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The Crystal and Molecular Structures of Bis[1,2-bis(methylthio)vinylenedithio]tetrathiafulvalene (TMTVT)

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Synopsis. An X-ray crystal structure analysis of the title molecule (TMTVT) was made. The central portion of tetrathio-TTF was shown to be almost planar, and the outer portions of the two bis(methylthio)vinylenes are bent toward opposite directions each other. TMTVT molecules form a columnar stack toward the *c*-axis with equal intermolecular spacings.

Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) is known to give several ambient presssure organic superconductors.[1] The most characteristic feature of BEDT-TTF salts is their two-dimensional electrical properties, which arise from S····S contacts that are shorter than the van der Waals distance between adjacent donor molecules in the crystal.[2] This crystal structure results in a suppression of a Peierls transition inherent in a one-dimensional system. TTF derivatives possessing multi-chalcogen atoms are attractive donor molecules, because they are expected to give complexes which are highly conductive down to low temperatures; this is a prerequisite for realizing organic superconductors. We have synthesized several TTF derivatives possessing eight or twelve chalcogen atoms.[3–7] This paper reports on an X-ray crystal structure analysis of bis[1,2-bis(methylthio)vinylenedithio]tetrathiafulvalene (TMTVT) which has the largest number of sulfur atoms (twelve)[5] in the TTF-derivatives ever known.

Experimental

$C_{14}H_{12}S_{12}$, M 565.04, monoclinic, space group $P2_1/n$, a=7.939(1), b=28.302(2), c=5.067(1) Å, β=95.74(1)°, V=1132.8(2) Å^3, D_c=1.657 g cm^{-3} for Z=2. The crystal used had a needle shape with 0.04×0.16×0.46 mm^3. Reflection intensities were measured by the θ-2θ scan technique up to 2θ=120° on a Rigaku rotating anode four-circle diffractometer using nickel-filtered Cu $K\alpha$ radiation. The scan rate was 4° min^{-1} and the scan width $\Delta\theta$=(1.4+0.15 tan θ)°. Backgrounds were counted for 3 s at both ends of each scan. No significant intensity decay of the standard reflections, which were measured after every 100 reflections, was detected. Of the 1997 reflections measured, 1564 were observed ($|F_o|>2\sigma(F_o)$). The usual Lorentz and polarization corrections were applied, but no absorption correction was made [μ(Cu $K\alpha$)=102.8 cm^{-1}].

Structure Solution and Refinement

The structure was solved by a direct method (*MULTAN* 78),[8] and was refined anisotropically by a block-diagonal least-squares procedure (*HBLS* V).[9] The function minimized was $\sum\omega(\Delta F)^2$. The weighting function used in the final stage of the refinement was $\omega=[\sigma^2(F_o)-0.0826|F_o|+0.0166|F_o|^2]^{-1}$. The hydrogen atoms could not be found on a D-map, which is probably due to either the rotation or the large amplitude of vibration of the methyl group. Therefore, the hydrogen atoms were not included in the final refinement. Atomic scattering factors were taken from those of International Tables for X-Ray Crystallography.[10] The final R index was 0.091. The atomic coordinates and equivalent isotropic temperature factors[11] are given in Table 1.† Bond lengths and bond angles are shown in Fig. 1, and the crystal structures in Figs. 2 and 3.

Table 1. Atomic Parameters of Nonhydrogen Atoms with Equivalent Isotropic Temperature Factors[11]

Atom	x	y	z	B_{eq}/Å^2
C(1)	0.9558(5)	0.0132(1)	0.0785(9)	3.77
C(2)	0.7200(5)	0.0521(1)	0.320(1)	3.84
C(3)	0.8654(5)	0.0710(1)	0.429(1)	4.09
C(4)	0.5610(6)	0.1337(2)	0.388(1)	4.42
C(5)	0.7065(6)	0.1530(2)	0.494(1)	4.30
C(6)	0.3231(9)	0.1415(3)	−0.051(1)	7.01
C(7)	0.9400(8)	0.2188(3)	0.350(2)	7.6
S(1)	0.7329(1)	0.01139(4)	0.0630(3)	4.14
S(2)	1.0537(1)	0.05421(4)	0.3074(3)	4.31
S(3)	0.5240(1)	0.07249(4)	0.3995(3)	4.29
S(4)	0.8665(2)	0.11692(5)	0.6626(3)	4.61
S(5)	0.3871(2)	0.16848(6)	0.2647(4)	5.99
S(6)	0.7490(2)	0.21363(5)	0.5121(4)	6.10

Results and Discussion

The TMTVT molecules are on the centers of symmetry. The central tetrathio-TTF portion of the TMTVT molecule is approximately planar; this plane is almost perpendicular to the *b*–*c* plane. Two bis(methylthio)vinylene portions at both ends of the molecule are bent toward opposite directions from each other (Fig. 1(b)). Both BEDT-TTF[14] and bis(vinylenedithio)tetrathiafulvalene (VT)[15] possess planar structures only at the central tetrathioethylene portion. Comparing the molecular structure of TMTVT with those of BEDT-TTF and VT, the central planar portion is extended more widely in the former molecule. The crystal structure is characterized by a face-to-face stack of TMTVT molecules toward the *c*-axis with equal intermolecular spacings (Fig. 2(a)). The interplanar distance between adjacent molecules is 3.53 Å. S····S contacts [3.700(3) Å] almost equal to the van der Waals radius (3.7 Å) are found between methylthio groups of TMTVT molecules belonging to the adjacent stacks [S(5)(x,y,z)····S(6)

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† Tables of anisotropic thermal parameters and observed and calculated structure factors are kept at the Chemical Society of Japan, Document No. 8880.

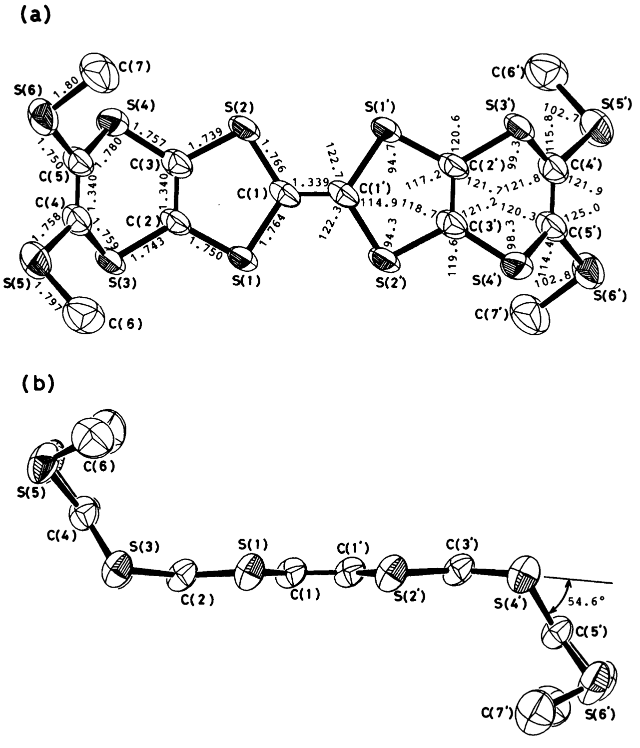

Fig. 1. Molecular structure of TMTVT.[12] (a) Over view, (b) side view. Nonhydrogen atoms are drawn as thermal ellipsoids with 50% probability level. Estimated standard deviations of the bond lengths and angles are 0.005—0.01 Å and 0.3—0.4°, respectively.

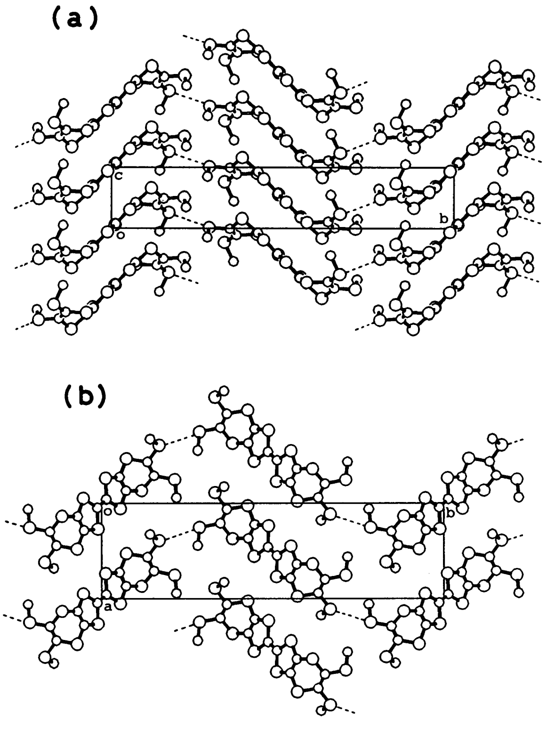

Fig. 2. Crystal structure of TMTVT[13] projected along the *a* axis (a) and the *c* axis (b). Dotted line indicates intermolecular S····S contact almost equal to the van der Waals distance (3.7 Å).

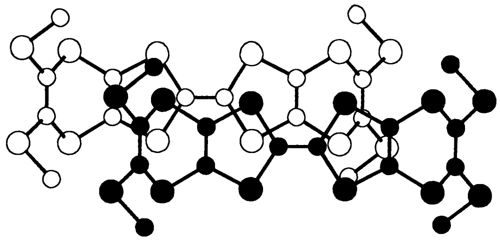

Fig. 3. Overlap of two TMTVT molecules.[13]

$(-0.5+x, 0.5-y, -0.5+z)$], and are shown by dotted lines in Fig. 2. All of the other S····S distances are longer than the van der Waals radius. Figure 2(b) shows a side-by-side arrangement of molecules of equal height. All of the side-by-side S····S distances are longer than the van der Waals radius, unlike the cases of BEDT-TTF salts.[2] Figure 3 shows the overlap of two TMTVT molecules projected normal to the molecular plane. The two molecules shift with each other in order to avoid direct overlap of carbon and sulfur atoms between them.

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