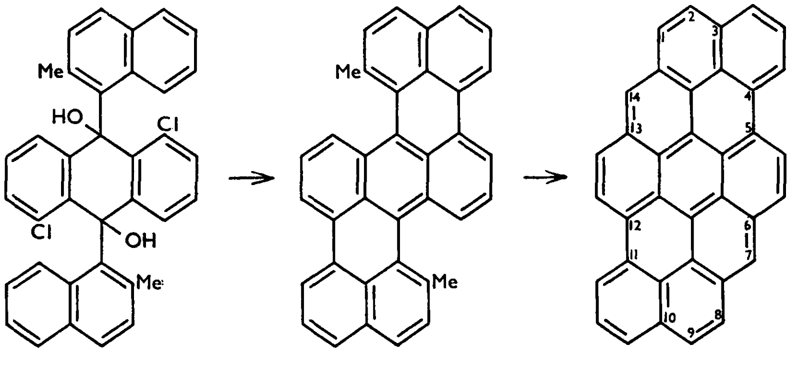
753. 3 : 4-5 : 6-10 : 11-12 : 13-*Tetrabenzoperopyrene.*

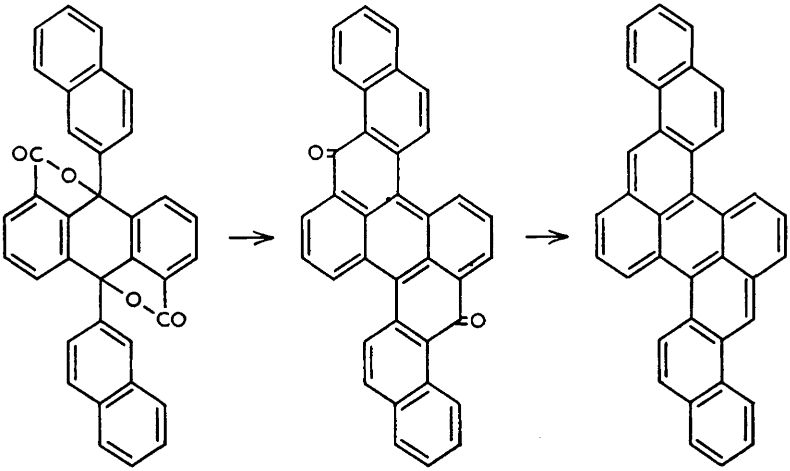
By E. Clar and W. Kelly.

Tetrabenzoperopyrene (III) was synthesised starting from 1 : 5-dichloroanthraquinone and 2-methyl-1-naphthylmagnesium bromide. The dimethyl compound (II) was obtained as an intermediate. The hydrocarbon (III) is different from Scholl and Meyer's dinaphthocoronene which is probably a dinaphthoperylene. It is also not identical with a hydrocarbon, claimed to be tetrabenzoperopyrene, obtained from the hydrogenation of coal.

1 : 5-Dichloroanthraquinone reacts with 2-methyl-1-naphthylmagnesium bromide to give the diol (I) which was reduced by hydriodic acid to the corresponding anthracene. When the latter was heated for a short time with potassium hydroxide in quinoline, preferably under nitrogen, the blue 7′ : 7″-dimethyl-1 : 9-5 : 10-di*peri*naphthylene-anthracene (II) was obtained. The hydrocarbon (II) has properties similar to those of the unmethylated hydrocarbon.[1] The absorption spectra of the two hydrocarbons are given in the Figure. The relatively small differences between the two spectra were to be expected from the overcrowding by the methyl groups in the derivative (II). This causes



(I) (II) (III)



(IV) (V) (VI)

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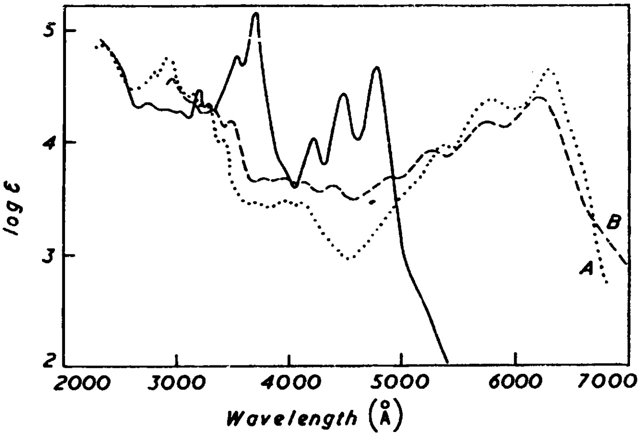
[1] Clar, Kelly, and Wright, *J.*, 1954, 1108.

a violet-shift of the long-wavelength bands and a flattening of the whole curve. This characteristic has also been observed in other cases.[2]

When 1 : 5-dichloro-9 : 10-di-(2-methyl-1-naphthyl)anthracene was heated for a longer time with potassium hydroxide and quinoline and in the presence of oxygen a further double cyclisation, involving the methyl groups, took place with the formation of the orange tetrabenzoperopyrene (III), the absorption spectrum of which, compared with that of the dimethyl compound (II), shows a large violet-shift. This compares strikingly with the strong red-shift which is observed when the two CH groups in the positions 7 and 14 were replaced by oxido-groups.[3]

The tetrabenzoperopyrene is not identical with the dinaphthocorene to which Scholl and Meyer[4] assign the same formula. The above synthesis does not allow any other course than the formation of (III). Scholl, Meyer, and Winkler,[5] however, assumed that the reaction of anthraquinone-1 : 5-dicarboxylic acid *pseudo*-chloride with naphthalene and aluminium chloride in nitrobenzene would give the di-α-naphthyl-dilactone. They failed to prove this and it is probable that the compound which they isolated was the di-β-naphthyl derivative (IV).



A, Absorption spectrum of 1 : 9-5 : 10-*di*peri*naphthyleneanthracene. Max.* (Å; log ε *in parentheses*) : 6300 (4·64), 5790 (4·40), 5360 (3·96); 4120 (3·47), 3920 (3·47), 3720 (3·47); 3420 (4·02), 3280 (4·36), 3120 (4·44), 2920 (4·76) *in benzene*; 2360 (4·88) *in alcohol.*

B, Absorption spectrum of 7′ : 7″-dimethyl-1 : 9-5 : 10-*di*peri*naphthyleneanthracene* (II). *Max.* : 6210 (4·40), 5780 (4·19), 5250 (3·92); 4390 (3·60), 3980 (3·66), 3780 (3·67); 3510 (4·18), 3320 (4·27), 3150 (4·34); 2960 (4·56), *in benzene.*

C. Absorption spectrum of 3 : 4-5 : 6-10 : 11-12 : 13-*tetrabenzoperopyrene* (III). *Max.* : 4780 (4·68), 4490 (4·44), 4220 (4·04); 3715 (5·14), 3540 (4·76) *in* 1-*methylnaphthalene*; 3200 (4·48), 3020 (4·32), 2750 (4·36) *in dioxan.*

Cyclisation of the lactone (IV) would yield only the dinaphthoperylenequinone (V), whereas the α-derivative would give, first, an isomeric dinaphthoperylenequinone and then dinaphthocoronenequinone. Scholl and Meyer claimed to have obtained the latter two quinones but reported that there was apparently no difference in their properties. It is suggested that they were actually the same compound, the dinaphthoperylenequinone (V). After reduction and dehydrogenation this could yield the dinaphthoperylene (VI). The reported properties of Scholl and Meyer's hydrocarbon are compatible with the structure (VI).

When coronene is prepared by hydrogenation of coal a more highly condensed hydrocarbon is obtained as a by-product which Fromherz, Thaler, and Wolf[6] consider to be

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[2] Brockmann and Randebrock, *Chem. Ber.*, 1951, **84**, 533.
[3] Clar, Kelly, Stewart, and Wright, *J.*, 1956, 2652.
[4] Scholl and Meyer, *Ber.*, 1934, **67**, 1229.
[5] Scholl, Meyer, and Winkler, *Annalen*, 1932, **494**, 220.
[6] Fromherz, Thaler, and Wolf, *Z. Elektrochem.*, 1943, **49**, 387.

identical with Scholl and Meyer's hydrocarbon. They do not report a direct comparison of the two hydrocarbons. The absorption spectrum of the hydrocarbon of Fromherz *et al.* is quite different from the spectrum of our compound (III). Therefore, their hydrocarbon must have some other structure.

EXPERIMENTAL

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

1 : 5-*Dichloro*-9 : 10-*dihydro*-9 : 10-*di*-(2-*methyl*-1-*naphthyl*)*anthracene*-9 : 10-*diol* (I).—A suspension of finely powdered 1 : 5-dichloroanthraquinone (35 g.) in benzene (300 ml.) was added with stirring during 30 min. to 2-methyl-1-naphthylmagnesium bromide prepared from 1-bromo-2-methylnaphthalene (110 g.) and magnesium (12 g.) in ether (250 ml.). The temperature was allowed to rise during the addition. 250 ml. of solvent were distilled from the mixture which was then heated under reflux on a water-bath for 2 hr. with continuous stirring. The thick suspension was decomposed by pouring it into dilute acetic acid containing ice. Benzene and some methylnaphthalene were removed by steam-distillation. The product was triturated with ether (1 l.) and digested twice with a large excess of alkaline sodium dithionite solution, a light fawn powder (26 g.) being obtained. Crystallisation from 1 : 2 : 4-trichlorobenzene gave the colourless *diol* (I), m. p. 329—330° (decomp.) (Found: C, 77·1; H, 4·8; Cl, 13·1. $C_{36}H_{26}O_2Cl_2$ requires C, 77·0; H, 4·7; Cl, 12·6%). It dissolved to give a green colour in concentrated sulphuric acid.

1 : 5-*Dichloro*-9 : 10-*di*-(2-*methyl*-1-*naphthyl*)*anthracene*.—A suspension of the diol (I) (10 g.) in acetic acid (70 ml.) and 55% hydriodic acid (7 ml.) was heated under reflux for 1 hr. The product was sublimed in a vacuum and the yellow sublimate (7 g.) was crystallised from 1 : 2 : 4-trichlorobenzene to give pale yellow 1 : 5-*dichloro*-9 : 10-*di*-(2-*methyl*-1-*naphthyl*)-*anthracene*, m. p. 359—360° (Found: C, 82·25; H, 5·1; Cl, 13·0. $C_{36}H_{24}Cl_2$ requires C, 82·0; H, 4·6; Cl, 13·4%).

7′ : 7″-*Dimethyl*-1 : 9-5 : 10-*di*peri*naphthyleneanthracene* (*Ring Index No.* 3943: 9 : 18-*Dimethyltetrabenzo*[de, hi, op, st]*pentacene*) (II).—A mixture of the reduced 1 : 5-dichloro-compound (2 g.), potassium hydroxide (5 g.), and quinoline (11 ml.) was heated under reflux for 23 min. in an atmosphere of nitrogen. The reddish-violet solution was poured into dilute hydrochloric acid and the dark blue precipitate was extracted with benzene (150 ml.). The extract was chromatographed on alumina, the column being protected from the light. Elution, under pressure, with benzene–light petroleum (b. p. 40—60°) (1 : 2) gave an orange solution with a green fluorescence of the monocyclised compound, the benzoperylene derivative. A second blue band was eluted with benzene and yielded deep blue crystals, m. p. 382—383°, of the *hydrocarbon* (II) (Found: C, 94·95; H, 4·8. $C_{36}H_{22}$ requires C, 95·1; H, 4·9%). The blue solution, which has a red fluorescence, was photo-oxidised quickly. The compound dissolved in concentrated sulphuric acid to give a reddish-brown solution.

3 : 4-5 : 6-10 : 11-12 : 13-*Tetrabenzoperopyrene* (III).—A mixture of the reduced dichloro-compound (5 g.), potassium hydroxide (25 g.), and quinoline (30 ml.) was heated under reflux for 90 min. The quinoline solution was poured into dilute hydrochloric acid, and the dark precipitate was extracted (Soxhlet) with xylene until the extract was almost colourless. The red xylene solution yielded a small quantity of a very soluble red mixture of compounds which were not identified. The residue from the xylene extraction was then extracted with 1 : 2 : 4-trichlorobenzene to give a low yield of orange-brown leaflets. They were dissolved in trichlorobenzene and chromatographed on alumina at 140° with trichlorobenzene as eluant. The yellow eluate had a strong green fluorescence and yielded orange feathery needles, m. p. 487—488°, of *tetrabenzoperopyrene* (Found: C, 96·3; H, 3·9. $C_{36}H_{16}$ requires C, 96·4; H, 3·6%). The compound dissolved in hot concentrated sulphuric acid to give a green solution.

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