Perylene-3:9-quinone

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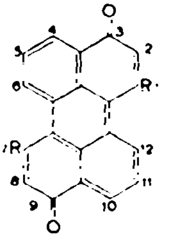
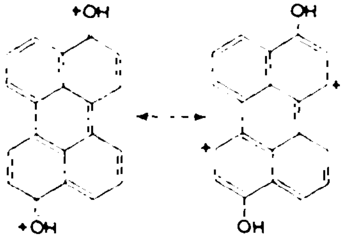
The chemistry of extended quinones has been little studied owing possibly to the difficulty of their preparation in quantity. Todd and co-workers examined the properties of perylene-3:10-quinone[1] and 4:9-dihydroxyperylene-3:10-quinone[2] as an aspect of the chemical studies of aphid pigments; the properties of perylene-3:9-quinone, (I, R = H), have been examined in an analogous manner.

Perylene-3:9-quinone has been prepared by a new method, namely the oxidation with iodine in pyridine of 3:9-diketo-1:2:3:7:8:9-hexahydroperylene,[3] the overall yield from anthracene being 40 per cent. Oxidation with chromic oxide in sulphuric acid gives anthraquinone-1:5-dicarboxylic acid[4] identified as its methylester;[5] reductive acetylation gives 3:9 diacetoxyperylene. Perylene-3:9-quinone reacts readily with piperidine and *cyclo*hexylamine at 90° in presence of air to give dipiperidino and di*cyclo*hexylamino derivatives, both of which are hygroscopic. With alkali a dihydroxy derivative is probably formed but this could only be isolated as its dihydrotetraacetyl derivative. This disubstitution with nucleophilic reagents contrasts with the monosubstitution of perylene-3:10-quinone where steric factors prohibit the attack of a second substituent.[1]

Quinone addition must occur on the 1:2 and 7:8 double bonds because of their relative stabilisation in the molecule and assuming normal addition as in perylene-3:10-quinone the substituents must be orientated at positions 1 and 7, (I, R = NC_5H_{10}, or NC_6H_{11}). This is borne out by the infra-red data, thus perylene-3:9-quinone has its carbonyl absorption at 1664 cm^{-1}--indicating less effective conjugation than other extended quinones--and those of its diamino derivatives at c.a. 1620 cm^{-1}. This lowering is due to the changed electron distribution in the carbonyl bonds under the influence of the electron repelling amino groups[6] at 1 and 7.



I



II

Perylene-3:9-quinone shows a bathychromic shift in its light absorption on change of solvent from chloroform to sulphuric acid and this is due to the contribution of the new electronic forms (II etc.), following protonation of the carbonyl groups. The spectra of the diamino derivatives is unchanged on similar treatment, the electron attracting --$\ddot{N}$H-- groups inhibit the mesomeric shifts leading to structures such as II, and also therefore protonation of the carbonyl groups.

EXPERIMENTAL

Since several of the compounds described do not have m.p., identification is based upon analysis and infra-red spectra.

Perylene-3:9-*quinone*. 3:9-Diketo-1:2:3:7:8:9-hexahydroperylene (1·0 g) was dissolved by warming in pyridine (25 cc) and then cooled to 10°. Addition of an ice cold solution of iodine in pyridine (0·5 g in 10 cc), gave a precipitate of perylene-3:9-quinone (0·9 g) which was filtered off after an hour. The quinone was purified in portions by extraction into chloroform in a soxhlet apparatus, evaporation to a small bulk (5 cc) and addition of hot methanol (20 cc); on standing overnight the quinone

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[1] B. R. Brown and A. R. Todd, *J. Chem. Soc* 1280 (1954).
[2] A. Calderbank, A. W. Johnson and A. R. Todd, *J. Chem. Soc.* 1285 (1954).
[3] I. Y. Postovskii and N. P. Bednyagina, *J. Gen. Chem. U.S.S.R.* 7, 2919, 2924 (1937).
[4] L. F. Feiser and H. Feiser, *J. Amer. Chem. Soc.* 55, 3010 (1933).
[5] A. W. Johnson, J. R. Quayle, T. S. Robinson, N. Sheppard and A. R. Todd, *J. Chem. Soc.* 2633 (1951).
[6] R. A. Durie and J. S. Shannon, *J. Austr. Chem. Soc* 170 (1958).

separated in fine black needles showing a violet reflex, m.p. >350°. Material dried at 120°/0·05 mm for 20 hr (Found: C, 84·8, H, 3·3; Calc. for $C_{20}H_{10}O_2$: C, 85·1, H, 3·6%). *Perylene*-3:9-*quinone* was sparingly soluble in organic solvents giving claret coloured solutions, in conc H_2SO_4 the solution was bichromatic appearing blue by direct and red by reflected light. Light absorption in $CHCl_3$: max at 244, 276, 427, 529, and 570 mμ; log ε 4·35, 4·90, 4·23, 4·64 and 4·78 respectively; min at 253, 325, 446, and 546 mμ; log ε 4·20, 3·45, 3·81, 4·33 respectively; inflexion at 365 mμ; log ε 3·84. Light absorption in conc H_2SO_4: max at 263, 292, 447, 575, and 636 mμ; log ε 4·72, 4·43, 4·45, 4·53 and 4·68 respectively; min at 279, 345–346, 485, and 596 mμ; log ε 4·37, 3·62, 4·21, and 4·37 respectively. The infra-red spectrum (KBr disk) showed max at 1098, 1149, 1193, 1212, 1271, 1306, 1354, 1395, 1455, 1545, 1597, 1664, and 2902 cm^{-1}.

3:9-*Diacetoxyperylene*. Perylene-3:9-quinone (250 mg), sodium acetate (30 mg), zinc dust (750 mg) and acetic anhydride (25 cc) were refluxed for 3 hr. The solution was filtered whilst still hot and the residue washed with acetic anhydride (10 cc); the combined washings and filtrate on cooling gave 3:9-*diacetoxyperylene* (150 mg). The product recrystallised as fine yellow needles from the same solvent, m.p. 272–273°. (Found: C, 77·9; H, 4·2; $C_{24}H_{16}O_4$ requires: C, 78·2; H, 4·4%). The compound dissolved in chloroform gave a yellow solution with a blue fluorescence. Light absorption in $CHCl_3$: max at 253, 396, 416, and 446 mμ; log ε 4·40, 4·16, 4·45, and 4·52 respectively; min at 318, 399, and 426 mμ; log ε 3·92, 4·12, and 4·25 respectively. The infra-red spectrum (KBr disk) showed a max at 1760 cm^{-1}.

1:7 *Dicyclohexylaminoperylene*-3:9-*quinone*. Finely powdered perylene-3:9-quinone (200 mg) was heated on a steam bath at 90° with pyridine (25 cc) and *cyclo*hexylamine (15 cc) for 36 hr when the solution was a deep brown colour. The solvents were removed under reduced pressure, the residue dissolved in chloroform (25 cc) and filtered free of insoluble material. Concentration of the chloroform solution and addition of hot methanol (15 cc) gave on cooling 1:7-*dicyclohexylaminoperylene*-3:9-*quinone* (170 mg) as small black needles. The compound was recrystallised from chloroform-methanol, m.p. >350°. (Found: 77·3, 77·4, H, 6·7, 6·4, N, 5·3; Calc. for $C_{32}H_{32}O_2N_2.H_2O$: C, 77·7, H, 6·9, N, 5·7%). After drying material at 110°/0·05 mm for 24 hr: (Found: C, 80·4, H, 6·5; Calc. for $C_{32}H_{32}O_2N_2$: C, 80·7; H, 6·7%). Light absorption in $CHCl_3$: max at 296, 455, and 481 mμ; log ε 4·92, 4·46, and 4·50 respectively; min at 374 and 462 mμ; log ε 4·32 and 4·45 respectively; inflexions at 430–435 and 472–474 mμ; log ε 4·39 and 4·48. Light absorption in conc H_2SO_4: max at 256 and 487 mμ; log ε 4·96 and 4·63; min at 394 mμ; log ε 4·34. Infra-red spectrum (KBr disk) showed max at 762, 821, 837, 886, 904, 927, 982, 1030, 1102, 1146, 1182, 1234, 1250, 1341, 1360, 1400, 1510, 1580, 1598, 1622, 2820, and 2880 cm^{-1}.

1:7-*Dipiperidinoperylene*-3:9-*quinone*. Perylene-3:9-quinone (150 mg) was heated for 6 hr at 90° with pyridine (5 cc) and redistilled piperidine (10 cc), at which stage the solution was a deep red colour. The residue on removal of the solvents under reduced pressure was dissolved in chloroform and filtered. Concentration of the chloroform and addition of hot methanol (20 cc) precipitated the product (100 mg) on cooling. 1:7-*Dipiperidinoperylene*-3:9-*quinone* crystallised as a black microcrystalline powder with a brown reflex from pyridine-methanol, m.p. >350°. (Found: C, 71·2, 71·6, H, 6·4, 6·6, N, 5·3; Calc. for $C_{30}H_{28}O_2N_2.3H_2O$: C, 71·7, H, 6·8, N, 5·67%). Material dried at 120°/0·03 mm for 30 hr (Found: C, 80·1, H, 6·3, N, 6·2; $C_{30}H_{28}O_2N_2$ requires: C, 80·4, H, 6·2, N, 6·2%). Solutions of the compound in organic solvents were pale red. Light absorption on $CHCl_3$: max at 251, 385, 404, 482, and 496 mμ; log ε 4·90, 4·48, 4·46, 4·50, and 4·50 respectively; min at 379, 395, 422, and 490 mμ; log ε 4·46, 4·44, 4·44, and 4·46. Light absorption in conc H_2SO_4: max at 270, 471, and 489 mμ; log ε 4·66, 4·48, and 4·48 respectively; min at 392 and 482 mμ; log ε 4·35 and 4·45. Infra-red spectrum (KBr disk) showed max at 805, 842, 1024, 1061, 1106, 1131, 1151, 1225, 1242, 1410, 1430, 1510, 1578, 1600, 1621, 2810, 2875 cm^{-1}.

1:3:7:9-*Tetra-acetoxyperylene*. A suspension of finely powdered perylene-3:9-quinone (600 mg) in dioxan (200 cc) containing sodium hydroxide (200 cc; 10%) was refluxed for 12 hr when the solution was a deep red. The solution was filtered and reduced to 50 cc bulk on a rotary evaporator, cooling to 0° overnight gave a black precipitate of the sodium salt which was filtered free and washed with water. The sodium salt was dissolved by boiling in 50 per cent aqueous ethanol, filtered and acidified with dil H_2SO_4. The hydroxyquinone separated as a black amorphous solid (150 mg), but was not amenable to recrystallisation because of its insolubility. Its solution in conc H_2SO_4 was violet in colour.

The crude hydroxy-quinone (150 mg) was boiled under reflux with acetic anhydride (50 cc), sodium acetate (25 mg) and zinc dust (750 mg) for 4 hr and the filtered solution poured into sodium acetate solution (2 N). After 1 hr the latter solution was extracted with chloroform (2 × 50 cc) and the chloroform extracts washed with sodium bicarbonate solution and water. Evaporation of the solvent gave a brown gum which was dissolved in benzene (5 cc) and absorbed on a column of precipitated silica (12 × 4 cm, in benzene) and the yellow orange band eluted with further benzene (350 cc). Evaporation of the benzene gave a light orange solid which crystallised from acetic anhydride as an orange powder (15 mg) m.p. 245–250° (d). (Found: C, 69·8, H, 4·4; Calc. for $C_{28}H_{20}O_8$: C, 69·4, H, 4·1%). Light absorption in $CHCl_3$: max at 396, 421, and 450 mμ; log ε 4·15, 4·40, and 4·51 respectively; min at 404 and 432 mμ; log ε 4·13 and 4·23.

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Electron transference in the attack of atoms or radicals upon carbon-hydrogen bonds

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Prof. J. Kenner has recently discussed a number of reactions wherein carbon-hydrogen bonds are broken and alkyl free radicals thereby generated.[1] His interpretation is that this process should always be formulated as involving two or more steps with electron transference being the dominant and initial process.

$$\mathrm{R\text{-}H \cdot X\cdot \longrightarrow \overset{+}{R}\cdot H\ \ X{:}^{-} \longrightarrow R\cdot \cdot H\text{--}X}$$

Although I agree in principle to the importance of electron transference in the reactions of atoms and radicals having a high electron affinity, I believe the details of the process have been incorrectly interpreted by Prof. Kenner. It is my belief that electron transference should be considered as a stabilizing factor in the transition state rather than the demanded reaction path.[2]

$$\begin{array}{c}\text{TRANSITION STATE}\\ \mathrm{R\text{-}H \cdot X\cdot \longrightarrow \left[\underset{\text{I}}{R{:}H\,X\cdot} \longleftrightarrow \underset{\text{II}}{R^{+}H\cdot X{:}^{-}} \longleftrightarrow \underset{\text{III}}{R\cdot H\text{-}\ X{:}^{-}}\right] \longrightarrow R\cdot + H\text{--}X}\end{array}$$

In terms of complete electron transference it is difficult to see why the relative reactivities of nuclear substituted toluenes or cumenes toward a free radical or atom should be dependent upon the structure of the radical or atom.

$$\mathrm{Y\text{--}C_6H_4\text{--}CH_3 + X\cdot \xrightarrow{k_s} Y\text{--}C_6H_4\text{--}CH_2\cdot + HX}$$

According to the Kenner postulate the polar effect (the effect of the polar nature of Y on k_s) in the reactions of atoms and radicals which have a high electron affinity (e.g. Cl·, Br·) or a low electron affinity (e.g. $CCl_3\cdot$) should be equivalent. In actual fact an appreciable polar effect is observed for chlorine and bromine atoms (k_s is reduced by electron-withdrawing substituents) whereas no polar effect has been detected in the reactions of trichloromethyl radicals.[3] In terms of resonance stabilization of the transition state these facts can be rationalized easily since the contribution of structure II should be most important when X· has the highest electron affinity.

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