

Thiophene-fused Tetracyanoquinodimethanes as Electron Acceptors for Conducting Charge-transfer Salts

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Four isomeric benzodithiophene analogues of 11,11,12,12-tetracyano-9,10-anthraquinodimethane (1)—(4) have been prepared, in which (1) and (2) exhibited excellent reduction potentials as electron acceptors and formed highly conducting charge-transfer complexes with tetrathiafulvalene.

The discovery of the metallic conductivity of tetrathiafulvalene (TTF)–tetracyanoquinodimethane (TCNQ) has stimulated the synthesis and study of numerous variants.¹ Of a variety of π -acceptor species recently explored, TCNQ-type acceptors fused with sulphur heterocycles are interesting structural modifications^{2,3} in terms of enhancing the interstack interactions in the solid state and reducing the intramolecular Coulombic repulsion as well. We now report the preparation and properties of an isomeric series of the thiophene-fused TCNQ compounds (1)—(4). The mode of fusion of the thiophene units in these molecules should affect the conductive properties of their charge-transfer salts and thereby provide useful information for the molecular design of synthetic metals.

The new acceptors were synthesized *via* the TiCl_4 -mediated condensation⁴ of the corresponding quinone⁵ and malononitrile. To a solution of the quinone, malononitrile (20 equiv.), and pyridine (40 equiv.) in chloroform TiCl_4 was added (2 equiv.) and the mixture was refluxed for 5 h. The crude product was chromatographed on a silica gel column (benzene–hexane), or alternatively recrystallized from acetonitrile, to afford the desired isomers in 15–37% yields: (1), orange–red prisms, m.p. 325 °C (decomp.); i.r. (Nujol) 2210

cm^{-1} ; ^1H n.m.r. δ (CDCl_3) 7.91, 7.92, 8.45, and 8.46 (*J* 5.7 Hz); (2), red prisms, m.p. 332 °C (decomp.); i.r. (Nujol) 2200 cm^{-1} ; ^1H n.m.r. δ (CDCl_3) 7.90, 7.91, 8.53, and 8.54 (*J* 5.7

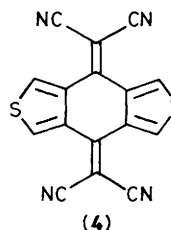
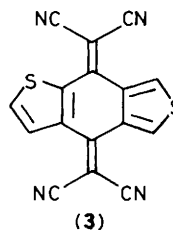
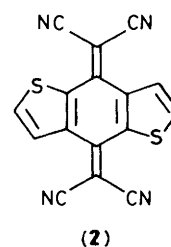
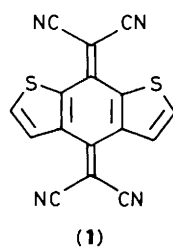
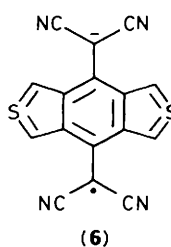
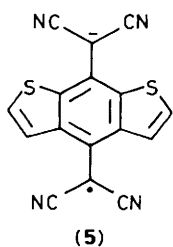


Table 1. Cyclic voltammetric data.^a

Compound	$E_{1/2}^1$	$E_{1/2}^2$	$\Delta E_{1/2}$
(1)	+0.13	-0.19	0.32
(2)	+0.13	-0.21	0.34
(3)	-0.14	-0.41	0.27
(4)	-0.49	-0.73	0.24

^a $E_{1/2}$ in V vs. standard calomel electrode, DMF solutions, 0.1 M Et_4NClO_4 , glassy carbon electrode, scan rate 100 mV s^{-1} .



Hz); (3), golden-yellow needles, m.p. 307°C (decomp.); i.r. (Nujol) 2210 cm⁻¹; ¹H n.m.r. δ (CDCl₃) 8.86, 8.87, 8.95, 8.96 (*J* 2.9 Hz), 7.91, 7.92, 8.33, and 8.34 (*J* 5.5 Hz); (4),² yellow needles, m.p. >320°C; i.r. (Nujol) 2225 cm⁻¹; ¹H n.m.r. δ (CDCl₃) 8.31.

Cyclic voltammetric studies (Table 1) were performed in dimethylformamide (DMF) with Et₄NClO₄ as the electrolyte using a standard calomel reference electrode. All the new acceptors exhibited two reversible one-electron reduction potentials. The first reduction potentials of (1) and (2) are comparable to that of TCNQ, while (3) and (4) are rather weak acceptors. This can be rationalized on the basis of the driving force for the formation of an aromatic system: upon one-electron reduction (1) and (2) can gain aromatic stabilization by generating a new aromatic benzodithiophene such as (5). In contrast, the radical-anion of (4) may be represented by the formula (6) involving tetravalent sulphur. Such non-classical condensed thiophenes are unstable as compared with classical Kekulé thiophenes,⁶ although a few have been isolated,⁷ including the benzo[1,2-*c*:4,5-*c'*]dithiophene ring system.⁸ Non-classical condensed thiophene units are also involved in one of the resonance contributions for (3).

The difference between the half-wave potentials for the first and second reductions decreases in the order: (1) ≈ (2) > (3) > (4). This trend suggests that the intramolecular Coulombic repulsion is reduced as the two sulphur atoms in the molecule are located further apart.

Compounds (1) and (2) were treated with TTF in acetonitrile to give charge-transfer complexes of 1:1 stoichiometry as fine black needles. However, (3) and (4), probably owing to their poor reduction potentials, did not

form crystalline complexes in spite of the indication that complexation occurred in MeCN solution from the colour change and electronic spectra. The conductivities of the TTF complexes of (1) and (2) were measured at room temperature on compressed pellets by the two-probe technique, and were found to be very high: (1)-TTF, 0.89 S cm⁻¹; (2)-TTF, 4.78 S cm⁻¹. Thus, we believe that compounds (1) and (2) are promising acceptors for synthetic metals.

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