5,8-Dihydroxy-9,10-dihydro-9,10-[1,2]benzenoanthracene-1,4-dione. An Intramolecular Triptycene Quinhydrone

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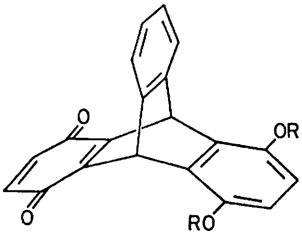
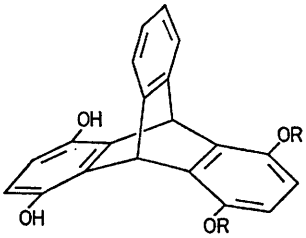
Summary The title compound (**1**) has been obtained either by the partial oxidation of the bishydroquinone (**4**) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone or by the reaction between (**4**) and the bisquinone (**5**); it has a strong transannular interaction in spite of the apparently disadvantageous framework.

In recent years the transannular interactions between the three benzene rings in triptycene molecule have been a matter of some uncertainty. The results of chemical reactions, and u.v., c.d., and e.s.r. spectra have been variously interpreted in terms of inductive effects, local excitation, exciton interaction, and/or transannular electron exchange. In one case, evidence for unexpectedly strong inter-ring interaction has been reported for a triptycene analogue in which the tropylium ring is substituted for a benzene ring.[1] The title compound (**1**) has now been prepared to study the strength and mechanism of the transannular interaction between the π-donor and acceptor groups incorporated into the apparently unfavourable triptycene framework.

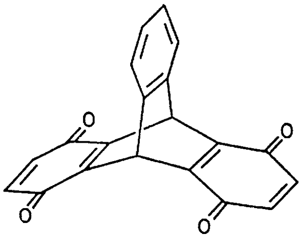
The Diels–Alder reaction of 1,4-dimethoxyanthracene with 5 mol. equiv. of *p*-benzoquinone in refluxing acetonitrile for 10 h gave the 9,10-adduct (yield 86%) which was a mixture of *endo*- and *exo*-isomers. Isomerization to the dimethoxyhydroquinone (**3**), m.p. >200 °C (decomp.),† took place quantitatively on treatment with potassium hydroxide in aqueous dioxan. Oxidation with freshly prepared silver oxide in dry acetone gave the dimethoxyquinone (**2**), m.p. 271·5—272·5 °C (70% yield), which was then treated with ceric ammonium nitrate in aqueous dioxan to effect oxidative demethylation.[2] The bisquinone (**5**), m.p. >220 °C (decomp.), thus obtained in 85% yield, was hydrogenated over Pd/C to give the bishydroquinone (**4**), m.p. >230 °C (decomp.). Partial oxidation of the latter with the calculated amount of dichlorodicyano-*p*-benzoquinone gave the intramolecular quinhydrone (**1**) as violet crystals, m.p. >250 °C; n.m.r. [$(CD_3)_2SO$] δ 6·01 (s, 2H), 6·33 (s, 2H), 6·70 (s, 2H), 6·9—7·1 (m, 2H), 7·3—7·5 (m, 2H), and 8·99 (s, 2H). Most intriguing was the spontaneous formation of (**1**), which precipitated when solutions of equimolar amounts of (**4**) and (**5**) in acetone were mixed and warmed briefly on a steam bath. No external quinhydrone was formed when triptycene monoquinone (**6**) and the corresponding hydroquinone were allowed to react.



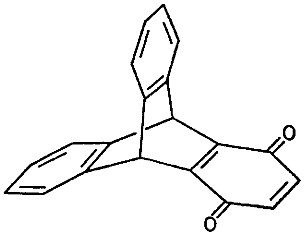
(1) R = H
(2) R = Me



(3) R = Me
(4) R = H

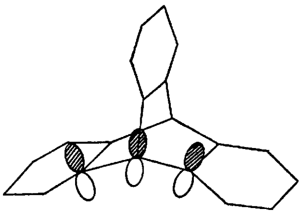


(5)

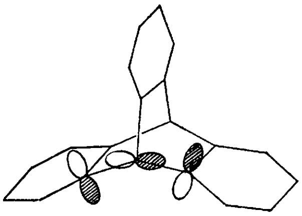


(6)

^{1}H N.m.r. spectroscopy shows that (**1**) is slightly dissociated into (**4**) and (**5**) in $(CD_3)_2SO$, with a free energy of formation ($\Delta G°$) from (**4**) and (**5**) of 10·0 kJ mol^{-1} at 27·0 °C. The charge-transfer band of (**1**) has a maximum at 430 nm (ϵ_{max} 425) in Me_2SO, extending as far as 550 nm and is almost comparable to that of quinhydrone itself (λ_{max} 440 nm; ϵ_{max} 890 in 0·05 M HCl).[3] [*Cf.* also (**2**): λ_{max} 411 nm; ϵ_{max} 450 in acetonitrile *vs.* *p*-benzoquinone–1,4-dimethoxybenzene: λ_{max} 413 nm; ϵ_{max} 370 in cyclohexane.[3]]



(7)



(8)

The first and second half-wave potentials of (**5**) in dimethylformamide with tetra-n-butylammonium perchlorate as supporting electrolyte are −0·23 and −0·48 V (with respect to the saturated calomel electrode), respectively. Compared to the first $E_{1/2}$ of (**6**), −0·37 V, the second quinonoid ring in (**5**) appears to have an electron-attracting effect on the electrolytic reduction of the first quinonoid ring and the intermediate semiquinone ring has an electron-donating effect on the reduction of the remaining quinone ring.

All the results clearly indicate that the electron donor–acceptor interaction between the hydroquinone and *p*-benzoquinone chromophores incorporated in the triptycene skeleton is almost as strong as that in the quinhydrone itself, the complex of the free component molecules. A simple through-space interaction between the donor and acceptor rings held at 120° to each other cannot explain the observed strong interaction, since the resonance interaction between the nearest $p\pi$ orbitals is estimated to be 0·2 β.[4] We propose a through-bond homoconjugative interaction between the donor and acceptor rings as depicted in (**7**) and (**8**). The occurrence of the σ(C–C)–π interaction may be rationalized by taking into account the rather high *p*-character and the 'banana bond' nature of the endocyclic bonds in the bicyclic framework of a triptycene molecule.[5]

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† Satisfactory elemental analyses were obtained for all new compounds.

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