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Crystal and Molecular Structure of Bis-1,2,5-thiadiazolotetracyanoquinodimethane. A Noval Acceptor Forming Highly Conductive Complexes

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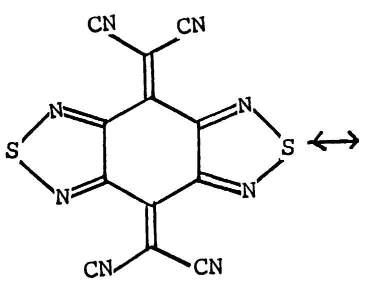
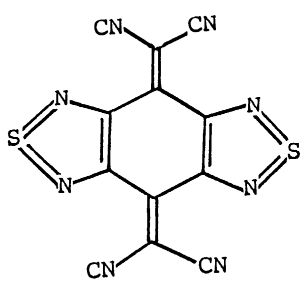
The crystal structure of bis-1,2,5-thiadiazolotetracyanoquinodimethane showed stacks of two-dimensionally expanded sheet-like networks, in which the roughly coplanar molesules are connected to one another by way of the rhombohedral linkage involving short S--NC contacts of 3.03 Å.

We have recently reported the preparation of bis-1,2,5-thiadiazolotetracyanoquinodimethane (BTDA-TCNQ) **1** along with the complex formation with various types of donors.[1,2] Among them, tetrathiatetracene(TTT) and dimethyldihydrophenazine (DMPH) are found to form highly conductive complexes,[3] while the complex with tetrathiafulvalene(TTF) exhibits a low conductivity. These findings suggest that the thiadiazole ring of **1** has an effect on the mode of stacking by way of the intermolecular interactions between hetero S and N atoms. In order to investigate such an effect in the crystal structure and elucidate the precise molecular structure of the BDTA-TCNQ itself, the present X-ray study has been carried out.

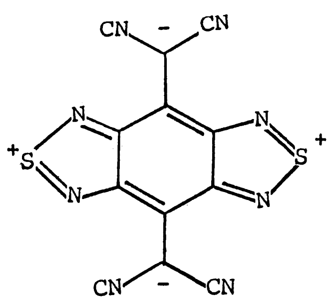
Crystal data of **1**: $C_{12}N_8S_2$, monoclinic, space group C2, a=8.990(1), b=13.042(1), c=5.538(1) Å, β=99.01(1)°, V=641.30 Å^3, Z=2, Dcalcd=1.66 g/cm^3. The intensity data were collected on a Rigaku automated four-circle diffractometer (AFC-5) with Mo-Kα radiation up to 2θ=55°. The structure was solved by the direct method and refined by the block-diagonal least-squares method. The final R value is 0.036 (Rw=0.039) for 601 non-zero reflections (measured: 664).



1a



1b



1c

Final atomic coordinates are given in Table 1 and ORTEP drawing of the molecule is shown in Fig. 1 together with bond lenghts and angles. The estimated standard deviations of the bond lengths and angles are 0.004-0.007 Å and 0.3-0.4°, respectively.

The molecule has crystallographically rigorous two-fold symmetry through the C(5), C(3), C(4),and C(6) atoms of the TCNQ nucleus. In addition, there is no significant difference in the lengths and angles for the chemically equivalent bonds such as S(1)-N(1) and S(1)-N(2). Therefore the average values are available for the following discussion. The molecule takes almost a planar conformation; the slight atom deviations indicate a tendency of butterfly form4) with the dihedral angle of 2.5° between the thiadiazole rings. In the thiadiazole ring, the S-N bond length 1.616 Å is intermediate between that of S-N single bond (av. 1.73 Å)5) and that of S=N double bond in sulfur diimides (1.53 Å).6) The C-N bond length 1.330 Å is equal to that found in the conjugated N-heterocycles (av. 1.33 Å).7) The annulated C-C bond length 1.422 Å reflects sufficient π-delocalization. It is clear that 1 has a structure described by the resonance forms of 1a and 1b, involving aromatic thiadiazole rings. Similar structure is found in the corresponding quinone, benzo-bis-thiadiazoledione (S-N: 1.624, C-N: 1.324, C-C: 1.426 Å).8) In the TCNQ nucleus, the C(1)-(3) bond length of 1.452 Å and the C(3)=C(5) bond length of 1.357 Å reflect partial single and double bond characters, respectively. There is no appreciable difference between these values and those of the TCNQ molecule (1.458 and 1.362 Å).9)

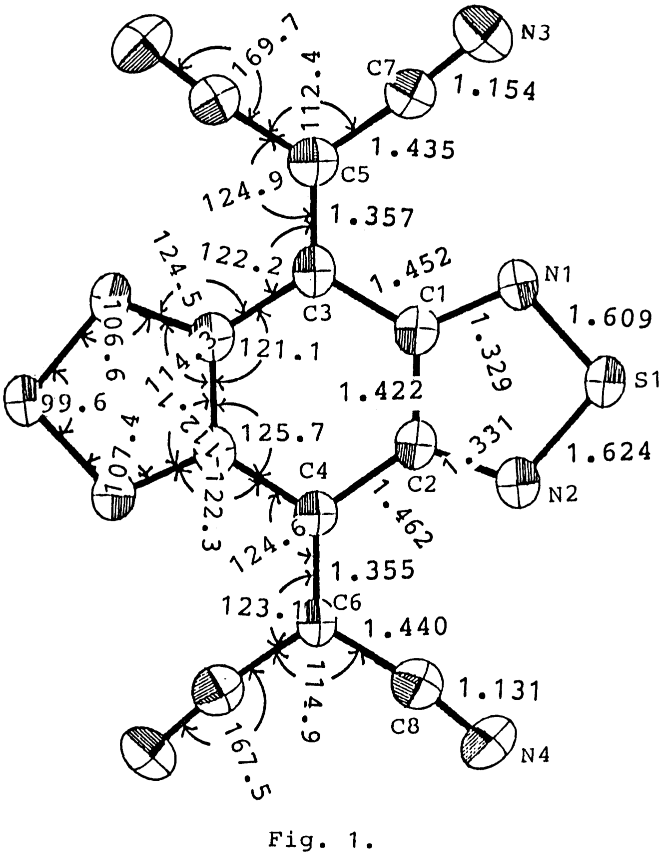


Fig. 1.

Table 1. Final atomic coordinates

atom	x/a	y/b	z/c
S(1)	0.2438(1)	0.4775(4)	0.4108(1)
N(1)	0.3219(3)	0.3828(2)	0.2924(5)
N(2)	0.4120(3)	0.4231(2)	0.1489(6)
C(1)	0.4115(3)	0.5321(2)	0.1420(6)
C(2)	0.3210(3)	0.5722(2)	0.2857(5)
C(3)	0.5	0.3638(4)	0.0
C(4)	0.5	0.5959(4)	0.0
C(5)	0.5	0.2598(4)	0.0
C(6)	0.5	0.6998(4)	0.0
C(7)	0.4141(4)	0.1986(3)	0.1398(6)
C(8)	0.4245(4)	0.7601(3)	0.1619(6)
N(3)	0.3657(4)	0.1410(3)	0.2693(7)
N(4)	0.3564(4)	0.8174(2)	0.2520(6)

Fig. 1. Molecular structure of 1 showing bond lengths(Å) and angles(°).

Figure 2 shows the crystal structure of 1 viewed along the b axis. The molecules are parallel closely to (201) plane and form stacks along the c axis. As shown in Fig. 3, in the stacked molecules, the direct overlapping occurs between the thiadiazole rings. However, the distance between the molecular planes is 3.68 Å, indicating no significant interaction. The most important feature in the present structure is transverse interaction between S atom of the thiadiazole ring and N atom of the TCNQ nucleus, thus forming a two-dimensionally expanded sheet-like network. The contact distance of 3.03 Å is significantly shorter than the sum of their van der Waals raddi (3.35 Å).[10] The mode of molecular connections in a sheet is shown in Fig. 4. The adjacent molecules such as A and B lie roughly on one plane; the displacement of the molecular planes is 0.7 Å (see Fig. 2). Since the molecules lie on the crystallographic symmetry axis, the arrangement is very symmetrical. Each molecule has eight short S--NC contacts by connecting to four neighbouring molecules in the sheet. Thus the network is connected tightly by way of the rhombohedral S--NCCCN--S--NCCCN linkage. It is well known that the short intermolecular S--N contacts occur in the compounds containing -NSN- rings, as exemplified by naphto-bis-thiadiazine.[11] It is notified that, in the present molecule, the interaction occurs between S atom of thiadiazole ring and N atom of cyano group. This fact indicates an appreciable contribution from the dipolar resonance forms such as 1c. It is possible to consider a charge transfer type electrostatic interaction and/or the bonding involving a partial rehybridization at sulfur atom with d orbital. The angle of 100.1° for C--S--C and that of 157.4° For C≡N--S angle in the linkage are geometrically reasonable for such a bonding.

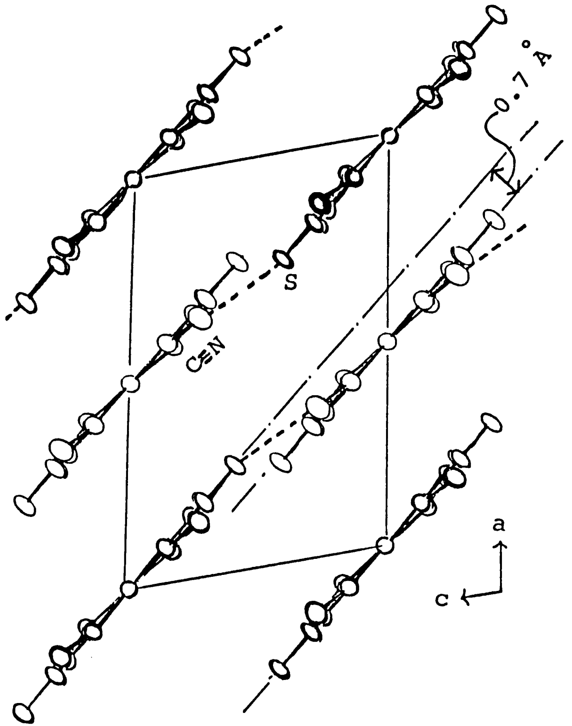


Fig. 2.

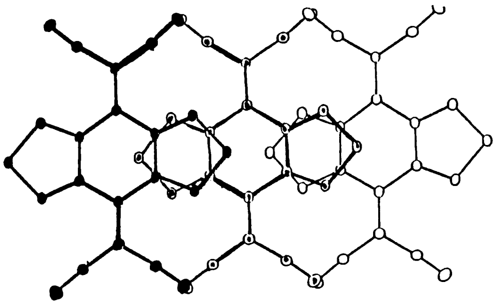


Fig. 3.

Fig. 2. Crystal structure of 1 viewed along b axis.

Fig. 3. Ovelappings of 1 projected on the molecular plane.

It is clarified that the BTDA-TCNQ molecule, characterized as a novel acceptor, has strongly transverse S--NC interactions to form a sheet-like network. This structural feature is important for the design of new conducting materials with electrically two or three-dimensional nature. The additional structural studies for the complexes of $\underset{\sim}{1}$ are in progress.

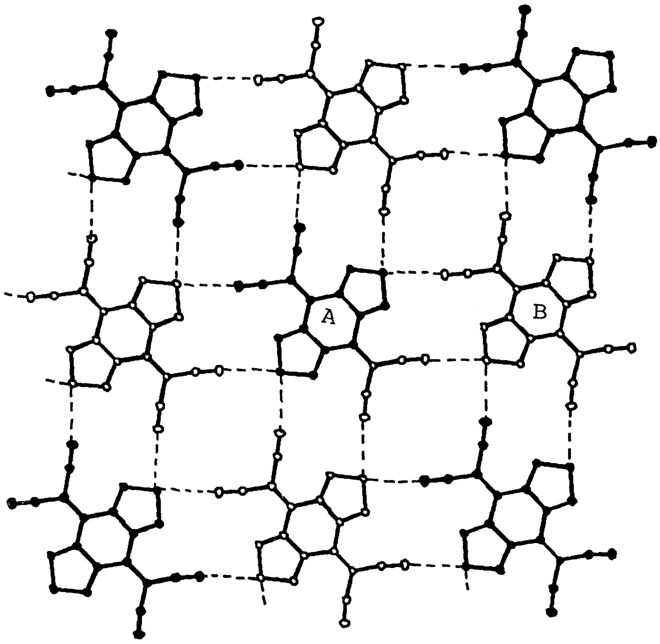


Fig. 4.
View of the sheet-like network projected on the molecular plane. A and B molecules are related by the equivalent positions of (x, y, z) and (1/2+x,1/2+y,1+z) to each other.

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