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2,3:4,5:8,9:10,11-TETRABENZOPERYLENE AND 1,2:3,4:7,8:9,10-TETRABENZOCORONENE

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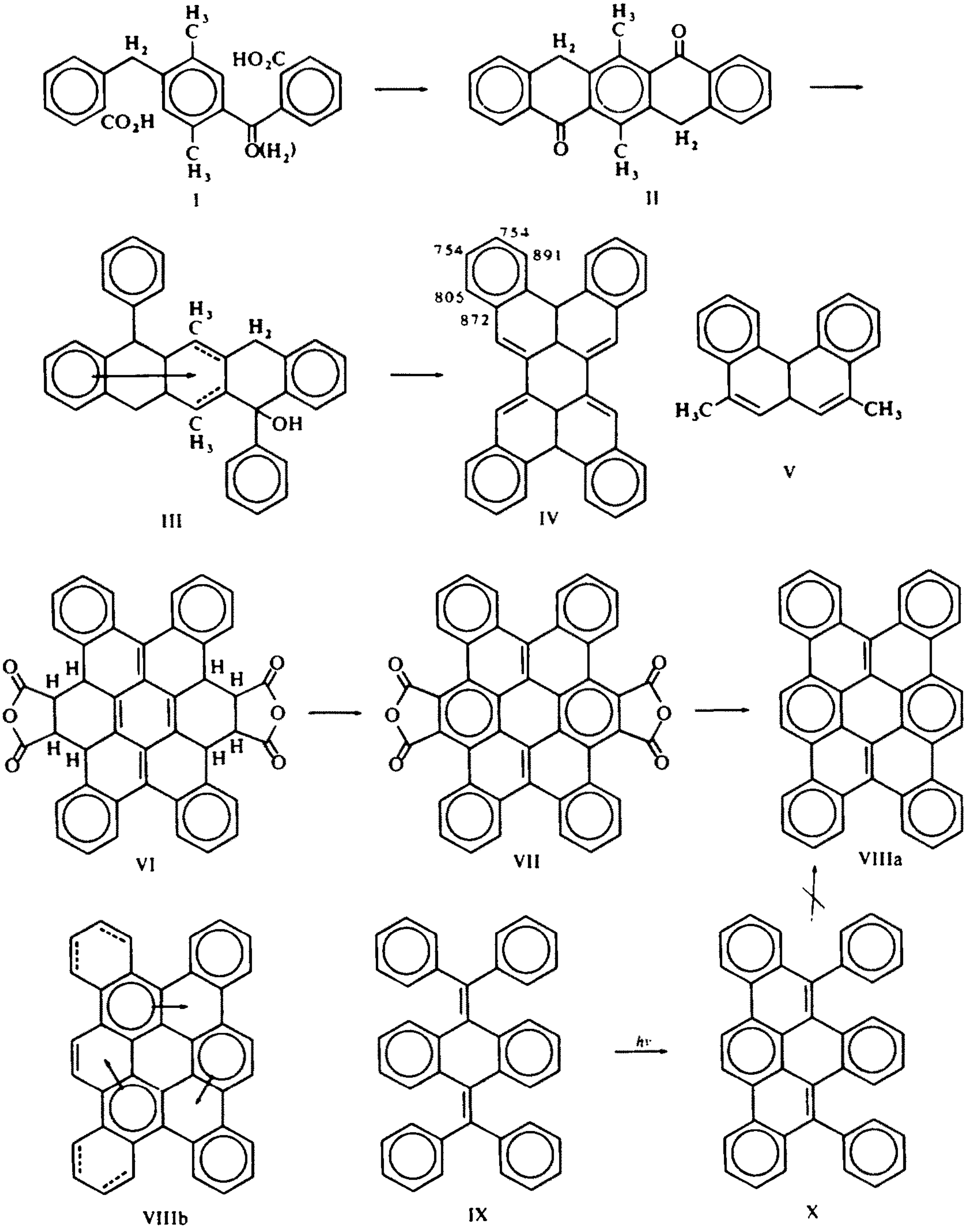
Abstract—Tetrabenzoperylene (IV) was synthesized in order to see whether it has fixed double bonds suitable for a double diene synthesis with maleic anhydride. This was found to be the case. From the double adduct (VI) tetrabenzocoronene (VIIIa) was obtained. It cannot have superaromaticity as shown in VIIIb. Attempts to obtain tetrabenzocoronene by photocyclization from IX gave diphenyltribenzopyrene (X).

THE CO group of the dicarboxylic acid (I)[1] was reduced to a CH_2 group and the resulting acid cyclized with $POCl_3$ and PCl_5 to the orange-brown double anthrone derivative (II). If the cyclization was carried out via the dichloride of the reduced dicarboxylic acid (I) with aluminium chloride a deep red isomeric compound was obtained which had the same composition, similar m.p. and *m/e*, but which had a completely different spectrum. We could not establish whether it is an enolized form of II, but we found that both compounds gave the same diphenyl-compound (III) with phenyl lithium. If the compound III was submitted to a melt with Cu powder at 400° tetrabenzoperylene (IV) was obtained.

This hydrocarbon shows a spectrum (Fig 1) which is related to perylene. However, it reacts with boiling maleic anhydride without a dehydrogenating agent to form an almost colourless adduct (VI). Perylene does not enter a similar reaction. This supports structure IV with the fixed double bonds in *cis*-butadiene positions. We found that the Me groups in dimethylbenzophenanthrene (V)[2] give doublets (separation 1.-Hz) in the NMR spectrum which is in agreement with the assumption of fixed double bonds as in formula V. Thus it might be justified to consider tetrabenzoperylene as composed of two benzophenanthrene complexes. In this case the centre ring in IV should be void of π-electrons. However, the NMR spectrum contradicts this view. The chemical shifts (in Hz from TMS at 100 MHz in CS_2) are recorded in formula IV. The "Bay" protons at 872 Hz form a sharp singlet which is indicative of π-electrons causing a ring current in the central ring.[3] Under the same conditions the bay protons in perylene (in 1,12 and 6,7-positions) which has an empty central ring, give a signal at 805 Hz and the bay protons of phenanthrene (in 4,5-position) at 850 Hz. The big chemical shift of 872 Hz in tetrabenzoperylene makes it impossible that it could have an empty ring.

This is confirmed by the electronic spectra. If perylene is composed of two naphthalene complexes connected by single bonds, there is a shift of the β-bands of 300 Å. This accounts well for the shift produced by two single bonds connecting the two moieties.

If tetrabenzoperylene (IV) is built up from two benzophenanthrene complexes a shift of 460 Å is recorded which is far too much for two single bonds. We shall deal



with this difference between perylene and tetrabenzoperylene in a different context in the near future.

If tetrabenzoperylene (IV) is submitted to a benzenogenic diene synthesis with

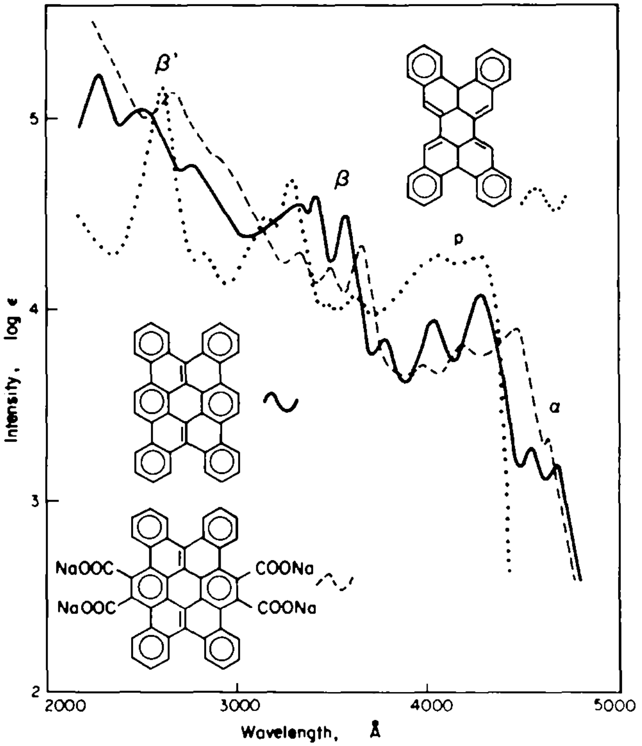


FIG 1. Absorption spectra with max (Å) and log ε in parentheses. ——— 1,2:3,4:7,8:9,10-Tetrabenzocoronene in 1,2,4-trichlorobenzene: α, 4660 (3·48), 4535 (3·26): p, 4260 (4·07), 4020 (3·93), 3770 (3·83): β, 3535 (4·48), 3380 (4·58), 3300 (4·54): in cyclohexane: 2730 (4·75), β', 2475 (5·06), 2250 (5·23). - - - - - Tetra-Na-salt of 1,2:3,4:7,8:9,10-tetrabenzocoronene-5,6,11,12-tetracarboxylic acid in 50% ethanol: α, 4620 (3·34): p, 4440 (3·92): 4180 (3·84), 3965 (3·73): β, 3625 (4·35), 3450 (4·23), 3285 (4·31): β', 2630 (5·16). ·········· 2,3:4,5:8,9:10,11-Tetrabenzoperylene in benzene: p, 4250 (4·28), 4040 (4·30), 3600 (4·07): β, 3270 (4·68), 3130 (4·51), 2860 (4·28): in cyclohexane: β', 2605 (5·16)

maleic anhydride and chloranil tetrabenzocoronene-tetracarboxylic dianhydride (VII) is formed. It has a spectrum closely related to tetrabenzocoronene (VIIIa), Fig 1. The latter is obtained by decarboxylation with soda-lime. It can be considered as composed of two picene complexes with two common fixed double bonds as shown in formula VIIIa. Formula VIIIb is less likely. This would have one sextet less than VIIIa if the sextets are to form a ring current as indicated by the arrows, i.e. it would display superaromaticity.[4] This is impossible, because the sextets in the external rings would have to migrate through space.

Attempts were made to obtain tetrabenzocoronene by photocyclization of anthraquinone-bis-diphenylmethide (IX). However, the cyclization stopped at 3,10-diphenyl-1,2:4,5:8,9-tribenzopyrene (X) which has a spectrum closely related to tribenzopyrene.[5] Fig 2 also shows the broadening of the bands which is typical for phenyl derivatives. Cyclization with NaCl-$AlCl_3$ was also unsuccessful. Splitting of the molecule occurred and the main constituent of the resulting mixture was a hydrocarbon which reacted with maleic anhydride and chloranil. This is possibly 2,3:8,9-dibenzo-6,7-*o*-phenylene-perylene.

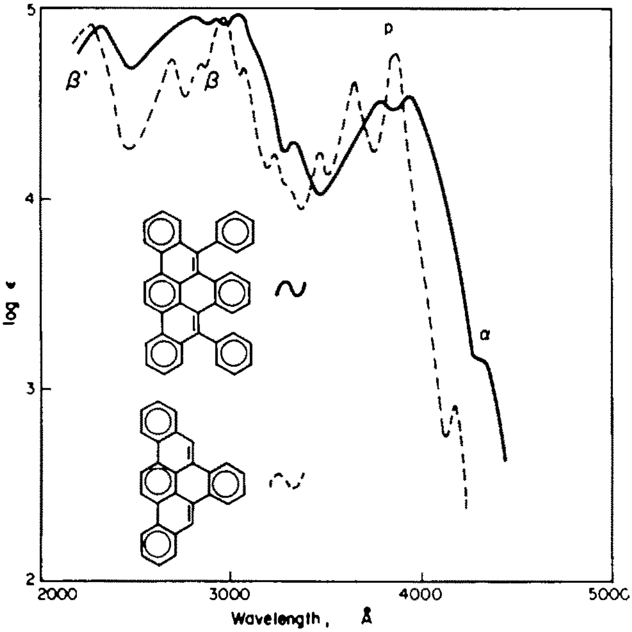


Fig 2. Absorption spectra with max (Å) and log ε in parentheses. ——— 3,10-Diphenyl-1,2:4,5:8,9-tribenzopyrene in cyclohexane: p, 3960 (4·53), 3775 (4·49); 3310 (4·28); β, 3020 (4·97), 2910 (4·95), 2800 (4·96); β', 2320 (4·91). - - - - - 1,2:4,5:8,9-Tribenzopyrene in cyclohexane: α, 4180 (2·86); p, 3850 (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)

EXPERIMENTAL*

1,4-*Di-(*o*-carboxybenzyl)-2,5-dimethylbenzene* (I). The acid I (CO unreduced; 250 g) was reduced with Cu activated Zn dust (375 g) in NaOH (8%, 3500 ml) by refluxing for 6 days. The Zn dust was added in portions (5 × 75 g) at intervals of 24 hr. The hot alkaline soln was filtered and acidified with conc HCl and the ppt filtered off. The dicarboxylic acid crystallized from AcOH as colourless needles (150 g), m.p. 304–305°, which dissolved in conc HSO_4 to give a red-orange soln which turned to green on warming; CO group: $_{\max}^{KBr}$ = 1690 cm^{-1}. (Found: C, 77·0; H, 6·10. $C_{24}H_{22}O_4$ requires: C, 77·0; H, 5·9%).

7,14-*Dihydro*-6,13-*dimethylpentacene*-5,12-*dione* (II). The above acid (37·4 g) and PCl_5 (39 g) were refluxed in freshly distilled $POCl_3$ (500 ml) for 30 min. HCl was evolved and the colour of the soln changed from yellow to orange, to red and finally to dark green. $POCl_3$ (250 ml) was distilled off, dry xylene added till the distillation temp rose to 135–140°. The ppt was filtered off, washed with benzene and dried. Crystallization from benzene-ethanol and then from dioxan yielded orange-brown clusters of prisms (25·5 g), m.p. 334–336° which dissolved in conc H_2SO_4 to form a yellow soln which changed to green on standing; MS, molecular ion *m/e* = 338; cal. M.W. 338; $\nu_{\max}^{KBr}$ = 1655 cm^{-1} (CO); UV spectrum in benzene: 3430 (3·62), 2970 (4·32), 2460 (4·15) Å. (Found: C, 85·4; H, 5·2. $C_{24}H_{18}O_2$ requires: C, 85·2; H, 5·4%).

Red Isomer of II. The reduced acid I (37·4 g) and PCl_5 (39 g) were warmed on a steam bath for 1 hr. $POCl_3$ was removed in vacuum and the remaining acid chloride suspended in dry benzene (250 ml). This

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

suspension was dropped on to finely divided $AlCl_3$ (32 g) in dry benzene (250 ml). The temp was kept below 10° and the complex refluxed with stirring for 12 hr. The mixture was decomposed with dil HCl, steam distilled and the reddish solid filtered off and dried. Crystallization from xylene gave lustrous reddish-purple needles (10·5), m.p. 335–336°, which dissolved in conc H_2SO_4 to give a yellow soln turning to green on standing; MS, molecular ion *m/e* = 338; Calc. M.W. = 338; ν_{max}^{KBr} = 1645 cm^{-1} (C=O); UV spectrum in benzene: 5590 (3·50), 5200 (3·35), 4910 (2·98), 3490 (3·95), 3360 (3·94), 3020 (4·91), 2910 (4·93) Å. (Found: C, 85·0; 85·1; H, 5·2; 5·1. $C_{24}H_{18}O_2$ requires: C, 85·2: H, 5·4%).

5-*Hydroxy*-5,12-*diphenyl*-5,14-*dihydro*-6,13-*dimethylpentacene* (III). Bromobenzene (15·7 g) was added to strips of Li metal (1·4 g) suspended in dry ether (250 ml) in a N_2 atm and the mixture refluxed until all the Li had dissolved (3–4 hr). The ethereal soln was filtered through glass wool into a very finely divided suspension of II (8·4 g) in dry benzene (250 ml). The mixture which was greenish-black (λ_{max} = 6325, 5840, 5435, 4105, 3920, 3695 Å) was refluxed for 12 hr. Decomposition with ice and dil AcOH followed by steam distillation left a buff-coloured residue. It was triturated with ether and yielded a dark yellow solid. Repeated crystallization from benzene-light petrol gave pale yellow crystals, m.p. 194–199° dec, which dissolved in conc HSO_4 to give a greenish-brown soln. Concentration of the mother liquor yielded a further 4 g, total yield 11·5 g: UV spectrum in cyclohexane: 3730 (3·57), 3200 (3·88), 3060 (3·85), 2580 (4·22), 2340 (4·16) Å. (Found: C, 90·6: H, 6·0. $C_{36}H_{28}O$ requires: C, 90·7: H, 5·9%).

An identical experiment was carried out with the purple isomeric compound of II. The product obtained was identical in all respects with III.

2,3:4,5:8,9:10,11-*Tetrabenzoperylene* (IV). The above III (2 g) and Cu powder (15 g) was heated under CO_2 at 400–410° for 2 hr. The cooled mixture was extracted with boiling xylene and chromatographed on Grade I Neutral Alumina (60 g). Elution with benzene gave firstly, a yellow, closely followed by an orange soln. Concentration of the yellow eluate gave long yellow-green needles (28 mg) and concentration of the orange eluate gave orange blades (11 mg). Both hydrocarbons yielded the same sublimate at 310–320°/0·04 mm. The crystals had m.p. 367–368° and dissolved in warm conc H_2SO_4 to give an apple-green soln. (Found (needles): C, 95·3; H, 4·7. Found (blades): C, 95·8; H, 4·4. $C_{36}H_{20}$ requires: C, 95·6; H, 4·4%).

1,2:3,4:7,8:9,10-*Tetrabenzocoronene*-5,6,11,12-*tetracarboxylic dianhydride* (VII). Tetrabenzoperylene (75 mg) and maleic anhydride (2·0 g) were refluxed for 30 min. The hydrocarbon was dissolved and a sample dissolved in dil NaOH showed a spectrum compatible with diadduct VI. Addition of chloranil (150 mg), followed by a further 30 min reflux, allowed the aromatic diadduct VII to crystallize from the hot soln. Dry xylene was added, the adduct filtered off and washed with benzene. The dark red dianhydride VII (90 mg) had m.p. 440–445°. It was sublimed at 310–320°/0·05 mm. (Found: C, 82·7; H, 2·9. $C_{44}H_{16}O_6$ requires: C, 82·5; H, 2·5%).

1,2:3,4:7,8:9,10-*Tetrabenzocoronene* (VIIIa). The above dianhydride (60 mg) was ground together with soda-lime (250 mg) and heated to 350° under N_2 for 1 hr. Sublimation (380–395°/0·03 mm) yielded an orange sublimate which was dissolved in 1,2,4-trichlorobenzene. Concentration allowed the hydrocarbon (1 mg) to crystallize as bright orange-brown needles or plates, m.p. 396–397°; MS, molecular ion *m/e* = 500: Calc. M.W. = 500; absorption spectrum, Fig 1.

Anthraquinone-bis-diphenylmethide (IX) was prepared following the description of Padova.[6] The cyclization attempt carried out with NaCl-$AlCl_3$ at 110–150°, followed by chromatography gave first a hydrocarbon, m.p. 309–312° which dissolved in conc H_2SO_4 to give a violet soln. When boiled with maleic anhydride and chloranil it gave an acid. (Found: C, 96·1; H, 4·2. $C_{34}H_{18}$ requires: C, 95·8; H, 4·2%). The hydrocarbon showed the following absorption bands in benzene soln: α, 4560 (3·94); p, 4250 (4·56), 4000 (4·48), 3800 (4·20) β, 3350 (4·64), 3200 (4·60), 3060 (4·70); in cyclohexane: β', 2400 (4·90) Å. From these results it appears possible that the hydrocarbon is 2,3:8,9-dibenzo-6,7-*o*-phenylene-perylene. It could have been formed by the loss of one phenyl group from IX and the cyclization of the other ones.

The following fraction of the chromatogram gave a mixture which according to the spectrum contained tetrabenzocoronene but which could not be obtained in a pure state.

(3,10-*Diphenyl*-1,2:4,5:8,9-*tribenzopyrene* (X). Compound IX (540 mg) was irradiated in dry benzene (500 ml) with a mercury vapour lamp in the presence of iodine. The progress of the reaction was followed by removing a standard portion and examining the UV spectrum. At the end of 10 days, the reaction appeared to be complete. The benzene was removed under vacuum, the residue dissolved in 1,2,4-trichlorobenzene and chromatographed on Grade I Neutral Alumina (25 g). Elution with xylene gave a yellow-green band with a strong blue-violet fluorescence which on concentration yielded pale yellow needles (52 mg), m.p. 332–334°. These dissolved in conc H_2SO_4 to give a bright blue colour, UV spectrums Fig 2. (Found: C, 95·0; H, 5·2. $C_{40}H_{24}$ requires: C, 95·2; H, 4·8%).

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