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Synthesis of Novel Truxenequinone Based Electron Acceptors

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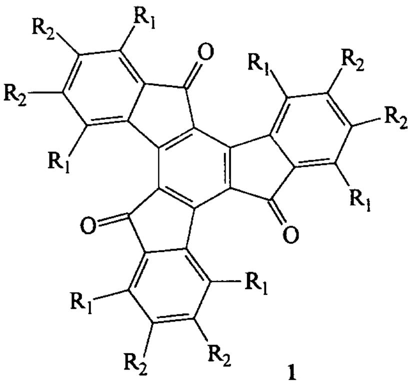
Abstract: Truxenequinones and their hexacyanotrimethylene derivatives exibit reversible multistep reduction in solution

Recently, 1,3-indandione derivatives were demonstrated to be valuable precursors for strong electron acceptors.[1] Truxenequinone **1a**, one of the products of 1,3-indandione self-condensation has been known for more than a century[2] and has attracted attention as one of possible precursors for the synthesis of C_{60}.[3] Here we report the synthesis of novel strong electron acceptors derived from this molecule.



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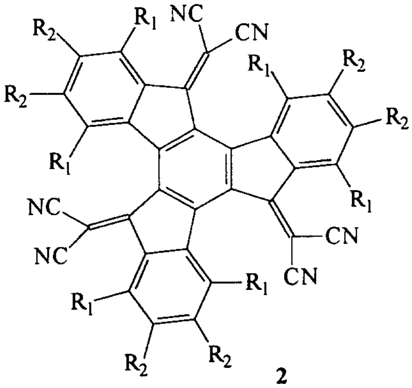

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a, $R_1 = R_2 = H$; **b**, $R_1 = H$, $R_2 = Cl$; **c**, $R_1 = R_2 = F$

We have found that truxenequinone (**1a**) undergoes three one-electron reduction steps of which the first one (-0.90 V, Ag/AgCl) is reversible. Its hexachloro derivative **1b** is a stronger acceptor (-0.76 V) whereas the perfluoro derivative (**1c**) is considerably stronger (-0.25 V) than *p*-benzoquinone (PBQ, -0.52 V)(Table).

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Unexpectedly, in spite of the strong steric hindrance, all carbonyl groups in derivatives **1** can easily be replaced by dicyanomethylene groups. In a typical experiment, 1 mmol of **1a** was dissolved in 50 ml of dry deoxygenated chlorobenzene. Then 6 mmol of malononitrile was added under Ar followed by a dropwise addition of 6 mmol of $TiCl_4$ and 12 mmol of dry pyridine during 2h under vigorous stirring. The reaction mixture was warmed to 70°C and stirred for another 4h. Water (30 ml) was added to the reaction mixture and the product was extracted with methylene chloride. Column chromatography (methylene chloride as the eluent) afforded di-, tetra- and hexacyano (**2a**) derivatives. The residue was recrystallized from chlorobenzene to afford **2a** as red crystals (m.p.> 250°C) in 42% yield. Derivatives **2b** and **2c** can be prepared analogously in 45% and 30% yields correspondingly.[4]

The structure of **2a** was confirmed by X-ray analysis.[5] The most interesting feature is the molecular structure of **2a**, which has an approximate C_{3v} symmetry with sphere-like shape of the truxene moiety and all-*cis* conformation of cyano groups protruding outside this sphere (Figure).

The cyclic voltammogram of derivative **2a** exhibits four one-electron reduction waves of which the first three are fully reversible. The first reduction potential is close to that of C_{60}.

Table. Peak reduction potentials of derivatives **1** and **2** (vs. Ag/AgCl, in benzonitrile, $TBABF_4$, glassy carbon working electrode, sweep rate 100 mV s^{-1}).

PBQ	-0.52	-1.17		
1a	-0.90	-1.05	-1.25	
1b	-0.76	-1.05	-1.28	
1c[a]	-0.25	-0.67	-0.80	
2a[a]	-0.33	-0.63	-0.85	-1.27
2b	-0.22	-0.75	-0.88	
2c	+~0.4	-0.11	-0.26	-0.44

[a] in acetonitrile

The electron accepting ability of **2b** is considerably higher than that of *p*-benzoquinone. Derivative **2c** exhibits very stong accepting properties and is highly sensitive to atmospheric moisture. We were able to isolate it only as a mixture with its anion radical. The first poorly resolved reduction peak was observed at about +0.4V. The relevant CV data are collated in the Table.

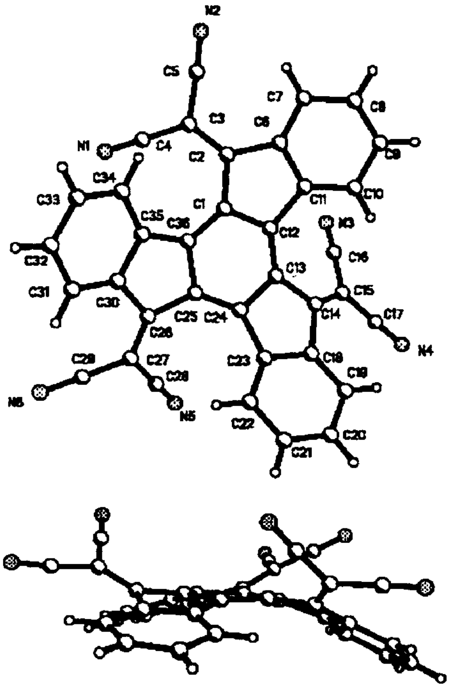

Figure. Molecular structure of **2a**.

Derivative **2a** is soluble in conc. sulfuric acid and subsequent addition of ice led to quantitative isolation of **1a**. Formation of charge transfer complexes between the new acceptors and electron donors of appropriate symmetry is currently under investigation.

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References and notes

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2. Gabriel, S.; Michael, A. *Ber. Dtsch. Chem. Ges.*, **1877**, *10*, 1557; 1878, *11*, 1009; Stobbe, H.; Zschoch, F. *Ber. Dtsch. Chem. Ges.*, **1927**, *60*, 457; Sbrogio, F; Fabris, F.; De Lucchi, O. *Synlett*, **1994**, 761; Plater, M. J.; Praveen, M. *Tetrahedron Lett.*, **1997**, *38*, 1081; Jacob, K.; Sigalov, M.; Becker, J. Y.; Ellern, A.; Khodorkovsky, V. *Eur. J. Org. Chem.*, **1999**, in press.
3. Diederich, F.; Rubin, Y. *Angew. Chem., Int. Ed. Engl.*, **1992**, *31*, 1101; Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.*, **1996**, *29*, 235.
4. Compounds **2b,c** were isolated chromatographically and gave satisfactory elemental analyses.
5. A dark-red transparent prism (0.45x0.40x0.3) has been used for X-ray structure analysis: $C_{36}H_{12}N_6$ $2(C_6H_5Cl)$, monoclinic, spase group $P2_1/n$ at 293K, a=10.683(4), b=19.910(6), c=17.480(4) Å, β=94.31°, V= 3708(2) $Å^3$, Z=4, F(000)= 1544. 3725 reflections were collected with Syntex P-1 diffractometer [$\lambda(MoK_\alpha)$=0.71069 Å], graphite monochromator, ω–2θ- scan, 2θ<40. 1455 reflections were observed with Fo > 4s(Fo) were observed from 3483 independent reflections. The structure was solved by direct methods. The very weak diffraction of the crystal and the absence of high-angle data as a result lead to the dramatically low value of observed reflection per non-hydrogen atom. Therefore the phenyl rings of two molecules of chlorobenzene solvent and three terminal phenylene rings of **2a** were determined as rigid hexagon with a=1.39 Å to decrease the number of refined parameters. The structure was refined by full-matrix least squares using anisotropic approximation for all other non-hydrogen atoms excluding the carbon atoms in the rigid groups. All hydrogen atoms were placed in calculated positions and refined using the "riding model" with fixed U_{iso} = 0.08 $Å^2$. 295 parameters, R1= 0.095, wR2= 0.25, GOF=1.01. SHELX86 and SHELX93 were used for all calculations. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic data Center.