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Structure of *N*-[2-(5-*tert*-Butyl-3*H*-1,2-dithiol-3-ylidene)ethylidene]-*N'*,*N'*-dimethylhydrazine,* $C_{11}H_{18}N_2S_2$

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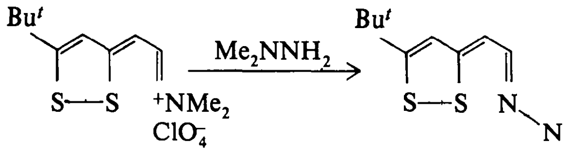
Abstract. $M_r = 242{\cdot}41$, triclinic, $P\bar{1}$, $a = 5{\cdot}998\,(2)$, $b = 9{\cdot}065\,(2)$, $c = 13{\cdot}078\,(3)$ Å, $\alpha = 72{\cdot}04\,(3)$, $\beta = 85{\cdot}18\,(4)$, $\gamma = 73{\cdot}35\,(4)°$, $U = 648{\cdot}06$ Å^3, $D_x = 1{\cdot}242$ Mg m^{-3}, $Z = 2$, $F(000) = 260$, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo }K\alpha) = 0{\cdot}335$ mm^{-1}, $R = 0{\cdot}0878$ for 2031 reflections with $F_o \geq 6\sigma(F_o)$. The structural assignment given in the title is confirmed and other isomeric forms are discussed. There are no short intermolecular contacts and no stacks formed by the 1,2-dithiol-3-ylidene rings.

Introduction. Treatment of the Vilsmeier salt (I) with *N*,*N*-dimethylhydrazine gave the title compound (II).



(I) (II)

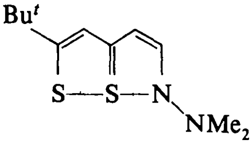
The present investigation was undertaken in order to determine its structural assignment.

Experimental. Crystal 0·5 × 0·25 × 0·2 mm, Stoe STADI-2 two-circle diffractometer, graphite-crystal-monochromatized Mo $K\alpha$ radiation, crystal about **a**, intensities of 2680 reflections in the hemisphere $+h$, $\pm k$ $\pm l$ with $2{\cdot}5 \leq \theta \leq 30°$, $h = 0$–8 ($0 \leq \mu \leq 28{\cdot}291°$) measured, ω–2θ scan mode, step width 0·01° in ω, 1·0 s per step, 160 steps per scan, backgrounds measured at both ends of the scan for 80·0 s each, standard reflections measured every 50 reflections and showed only small random deviations from their means, no corrections for absorption.

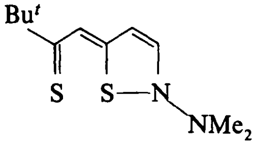
The structure was solved using the automatic centrosymmetric direct-methods program in *SHELX* 76 (Sheldrick, 1976), which gave the positions of all the non-H atoms in the molecule. Full-matrix least-squares refinement with anisotropic temperature parameters for all non-H atoms reduced R $(= \sum\Delta/\sum F_o,\ \Delta = |F_o - |F_c||)$ from an initial value of 0·38 to 0·1113 and R_G $[= (\sum w\Delta^2/\sum wF_o^2)^{\frac{1}{2}}]$ from 0·37 to 0·1158 $[w = 1/\sigma^2(F)]$. H-atom positions were obtained from a difference Fourier synthesis and included in the refinement with separate common isotropic temperature parameters for the H atoms on the main skeleton, those in the *tert*-butyl group, and those in the *N*-dimethyl group, yielding final values of $R = 0{\cdot}0878$ and $R_G = 0{\cdot}0888$ for 2031 reflections with $F_o \geq 6\sigma(F_o)$.‡ In the final cycles of refinement 193 parameters were simultaneously varied, comprising 99 positional coordinates, 90 anisotropic temperature-factor components, 3 common isotropic temperature factors and 1 overall scale factor: a final difference map showed no significant residual features. Complex neutral-atom scattering factors were used for all atoms (Cromer & Mann, 1968; Cromer & Liberman, 1970). The reduction in R_G at all stages of the refinement was significant at the 99·5% level (Hamilton, 1965).

Discussion. The final atomic coordinates are given in Table 1. These, together with the full covariance matrix, were used to calculate the bond lengths and bond angles given in Table 2. Fig. 1 shows the molecule and the atom numbering scheme.

The S—S distance of 2·116 (2) Å and the S(2)···N(1) distance of 2·541 (5) Å show clearly that the compound should be represented as (II) rather than as (III) or (IV).



(III)



(IV)

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* Alternative name: (5-*tert*-butyl-3*H*-1,2-dithiol-3-ylidene)-acetaldehyde dimethylhydrazone.

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‡ Lists of structure factors anisotropic thermal parameters and least-squares-planes data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38135 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates* ($\times 10^4$, $\times 10^3$ *for* H) *and equivalent isotropic temperature parameters* ($\times 10^3$)

The equivalent isotropic temperature parameters are defined as the geometric mean of the diagonal components of the diagonalized matrix of U_{ij}.

	x	y	z	U_{eq}(Å^2)
S(1)	3732 (3)	3038 (2)	2303 (1)	42 (1)
S(2)	3176 (3)	4982 (2)	2953 (1)	38 (1)
N(1)	3140 (9)	7292 (6)	3672 (4)	38 (3)
N(2)	1841 (9)	8037 (6)	4385 (4)	39 (3)
C(1)	5655 (10)	5552 (7)	2340 (5)	34 (3)
C(2)	6936 (11)	4550 (7)	1712 (5)	37 (3)
C(3)	6309 (10)	3289 (7)	1621 (4)	33 (3)
C(4)	6229 (12)	6798 (7)	2519 (5)	40 (4)
C(5)	4977 (12)	7662 (7)	3233 (5)	41 (4)
C(6)	583 (17)	6980 (10)	5086 (7)	56 (5)
C(7)	3035 (16)	8778 (10)	4928 (7)	54 (5)
C(8)	7609 (10)	2051 (7)	1072 (4)	34 (3)
C(9)	5929 (14)	1440 (10)	595 (6)	51 (5)
C(10)	9085 (13)	2810 (9)	160 (5)	46 (4)
C(11)	9203 (13)	633 (9)	1897 (6)	48 (4)
H(2)	814 (11)	471 (7)	138 (5)	42 (10)
H(4)	780 (10)	708 (7)	225 (5)	42 (10)
H(5)	550 (10)	848 (7)	338 (5)	42 (10)
H(61)	–42 (15)	661 (10)	461 (7)	91 (12)
H(62)	160 (16)	611 (11)	558 (7)	91 (12)
H(63)	–57 (16)	755 (11)	540 (7)	91 (12)
H(71)	453 (16)	798 (10)	530 (7)	91 (12)
H(72)	182 (15)	927 (10)	542 (7)	91 (12)
H(73)	329 (15)	987 (11)	440 (7)	91 (12)
H(91)	495 (15)	108 (10)	112 (7)	81 (9)
H(92)	670 (15)	56 (10)	46 (7)	81 (9)
H(93)	474 (14)	238 (9)	–22 (6)	81 (9)
H(101)	813 (14)	372 (10)	–49 (7)	81 (9)
H(102)	981 (15)	209 (10)	–22 (6)	81 (9)
H(103)	1062 (14)	305 (9)	51 (6)	81 (9)
H(111)	987 (14)	–9 (10)	146 (7)	81 (9)
H(112)	1014 (15)	101 (10)	211 (7)	81 (9)
H(113)	814 (15)	15 (9)	247 (7)	81 (9)

Table 2. *Bond lengths* (Å) *and angles* (°)

S(2)···N(1)	2·541 (5)				
S(1)–S(2)	2·116 (2)	S(1)–C(3)	1·755 (5)	S(2)–C(1)	1·762 (6)
N(1)–N(2)	1·377 (6)	N(1)–C(5)	1·282 (8)	N(2)–C(6)	1·444 (9)
N(2)–C(7)	1·457 (9)	C(1)–C(2)	1·430 (8)	C(1)–C(4)	1·359 (8)
C(2)–C(3)	1·342 (8)	C(3)–C(8)	1·512 (8)	C(4)–C(5)	1·431 (8)
C(8)–C(9)	1·533 (9)	C(8)–C(10)	1·531 (8)	C(8)–C(11)	1·531 (9)
C(2)–H(2)	0·84 (6)	C(4)–H(4)	1·05 (6)	C(5)–H(5)	0·96 (6)
C(6)–H(61)	1·08 (9)	C(6)–H(62)	0·94 (9)	C(6)–H(63)	0·89 (9)
C(7)–H(71)	1·02 (9)	C(7)–H(72)	1·03 (9)	C(7)–H(73)	1·06 (9)
C(9)–H(91)	0·91 (8)	C(9)–H(92)	0·86 (9)	C(9)–H(93)	1·26 (9)
C(10)–H(101)	1·06 (8)	C(10)–H(102)	0·93 (8)	C(10)–H(103)	1·16 (8)
C(11)–H(111)	0·99 (9)	C(11)–H(112)	0·84 (9)	C(11)–H(113)	1·02 (8)

S(2)–S(1)–C(3)	96·2 (2)	S(1)–S(2)–C(1)	94·0 (2)
S(1)–S(2)···N(1)	171·5 (3)	N(2)–N(1)–C(5)	121·7 (5)
N(1)–N(2)–C(6)	109·3 (5)	N(1)–N(2)–C(7)	116·6 (6)
C(6)–N(2)–C(7)	114·9 (6)	S(2)–C(1)–C(2)	113·3 (4)
S(2)–C(1)–C(4)	120·2 (5)	C(2)–C(1)–C(4)	126·4 (6)
C(1)–C(2)–C(3)	122·6 (5)	S(1)–C(3)–C(2)	113·8 (4)
S(1)–C(3)–C(8)	118·1 (4)	C(2)–C(3)–C(8)	128·0 (5)
C(1–C(4)–C(5)	123·5 (6)	N(1)–C(5)–C(4)	117·5 (6)
C(3)–C(8)–C(9)	111·3 (5)	C(3)–C(8)–C(10)	109·5 (5)
C(3)–C(8)–C(11)	108·7 (5)	C(9)–C(8)–C(10)	108·5 (6)
C(9)–C(8)–C(11)	109·5 (6)	C(10)–C(8)–C(11)	109·3 (5)

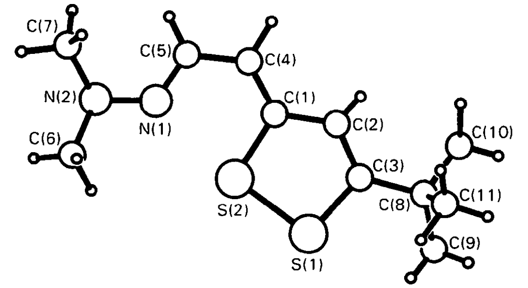
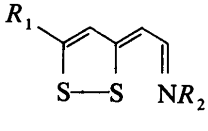


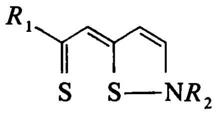
Fig. 1. The molecule showing the atom-numbering scheme.

The S–S and S···N distances are similar to those in a number of other SSN triheterapentalene analogues (see Cuthbertson, Glidewell & Liles, 1982). Although too long to be regarded as a bond, the S···N distance is shorter than the sum of the van der Waals radii of S and N, 3·35 Å (Pauling, 1960).

In order to assess the relative stabilities of the two isomeric forms (II) and (IV), we have performed calculations for the model compounds (V) and (VI) for $R_1 = \mathrm{H}$, using the MNDO method (Dewar & Thiel, 1977): we have previously shown (Cuthbertson, Glidewell & Liles, 1982) that when $R_2 = \mathrm{H}$ alteration of the group R_1 from Bu^t to H causes rather little difference in the energy differences between isomeric pairs.



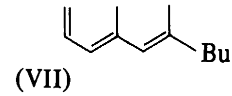
(V*a*) $R_2 = \mathrm{H}$
(V*b*) $R_2 = \mathrm{NMe_2}$
(V*c*) $R_2 = \mathrm{NH_2}$



(VI*a*) $R_2 = \mathrm{H}$
(VI*b*) $R_2 = \mathrm{NMe_2}$
(VI*c*) $R_2 = \mathrm{NH_2}$

When $R_2 = \mathrm{H}$, (V*a*) is more stable than (VI*a*) by some 40 kJ mol^{-1} (Cuthbertson, Glidewell & Liles, 1982); when $R_2 = \mathrm{NMe_2}$, the ΔH_f^0 values for (V*b*) and (VI*b*) are +293·9 and +402·0 kJ mol^{-1} respectively, a difference of some 108 kJ mol^{-1}, while for $R_2 = \mathrm{NH_2}$, although a stable minimum was found for (V*c*) having ΔH_f^0 of +270·7 kJ mol^{-1}, in all attempts to find a minimum corresponding to (VI*c*), the optimizations converged to (V*c*). In the sequence $R_2 = \mathrm{H}$, $\mathrm{NMe_2}$, $\mathrm{NH_2}$, the structure (VI) is steadily destabilized relative to (V).

In (II) the conformation of the Bu^t group differs from that in the comparable molecule (VII) (Cuthbertson, Glidewell & Liles, 1982) in being rotated through 90° relative to the plane of the heterocycle. MNDO calculations show that, for isolated molecules of (II), there is free rotation of the Bu^t group about the C(3)–C(8) bond.



(VII)

The molecular skeleton of (II) is almost planar, the dihedral angle between the heterocyclic ring and the plane of the side chain being 3·2 (3)°. The three-coordinate N atom N(2) is pyramidal with a sum of bond angles of 340·8° and with both *N*-methyl groups on the same side of the molecular plane (Fig. 1). The MNDO calculations show that the barrier to rotation about the N(1)—N(2) bond is only 4·1 kJ mol^{-1}, while the barrier to planarity at N(2) is only 2·5 kJ mol^{-1}.

The overall conformation observed in the crystal is therefore largely a consequence of intermolecular forces. There are no short intermolecular contacts: in particular, there are no stacks formed by the 1,2-dithiol-3-ylidene rings, in contrast to (VII).

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3,4,5,6-Tetrahydro-2*H*-1-benzothiocin 1,1-Dioxide, $C_{11}H_{14}O_2S$

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Abstract. $M_r = 210\cdot3$, monoclinic, $P2_1/n$, $a = 7\cdot527$ (3), $b = 9\cdot928$ (3), $c = 13\cdot863$ (6) Å, $\beta = 98\cdot80$ (3)°, $V = 1023\cdot8$ (7) Å^3, $Z = 4$, $D_x = 1\cdot364$ (1) Mg m^{-3}, μ(Mo $K\alpha$) = 0·28 mm^{-1}, λ(Mo $K\alpha$) = 0·71069 Å, $T = 293$ K, $R = 0\cdot046$ for 1176 diffractometer data. The dihedral angle between the benzo plane and the C—S—C plane in the thiocin ring is 71·4 (2)°.

Introduction. The main reason for the study was to investigate the influence of the dihedral angle between the phenyl plane and the C—S—C plane on the cathodic cleavage of the eight-membered ring and to make a comparison with corresponding sulfones.

Experimental. The compound was prepared and crystallized by Lamm & Aurell (1982). It was obtained by oxidation of the corresponding sulfide with peracetic acid. The sulfide was prepared in 79% yield *via* reductive cyclization of a disulfide mesylate under high-dilution conditions (Ohtsuka & Oishi, 1979).

Colourless prisms 0·22 × 0·08 × 0·10 mm, Syntex $P2_1$, graphite-monochromatized Mo $K\alpha$, lattice parameters from settings of 15 reflections with $5\cdot82 < 2\theta < 12\cdot0°$, 2479 reflections ($hkl$ and $hk\bar{l}$) with $2\theta < 52\cdot0°$, 1176 independent with $I > 3\sigma(I)$, intensities from profile analysis of $\omega/2\theta$ scans (*cf.* Lindqvist & Ljungström, 1979) according to Lehmann & Larsen (1974), 2θ-scan intervals 2·0–3·0°, standard reflections 122 and $0\bar{2}0$ stable, systematic absences: $h0l$ for $h + l$ odd and $0k0$ for k odd, Lp correction (Syntex, 1973), absorption ignored, direct methods (Main, Lessinger, Woolfson, Germain & Declercq, 1977), H located from difference map, anisotropic and isotropic block-diagonal least-squares refinement (Lindgren, 1977) for non-hydrogen and H atoms, respectively, minimizing $\sum w(|F_o| - |F_c|)^2$, final $R = 0\cdot046$,* $R_w = 0\cdot05$; weights $w = 1/(a + F_o + cF_o^2)$ with $a = 20\cdot0$ and $c = 0\cdot025$ gave acceptable weight analysis, $F(000) = 456$, scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic coordinates are given in Table 1 and bond lengths and angles in Table 2. All bond distances and angles have normal values. The thiocin ring has a puckered conformation (*cf.* Fig. 1). Lamm &

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38156 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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