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5-*R*-3*H*-1,2-Dithiole-3-thione (*R* = Ethylthio and Methylthio)

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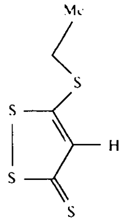
Abstract

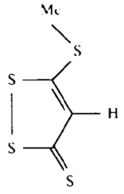
The title compounds, 5-ethylthio-3*H*-1,2-dithiole-3-thione [$C_5H_6S_4$, (2)] and 5-methylthio-3*H*-1,2-dithiole-3-thione, [$C_4H_4S_4$, (3)] crystallize in space groups *C*2/*c* and *P*2$_1$/*n*, respectively. The molecules are planar, with heterocyclic characteristics similar to those shown by other members of the 3*H*-1,2-dithiole-3-thione family. The striking difference between the corresponding melting points [340–341 K for (2) and 438–440 K for (3)] does not seem to arise from the rather similar main intermolecular interactions but rather from apparently much weaker ones.

Comment

In spite of the fact that drugs containing the 3*H*-1,2-dithiole-3-thione unit have been found to show important chemotherapeutic properties, few structural studies have been carried out. A brief summary can be found in a report by Baggio *et al.* (1997, and references therein), where the structure of 4-benzyl-5-ethylthio-3*H*-1,2-dithiole-3-thione [hereafter (1)] is reported. This was the first structure to be determined as part of a planned long-term project concerning the crystal structure determination of new 3*H*-1,2-dithiole-3-thione derivatives obtained through a novel synthetic route for 5-alkylthio derivatives (Aimar & de Rossi, 1996). In this second report, we present the crystal structures of 5-ethylthio-3*H*-1,2-dithiole-3-thione, (2), and 5-methylthio-3*H*-1,2-dithiole-3-thione, (3); these two apparently very similar structures present, however, quite different properties in the solid state, *viz*., melting points differing by *ca* 100 K [340–341 K for (2) and 438–440 K for (3)].



(2)



(3)

Both structures are monoclinic; compound (2) crystallizes in space group *C*2/*c*, while (3) crystallizes in *P*2$_1$/*n*. Molecular diagrams for the two compounds showing the common numbering scheme are presented in Fig. 1. The great similarity of the two 3*H*-1,2-dithiole-3-thione moieties is apparent both by inspection of Fig. 1 and by analysis of their interatomic bond distances and angles; the structural characteristics thoroughly discussed by Baggio *et al.* (1997) for compound (1) (*i.e.* absolute planarity of the cycle, angle at S2 larger than that at S1, *etc.*) are also found here. It is perhaps worth pointing out that the difference arising between the corresponding U_{eq} values [*e.g.* 0.047 Å^2 for (2) and 0.039 Å^2 for (3)] is in clear accord with (2) being 'softer' at room temperature.

The ethylthio group in (2), as well as the homologous methylthio group in (3), lie in the planes of their respective heterocycles, as shown by the relevant torsion angles [C4—C5—S7—C8 −179.6 (1) in (2) and 177.7 (2)° in (3); C5—S7—C8—C9 −174.7 (2)° in (2)], making the two molecules basically planar.

As usual in this type of compound, packing appears to be governed by S···S interactions, the closest intermolecular approaches being reported in Table 5. The shortest S···S distances present in (2) [3.385 (1) Å] and (3) [3.384 (1) Å] are comparable with the shortest distances found in related structures [*e.g.* 3.374 (1) and 3.363 (1) Å in phenyl-3*H*-1,2-dithiole-3-thione (Wei, 1986)] and contribute to the formation of zigzag chains, which evolve in a severely twisted fashion along the unique monoclinic axis; these chains, in turn, are interconnected through weaker interactions (see below).

This solid-state packing with rather short S···S intermolecular distances appears to be a characteristic of compounds containing the dithiole–thione ring; the effect has already been observed in (1) and in many other members of the family, *e.g.* 3*H*-1,2-dithiole-3-thione (Wei, 1985), phenyl-3*H*-1,2-dithiole-3-thione (Wei, 1986) and oltipraz (Wei, 1983), as well as in some other compounds containing sulfur in the ring (Lu *et al.*, 1989).

As already mentioned, an intriguing feature of these two otherwise quite similar structures is the fact that they exhibit melting points differing by *ca* 100 K, that of (3) being the higher. In order to find some clue for such a difference, the crystal-packing motifs were scrutinized, searching for any additional interactions in the methylthio derivative strong enough to be responsible for its stronger cohesion.

For this purpose, the intermolecular interactions were ranked according to their relative strength (as roughly measured by the interatomic distance) and compared. In spite of what could have been guessed beforehand, the main interactions (those unambiguously shorter than the sum of the corresponding van der Waals radii, *i.e.* $S\cdots S \leq 3.70$ Å) were found to be basically the same in both structures, not only in number, but in length as well. It is, instead, in a number of weak interactions (say $3.70 < S\cdots S < 4.00$ Å) that the difference seems to reside. Further analysis, perhaps through a review of crystal data of related structures on the Cambridge Structural Database (CSD; Allen & Kennard, 1993), might be required before a definite conclusion can be reached.

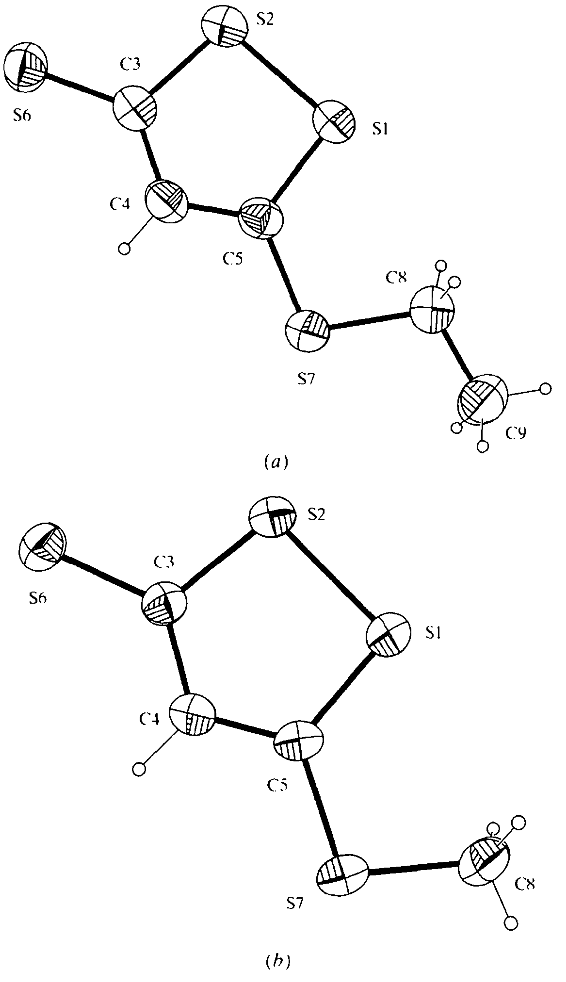


Fig. 1. Molecular diagrams showing the numbering of atoms of (*a*) compound (2) and (*b*) compound (3), with displacement ellipsoids at the 50% probability level.

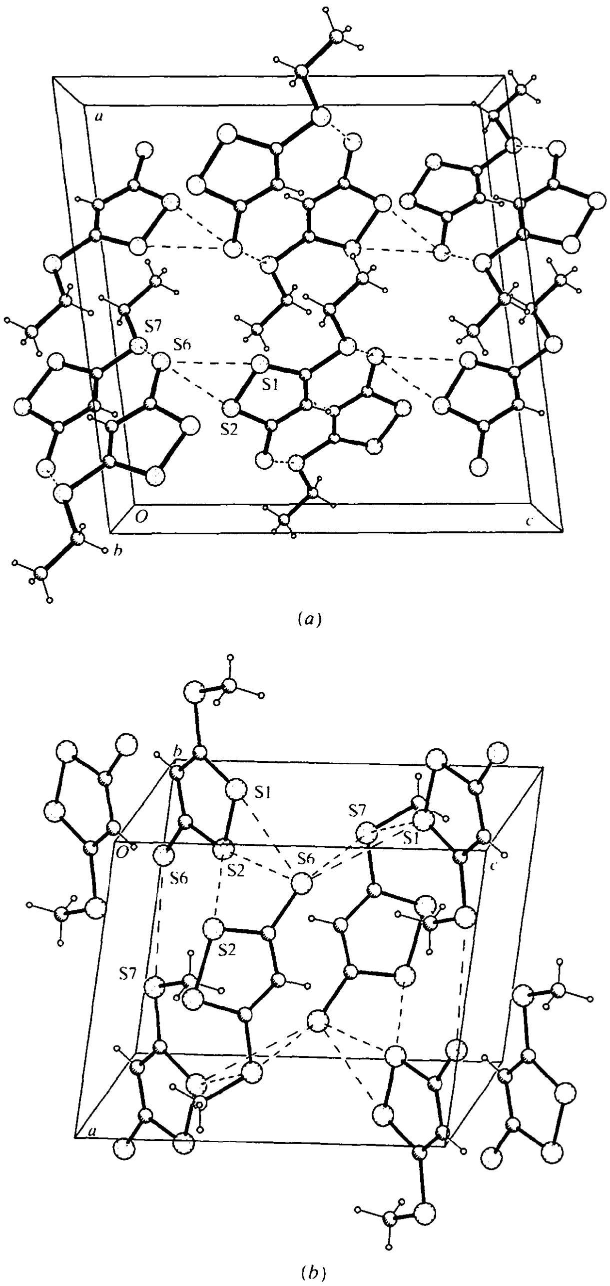


Fig. 2. Packing diagrams of (*a*) compound (2) and (*b*) compound (3), depicting close intermolecular approaches ($S\cdots S < 4.00$ Å).

Experimental

The title compounds were prepared according to procedures described by Aimar & de Rossi (1996). Crystals suitable for X-ray diffraction were obtained by very slow evaporation from acetone solutions of the compounds.

Compound (2)

Crystal data

$C_5H_6S_4$
$M_r = 194.34$
Monoclinic
$C2/c$
$a = 14.566$ (3) Å
$b = 7.886$ (2) Å
$c = 14.395$ (3) Å
$\beta = 96.84$ (3)°
$V = 1641.7$ (6) Å^3
$Z = 8$
$D_x = 1.573$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5$–12.5°
$\mu = 1.067$ mm^{-1}
$T = 293$ (2) K
Block
0.18 × 0.14 × 0.14 mm
Light orange

Data collection

Rigaku AFC-7S diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (Molecular Structure Corporation, 1988)
$T_{\min} = 0.82$, $T_{\max} = 0.85$
1959 measured reflections
1885 independent reflections
1590 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 27.49°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 10$
$l = -18 \rightarrow 18$
2 standard reflections every 98 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.073$
$S = 1.04$
1885 reflections
82 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.034P)^2 + 0.826P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.01$
$\Delta\rho_{\max} = 0.245$ e Å^{-3}
$\Delta\rho_{\min} = -0.258$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S1	0.13490 (3)	0.18654 (6)	0.12638 (3)	0.04659 (13)
S2	0.23951 (3)	0.06638 (6)	0.21010 (3)	0.04568 (13)
C3	0.28348 (11)	−0.0475 (2)	0.12214 (11)	0.0387 (3)
C4	0.23501 (12)	−0.0191 (2)	0.03288 (11)	0.0409 (4)
C5	0.16145 (12)	0.0898 (2)	0.02497 (11)	0.0387 (3)
S6	0.37385 (3)	−0.17431 (7)	0.15238 (3)	0.05046 (14)
S7	0.09542 (4)	0.12994 (6)	−0.08057 (3)	0.05074 (14)
C8	0.01097 (14)	0.2803 (3)	−0.04911 (13)	0.0506 (4)
C9	−0.05875 (15)	0.3171 (3)	−0.13264 (15)	0.0593 (5)

Table 2. *Selected bond lengths (Å) for (2)*

S1—C5	1.7312 (17)	C4—C5	1.367 (2)
S1—S2	2.0578 (8)	C5—S7	1.7278 (18)
S2—C3	1.7360 (17)	S7—C8	1.8045 (19)
C3—C4	1.408 (2)	C8—C9	1.507 (3)
C3—S6	1.6689 (18)		

Compound (3)

Crystal data

$C_4H_4S_4$
$M_r = 180.31$
Monoclinic
$P2_1/n$
$a = 8.831$ (2) Å
$b = 7.454$ (2) Å
$c = 10.769$ (2) Å
$\beta = 100.74$ (3)°
$V = 696.5$ (2) Å^3
$Z = 4$
$D_x = 1.720$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5$–12.5°
$\mu = 1.250$ mm^{-1}
$T = 293$ (2) K
Block
0.16 × 0.14 × 0.12 mm
Brown–orange

Data collection

Rigaku AFC-7S diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (Molecular Structure Corporation, 1988)
$T_{\min} = 0.82$, $T_{\max} = 0.86$
1693 measured reflections
1594 independent reflections
1278 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$
$\theta_{\max} = 27.50°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 9$
$l = -13 \rightarrow 13$
2 standard reflections every 98 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.096$
$S = 1.10$
1594 reflections
73 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.051P)^2 + 0.255P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.01$
$\Delta\rho_{\max} = 0.45$ e Å^{-3}
$\Delta\rho_{\min} = -0.42$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (3)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S1	0.53388 (6)	0.03621 (9)	0.26287 (6)	0.03901 (18)
S2	0.31380 (6)	0.10161 (9)	0.28357 (6)	0.04029 (18)
C3	0.3638 (3)	0.2379 (3)	0.4160 (2)	0.0320 (5)
C4	0.5239 (2)	0.2522 (3)	0.4575 (2)	0.0351 (5)
C5	0.6196 (3)	0.1637 (3)	0.3916 (2)	0.0332 (5)
S6	0.22108 (7)	0.33401 (9)	0.47409 (6)	0.04063 (18)
S7	0.81784 (7)	0.18180 (10)	0.43026 (6)	0.04360 (19)
C8	0.8829 (3)	0.0341 (4)	0.3198 (3)	0.0455 (6)

Table 4. *Selected bond lengths (Å) for (3)*

S1—C5	1.735 (2)	C3—S6	1.669 (2)
S1—S2	2.0558 (9)	C4—C5	1.369 (3)
S2—C3	1.740 (2)	C5—S7	1.727 (2)
C3—C4	1.406 (3)	S7—C8	1.792 (3)

Table 5. *Short interatomic distances (Å) for (2) and (3)*

(2)			
S1···S6^{i}	3.385 (1)	S6···S7^{ii}	3.780 (1)
S2···S6^{i}	3.407 (1)		
(3)			
S2···S6^{iii}	3.384 (1)	S6···S7^{vi}	3.786 (1)
S1···S6^{iii}	3.422 (1)	S1···S6^{vii}	3.906 (1)
S6···S7^{iv}	3.683 (1)	S2···S2^{iii}	3.928 (1)
S1···S7^{v}	3.746 (1)		

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, -\frac{1}{2} - y, -z$; (iii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $x - 1, y, z$; (v) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (vi) $1 - x, 1 - y, 1 - z$; (vii) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$.

The structures were solved by direct methods and completed through successive cycles of ΔF synthesis (including all of the H atoms). Anisotropic displacement parameters were used for non-H atoms, while an isotropic riding model was used for H atoms.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997*b*); molecular graphics: *XP* (*SHELXTL/PC*; Sheldrick, 1994); software used to prepare material for publication: *PARST* (Nardelli, 1983). Literature search: CSD (Allen & Kennard, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1396). Services for accessing these data are described at the back of the journal.

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Thiabendazolium Nitrate, an Anthelmintic Compound

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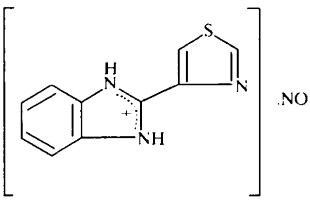
Abstract

In the crystal structure of 2-(thiazol-4-yl)-1*H*-benzimidazolium nitrate, $C_{10}H_8N_3S^+.NO_3^-$, the benzimidazole moiety is protonated. The benzimidazole and thiazole systems are coplanar. Both N—H groups of the protonated benzimidazole are involved in N—H···O hydrogen bonds with the nitrate anion.

Comment

Substituted benzimidazoles show antiviral action and anthelmintic activity. This has been attributed to their metal-chelating ability (Margaret *et al.*, 1985). Thiabendazole [2-(thiazol-4-yl)-1*H*-benzimidazole] is a broad-spectrum anthelmintic compound useful in the treatment of parasitic diseases of humans and animals. It is also useful as a fungicide for spoilage control of citrus fruit (Windholz, 1983). In its metal-chelating behaviour, it is similar to both 2,2′-bipyridine and 1,10-phenanthroline. The crystal structure of thiabendazole (Trus & Marsh, 1973), and its complexes with cobalt (Kowala & Wunderlich, 1973; Umadevi *et al.*, 1995), copper (Udupa & Krebs, 1979) and platinum (Rong *et al.*, 1991) have been reported. This paper deals with the crystal structure of a protonated thiabendazole moiety, namely, thiabendazolium nitrate, (I).



(I)

The N atom of the benzimidazole moiety rather than that of the thiazole group is protonated. This protonation leads to equalization of the bond angles at the two N atoms of the benzimidazole group, in contrast to the benzimidazole group in the crystal structure of free thiabendazole where the two bond angles are different (Trus & Marsh, 1973). The C—C bond connecting the two

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