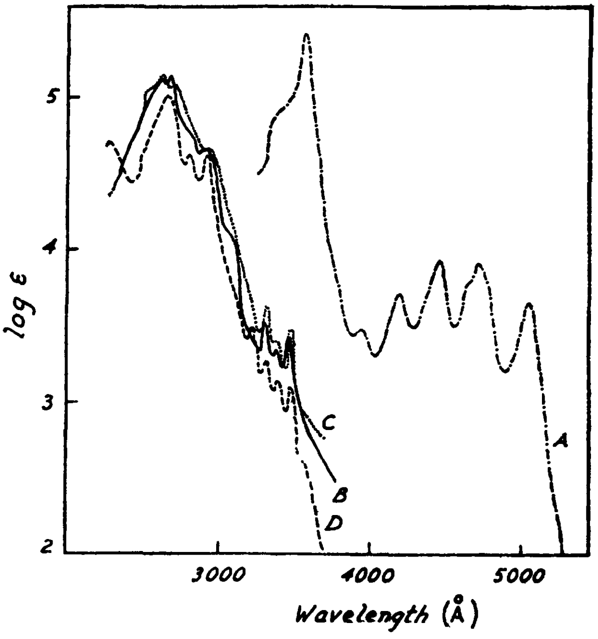
359. 1 : 2-3 : 4-8 : 9-10 : 11-*Tetrabenzopentacene.*

By E. Clar, W. Kelly, and W. G. Niven.

Tetrabenzopentacene (III) has been synthesised from (*a*) 1:2:3:4:5:6:7:8-octahydrophenanthrene and (*b*) phenanthrene and pyromellitic anhydride. The mono- and the di-quinone of the hydrocarbon and its addition product with maleic anhydride have been prepared.

Pyromellitic anhydride has been condensed twice with 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenanthrene in the presence of aluminium chloride. The product, which is a mixture of (I) and the corresponding *iso*phthalic acid, was cyclised in a melt of sodium chloride and zinc chloride [cf. the cyclisation of *o*-(octahydro-9-phenanthroyl)benzoic acid [1]]. The product was not tetrahydrotetrabenzopentacene, as expected, but 6 : 13-dihydrotetrabenzopentacene (II), probably owing to oxidation by air during the reaction. A small quantity of the tetrabenzopentacene (III) which was also formed was removed during recrystallisation by the addition of some maleic anhydride.



Absorption spectra of:

(*A*) 1 : 2-3 : 4-8 : 9-10 : 11-*Tetrabenzopentacene* (III) *in* 1-*methylnaphthalene. Max.* (Å; log ε *in parentheses*): 5050 (3·67), 4720 (3·93), 4470 (3·95), 4200 (3·73), 3950 (3·49), 3570 (5·41).

(*B*) 6 : 13-*Dihydro*-1 : 2-3 : 4-8 : 9-10 : 11-*tetrabenzopentacene* (II) *in dioxan. Max.*: 3470 (3·43), 3380 (3·34), 3310 (3·51), 2910 (4·66), 2680 (5·14), 2620 (5·12).

(*C*) *Dipotassium salt from the maleic anhydride adduct* (VII) *in alcohol. Max.*: 3480 (3·48), 3390 (3·40), 3330 (3·63), 2930 (4·66), 2700 (5·09), 2620 (5·15).

(*D*) *Disodium salt from the maleic anhydride adduct of* 1 : 2-3 : 4-*dibenzopentacene* [2] *in water. Max.*: 3470 (3·11), 3380 (3·16), 3310 (3·28), 3205 (3·51), 2915 (4·62), 2800 (4·63), 2650 (5·02).

The same dihydrotetrabenzopentacene was synthesised from pyromellitic anhydride, phenanthrene, and aluminium chloride. Although the Friedel–Crafts reaction should

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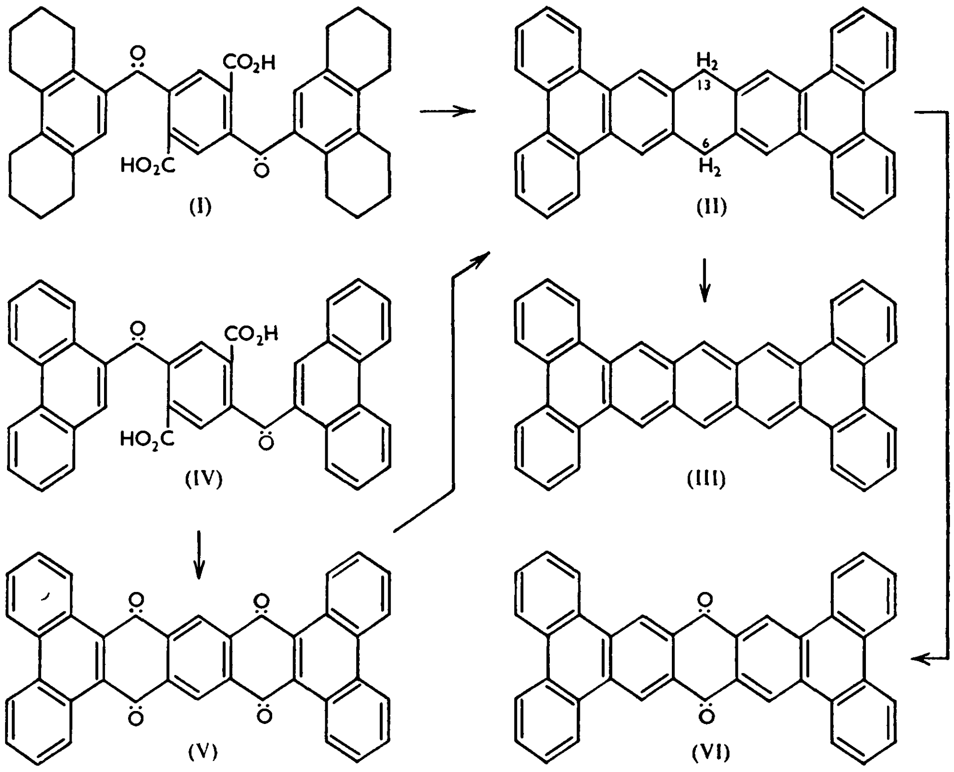
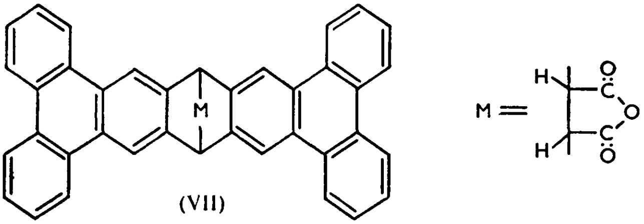
[1] Clar, *J.*, 1949, 2168.

yield numerous isomers, only one dicarboxylic acid was obtained, being either the terephthalic acid (IV) or the isomeric *iso*phthalic acid.

Ring closure with benzoyl chloride and sulphuric acid gave the diquinone (V) which was reduced by pyridine, zinc dust, and acetic acid to 6 : 13-dihydrotetrabenzopentacene (II). This was identical with the hydrocarbon obtained as above.





(VII)

1 : 2-3 : 4-8 : 9-10 : 11-Tetrabenzopentacene (III) was obtained from the dihydro-compound (II) by dehydrogenation over palladium–charcoal at 370°. It is an orange-red hydrocarbon which, as expected, is considerably less reactive than pentacene, but it still reacted very quickly with maleic anhydride to form the colourless adduct (VII). The adduct and the dihydro-compound (II) contain the aromatic complexes of two triphenylene molecules, as shown by the close similarity (see Figure) between the absorption spectra of (II) and (VII), and that of the maleic anhydride adduct of 1 : 2-3 : 4-dibenzopentacene.[2]

The dihydro-compound (II) was oxidised by selenium dioxide in boiling nitrobenzene to the monoquinone (VI).

Clar and Frommel, *Ber.*, 1948, **81**, 163.

EXPERIMENTAL

M. p.s were taken in evacuated capillaries. Microanalyses are by Mr. J. M. L. Cameron and Miss M. W. Christie.

Di-(1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydro*-9-*phenanthroyl*)*benzenedicarboxylic Acids* (I and an isomer).—A mixture of the octahydrophenanthrene (21 g.), pyromellitic anhydride (11 g.), and powdered aluminium chloride (27 g.) was heated in tetrachloroethane (120 ml.). The reaction became vigorous at 60° and was continued until evolution of hydrogen chloride ceased, the final temperature being 80—85°. After the mixture had been cooled and decomposed, the tetrachloroethane solution was washed with dilute hydrochloric acid, then extracted several times with dilute aqueous ammonia, and the combined extracts were acidified with hydrochloric acid. The light fawn mixture of isomers (10 g.) crystallised with difficulty from nitrobenzene or acetic acid as a non-uniform powder of unsharp m. p. (Found : C, 78·2; H, 5·7. Calc. for $C_{38}H_{38}O_6$: C, 77·3; H, 6·5%). This product, in concentrated sulphuric acid, gave a brownish-yellow solution, which, on being heated, changed through brownish-orange to a light brown.

6 : 13-*Dihydro*-1 : 2-3 : 4-8 : 9-10 : 11-*tetrabenzopentacene* (II).—A mixture of powdered acid (I) (6 g.), sodium chloride (1·2 g.), and finely divided zinc chloride (6 g.) was heated to 330° during 10—15 min. The cooled solid melt was powdered and extracted with boiling dilute hydrochloric acid and then with hot dilute ammonia solution. The residue was dried and sublimed *in vacuo*. The orange sublimate crystallised from xylene as orange needles. When a small quantity of maleic anhydride was added during crystallisation, colourless needles, m. p. 426—428°, of the *dihydro-compound* (II) were obtained (Found : C, 94·8; H, 5·0. $C_{38}H_{24}$ requires C, 95·0; H, 5·0%). Before melting, the colourless crystals became pale orange and they melted to give a reddish-orange melt.

1 : 2-3 : 4-8 : 9-10 : 11-*Tetrabenzopentacene* (III).—The dihydro-compound (II) (0·1 g.) was sublimed *in vacuo* through an electrically heated tube of granulated palladium–charcoal (20%) in a slow stream of carbon dioxide at 370°. The sublimate of red needles (0·06 g.) crystallised from 1 : 2 : 4-trichlorobenzene in red needles, m. p. 498—499°, being the *tetrabenzopentacene* (Found : C, 95·4; H, 4·5. $C_{38}H_{22}$ requires C, 95·4; H, 4·6%). Its orange solution in trichlorobenzene had a green fluorescence. It was insoluble in cold concentrated sulphuric acid but, on being heated, dissolved to give a green solution which changed to red.

Di-9-*phenanthroylbenzenedicarboxylic Acid* (IV or an isomer).—A solution of phenanthrene (40 g.) in tetrachloroethane (150 ml.) was added to a mixture of powdered pyromellitic anhydride (22 g.) and powdered aluminium chloride (60 g.) in tetrachloroethane (150 ml.). The temperature was raised to 75°, at which a vigorous evolution of hydrogen chloride took place and the initial orange colour of the mixture became dark brown. This temperature was maintained for 30 min. with frequent shaking, and, after being cooled, the mixture was decomposed. The organic layer was separated and washed several times with hot dilute hydrochloric acid and hot water. Xylene (400 ml.) was added to the tetrachloroethane solution, and the light brown precipitate was washed with xylene, dried, and extracted with dilute aqueous ammonia. The ammonia solution was acidified with hydrochloric acid to give 34 g. of precipitate. Crystallisation from nitrobenzene several times gave uniform colourless needles, m. p. 377—378° (decomp.), of an *acid* (Found : C, 79·1; H, 3·9. $C_{38}H_{22}O_6$ requires C, 79·4; H, 3·9%) which dissolved in hot concentrated sulphuric acid to give a brownish-orange solution which changed to brownish-yellow. Similar results were obtained when benzene was used as solvent instead of tetrachloroethane.

1 : 2-3 : 4-8 : 9-10 : 11-*Tetrabenzopentacene*-5 : 14-7 : 12-*diquinone* (V).—The crude acid (IV) (10 g.) was heated under reflux with benzoyl chloride (200 ml.). Concentrated sulphuric acid was added dropwise. Each drop of sulphuric acid produced a transient green colour. Acid was added until the green colour was no longer produced. The solution was boiled for a further 10 min. Fine brownish-red needles (6 g.) separated from the boiling solution. These were sublimed *in vacuo* and recrystallised from 1 : 2 : 4-trichlorobenzene, to give small red needles, m. p. 486—487°, of the *diquinone* (V) (Found : C, 84·5; H, 3·2. $C_{38}H_{18}O_4$ requires C, 84·75; H, 3·4%). It gave a green colour in hot concentrated sulphuric acid; in alkaline sodium dithionite solution it gave a violet vat from which the diquinone could be recovered by shaking with air.

6 : 13-*Dihydro*-1 : 2-3 : 4-8 : 9-10 : 11-*tetrabenzopentacene* (II).—The diquinone (0·7 g.), zinc dust (10 g.), and pyridine (150 ml.) were heated under reflux and acetic acid (80%, 25 ml.) was added during 5 hr. The dark red solution quickly changed to a transiently violet one and then slowly from reddish-orange to pale yellow. Orange-yellow plates crystallised during the

reaction. After being filtered off, the crystals were separated from the zinc dust by treatment with hydrochloric acid. Sublimation of the residue *in vacuo* gave pale yellow crystals (0·15 g.). Crystallisation from xylene containing small amounts of maleic anhydride gave colourless needles of the hydrocarbon (II), m. p. 425—427° (Found : C, 94·9; H, 4·8%). There was no depression of the m. p. when this compound was mixed with the dihydro-compound obtained as above. The ultraviolet spectra of the two compounds were identical. Dilution of the pyridine mother-liquor, with water, from the above filtration yielded a further 0·3 g. of the dihydro-compound.

1 : 2-3 : 4-8 : 9-10 : 11-*Tetrabenzopentacene*-6 : 13-*quinone* (VI).—A solution of the dihydro-compound (II) (0·2 g.) in nitrobenzene (15 ml.) was heated under reflux with selenium dioxide (0·18 g.) for 30 min. The reddish-brown needles which crystallised during the reaction were filtered from the hot solution and sublimed *in vacuo.* The small quantity of selenium, mixed with the needles, sublimed at a much lower temperature and was easily separated from them. The sublimate crystallised from nitrobenzene in orange feathery needles, m. p. >550°, of the *quinone* (Found : C, 90·0; H, 4·0. $C_{38}H_{20}O_2$ requires C, 89·7; H, 4·0%). It gave a red solution in hot concentrated sulphuric acid. As with other pentacene quinones, it did not form a vat with alkaline sodium dithionite.

Maleic Anhydride Adduct (VII).—A suspension of the powdered hydrocarbon (III) (30 mg.) in xylene (20 ml.) was heated under reflux with excess of maleic anhydride until the hydrocarbon had dissolved and the solution had become a faint yellow colour. The *adduct* crystallised as colourless prisms which decomposed without melting above 310° to give the red hydrocarbon (Found : C, 87·0; H, 4·5. $C_{42}H_{24}O_3$ requires C, 87·5; H, 4·2%). It dissolved in warm concentrated sulphuric acid to give a blue solution which changed to purple.

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