PREPARATION AND PROPERTIES OF BIS[1,2,5]THIADIAZOLO-TETRATHIAFULVALENE†

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Abstract - Bis[1,2,5]thiadiazolotetrathiafulvalene (**1**) was prepared by desulfurization of the corresponding 1,3-dithiole-2-thione (**2**) with triphenylphosphine. It showed relatively high oxidation potentials due to the electron-withdrawing thiadiazole ring. The X-ray structural analysis revealed that there exist short intermolecular S---S and S---N contacts in the crystal.

Heterocycles containing sulfur or nitrogen atoms are useful as components of organic conductors because heteroatoms in their rings are helpful to stabilize ions or ion-radical species, and extended π-conjugation decreases Coulombic repulsion.[1] In addition, intermolecular interactions caused by heteroatom contacts can be expected to form unique molecular assemblies.[2] From this viewpoint, we have prepared novel electron donors and acceptors containing fused 1,2,5-thiadiazole units, and found that the thiadiazole ring plays an important role in forming two-dimensional networks in crystals.[3] In this connection, tetrathiafulvalene (TTF) derivatives containing fused 1,2,5-thiadiazole rings are interesting electron donors since TTF is a strong electron donor and a pyrazine-fused TTF derivative affords a three-dimensional conductor.[4] We have now succeeded in preparing bis[1,2,5]thiadiazolotetrathiafulvalene (**1**) and investigated its properties.

The TTF derivative (**1**) was prepared as follows. Dithiolate (**2**) obtained by the reaction of 3,4-dichloro-1,2,5-thiadiazole with sodium sulfide[5] was reacted with thiophosgene to give [1,2,5]thiadiazolo-1,3-dithiole-2-thione (**3**) in 37% yield. Although the reaction of **3** with trialkylphosphite gave a complicated mixture of products, the reaction of **3** with triphenylphosphine (10 equiv.) in refluxing toluene afforded **1** in 63% yield. The structure of **1** was determined on the basis of the spectral data along with elemental analysis.[6] The oxidation potentials of **1**

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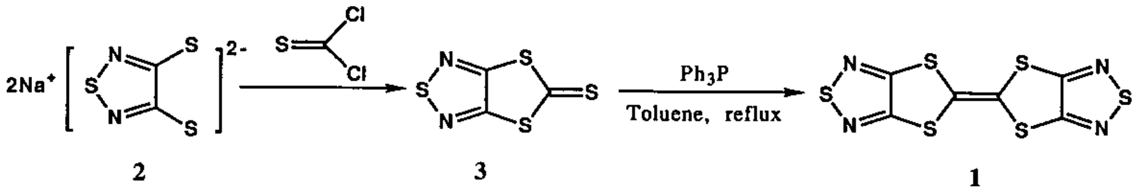
†Dedicated to Prof. Edward C. Taylor on the occasion of his 70th birthday.



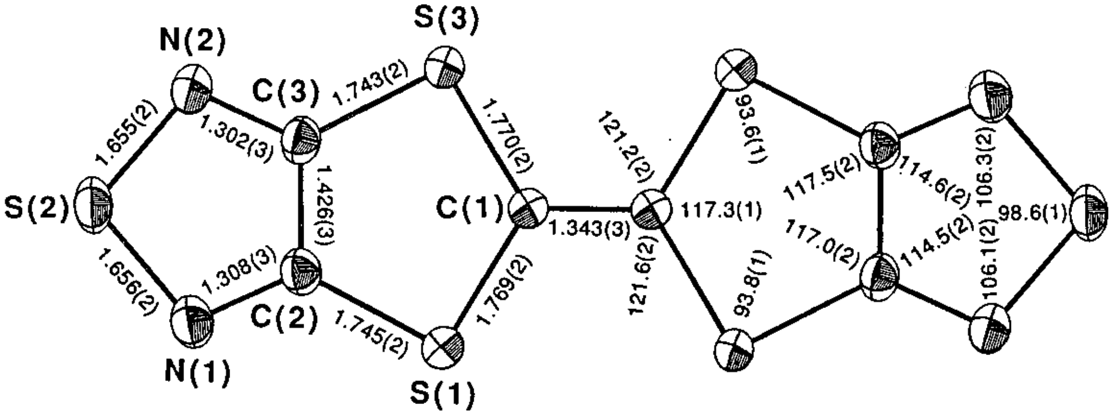


Figure 1. ORTEP drawing of 1 along with bond lengths (Å) and angles (°).

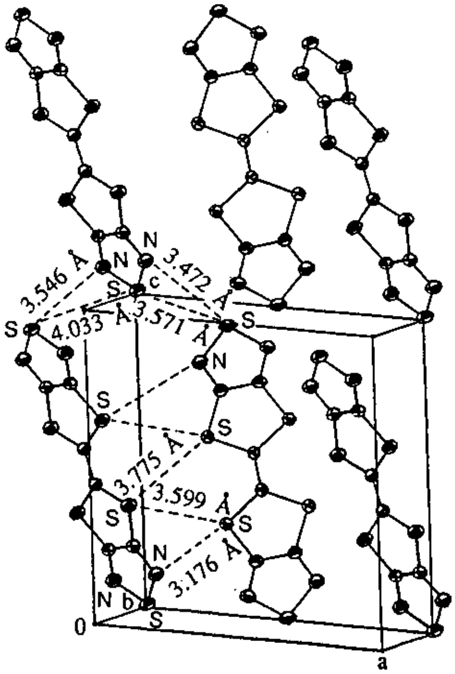


Figure 2. Crystal structure of 1.

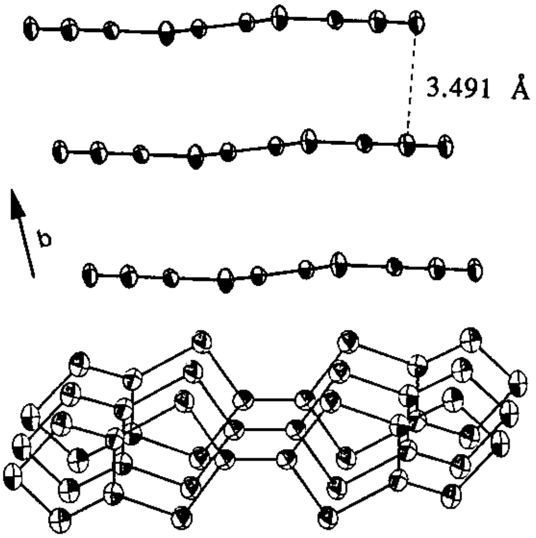
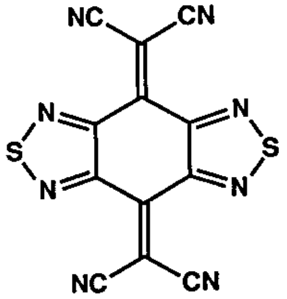


Figure 3. Stacking mode of 1.

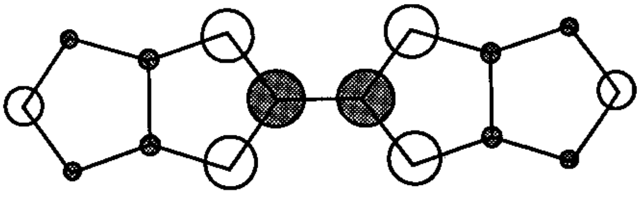
measured by cyclic voltammetry in dichloromethane[7] were +1.42 (rev.) and +1.63 (irrev.) V vs. SCE. The higher values compared with those of TTF (+0.52, +0.87 V vs. SCE) reflect the electron-withdrawing property of 1,2,5-thiadiazole.

In order to investigate the molecular structure of **1** as well as the possible interheteroatom interactions, the X-ray structural analysis was carried out.[8] The molecule has a planar geometry with the max. deviation of 0.151 Å from the mean plane. The bond lengths and angles are shown in Figure 1. The bond lengths show a pronounced bond alternation. Thus the S-N and C-N bonds of the thiadiazole ring are longer and shorter, respectively, than the corresponding bonds of 1,2,5-thiadiazoles.[9] In bis[1,2,5]thiadiazolotetracyanoquinodimethane (BTDA-TCNQ), for example, the S-N and C-N bond lengths of the thiadiazole ring are 1.616 and 1.330 Å, respectively.[10] The crystal structures are shown in Figure 2. The most striking feature in the crystal is the formation of a network by heteroatom contacts. The S---N contact distance (3.176 Å) and S---S ones (3.571 and 3.599 Å) are shorter than the sum of the van der Waals distances (3.35 and 3.70 Å, respectively). The molecules of **1** are uniformly stacked along the b axis with good overlapping as shown in Figure 3, where the shortest S---N distance is 3.491 Å.

The HOMO of **1** is similar to that of TTF,[11] but the sulfur atom of the thiadiazole has a fairly large coefficient.[12] This property is favorable for construction of multi-dimensional conductors. However, the donor (**1**) formed no complexes with TCNQ, BTDA-TCNQ, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) probably due to its high oxidation potentials. The preparation of cation-radical salts by electrochemical oxidation is now in progress.



BTDA-TCNQ



HOMO of **1**

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6. **1**: mp 307-308 °C (decomp.) (tetrachloroethylene); ir (KBr) 1372, 1354, 1248, 1228, 1023, 777 cm^{-1}; ms m/z 320 (M^+); uv (CH_2Cl_2) λmax (log ε) 276 (3.93), 371 (3.89). Anal. Calcd for $C_6N_4S_6$: C, 22.49; N, 17.48. Found: C, 22.25, N, 17.63.
7. Measured at a Pt electrode with 0.1 mol dm^{-3} Bu_4NBF_4 as a supporting electrolyte; scan rate 100 mV s^{-1}.
8. The single crystal was obtained by recrystallization from tetrachloroethylene. Crystal data for **1**: $C_6N_4S_6$, M=320.49, monoclinic, space group $P2_1/a$, a=11.607(3), b=3.918(1), c=11.349(3) Å, β=91.78(2)°, V=515.8(2) $Å^3$, Z=2, D_{calcd}=2.063 g cm^{-1}, MoK_α radiation. The final R value is 2.65% for 933 reflections with $|Fo| > 3\sigma|Fo|$.
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11. D. L. Lichtenberger, R. L. Johnston, K. Hinkelmann, T. Suzuki, and F. Wudl, *J. Am. Chem. Soc.*, 1990, **112**, 3302.
12. The HOMO was calculated by the MNDO method [MOPAC program: J. J. P. Stewart, *Q. C. P. E. Bull.*, 1983, **3**, 439], which was performed by using the geometry determined from the X-ray analysis. This calculation was carried out at the Computer Center of the Institute for Molecular Science.

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