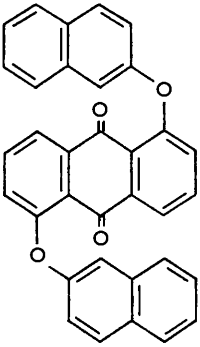
522. *Benzo*[a]*perylene and Some of its Derivatives.*

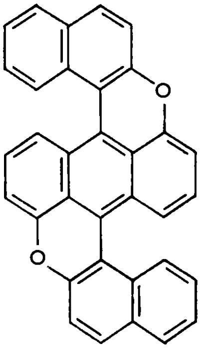
By E. Clar, W. Kelly, D. G. Stewart, and (in part) J. W. Wright.

Dinaphthyloxyanthraquinone (I) was condensed in a sodium chloride–aluminium chloride melt to the polycyclic oxides (II), (III), and (IV). Reduction of one of these (III), with hydriodic acid and red phosphorus followed by dehydrogenation with palladium charcoal gave benzo[*a*]perylene (VI), which was also obtained from dinaphthylanthracene (V) by drastic treatment in a sodium chloride–aluminium melt. If the ring closure of 9 : 10-dihydro-9 : 10-dihydroxy-9 : 10-di-1′-naphthylanthracene (IX) was carried out under milder conditions, 3-1′-naphthylbenzo[*a*]perylene (VIII) was formed. This compound was also obtained by ring closure of 1-chloro-9 : 10-di-1′-naphthylanthracene.

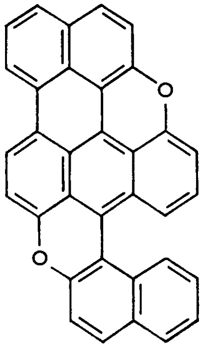
Ring closure of 1 : 5-di-2′-naphthyloxyanthraquinone (I) in a sodium chloride–aluminium chloride melt gave the red nonacyclic dioxide (II), the blue decacyclic dioxide (III), and the green undecacyclic dioxide (IV) according to the conditions applied. The absorption spectra of the three condensation products are shown in Fig. 1. Each ring closure causes a strong shift of the first group of bands to the red, whilst the intense band near 3000 Å remains relatively unaltered.



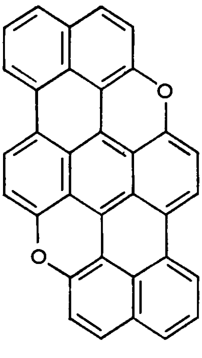
(I)



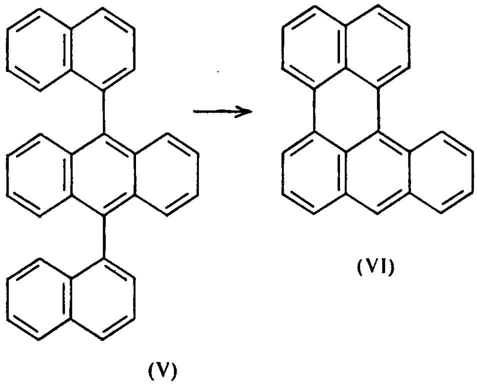
(II)



(III)



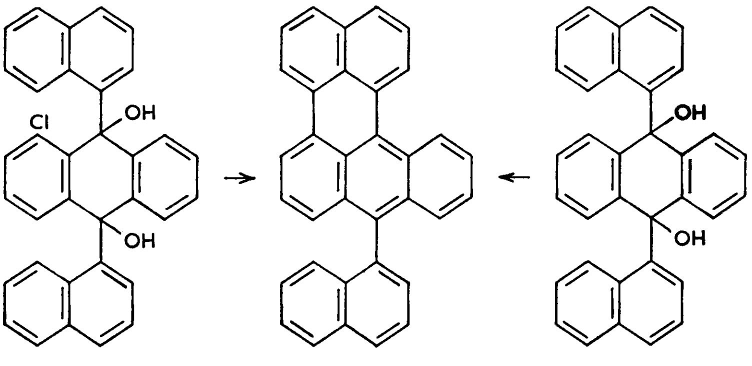
(IV)



(V)

(VI)

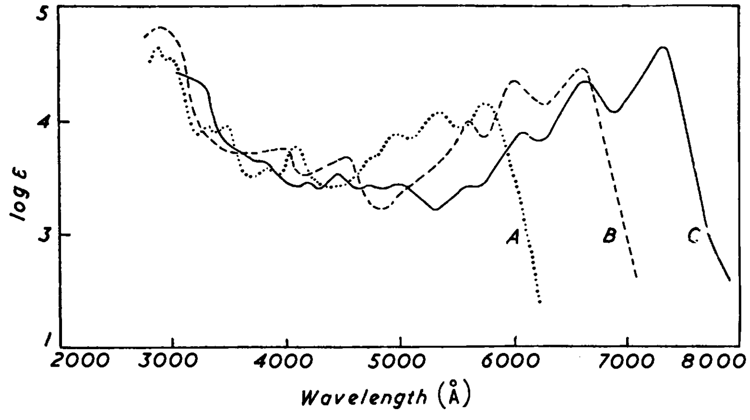
Reduction of the blue compound (III) with hydriodic acid and red phosphorus at 210° yielded a pale yellow resin which was dehydrogenated with palladium–charcoal to a red hydrocarbon. The absorption spectrum of this compound is identical with that of the non-crystalline hydrocarbon obtained on reduction of benzo[*a*]perylene-3 : 10-quinone.[1] Benzo[*a*]perylene (VI) was synthesised by heating 9 : 10-dinaphthylanthracene (V) in a sodium chloride–aluminium chloride melt at 160°. One naphthyl radical is split off during the reaction but the main product of the reaction is 1 : 9-4 : 10-di*peri*naphthyleneanthracene,[2] together with some anthracene and perylene. The benzoperylene was identical with the red hydrocarbon obtained from the dehydrogenation. It gives a colourless adduct with maleic anhydride.



(VII) (VIII) (IX)

3-1′-Naphthylbenzo[*a*]perylene (VIII) is a possible product of the above reactions and, in order to exclude this possibility, this hydrocarbon was synthesised by heating the diol (IX) in sodium chloride–aluminium chloride at a much lower temperature (110°). The hydrocarbon (VIII) was also prepared by heating 1-chloro-9 : 10-di-1′-naphthylanthracene, obtained by reduction of the diol (VII) with quinoline and potassium hydroxide.

FIG. 1. *Absorption max.* (Å) *and* log ε (*in parentheses*).



A, Compound (II) in C_6H_6, 5760 (4·16), 5370 (4·06), 4950 (3·88); 4090 (3·78), 3840 (3·58), 3470 (3·96), 3310 (3·94); 2990 (4·56), 2860 (4·64).
B, Compound (III) in C_6H_6, 6600 (4·46), 6050 (4·33), 5600 (3·97); 4550 (3·68), 3940 (3·76); 2900 (4·82).
C, Compound (IV) in 1 : 2 : 4-*trichlorobenzene*, 7320 (4·65), 6630 (4·34), 6100 (3·89); 500 (3·45); 4450 (3·52), 4210 (3·45), 3800 (3·64).

The absorption spectra of benzo[*a*]perylene (VI) and its naphthyl derivative (VIII) are given in Fig. 2. They are in accordance with the assumed formulæ. It is noteworthy that the first band of benzo[*a*]perylene is shifted by the same amount (6·1$\sqrt{}$Å) in passage

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[1] Clar, *Chem. Ber.*, 1949, **82**, 59.

to 12 : 1′-oxido-1 : 2-benzoperylene [3] (first band in benzene at 5990 Å) as in passage from 1 : 9-4 : 10-di*peri*naphthyleneanthracene [2] (first band in benzene at 6300 Å) to the green compound (IV). This indicates that the annelation principle also applies in the above cases where oxygen-containing rings are involved.

EXPERIMENTAL

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

1 : 5-*Di-2′-naphthyloxyanthraquinone* (I).—This was prepared by a modification of the method described in the literature.[4,5] An intimate mixture of 1 : 5-dichloroanthraquinone (37 g.), β-naphthol (75 g.), and powdered potassium hydroxide (22 g.) was heated at 145° for 2 hr. The melt, mobile at first, became very viscous. The cold melt was extracted with boiling, dilute, aqueous potassium hydroxide and crystallised from nitrobenzene to give large yellow prisms (65 g.), m. p. 245—247° (lit., 243—245°) (Found : C, 82·8; H, 4·3. Calc. for $C_{34}H_{20}O_4$: C, 82·9; H, 4·1%). The compound dissolved in concentrated sulphuric acid to a violet-blue solution and gave a yellow vat in alkaline sodium dithionite solution.

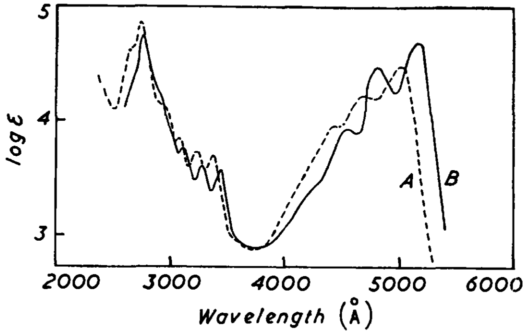

FIG. 2. *Absorption max.* (Å) *and* log ε (*in parentheses*).

A, Compound (VI) in EtOH, 5030 (4·47), 4730 (4·27), 4450 (3·95), 3390 (3·70), 3230 (3·74), 3080 (3·85), 2760 (4·86).

B, Compound (VIII) in C_6H_{14} 5140 (4·68), 4800 (4·46), 4540 (3·91), 3420 (3·55), 3260 (3·58), 3100 (3·74), 2760 (4·73).

7 : 17-*Dioxanaphtho*[1, 2-a, 1′, 2′-j]*perylene* (II) *and* 6 : 16-*dioxanaphtho*[1, 2-*a*]*perinaphtheno*-[1, 2, 3, 3*a*, 4-g, h, i, j]*perylene* (III).—A mixture of the dinaphthyloxyanthraquinone (I) (30 g.), sodium chloride (30 g.), and aluminium chloride (150 g.) was heated with stirring at 180° for 10 min., and then at 145° for 15 min. After cooling to 110°, the melt was poured into dilute hydrochloric acid. The dark blue precipitate was extracted with warm alkaline sodium dithionite solution and dried. The residue was extracted several times with cold benzene and the blue solution chromatographed on alumina. A first, red band, on elution with benzene, gave a brilliant violet-red solution, with a red fluorescence, which on concentration yielded dark red prisms (4 g.), m. p. 255—256°, of the *dioxide* (II) (Found : C, 88·9; H, 4·1. $C_{34}H_{18}O_2$ requires C, 89·1; H, 4·0%). The compound, which photo-oxidised rapidly, dissolved in concentrated sulphuric acid to a violet-red solution. A second, blue band from the chromatogram, on elution and concentration, gave blue crystals (2 g.), m. p. >400°, of the *dioxide* (III) (Found : C, 88·9; H, 3·6. $C_{34}H_{16}O_2$ requires C, 89·5; H, 3·5%). A further portion (15 g.) of this blue compound was obtained by extracting the residue from the benzene extraction with xylene in a Soxhlet apparatus. It sublimed in a vacuum without decomposition and dissolved in concentrated sulphuric acid to a violet solution with a red fluorescence.

Heating the compound (II) in sodium chloride–aluminium chloride at 175° gave the blue compound (III).

6 : 14-*Dioxadinaphtho*[1, 8a, 8, 7-a, b, c ; 1′, 8a′, 8′, 7′-j, k, l]*coronene* (IV).—A mixture of the dinaphthyloxyanthraquinone (I) (26 g.), sodium chloride (26 g.), and aluminium chloride (140 g.) was heated at 175—180° for 35 min. The melt was decomposed and washed as above. The blue-black precipitate contained no red compound (II). The blue compound (2·5 g.) was extracted in a Soxhlet apparatus with xylene. The residue was sublimed in vacuum at 400°/8 × 10^{-5} mm. The blue-green sublimate was extracted with boiling xylene and crystallised from

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

[3] Clar, *Ber.*, 1940, **73**, 351.

[4] Bayer, G.P. 158,531; *Chem. Zentr.*, 1905, **1**, 1517.

[5] Scholl, Böttger, and Wanka, *Ber.*, 1934, **67**, 603.

1 : 2 : 4-trichlorobenzene. It was resublimed and recrystallised several times, to give dark greenish-blue needles, m. p. 515—516°, of the *dioxide* (IV) (Found : C, 90·0; H, 3·8. $C_{34}H_{14}O_2$ requires C, 89·85; H, 3·1%). It dissolves in concentrated sulphuric acid to a blue solution with a very strong red fluorescence.

Benzo[a]*perylene* (VI).—(a) *From the compound* (III). A mixture of compound (III) (0·75 g.), red phosphorus (1 g.), potassium iodide (0·5 g.), and hydriodic acid (55%, 10 ml.) was heated in a sealed tube at 210° for 10 hr. The light brown resin was washed with water and chromatographed in benzene on alumina. The pale yellow resin which was obtained did not crystallise. The resin (0·5 g.) was heated at 230° for 5 hr. with 20% palladium–charcoal (0·5 g.). The charcoal was extracted with benzene and the extract was chromatographed. A colourless band, blue-violet in ultraviolet light, was eluted with benzene–light petroleum (b. p. 40—60°; 1 : 4). Concentration gave a colourless oil. An orange band was eluted with benzene. The orange solution, which had a green fluorescence, was taken to dryness to give a red resin which crystallised from light petroleum (b. p. 60—80°) as red needles, m. p. 115—116°, of *benzo*[a]*perylene* (VI) [Found : C, 94·9; H, 4·8%; *M* (Rast), 310. $C_{24}H_{14}$ requires C, 95·3; H, 4·7%; *M*, 302]. It dissolves in concentrated sulphuric acid to a green solution with a red fluorescence. It photo-oxidised quite quickly. (b) *From the compound* (V). The dinaphthylanthracene (44 g.) was added to sodium chloride (45 g.) and aluminium chloride (230 g.) at 125°, heated to 160° during 5 min., cooled, and poured into dilute hydrochloric acid. The blue-black precipitate was dried and extracted with 400 ml. of cold benzene. The extract was taken to dryness and the residue was distilled in a high vacuum, giving a first, colourless fraction (mainly anthracene) and a second, red, resinous fraction (4 g.). The residue in the flask was mainly 1 : 9-4 : 10-di*peri*naphthyleneanthracene. The second fraction was redistilled into two fractions, the first of which was washed with a little benzene and crystallised from benzene, to give yellow plates, m. p. 268—270°, of perylene. The second was very slowly fractionally sublimed; the yellow portion which sublimed first was perylene; the red fraction which sublimed as droplets was dissolved in benzene and chromatographed; the benzene eluate of the orange band was taken to dryness and the residue crystallised from light petroleum (b. p. 60—80°) to give red needles, m. p. 115—116°, of benzo[*a*]perylene.

Adduct of Benzo[a]*perylene and Maleic Anhydride.*—Benzo[*a*]perylene (VI) was heated under reflux in benzene with a large excess of maleic anhydride until the solution became colourless. The *adduct* recrystallised from acetic anhydride as colourless prisms, m. p. 300—306° (decomp.) (Found : 83·6; H, 4·4. $C_{28}H_{16}O_3$ requires C, 84·0; H, 4·0%). It dissolved in hot concentrated sulphuric acid to a green solution with a red fluorescence. The spectrum of the dipotassium salt of the adduct in water compares well with that of benzanthrene (in alcohol) as expected. Maxima of salt : 3450, 3290, and 3140 Å (log ε 4·22, 4·22, 4·06). Maxima of benzanthrene : 3440, 3290, and 3120 Å (log ε 4·14, 4·22, 4·08).

1-*Chloro*-9 : 10-*dihydro*-9 : 10-*di*-1′-*naphthylanthracene*-9 : 10-*diol* (VII).—A suspension of finely powdered 1-chloroanthraquinone (12·1 g.) in benzene (100 ml.) was slowly added with stirring to 1-naphthylmagnesium bromide prepared from 1-bromonaphthalene (41·4 g.) and magnesium (4·8 g.) in ether (70 ml.). The temperature was allowed to rise during the addition. 70 ml. of solvent were distilled from the mixture which was then heated under reflux for 2 hr. with stirring. The suspension was poured into dilute acetic acid. The residue remaining after steam-distillation was washed with ether and digested thoroughly with alkaline sodium dithionite solution, an almost colourless powder (12·3 g.) being obtained. Crystallisation from xylene gave colourless prisms, m. p. 291—292° (decomp.), of the *diol* (VII) (Found : C, 81·6; H, 4·8; Cl, 6·9. $C_{34}H_{23}O_2Cl$ requires C, 81·8; H, 4·65; Cl, 7·1%). In concentrated sulphuric acid it dissolved to a green solution.

1-*Chloro*-9 : 10-*di*-1′-*naphthylanthracene.*—A suspension of the diol (VII) (5 g.) in acetic acid (30 ml.) and hydriodic acid (55%, 4·5 ml.) was heated under reflux for 15 min. A pale yellowish powder (3·9 g.) was obtained which crystallised from xylene as yellow prisms, m. p. 297—298°, of 1-*chloro*-9 : 10-*di*-1′-*naphthylanthracene* (Found : C, 88·1; H, 4·45; Cl, 7·4. $C_{34}H_{21}Cl$ requires C, 87·8; H, 4·55; Cl, 7·6%). It was insoluble in concentrated sulphuric acid.

3-1′-*Naphthylbenzo*[a]*perylene* (VIII).—(a) 1-Chloro-9 : 10-di-1′-naphthylanthracene (2 g.) in quinoline (15 ml.) was heated under reflux with potassium hydroxide (10 g.) for 7 min. The quinoline solution, which had quickly become red with a green fluorescence, was decanted into dilute hydrochloric acid. The orange-red precipitate was sublimed in a vacuum. The sublimate was dissolved in benzene and the solution chromatographed. An orange-red band was eluted with benzene–light petroleum (b. p. 40—60°; 3 : 1). Crystallisation from light petroleum (b. p. 80—100°), by adding the petroleum to the benzene concentrate and distilling off the benzene, gave red prisms, m. p. 198—200°, of 3-1′-*naphthylbenzo*[a]*perylene* (VIII) [Found: C, 95·3; H, 4·8%; *M* (Rast), 436. $C_{34}H_{20}$ requires C, 95·3; H, 4·7%; *M*, 428]. The solution of the compound was orange with a green fluorescence and it photo-oxidised rapidly. The hydrocarbon dissolved in concentrated sulphuric acid give a green solution with a red fluorescence.

(b) 9 : 10-Dihydro-9 : 10-di-1′-naphthylanthracene-9 : 10-diol (IX) (6 g.) was added to sodium chloride (9 g.) and aluminium chloride (45 g.) at 110°. After 5 min. the melt was poured into dilute hydrochloric acid. The blue-black precipitate was dried and extracted with a small quantity of benzene which was chromatographed. An orange-red band yielded the naphthylbenzoperylene as red prisms.

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