Structure of N,N'-Bis[2-(5-*tert*-butyl-3H-1,2-dithiol-3-ylidene)ethylidene]hydrazine*

By Alastair F. Cuthbertson, Christopher Glidewell† and David C. Liles

Chemistry Department, University of St. Andrews, St. Andrews, Fife KY16 9ST, Scotland

Abstract. $C_{18}H_{24}N_2S_4$, triclinic, $P\bar{1}$, $a = 5\cdot929$ (3), $b = 8\cdot898$ (3), $c = 9\cdot954$ (2) Å, $\alpha = 92\cdot05$ (3), $\beta = 102\cdot12$ (4), $\gamma = 104\cdot73$ (4)°, $U = 494\cdot34$ Å^3, $M_r = 396\cdot66$, $D_c = 1\cdot332$ Mg m^{-3} for $Z = 1$, $F(000) = 210$, Mo $K\alpha$ radiation, $\lambda = 0\cdot71069$ Å, μ(Mo $K\alpha$) $= 0\cdot428$ mm^{-1}, $R = 0\cdot0959$ for 1407 reflections with $F_o \geq 6\sigma(F_o)$. The molecule lies across a centre of inversion and is planar apart from the *tert*-butyl groups.

Introduction. Treatment of the Vilsmeier salt (I) with hydrazinium hydroxide gave the title compound (II). Crystals suitable for X-ray investigation were provided by Professor D. H. Reid and Mr A. McRoberts.

(I)

(II)
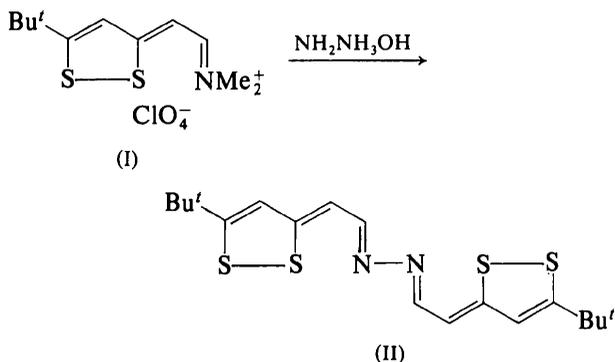
Data were collected using a Stoe STADI-2 two-circle diffractometer with graphite-crystal-monochromatized Mo $K\alpha$ radiation for a crystal of dimensions $0\cdot1 \times 0\cdot1 \times 0\cdot3$ mm mounted about **a**. The intensities of 1637 reflections in the hemisphere $+h,\pm k,\pm l$ with $2\cdot5 < \theta < 30°$, $h = 0$–8 ($0 \leq \mu \leq 28\cdot650°$) were measured using the ω–2θ scan mode with a step width of $0\cdot01°$ in ω, a time of $1\cdot0$ s per step and 200 steps per scan. Backgrounds were measured at both ends of the scan for $100\cdot0$ s. Standard reflections were measured every 50 reflections and showed only small random deviations from their means. No correction for absorption was made.

The structure was solved using the fast centrosymmetric direct-methods program in *SHELX* 76 (Shel-

drick, 1976). The best E map gave the positions of all non-H atoms in the asymmetric unit. A subsequent difference synthesis provided the H-atom positions. Full-matrix least-squares refinement with anisotropic temperature parameters for all non-H atoms, and with separate common isotropic temperature parameters for the H's on the main skeleton and those in the *tert*-butyl group, converged to give R ($= \sum \Delta / \sum F_o$, $\Delta = |F_o - |F_c||$) of $0\cdot0959$ and R_G [$= (\sum w\Delta^2 / \sum wF_o^2)^{1/2}$] of $0\cdot0992$ for 1407 independent reflections with $F_o \geq 6\sigma(F_o)$. In the final cycles of refinement 147 parameters were simultaneously varied, comprising 72 positional coordinates, 72 anisotropic temperature factor components, two common isotropic temperature factors and one overall scale factor: a final difference map showed no signifi-

Table 1. *Fractional atomic coordinates* ($\times 10^4$, $\times 10^3$ *for* H) *and the equivalent isotropic temperature parameters* (U_{eq}) (*common isotropic U's for* H) (Å$^2 \times 10^3$)

U_{eq} is defined as the geometric mean of the diagonal components of the diagonalized matrix of U_{ij}.

	x	y	z	U_{eq}/U
S(1)	1560 (4)	3458 (2)	1135 (2)	39 (1)
S(2)	2623 (4)	5830 (2)	1961 (2)	44 (1)
N(1)	812 (12)	643 (6)	381 (6)	30 (3)
C(1)	5453 (13)	5823 (8)	2869 (7)	29 (3)
C(2)	5971 (14)	4460 (8)	2714 (7)	31 (3)
C(3)	4310 (13)	3130 (8)	1890 (7)	29 (3)
C(4)	4659 (16)	1686 (8)	1703 (8)	38 (4)
C(5)	2864 (15)	411 (8)	921 (8)	36 (4)
C(6)	7053 (13)	7336 (8)	3682 (7)	28 (3)
C(7)	8964 (16)	6970 (9)	4824 (8)	37 (4)
C(8)	5619 (19)	8194 (10)	4350 (9)	46 (5)
C(9)	8244 (20)	8365 (10)	2694 (10)	43 (5)
H(1)	748 (15)	443 (9)	309 (8)	46 (13)
H(2)	606 (15)	150 (9)	211 (8)	46 (13)
H(3)	324 (15)	−58 (9)	67 (8)	46 (13)
H(4)	815 (18)	629 (12)	537 (10)	71 (10)
H(5)	1002 (18)	799 (11)	535 (10)	71 (10)
H(6)	1028 (18)	670 (11)	436 (10)	71 (10)
H(7)	429 (18)	840 (11)	371 (10)	71 (10)
H(8)	689 (18)	936 (11)	497 (9)	71 (10)
H(9)	474 (18)	775 (11)	520 (10)	71 (10)
H(10)	916 (18)	933 (12)	317 (10)	71 (10)
H(11)	904 (19)	790 (12)	232 (10)	71 (10)
H(12)	699 (19)	863 (11)	192 (10)	71 (10)

Table 2. Bond distances (Å)

S(1)···N(1)	2·489 (6)				
S(1)–S(2)	2·124 (3)	S(1)–C(3)	1·747 (7)	S(2)–C(1)	1·732 (7)
N(1)–N(1')	1·372 (10)	N(1)–C(5)	1·293 (10)		
C(1)–C(2)	1·335 (10)	C(1)–C(6)	1·522 (9)	C(2)–C(3)	1·429 (9)
C(3)–C(4)	1·365 (10)	C(4)–C(5)	1·415 (10)	C(6)–C(7)	1·534 (10)
C(6)–C(8)	1·510 (12)	C(6)–C(9)	1·527 (11)		
C(2)–H(1)	0·91 (8)	C(4)–H(2)	0·90 (8)	C(5)–H(3)	1·00 (8)
C(7)–H(4)	0·94 (10)	C(7)–H(5)	1·02 (10)	C(7)–H(6)	1·06 (10)
C(8)–H(7)	0·96 (10)	C(8)–H(8)	1·18 (10)	C(8)–H(9)	1·12 (10)
C(9)–H(10)	0·94 (10)	C(9)–H(11)	0·84 (10)	C(9)–H(12)	1·03 (10)

Table 3. Bond angles (°)

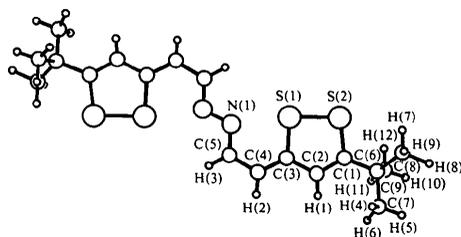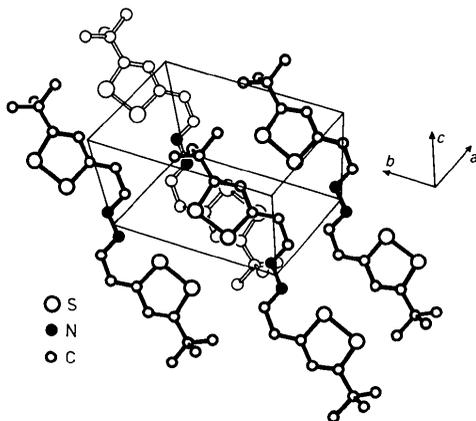|			
S(2)–S(1)–C(3)	93·5 (2)	S(1)–S(2)–C(1)	96·4 (2)
S(2)–C(1)–C(2)	113·9 (5)	S(2)–C(1)–C(6)	117·9 (5)
C(2)–C(1)–C(6)	128·2 (7)	C(1)–C(2)–C(3)	122·5 (7)
S(1)–C(3)–C(2)	113·6 (5)	S(1)–C(3)–C(4)	119·7 (6)
C(2)–C(3)–C(4)	126·6 (7)	C(3)–C(4)–C(5)	122·7 (8)
N(1)–C(5)–C(4)	117·6 (7)	N(1')–N(1)–C(5)	114·0 (7)
C(1)–C(6)–C(7)	109·6 (6)	C(1)–C(6)–C(8)	111·0 (7)
C(1)–C(6)–C(9)	108·6 (6)	C(7)–C(6)–C(8)	108·2 (7)
C(7)–C(6)–C(9)	110·1 (7)	C(8)–C(6)–C(9)	109·3 (7)

Fig. 1. A perspective view of the molecule showing the atom numbering scheme.

Fig. 2. A perspective view of the unit cell viewed perpendicular to the plane of the molecule. The four molecules whose centres lie in the range −0·5 to 1·5 in x and y and −0·5 to 0·5 in z are shown: that centred at 1,1,0 is drawn with light lines for clarity.

cant residual features. Complex neutral-atom scattering factors were used for all atoms (Cromer & Mann, 1968; Cromer & Liberman, 1970). The reductions in R_G at all stages of the refinement were significant at the 99·5% level (Hamilton, 1965).

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 Tables 2 and 3. Fig. 1 shows the molecule and the atom numbering scheme. Fig. 2 shows the unit-cell contents viewed perpendicular to the plane of the molecule.*

Discussion. The S—S distance of 2·124 (3) Å and the S(1)···N(1) distance of 2·489 (6) Å show that the compound should be represented as (II), rather than as (III) or (IV). The S—S and S—N distances are similar to those in (V) [2·121 and 2·324 Å respectively (Butler, Glidewell & Liles, 1978)] and (VI) [2·155 and 2·282 Å (Glidewell & Liles, 1981)]. Although it is 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). The molecule is centrosymmetric, and apart from the butyl group is planar.
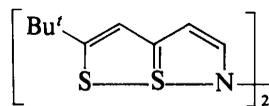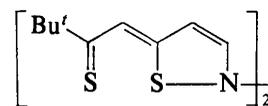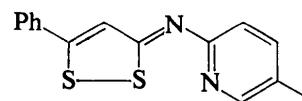

(III)   (IV)
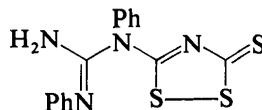
(V)   (VI)

In order to assess the relative stabilities of the two isomeric forms (II) and (IV), we have calculated ΔH_f^0 values for the model compounds (VII) and (VIII), using the MNDO method (Dewar & Thiel, 1977): for the simplest models, having R = H, the values of ΔH_f^0 for (VIIa) and (VIIIa) are +218·5 and +279·6 kJ mol⁻¹ while, when R = tert-butyl, the values for (VIIb) and (VIIIb) are +175·6 and +215·4 kJ mol⁻¹, in each case indicating that the observed S—S bonded form is the thermodynamically stable isomer.
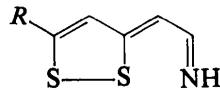
(VIIa) R = H
(VIIb) R = tert-butyl
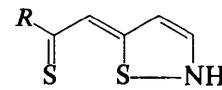
(VIIIa) R = H
(VIIIb) R = tert-butyl

In molecule (II), the acyclic chain contains three single bonds, and for each of these the two principal substituents may be mutually either *cisoid*, *c*, or *transoid*, *t*, while retaining the overall skeletal planarity. There are then six possible planar conformers of (II) in which the observed configurations about the double bonds are preserved; these may be denoted *ttt*, *ttc*, *ctc*, *tct*, *tcc*, and *ccc*. MNDO calculations on simple model compounds with $R = H$ rather than *tert*-butyl [since investigations of (VII) and (VIII) indicated no major influence of the group R] indicate that the dominant factor is the conformation about the central N—N bond: when this is *c* the ΔH_f^0 is *ca* 40 kJ mol^{-1} higher than when the conformation is *t*, regardless of the conformation of the other two bonds. On the other hand, a change of conformation at either of the other two single bonds from *c* to *t* causes a decrease in ΔH_f^0 of only 1–2 kJ mol^{-1}. Overall the most stable conformation, as an isolated molecule, is *ttt*, with the observed *ctc* only 3·0 kJ mol^{-1} higher in energy: this difference in isolated-molecule energies can easily be compensated for by intermolecular forces in the crystal.

The stacking of the molecules in the crystals is of some interest. The hetero rings of the molecule centred at (0,0,0) overlap one ring each of the molecules centred at (1,1,0) and (−1,−1,0), the overlapping rings being related by the centres of inversion at ($\frac{1}{2},\frac{1}{2}$,0) and (−$\frac{1}{2}$,−$\frac{1}{2}$,0) respectively (see Fig. 2), so that the sulphur atoms of one ring lie over the C=C double bonds associated with the other: one sulphur lies over the endocyclic double bond and one over the exocyclic double bond. The inter-ring spacing is only 4·61 (2) Å; the closeness of the intermolecular contact between the rings, and the conjugated chain between the two rings of each molecule suggest that this compound may have interesting electrical properties.

The structures are known of several compounds which contain a single 1,2-dithiol-3-ylidene ring, rather than two such rings as here: these include (IX) and (X) (Johnson, Reid & Paul, 1971), (XI) (Reid & Paul, 1971), (XII) (Hordvik, Sletten & Sletten, 1969) and (XIII) (Nguyen-Huy-Dung & Etienne, 1978). In none of these molecules does the closest intramolecular contact between the heterocyclic rings

resemble that found here: in particular there are no centrosymmetric ring overlaps which could give rise to charge-transfer interactions.
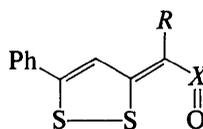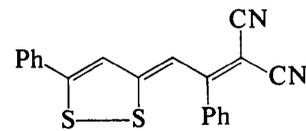

	R	X
(IX)	PhCO	N
(X)	NO$_2$	N
(XI)	Br	NO
(XII)	Ph	CH

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