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4,5-Dimethyl-1,3-dithiole-2-thione

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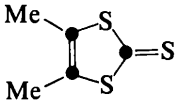
Abstract. $C_5H_6S_3$, $M_r = 162{\cdot}3$, orthorhombic, *Pmnb*, $a = 10{\cdot}861$ (5), $b = 11{\cdot}484$ (6), $c = 5{\cdot}927$ (4) Å, $V = 739{\cdot}3$ (7) Å^3, $Z = 4$, $D_c = 1{\cdot}458$ Mg m^{-3}, $T = 294$ K, λ(Mo $K\alpha_1$) = 0·70926 Å, μ(Mo $K\alpha$) = 0·86 mm^{-1}, $F(000) = 336$. The structure was solved from diffractometer data by the heavy-atom method and refined by full-matrix least squares to $R = 0{\cdot}037$. The S–C bond lengths (1·651, 1·717, 1·736 Å) indicate that there is considerable resonance between the thione sulfur and the ring resulting in a separation of charge and a dipolar ground state.

Introduction. In recent years, a large number of highly conducting, organic, donor–acceptor complexes have been studied (Perlstein, 1977). Among the better conductors are radical-cation salts of the tetrathiafulvalenes (TTF), which have revived interest in the aromaticity and other electronic properties of the 1,3-dithiole-2-thiones, starting materials in the TTF synthesis (Campaigne & Hamilton, 1970; Spanget-Larsen, Gleiter, Kobayashi, Engler, Shu & Cowan, 1977).

Yellow, long prismatic (*c*) crystals of the title compound (DMDTT)



were grown by slow evaporation of a solution in petroleum ether. Systematic absences (*h*0*l*, *h* + *l* odd; *hk*0, *k* odd) from precession films indicated possible space groups *Pmnb* and $P2_1nb$. A crystal 0·28 × 0·30 × 0·61 mm, sealed in a glass capillary to prevent sublimation, was used for data collection with Zr-filtered Mo radiation on a card-controlled Picker diffractometer. Cell dimensions were determined by a least-squares refinement of 13 carefully centered reflections, and intensities were measured by θ–2θ scans (1° min^{-1}, 20 s backgrounds). Of the 1141 unique reflections measured ($2\theta < 60°$), 873 had $I \geq 2\sigma(I)$. The rest were set equal to $2\sigma(I)$, corrected to $F_{\rm lim}$, and were included in the refinement only if $|F_c| > F_{\rm lim}$. Absorption corrections were not made.

The statistical averages and distribution of the normalized structure factors strongly supported the centrosymmetric space group. With $c < 6$ Å and $Z = 4$, the molecule had to lie on the mirror plane at $x = \frac{1}{4}$ with its plane perpendicular to the mirror plane. This orientation was verified by an $E^2 - 1$ Patterson map. The Patterson map and a subsequent electron density map gave the structure which was then refined in the centrosymmetric space group by full-matrix least squares (Busing, Martin & Levy, 1962; Luss & Smith, 1973). A difference map yielded the H atoms. The largest structure factors were obviously affected by extinction, so the 102 largest F's were used to refine an extinction parameter g (Larson, 1967). Refinement with anisotropic thermal parameters for C and S and isotropic thermal parameters for H was concluded when all parameter shifts were less than $0{\cdot}1\sigma$. For 873 observed reflections plus 27 unobserved reflections with $|F_c| > F_{\rm lim}$, the final agreement index was $R = 0{\cdot}037$. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma^2(F_o) + (0{\cdot}024F_o)^2$. The extinction parameter g was $5{\cdot}7\ (3) \times 10^{-6}$. The atomic scattering factors were obtained from Stewart, Davidson & Simpson (1965) for H and *International Tables for X-ray Crystallography* (1962) for S and C. The anomalous scattering factor corrections for S (Cromer & Liberman, 1970) were applied. The final positional parameters are given in Table 1.*

Discussion. The atomic labeling and the bond distances and angles for DMDTT are shown in Fig. 1. The

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34807 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* (×10^3 *for* H *atoms and* ×10^4 *for all others*)

	x	y	z
S(1)	2500	3541·6 (9)	3737·5 (16)
S(2)	3811·1 (4)	2041·1 (5)	431·9 (10)
C(1)	2500	2590 (2)	1651 (4)
C(2)	3116 (2)	1158 (1)	−1574 (3)
C(3)	3936 (3)	473 (3)	−3113 (6)
H(1)	415 (4)	94 (3)	−425 (7)
H(2)	347 (4)	2 (4)	−422 (7)
H(3)	467 (5)	48 (3)	−251 (8)

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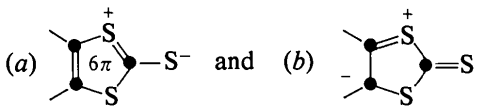
C(2)–C(2′) distance (1·338 Å) is normal for a double bond (1·335 Å expected). Comparison of S(1)–C(1) (1·651 Å) with the expected 1·61 Å for a double bond and of S(2)–C(1) (1·717 Å) and S(2)–C(2) (1·736 Å) with the expected value of 1·78 Å for a single bond indicates appreciable resonance interactions in the molecule in which polar structures of the types



are important. In (*a*), the dithiole ring, by transfer of one electron to the thione sulfur, has formed a sextet of π electrons which should confer some aromatic stability on this polar structure. The S(2)–C(1) bond is significantly (7σ) shorter than S(2)–C(2), and structure (*a*) is therefore considerably more important than (*b*).

The crystal structures of many complexes of TTF derivatives, particularly with TCNQ, have been determined. For a given complex stoichiometry, the dimensions of the TTF moieties agree reasonably well, and the dimensions show that the aromaticity of the dithiole ring increases with the formal cationic charge (Kistenmacher, Phillips, Cowan, Ferraris & Bloch, 1976; Galigné, Fabre & Giral, 1977). In Table 2, some distances and angles in DMDTT are compared with similarly situated distances in a selected group of TTF derivatives, both complexed and uncomplexed. The obvious trend is that DMDTT resembles most closely the more highly charged and hence more aromatic TTF moieties. The trend occurs for both the distances and the angles, with an indication that DMDTT is about as aromatic as TETTF in TETTF.$TCNQ_2$.

The DMDTT molecule is only approximately planar with maximum and r.m.s. deviations of 0·012 and 0·007 Å, respectively, from a least-squares plane. The deviations from this plane are systematic and indicate a bend at S(2) into two planes, one through S(1), C(1), S(2), and S(2′) and another through C(2), C(2′), C(3), C(3′), S(2), and S(2′), both with a maximum deviation

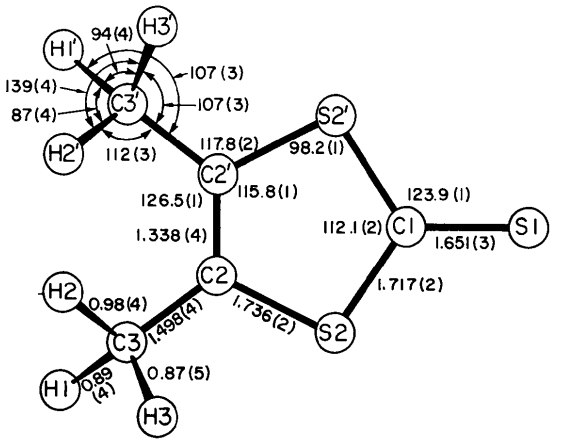


Fig. 1. Atomic labeling and bond distances (Å) and angles (°). E.s.d.'s are given in parentheses.

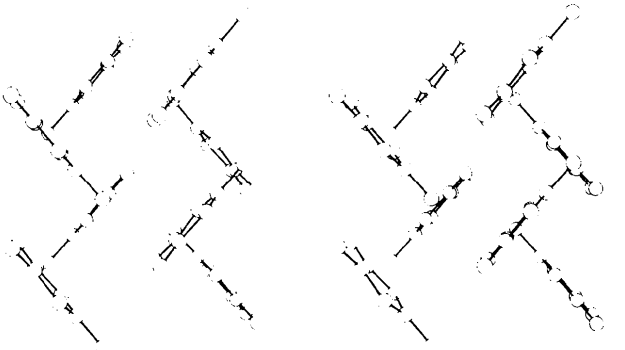
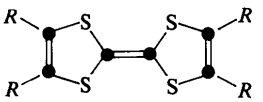


Fig. 2. (100) stereoscopic view of the molecular packing. The *b* axis is horizontal, left to right, and *c* is vertical, top to bottom.

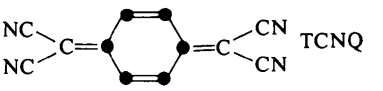
Table 2. *Comparison of averaged bond lengths* (Å) *and angles* (°) *in similar molecules*

	DMDTT[a]	$TCNQ_2$.- TETTF[b]	$TCNQ_2$.- $TMTTF_{1\cdot3}$[c]	TCNQ.- TMTTF[d]	TCMTTF[e]	TTF[f]
S(2)–C(1)	1·717	1·716	1·723	1·739	1·762	1·757
S(2)–C(2)	1·736	1·740	1·747	1·742	1·735	1·730
C(2)–C(2′)	1·338	1·371	1·344	1·360	1·355	1·314
C(1)–S(2)–C(2)	98·2	96·4	95·8	96·2	94·3	94·4
S(2)–C(1)–S(2′)	112·1	115·2	115·2	114·4	115·5	114·5
S(2)–C(2)–C(2′)	115·8	116·0	116·6	116·7	117·9	118·3
Ring bend	1·1	2·3	1·4	2·2	–	2·1

References: (*a*) This work; (*b*) Galigné, Fabre & Giral (1977); (*c*) Kistenmacher *et al.* (1976); (*d*) Phillips, Kistenmacher, Bloch, Ferraris & Cowan (1977); (*e*) Belsky & Voet (1976); (*f*) Cooper, Kenny, Edmonds, Nagel, Wudl & Coppens (1971); Cooper, Edmonds, Wudl & Coppens (1974).



TTF: R = H; TCMTTF: $R = COOCH_3$
TMTTF: $R = CH_3$; TETTF: $R = C_2H_5$



of 0·003 Å. The dihedral angle between the planes is 1·1°. Similar bends have been found for TTF molecules and are listed in Table 2 for the compounds compared there.

There are no intermolecular contacts less than the sums of the van der Waals radii. A stereoscopic view (Johnson, 1971) of the packing is given in Fig. 2. The molecules pack on edge in sheets [the (100) mirror planes]. The plane-to-plane separation is 3·88 Å but the molecular overlap is minimal, and the prominent feature appears to be that each thione S is surrounded by three C(2)=C(2′) bonds at 3·44, 3·90, and 5·20 Å.

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Structure of 3-Bromopyridinium Perchlorate Hemihydrate

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Abstract. $C_5H_5BrN^+.ClO_4^-.\frac{1}{2}H_2O$, monoclinic, $P2_1/n$ ($P2_1/c$ in standard setting), a = 12·181 (2), b = 8·085 (3), c = 18·973 (2) Å, β = 103·66 (1)°, V = 1816·15 Å^3, Z = 8, D_m (flotation) = 1·89, D_c = 1·94 Mg m^{-3}. The structure was solved using the heavy-atom technique and refined by the full-matrix least-squares method to a final $R(F)$ value of 5·7%. The 3-bromopyridinium cations are linked in pairs by means of N–H···O hydrogen bonds to a bridging H_2O molecule [N···O distances are 2·89 (2) and 2·80 (2) Å].

Introduction. The 3-bromopyridine (BrPy)–perchloric acid system has already been investigated by DTA, IR spectroscopy and X-ray diffraction (Belin & Pichvai, 1978). Both 1:1 and 2:1 adducts have been characterized; the latter displays a homoconjugated cation $(BrPy.H.PyBr)^+$ with non-symmetrical NHN hydrogen bonding.

The present research was initiated to determine whether the 3-bromopyridine–perchloric acid–water ternary system would also lead to bromopyridinium homoconjugated cations or to heterocations $(BrPy.H.OH_2)^+$ including water molecules. So far no evidence of a higher hydrate has been found in the system.

The title compound was synthesized from BrPy and commercial (≃ 70%) perchloric acid and then recrystallized in a water–acetone solution to yield large, flat, plate-shaped crystals.

A crystal of dimensions 0·45 × 0·20 × 0·40 mm was selected under polarizing microscope and mounted

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