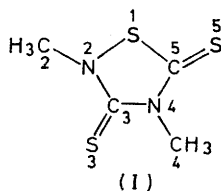


## Crystal Structure of 2,4-Dimethyl-1,2,4-thiadiazolidine-3,5-dithione

By **Colin L. Raston, Allan H. White,\*** and **Anthony C. Willis**, Department of Chemistry, University of Western Australia, Nedlands, 6009 Western Australia, Australia  
**Jose N. Varghese**, Department of Physics, University of Western Australia, Nedlands, 6009 Western Australia, Australia

The crystal structure of the title compound has been determined from *X*-ray diffractometer data and refined by least squares to *R* 0.035 (749 reflections). Crystals are monoclinic,  $P2_1/n$ ,  $a = 7.812(1)$ ,  $b = 15.276(3)$ ,  $c = 6.271(2)$  Å,  $\beta = 96.41(1)^\circ$ ,  $Z = 4$ . The non-hydrogen atom geometry of the planar system has been corrected throughout for thermal motion; the conjugation is extensive throughout the S·CS·N·CS·N part of the ring but not in the N–S bond. Considerable repulsion distorts the geometry of the peripheral sulphur and methyl groups.

SUCCESSIVE oxidation of the *N*-alkyldithiocarbamate ion,  $\text{RNH}\cdot\text{CS}_2^-$ , leads to the formation of the *NN'*-dialkylthiuram disulphides,  $\text{RNH}\cdot\text{CS}\cdot\text{SS}\cdot\text{CS}\cdot\text{NHR}$ , and then to the 4,5-dialkyl-5-imino-1,2,4-dithiazolidine-3-thione,  $\overline{\text{S}\cdot\text{S}\cdot\text{CS}\cdot\text{NR}\cdot\text{C}\cdot\text{NR}}$ , which can be isomerized in alcoholic ammonia to the 2,4-dialkyl-1,2,4-thiadiazolidine-3,5-dithiones of which the title compound is a representative.<sup>1</sup>



Such compounds are of interest because of their fungicidal activity but have been little studied structurally, although well characterized spectroscopically; they are of interest to us because they provide further information about the geometry of the dithiocarbamate system

<sup>1</sup> G. D. Thorn and R. A. Ludwig, 'The Dithiocarbamates and Related Compounds,' Elsevier, Amsterdam, 1961, p. 76.

in a pseudo-monodentate system. Accordingly, the structure of the title compound, (I) was determined; it was prepared by the standard method of Freund<sup>2,3</sup> and recrystallized from ethanol as needles elongated along *a*; a needle section  $0.30 \times 0.20 \times 0.26$  mm was used for data collection.

### EXPERIMENTAL

Cell dimensions were obtained by a least squares fit of the angular parameters of 15 reflections centred in the counter aperture of a Syntex P1 diffractometer at 295 K; a unique set of data in the range  $2\theta < 100^\circ$  was collected using a conventional  $2\theta/\theta$  scan yielding 749 reflections, all of which were used with unit weights in the structure solution and refinement, after correction for absorption.

*Crystal Data.*— $\text{C}_4\text{H}_6\text{N}_2\text{S}_3$ ,  $M = 178.3$ . Monoclinic, space group  $P2_1/n$  ( $C_{2h}^5$ , No. 14),  $a = 7.812(1)$ ,  $b = 15.276(3)$ ,  $c = 6.271(2)$  Å,  $\beta = 96.41(1)^\circ$ ,  $U = 743.6$  Å<sup>3</sup>,  $D_m = 1.58$ ,  $Z = 4$ ,  $D_c = 1.59$ ,  $g \text{ cm}^{-3}$ ,  $F(000) = 368$ . Ni filtered Cu- $K_\alpha$  radiation,  $\lambda = 1.5418$  Å,  $\mu = 80.4 \text{ cm}^{-1}$ .

The structure was solved by direct methods and refined

<sup>2</sup> M. Freund, *Annalen*, 1895, **285**, 154.

<sup>3</sup> M. Freund and G. Bachrach, *Annalen*, 1895, **285**, 184.

by full matrix least squares to  $R(=\Sigma|F_o| - |F_o|/\Sigma|F_o|)$  0.035, and  $R'[(\Sigma|F_o| - |F_o|)^2/\Sigma|F_o|^2]^{1/2}$  0.038, with anisotropic thermal parameters of the form  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}hkb^*c^*)]$  being employed for the non-hydrogen atoms, the hydrogen atoms being refined isotropically with  $U$  constrained at 0.089 Å<sup>2</sup>. In the final least squares cycle, no parameter shift exceeded 0.2σ; a final difference map showed no significant features. Scattering factors

termination were fitted by least squares to the libration (L), screw displacement (S), and translation (T) tensors, giving  $R[(\Sigma(U_{ij})_o - (U_{ij})_c)/\Sigma(U_{ij})_c]$  0.07, indicative of a reasonable description of the thermal motion. The principal mean square librations are: 0.0031(3) rad<sup>2</sup> perpendicular to the molecular plane, 0.0045(9) rad<sup>2</sup> along C(5) ··· N(2) in the molecular plane, and 0.0047(5) rad<sup>2</sup> normal to the above two. Rigid body interatomic distances and angles corrected for the effect of rigid body

TABLE 1

Final atomic fractional cell parameters (a preceding decimal point is implied), and thermal parameters ( $\times 10^3$  Å<sup>2</sup>). Least squares e.s.d.'s in parentheses

Atom	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
S(1)	7525(1)	2613(1)	6304(2)	56(1)	42(1)	39(1)	0(1)	5(1)	2(1)
C(2)	8285(8)	4267(3)	7793(9)	66(4)	35(3)	68(4)	2(3)	-5(3)	7(3)
N(2)	8377(5)	3329(2)	8216(5)	57(2)	28(2)	40(2)	0(2)	-6(2)	4(2)
S(3)	1.0182(2)	3468(1)	1.2076(2)	64(1)	43(1)	46(1)	-9(1)	-7(1)	-1(1)
C(3)	9209(5)	2945(3)	9967(7)	41(3)	34(3)	41(3)	-3(2)	4(2)	1(2)
C(4)	9851(7)	1450(3)	1.1427(9)	57(3)	42(3)	54(3)	2(3)	-3(3)	11(3)
N(4)	9128(4)	2041(2)	9722(5)	43(2)	29(2)	35(2)	0(2)	0(2)	5(2)
S(5)	8061(2)	0717(1)	7022(2)	89(1)	38(1)	60(1)	-2(1)	-6(1)	-8(1)
C(5)	8306(5)	1730(3)	7833(7)	45(3)	36(3)	40(3)	1(2)	5(2)	2(2)
H(21)	932(7)	440(4)	744(9)	*					
H(22)	735(7)	439(4)	710(9)	*					
H(23)	829(7)	460(4)	898(9)	*					
H(41)	994(7)	085(4)	1.083(8)	*					
H(42)	905(7)	140(4)	1.232(9)	*					
H(43)	1.099(7)	157(4)	1.168(9)	*					

\* Constrained (see text).

employed were for the neutral atoms, that for S being corrected for anomalous dispersion ( $\Delta f'$ ,  $\Delta f''$ ).<sup>4,5</sup> No pronounced extinction effects were observed and no correction applied.

TABLE 2

(a) Interatomic distances (Å) and angles (deg); the values corrected for thermal motion (see text) follow the uncorrected values

S(1)-N(2)	1.702(4), 1.709	S(1)-N(2)-C(2)	119.7(3), 119.7
N(2)-C(2)	1.456(6), 1.463	S(1)-N(2)-C(3)	114.2(3), 114.2
N(2)-C(3)	1.347(5), 1.351	C(2)-N(2)-C(3)	125.9(4), 125.9
C(3)-S(3)	1.655(4), 1.662	N(2)-C(3)-N(4)	109.3(3), 109.3
C(3)-N(4)	1.390(5), 1.396	N(2)-C(3)-S(3)	125.3(3), 125.3
N(4)-C(4)	1.464(6), 1.469	S(3)-C(3)-N(4)	125.3(3), 125.4
N(4)-C(5)	1.368(5), 1.373	C(3)-N(4)-C(4)	121.5(3), 121.5
C(5)-S(5)	1.634(4), 1.640	C(3)-N(4)-C(5)	116.9(3), 116.9
C(5)-S(1)	1.727(4), 1.733	C(4)-N(4)-C(5)	121.6(3), 121.6
S(3) ··· C(4)	3.116(5)	N(4)-C(5)-S(1)	108.2(3), 108.1
S(3) ··· C(2)	3.164(6)	N(4)-C(5)-S(5)	128.7(3), 128.8
C(4) ··· S(5)	3.159(5)	S(5)-C(5)-S(1)	123.1(2), 123.0
		N(2)-S(1)-C(5)	91.5(2), 91.4

(b) Least squares plane through the five-membered ring referred to the orthogonal frame (Å):  $X = ax + cz \cos \beta$ ,  $Y = by$ ,  $Z = cz \sin \beta$

$$0.9063 X + 0.0271 Y - 0.4219 Z = 3.385$$

Atomic deviations (Å)

(i) defining atoms: N(2), C(3), 0.00; S(1), N(4), -0.01; C(5), 0.01 Å;  $\sigma = 0.009$  Å.

(ii) others: C(2), 0.11; S(3), 0.02; C(4), -0.08; S(5), 0.06 Å

A rigid body thermal motion analysis was carried out using the Schomaker-Trueblood formalism,<sup>6</sup> the non-hydrogen atom system being considered as the rigid body. The thermal parameters derived from the structure de-

\* For details see Notice to Authors No. 7, in *J.C.S. Perkin II*, 1973, Index issue.

<sup>4</sup> D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **24A**, 321.

<sup>5</sup> D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

libration were calculated using the Johnson-Levy formalism.<sup>7</sup> The angle corrections are negligible as expected from the relatively isotropic libration, while bond corrections are also small, being of the order of the standard deviations.

TABLE 3

The molecular T, S, and L tensors relative to the 'centre of reaction',  $\rho$ ,<sup>7</sup>  $\rho$  being located at (0.8622, 0.2552, 0.9267) and approximately coincident with the centre of mass

$$T = \begin{bmatrix} 0.0320(14) & -0.0027(13) & 0.0010(15) \\ & 0.0384(16) & -0.0026(16) \\ & & 0.0378(23) \end{bmatrix}$$

$$S = \begin{bmatrix} 0.0010(11) & -0.0001(8) & -0.0005(5) \\ & -0.0009(6) & -0.0003(4) \\ & & -0.0001(4) \end{bmatrix}$$

$$L = \begin{bmatrix} 0.0045(8) & 0.0003(3) & -0.0008(5) \\ & 0.0047(5) & 0.0002(4) \\ & & 0.0031(3) \end{bmatrix}$$

Data processing and computation were carried out using the X-Ray 72 System<sup>8</sup> implemented on the CDC 6200 computer at this University. Structure factor tables and calculated  $U_{ij}$  values are deposited as Supplementary Publication No. SUP 20998 (7 pp.).\*

## DISCUSSION

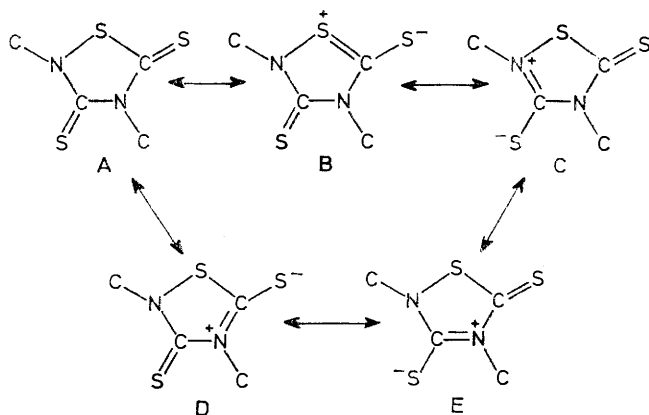
The atoms comprising the five-membered ring are rigorously planar within the limits of error; this observation together with the observed bond lengths suggest that, with the exception of the N(2,4)-C(2,4)

<sup>6</sup> V. N. Schomaker and K. N. Trueblood, *Acta Cryst.*, 1968, **24B**, 63.

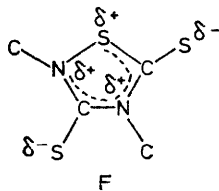
<sup>7</sup> R. D. Ellison, C. K. Johnson, and H. A. Levy, *Acta Cryst.*, 1971, **27B**, 341.

<sup>8</sup> 'X-Ray System,' Technical Report TR-192, University of Maryland Computer Science Centre, June 1972.

distances which are normal single bonds (*ca.* 1.46 Å), conjugation is rife throughout the system as a consequence of ring constraints, nitrogen atom lone pairs, carbon-sulphur double bonds, and the presence of  $p_\pi$  and  $d_\pi$  orbitals on S(1), leading to the possibility of a large number of contributing 'canonical forms', *e.g.* A—E.



It will be noted that the possibilities do not include a form with a double bond between S(1) and N(2); while all other intra-ring distances are appreciably less than normal single bonds, the N(2)—S(1) distance is not greatly diminished from the sum of the Pauling covalent radii of 1.74 Å [measured, 1.709(4)].<sup>9</sup> The molecule is thus best represented as F.

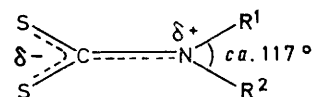


The peripheral atoms of the system are appreciably distorted due to the lack of substituent on S(1); whereas the extracyclic angles at C(3) and N(4) are symmetrically disposed, considerable distortions are observed in those at N(2) and C(5) where the C(2)—N(2)—S(1) and S(5)—C(5)—S(1) angles are diminished with respect to C(2)—N(2)—C(3) and S(5)—C(5)—N(4) by some 6°. This is reflected in the distances C(2)···S(3) and C(4)···S(5) which exceed S(3)···C(4) by *ca.* 0.04 Å; all these distances are considerably less than the van der Waals methyl-

<sup>9</sup> L. Pauling, 'The Nature of the Chemical Bond,' Cornell, Ithaca, 1960, p. 224.

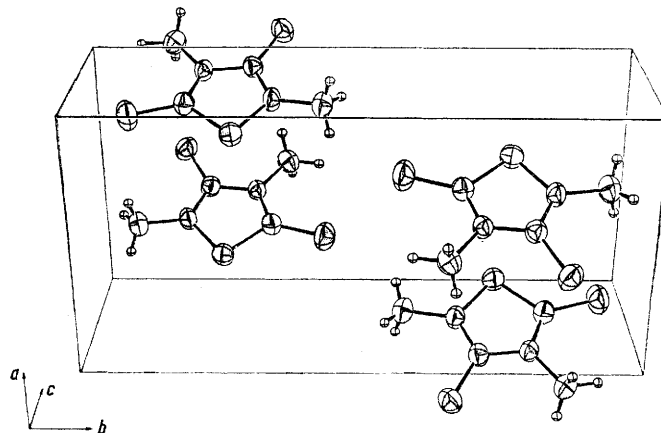
<sup>10</sup> Ref. 9, p. 260.

sulphur contact of 3.85 Å.<sup>10</sup> The intra-ring angles at N(2) and N(4) are appreciably greater than those at C(3) and C(5); this effect appears to be the usual one whereby the magnitude of an angle opposite a double bond is diminished below the expected 120°. Apparently the effect is greatly exacerbated by ring strain, since the usual diminution is only by some 3 or 4°; *e.g.* in the dithiocarbamate system, the angle between the pair of nitrogen substituents is usually *ca.* 117° (which is a typical order of magnitude) provided that



$R^1$  and  $R^2$  do not participate in a strained cyclic system themselves.<sup>11</sup>

The angle at the ring sulphur atom is far less than the others, being the usual pseudo-right angle found in five-membered hetero (sulphur) rings. Within the  $C_2N_2CS_2$  part of the system, the cyclic  $\langle C-S \rangle$  distance of 1.730 Å is shorter than the comparable (single-bond) distance of 1.815 Å found in tetraethylthiuram disulphide,<sup>11</sup> and is more in keeping with that occurring in the conjugated symmetrically chelated dithiocarbamate-transition metal complexes;<sup>11</sup> the  $\langle C=S \rangle$  bond length is 1.637 Å, in very close agreement with that observed in the tetraethylthiuram disulphide, 1.648,<sup>11</sup> indicative of a very considerable double bond character.<sup>9</sup>



An ORTEP diagram of the cell contents (50% ellipsoids); hydrogen atom amplitudes are set arbitrarily at 0.1 Å radius

[3/2630 Received, 31st December, 1973]

<sup>11</sup> R. Eisenberg, *Progr. Inorg. Chem.*, 1970, **12**, 295 and references therein.