Preparation, Properties, and Crystal Structure of a 1,2,5-Thiadiazolotetracyanoquinodimethane

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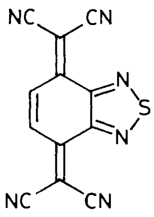
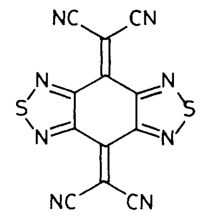
The title electron acceptor forms a coplanar dyad in the crystal by hydrogen bonding, and the charge-transfer complexes with tetrathiafulvalene derivatives exhibit high electrical conductivities.

Electron acceptors containing chalcogen atoms are of interest since the interheteroatom interactions may suppress the metal–insulator transitions.[1] Recently we have found that the anion radical salts of BTDA (**2**)† containing two thiadiazole units exhibit two-dimensional electrical conductivity because of interheteroatom S · · · N≡C interactions.[2] However, the charge transfer (CT) complexes of (**2**) with tetrathiafulvalene (TTF) and its analogues are semi-conductors owing to mixed stack formation, which is facilitated by the inclusion behaviour of (**2**) and by interactions between heteroatoms.[3] To overcome this disadvantage of inclusion behaviour, one of the heterocyclic components of (**2**) needs to be removed. We report here the properties and crystal structure of TDA (**1**),† fused with only one heterocyclic ring.

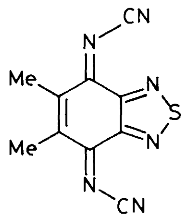
Compound (**1**) (decomp. 289—300 °C) was prepared in 45% yield by Takahashi's method[4] from 4,7-dibromobenzothiadiazole[5] followed by oxidation with PbO_2. The *X*-ray structural analysis‡ showed that (**1**) is a planar molecule and forms a coplanar dyad by hydrogen bonding of cyano groups[6] [N(6) · · · H(5) 2.53 Å], which may cause the bowing of dicyanomethylene groups to the opposite direction from the heterocyclic ring (Figure 1). Although there is no S · · · S or S · · · N heteroatom interaction in the crystal, the dyad formation of (**1**) shows the possibility that the negative charge can be delocalized over the two molecules in the anion radical salts, which is another approach to reducing the on-site Coulomb repulsion, besides enlargement of the π-electron system of the independent molecule. The first (E_1) and second (E_2) reduction potentials of (**1**) measured by cyclic voltammetry are +0.12 and −0.38 V *vs.* standard calomel electrode (S.C.E.), respectively, showing that (**1**) is a stronger acceptor than (**2**) (E_1 −0.02 V). Although the semiquinone formation constant (log K_{sem}) for (**1**) (9.14) is larger than that of (**2**) (8.10), it is smaller than that of tetracyanoquinodimethane (TCNQ) 9.31, so that the on-site Coulomb repulsion is decreased in $(\mathbf{1})^{\overline{\cdot}}$ compared with $TCNQ^{\overline{\cdot}}$ by fusing a heterocyclic ring. In contrast to (**2**), (**1**) gave highly conductive CT complexes with TTF and its derivatives (Table 1), indicating that the inclusion behaviour of (**2**) is diminished, as expected, by eliminating one heterocycle, preventing formation of inclusion cavities. The hydrogen bonding in (**1**) may be important in forming highly conductive complexes since the



TDA (**1**)



BTDA (**2**)



(**3**)

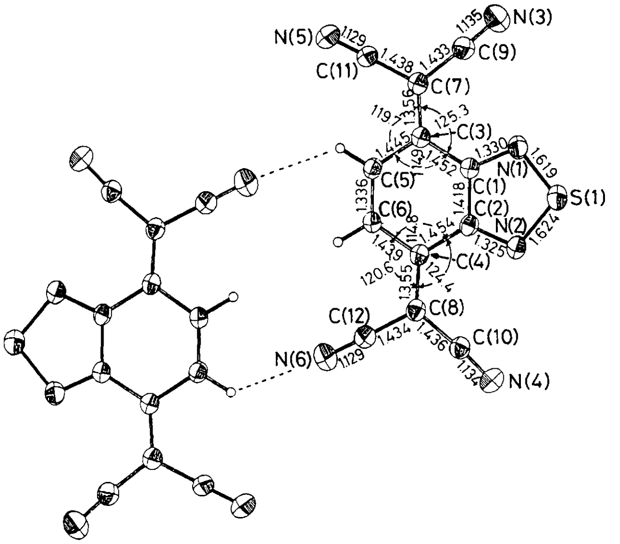


Figure 1. Dyad formation in (**1**) with selected bond lengths and angles. Molecules in the dyad are related by a centre of symmetry and lie in the same plane (deviation 0.34 Å). Hydrogen bonding of N(6) · · · H(5) (2.53 Å) is shown by a broken line.

Table 1. Molar ratios,[a] oxidation potentials of donors, and electrical resistivities[b] of the CT complexes of TDA (**1**).

Donor	$(E^{ox})^c$	Ratio[a]	ρ/Ω cm
Tetrathiafulvalene (TTF)	(0.31 V)	1:1	0.78
Tetramethyltetraselenafulvalene	(0.41 V)	1:1	1.4
Bis(methylenedithio)-TTF	(0.45 V)	3:2	6.3
Bis(ethylenedithio)-TTF	(0.45 V)	1:1	1.6×10^6
Tetrakis(methylthio)-TTF	(0.47 V)	1:1	$>10^8$
Dibenzo-TTF	(0.57 V)	1:1	$>10^8$

[a] Donor : acceptor ratio, based on the elemental analyses. [b] Measured at room temperature on compressed pellets by the two-probe technique. [c] V *vs.* S.C.E., 0.1 mol dm^{-3} Et_4NClO_4 in MeCN.

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† (**1**), 4,7-bis(dicyanomethylene)-4,7-dihydro-2,1,3-benzothiadiazole; (**2**), 4,7-bis(dicyanomethylene)-4*H*,7*H*-[1,2,5]thiadiazolo[3,4-*f*]-2,1,3-benzothiadiazole; (**3**), 4,7-bis(cyanoimino)-4,7-dihydro-4,7-dihydro-5,6-dimethyl-2,1,3-benzothiadiazole.

‡ *Crystal data* for (**1**): $C_{12}H_2N_6S$, M = 262.25, monoclinic, space group $P2_1/n$, a = 14.325(2), b = 10.515(1), c = 7.765(1) Å, β = 95.28(1)°, U = 1164.6(3) Å^3, Z = 4, D_c = 1.496 g cm^{-1}. The final R value is 4.70% for 1881 reflections with $|F_o| > 3\sigma|F_o|$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Table 2. Molar ratios[a] and electrical resistivities[b] of the anion radical salts of TDA (**1**).

Cation	Ratio	ρ/Ω cm
H_4N^+	1:1	9.6×10^2
Me_4N^+	1:1	12
Et_4N^+	1:2	5.7×10^2
$Pr^n{}_4N^+$	1:2	28
$Bu^n{}_4N^+$	1:2	5.6×10^4

[a] Based on the elemental analyses. [b] Measured at room temperature on compressed pellets by the two-probe technique.

reference compound (**3**)† (decomp. 140—160 °C),§ which cannot exhibit hydrogen bonding, did not afford a CT complex with tetramethyltetraselenafulvalene, and the complex TTF–(**3**) was an insulator (1:1, $\rho > 10^8$ Ω cm). Compound (**1**) gave anion radical species on reduction with iodides in MeCN, which could be isolated as stable salts [λ_{max}(MeCN) 810 (log ε 3.99), 658 (4.74), 366 (4.24), 352 (4.26), 290 (4.10), 284 (4.07) 280sh (4.07), and 234 (3.83) nm] (Table 2). Among them, the Me_4N^+ salt is interesting since it exhibits good electrical conductivity although it is a 1:1 salt with a complete charge transfer state. This fact may be attributed to the reduced on-site Coulomb repulsion of (**1**)$^{\overline{\cdot}}$ as well as the molecular interactions in the crystal.

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§ (**3**) is expected to be planar, and possesses similar electron affinity to (**1**) (E_1 −0.01; E_2 −0.55 V *vs.* S.C.E.).

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