Synthesis of Cyclobutane-fused Tetracyanoquinodimethanes

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The preparation of the title π-acceptors (**1**)—(**3**) from the corresponding cyclohexane-1,4-diones and the electrical conductivities of their charge transfer complexes with tetrathiafulvalene are described.

Since the discovery of the metallic conductivity of tetrathiafulvalene (TTF)–tetracyanoquinodimethane (TCNQ), much effort has been made to prepare related organic charge transfer (CT) complexes. A wide variety of π-donors have been explored, but rather fewer π-acceptors are known.

We now report the synthesis of the cyclobutane-fused TCNQ compounds, (**1**)—(**3**). They were designed in order that the condensed cyclobutane ring would influence to some extent the interplanar distances in segregated columns of TCNQ complexes without significantly changing the electronic state of the parent TCNQ molecule and, consequently, would not bring about an alteration in the electrical properties of these complexes.

Although the synthetic method of Wheland and Martin[1] was unfruitful, we successfully synthesised the desired compounds (**1**)—(**3**) using a procedure similar to the first synthesis of TCNQ by Acker and Hertler.[2] The diketone (**4**),[3] obtained by a four-step sequence from benzoquinone, was treated with malononitrile and a catalytic amount of β-alanine at about 60 °C for 2 h to give (**5**) in 60% yield. Bromination of (**5**) with *N*-bromosuccinimide at 0 °C in CH_2Cl_2–MeCN and subsequent dehydrobromination with pyridine at 0 °C gave (**1**)† in 69% yield [(**1**): orange plates from CCl_4–$CHCl_3$, m.p. 170—172 °C; ^{1}H n.m.r. δ ($CDCl_3$) 3.37 (s, 4H) and 7.30 (s, 2H); λ_{max} (MeCN) 392 (log ε 4.63) nm; ν_{max} (KBr) 2210 cm^{-1}]. Similarly, (**2**) and (**3**) were synthesized from (**6**)[4] and (**7**),[5] respectively [(**2**): red needles from CCl_4–$CHCl_3$, decomp. >218 °C; ^{1}H n.m.r. δ ($CDCl_3$) 3.26 (s); λ_{max} (MeCN) 410 (log ε 4.80) nm; ν_{max} (KBr) 2200 cm^{-1}. (**3**): orange prisms from benzene, m.p. 184—186 °C; ^{1}H n.m.r. δ ($CDCl_3$) 3.59 (s, 4H), 7.68 and 8.82 (AA'BB', 4H); λ_{max} (MeCN) 272 (log ε 3.84), 412 (4.48), 522 (3.61), and 558 (3.32) nm; ν_{max} (KBr) 2205 cm^{-1}].

Cyclic voltammetry of (**1**)—(**3**) (Table 1) shows two reversible one-electron reductions. The potentials of (**1**) are very close to those of TCNQ, suggesting that the ethano-group has little influence upon the electronic nature of TCNQ, as we predicted.

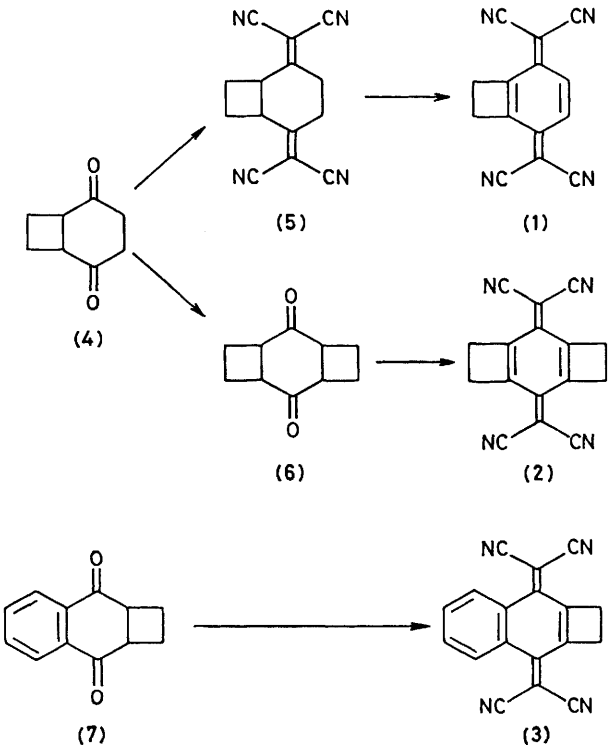

Table 1. Cyclic voltammetry data showing two reversible one-electron reductions (a) and (b).[a]

Compound	$E_{1/2}$(a)/V	$E_{1/2}$(b)/V
TCNQ	0.08	−0.48
(**1**)	0.07	−0.48
Me_2TCNQ[b]	0.05	−0.42
(**2**)	0.04	−0.49
$(MeO)_2$TCNQ[c]	−0.08	−0.55
(**3**)	−0.10	−0.47

[a]Volts *vs.* standard calomel electrode at a glassy carbon electrode; 0.1 M Et_4NClO_4–MeCN, scan rate 100 mV s^{-1}. [b]Me_2TCNQ = 2,5-dimethyltetracyanoquinodimethane. [c] $(MeO)_2$TCNQ = 2,5-dimethoxytetracyanoquinodimethane.

† All new compounds gave satisfactory elemental analyses (C,H, and N) and mass spectra.

Table 2. Properties of the TTF complexes of (**1**) and (**3**).

Complex	Conductivity[a] /Ω^{-1} cm^{-1}	$\nu_{C\equiv N}$/cm^{-1}
(**1**)–TTF[b]	0.30	2190
(**3**)–TTF[c]	2.7×10^{-6}	2205

[a]Measured at room temperature on compressed pellets for (**1**)–TTF and on a single crystal for (**3**)–TTF. [b]Fine black needles. [c]Dark reddish brown needles.

Compounds (**1**) and (**3**) were treated with TTF to give CT complexes of 1:1 stoicheiometry. However, (**2**) did not form a TTF complex, probably owing to steric reasons. The conductivity (Table 2) of (**1**)–TTF is comparable to that of TTF–TCNQ measured under the same conditions. On the other hand, the complex of (**3**) shows an energy gap, probably based on the electronic state of (**3**) in origin.

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