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Synthesis and Properties of a Novel Electron Acceptor Derived from *p*-Benzoquinone

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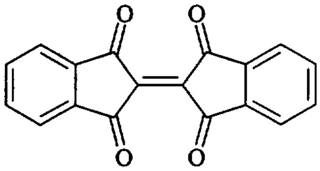
Abstract: Oxidation of *p*-hydroxyphenyl indandione affords 2-(cyclohexa-2',5'-dienylidene) indan-1,3,4'-trione, a new strong electron acceptor that exhibits two reversible one-electron reduction steps in solution.

Keywords: Quinoid compound

A majority of strong organic electron acceptors employed in the synthesis of donor-acceptor charge transfer complexes are based on the *p*-benzoquinone parent system.[1] Recently, we demonstrated that 2,2'-biindanylidene-1,3,1'3'-tetraone (BIT, **1**) exhibits strong electron accepting properties comparable to that of chloranil.[2] Further extension of the conjugated system of **1** can afford a series of *p*-benzoquinone and tetracyano-*p*-quinodimethane analogs involving the 1,3-indandione moiety.



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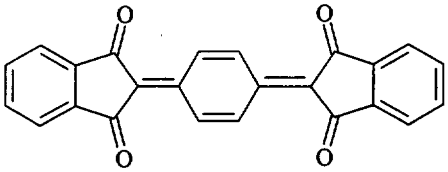

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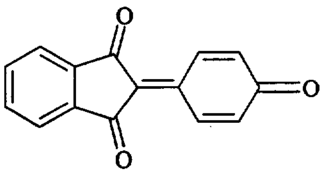

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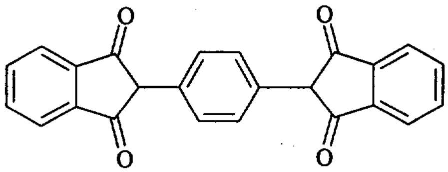

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Here we report on hybrids of BIT and *p*-benzoquinone (PBQ) molecules: the attempted synthesis of cyclohexa-2",5"-diene-1",4"-diylidene-di-2,2'-indane-1,1',3,3'-tetraone (**2**) and properties and crystal structure of 2-(cyclohexa-2',5'-dienylidene) indane-1,3,4'-trione (**3**).

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Oxidation of 1,4-phenylene di-2,2'-indane-1,1',3,3'-tetraone[3] (4) using DDQ (excess) in acetonitrile (c = 10^{-3} molL^{-1}) at room temperature led to the formation of red-violet poorly soluble microcrystals. In the presence of solvents the product is unstable and turns slowly into a colorless powder. All attempts at crystallization also afforded the colorless amorphous powder. IR spectra of both colorless samples showed the presence of carbonyl groups and benzene rings. Mass spectra of the colorless samples exhibited polymer-like features. The instability of **2** is reminiscent of tetrakis-(methoxycarbonyl)-quinodimethane, which although somewhat more stable, forms an insoluble product upon heating or storing in light.[4]

The synthesis of **3** has previously been attempted using silver oxide during the search for antioxidant agents,[5] but the clean product has never been isolated and characterized. Derivatives of **3** were also postulated to form as a result of disproportionation of radicals generated from 2-*p*-hydroxyphenyl-1,3-indandiones by impulse photolysis.[6] However, upon oxidation of *p*-hydroxyphenyl-1,3-indandiones[7-9] using iron (III) chloride, only the corresponding dimers have been isolated.[9]

We found that oxidation of 2-*p*-hydroxyphenyl-1,3-indandione using DDQ affords orange platelets of **3** in good yields. In a typical procedure, to a warm solution of 1 mmol of *p*-hydroxyphenylindandione in 10 ml of acetonitrile, a solution of 1 mmol of DDQ in 5 ml of acetonitrile was added. The mixture was heated to the boiling point and, after the color changed to red-orange, filtered and left overnight in a refrigerator. The product (0.16 g, 67%) was filtered and crystallized from acetonitrile, m.p. 194-199^{0} C (decomp.). Derivative **3** is highly soluble in toluene, chloroform, methylene chloride, less soluble in ethanol and unlike **2** is very stable in both the solid state and in solution.

The electronic absorption spectra of **3** in methylene chloride exhibits a broad absorption band between 440 and 570 nm ($\varepsilon = 460$) and an intensive band at 356 nm ($\varepsilon = 43{,}000$). ^{1}H and ^{13}C-nmr spectra were consistent with the structure **3**.[10]

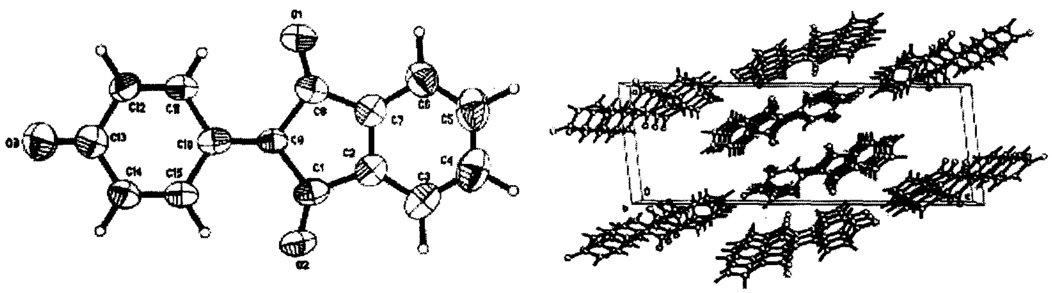

Figure. Molecular structure and crystal packing of **3** along the *b*-axis; selected bond lengths [Å]: C1-C2 1.498(6), C1-C9 1.498(6), C1-O2 1.219(5), C9-C10 1.359(6), C13-O3 1.230(5). Displacement ellipsoids are drawn at 50% probability level.

Finally, the structure of **3** was confirmed by X-Ray analysis[11]. Molecules of **3** in crystals are planar (Rms is 0.0167Å)(Figure). The bond lengths and angles are in a good agreement with the results obtained for both PBQ[12] and BIT[2]. The intramolecular distance O(1)...C(11)H is equal to 2.18Å evidencing the presence of the hydrogen bond.

The molecules in a crystal form infinite stacks along the short *b*-axis. No short intermolecular contacts are found in the crystal of **3** and all intermolecular O...H distances are longer than 2.51Å.

Quantum mechanical calculations using both AM1//AM1 and B3LYP/6-31G(d)//B3LYP/6-31G(d) model chemistries[13] (zero-point correction was taken into account in the latter case) predict that **3** should exhibit strong electron accepting properties considerably exceeding that of PBQ. This prediction is confirmed by the results of electrochemical studies (Table).

Table. Calculated electron affinities and CVA data for PBQ, **3** and BIT (in acetonitrile, at r.t., Bu_4NClO_4 electrolyte, scan rate100 mV/s).

	EA (eV)[a]	EA(eV)[b]	E^1_{red} (V)	E^2_{red} (V)
PBQ	2.25	1.58	-0.54	-1.19 (SCE)
3	2.97	2.33	-0.18	-0.59 (SCE)
BIT	2.58	2.13	-0.08	-0.28 (Ag/AgCl)

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[a] AM1//AM1. [b] B3LYP/6-31G(d)//B3LYP/6-31G(d).

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10. ^{1}H-Nmr (500 MHz, $CDCl_3$) δ 6.64 (d, J=3 Hz, 2H, 3',5'-CH), 7.85-7.9 (m, 2H), 7.99-8.05 (m, 2H), 9.02 (d, J=3 Hz, 2H, 2',6'-CH); ^{13}C-NMR δ 123.76 (5-C), 130.84 (2-C), 133.93 (5'-C), 134.55 (6'-C), 136.37 (4'-C), 141.94 (1'-C), 142.40, 186.98 (4'-C), 190.17 (1-C).

11. X-ray data for **3** (orange plate, size 0.4x0.3x0.15 mm); $C_{15}H_8O_3$, M= 236.2, monoclinic, space group $P2_1/n$; at 293K, a= 8.527(3), b=5.356(2), c=24.463(9) Å, β= 96.93(2)°, V=1109.1(7)A^3, Z=4, ρ_c=1.415 Mg/m^3,$\mu(MoK_\alpha)$= 0.099 mm^{-1}. 1550 independent reflections were measured with "Syntex P-1 " difractometer ($\lambda(MoK_\alpha)$ = 0.71069, graphite monochromator, $\omega/2\theta$-scan, 2θ<50°) of which 1079 were observed with F_o>4$\sigma(F_o)$. The structure was solved by direct methods and refined by least-squares in anisotropic approximation to R = 7.24, wR2 = 16.37. All calculations were carried out using the SHELXTL programs (Bruker, 1998). Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Center.

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