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Tetrathio-Derivatives of *p*-Quinodimethanes Fused with 1,2,5-Thiadiazoles. A Novel Type of Organic Semiconductors

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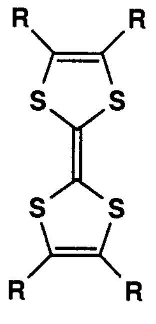
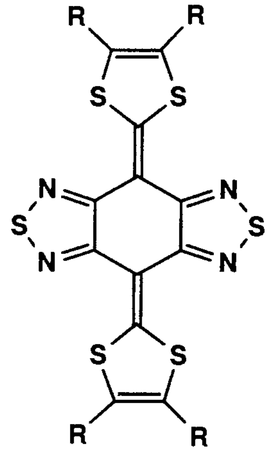
Bis[1,2,5]thiadiazolo-*p*-quinobis(1,3-dithiole) (BTQBT) was prepared by a Wittig-Horner reaction of 2-dimethylphosphono-1,3-dithiole with the corresponding dione. BTQBT is a red-violet crystal with a high melting point and the conductivity is unusually high (10^{-3} S cm^{-1}) as a single component. The X-ray structural analysis reveals that the molecule is completely planar and forms a sheet-like network by short S---S contacts.

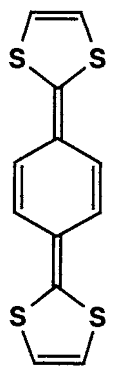
Although usual organic compounds are insulators as single components, tetrathiafulvalene (TTF) derivatives **1a,b** containing long alkyl chains$^{1)}$ or methyltelluoro substituents$^{2)}$ exhibit moderate electrical conductivities. These novel properties are considered to come from strong molecular interactions between adjacent molecules. Therefore, molecules with strong intermolecular interactions seem promising for single-component electron conductors. In this connection, heterocyclic compounds are of interest since interheteroatom contacts are expected to lead to strong intermolecular interactions. We have prepared novel electron acceptors or donors containing fused 1,2,5-thiadiazole rings, which form unique molecular assemblies by interheteroatom contacts.$^{3)}$ In the continuation of these works, we have now designed a novel compound, bis[1,2,5]thiadiazolo-*p*-quinobis(1,3-dithiole) (BTQBT) (**2a**),$^{4)}$ in which the electron withdrawing heterocycles are fused to the skeleton of a very strong electron donor, 2,2'-*p*-quinobis(1,3-dithiole) (QBT) (**3**).$^{5)}$ In addition to the advantage of the strong intermolecular interactions, **2a** with an extended π-conjugation has a reduced on-site Coulomb



1a; R=S$(CH_2)_9CH_3$
1b; R=TeCH_3



2a; R=H (BTQBT)
2b; R=CH_3
2c; R,R=benzo



3 (QBT)

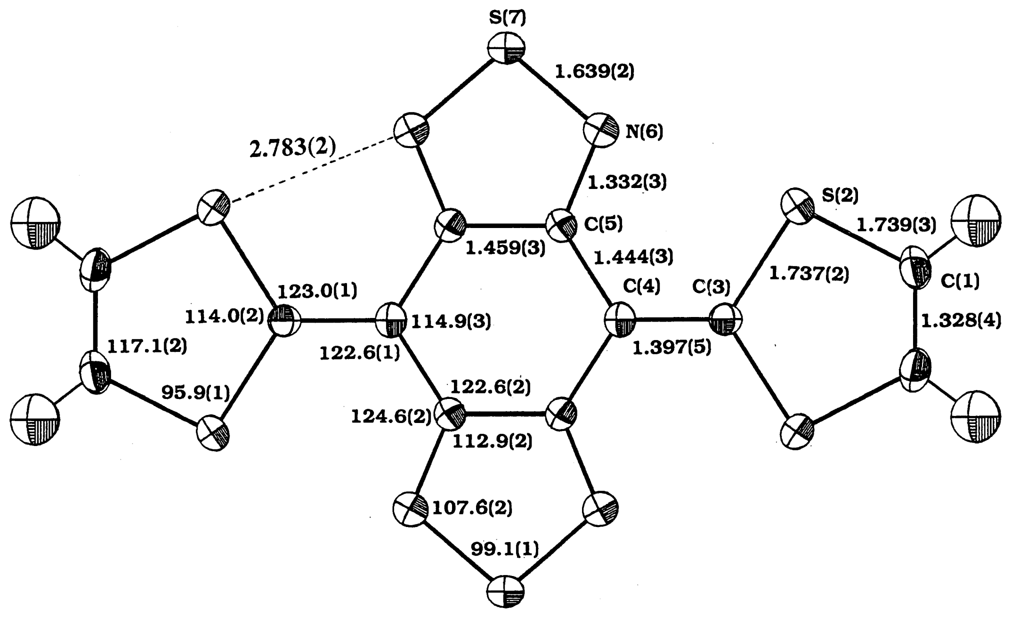


Fig. 1. Molecular structure of **2a** with bond lengths [Å] and angles [°] (ORTEP).

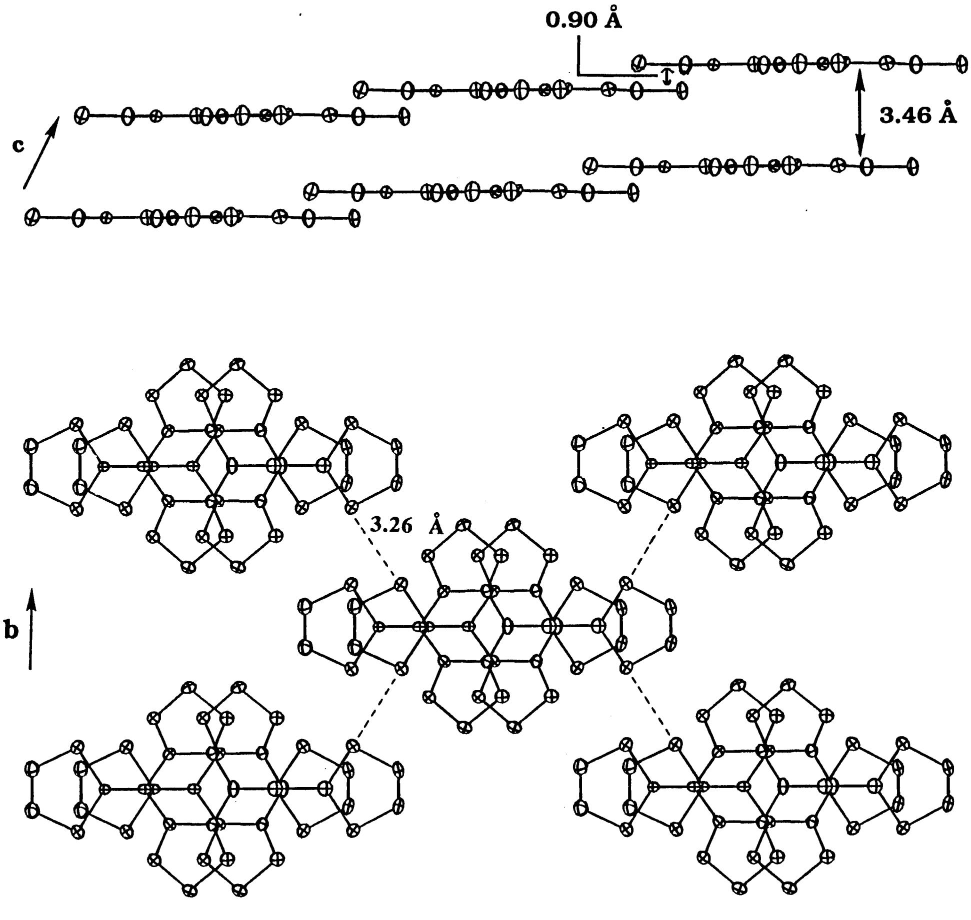


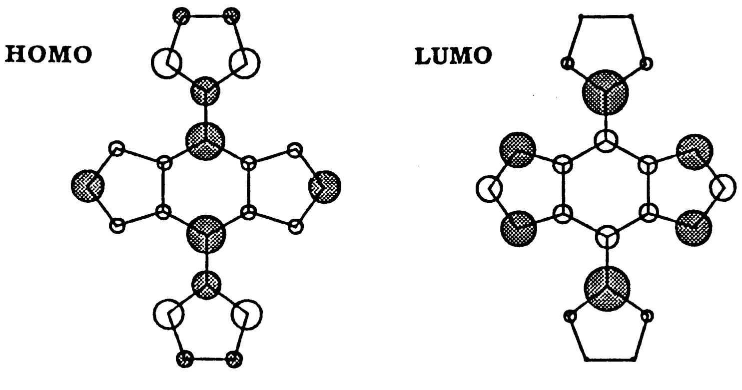
Fig. 2. Crystal structure of **2a**.

repulsion. Furthermore, **2a** is highly polarized and expected to have a relatively small HOMO-LUMO gap. We report here the preparation, structure, and physical properties of **2a**.

BTQBT **2a** was obtained in 48% yield by a Wittig-Horner reaction of 2-dimethylphosphono-1,3-dithiole[5] with 4H,8H-benzo[1,2-c;4,5-c']bis[1,2,5]thiadiazole-4,8-dione.[6] BTQBT has a very high melting point (>450 °C) and is sublimed at 350 °C/0.1 Torr. The color of the solid is red-violet and the absorption maxima are observed at 470 and 542 (sh) nm in a KBr disk. The solubilities in any solvents are very low,[7] while it is a little dissolved in nitrobenzene upon heating. A single crystal of BTQBT was obtained by recrystallization from nitrobenzene.

In order to investigate the molecular structure of BTQBT as well as the intermolecular interactions, the X-ray structural analysis was carried out.[8] The molecule is completely planar. The bond lengths and angles are shown in Fig. 1. It should be noted here that the distance between the S of the dithiole and the N of the thiadiazole (2.78 Å) is significantly shorter than the sum of the van der Waals distance (3.35 Å), indicating the possibility of the delocalization of electrons through the S---N contacts. The short contacts may play an important role in making the molecule planar.

The BTQBT molecules form a sheet-like network by S---S contacts as shown in Fig. 2. The S---S contact distance of 3.26 Å is much shorter than the sum of their van der Waals radii (3.70 Å). The contacts of the heteroatoms in the thiadiazoles, which are often seen in heterocycles containing thiadiazole rings,[3] are not observed in this network. Although the sheet is roughly planar, there is a little deviation of 0.90 Å between adjacent molecules. The sheet is overlapped according to the manner shown in Fig. 2. The distance between the molecular planes is 3.46 Å. The overlapping mode in the crystal structure is in accord with that of the most effective interaction between the HOMO and LUMO,[9] suggesting that the charge-transfer interaction is important for the overlap. The net atomic charge of the sulfur atoms in the 1,3-dithioles was calculated by the MNDO method to be +0.160, which is more positive than that for **3** (+0.099). This fact indicates that the molecule is polarized due to the electron withdrawing thiadiazoles.



BTQBT exhibited an unusually high electrical conductivity of 1.0 x 10^{-3} S cm^{-1} at room temperature as a single component, which is higher than those of the TTF derivatives **1a,b**. The value was measured along the stacking direction at a single crystal recrystallized from nitrobenzene. The temperature dependence of the conductivity showed a semiconductive behavior with *Ea* of 0.21 eV.[10] Interestingly, the thin film (1000 Å) prepared by sublimation also showed a high conductivity of 3.7 x 10^{-3} S cm^{-1}. This unusual electrical property may be attributed to the strong intermolecular interactions whose presence is suggested by the crystal structure as well as the very low ionization potential in solid state (4.58 eV).[11] For comparisons, the derivatives **2b** and **2c** were prepared by the reaction of the corresponding Wittig-Horner reagents[12] with the diones.[13] Their electrical conductivities as compaction pellets are very low (**2b**; 7x10^{-10} S cm^{-1}, **2c**; <10^{-10} S cm^{-1}).[14] This fact supports that the crystal structure of BTQBT is necessary for the good conductivity since it is impossible for **2b,c** to take such structures due to the substituents.[15] The more detailed studies on the physical properties of BTQBT are now in progress.

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7) The redox potentials of BTQBT could not be measured due to the low solubility.

8) X-ray structure data for **2a**: monoclinic, space group *C 2/m*, a=16.226(4), b=11.191(2), c=3.833(1) Å, β=96.88(2) °, V=691.0(3) Å^3, Z=2, ρ_{calcd}=1.91 g cm^{-3}. Rigaku AFC-5R, MoKα radiation, 1202 reflections for $2\theta_{max}$=60 °; solution of structure by direct methods; refinement by block-diagonal least-squares method to R=0.0396 for 814 reflections with $|F_o| > 3\sigma |F_o|$.

9) MNDO calculations [MOPAC program: J. J. P. Stewart, *Q. C. P. E. Bull.*, **3**, 439 (1983)] were performed by using the geometry determined from the X-ray analysis. These calculations were carried out at the Computer Center of the Institute for Molecular Science.

10) Electrical conductivities were measured by two-probe technique between 100 K and room temperature.

11) The ionization potential was determined with the photoelectron spectroscopical method by Drs. K. Kamiya, H. Fujimoto, and K. Seki. The detail will be reported elsewhere.

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13) The melting points of **2b,c** are high (400 °C) and sublimed around 400 °C/0.1 Torr.

14) The conductivity of BTQBT as a compaction pellet is 5x10^{-6} S cm^{-1}.

15) The fact that BTQBT is stable to oxygen and the conductivity does not change upon standing in air for a long time suggests that the observed conductivity is intrinsic. Further studies to clarify this point are under way.

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