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3,7-DIHALO-2H,6H-BENZO[1,2-b:4,5-b']DITHIOPHENE-2,6-DIONE. NEW WURSTER-TYPE ACCEPTORS ISOELECTRONIC WITH 2,6-ANTHRAQUINONE

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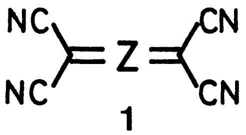
We describe the syntheses and properties of the new Wurster-type acceptors, 3,7-dihalo-2H,6H-benzo[1,2-b:4,5-b']dithiophene-2,6-diones (**2a**) and (**2b**), which have C_{2h} molecular symmetry with two sulfur atoms, together with the electrical resistivities of their CT complexes.

The rapidly growing family of new multi-stage redox system[1)] has attracted much interests due to the wide spectrum of their usage for preparation of conducting charge-transfer (CT) complexes,[2)] and this has consequently stimulated synthetic efforts.[3)]

Many structural modifications to the well-known acceptor, tetracyanoethylene (TCNE), have been carried out by insertion of conjugated segment, **Z**, into the double bond of TCNE, e.g. **1a**, **1b**, and other several conjugated systems,[4)] to reduce on-site Coulomb repulsion by extending the conjugation and to gain aromaticity in their reduced forms. The extensively studied acceptor, TCNQ **1a**, has a high molecular symmetry D_{2h}. Furthermore, a few acceptors with enhanced polarizability derived from the introduction of sulfur atom(s) such as **1c**[5)] and **1d**[6)] have also been synthesized. Most of highly conducting organic metals consist of donors containing charcogenide atoms.[7)] We now describe the synthesis of the new quinone-type acceptor **2** which has a C_{2h} molecular symmetry like TNAP **1b** and contains sulfur atoms in its conjugated system.



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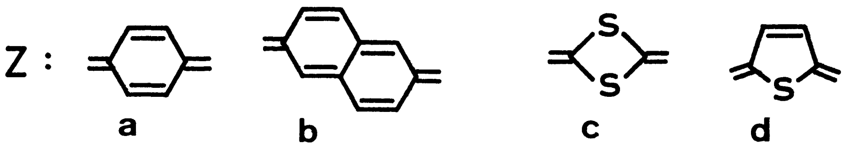
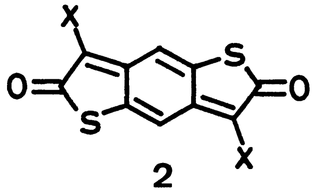
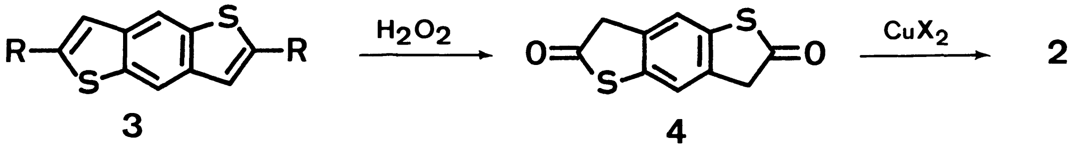




2

a, X = Br
b, X = Cl

The key intermediate **4** was synthesized modelled after Gronowitz's procedure for the preparation of the keto tautomers of 2-hydroxythiophenes.[8)] Thus, benzodithiophene **3a** was lithiated (BuLi in THF/TMEDA, -70 °C) and the resulting solution was treated with tri-n-butylborate at 0 °C to afford **3b**. Treatment of the crude **3b** with 30% hydrogen peroxide gave **4** in 73% yield based on **3a** as colorless needles, mp 272-274 °C (decomp); m/e 222 (M^+), 194 (M^+-CO), 166 (M^+-2CO); δ_H (CD_2Cl_2) 4.00 (4H, s), 7.31 (2H, s); ν (KBr) 1700 cm^{-1}. Interestingly, bromination of **4** with cupric bromide[9)] in methanol afforded the desired 3,7-dibromo-2H,6H-benzo[1,2-b:4,5-b']dithiophene-2,6-dione (**2a**) in 83% yield as deep violet needles, mp 204-208 °C (decomp); m/e 376, 378, 380 (1:2:1, M^+); δ_H (CD_2Cl_2) 7.18 (s); ν (KBr) 1670 cm^{-1}; λ_{max} (CH_2Cl_2) 488 sh nm (log ε, 2.88), 442 (4.59), 421 (4.56), 402 sh (4.34), 374 sh (4.07), 242 (4.37). The dichloro derivative **2b** was also obtained by treatment of **4** with cupric chloride in DMF as deep violet needles in 33% yield, mp 256-258 °C (decomp); m/e 288, 290, 292 (10:6:1, M^+); δ_H (CD_2Cl_2) 7.22 (s); ν (KBr) 1665 cm^{-1}; λ_{max} (CH_2Cl_2) 478 sh nm (log ε, 2.83), 431 (4.58), 411 (4.56), 391 sh (4.35), 374 sh (4.16), 243 (4.38).



3 **4**

a, R = H

b, R = $B(OH)_2$

The cyclic voltammograms of **2a** and **2b**, although the peak potentials of the first cathodic reduction wave appeared clearly at -0.04 V and -0.06 V (vs. SCE),[10)] respectively, exhibited irreversible redox waves because the electrode is immediately coated with an insoluble material. However, the potential for the first electron transfer yields electron affinities(E_A) of 2.43 eV and 2.41 eV, in excellent agreement with those estimated from the solution CT bands of their pyrene complexes, 2.41 eV and 2.39 eV for **2a** and **2b**, respectively [using E_A(p-chloranil)= 2.48 eV].[11)] These electron affinities are comparable to those of the moderately strong acceptor; trichloro- or tribromo-p-benzoquinone (2.41 eV). Compared with the dicyanomethylene-based acceptor **1c** [E_A=2.06 eV], which also contains two sulfur atoms, the electron accepting ability of these carbonyl-based acceptors **2** is remarkably enhanced due to the resonance stabilization of the anion radicals of **2** or formation of a new aromatic sextet by one electron reduction in addition to the presence of halogen atoms. The reduction potentials and the electron affinities of **2a** and **2b** can be used as a measure to estimate the acceptor strength and a guide to design new acceptor systems containing charcogenide atoms. The basic physical properties of **2a** and **2b** are summarized in Table 1.

Table 1. Physical properties of the acceptors, **2a** and **2b**.

Compd	Mp, °C (decomp)	λ_{max} (CH_2Cl_2) nm (log ε)	Reduction potentials[a)]	Electron affinities
2a	204-208	488(2.88) 442(4.59) 421(4.56)	-0.04[b)]	2.41[d)]
2b	256-258	478(2.83) 431(4.58) 411(4.56)	-0.06[b)]	2.39[d)]
p-chloranil			0.01[c)]	2.48[e)]

a) V vs. SCE. b) See Ref. 10. c) See Ref. 15. d) Values deduced from CT bands of their pyrene complexes, see text. e) Ref. 11.

Preliminary experiments to prepare the CT complexes are as follows. Reaction of TTT[12)] with **2a** in 1,2,4-trichlorobenzene gave the 2:1 complex as a dark reddish violet solid. The room temperature compaction resistivity (ρ_{RT}) is 26 Ωcm. Several other complexes with TTF[12)] and HMTTF[12)] which gave no simple stoichiometry from elemental analysis were obtained: TTF **2a**, ρ_{RT} 2.6×10^3 Ωcm (E_a, 0.09 eV); HMTTF·**2a**, ρ_{RT} 1.3×10^7 Ωcm (0.48 eV); TTT·**2b**, ρ_{RT} 6.7×10^4 Ωcm (0.09 eV); HMTTF·**2b**, ρ_{RT} 8.3×10^5 Ωcm (0.27 eV).

The solid state properties of the CT complexes essentially depend not only on the molecular structure of the components but also on the characteristic of the crystal structure. **2a** and **2b** have following structural features: (a) relatively strong electron accepting ability, (b) decreased on-site Coulomb repulsive energy, (c) a C_{2h} molecular symmetry, and (d) incorporation of charcogenide atoms. The features (c) and (d) are important for the study of CT complexes from following reasons.

Firstly, Torrance and his co-workers have recently pointed out that the symmetry property of HOMO of the donor and LUMO of the acceptor plays a role to select stacking mode of the components in the CT complexes. Using tetrahalo-p-benzoquinones as acceptors, this idea has been realized by the preparation of the first highly conducting 1:1 p-benzoquinone-based CT complexes.[13)] As many acceptors synthesized have a high molecular symmetry (D_{2h}), it is therefore worth searching new acceptors belonging to symmetries other than D_{2h} for the detailed understanding of how a crystal structure is influenced by the frontier orbitals of the components.

Secondly, it has been known that some donors containing charcogenide atoms give organic metals with pronounced metallic character even at low temperatures and also give organic superconductors in which cation radicals of the donor are making channels for the electrical conduction.[7,14)] One of the reasons of these novel behaviors has been ascribed to the enhanced intra- and interchain interaction due to the strong interheteroatom contacts. Therefore the incorporation of charcogenide atom into the acceptor moiety in turn may also produce strong intermolecular interaction in their complexes. Consequently it is, also, worth exploring new acceptors which contain charcogenide atoms in pursuit of organic conductors in which anion radicals of the acceptors play the essential role.

Apparently, it is desirable to prepare single crystals of CT complexes containing **2** as an acceptor.

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