

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

By HIIZU IWAMURA* and KATSUMI MAKINO

(Division of Applied Molecular Science, Institute for Molecular Science, Myodaiji, Okazaki 444, Japan and Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan)

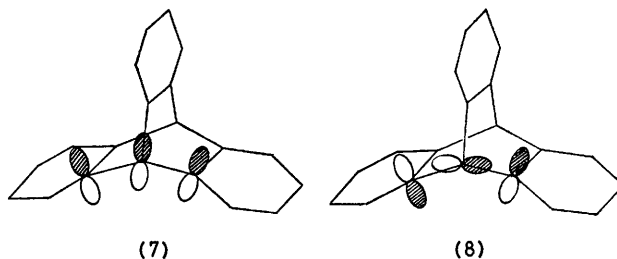
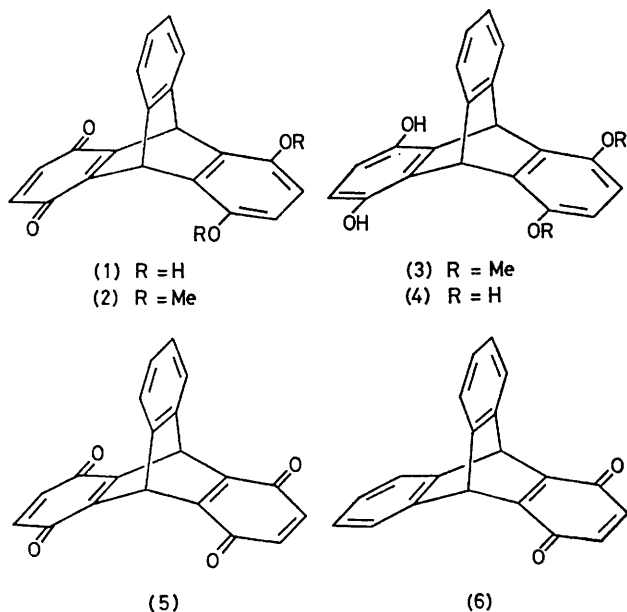
Summary The title compound (1) has been obtained either by the partial oxidation of the bishydroquinone (4) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone or by the reaction between (4) and the bisquinone (5); it has a strong transannular interaction in spite of the apparently disadvantageous framework.

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.

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

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

¹H N.m.r. spectroscopy shows that (1) is slightly dissociated into (4) and (5) in (CD₃)₂SO, with a free energy of formation (ΔG°) 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 Me₂SO, 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]



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 0.2β .⁴ We propose a through-bond homoconjugative interaction between the donor and acceptor rings as depicted in (7) and (8). The occurrence of the $\sigma(\text{C}-\text{C})-\pi$ 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

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. [(CD₃)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.

(Received, 3rd May 1978; Com, 473.)

† Satisfactory elemental analyses were obtained for all new compounds.

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