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THE SYNTHESIS OF 1:2, 3:4, 5:6, 7:8, 9:10, 11:12-HEXABENZOCORONENE

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Abstract—The acid (I) was condensed with phthalic anhydride to the dicarboxylic acid (II). One sided cyclization yielded the acid (III) which was reduced to (IV). A second cyclization gave the pentacene derivative (V) which was oxidized to the diquinone (VI). Compound VI reacted with phenyl lithium to form the tetraol (VII) which was condensed to hexabenzocoronene (VIII) by heating with copper powder.

o-(1,4,5-Xyloyl)-BENZOIC ACID was easily obtained by condensing *p*-xylene with phthalic anhydride and aluminium chloride.[1] Reduction with zinc dust and sodium hydroxide solution gave the acid (I). This was condensed again with phthalic anhydride and aluminium chloride to yield the dicarboxylic acid (II). Concentrated sulphuric acid effected semicyclization to the acid (III) which was reduced to the acid (IV) with zinc dust and potassium hydroxide solution. A milder reduction gave the phthalide like lactone $C_{24}H_{18}O_2$.

The cyclization of the acid (IV) to the pentacene derivative (V) was carried out with boiling phosphorus oxychloride. The oxidation of V with excess chromic acid in acetic acid yielded dimethylpentacenediquinone (VI). The diquinone (VI) was condensed with phenyl lithium to the tetraol (VII). Condensation to hexabenzocoronene (VIII) took place when the tetraol (VII) was heated with copper powder at 400°.

1:2, 3:4, 5:6, 7:8, 9:10, 11:12-Hexabenzocoronene (VIII) is a yellow hydrocarbon which melts as 516° and can be sublimed *in vacuo* at 500°. It can be recrystallized from boiling xylene and dissolved slowly in concentrated sulphuric acid to form a brown solution. As a hydrocarbon with six aromatic sextets it shows an intense red phosphorescence with emission bands at 6160 and 6270 Å in a glassy frozen solution of methylcyclohexane and isopentane after irradiation. The phosphorescence is similar to that of pyrene[2] (bands at 5940 and 6050 Å); however the life of phosphorescence of hexabenzocoronene (VIII) is very much longer than that of pyrene.

The absorption spectra of 1:2, 3:4, 5:6, 7:8, 9:10, 11:12-hexabenzocoronene (VIII) and of the 1:12, 2:3, 4:5, 6:7, 8:9, 10:11-hexaperibenzocoronene[3] (IX) are recorded in Fig. 1. These spectra are at relatively short wavelength when compared with the number of π-electrons in VIII and IX which amount to 48 and 42 respectively. This can be explained by assuming that only a fraction of the number of rings are in aromatic conjugation whilst some sextets are connected to the system by single bonds forming empty rings (E). The aromatic conjugated system is that of naphthopentaphene (trinaphthylene) in VIII and is that of triphenylene in IX.[4] The IR spectrum of

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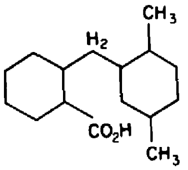
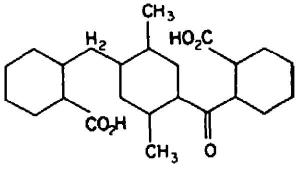
[1] Franz Meyer, *Ber. Dtsch. Chem. Ges.* **15**, 636 (1882); K. Elbs, *J. Prakt. Chem.* (2) **41**, 27 (1890).
[2] E. Clar and M. Zander, *Chem. Ber.* **89**, 749 (1956).
[3] E. Clar and C. T. Ironside, *Proc. Chem. Soc.* 150 (1958); E. Clar, C. T. Ironside and M. Zander, *J. Chem. Soc.* 142 (1959).
[4] E. Clar, *Polycyclic Hydrocarbons* p. 80. Academic Press (1964).



I



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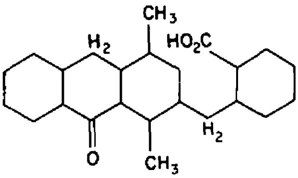

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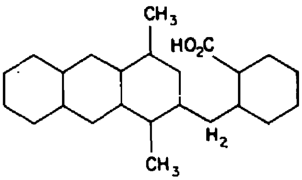

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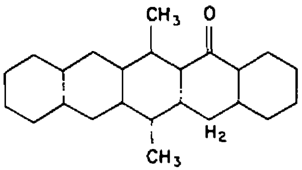
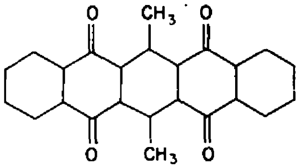
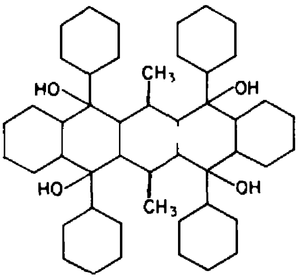


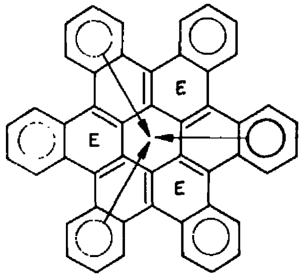
V



VI



VII



VIII

hexabenzocoronene (VIII) shows two absorption bands at 767 and 807 cm^{-1} which must be classified as γ-vibrations.

Hexaperibenzocoronene (IX in Fig. 1) which does not melt even above 700°, is insoluble in all conventional solvents and can be formulated with sextets only, can therefore be considered as a particle of graphite.[3] This is not so in hexabenzocoronene (VIII) which melts at 516°, can be recrystallized from xylene and is not a fully benzenoid hydrocarbon. It has twelve overcrowded positions which makes it most unlikely that the hydrocarbon is uniplanar. It cannot therefore be compared with a particle of graphite.

EXPERIMENTAL*

1-(o-*Carboxybenzyl*)-*2,5-dimethylbenzene* (I). 1-(*o*-carboxybenzoyl)-2,5-dimethylbenzene (50 g) was reduced with Cu activated Zn dust (75 g) and NaOH aq (8%; 1500 ml) by refluxing for 3½ days. Zn dust (75 g) was added in portions (3 × 25 g) at intervals of 24 hr. The hot alkaline solution was filtered from excess Zn, acidified with conc. HCl and the precipitated acid (41 g) crystallized from benzene. A second crystallization from pet. ether 60–80° gave I as colourless needles, m.p. 130–132°; (I) dissolves in conc. H_2SO_4 to give a yellow solution. (Found: C, 80·30; H, 6·9. $C_{16}H_{16}O_2$ requires: C, 80·00; H, 6·7%).

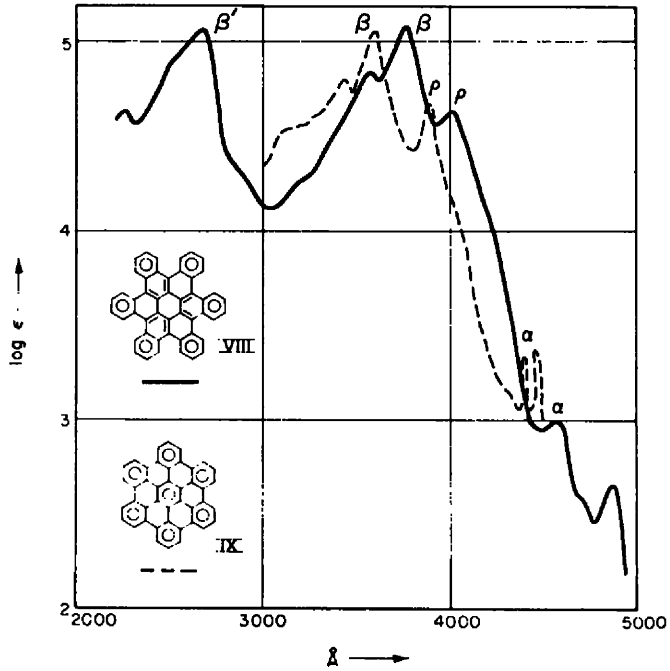


FIG. 1. Absorption max (Å) and log ε (in parentheses) 1:2, 3:4, 5:6, 7:8, 9:10, 11:12-Hexabenzocoronene (VIII) in benzene. α: 4860 (2·64, 4560 (3·01); *p*: 4020 (4·63); β: 3760 (5·07), 3570 (4·83); in cyclohexane, β': 2680 (5·08), 2260 (4·64).
1:12, 2:3, 4:5, 6:7, 8:9, 10:11-Hexaperibenzocoronene (IX) in trichlorobenzene. Owing to the very low solubility the absolute intensities are uncertain: (log ε + X), *p*: 3875 (4·68); β: 3600 (5·06), 3425 (4·80). α-Bands were observed visually with a 100 cm cell: 4440, 4380 (very sharp).

1-(o-*Carboxybenzyl*)-4-(o-*carboxbenzoyl*)-*2,5-dimethylbenzene* (II) Powdered I (26 g) was added to a suspension of finely ground $AlCl_3$ (64 g) and phthalic anhydride (17·7 g) in tetrachloroethane (78 ml). The solution became yellow and HCl was evolved. After 5 min at room temp, the reaction vessel was immersed in a water bath at 60°. A vigorous evolution of HCl occurred and the solution became wine red in colour. When the evolution of HCl had ceased (ca. 25 min) the viscous red complex was decomposed with dil. HCl aq and the precipitated condensation product (31 g) was filtered off and washed with benzene and hot water. Crystallization from glacial acetic acid afforded II as clusters of colourless needles, m.p. 249–250° which dissolve in conc. H_2SO_4 to give a yellow solution which rapidly changes to orange and then to red on standing. (Found. C, 74·15; H, 5·2. $C_{24}H_{20}O_5$ requires: C, 74·2; H, 5·2%).

2-(o-*Carboxybenzoyl*)-*1,4-dimethylanthrone*-(9) (III). Finely divided II (33 g) was added with stirring to conc. H_2SO_4 (250 ml) and the mixture was heated at 80° for 5 min. The solution initially

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

orange-red in colour became brown. The cold mixture was poured on to ice and the crude cyclization product (III; 28 g) was filtered off and washed with water. Compound III was readily oxidized, could not be obtained in a pure state and was used in the crude form for the next stage.

2-(o-*Carboxybenzyl*)-1,4-*dimethylanthracene* (IV). Crude III (48 g) was dissolved in KOH aq (5% 2500 ml), Zn dust (70 g) added and the mixture heated under reflux. The initial dark red colour was rapidly discharged and a yellow solution resulted. Reduction was prolonged for 5 days and an additional 120 g Zn dust was added in portions (4 × 30 g) at intervals of 24 hr. The alkaline solution was filtered hot from excess Zn and acidified with conc. HCl. The Zn was destroyed with conc. HCl and the residue was combined with the above precipitated acid to give crude IV (36 g) which crystallized from xylene in small yellow needles, m.p. 243–244° and dissolves in conc. H_2SO_4 to give an orange solution which changes to brown green and finally to green on standing. (Found: C, 84·8; H, 6·3. $C_{24}H_{20}O_2$ requires: C, 84·7; H, 5·9%). The UV absorption data (in 50% ethanol water) for IV are summarized: absorption maxima (Å) and log ε in parentheses. p: 3860 (3·56), 3670 (3·66), 3400 (3·58); β: 2600 (4·97), 2260 (4·24).

6,13-*Dimethylpentacenone*-(5) (V). The carboxylic acid (IV; 20 g) was dissolved in $POCl_3$ (400 ml) and the mixture heated under reflux for 5 min. The $POCl_3$ (300 ml) was distilled off, xylene (300 ml) added and the mixture redistilled until about 300 ml of distillate was obtained. The mixture still contained $POCl_3$ and was poured into water and the xylene steam distilled off. Crystallization of the material thus obtained from xylene gave V (8·6 g) as golden brown ferns, m.p. 268–270°. Compound V dissolves in conc. H_2SO_4 to give a green colour. (Found: C, 89·7; H, 5·8. $C_{24}H_{18}O$ requires: C, 89·4; H, 5·6%).

6,13-*Dimethylpentacene*-5,14, 7,12-diquinone (VI). Finely powdered V (10 g) was suspended in hot glacial acetic acid (300 ml) and chromic acid (21 g) was added rapidly so that the mixture refluxed vigorously. Compound V dissolved and the diquinone (VI) began to precipitate from the boiling solution. Refluxing was continued for a further 30 min when the precipitated VI (7·8 g) was filtered off and washed with acetic acid and water. Dilution of the acetic acid mother liquor furnished an additional (450 mg) of VI which crystallizes in large green yellow needles from 1,2,4-trichlorobenzene which darken at 300° and melt at 320–322° with dec. Compound VI gives a violet vat with alkaline sodium dithionite and dissolves in conc. H_2SO_4 to give a yellow solution which changes to orange and then to green on standing. (Found: C, 78·7; H, 4·1. $C_{24}H_{14}O_4$ requires: C, 78·7; H, 3·85%).

5,7,12,14-*Tetraphenyl*-5,7,12,14-*tetrahydroxy*-5,7,12,14-*tetrahydro*-6,13-*dimethylpentacene* (VII). Bromobenzene (25·84 g) was added to strips of Li metal (2·30 g) suspended in dry ether (200 ml) in a N_2 atm. and the mixture refluxed until all the Li had reacted (2–3 hr). The ethereal solution was then filtered through glass wool into a suspension of very finely divided 6,13-dimethylpentacene-5·14, 7·12-diquinone in dry benzene prepared by shaking the diquinone (10 g), a handful of glass beads and dry benzene (200 ml) in a thick walled glass bottle for 12 hr. The reaction vessel was securely corked and the mixture was shaken for 48 hr. The brown colour which developed immediately changed to red as the reaction proceeded. Decomposition with ice and dil. acetic acid aq followed by steam distillation of the benzene gave a violet brown product which was washed with ether. The ether insoluble material (3 g) was filtered off, given a washing with pyridine and the pyridine mother liquor decanted leaving behind unchanged VI (2·05 g). Dilution of the pyridine mother liquor with water gave crude tetraol (VII; 500 mg). Slow evaporation of the ether from the ether washing furnished after 7 days (1·02 g) of crude tetraol. No more crystallization took place from the ether and the ether was replaced with benzene and pet. ether 100–120° added to the hot benzene solution. In this way an additional 4·5 g of tetraol were obtained, total yield (6·02 g). Repeated crystallization from acetone-ethylacetate mixture gave the tetraol as colourless needles, m.p. 312–318 dec. which dissolve in conc. H_2SO_4 to give a violet solution. (Found: C, 84·4; H, 5·6. $C_{48}H_{38}O_4$ requires: C, 84·9; H, 5·65%).

1:2, 3:4, 5:6, 7:8, 9:10, 11:12—*Hexabenzocoronene* (VIII). An intimate mixture of the tetraol (1 g) and Cu powder was pyrolysed in a CO_2 atm. at 400–440° for 2 hr. The Cu was extracted with xylene and the extract chromatographed on grade I alumina. Eluting with xylene gave a yellow red eluate which yielded small yellow prisms of hexabenzocoronene (20 mg). (Found: C, 95·6; H, 4·2. $C_{48}H_{24}$ requires: C, 96·0; H, 4·0%). The properties of the hydrocarbon are described in the theoretical part.