

Structures of 4,5-Bis(methylthio)-3*H*-1,2-dithiole-3-thione and 1,2-Dithiole-3-thione-[5,4-*b*]-5,6-dihydro-1,4-dithiin*

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Abstract. 4,5-Bis(methylthio)-3*H*-1,2-dithiole-3-thione, C₅H₆OS₄ (BMDT), $M_r = 210.34$, monoclinic, $P2_1/c$, $a = 8.975$ (1), $b = 14.727$ (1), $c = 13.151$ (3) Å, $\beta = 93.46$ (1)°, $V = 1735$ (1) Å³, $Z = 8$, $D_m = 1.62$ (1), $D_x = 1.610$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.99$ mm⁻¹, $F(000) = 864$, $T = 295$ K, $R = 0.033$, $wR = 0.051$ for 3712 unique observed reflections with $I > 2.5\sigma(I)$. 1,2-Dithiole-3-thione-[5,4-*b*]-5,6-dihydro-1,4-dithiin, C₅H₄S₅ (DTDD), $M_r = 224.39$, monoclinic, $P2_1/c$, $a = 12.099$ (2), $b = 17.613$ (2), $c = 8.201$ (3) Å, $\beta = 108.43$ (2)°, $V = 1658$ (1) Å³, $Z = 8$, $D_m = 1.79$ (1), $D_x = 1.798$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.26$ mm⁻¹, $F(000) = 912$, $T = 295$ K, $R = 0.044$, $wR = 0.044$ for 3271 unique observed reflections with $I > 2.5\sigma(I)$. The two BMDT molecules in the asymmetric unit have nearly identical bond lengths and bond angles, whereas the two symmetry independent DTDD molecules differ with respect to the —S—CH₂—CH₂—S fragment. The carbonyl O atom in BMDT and the thione S atom in DTDD are involved in rather short intermolecular contact distances probably due to delocalization of π -electron density in the all-*trans* system (S,O)=C—C=C—S—.



Introduction. Over the past few years there has been intense activity concerning the preparation and properties of organic metals and organic superconductors based on 3,4,3',4'-bis(ethylenedithio)-2,2',5,5'-tetrathiafulvalene (BEDT-TTF). The superconducting transition temperature T_c of these materials has recently been raised to 11.6 K in κ -(BEDT-TTF)₂Cu[N(CN)₂]Br (Williams, Kini, Geiser, Wang, Carlson, Kwok, Vandervoort, Thompson, Stupka, Jung & Whangbo, 1990). Metal

complexes of the related ligand dmit, also gives rise to molecular metals and superconductors (Kobayashi, Kim, Sasaki, Kato, Kobayashi, Moriyama, Nichio, Kajita & Sasaki, 1987; Clark, Underhill, Parker & Friend, 1989). There is considerable interest in the study of possible chemical modifications of the molecular framework of BEDT-TTF and of the dmit ligand and the influence of such changes on the properties of the charge-transfer salts and metal complexes. We now wish to report the crystal structures of two compounds closely related to molecular fragments of BEDT-TTF and dmit, but containing a 1,2-dithiole in place of the 1,3-dithiole ring found in the latter two compounds.

Experimental. *X-ray crystal structure analyses.* The crystals of 4,5-bis(methylthio)-3*H*-1,2-dithiole-3-thione (BMDT) used in the X-ray investigation were recrystallized from chloroform/methanol and separated as pale-yellow prisms. A crystal with approximate dimensions 0.33 × 0.33 × 0.23 mm was selected for X-ray diffraction. The crystals of 1,2-dithiole-3-thione[5,4-*b*]-5,6-dihydro-1,4-dithiin (DTDD) selected for the X-ray investigation were recrystallized from absolute ethanol and separated as yellow needles. Crystal of size 0.10 × 0.23 × 0.36 mm was used. Crystals of both compounds were mounted on an Enraf–Nonius CAD-4F diffractometer, graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Both BMDT and DTDD crystallize in space group $P2_1/c$ (deduced from systematic extinctions) and both with $Z = 8$ corresponding to two molecules in the asymmetric unit. The lattice parameters were determined from setting angles for 24 reflections (BMDT) with $11.30 < \theta < 14.33^\circ$ and 25 reflections (DTDD) with $11.71 < \theta < 13.80^\circ$. Density was determined by flotation in CH₂BrCl and CCl₄. The intensities of 5054 unique reflections ($R_{int} = 0.02$) were measured for BMDT ($h: 0 \rightarrow 12, k: 0 \rightarrow 20, l: -18 \rightarrow 18$) with $2.0 < \theta < 30.0^\circ$. 3712 reflections

* IUPAC name: 5,6-dihydro[1,2]dithiolo[3,4-*b*][1,4]dithiin-3-thione.

with $I > 2.5\sigma(I)$ were used in the refinement process together with less-than reflections [$I < 2.5\sigma(I)$] with calculated values greater than the observed (4685 contributing reflections). Intensities of 4810 unique reflections for DTDD ($h: 0 \rightarrow 16, k: 0 \rightarrow 24, l: -11 \rightarrow 10$) with $2.0 < \theta < 30.0^\circ$, 3271 with $I < 2.5\sigma(I)$ were used in the refinement process together with less-than reflections [$I < 2.5\sigma(I)$] with calculated values greater than the observed (4374 contributing reflections). $\omega/2\theta$ scan technique was used with scan angles $\Delta\omega = (1.20 + 0.35\tan\theta)^\circ$ for both structures. Three reflections were used for orientation control every 100 reflections (BMDT: 455, 085, 515; DTDD: 283, 652, 532). An intensity stability check was made every third hour of exposure time by using 515 (BMDT) and 652 (DTDD). During the data collection the standard intensity decreased by 8% for BMDT and 2.5% for DTDD. Correction for decay was applied in both cases. The intensities were corrected for Lorentz and polarization effects. Absorption was ignored. The structures were solved with direct methods and refined by full-matrix least squares for anisotropic non-H atoms. The function $\sum w(\Delta|F|)^2$ was minimized. Average $(w\Delta|F|)^2$ was almost independent of $|F_o|$ by using $w = 1$ when $|F_o| < 30.0$, else $w = (30.0/F_o)^2$ for BMDT and $w = \{1 + [(F_o - 32)/85]^2\}^{-1}$ for DTDD. Positional H-atom parameters (BMDT) from $\Delta\rho$ maps. Refinements of H(x, y, z) using reflections with $\sin\theta/\lambda < 0.40 \text{ \AA}^{-1}$, and fixed isotropic temperature factors. The atoms C(26) and C(27) (DTDD) are disordered and all positional H-atom parameters (DTDD) were calculated.

The refinement converged, with 217 parameters varied, to final $R = 0.033$, $wR = 0.051$, $S = 1.07$ and $(\Delta/\sigma)_{\max} = 0.005$ for BMDT and, with 196 parameters varied, to $R = 0.044$, $wR = 0.044$, $S = 1.70$ and $(\Delta/\sigma)_{\max} = 0.009$ for DTDD [except for two disordered C atoms, C(26) and C(27), where $(\Delta/\sigma)_{\max} = 0.269$]. Min. and max. values in final $\Delta\rho$ maps were -0.41 and 0.24 e \AA^{-3} for BMDT and -0.68 and 0.72 e \AA^{-3} for DTDD. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99 and 149). Computer programs from *SHELXS86* (Sheldrick, 1986) and *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). The fractional coordinates for the molecules in the structures of DTDD and BMDT are given in Table 1.*

Discussion. The bond distances and bond angles for the two symmetry independent molecules in the

* Lists of structure factors, anisotropic displacement parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53976 (60 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates and equivalent isotropic thermal parameters of non-H atoms in the structures of DTDD and BMDT

E.s.d.'s in parentheses.				
$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$.				
	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
BMDT1				
S(1)	0.27084 (3)	0.38462 (2)	0.32013 (2)	4.00 (2)
S(2)	0.22590 (3)	0.45397 (2)	0.44954 (2)	3.79 (2)
S(3)	0.35324 (4)	0.63537 (2)	0.51051 (2)	4.36 (2)
S(4)	0.55207 (4)	0.62674 (2)	0.31629 (3)	5.01 (2)
O(5)	0.4764 (1)	0.44301 (6)	0.20320 (6)	4.96 (7)
C(3)	0.3417 (1)	0.54483 (6)	0.42632 (7)	3.22 (6)
C(4)	0.4234 (1)	0.54134 (7)	0.34199 (7)	3.35 (6)
C(5)	0.4093 (1)	0.46196 (7)	0.27846 (8)	3.73 (7)
C(31)	0.2267 (2)	0.6040 (1)	0.6064 (1)	5.3 (1)
C(41)	0.4851 (2)	0.6641 (1)	0.1912 (1)	6.2 (1)
BMDT2				
S(11)	0.26424 (3)	0.17169 (2)	0.54413 (2)	4.23 (2)
S(12)	0.28149 (3)	0.03546 (2)	0.51617 (2)	3.97 (2)
S(13)	0.10258 (4)	-0.06708 (2)	0.35600 (2)	4.43 (2)
S(14)	-0.07105 (3)	0.11729 (2)	0.29618 (2)	4.69 (2)
O(15)	0.0616 (1)	0.26910 (6)	0.44334 (8)	5.28 (7)
C(13)	0.1455 (1)	0.03387 (6)	0.41736 (7)	3.20 (6)
C(14)	0.0729 (1)	0.11316 (7)	0.39281 (7)	3.40 (6)
C(15)	0.1134 (1)	0.19305 (7)	0.45076 (8)	3.67 (7)
C(131)	0.2397 (2)	-0.1443 (1)	0.4138 (1)	5.8 (1)
C(141)	0.0259 (2)	0.1647 (1)	0.1939 (1)	6.5 (1)
DTDD1				
S(11)	0.82687 (6)	0.26059 (4)	0.0026 (1)	3.63 (5)
S(12)	0.90616 (6)	0.16022 (4)	0.0999 (1)	3.74 (5)
C(13)	1.0314 (2)	0.1991 (2)	0.2415 (3)	3.0 (2)
S(13)	1.13528 (7)	0.14172 (5)	0.3572 (1)	4.30 (6)
C(14)	1.0318 (2)	0.2800 (2)	0.2453 (3)	2.8 (2)
S(15)	1.15418 (6)	0.32193 (4)	0.39243 (9)	3.68 (5)
C(16)	1.1130 (3)	0.4200 (2)	0.3866 (4)	4.2 (2)
C(17)	1.0556 (3)	0.4506 (2)	0.2087 (4)	4.1 (2)
S(18)	0.91016 (6)	0.41268 (4)	0.1060 (1)	4.09 (5)
C(19)	0.9372 (2)	0.3163 (1)	0.1341 (3)	2.9 (2)
DTDD2				
S(21)	0.31435 (6)	0.00766 (4)	0.29221 (9)	3.46 (5)
S(22)	0.41426 (6)	0.09780 (4)	0.2638 (1)	3.59 (5)
C(23)	0.5309 (2)	0.0460 (2)	0.2443 (3)	3.0 (2)
S(23)	0.64517 (6)	0.09070 (4)	0.2194 (1)	4.21 (6)
C(24)	0.5169 (2)	-0.0343 (1)	0.2552 (3)	2.7 (2)
S(25)	0.63315 (6)	-0.09008 (4)	0.2385 (1)	3.71 (5)
C(26)	0.5885 (4)	-0.1839 (2)	0.2717 (8)	8.1 (5)
C(27)	0.4717 (4)	-0.2043 (2)	0.2187 (8)	8.0 (5)
S(28)	0.36958 (6)	-0.15214 (4)	0.2899 (1)	3.90 (5)
C(29)	0.4144 (2)	-0.0594 (2)	0.2768 (3)	2.80 (5)

DTDD structure are shown in Figs. 1(c) and 1(d) together with the atom-numbering scheme. The dithiole ring in both molecules of the asymmetric unit is essentially planar as the maximum deviations from a least-squares plane defined by the dithiole ring atoms are 0.02 (2) and 0.005 (4) Å, respectively, for DTDD1 and DTDD2. The dithiole rings associated with the symmetry independent BMDT molecules (Figs. 1a and 1b) are nearly planar with -0.04 (3) Å (BMDT1) and 0.02 (2) Å (BMDT2) as maximum deviations from the respective least-squares planes. Generally the molecules BMDT1 and BMDT2 have nearly the same bond distances and bond angles and it is also the case for the two molecules DTDD1 and DTDD2 except with respect to the $-\text{S}-\text{CH}_2-\text{CH}_2-\text{S}-$ part which has disordered C atoms in DTDD2. C(26) and C(27) have extraordinarily large temperature factors and the

DTDD and BMDT in such a way that the shortest C_{sp²}—S bond is in a *trans* position to the O, S=C < fragment.

On the basis of the preceding considerations we suggest the existence of some intramolecular π -electron delocalization over the systems S(X3)=C(X3)—C(X4)=C(X9)—S(X8) (X=1;2) (DTDD) and O(Y5)=C(Y5)—C(Y4)=C(Y3)—S(Y3) (Y=0;1) (BMDT). These delocalizations of π electrons are probably responsible for a different pattern of S...S and S...O interactions in DTDD and BMDT compared to BTDTT and BTDTO. The two former structures have intermolecular S...S and S...O contacts involving the thione and carbonyl groups (Figs. 2 and 3), whereas this is not the case for the latter two structures.

The density of the DTDD crystals (1.79 g cm⁻³) is markedly higher than those of the related compounds (BMDT), (BTDTT) and (BTDTO) which all have a measured density of 1.62 g cm⁻³. The DTDD structure has five intermolecular S...S contact distances less than 3.7 Å. Two of them are rather short, S(13)...S(21; 1 + x, y, z) 3.359 (1), S(11)...S(28; 1 - x, -y, -z) 3.383 (1) Å. The remaining three are: S(15)...S(25; 2 - x, 0.5 + y, 0.5 - z) 3.453 (1), S(18)...S(21; 1 - x, 0.5 + y, 0.5 - z) 3.508 (1) and

S(11)...S(28; 1 - x, 0.5 + y, 0.5 - z) 3.670 (1) Å. The BMDT structure has four intermolecular S...O contact distances less than 3.25 Å with S(12)...O(5; x, 0.5 - y, 0.5 - z) 2.949 (1) Å as the strongest, S(1)...O(15) 3.071 (1), S(2)...O(15) 3.098 (1), S(11)...O(5; x, 0.5 - y, 0.5 + z) 3.225 (1) Å.

References

- CLARK, A., UNDERHILL, A. E., PARKER, I. D. & FRIEND, R. H. (1989). *J. Chem. Soc. Chem. Commun.* pp. 228–229.
 DOWTY, E. (1989). *ATOMS. A Computer Program for Displaying Atomic Structures*. IBM-PC, Version 1.0. Copyright E. Dowty, 521 Hidden Valley Road, Kingsport, TN 37663, USA.
 KOBAYASHI, A., KIM, H., SASAKI, Y., KATO, R., KOBAYASHI, H., MORIYAMA, S., NICHIO, Y., KAJITA, K. & SASAKI, W. (1987). *Chem. Lett.* pp. 1819–1822.
 SHELDRICK, G. M. (1986). *SHELXS86*. Program system for the solution of crystal structures. Univ. of Göttingen, Germany.
 SIMONSEN, O., VARMA, K. S., CLARK, A. & UNDERHILL, A. E. (1990). *Acta Cryst.* **C46**, 804–807.
 STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The *XRAY76* system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.
 WILLIAMS, J. M., KINI, A. M., GEISER, U., WANG, H. H., CARLSON, K. D., KWOK, W. K., VANDERVOORT, K. G., THOMPSON, J. E., STUPKA, D. J., JUNG, D. & WHANGBO, M.-H. (1990). *Proc. Int. Conf. on Organic Superconductors*, May 1990, South Lake Tahoe, USA. Plenum Press. Pre-print.

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X-ray Study of 2-(3,5-Dimethylpyrazolyl)-1,3-benzothiazole

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Abstract. C₁₂H₁₁N₃S, *M_r* = 229.3, orthorhombic, *Pbca*, *a* = 16.841 (5), *b* = 12.189 (4), *c* = 10.842 (2) Å, *V* = 2225.6 (2) Å³, *Z* = 8, *D_x* = 1.37, *D_m* (floatation) = 1.43 g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178 \text{ \AA}$, $\mu = 23.77 \text{ cm}^{-1}$, *F*(000) = 960, *R* = 0.038 for 1208 unique observed reflections [*I* > 2 σ (*I*)]. The molecule consists of a five-membered dimethylpyrazole ring rather than a seven-membered ring. The S—C average bond distance, 1.746 Å, is shorter than for a single bond. The benzothiazole nucleus adopts an almost planar conformation with a dihedral angle between the mean planes of the two individual rings of 1.5°. The dimethylpyrazole ring does not deviate much from planarity and is inclined at an angle of 13° to

the benzothiazole ring. The molecules are well separated and stacked in parallel rows along the crystallographic axes.

Introduction. There has been considerable interest in studies of the structural configuration of the products obtained by the reaction of heterocyclic hydrazines with β -dicarbonyl compounds, and their biological activities. In the cases of 4-aryl-2-hydrazines (Singh, Vaid, Prakash & Prakash, 1986) and 2-hydrazinequinolines (Singh, Sehgal, Singh & Dhawan, 1987), a five-membered ring formation (1) of the pyrazole group has been suggested for the compounds obtained on treatment with pentane-2,4-dione. However, an isomeric seven-membered ring formation (2) has been proposed for the same compounds by other groups of workers (Mahajan,

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