. Bergmann, H. E. Eschinasi and M. Weeman, *J. Org. Chem.* **8**, 179 (1943).

[2] E. Clar and M. Zander, *J. Chem. Soc.* 1861 (1958).

[3] J. M. L. Cameron, J. W. Cook and W. Graham, *J. Chem. Soc.* 286 (1945).

[4] J. van de Kamp, A. Burger and E. Mossetig, *J. Amer. Chem. Soc.* **60**, 1312 (1938).

be formulated with aromatic sextets only. In accordance with this they are extremely stable and do not react with boiling maleic anhydride and chloranil. Further they do not dissolve in concentrated sulphuric acid and they show a phosphorescence of very long life in solid solution at low temperature. These properties are typical of hydrocarbons of this type.[5]



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[5] E. Clar, *Tetrahedron* **9**, 202 (1960); E. Clar and M. Zander, *Proc. Chem. Soc.* 150 (1958); E. Clar, C. T. Ironside and M. Zander, *J. Chem. Soc.* 142 (1959); M. Zander, *Ber. Dtsch. Chem. Ges.* **92**, 2744 (1959); E. Clar, G. S. Fell and M. H. Richmond, *Tetrahedron* **9**, 105 (1960).

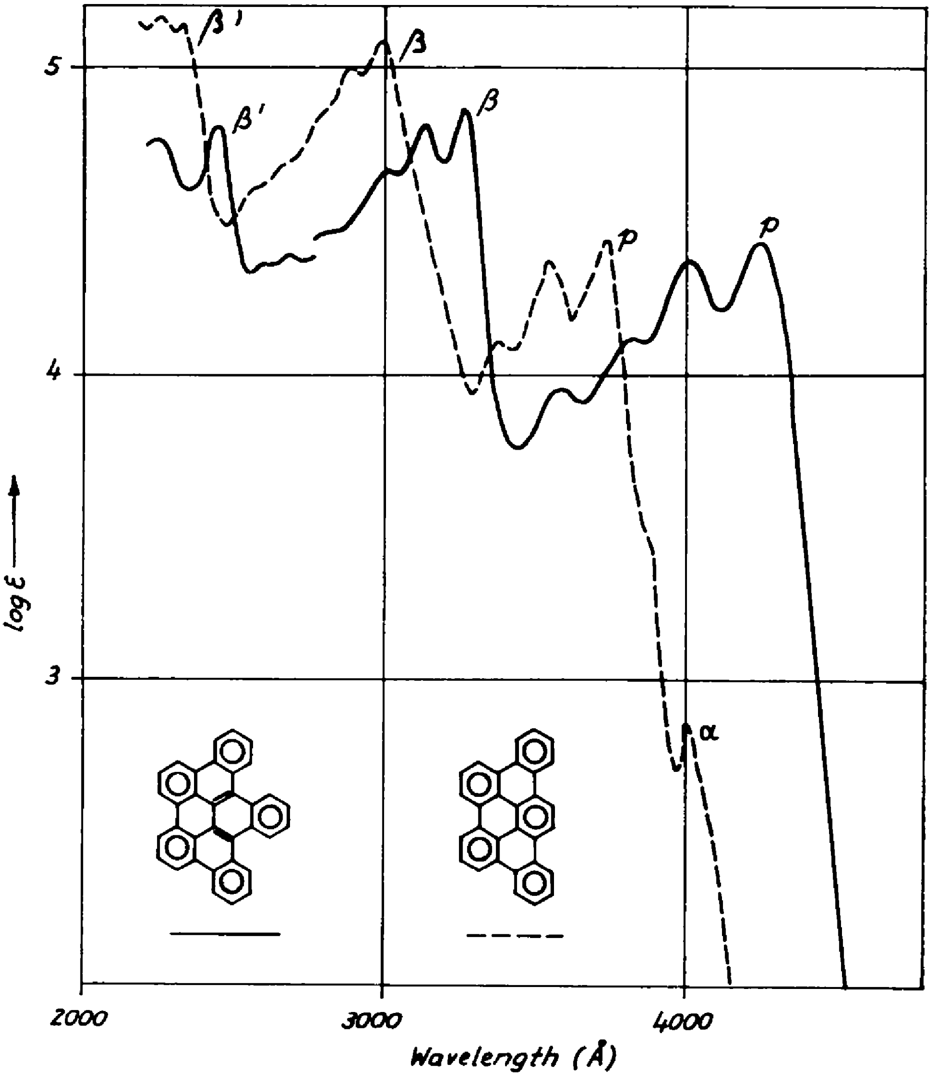

FIG. 1. Absorption max (Å) and log ε (in parentheses). 1,12-(o-Phenylene)-2:3,10:11-dibenzoperylene (IV) in benzene, p:4260 (4·43), 4020 (4·37), 3820 (4·11), 3580 (3·95); β:3260 (4·87), 3130 (4·82), 3010 (4·67); β:2450 (4·80). From 2800 Å in cyclohexane. 1:12,2:3,10:11-Tribenzoperylene in trichlorobenzene, α:4010 (2·86); p:3740 (4·45), 3540 (4·37), 3380 (4·11); β:3000 (5·09), 2880 (5·00); β:2340 (5·14). From 3000 Å in ethanol.

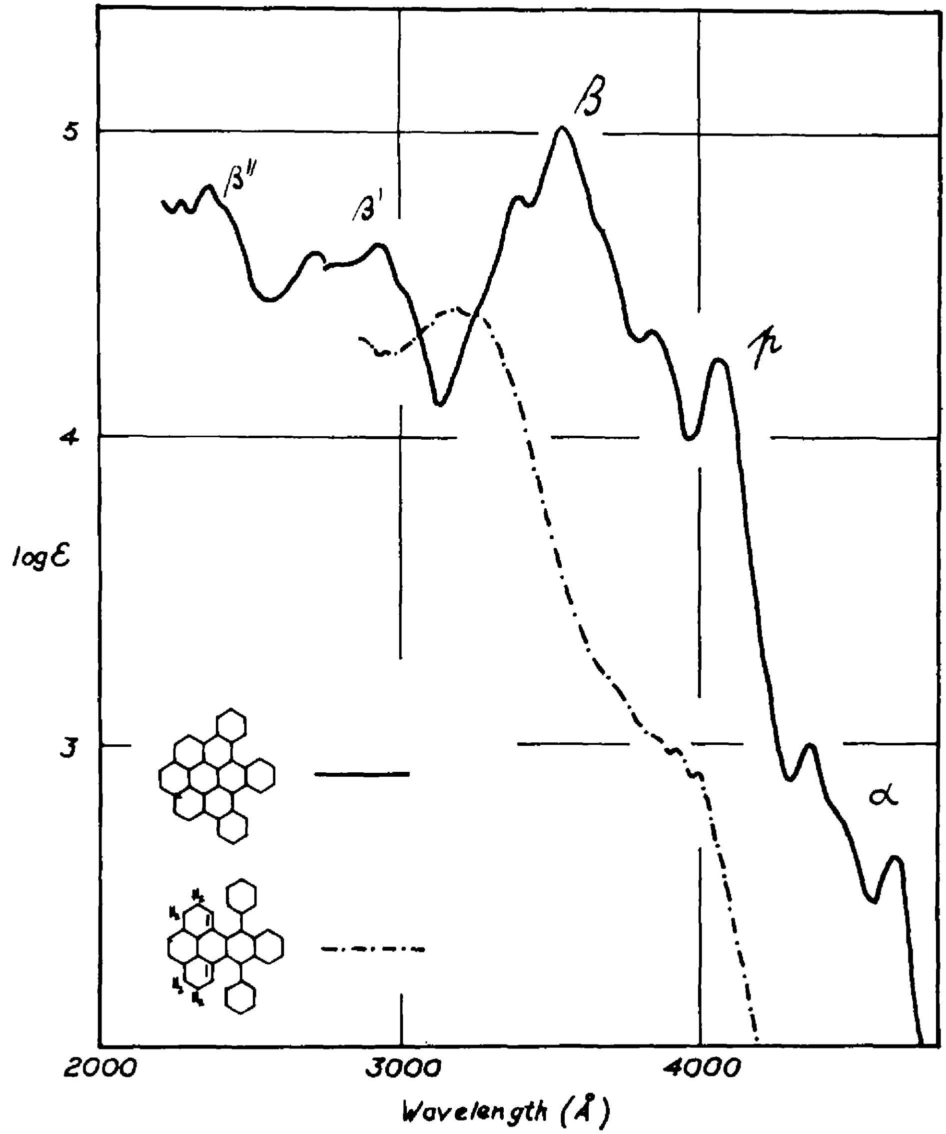

FIG. 2. Absorptions max (Å) and log ε (in parentheses). 1:2,3:4,5:6-Tribenzocoronene (VIII) in benzene, α: 4640 (2·62), 4360 (2·98); p: 4070 (4·25), 3840 (4·34); β: 3540 (5·00), 3400 (4·78); β'': 2930 (4·62); 2720 (4·60); in cyclohexane β'': 2360 (4·81). 1',4'-Diphenyl-naptho-(2',3': 1,2)-4,5,8,9-tetrahydro-pyrene (VII) in benzene, 3190 (4·41).

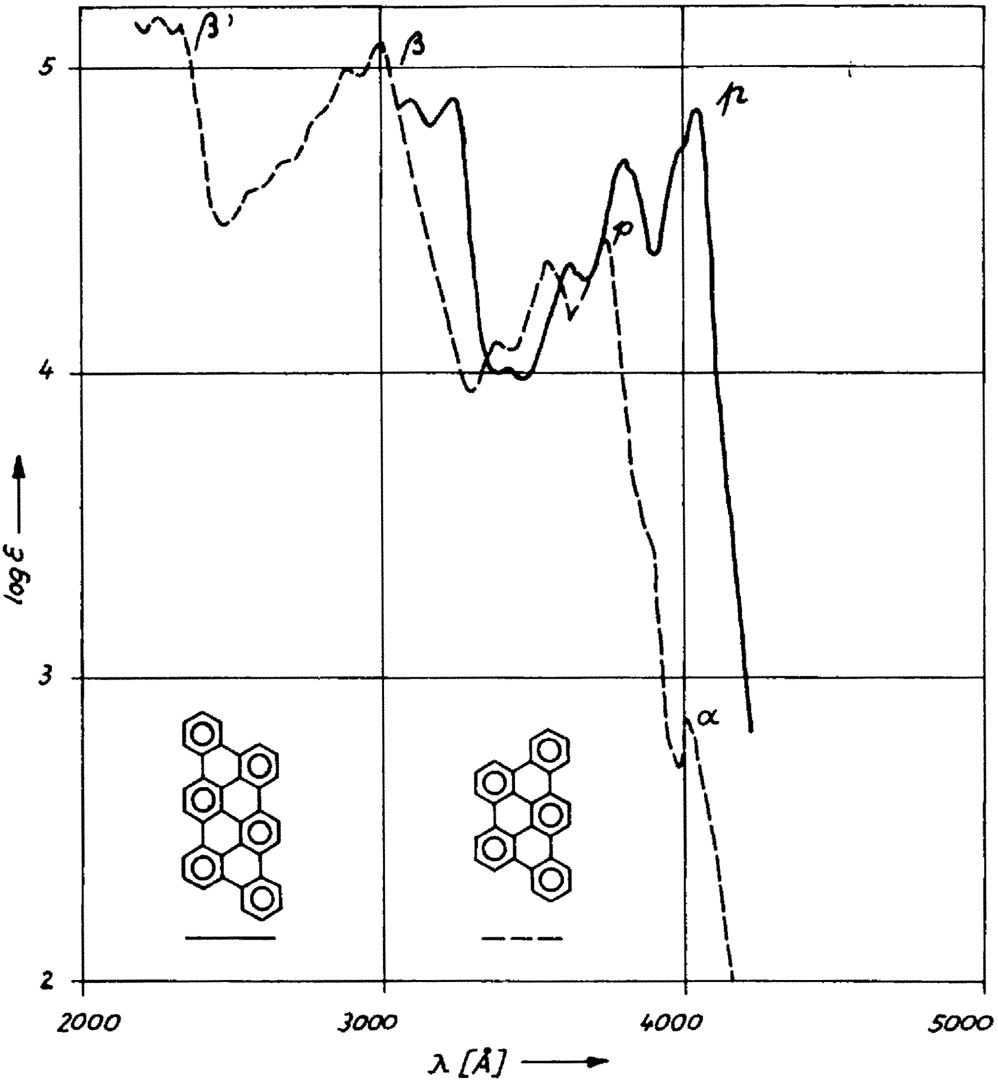

FIG. 3. Absorption max (Å) and log ε (in parentheses). 1:12,2:3,6:7,8:9-Tetrabenzanthanthrene (XII) in trichlorobenzene, p:4040 (4·86), 3800 (4·69), 3620 (4·35); β:3240 (4·89), 3090 (4·88). 1:12,2:3,10:11-Tribenzoperylene in trichlorobenzene, α:4010 (2·86) p:3740 (4·45), 3540 (4·37), 3380 (4·11); β:3000 (5·09), 2880 (5·00); β:2340(5·14). From 3000 Å in ethanol.

EXPERIMENTAL*

1′,2′,3′,4′,1″,2″,3″,4″*Octahydro*-1,2,3,4-*dibenzanthraquinone* (I). The condensation of phthalic anhydride with octahydropenanthrene and $AlCl_3$ was carried out with benzene as solvent and gave the keto-acid in high yield. The m.p. was 201–202° (Lit. 200°)[1] when recrystallized from xylene. The keto-acid (10 g) was slowly added to anhydrous HF (200 ml), the colour darkening rapidly from the original yellow-brown. After 18 hr, the solution was decomposed with ice-water and the pale yellow solid obtained extracted with dil. Na_2CO_3 aq. The residue (5 g) crystallized from xylene as long pale yellow prisms, m.p. 242–244° (Lit. 238–239°).[1] The quinone (I) dissolved in conc. H_2SO_4 to give a red solution and did not form a vat with alkaline sodium dithionate.

1′,2′,3′,4′,1″,2″,3″,4″-*Octahydro*-1,2:3,4-*dibenzo*-9,10-*diphenyl-dihydroxy-anthracene* (II). A solution of the quinone (I; 3 g) in dry benzene (50 ml) was slowly added to an ethereal solution of phenyl lithium which was prepared from bromobenzene (4 g) and Li (0·4 g). The mixture was refluxed 2 hr and then decomposed with ice-water. The benzene was distilled off and the residue, after washing with dil. acetic acid, treated with ether. The solid diol (2·5 g) was recrystallized from benzene and formed colorless prisms, m.p. 260–264° (dec) which dissolved in conc H_2SO_4 acid to give a green solution changing to brown in standing. (Found: C, 86·5; H, 6·7. $C_{34}H_{32}O_2$ requires: C, 86·4; H, 6·8%.)

2′,3′,4′,2″,3″,4″-*Hexahydro*-1,2:3,4-*dibenzo*-9,10-*diphenylanthracene* (III). The diol (1 g) was dissolved in glacial acetic acid and 1 drop conc. HCl added. The solution immediately became yellow and on refluxing for 10 min a yellow precipitate formed. This was filtered off and crystallized from benzene. It formed greenish-yellow needles (0·5 g), m.p. 281–282 which dissolved in conc. H_2SO_4 to give a pink solution which turned to red with a red fluorescence on standing. (Found: C, 93·8; H, 5·9. $C_{34}H_{28}$ requires: C, 93·9; H, 6·1%.)

1,12-*o-Phenylene*-2,3:10,11-*dibenzoperylene* (IV). The diol (2 g) was ground with Cu powder and heated at 400° for 30 min under protection (stream of CO_2). A yellow oil was obtained and this and the Cu powder were extracted with benzene and the solution chromatographed on alumina. Concentration of the solution gave a yellow solid which was sublimed. The sublimate crystallized from benzene in yellow leaflets (0·7 g), m.p. 324–324·5°, which dissolved very slowly in conc H_2SO_4 to form a blue solution. The hydrocarbon did not react when boiled with maleic anhydride and chloranil for 5 hr. (Found: C, 95·7; H, 4·4. $C_{34}H_{18}$ requires: C, 95·7; H, 4·3%.)

3,4,5,8,9,10-*Hexahydro-naphtho*-(2′,3′:1,2)-*pyrene*-1′,4′-*quinone* (V). The keto-acid[3] was prepared from phthalic anhydride, hexahydropyrene and $AlCl_3$ in benzene. The keto-acid (5 g) dissolved in anhydrous HF (100 ml) to give a violet solution which soon became green. After 20 hr the solution was decomposed with ice-water and the yellow solid filtered off. Crystallization from xylene gave bright yellow needles (3·9 g) of the quinone, m.p. 197–198° which dissolved in conc H_2SO_4 to give a green-blue solution. The quinone (V) did not form a vat with alkaline sodium dithionate. (Found: C, 85·1; H, 5·7. $C_{24}H_{18}O_2$ requires: C, 85·2; H, 5·4%.)

1′,4′-*Diphenyl-naphtho*-(2′,3′:1,2)-4,5,8,9-*tetrahydro-pyrene* (VII). A solution of the quinone (V; 2 g) in benzene was added to an ethereal solution of phenyl lithium which was prepared from bromobenzene (3 g) and Li (0·4 g). The mixture which became red, was refluxed for 15 min and then decomposed with ice-water and dil. acetic acid. The benzene was removed by steam distillation and then treated with ether. A red product went into solution and the hydrocarbon (0·4 g) remained undissolved. It gave colourless needles, m.p. 312–314° on crystallization from benzene and dissolved in conc H_2SO_4 to form a green solution. (Found: C, 94·5; H, 5·4. $C_{36}H_{26}$ requires: C, 94·3; H, 5·7%.)

The ethereal solution after evaporation gave a red solid which proved to be a hydrocarbon. Due to its sensitivity to light and air it could not be obtained in a pure state. It is probably a tetracene derivative. (Found: C, 94·0; H, 6·1. $C_{36}H_{28}$ requires: C, 93·9; H, 6·1%.)

1,2:3,4:5,6-*Tribenzocoronene* (VIII). The above crude hydrocarbon (1 g) was ground with Cu powder and heated (under CO_2) at 420° for 1 hr. The Cu powder was extracted with benzene and the solution chromatographed on alumina. Concentration yielded a dark yellow product which was sublimed at $330°/10^{-2}$ mm. The sublimate crystallized from benzene to give yellow needles, m.p. 350–351° (0·15 g) which did not dissolve in conc H_2SO_4. (Found: C, 95·9; H, 4·3. $C_{36}H_{18}$ requires: C, 96·0; H, 4·0%.)

β-9-(1,2,3,4,5,6,7,8-*Octahydrophenanthroyl*)-*propionic acid.* Powdered $AlCl_3$ (40 g) was added to a solution of octahydrophenanthrene (30 g) and succinic anhydride (20 g) in benzene (100 ml).

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

After agitation for 2½ hr at room temp, the red mixture was decomposed with dil. HCl and ice and the pale green solid isolated. It was dissolved in dil. KOH aq. and the hot, filtered solution acidified to give the keto-acid (41 g). It crystallized from xylene to yield large white blades (38 g), m.p. 142–43° (Lit. 143–144°) which dissolved in conc. H_2SO_4 to form a yellow solution.

γ-9-(1,2,3,4,5,6,7,8-*Octahydrophenanthryl*)-*butyric acid*. The above acid (20 g) was added to conc. HCl (120 ml), glacial acetic acid (120 ml), xylene (100 ml) and Zn wool (200 g). The mixture was refluxed for 6 hr, two 40 ml portions of conc. HCl being added during this period. The xylene layer was removed and concentrated, and the resulting colourless acid crystallized from cyclohexane. It formed white needles (14·8 g), m.p. 127–128° (Lit, 128–129°) and gave a yellow solution with conc. H_2SO_4.

1-*Keto*-1,2,3,4,5,6,7,8,9,10,11,12-*dodecahydrotriphenylene* (IX). The above acid (10 g) was added to anhydrous HF (150 ml), a yellow coloration developing. After 3 hr, the solution was decomposed with ice-water and the white solid obtained filtered off. This crystallized from 50% ethanol-benzene in long white needles (7·9 g) m.p. 222–223° (Lit. 222–222·5°)[4] which dissolved in conc H_2SO_4 to give a green solution.

1,1′-*Di*-(3,4,5,6,7,8,9,10,11,12-*Octahydrotriphenylenyl*) (XI). Absolute ethanol (10 ml) was added to dry benzene (120 ml) and about 15 ml of the resulting solution was distilled off. Freshly scratched thin Al foil (4 g), $HgCl_2$ (0·6 g), and finally the above ketone (12 g) were added in rapid succession. The mixture was refluxed 24 hr and the supernatant liquid decanted from the metal. On cooling, the solution deposited crystals of unreacted ketone and these were filtered off and the solvents removed. The white residue was refluxed 3 hr with a 1:1 mixture of acetic anhydride and acetic acid. White prismatic crystals (1·3 g) precipitated from solution at the beginning of ebullition. These were recrystallized from benzene, had m.p. 236–237° and dissolved in conc. H_2SO_4 to give a ruby red solution. (Found: C, 91·1; H, 8·9. $C_{36}H_{42}$ requires: C, 91·3; H, 8·9%.)

1,12:2,3:6,7:8,9-*Tetrabenzanthanthrene* (XII). The above hydrocarbon (XI) was dehydrogenated with Cu powder (under CO_2) at 420° for 70 min. Sublimation of the mixture at 400° and 10^{-3} yielded yellow plates (15 mg). These were extracted with boiling trichlorobenzene and the residue re-sublimed. The pale yellow plates, m.p. 530°, did not dissolve in conc. H_2SO_4 and showed an orange phosphorescence of very long life in solid solution in 1,2,4-trichlorobenzene, cooled in liquid air. (Found: C, 95·7; H, 4·2. $C_{36}H_{18}$ requires: C, 96·0; H, 4·0%.)