Colouring Matters of the Aphididæ. Part X. Preparation and Properties of 4 : 9-Dihydroxyperylene-3 : 10-quinone.*

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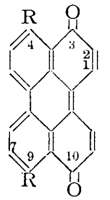
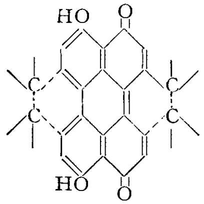
The compound described in the literature as perylene-3 : 4 : 9 : 10-diquinone has been shown to be 4 : 9-dihydroxyperylene-3 : 10-quinone. The similarity of the ultra-violet absorption spectrum of this compound to that of erythroaphin-*fb* confirms that this ring system is the chromophore of the aphin. Di*cyclo*hexylamino-, dipiperidino-, and tetrabromo-derivatives of the dihydroxyperylene-quinone have been prepared as well as 3 : 4 : 9 : 10-tetra-acetoxyperylene, the ultra-violet absorption spectrum of which closely resembles that of tetra-acetyldihydroerythroaphin-*fb*.

The experiments described in Part IX* showed that perylene-3 : 10-quinone (I; R = H), like erythroaphin-*fb* (Part VII, *J.*, 1952, 4928), undergoes a variety of nucleophilic addition reactions. Thus *cyclo*hexylamine, piperidine, and sodium hydroxide in the presence of air gave 1-*cyclo*hexylamino-, 1-piperidino-, and 1-hydroxy-perylene-3 : 10-quinone respectively.



(I)



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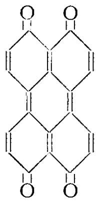

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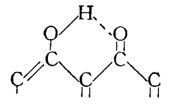

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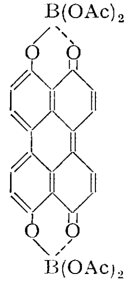

(V)

It was clearly desirable to investigate also the analogous reactions with the undescribed 4 : 9-dihydroxyperylene-3 : 10-quinone (I; R = OH) which resembles the proposed erythroaphin structure (II; Part VIII, *J.*, 1954, 107) even more closely. In 1929, Zinke, Hirsch, and Brozek (*Monatsh.*, **51**, 205; **52**, 13) obtained a compound which, they claimed, gave analyses for $C_{20}H_8O_4$, by the action of sulphuric acid at 150° on 3 : 4 : 9 : 10-tetrachloro-, 3 : 4 : 9 : 10-tetranitro-, 3 : 9-dichloro-4 : 10-dinitro-, or 3 : 10-dinitro-perylene. This product they formulated as perylene-3 : 4 : 9 : 10-diquinone (III). Reductive benzoylation gave 3 : 4 : 9 : 10-tetrabenzoyloxyperylene, oxidation with nitric acid gave mellitic acid, and the compound was stated to be insoluble in alkali. The marked stability of their product was a little surprising for a diquinone structure of this type. 1 : 4 : 5 : 8-Naphthadiquinone is rather unstable and is readily reduced to naphthazarin (Zahn and Ochwat, *Annalen*, 1928, **462**, 72, 86) and we have failed consistently to obtain the corresponding diquinone from erythroaphin, *e.g.*, on oxidation with lead tetra-acetate in glacial acetic acid. The preparation of Zinke's perylenediquinone by the action of sulphuric acid

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* Part IX, preceding paper.

on 3 : 4 : 9 : 10-tetranitroperylene has therefore been repeated. A new pentanitroperylene has been isolated from the nitration products of perylene by Zinke and Unterkreuter's procedure (*Monatsh.*, 1919, **40**, 405) and a rather better yield of the tetranitro-compound has been obtained by modifying the strength of the nitric acid employed. The product isolated from the acid hydrolysis of tetranitroperylene gave analyses for $C_{20}H_{10}O_4$ and is 4 : 9-dihydroxyperylene-3 : 10-quinone (I; R = OH), and not the diquinone as Zinke believed. The dihydroxy-quinone, like erythroaphin, forms a very sparingly soluble greenish-blue sodium salt which probably led the earlier workers to think that the free quinone did not react with alkali. The sodium derivative is non-volatile, whereas the parent dihydroxy-quinone can be sublimed at 260—280°/10^{-4} mm.

The existence of a hydroxyl group in a *peri*-position to a quinone-carbonyl group causes the formation of a six-membered hydrogen-bonded ring (IV) which can be recognised by its effect on the infra-red spectrum (Flett, *J.*, 1948, 1441; Part V, Johnson, Quayle, Robinson, Sheppard, and Todd, *J.*, 1951, 2633). The intensity of the hydroxyl band is greatly diminished if it appears at all, and the carbonyl band is displaced to longer wave-lengths. This phenomenon was noted in erythroaphin (Part V, *loc. cit.*) and it has also been observed with 4 : 9-dihydroxyperylene-3 : 10-quinone, which shows no hydroxyl band and has the main carbonyl band at 1631 cm.$^{-1}$ (cf. erythroaphin-*fb* at 1625 cm.$^{-1}$ and perylene-3 : 10-quinone at 1650 cm.$^{-1}$). Further, with boroacetate (cf. Dimroth and Faust, *Ber.*, 1921, **54**, 3020), 4 : 9-dihydroxyperylene-3 : 10-quinone gave a crystalline complex of structure (V). Hydrolysis regenerated the original quinone. A similar reaction with erythroaphin caused a marked change in the visible spectrum, similar to that observed with the dihydroxyperylenequinone, but the complex proved to be too unstable to be isolated in the crystalline state.

FIG. 1.

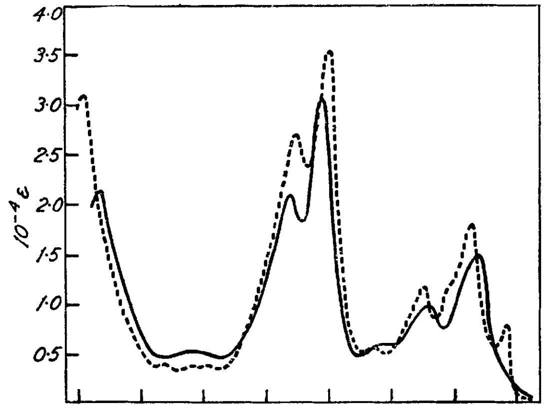

FIG. 2.

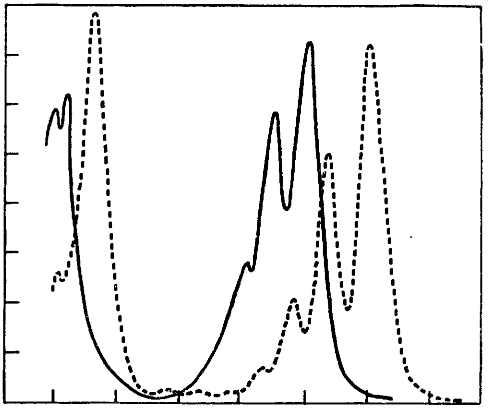

FIG. 1. *Ultra-violet absorption spectra of erythroaphin*-fb (– – – – –) *and* 4 : 9-*dihydroxyperylene*-3 : 10-*quinone* (————) *in tetrachloroethane.*

FIG. 2. *Ultra-violet absorption spectra of tetra-acetyldihydroerythroaphin*-fb (– – – – –) *and* 3 : 4 : 9 : 10-*tetra-acetoxyperylene* (————) *in chloroform.*

The close resemblance of the ultra-violet absorption spectrum of 4 : 9-dihydroxyperylene-3 : 10-quinone to that of erythroaphin-*fb* is so striking as to leave no further doubts as to the nature of the chromophore of the erythroaphin (Figs. 1 and 2).

Because of the sparing solubility of 4 : 9-dihydroxyperylene-3 : 10-quinone in common organic solvents, addition reactions, particularly addition of amines, have been carried out with a suspension of the quinone in pyridine. As with erythroaphin-*fb* (Part VII, *loc. cit.*), two mols. of *cyclo*hexylamine or piperidine were added to the quinone to give substituted diamino-4 : 9-dihydroxyperylene-3 : 10-quinones, dark microcrystalline solids which were only sparingly soluble in hydrochloric acid. This was in contrast to the behaviour of perylene-3 : 10-quinone (Part IX), which formed only monoamino-adducts, the substitution occurring in the 1-position. From this evidence it is probable that in the 4 : 9-dihydroxyperylene-3 : 10-quinone series the amino-substituents occur in the 1 : 6- or 1 : 7-positions, thus emphasising the near-equivalence of the oxygen atoms in the *peri*-hydroxy-quinone system. Reaction of the dihydroxy-quinone with bromine gave a tetrabromo-derivative which was not orientated, although it should be noted that steric considerations would forbid the entry of bromines into both the 1- and the 12- (or 6- and 7-)positions.

Reductive acetylation of 4 : 9-dihydroxyperylene-3 : 10-quinone gave 3 : 4 : 9 : 10-tetra-acetoxyperylene, the ultra-violet absorption spectrum of which closely resembles that of tetra-acetyldihydroerythroaphin-*fb* (Part II, *J.*, 1950, 477) in general shape (Fig. 2). The displacement of the latter spectrum to longer wave-lengths is in accord with the presence of the additional nuclear substituents in the aphin derivative.

EXPERIMENTAL

3 : 4 : 9 : 10-*Tetranitroperylene*.—(*a*) Finely powdered perylene (4·0 g.) was nitrated with nitric acid (*d* 1·42; 280 c.c.) according to Zinke and Unterkreuter's method (*loc. cit.*). The insoluble portion of the reaction mixture was separated by filtration and washed and the combined filtrates were cooled; bright red needles of *pentanitroperylene* (0·47 g.) crystallised. These were recrystallised from nitrobenzene (5 c.c.), washed with boiling ethanol, and, for analysis, dried at 145°/0·2 mm. for 7 hr. (Found : C, 50·4, 50·1; H, 1·8, 2·0; N, 14·9. $C_{20}H_7O_{10}N_5$ requires C, 50·3; H, 1·5; N, 14·7%). The pentanitroperylene is sparingly soluble in chloroform but soluble in sulphuric acid, ethyl benzoate, or nitrobenzene, especially on warming. The absorption spectrum of a chloroform solution showed maxima at 322—323 and 480 mμ. The insoluble residue (3·76 g.) was powdered and stirred at 60—70° for 1 hr. with nitrobenzene (75 c.c.) in order to extract most of the remaining pentanitroperylene, which was precipitated from the filtrate by addition of ethanol (150 c.c.). The dried precipitate (487 mg.) was twice recrystallised from nitrobenzene, to give red needles of pentanitroperylene (266 mg.) (Found : N, 14·7%).

The residue (3·0 g.) was dissolved in boiling nitrobenzene (180 c.c.) as far as possible and the filtrate on cooling depositied red needles (1·38 g.) of 3 : 4 : 9 : 10-tetranitroperylene. For analysis, this was recrystallised from nitrobenzene, washed with boiling ethanol, and dried at 150°/0·15 mm. overnight (Found : C, 55·6; H, 1·9; N, 13·1. Calc. for $C_{20}H_8O_8N_4$: C, 55·5; H, 1·9; N, 13·0%). It formed a yellow-red solution in warm sulphuric acid and was soluble in 100 parts of boiling nitrobenzene and sparingly soluble in chloroform. The ultra-violet absorption spectrum of a chloroform solution showed maxima at 454 and 483 mμ.

(*b*) Finely powdered perylene (4·0 g.) was heated under reflux for 1 hr. with nitric acid (250 c.c.; *d* 1·39). After cooling, the red nitration product was separated, washed with nitric acid and water, dried (4·35 g.), and recrystallised from nitrobenzene (300 c.c.). The product, which formed small brick-red needles, was washed and dried (2·93 g.). For analysis it was again crystallised from nitrobenzene and was dried at 130°/0·15 mm. (Found : N, 13·1%).

4 : 9-*Dihydroxyperylene*-3 : 10-*quinone*.—3 : 4 : 9 : 10-Tetranitroperylene (1·36 g.) was heated with concentrated sulphuric acid (95 c.c.) at 130—140° for 6 hr. (cf. Zinke, Hirsch, and Brozek, *Monatsh.*, 1929, **51**, 205). After cooling and dilution, the deep red acid solution showed absorption in the visible region at 490, 536, and 578 mμ. The reaction product was added to water (1400 c.c.), and the flocculent brown precipitate separated on the centrifuge, washed, and then stirred with 10% sodium hydroxide solution (150 c.c.) for 10 min. The insoluble greenish sodium salt was separated (centrifuge) and suspended in more 10% sodium hydroxide solution (100 c.c.), and to the suspension sodium dithionite (5 g.) was added. The mixture was warmed on the steam-bath in an atmosphere of nitrogen until the quinone was completely reduced and the solution so obtained was quickly filtered through a thin layer of carbon. The reddish-brown vat, which showed a greenish fluorescence, was oxidised by bubbling air through the solution for 3 hr., and the greenish-blue precipitate which formed was separated on the centrifuge, washed, and dried (740 mg.). The product which was the sodium salt of the dihydroxyperylene-quinone was insoluble in nitrobenzene and did not sublime at 270°/10^{-4} mm. It was digested with warm dilute acid and the reddish-brown suspension separated, washed, and dried (550 mg.). After crystallisation of the product (100 mg.) from nitrobenzene (60 c.c.), very small, red,

solvated needles of 4 : 9-*dihydroxyperylene*-3 : 10-*quinone* (50 mg.) were obtained which were washed with boiling ethanol and dried at 150°/0·15 mm. for 12 hr. (Found : C, 74·7; H, 3·6; N, 2·4. $C_{20}H_{10}O_4,C_6H_5{\cdot}NO_2$ requires C, 71·3; H, 3·4; N, 3·2%). The product was then sublimed at 270—290°/10^{-4}—10^{-5} mm.; it formed black metallic needles (20 mg. in 24 hr.) (Found : C, 76·2; H, 3·2. $C_{20}H_{10}O_4$ requires C, 76·4; H, 3·2%). The product was soluble in 600 parts of boiling nitrobenzene and dissolved in concentrated sulphuric acid forming a pinkish red-fluorescent solution which showed bands in the visible spectrum at 490, 536, and 578 mμ (hand spectroscope). In *sym*-tetrachloroethane, the product showed absorption at 265—266, 340, 419, 444, 493, 526, and 567 mμ; log $\varepsilon_{\max.}$ 4·33, 3·73, 4·32, 4·50, 3·77, 4·00, and 4·17 respectively (Fig. 1). The infra-red spectrum determined on a mull in Nujol showed maxima at 1631 (s), 1290 (s), 1242, 1186, 1145, 1072 (s), 926, 840, 787, and 673 cm.$^{-1}$.

3 : 4 : 9 : 10-*Tetra-acetoxyperylene.*—Anhydrous sodium acetate (200 mg.) and zinc dust (850 mg.) were added to a suspension of finely powdered 4 : 9-dihydroxyperylene-3 : 10-quinone in acetic anhydride (5 c.c.) and acetic acid (3 c.c.), and the mixture was vigorously stirred and heated under reflux for 20 min. After a few minutes the insoluble material dissolved to a reddish-brown solution but a precipitate was formed towards the end of the reaction. After cooling, excess of zinc was removed by decantation and the solid material in the product was separated, washed with cold dilute acetic acid and water, and dried (yield 375 mg.). It was easily soluble in hot nitrobenzene, moderately soluble in acetic anhydride, and sparingly soluble in xylene, carbon disulphide, and chloroform. Recrystallisation of a portion of the product (60 mg.) from nitrobenzene (5 c.c.) gave a *solvate* as reddish prisms (17 mg.) which were washed with boiling ethanol and dried at 135—150°/0·2 mm. for 16 hr. The product decomposed >350° (Found : C, 68·4; H, 4·5. $C_{28}H_{20}O_8,C_6H_5{\cdot}NO_2$ requires C, 68·3; H, 4·1%). The remainder of the crude product (315 mg.) was recrystallised from acetic anhydride (130 c.c.) and formed bronze-coloured leaflets (120 mg.) which were washed with acetic acid and then ethanol. After two further recrystallisations from ethyl benzoate (80 c.c. then 40 c.c.) *tetra-acetoxyperylene* was obtained as reddish-brown plates (40 mg.) (Found : C, 69·2; H, 4·4. $C_{28}H_{20}O_8$ requires C, 69·3; H, 4·1%). Light absorption in $CHCl_3$: max. at 251, 259, 403, 425, and 452 mμ; log ε 4·47, 4·49, 4·14, 4·47, and 4·56 respectively. The infra-red spectrum (Nujol mull) showed max. at 1764, 1600, 1408, 1302, 1208, 1186, 1131, 1039, 1014, 952, 946, 935, 893, 826, 800, and 746 cm.$^{-1}$.

Hydrolysis of 3 : 4 : 9 : 10-*Tetra-acetoxyperylene.*—The acetoxy-compound was suspended in 95% ethanol (7 c.c.), alcoholic sodium hydroxide (2 c.c.; 10%) was added, and the mixture heated under reflux for 15 min. Air was bubbled through the solution for 10 min. to complete the oxidation, and the insoluble sodium salt separated and washed. Acidification of an aqueous suspension of the salt with dilute acetic acid, as before, gave 4 : 9-dihydroxyperylene-3 : 10-quinone, which was purified by sublimation as described above (Found : C, 76·7; H, 3·5%).

4 : 9-*Dihydroxyperylene*-3 : 10-*quinone Bisboroacetate.*—A solution of boric acid (16 mg.) in acetic anhydride (3 c.c.) was added to a suspension of finely divided sublimed 3 : 10-dihydroxyperylene-4 : 9-quinone (16 mg.) in acetic anhydride (3 c.c.) at 60—70°. The mixture was kept at 100° for 30 min. with occasional shaking, the quinone slowly dissolving and a dark red crystalline complex separating from the hot solution. The *product* (21 mg.) was separated, washed with acetic anhydride and ether, and dried *in vacuo* at room temperature [Found : C, 59·1; H, 3·8; B, 3·9 (weighed as B_2O_3). $C_{28}H_{20}O_{12}B_2$ requires C, 59·0; H, 3·5; B, 3·8%]. The complex had no definite m. p. and was sparingly soluble in most organic solvents. A solution in acetic anhydride showed maxima in the visible spectrum (hand spectroscope) at 470, 538, and 583 mμ (cf. the visible spectrum of 4 : 9-dihydroxyperylene-3 : 10-quinone in acetic anhydride which shows bands at 445, 521, and 561 mμ). A solution of the boroacetate of erythroaphin-*sl* in acetic anhydride showed bands in the visible spectrum at 470, 537, and 582 mμ whereas the original quinone under similar conditions absorbed at 445, 518, and 559 mu. Light absorption of 4 : 9-dihydroxyperylene-3 : 10-quinone bisboroacetate in $CHCl_3$: max. at 261, 416, 442, 470, 506, 530, 544, 570, and 588 mμ; log ε 4·58, 3·82, 4·30, 4·88, 3·49, 3·36, 4·00, 3·51, and 4·35 respectively. The infra-red spectrum, determined as a mull in Nujol, showed max. at 1715, 1701, 1631, 1575, 1531, 1427, 1389, 1316, 1294, 1274, 1198, 1103, 1075, 990, 962, 870, 855, 807, 794, 735, and 699 cm.$^{-1}$.

4 : 9-*Dihydroxydipiperidinoperylene*-3 : 10-*quinone.*—Redistilled piperidine (5 c.c.) was shaken with a suspension of finely powdered 4 : 9-dihydroxyperylene-3 : 10-quinone in dry pyridine (15 c.c.) at room temperature for one week. The solid slowly dissolved, forming a purple solution which was filtered and evaporated almost to dryness *in vacuo.* The residue was thoroughly extracted with chloroform (35 c.c.), the insoluble material (102 mg.; insoluble also

in 50% hydrochloric acid) separated, and the filtrate concentrated (to 5 c.c.) and diluted with hot 95% ethanol to precipitate the product. Next morning, the dark precipitate (90 mg.) was separated, washed with ethanol, and crystallised from pyridine–aqueous methanol. The *product* (42 mg.), which was an almost black granular solid, was separated, washed with hot water and methanol, and dried at 130°/0·4 mm. (Found : C, 74·7; H, 5·8; N, 5·4. $C_{30}H_{28}O_4N_2$ requires C, 75·0; H, 5·8; N, 5·8%). It was soluble in pyridine to a purple solution, sparingly soluble in chloroform, and not easily soluble in acids. Light absorption in $(CHCl_2)_2$: max. at 258—259, 430, 454, and 540—554 mμ; log ε 4·49, 4·09, 4·12, and 4·00 respectively. The infra-red spectrum (Nujol mull) showed max. at 3344, 1626, 1550, 1515, 1235, 1155, 1130, 1024, 990, 926, 862, 840, 807, 764, and 752 cm.$^{-1}$.

*Di*cyclo*hexylamino-*4 : 9-*dihydroxyperylene-*3 : 10-*quinone*.—A suspension of 4 : 9-dihydroxyperylene-3 : 10-quinone in dry pyridine (10 c.c.) and *cyclo*hexylamine (8 c.c.) was stirred at room temperature for 6 days. The green solution was then warmed on the steam-bath for 48 hr., during which time the colour changed to purple. The filtrate of the final mixture was evaporated almost to dryness under reduced pressure, and the residue dissolved in warm chloroform (15 c.c.) and again filtered. The chloroform solution was concentrated, diluted with hot 95% ethanol, boiled for 5 min., and then kept overnight. The black granular solid (213 mg.) was separated, washed, and dried, the purification from chloroform (10 c.c.)–ethanol was repeated, and the product (80 mg.) crystallised from pyridine–50% aqueous ethanol. For analysis the *di*cyclo*hexylamino*-compound was dried at 140°/0·5 mm. (Found : N, 5·5. $C_{32}H_{32}O_4N_2$ requires N, 5·5%). A solution in $CHCl_3$ showed max. at 264, 394—398, 440, 568, 576, and 588 mμ. The infra-red spectrum determined as a mull in Nujol showed max. at 3333, 1626, 1600, 1550, 1508, 1342, 1271, 1235, 1212, 890, 830, 820, and 754 cm.$^{-1}$.

*Tetrabromo-*4 : 9-*dihydroxyperylene-*3 : 10-*quinone*.—Finely powdered 4 : 9-dihydroxyperylene-3 : 10-quinone (250 mg.) was brominated according to Zinke, Hirsch, and Brozek's directions (*loc. cit.*). The dark-brown bromo-compound (100 mg.) was recrystallised from nitrobenzene, washed with hot ethanol, and finally recrystallised from ethyl benzoate (40 c.c.), to give dark maroon-coloured needles with a metallic lustre. These (62 mg.) were washed and dried at 150°/0·5 mm. for 12 hr. As a result of analysis (Found : C, 40·3; H, 1·7%), the sample was sublimed at 290—295°/5 × 10^{-5} mm., 10 mg. being obtained as short dark brown needles after 30 hr. (Found : C, 38·5; H, 1·0; Br, 50·7. Calc. for $C_{20}H_6O_4Br_4$: C, 38·1; H, 1·0; Br, 50·7%). Light absorption in $(CHCl_2)_2$: max. at 359, 450, 480, 534, and 576 mμ; log ε 3·80, 4·54, 4·73 4·12, and 4·22 respectively; infl. at 350—356 mμ; log ε 3·79.

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