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Structural and Electronic-Spectral Studies of 1,1′-Trimethylenedi-2-imidazolidinethione

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Abstract. $C_9H_{16}N_4S_2$, triclinic, $P\bar{1}$, $a = 7{\cdot}785\,(2)$, $b = 8{\cdot}653\,(2)$, $c = 10{\cdot}325\,(2)$ Å, $\alpha = 106{\cdot}88\,(2)$, $\beta = 74{\cdot}24\,(2)$, $\gamma = 116{\cdot}16\,(2)°$, $Z = 2$, $D_o = 1{\cdot}378\,(2)$, $D_c = 1{\cdot}379$ Mg m^{-3}. The structure contains two eight-membered $(SCNH)_2$ rings, each with two nearly linear N—H⋯S hydrogen bonds. In addition, thiourea chromophores on adjacent molecules are separated by a S⋯S contact [3·586 (2) Å] which is substantially shorter than corresponding distances in related thiourea derivatives.

Introduction. The vast majority of thiourea derivatives which have been characterized are colorless both in the solid state and in solution. Our curiosity as to why crystals of the title compound (1) were conspicuously yellow led to the present structural investigation. Crystals of (1) were prepared by a published procedure (van Alphen, 1936) and recrystallized from ethanol.

Analysis: calculated for $C_9H_{16}N_4S_2$: C, 44·23; H, 6·60; N, 22·93; S, 26·24%; found: C, 44·26; H, 6·94; N, 22·88; S, 25·85%.

A cleaved fragment of dimensions 0·52 × 0·26 × 0·17 mm was mounted on a glass fiber and centered on a Syntex $P2_1$ computer-controlled diffractometer. Diffractometer examination of the reciprocal lattice revealed no systematic absences, and successful refinement of the structure was achieved in space group $P\bar{1}$. Using a θ–2θ scan and Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å), intensity data were collected at 295 ± 1 K to a maximum $2\theta = 120°$. Three standard reflections, measured at 27-reflection intervals, remained constant to within ±2% during the data-collection period. Of the 1491 unique reflections measured, 1304 with $F^2 \geq 3\sigma(F^2)$ (counting statistics) were used in the structure solution and refinement. A total of 22 reflections with $3\sigma(F^2) < F^2 < 5\sigma(F^2)$ and scattering vectors distributed randomly in reciprocal space were rejected on the basis of profile scans. The profile-scan test compares the intensity in the central portion of the scan range with that at either end and leads to rejection of poorly centered reflections or those with unusually shaped profiles. The data were corrected for Lp and absorption effects ($\mu = 3{\cdot}75$ mm^{-1} for Cu $K\alpha$); absorption factors ranged from 1·192 to 1·834.

The structure was solved by direct methods and refined by full-matrix least-squares techniques using programs described previously (Fawcett, Ushay, Rose, Lalancette, Potenza & Schugar, 1979). An initial E map revealed all but one of the non-hydrogen atoms; the remaining atom was located on a subsequent difference Fourier map. Neutral-atom scattering factors and anomalous-dispersion corrections for C, N, and S were obtained from *International Tables for X-ray Crystallography* (1974). Refinement was based on F and the function minimized was $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, where $w = 1/\sigma^2(F)$ and $\sigma^2(F) = \frac{1}{2}[N_t + (0{\cdot}03N_n)^2]/\mathrm{Lp}N_n$. H atom coordinates were calculated by methods described previously (Fawcett, Ou, Potenza & Schugar, 1978) and confirmed using difference Fourier maps; all H atoms were located at positions of high electron density on a difference Fourier map. H atoms were assigned fixed isotropic temperature factors equal to $B_N + 1$ where B_N is the temperature factor of the atom bonded to H.

Anisotropic refinement of all non-hydrogen atoms and refinement of all H atom coordinates reduced $R_F = \sum||F_o| - |F_c||/\sum|F_o|$ to 0·063 and R_{wF} to 0·075.[*] For the final refinement cycle, all parameter changes were less than 0·6σ for non-hydrogen atoms and 1·4σ for H atoms, where σ is the e.s.d. obtained from the inverse matrix. A final difference Fourier map showed a general background of ±0·3 e Å^{-3} and no significant features. Atomic parameters are listed in Table 1, while a view of the molecule, showing the atom-numbering scheme and bond distances and angles, is given in Fig. 1. A stereoview showing the molecular packing is given in Fig. 2.

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[*] Lists of structure factors, H atom coordinates, thermal parameters, and bond distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34915 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Discussion. The structure contains discrete, centrosymmetrically related molecules of (1), each consisting of two ethylenethiourea rings joined by a propyl bridge. Within each molecule, the C–S distances are equivalent; they are significantly shorter than those reported for ethylenethiourea [1·708 (4) Å, Wheatley, 1953] and trimethylenethiourea [1·722 (7) Å, Dias & Truter, 1964], and more closely approximate the value of 1·66 (1) Å reported for allylthiourea (Dragonette & Karle, 1965). The remaining bond distances in the ethylenethiourea fragments are comparable (to within ±0·01–0·02 Å) to those reported for ethylenethiourea and trimethylenethiourea. Each thiourea (SCN_2) unit is planar within experimental error (maximum deviation 0·004 Å) while the carbons of the bridging ethylene units C(2)–C(3) and C(7)–C(8) deviate significantly (0·01 to 0·12 Å), and in opposite directions, from these planes.

Table 1. *Fractional coordinates of non-hydrogen atoms*

Estimated standard deviations, obtained from the least-squares refinement, are given in parentheses. Coordinate values are × 10^4.

	x	*y*	*z*
S(1)	−1213 (2)	7565 (2)	3438 (1)
S(2)	7170 (2)	9331 (2)	1484 (1)
N(1)	1394 (7)	8296 (6)	5016 (4)
N(2)	1246 (5)	6086 (4)	3308 (3)
N(3)	4785 (5)	7736 (4)	−397 (3)
N(4)	7845 (5)	8929 (5)	−1263 (4)
C(1)	513 (6)	7300 (5)	3922 (4)
C(2)	2808 (8)	7765 (7)	5188 (6)
C(3)	2797 (7)	6294 (6)	3973 (5)
C(4)	825 (7)	4863 (6)	2014 (4)
C(5)	2512 (6)	5341 (6)	838 (4)
C(6)	3050 (6)	7157 (5)	592 (4)
C(7)	4801 (7)	7270 (7)	−1873 (4)
C(8)	6892 (7)	8329 (6)	−2438 (4)
C(9)	6605 (6)	8664 (5)	−99 (4)

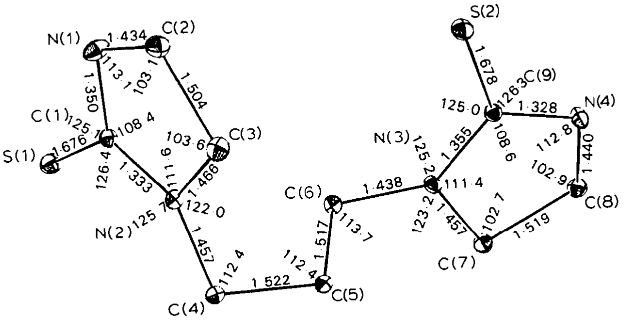

Fig. 1. Molecular structure of (1) showing the atom-numbering scheme and bond distances (Å) and angles (°). E.s.d.'s for the derived parameters are: S–C, 0·005; N–C and C–C, 0·006 Å; S–C–N, 0·3; N–C–N, N–C–C, C–N–C, and C–C–C, 0·4°. Torsional angles are as follows: C(1)–N(2)–C(4)–C(5), 73·6; N(2)–C(4)–C(5)–C(6), 59·6; C(4)–C(5)–C(6)–N(3), 172·8; and C(5)–C(6)–N(3)–C(9), 85·3°.

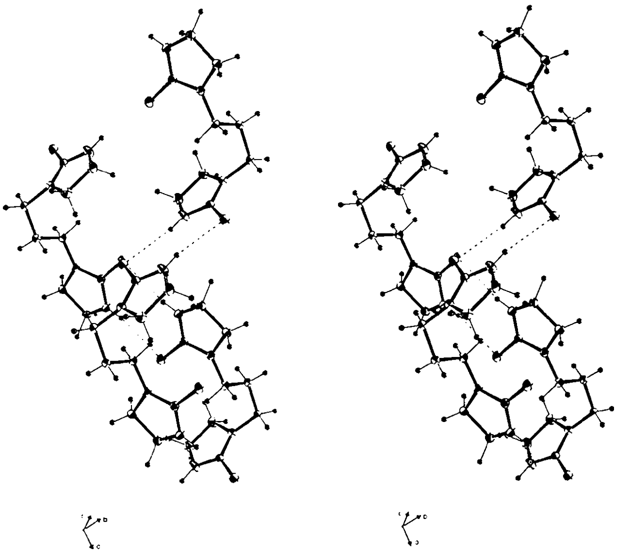

Fig. 2. Stereoview showing the molecular packing viewed along S(1)···S(2′). Hydrogen bonds are indicated by dashed lines and the origin of the coordinate system shown is 0,−1,0.

Centers of symmetry at (0,0,½) and (0,0,0) relate thiourea units of adjacent molecules and give rise to eight-membered $(SCNH)_2$ rings each of which contains two symmetry-related, nearly linear N–H···S hydrogen bonds (Table 2). There are two unique eight-membered rings in the structure, one comprised of atoms S(1), C(1), N(1) and H(N1) and one containing atoms S(2), C(9), N(4) and H(N4); atoms S(1) and S(2) are not related to each other by this hydrogen-bonding network. Each S atom is involved in one hydrogen bond, in contrast to both trimethylenethiourea and ethylenethiourea which form one hydrogen bond per N atom or two hydrogen bonds per S atom. The N···S distances [3·521 (5), 3·456 (4) Å] are substantially longer than those reported for trimethylenethiourea (3·30 Å) and thiourea [3·397 (4), 3·394 (5) Å, Mullen, Heger & Treutmann, 1978] and are more nearly comparable to those given for ethylenethiourea (3·44, 3·48 Å).

In addition to forming hydrogen bonds, the unique thiourea units of adjacent molecules appear to interact weakly *via* the S atoms. The S(1)···S(2′) distance of 3·586 (2) Å is slightly shorter than the van der Waals radius (3·70 Å) and is substantially shorter than the values of 4·20, 4·28 and 3·845 Å found, respectively, for ethylenethiourea, allylthiourea, and trimethylenethiourea. Further, the orientation of these thiourea

Table 2. *Hydrogen-bond parameters*

Donor (*D*)	Hydrogen (H)	Acceptor (*A*)	*D*–H···*A* (°)	*D*···*A* (Å)	H···*A* (Å)	*D*–H (Å)
N(1)	H1(N1)	S(1)^{i}	169 (7)	3·521 (5)	2·67 (8)	0·85 (7)
N(4)	H1(N4)	S(2)^{ii}	166 (6)	3·456 (4)	2·66 (7)	0·81 (6)

Symmetry code: (i) −*x*, 2 − *y*, 1 − *z*; (ii) 2 − *x*, 2 − *y*, −*z*.

chromophores (Fig. 2) is such as to encourage overlap of the lone-pair S orbitals with each other and with the thiourea π systems. Spatial interaction between S lone pairs separated by methylene bridges in dithiaalkanes is well known (Bock & Wagner, 1972; Wagner & Bock, 1974) and leads, *via* symmetric and antisymmetric combination of S lone-pair orbitals, to a splitting of vertical photoelectron ionization potentials. With ruthenium disulfide complexes, recent work has revealed absorption at energies much lower than those characteristic of simple sulfur-containing ligands (Stein & Taube, 1979). Lowering of the absorption energy in these complexes has been attributed to S 'lone-pair perturbations' which are also encountered when atoms are not directly bonded. Therefore, it appears that weak $S\cdots S$ interactions can affect the appearance of spectra significantly.

Methanolic solutions of (1) are colorless and exhibit absorptions (Fig. 3) at 205, 240 and 390 nm. The latter band is relatively weak ($\varepsilon \sim 5$) and is not evident in Fig. 3. These spectral features are characteristic of alkyl thiourea derivatives and of thiourea (Barrett & Deghaidy, 1975). Mull spectra of (1) (Fig. 3) reveal the source of its yellow color in the solid state; the relatively weak absorption exhibited by the solvated compound at ~390 nm apparently has achieved considerable prominence in the polycrystalline material. Moreover, the absorption of the solution species at 240 nm has been red-shifted and broadened considerably in the solid state. Polycrystalline thiourea (colorless) shows a corresponding broad absorption at ~270 nm (Fig. 3) which is not accompanied by longer-wavelength absorptions. Thus, the yellow color of (1) originates from enhancement of the band at 390 nm and not merely from tailing of the more intense band centered at ~260 nm. Solvated thiourea exhibits a corresponding weak absorption ($\varepsilon = 5{\cdot}3$) that has been attributed to excitation of a S lone-pair electron into a delocalized antibonding orbital extending over the thiourea chromophore (${}^1n_S \rightarrow {}^3\pi^*$, Barrett & Deghaidy, 1975). Apparently, intermolecular electronic interacion of adjacent SCN_2 chromophores in (1) *via* the short $S\cdots S$ contact makes this transition more allowed and leads to the yellow color.

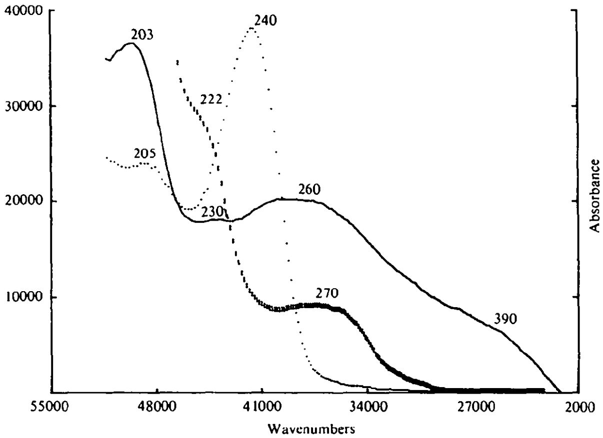

Fig. 3. Spectra of (1) in methanol (····) and dispersed as a mineral oil mull (——) at 298 K. The reference mull spectrum of thiourea (|||||||||||) is also shown. Spectra were recorded using a Cary 18 spectrometer. Band maxima are given in nm.

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