compounds be discussed but also the deviations of the structures from the cubic symmetry found with inorganic cations. With the amino acid, Te atoms are at the apex of an *A* face-centred monoclinic lattice. The contacts between Br atoms in different anions range from 3·943 to 4·134 Å, which are larger than van der Waals contacts. With the succinamide, Te atoms are 0·515 Å away from the apex of the *C* face-centred lattice. The van der Waals contacts between Br atoms in different $TeBr_6^{2-}$ ions are grouped into four short contacts of 3·705 and two longer contacts of 3·953 Å. A larger organic cation tends to distort the octahedra network but does not deform it fundamentally.

In the two structures, the cohesion is governed by hydrogen bonds and Br···Br intermolecular van der Waals contacts. The packing of the molecules approaches close packing, with the octahedra in contact, and the cavities occupied by the organic cations.

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References

AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). NRC Crystallographic Programs for the IBM/360 System. *Word List of Crystallographic Computer Programs*, p. 52. Utrecht: Oosthoek.

BROWN, I. D. (1964). *Canad. J. Chem.* **42**, 2758–2767.

BUJEWSKI, A. & DOBROWOLSKI, J. (1973). *Rocz. Chem.* **47**, 401–405.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak-Ridge National Laboratory Report ORNL-TM-305.

DAHAN, F. & LEFÈBVRE-SOUBEYRAN, O. (1976). B**32**, 2859–2862.

DAS, A. K. & BROWN, I. D. (1966). *Canad. J. Chem.* **44**, 939–943.

DAVIES, D. R. & PASTERNAK, R. A. (1956). *Acta Cryst.* **9**, 334–340.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–215. Birmingham: Kynoch Press.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., pp. 244–264. Ithaca: Cornell Univ. Press.

SRIVASTAVA, B. B., DUBLISH, A. K. & PANDEY, A. N. (1974). *Z. Naturforsch.* **29a**, 602–604.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1976). B**32**, 2866

The Crystal Structure of 2,5-Dimercaptothiadiazole

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The crystal structure of 2,5-dimercaptothiadiazole ($C_2H_2N_2S_3$) has been determined at room temperature. The compound has the space group $P2_1/c$, with $a=6{\cdot}225$ (1), $b=10{\cdot}593$ (3), $c=9{\cdot}248$ (3) Å and $\beta=113{\cdot}65$ (2)°. The compound crystallizes as thiadiazole-2-thiol-5-thione, as a result of proton transfer in one of the two S–H···N hydrogen bonds. Difference density maps based on atomic parameters from a conventional and a high-order X-ray refinement have been calculated and interpreted in terms of bonding effects in the molecule.

Introduction

With the improvement in accuracy of X-ray diffraction analyses, several studies have recently been concerned with the determination of electron densities in solids (see Coppens, 1976). In the field of the determination of the nature of the bonding of the sulfur atom, electron density studies have been applied to orthorhombic sulfur (Blessing, Cooper, Yang & Coppens, 1973), sulfamic acid (Bats, Coppens & Koetzle, 1977), and Na sulfanilate.$2H_2O$ (Bats, 1977).

As a continuation in this field, it seemed interesting to study 2,5-dimercaptothiadiazole, in which the sulfur atom is involved in some type of bonding not present in other compounds studied.

The present work is concerned with the determination of the structure of the title compound at room temperature (295 K), in order to investigate the suitability of the structure for electron density studies.

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Experimental

Clusters of transparent yellow crystals of 2,5-dimercaptothiadiazole (Aldrich Chemical Co.) were grown from methanol. It took some effort to select a crystal of sufficient quality for data collection. A crystal with dimensions about 0·35 × 0·35 × 0·50 mm was found suitable and sealed in a glass capillary as the crystals underwent slow deterioration in air.

Precession photographs showed the monoclinic space group $P2_1/c$. The cell dimensions and general information are given in Table 1.

Table 1. *General information*

a	6·225 (1) Å	Space group	$P2_1/c$
b	10·593 (3)	Absorption coefficient	11·41 cm^{-1}
c	9·248 (3)	Transmission range	0·699–0·761
β	113·65 (1)°	Number of observations	3203
V	558·6 (3) Å^3	Unique reflections	2411
		Unique reflections with $F_o^2>0$	2242

Data in one quadrant of reciprocal space were measured on a Picker diffractometer with Nb-filtered Mo $K\alpha$ radiation up to $\sin\theta/\lambda=0{\cdot}75$ Å^{-1}, yielding 2540 reflections. Once the structure had been determined, an additional 331 reflections with $0{\cdot}75<\sin\theta/\lambda<0{\cdot}90$ Å^{-1}, which were calculated to be measurable, were collected twice; these reflections were, however, rather weak. Data collection was performed in a step scanning mode (Blessing, Coppens & Becker, 1974). Fluctuations in incident-beam intensity and counter response were corrected by measuring three different standard reflections after every 35 reflections and rescaling the data with respect to these standards (maximum fluctuation of the standards was about 3%). The reflections were corrected for Lorentz, polarization and absorption effects, while a correction for deviations from the counter linearity was taken into account (Chipman, 1969). Averaging doubly observed reflections and eliminating reflections with negative net intensities resulted in 2242 unique reflections for the structure refinement.

Table 2. *Least-squares refinements*

	Conventional	High-order
$(\sin\theta/\lambda)_{\min}$ (Å^{-1})	0·00	0·60
$(\sin\theta/\lambda)_{\max}$ (Å^{-1})	0·90	0·90
Number of observations	2242	1266
Number of parameters	72	64
Scale factor	6·63 (1)	6·52 (6)
$R(F)$ (%)	5·3	9·4
$R_w(F)$ (%)	4·1	5·1
Goodness-of-fit	1·70	1·17

Table 3. *Positional and thermal parameters*

Conventional refinement

	x	y	z
S(1)	−0·09112 (8)	0·04020 (5)	0·23687 (6)
S(2)	0·30913 (7)	−0·11056 (4)	0·21634 (5)
S(3)	0·73629 (7)	−0·27596 (5)	0·40471 (6)
C(1)	0·14474 (26)	−0·05215 (16)	0·31560 (19)
C(2)	0·49084 (24)	−0·18767 (15)	0·38744 (19)
N(1)	0·24190 (24)	−0·09625 (15)	0·46342 (18)
N(2)	0·43505 (22)	−0·17225 (14)	0·50696 (17)
H(1)	0·2044 (31)	−0·0800 (18)	0·5206 (27)
H(2)	0·6897 (31)	−0·2826 (20)	0·2654 (29)

High-order refinement

	x	y	z
S(1)	−0·09072 (16)	0·04052 (11)	0·23670 (10)
S(2)	0·30931 (14)	−0·11063 (8)	0·21636 (8)
S(3)	0·73734 (15)	−0·27541 (9)	0·40484 (11)
C(1)	0·14467 (44)	−0·05185 (26)	0·31544 (28)
C(2)	0·49125 (41)	−0·18803 (25)	0·38763 (27)
N(1)	0·24203 (48)	−0·09581 (29)	0·46498 (27)
N(2)	0·43426 (46)	−0·17245 (31)	0·50734 (26)

Table 3 (*cont.*)

Conventional refinement

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0·0437 (2)	0·0591 (3)	0·0392 (2)	0·0164 (2)	0·0193 (2)	0·0073 (2)
S(2)	0·0404 (2)	0·0474 (2)	0·0275 (2)	0·0093 (2)	0·0148 (2)	0·0019 (2)
S(3)	0·0392 (2)	0·0515 (3)	0·0430 (3)	0·0108 (2)	0·0130 (2)	0·0015 (2)
C(1)	0·0338 (6)	0·0380 (8)	0·0298 (7)	−0·0011 (6)	0·0143 (6)	−0·0010 (6)
C(2)	0·0297 (6)	0·0326 (7)	0·0305 (7)	−0·0021 (5)	0·0092 (5)	−0·0006 (6)
N(1)	0·0362 (6)	0·0504 (9)	0·0298 (6)	0·0024 (6)	0·0177 (6)	0·0009 (6)
N(2)	0·0350 (6)	0·0474 (8)	0·0317 (7)	0·0025 (6)	0·0124 (6)	0·0053 (6)
H(1)	0·042 (6)					
H(2)	0·063 (7)					

High-order refinement

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0·0436 (4)	0·0586 (5)	0·0388 (4)	0·0163 (3)	0·0195 (3)	0·0073 (3)
S(2)	0·0403 (3)	0·0462 (4)	0·0273 (3)	0·0088 (2)	0·0149 (2)	0·0025 (2)
S(3)	0·0385 (4)	0·0496 (4)	0·0415 (4)	0·0100 (3)	0·0131 (3)	0·0016 (3)
C(1)	0·0334 (8)	0·0379 (10)	0·0301 (8)	0·0007 (7)	0·0145 (7)	−0·0008 (7)
C(2)	0·0308 (8)	0·0328 (9)	0·0287 (7)	−0·0004 (6)	0·0101 (6)	−0·0004 (6)
N(1)	0·0377 (8)	0·0486 (12)	0·0288 (7)	0·0024 (8)	0·0164 (6)	0·0015 (7)
N(2)	0·0356 (9)	0·0489 (12)	0·0289 (8)	0·0038 (8)	0·0131 (7)	0·0034 (7)

The standard deviation assigned to each observation was taken as $\sigma(I-B)=\{(I+B)+k^2(I-B)^2\}^{1/2}$, with $k=0{\cdot}03$; I is the integrated intensity and B the background.

Structure refinement

The structure was determined by direct methods, using *MULTAN* (Main, Woolfson & Germain 1970). The first E map showed all non-hydrogen atoms, while a difference Fourier synthesis based on these atoms showed both H atoms.

Scattering factors for the non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1974) and those for the H atoms from Stewart, Davidson & Simpson (1965). For the S atoms the anomalous scattering factors of Cromer & Liberman (1970) were used. Extinction was found to be negligible.

As atomic parameters from a high-order X-ray refinement are known to be considerably less affected by bonding effects than the parameters from conventional X-ray refinements, a high-order X-ray refinement was performed on the data with $\sin\theta/\lambda > 0{\cdot}60$ Å^{-1}, in addition to the conventional refinement. The atomic parameters of the H atoms were not varied in the high-order refinement. The unweighted R value was high in the latter refinement as a result of the weakness of most high-order reflections. Information concerning the least-squares refinements is given in Table 2. Table 3 gives the positional and thermal parameters of the atoms.*

Discussion

The bond lengths and angles are given in Figs. 1 and 2. A librational correction to the bond lengths, based on the **TLS** method of Schomaker & Trueblood (1968), is included in Fig. 1. A stereoscopic view of the molecular packing is shown in Fig. 3.

Consideration of the bond lengths shows that 2,5-dimercaptothiadiazole in the crystalline state has mainly the resonance structures shown in Fig. 4, with partly double S(1)–C(1) and C(1)–N(1) bonds and a completely double C(2)–N(2) bond, while Fig. 1 also indicates some conjugation of the π-system in the molecule.

The molecular packing of 2,5-dimercaptothiadiazole is similar to that found in 5-aminothiadiazole-2-thiol

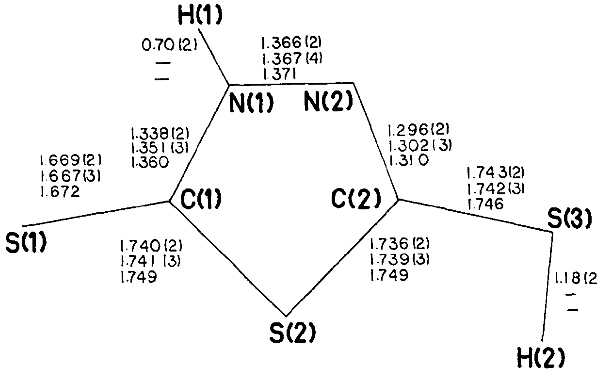

Fig. 1. Bond lengths. First row from conventional refinement, second row from high-order refinement, third row from high-order refinement and including corrections for libration.

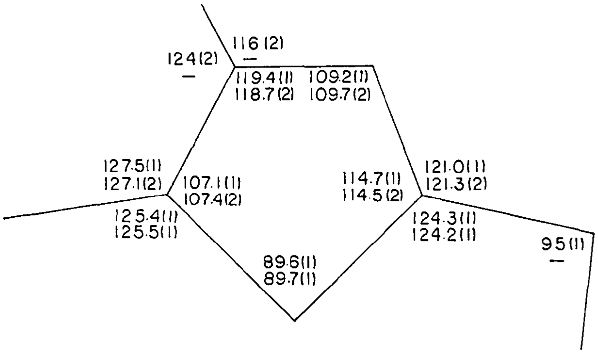

Fig. 2. Bond angles. First row from conventional refinement, second row from high-order refinement.

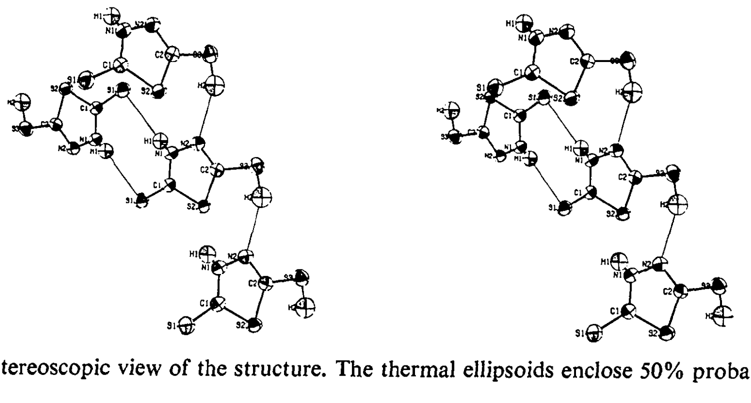

Fig. 3. Stereoscopic view of the structure. The thermal ellipsoids enclose 50% probability.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31858 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

(Downie, Harrison, Raper & Hepworth, 1972), while all bond lengths in the thiadiazolethione groups of both compounds agree within 2σ and the bond angles within 1 or 2°. Although in 5-aminothiadiazole-2-thiol the positions of the H atoms were not clear it is obvious from a consideration of the molecular dimensions that the compound crystallizes as a thione as suggested by Downie *et al.*

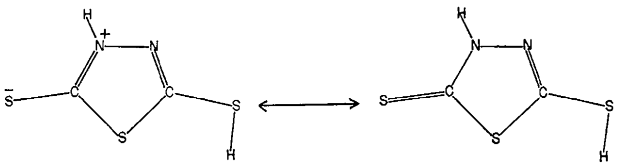
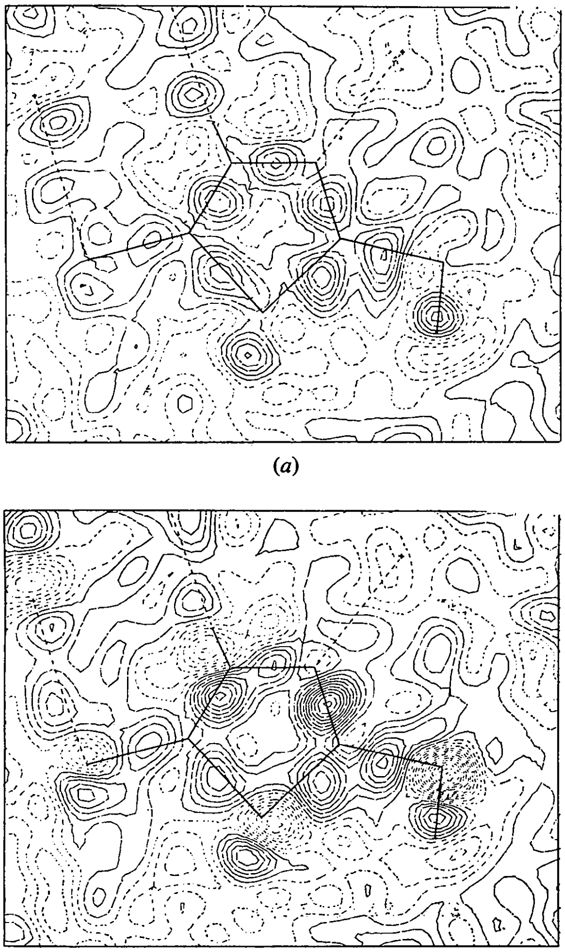
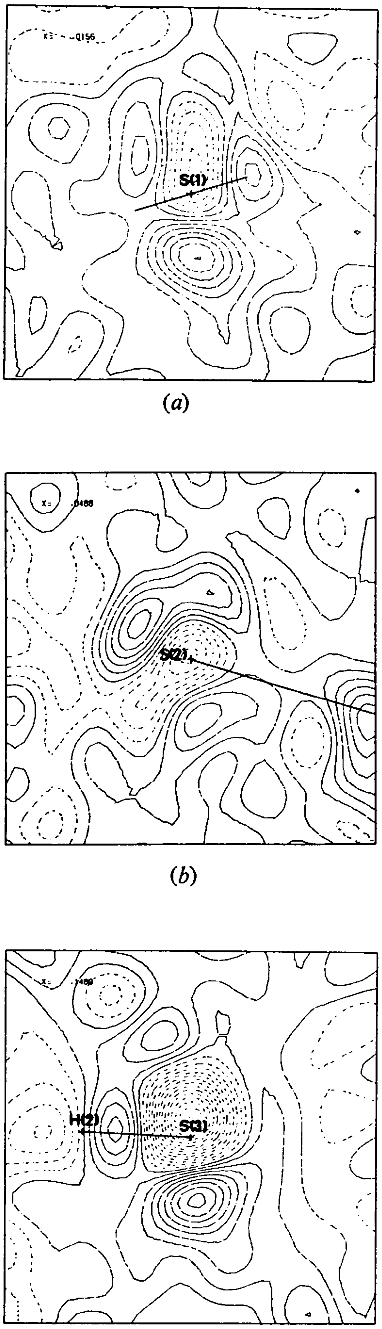


Fig. 4. Main resonance structures of crystalline 2,5-dimercaptothiadiazole.


(*a*)

(*b*)

Fig. 5. Deformation density in a section through the molecular plane, (*a*) after conventional refinement, (*b*) after high-order refinement. Data cut-off in Fourier synthesis: $\sin\theta/\lambda = 0{\cdot}65$ Å^{-1}. Contour interval 0·05 e Å^{-3}; negative contours broken.



(*a*)

(*b*)

(*c*)

Fig. 6. Deformation density in cross-sections through the sulfur atoms normal to the molecular plane, (*a*) through S(1) normal to the C(1)–S(1) bond, (*b*) through S(2) and its lone pair peak, (*c*) through S(3) normal to the C(2)–S(3) bond. Contours as in Fig. 5.

Table 4. *Hydrogen bonds*

X–H···*Y*	*X*···*Y* (Å)	H···*Y* (Å)	*X*–H–*Y* (°)
N(1)–H(1)···S(1′)	3·317 (2)	2·62 (2)	174 (2)
S(3) –H(2)···N(2′)	3·437 (2)	2·34 (2)	153 (1)

The molecule, with the exception of H(2), is almost planar; the largest torsion angle in the five-membered ring is 0·30°. Both H atoms are involved in a S–H···N hydrogen bond, listed in Table 4. In the S(3)–H(2)···N(2′) hydrogen bond the H atom is still mainly bonded to the S atom. In the N(1)–H(1)···S(1′) hydrogen bond, which is about 0·12 Å shorter, H has moved towards N. This protonation of N(1) makes the molecule rather asymmetric compared with 2,5-dimethylthiadiazole (Povet'eva & Zvonkova, 1972) and 1,3,4-thiadiazole (La Cour, 1974), which both have approximately C_{2v} symmetry.

Both C–N bonds are found to be longer in the high-order refinement than in the conventional refinement, mainly as a result of a shift of the N atoms into the C–N bonds in the conventional refinement.

Fig. 5(*a*) and (*b*) shows difference Fourier syntheses in the plane through the five-membered ring obtained with the atomic parameters from the conventional and high-order refinement respectively. The scale factor from the conventional X-ray refinement has been used in the calculation of both maps as it has a much lower standard deviation than the high-order scale factor and gave a reasonable appearance of both maps.

Bond populations are clearly shown in all bonds not including H and tend to be stronger, when the high-order parameters are used, especially in the case of the C–N bonds. The peak in the the N–N bond is lower than the peaks in the C–N bonds.

Fig. 6 shows the deformation density in cross-sections through the sulfur atoms. All three sections show concentrations of density at about 0·6–0·8 Å from the S nuclei, which has probably to be attributed to sulfur lone pair density.

It should, however, be mentioned that the present study is not accurate enough to make final conclusions about details of the deformation density.

An accurate redetermination of 2,5-dimercaptothiadiazole at reduced temperature seems desirable and is expected to elucidate further the nature of the sulfur bonding.

References

BATS, J. W. (1977).

BATS, J. W., COPPENS, P. & KOETZLE, T. F. (1977). *Acta Cryst.* **B33**. In the press.

BLESSING, R. H., COOPER, W. F., YANG, Y. W. & COPPENS, P. (1973). *ACA Conf. Abs. Ser.* 2, **1**, 200.

BLESSING, R. H., COPPENS, P. & BECKER, P. (1974). *J. Appl. Cryst.* **7**, 488–492.

CHIPMAN, D. R. (1969). *Acta Cryst.* **A25**, 209–213.

COPPENS, P. (1976). *Measurement of Electron Densities in Solids by X-ray Diffraction. MTP International Review of Science*. London: Butterworths. In the press.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

DOWNIE, T. G., HARRISON, W., RAPER, E. S. & HEPWORTH, M. A. (1972). *Acta Cryst.* **B28**, 1584–1590.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

LA COUR, T. (1974). *Acta Cryst.* **B30**, 1642–1643.

MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1970). *MULTAN. A Computer Program for the Automatic Solution of Crystal Structures*. Univ. of York Printing Unit, York.

POVET'EVA, Z. P. & ZVONKOVA, Z. V. (1972). *Sov. Phys. Crystallogr.* **16**, 899–901.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.