

*Colouring Matters of the Aphididae. Part IX.\* Some Reactions of Extended Quinones.*

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The reactions of some "extended" quinones with amines and with alkali in presence of air have been examined. Perylene-3 : 10-quinone reacts with *cyclohexylamine*, piperidine, and sodium hydroxide solution in presence of air to give respectively 1-*cyclohexylamino*-, 1-piperidino-, and 1-hydroxy-*perylene-3 : 10-quinone*. Details in the infra-red spectrum of the last-named compound are discussed and 2 : 11-dihydroxyperylene-3 : 10-quinone is also shown to yield a monopiperidino-derivative. These findings support the view expressed in earlier papers from this laboratory that the erythroaphins are derivatives of perylene-3 : 10-quinone.

On the basis of all available evidence it was postulated in Part VII of this series (Brown, Johnson, MacDonald, Quayle, and Todd, *J.*, 1952, 4298) that the erythroaphins, a group of deep red colouring matters derived from a variety of dark-coloured aphids, are extended quinones (*i.e.*, polycyclic quinones in which the carbonyl groups occur in different rings) in which the quinonoid carbonyls are in peripheral rings of the polycyclic system. The simplest of such structures formulates them as derivatives of perylene-3 : 10-quinone. A significant factor in arriving at this conclusion was the ease with which erythroaphin-*fb* appeared to undergo the Thiele acetylation reaction and to react with ammonia or amines in presence of air giving diamino- or substituted diamino-derivatives. Such reactions are typical of simple *p*-quinones (Leicester, *Ber.*, 1890, 23, 2793) and *mesobenzanthrones* (Bradley and Sutcliffe, *J.*, 1952, 1247) but, apart from the fact that 3 : 5 : 3' : 5'-tetramethyldiphenquinone (I; R = Me) undergoes the Thiele acetylation reaction (Erdtman, *Proc. Roy. Soc., A*, 1933—34, 143, 177), no record of similar behaviour among extended quinones exists. Indeed, such quinones as diphenquinone (I; R = H) and perylene-3 : 10-quinone (II; R = H) have been little studied, possibly owing to the difficulty involved in preparing them in quantity. It was therefore necessary to examine their reactions in order to establish whether they undergo reactions with nucleophilic reagents in a manner analogous to the erythroaphins, as an aspect of structural studies on the aphid colouring matters.

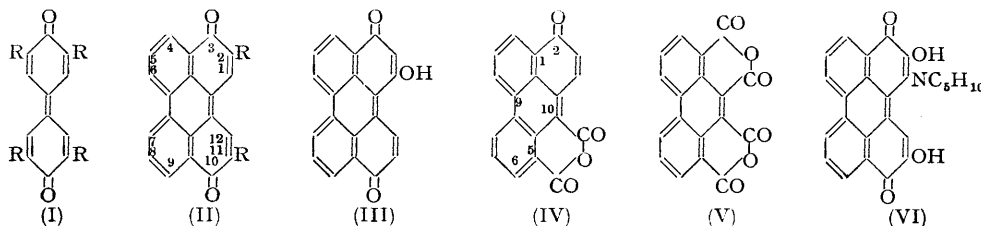
Diphenquinone (I; R = H) was prepared by a new method, *viz.*, oxidation of 4 : 4'-dihydroxydiphenyl with lead tetra-acetate in glacial acetic acid at room temperature. The yield was about 75% and the method proved much superior to that of Willstätter and Kalb (*Ber.*, 1905, 38, 1235) which employed lead dioxide in benzene. Fieser (*J. Amer. Chem. Soc.*, 1930, 52, 5204) has recorded for diphenquinone the very high oxidation-reduction potential of 954 mv, indicative of great reactivity as an oxidising agent. It was therefore not surprising to find that diphenquinone would not undergo addition reactions with amines; reaction with *cyclohexylamine*, piperidine, or morpholine in air at room temperature yielded only its reduction product 4 : 4'-dihydroxydiphenyl. In the same way it yielded only 4 : 4'-diacetyldiphenyl under the conditions normally employed for Thiele acetylation. 3 : 5 : 3' : 5'-Tetramethyldiphenquinone (I; R = Me) has a lower oxidation-reduction potential (calculated to be *ca.* 754 mv) but, although it undergoes Thiele acetylation (Erdtman, *loc. cit.*), reaction with *cyclohexylamine*, piperidine, or morpholine in air yielded only its reduction product 4 : 4'-dihydroxy-3 : 5 : 3' : 5'-tetramethyldiphenyl.

Perylene-3 : 10-quinone (II; R = H), however, with a lower oxidation-reduction potential of 534 mv (Gupta, *J.*, 1952, 3479) reacts readily with *cyclohexylamine* or piperidine at 100° in presence of air, to give monocyclohexylamino- or monopiperidino-derivatives, and with alkali in presence of air to yield a monohydroxyperylene-3 : 10-quinone. The

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same monohydroxy-quinone is formed on hydrolysis of the monocyclohexylamino-quinone, indicating that the hydroxy- and amino-compounds have the same orientation.

2 : 11-Dihydroxyperylene-3 : 10-quinone (II; R = OH) condenses readily with 2 mols. of *o*-phenylenediamine, a fact taken to prove the location of the hydroxyl groups in this compound (Zinke, Stimler, and Reuss, *Monatsh.*, 1934, **64**, 415). With *o*-phenylenediamine under the same conditions the monohydroxyperylene-3 : 10-quinone obtained above does not react and can be recovered unchanged. This observation indicates that the compound should be formulated as 1-hydroxyperylene-3 : 10-quinone (III) and that the cyclohexylamino- and piperidino-compounds are also 1-substituted compounds. This conclusion is supported by the fact that in the reactions described perylene-3 : 10-quinone



yields only monosubstituted derivatives. If the substituent group entered the 2-position it would be expected that under the conditions employed (*i.e.*, in presence of excess of reagent and air) the quinone would yield a 2 : 11-disubstituted product (II; R = OH, cyclohexylamino, or piperidino). On the other hand, examination of models shows that with the first substituent in the 1-position it would be very difficult on steric grounds to introduce a second substituent into the other angular (*i.e.*, 12-) position. Moreover, substitution in the 1-position occurs readily in 2 : 11-dihydroxyperylene-3 : 10-quinone (II; R = OH) which, with piperidine, yields 2 : 11-dihydroxy-1-piperidinoperylene-3 : 10-quinone (VI).

Perylene-3 : 10-quinone undergoes Thiele acetylation but the course of reaction is unusual. Treatment with acetic anhydride and perchloric acid at 35° for several days, followed by hydrolysis and aerial oxidation, gave a compound which from its analysis and infra-red spectrum appeared to be identical with that formulated by Zinke, Hirsch, and Brodek (*Monatsh.*, 1929, **51**, 205) as perylene-3 : 4 : 9 : 10-diquinone. Further discussion of the true nature of this compound is reserved for a later communication.

Oxidation of perylene-3 : 10-quinone with potassium permanganate in aqueous pyridine yielded 2-oxobenzanthrene-5 : 10-dicarboxylic anhydride (IV) and phenanthrene-1 : 8 : 9 : 10-tetracarboxylic dianhydride (V); it seems likely that 1-hydroxyperylene-3 : 10-quinone is an intermediate in this oxidation.

In agreement with observations recorded for other extended quinones (Josien and Fuson, *J. Amer. Chem. Soc.*, 1951, **73**, 478; Hadzi and Sheppard, *ibid.*, p. 5460; Johnson, Quayle, Robinson, Sheppard, and Todd, *J.*, 1951, 2633) the carbonyl frequency in the infra-red spectrum of perylene-3 : 10-quinone (1650  $\text{cm}^{-1}$ ) was found to be lower than that of a simple *p*-quinone (1660—1680  $\text{cm}^{-1}$ ). In 2 : 11-dihydroxyperylene-3 : 10-quinone the carbonyl frequency is shifted even further (1621  $\text{cm}^{-1}$ ) owing to the presence of the *o*-hydroxyl groups. However, unlike quinones with *peri*-hydroxyl groups (Flett, *J.*, 1948, 1441; Johnson *et al.*, *loc. cit.*) the shift is not accompanied by disappearance of the hydroxyl frequency (*ca.* 3300  $\text{cm}^{-1}$ ), for 2 : 11-dihydroxyperylene-3 : 10-quinone shows a strong hydroxyl band at 3280  $\text{cm}^{-1}$ . The compound here formulated as 1-hydroxyperylene-3 : 10-quinone shows a double carbonyl band with maxima at 1647 and 1621  $\text{cm}^{-1}$  and a strong hydroxyl band at 3322  $\text{cm}^{-1}$ . A similar splitting of the carbonyl band is observed in 2-hydroxynaphthalene-1 : 4-quinone which shows maxima at 1680 and 1645  $\text{cm}^{-1}$ , as well as a hydroxyl band at 3080  $\text{cm}^{-1}$ . That the lowering of the carbonyl frequency is due to electron distribution and not solely to chelation is indicated by the facts that the hydroxyl frequency, though modified, does not disappear completely as it does in quinones having *peri*-hydroxyl groups, and that compounds which have no hydrogen available for

chelation still show the effect, *e.g.*, the carbonyl frequency for *p*-benzoquinone is 1660  $\text{cm}^{-1}$  whereas for 2 : 5-bisdimethylamino-*p*-benzoquinone it is 1630  $\text{cm}^{-1}$ .

The infra-red data quoted cannot be used to differentiate between 1- and 2-substituted perylene-3 : 10-quinones since resonance can operate equally well for substituents in both these positions. Analogous effects have been observed in 2-aminoanthraquinone (Flett, *loc. cit.*) and in *o*-substituted acetophenones (Hegert and Kurth, *J. Amer. Chem. Soc.*, 1953, 75, 1622).

#### EXPERIMENTAL

Since the majority of the compounds described do not have m. p.s, characterisation and identification are based upon analysis and infra-red spectra, which were determined in Nujol mulls with a Perkin-Elmer Model 21 double-beam instrument.

*Diphenoquinone* (I; R = H).—4 : 4'-Dihydroxydiphenyl (1.0 g.) was dissolved in hot acetic acid (60 c.c.) and cooled carefully to 30° to obtain a supersaturated solution, which was added quickly to a suspension of lead tetra-acetate (3.0 g.) in acetic acid (40 c.c.) at 30°. The mixture was kept at room temperature overnight, and the scarlet needles of diphenoquinone (0.75 g.) were separated, washed with acetic acid and with light petroleum, and recrystallised from benzene. The quinone separated as either feathery yellow needles or scarlet plates, which decomposed at about 160° yielding a white crystalline sublimate of 4 : 4'-dihydroxydiphenyl and a refractory brown residue (Found : C, 78.4; H, 4.6. Calc. for  $\text{C}_{12}\text{H}_8\text{O}_2$  : C, 78.3; H, 4.4%). Light absorption in  $\text{CHCl}_3$  : max. at 253, 263, and 398  $\text{m}\mu$ ;  $\log \epsilon$  3.40, 3.37, and 4.84 respectively; min. at 249, 260, and 270  $\text{m}\mu$ ;  $\log \epsilon$  3.29, 3.17, and 2.51 respectively. The infra-red spectrum showed max. at 722, 736, 786, 857, 968, 992, 1107, 1171, 1258, 1282, 1550, 1597, and 1639  $\text{cm}^{-1}$ .

3 : 5 : 3' : 5'-Tetramethylidiphenoquinone (I; R = Me).—Prepared according to Bamberger (*Ber.*, 1903, 36, 2036), the quinone separated from acetic acid as small red needles, m. p. 208° (decomp.). The infra-red spectrum showed max. at 722, 775, 830, 913, 939, 1047, 1218, 1250, 1277, 1563, 1597, and 1645  $\text{cm}^{-1}$ .

*Perylene-3 : 10-quinone* (II; R = H).—Prepared according to Zinke and Unterkreuter (*Monatsh.*, 1919, 40, 405), the quinone separated from nitrobenzene as yellow needles (Found, in material dried at 180°/0.2 mm. for 20 hr. : C, 84.8; H, 3.5. Calc. for  $\text{C}_{20}\text{H}_{10}\text{O}_2$  : C, 85.1; H, 3.6%). Light absorption in concentrated  $\text{H}_2\text{SO}_4$  : max. at 285, 347, 362, 489, and 584  $\text{m}\mu$ ;  $\log \epsilon$  4.12, 3.70, 3.71, 4.57, and 3.84 respectively; min. at 271, 315, 354, 375, and 569  $\text{m}\mu$ ;  $\log \epsilon$  4.01, 3.48, 3.64, 3.06, and 3.73 respectively; infl. at 543  $\text{m}\mu$ ;  $\log \epsilon$  4.01. The infra-red spectrum showed max. at 763, 792, 844, 896, 1036, 1054, 1149, 1190, 1259, 1294, 1339, 1353, 1560, 1590, 1603, and 1650  $\text{cm}^{-1}$ .

3 : 10-Diacetoxyperylene.—Perylene-3 : 10-quinone (300 mg.), acetic anhydride (25 c.c.), and excess of zinc dust were boiled under reflux for 2 hr. and filtered hot. The residue was extracted with hot acetic anhydride (25 c.c.). The combined filtrate and extracts yielded 3 : 10-diacetoxyperylene (288 mg.) as yellow plates, m. p. 265—270° (decomp.) after recrystallisation from acetic anhydride (Found, in material dried at 140°/0.1 mm. for 16 hr. : C, 78.1; H, 4.3.  $\text{C}_{24}\text{H}_{16}\text{O}_4$  requires C, 78.2; H, 4.4%). Solutions of the compound in organic solvents are yellow with a strong blue fluorescence. Light absorption in  $\text{CHCl}_3$  : max. at 323, 325, 328, 396, 419, and 446  $\text{m}\mu$ ;  $\log \epsilon$  2.89, 2.90, 2.89, 4.11, 4.45, and 4.54 respectively; min. at 319, 324, 327, 333, 403, and 430  $\text{m}\mu$ ;  $\log \epsilon$  2.87, 2.88, 2.89, 2.87, 4.06, and 4.20 respectively; infl. at 374—378  $\text{m}\mu$ ;  $\log \epsilon$  3.68. The infra-red spectrum showed max. at 692, 760, 769, 803, 811, 870, 920, 938, 1007, 1021, 1036, 1076, 1129, 1143, 1157, 1182, 1209, 1220, 1282, 1309, 1391, 1506, 1603, and 1764  $\text{cm}^{-1}$ .

2-Oxobenzanthrene-5 : 10-dicarboxylic Anhydride (IV) (Zinke and Wenger, *Monatsh.*, 1930, 56, 147).—Sublimation at 260°/5  $\times 10^{-3}$  mm. yielded orange-brown needles (Found : C, 75.6; H, 2.7. Calc. for  $\text{C}_{19}\text{H}_8\text{O}_4$  : C, 76.0; H, 2.7%). Light absorption in concentrated  $\text{H}_2\text{SO}_4$  : max. at 230, 311, and 470  $\text{m}\mu$ ;  $\log \epsilon$  4.56, 3.98, and 4.37 respectively; min. at 215, 290, and 363  $\text{m}\mu$ ;  $\log \epsilon$  4.49, 3.86, and 3.18 respectively; infl. at 278—283  $\text{m}\mu$ ;  $\log \epsilon$  3.88. Light absorption in *N*-NaOH : max. at 266, 297, 309, 424, and 474  $\text{m}\mu$ ;  $\log \epsilon$  4.36, 4.00, 3.99, 4.14, and 4.07 respectively; min. at 254, 292, 304, 326, and 463  $\text{m}\mu$ ;  $\log \epsilon$  4.27, 3.98, 3.88, 3.52, and 3.97 respectively. The infra-red spectrum showed max. at 729, 742, 768, 811, 841, 873, 917, 932, 970, 1031, 1053, 1093, 1115, 1144, 1181, 1200, 1241, 1277, 1294, 1330, 1577, 1608, 1645, 1736, and 1770  $\text{cm}^{-1}$ .

*Aerial Oxidation of Perylene-3 : 10-quinone in Alkaline Solution.*—Sodium hydroxide solu-

tion (300 c.c.; 10%) was added to a hot suspension of finely powdered perylene-3 : 10-quinone (1.0 g.) in dioxan (250 c.c.), and the mixture was heated under reflux for 6 hr. The solution quickly became deep purple and then deep green. Air was passed through the mixture for 5 hr. and the dioxan allowed to evaporate slowly. The solution was cooled overnight, and the insoluble black sodium salt was collected and washed with 10% sodium hydroxide solution until the washings no longer showed an oily green fluorescence. Extraction of the sodium salt with boiling water yielded a deep green non-fluorescent solution which gave a dark brown precipitate when excess of dilute sulphuric acid was added. The dry precipitate was recrystallised several times from nitrobenzene, to yield a black crystalline powder (0.60 g.) (Found, in material dried at 150°/0.05 mm. for 21 hr. : C, 79.0; H, 3.5%). Successive crystallisations from nitrobenzene effected no further purification. The compound was therefore reductively acetylated.

**1 : 3 : 10-Triacetoxyperylene.**—The above crude hydroxy-quinone (200 mg.) was boiled under reflux with acetic anhydride (50 c.c.), sodium acetate (200 mg.), and excess of zinc dust for 2 hr. Filtration yielded a reddish-brown solution with a bluish-green fluorescence, which was stirred with ice-cold sodium acetate solution for 1 hr., and the dark brown solid was collected, washed, and dried *in vacuo* over phosphoric oxide at room temperature. The crude acetoxy-compound was dissolved in benzene (50 c.c.) and put on a column of silica (5.5 × 15 cm.). The impurities formed an upper dark brown band, and the product was eluted with benzene (2 l.) as a yellow, blue-fluorescent band. Evaporation of the benzene, a repetition of chromatography on silica, and several recrystallisations from acetic anhydride or benzene yielded 1 : 3 : 10-triacetoxyperylene (130 mg.) as bright yellow, small, hair-like needles, m. p. 238—239° (decomp.) (Found : C, 73.3, 73.1, 73.5; H, 4.2, 4.3, 4.5. C<sub>26</sub>H<sub>18</sub>O<sub>6</sub> requires C, 73.3; H, 4.2%). The compound is readily soluble in chloroform, yielding a yellow solution with a blue fluorescence. Light absorption in CHCl<sub>3</sub> : max. at 250, 256, 296, 308, 397, 419, and 446 mμ; log ε 4.66, 4.68, 4.03, 3.98, 4.22, 4.46, and 4.52 respectively; min. at 251, 292, 304, 328, 402, and 430 mμ; log ε 4.65, 4.02, 3.96, 3.71, 4.19, and 4.26 respectively. The infra-red spectrum showed max. at 743, 761, 769, 781, 804, 825, 838, 856, 872, 895, 915, 990, 1024, 1081, 1100, 1148, 1160, 1205, 1600, and 1770 cm.<sup>-1</sup>.

**1-Hydroxyperylene-3 : 10-quinone (III).**—1 : 3 : 10-Triacetoxyperylene in chloroform was treated with methanol containing a few drops of 10% aqueous sodium hydroxide. The solution immediately became deep blue and deposited a blue sodium salt. This salt was dissolved in water and treated with excess of dilute sulphuric acid, and the mixture shaken with air. The orange-red precipitate was sublimed at 260°/5 × 10<sup>-3</sup> mm., to yield 1-hydroxyperylene-3 : 10-quinone as flat red needles, which did not melt below 350° (Found : C, 80.0; H, 3.3. C<sub>26</sub>H<sub>10</sub>O<sub>3</sub> requires C, 80.6; H, 3.4%). Light absorption in concentrated H<sub>2</sub>SO<sub>4</sub> (magenta solution) : max. at 219, 237, 304, and 508 mμ; log ε 4.54, 4.51, 4.08, and 4.37 respectively; min. at 229, 375, and 370 mμ; log ε 4.49, 3.95, and 3.30 respectively. The infra-red spectrum showed max. at 703, 763, 811, 843, 849, 873, 896, 1008, 1099, 1176, 1244, 1299, 1414, 1582, 1621, 1647, and 3322 cm.<sup>-1</sup>.

**1-cycloHexylaminoperylene-3 : 10-quinone.**—Perylene-3 : 10-quinone (200 mg.) was heated at 80° for 24 hr. with pyridine (20 c.c.) and cyclohexylamine (10 c.c.). The resulting deep purple solution was diluted with water, and the product extracted with chloroform. The extract was washed free from pyridine and cyclohexylamine with dilute sulphuric acid and water, dried, evaporated to small bulk (4 c.c.), and diluted with hot methanol (16 c.c.). 1-cycloHexylaminoperylene-3 : 10-quinone (217 mg.) separated as clusters of flat purple needles having a red-brown metallic sheen. The compound was recrystallised from methanol-chloroform or from anhydrous methanol (Found, in material dried at 100°/0.5 mm. for 24 hr. : C, 82.0, 82.0; H, 5.0, 5.4; N, 3.8, 3.8. C<sub>26</sub>H<sub>21</sub>O<sub>2</sub>N requires C, 82.4; H, 5.4; N, 3.7%). The compound, which on being heated decomposes without melting, is hygroscopic and in air absorbs water to constant weight (Found : C, 80.8; H, 5.4; N, 3.75. C<sub>26</sub>H<sub>21</sub>O<sub>2</sub>N,  $\frac{1}{2}$ H<sub>2</sub>O requires C, 80.4; H, 5.7; N, 3.6%). It is soluble in acetic acid or chloroform, giving purplish-blue solutions. Its solution in concentrated sulphuric acid is blood-red with a red fluorescence; on dilution with water the colour changes to deep green and a green sulphate separates; further dilution yields the original purple solid. Light absorption in CHCl<sub>3</sub> : max. at 285, 328, 402, 454, 490, 568, 578, and 586 mμ; log ε 4.55, 3.92, 4.21, 3.78, 3.90, 4.29, 4.30, and 4.30 respectively; min. at 323, 339, 444, 467, 497, 570, and 580 mμ; log ε 3.87, 3.56, 3.76, 3.73, 3.89, 4.29, and 4.29 respectively; infl. at 498—500 and 572—576 mμ; log ε 3.89 and 4.29. Light absorption in concentrated H<sub>2</sub>SO<sub>4</sub> : max. at 341—343, 488, and 558 mμ; log ε 3.77, 4.54, and 3.99 respectively; min. at 310, 376, and 553, mμ; log ε 3.60, 3.61, and 3.97 respectively; infl. at 354—357 mμ; log ε 3.71.

The infra-red spectrum showed max. at 769, 807, 1028, 1122, 1232, 1244, 1292, 1335, 1515, 1563, 1587, 1603, 1645, and 3300  $\text{cm}^{-1}$ .

*Hydrolysis of 1-cyclohexylaminoperylene-3 : 10-quinone.*—Sodium hydroxide solution (20 c.c.; 5%) was added to a boiling solution of *cyclohexylaminoperylene-3 : 10-quinone* (200 mg.) in dioxan (20 c.c.), and the mixture was boiled under reflux for 5½ hr. The cooled mixture was filtered, the bluish-purple solid washed with water, and the alkaline filtrate washed with chloroform until free from purple starting material. From the residual purple solid and the chloroform extracts, unchanged crystalline *cyclohexylaminoperylene-3 : 10-quinone* (60 mg.) was isolated. The deep green, non-fluorescent, alkaline filtrate was acidified, and the brown precipitate separated, dried, and recrystallised several times from boiling nitrobenzene. 1-Hydroxyperylene-3 : 10-quinone (24 mg.) was obtained as reddish-brown rectangular plates (Found, in material dried at  $170^\circ/4 \times 10^{-4}$  mm. for 6 hr. : C, 79.8; H, 3.7. Calc. for  $\text{C}_{26}\text{H}_{10}\text{O}_3$  : C, 80.6; H, 3.4%). The compound was identical with 1-hydroxyperylene-3 : 10-quinone in its ultra-violet and infra-red spectra.

*1-Piperidinoperylene-3 : 10-quinone.*—Perylene-3 : 10-quinone (88 mg.) was heated at  $80^\circ$  with redistilled piperidine (10 c.c.) for 45 min. The quinone dissolved and a deep purple solution resulted, which deposited purple crystals (45 mg.) on being cooled to  $0^\circ$ . Recrystallisation from pyridine-methanol (1 : 1) yielded *1-piperidinoperylene-3 : 10-quinone* as small purple plates which decomposed without melting; the crystals had a brown reflex. In air the compound absorbed water to constant weight (Found : C, 80.4, 80.9, 80.5; H, 5.0, 5.3, 5.0; N, 3.6, 3.7.  $\text{C}_{25}\text{H}_{10}\text{O}_2\text{N}, \frac{1}{2}\text{H}_2\text{O}$  requires C, 80.3; H, 5.4; N, 3.8%). Light absorption in concentrated  $\text{H}_2\text{SO}_4$  (blood-red solution) : max. at 340 and 486  $\text{m}\mu$ ;  $\log \epsilon$  3.73 and 4.50; min. at 308 and 376  $\text{m}\mu$ ;  $\log \epsilon$  3.64 and 3.45; infl. at 324—336  $\text{m}\mu$   $\log \epsilon$  3.71. Light absorption in  $\text{CHCl}_3$  : max. at 280, 401, 476, and 542  $\text{m}\mu$ ;  $\log \epsilon$  4.28, 4.22, 3.98, and 4.09; min. at 254, 343, 454, and 492;  $\log \epsilon$  4.20, 3.73, 3.92, and 3.97; infl. at 434—444  $\text{m}\mu$ ;  $\log \epsilon$  3.94. The infra-red spectrum showed max. at 768, 781, 809, 835, 851, 864, 895, 986, 1033, 1049, 1088, 1104, 1133, 1188, 1239, 1247, 1294, 1332, 1553, 1585, and 1637  $\text{cm}^{-1}$ .

*Permanganate Oxidation of Perylene-3 : 10-quinone.*—A mixture of finely powdered perylene-3 : 10-quinone (400 mg.), finely powdered potassium permanganate (400 mg.), redistilled pyridine (30 c.c.), and a few drops of water was heated at  $90^\circ$  for 30 min., and filtered hot from manganese dioxide. The yellow filtrate, which had a strong green fluorescence, was kept at  $0^\circ$  for 45 min. and the brownish-yellow needles (30 mg.) of unchanged perylenequinone were separated. The manganese dioxide was washed with hot dilute sodium hydroxide solution, and the combined filtrate and washings were cooled and acidified. The resulting brown solid was crystallised from nitrobenzene, to yield orange needles (40 mg.) (Found, in material dried at  $120^\circ/0.5$  mm. for 20 hr. : C, 75.8; H, 2.7. Calc. for  $\text{C}_{19}\text{H}_8\text{O}_4$  : C, 76.0; H, 2.7%). This compound was identical with 2-xobenzanthrene-5 : 10-dicarboxylic anhydride (IV) in its infra-red and ultra-violet spectra.

Addition of methanol to the hot nitrobenzene mother-liquor from the above crystallisation yielded bronze needles (60 mg.) of phenanthrene-1 : 8 : 9 : 10-tetracarboxylic dianhydride (V) (Found, in material dried at  $170^\circ/0.2$  mm. for 15 hr. : C, 68.0; H, 2.2. Calc. for  $\text{C}_{18}\text{H}_6\text{O}_4$  : C, 67.9; H, 1.9%). Light absorption in concentrated  $\text{H}_2\text{SO}_4$  : max. at 303, 314, and 406  $\text{m}\mu$ ;  $\log \epsilon$  4.05, 4.06, and 4.16 respectively; min. at 276, 305, and 315  $\text{m}\mu$ ;  $\log \epsilon$  3.86, 4.02, and 3.48 respectively. Light absorption in aq. NaOH : max. at 265, 305, and 315  $\text{m}\mu$ ; min. at 238, 291, and 312  $\text{m}\mu$ . The infra-red spectrum showed max. at 730, 741, 760, 775, 807, 833, 864, 885, 904, 940, 979, 1017, 1045, 1091, 1103, 1133, 1149, 1152, 1205, 1245, 1264, 1282, 1339, 1401, 1636, 1575, 1592, 1608, 1667, 1745, and 1779  $\text{cm}^{-1}$ .

*2 : 11-Dihydroxyperylene-3 : 10-quinone* (II; R = OH). Prepared according to Zinke, Stimler, and Reuss (*Monatsh.*, 1933, **62**, 415) and recrystallised several times from nitrobenzene, the dihydroxy-quinone formed minute black crystals (Found, in material dried at  $150^\circ/1.0$  mm. for 18 hr. : C, 76.4; H, 3.5. Calc. for  $\text{C}_{20}\text{H}_{10}\text{O}_4$  : C, 76.4; H, 3.2%). Light absorption in concentrated  $\text{H}_2\text{SO}_4$  : max. at 308 and 521  $\text{m}\mu$ ;  $\log \epsilon$  4.04 and 4.19; min. at 290 and 392—406  $\text{m}\mu$ ;  $\log \epsilon$  3.97 and 3.75; infl. at 361—365 and 574—585  $\text{m}\mu$ ;  $\log \epsilon$  3.83, and 4.08. The infra-red spectrum showed max. at 731, 761, 852, 885, 921, 1031, 1062, 1104, 1205, 1232, 1259, 1287, 1339, 1408, 1587, 1621, and 3279  $\text{cm}^{-1}$ .

*2 : 11-Dihydroxy-1-piperidinoperylene-3 : 10-quinone* (VI).—The dihydroxy-quinone (100 mg.) readily dissolved in piperidine (10 c.c.), yielding a deep blue solution. After several days in contact with air, this solution, then deep purple, was poured into water and made just acid to litmus. The purple solid was collected, dried, and recrystallised several times from nitrobenzene, and the hygroscopic black-brown glistening crystals of *1-piperidino-2 : 11-dihydroxy-*

*perylene-3 : 10-quinone* were well washed with methanol (Found in material dried at 140°/0.1 mm. for 20 hr. : N, 3.7.  $C_{25}H_{19}O_4N$  requires N, 3.6%).

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