

5. 2 : 3-5 : 6-8 : 9-Tribenzoperinaphthene.

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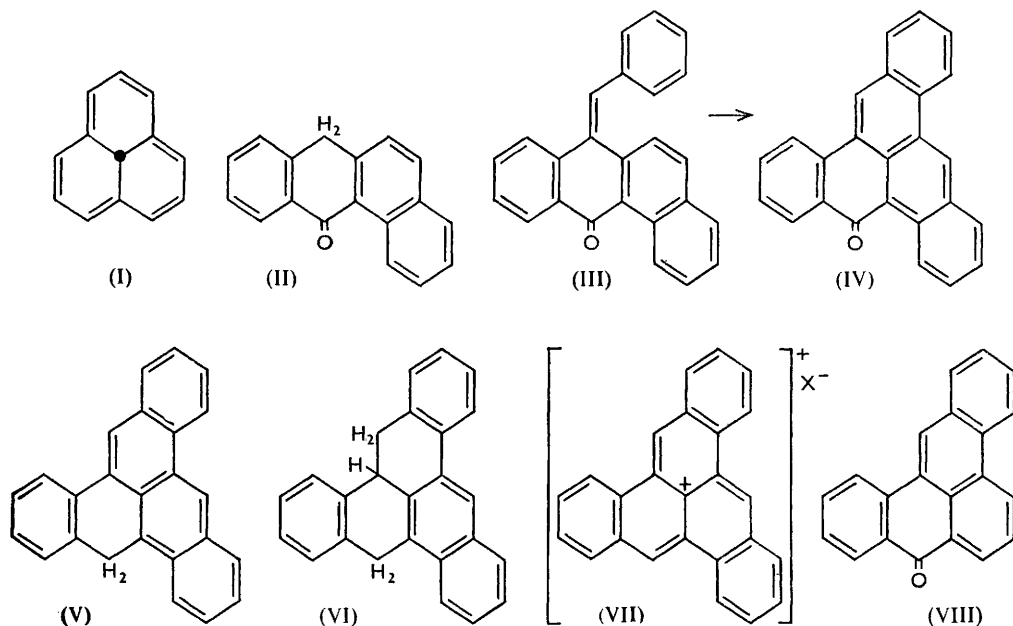
1 : 2-Benzanthr-9-one gave the 10-benzylidene derivative (III), ring closure of which with aluminium chloride led to the hexacyclic ketone (IV). The reduction of this yielded the tribenzoperinaphthene (V) which was oxidised in the presence of acids to salts of type (VII).

THE skeleton of perinaphthene tends to form an aromatic framework with external, alternating single and double bonds and an odd electron or a positive charge in the centre (cf. I) Evidence for this assumption has accumulated recently.¹ We have now synthesised tribenzoperinaphthene derivatives and found that the same tendency occurs in this centrosymmetrical system.

1 : 2-Benzanthr-9-one (II) condensed smoothly with benzaldehyde in pyridine under the influence of piperidine, to form the derivative (III). Ring closure was then carried out with aluminium chloride in boiling benzene and is assumed to have yielded the hexacyclic ketone (IV), involving the more reactive naphthalene complex rather than the benzene complex. A by-product containing four hydrogen atoms more was also obtained, which could have a different skeleton since it could not be dehydrogenated to the ketone (IV). 2 : 3-5 : 6-8 : 9-Tribenzoperinaphthenone (IV) has basic properties: it forms a

¹ Boekelheide and Larrabee, *J. Amer. Chem. Soc.*, 1950, **72**, 1240, 1245; Clar, "Aromatische Kohlenwasserstoffe," Springer-Verlag, 1952, p. 431; Beckmann and Silberman, *Chem. and Ind.*, 1955, 1635; Sogo, Nokazaki, and Calvin, *J. Chem. Phys.*, 1957, **26**, 1343.

stable perchlorate. Reduction with hydriodic acid and red phosphorus gave, depending on the time of reaction, either 2 : 3-5 : 6-8 : 9-tribenzoperinaphthene (V) or its dihydro-derivative (probably VI). Whilst the tribenzoperinaphthene is fairly stable in neutral



solvents, it is quickly oxidised in acid by atmospheric oxygen. The solution in acetic acid became deep violet-blue when boiled in the presence of air or when selenium dioxide was added. The violet-blue solution was not stable, but was further oxidised to the

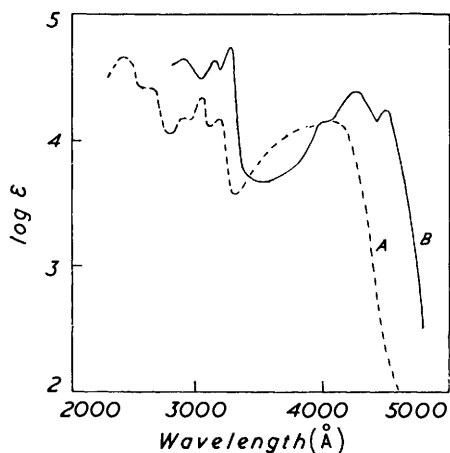


FIG. 1. Absorption max. (Å) and $\log \epsilon$ (in parentheses).
 A, 2 : 3-5 : 6-Dibenzoperinaphthenone in EtOH: 4040 (4.16); 3180 (4.15), 3030 (4.34), 2900 (4.18); 2410 (4.66).
 B, 2 : 3-5 : 6-8 : 9-Tribenzoperinaphthenone in C_6H_6 : 4520 (4.24), 4260 (4.40); 3260 (4.74), 3120 (4.64); 2860 (4.65).

tribenzoperinaphthene (IV). However, it was stabilised by hydrochloric or perchloric acid. The crystalline, deep violet-blue perchlorate was not paramagnetic when tested with the microwave resonance absorption method.* This does not support a formula with an odd electron and proton in the centre of the molecule, and formula (VII) which

* This investigation was kindly carried out by Professor J. Weiss and Dr. P. A. Forrester, King's College, Newcastle.

has no radical character apparently accounts best for the properties of the tribenzoperinaphthylum perchlorate. The perchlorate gave a violet-blue solution in nitromethane; when alkali or pyridine was added the colour disappeared immediately, but if perchloric acid was then also added without delay the colour was restored. This also supports formula (VII) rather than the structure of a protonated radical.

The absorption spectra are in accordance with the structures here assumed. The long-wave absorption of the tribenzoperinaphthenone (IV) is much shifted towards the red in comparison with that of 2 : 3-5 : 6-dibenzoperinaphthenone² (VIII) (Fig. 1); this is to be expected owing to the annellation effect of a benzene ring fused linearly to the phenanthrene complex in (VIII) and extended to a 1 : 2-benzanthracene complex in

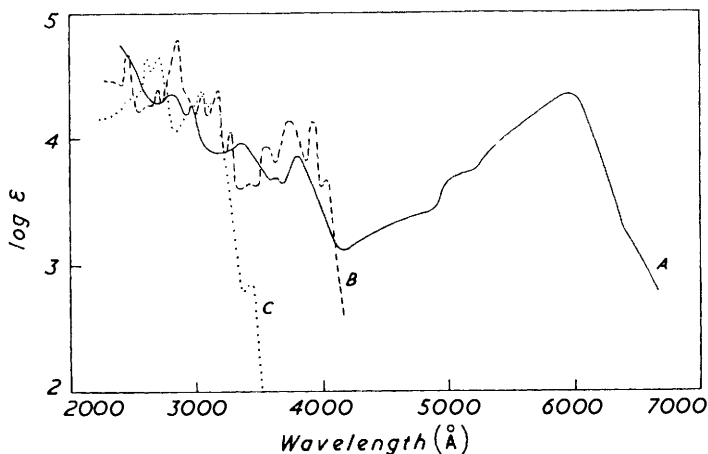


FIG. 2. Absorption max. (Å) and $\log \epsilon$ (in parentheses).

- A, 2 : 3-5 : 6-8 : 9-Tribenzoperinaphthylum chloride in 17% HCl: 5960 (4.36); 3820 (3.88), 3600 (3.70); 3350 (3.98); 2960 (4.26), 2780 (4.37).
 B, 2 : 3-5 : 6-8 : 9-Tribenzoperinaphthene in EtOH: 4020 (3.68), 3930 (4.14), 3730 (4.16), 3540 (3.95); 3260 (4.04); 3160 (4.39), 3040 (4.33); 2840 (4.79), 2740 (4.50); 2460 (4.66).
 C, Dihydro-2 : 3-5 : 6-8 : 9-tribenzoperinaphthene in EtOH: 3420 (2.87); 3160 (4.34), 3050 (4.37); 2690 (4.65), 2610 (4.64).

(IV). Also expected is the violet shift when the tribenzoperinaphthene (V) is compared with its dihydro-derivative (VI). The chloride (VII) (X = Cl), however, has an entirely different type of absorption (Fig. 2).

EXPERIMENTAL

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

10-Benzylidene-1 : 2-benzanthrone (III).—1 : 2-Benzanthrone³ (II) (48 g.), benzaldehyde (25 g.), pyridine (125 c.c.), and piperidine (1.25 c.c.) were boiled together for 4 hr. The solvent was then distilled off and the residue dried at 140° in a vacuum till free from benzaldehyde. The glassy product was dissolved in benzene and thoroughly extracted with warm alkaline sodium dithionite solution, till the red vat of the quinone was no longer formed. After being washed and dried, the benzene was removed and crystallisation from acetic acid gave yellow prisms (50 g.), m. p. 144—145°, of 10-benzylidene-1 : 2-benzanthrone (III) (Found: C, 90.1; H, 5.1. C₂₅H₁₆O requires C, 90.3; H, 4.85%) which gave a magenta solution (no fluorescence) in concentrated sulphuric acid.

2 : 3-5 : 6-8 : 9-Tribenzoperinaphthenone (IV).—Powdered aluminium chloride (50 g.) was added to a solution of the ketone (III) (10 g.) in benzene (150 c.c.), and the deep red solution refluxed for 30 min. After decomposition the benzene layer was separated, washed, and dried.

² Clar, *Ber.*, 1943, **76**, 609.

³ Cook, *J.*, 1930, 1087.

Chromatography on alumina with benzene as eluant gave first a colourless, non-fluorescent solution; concentration and crystallisation from xylene yielded colourless prisms (3 g.), m. p. 276—278° (Found: C, 89.7; H, 5.7. $C_{25}H_{18}O$ requires C, 89.75; H, 5.4%). The compound sublimed without decomposition in a vacuum, forming needles, m. p. 276—278°; it did not yield an acetate with acetic anhydride and gave a bright yellow, green-fluorescent solution in concentrated sulphuric acid. It was insoluble in alkaline solution and did not form a perchlorate. Attempts to dehydrogenate it with chloranil or palladium-charcoal and to oxidise it with selenium dioxide or chromic acid were unsuccessful. The second, yellow band in the chromatogram gave a clear yellow eluate whence concentration and crystallisation from acetic acid or benzene yielded orange-yellow needles (4 g.), m. p. 260—261°, of the *tribenzoperinaphthenone* (IV) (Found: C, 91.0; H, 4.3. $C_{25}H_{14}O$ requires C, 90.9; H, 4.3%) which gave a violet-red solution, with an orange fluorescence, in concentrated sulphuric acid. The compound, which gave stable brown needles on addition of a little bromine to its benzene solution, was not readily reduced and was recovered unchanged after 1 hour's boiling with zinc dust in pyridine and acetic acid.

2:3-5:6-8:9-Tribenzoperinaphthenone Perchlorate.—Perchloric acid (1 c.c.) in acetic anhydride (2 c.c.) was added to a boiling solution of the product (IV) (1 g.) in acetic acid. When cold, the dark reddish-brown needles were filtered off, washed with acetic acid and benzene, and dried in a vacuum at 100°. The *perchlorate* (Found: Cl, 8.4. $C_{25}H_{15}O_5Cl$ requires Cl, 8.25%) was readily hydrolysed and the tribenzoperinaphthenone (IV) recovered from it by means of warm dilute alkaline solution. The yields from these reactions were theoretical.

2:3-5:6-8:9-Tribenzoperinaphthene (V).—The tribenzoperinaphthenone (IV) (1 g.), red phosphorus (2.5 g.), and potassium iodide (1 g.) were added to 55% hydriodic acid (25 c.c.) covered with xylene (25 c.c.). After 48 hours' refluxing, the mixture was diluted with water, and the phosphorus filtered off from the hot solution. The xylene layer was separated, washed thoroughly with warm alkaline sodium dithionite solution, concentrated, and chromatographed on alumina. As the hydrocarbon was oxidisable, the column was protected against light and pressure was applied to the top. By using benzene as eluant, a pale yellow solution with a bright blue fluorescence was obtained which on concentration and crystallisation from benzene or methyl alcohol yielded pale yellow needles (0.6 g.), m. p. 253—255°, of the *tribenzoperinaphthene* (V) (Found: C, 94.4; H, 5.2. $C_{25}H_{16}$ requires C, 94.9; H, 5.1%). The hydrocarbon did not dissolve readily in concentrated sulphuric acid, but, on gentle warming, a violet-blue solution with a red fluorescence was obtained. A solution having the same colour was obtained by boiling the hydrocarbon in acetic acid in contact with air.

The hydrocarbon (0.2 g.) was dissolved in acetic acid (30 c.c.) containing perchloric acid (1 c.c.). A stream of oxygen was passed through the boiling solution, which rapidly assumed a deep violet-blue colour. After 15 min. the solution was allowed to cool and violet-blue crystals of the *perchlorate* were obtained, which were filtered off, washed with dry benzene, and dried in a vacuum (KOH) (Found: C, 71.5; H, 3.9. $C_{25}H_{16}O_4Cl$ requires C, 72.4; H, 3.6%). The blue solid was quickly decomposed by water to a yellow compound. The perchlorate was soluble in nitromethane, giving a violet-blue solution (red fluorescence), which became pale yellow on the addition of alkali or basic solvents such as pyridine. The initial colour of the solution was restored, however, by the addition of perchloric acid. The addition of perchloric acid to the solution after 15—30 min. gave the deep red colour of the perchlorate of tribenzoperinaphthenone (IV) and not that of the hydrocarbon perchlorate (V). The perchlorate in acetic acid was rapidly reduced by boiling it with zinc dust, and a colourless solution with a blue fluorescence was obtained which was re-oxidised on storage.

(? 3a:4-)Dihydro-2:3-5:6-8:9-tribenzoperinaphthene (VI).—The tribenzoperinaphthenone (IV) (1 g.) was reduced for 5 days, under the conditions used for preparation of the tribenzoperinaphthene (V). The mixture was treated as described and the concentrated xylene layer was chromatographed on alumina with light petroleum (b. p. 40—60°) as eluant. A colourless non-fluorescent solution was obtained. Concentration and crystallisation from methyl alcohol gave yellow plates (0.5 g.), m. p. 178—180°, of the *dihydro-compound* (VI) (Found: C, 94.0; H, 5.7. $C_{25}H_{18}$ requires C, 94.3; H, 5.7%). This hydrocarbon did not dissolve in cold concentrated sulphuric acid but, on heating, a violet-blue solution with a red fluorescence was obtained. Boiling it in acetic acid in contact with oxygen did not affect the compound, but addition of a little selenium dioxide gave a violet-blue solution.