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Oxidative Ring Opening and Rearrangement of an Anthroquinocyclopropene. Molecular Structure of a Novel Spiro-3-Furanone

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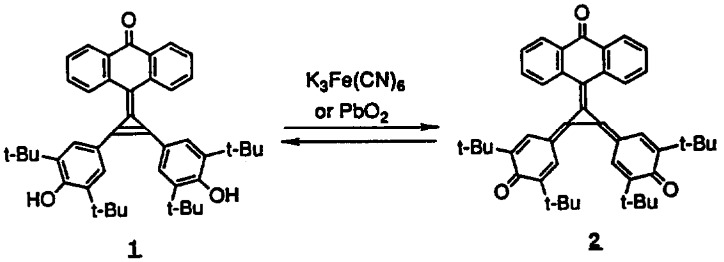
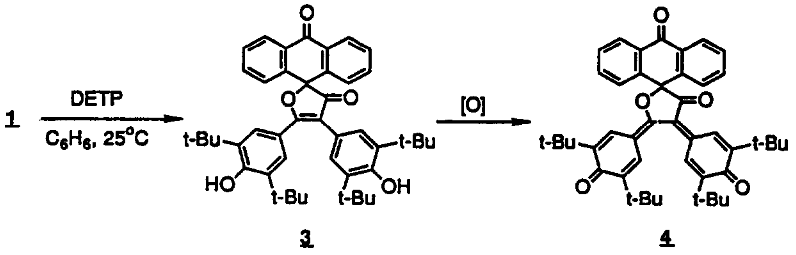
Reaction of anthraquinone **1** with diethyl dithiophosphate led to oxidative ring opening with the formation of spiro-3-furanone **3**; subsequent oxidation of **3** with alkaline potassium ferricyanide gave a 4,5-bis(quino)-3-furanone, **4**, whose structure was established by x-ray crystallography.

Earlier we have reported the synthesis of various polyquinocycloalkanes, radialene-like molecules with strong, low energy electronic transitions.[1] An example is the anthraquinocyclopropane **2**, made by oxidation of the corresponding dihydro compound, **1**.[2]



In an attempt to replace an oxygen atom in **1** with sulfur, this compound was treated with diethyl dithiophosphate (DETP) in benzene. The surprising product was the spiro-3-furanone compound **3**, which upon oxidation yielded the diquino derivative **4**. Both structures are unprecedented. Compounds **3** and **4** each contain the structural elements of an enol ether and a conjugated ketone, and are unique both because of the spiro-anthrone moiety and the di(hydro)quinoethylene functionality at positions 4 and 5.



In a typical procedure, diethyl dithiophosphate (0.30 g, 1.6 mmol) was added via syringe to a dark red suspension of **1** (1.0 g, 1.6 mmol) in 25 mL of dry benzene under a nitrogen atmosphere. After 15 h at room temperature, the reaction mixture was pale orange and no remaining cyclopropene was detected by tlc analysis. Following evaporation of solvent, crystallization from acetonitrile solution gave 0.26 g (24%) of **3** as yellow crystals. The spectroscopic data is entirely consistent with the proposed furan-3(2H)-one structure.[†]

It was found that the 1,2-dihydroquinoethylene moiety in **3** can undergo two-electron oxidation, characteristic of dihydroquinones, to give the diquinoradialene **4**.[‡] In a typical procedure, a yellow solution of 150 mg (0.22 mmol) of **3** in 20 mL of chloroform was treated with 20 mL (0.66 g, 2 mmol) of potassium ferricyanide in 1 N aqueous potassium hydroxide. The resultant bright green organic layer was separated, dried, and evaporated to a green residue. Crystallization from acetonitrile gave birefringent, metallic-appearing crystals, reflecting purple from some faces and green from others. An x-ray crystallographic analysis was carried out for **4**;[§] a thermal ellipsoid diagram is shown in Figure 1.

[†] Analytical data for 4',5'-bis[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]-spiro[anthracene-9(10H), 2'(3'H)-furan]-3'-10-dione (**3**): Mp 264-266°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.36 (bs, 36H), 5.77 (s, 1H, -OH), 5.22 (s, 1H, -OH), 7.00 (s, 2H), 7.7-7.5 (m, 6H), 7.83 (s, 2H), 8.5-8.3 (m, 2H). Mass spectrum (30eV) calcd for $C_{45}H_{50}O_5$ m/z 670.3658, found m/z 670.3776. Anal. Calcd: C, 80.56; H, 7.51. Found: C, 79.97; H, 7.38.

[‡] Analytical data for 4',5'-bis[3,5-bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadien-1-ylidene]-4',5'-dihydrospiro[anthracene-9(10H), 2'(3'H)-furan]-3',10-dione (**4**): Crystals from CH_3CN; mp 250°C dec; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.26 (bs, 18H), 1.30 (s, 9H), 1.40 (s, 9H), 7.0-8.5 (m, 12H). ^{13}C NMR (90 MHz, $CDCl_3$) δ 182.7, 186.4, 186.8, 194.6 (C=O). Mass spectrum (30 eV) calculated for $C_{45}H_{48}O_5$ m/z 668.3504, found m/z 668.3354. UV ($CHCl_3$) λ_{max} 682 nm.

[§] Crystal data for **4**: $C_{45}H_{48}O_5 \cdot CH_3CN$, M = 709.9; monoclinic, space group $P2_{1/n}$, a = 17.998(4), b = 9.861(2), c = 24.655(5) Å, $\beta = 111.15(2)^\circ$, T = 294 ± 1 K, λ (Mo-K_α) = 0.71073 Å; U = 4081(2) Å^3, $D_o = 1.15$ g cm^{-3}, and Z = 4. The structure was solved by direct methods and refined by blocked-cascade least squares refinement[3] based on 3468 unique reflections with $F_o > 3$ I(F_o)I. The acetonitrile of crystallization was disordered into three overlapping positions which were included in the refinement as idealized rigid groups with individual atom thermal parameters; final discrepancy indices R = 0.070, $R_w = 0.078$, goodness of fit = 1.54. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center. See Notice to Authors, Issue No. 1.

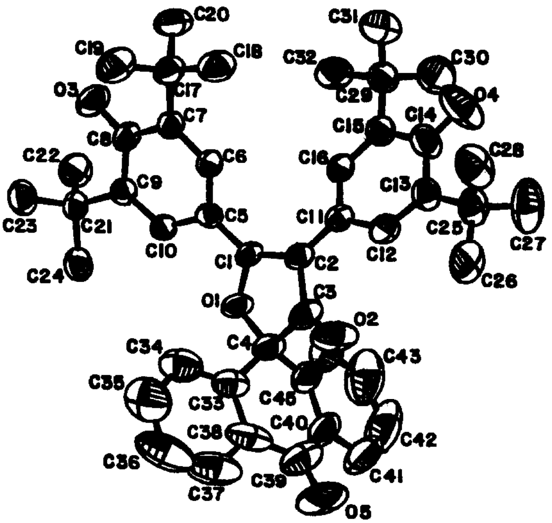
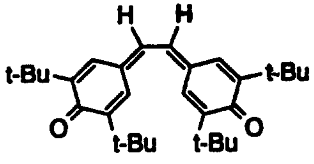


Figure 1. Thermal ellipsoid diagram from crystal structure of **4**. Hydrogen atoms have been omitted for clarity.

The intense color of compound **4** is due to a low energy UV absorption band (λ_{max} 682 nm in $CHCl_3$ solution) evidently resulting from an electronic transition of the extended pi-electron system. Similar long wavelength absorption has been observed for the polyquinoalkanes such as **2**, but the transition energy for **4** is exceptionally low for a diquino compound. Suitable model compounds are **5**, λ_{max} 447 nm,[4] and **6**, λ_{max} 542 nm.



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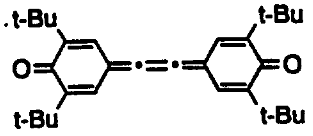

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The low-energy transition in **4** may reflect destabilization of the ground state due to twisting of the quinonoid rings. In the solid state, the dihedral angle between the planes of these rings in **4** is 45.6°. The deviation from coplanarity probably results from steric interactions between the hydrogens at C(6) and C(16), and the *tert*-butyl groups at C(7) and C(15). Atoms C(1), C(2), C(3) and O(2) are nearly coplanar, and lie in the mean plane of the quinonoid rings. Additional conjugation involving the carbonyl group, as well as a lone pair of electrons on O(1), may also contribute to the low transition energy. The contribution of the anthraquinoid moiety to conjugation is probably negligible, since it is nearly orthogonal to the mean plane of the furanone ring.

Detailed steps in the reaction pathway leading from **1** to **3** are unknown. There is precedent for the opening of the three-membered ring in the disubstituted quinocyclopropenes under acidic conditions,[5] but not for subsequent closure to a furanone. We hope to report on the reaction mechanism of this surprising transformation in the future.

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