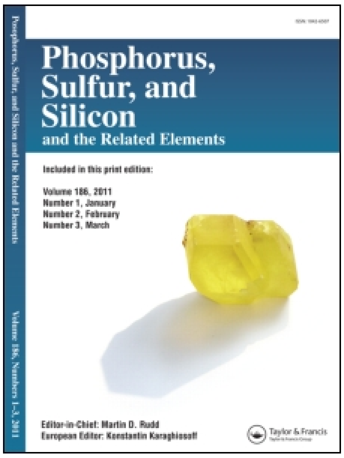

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2-(2-THIOXO-1,3-THIAZOLIDIN-3-YL)-4,5-DIHYDRO-1,3-THIAZOLIUM BROMIDE. ^{1}HNMR, MASS SPECTRAL, X-PES STUDIES AND CRYSTAL STRUCTURE DETERMINATION

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The title compound is formed by the rearrangement of 2,2′-dithiobis[4,5-dihydrothiazole] with the extrusion of one sulfur in dilute hydrobromic acid medium. ^{1}HNMR, Mass spectral, X-PES studies and crystal structure determination have been carried out. While the Mass spectrum showed the presence of three sulfurs in the molecule, the presence of four triplets in the ^{1}HNMR spectrum ruled out the symmetrical sulfide isomer. The unit cell is monoclinic, $P2_1/c$, with $a = 11.236(1)$, $b = 10.138(1)$, $c = 9.571(1)$Å, $\beta = 111.89°(1)$, $V = 1011.63$Å^3, $D_m = 1.85$ Mg/m^3, $D_c = 1.86$ Mg/m^3, at 296 K for four molecules per unit cell. From 1498 unique reflections for which $I > 3\sigma(I)$, $R = 0.051$, with anisotropic thermal parameters for all non-hydrogen atoms. Both the five membered heterocyclic rings adopt the half chair conformation. Hydrogen bonding occurs involving the dihydrothiazolyl nitrogen, the proton attached to it and the bromide.

Key words: 2-(2-Thioxo-1,3-thiazolidin-3-yl)-4,5-dihydro-1,3-thiazolium bromide; NMR, mass spectra; X-ray structure.

INTRODUCTION

The oxidation of thiols to the corresponding disulfides by an electron transfer is well understood.[1] The disulfide 2,2′-dithiobis[4,5-dihydrothiazole] formed by the oxidation of **1** is known to rearrange on acid catalysis giving the thiocarbonyl derivative,[2]§ **3a**. Clark[3] *et al.* have prepared **3a** by the hydrogen peroxide oxidation of **1** in dilute hydrochloric acid medium. Fujita[4] *et al.* have isolated **3a** as one of the major products of the reaction of the Thallium salt of **1** with thiophosgene. Eric[5] *et al.* have found Copper(II) ions promoting this rearrangement in nitromethane as solvent with subsequent complexation of **3a** by copper(I). Kubiak[6] *et al.* have reported the crystal structure of trichlorozincate of **3a**.

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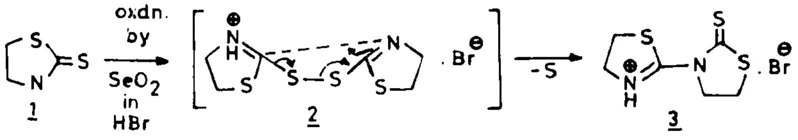
§ The structure of 1 given in page 665 is incorrect. One heterocyclic sulfur is missing.



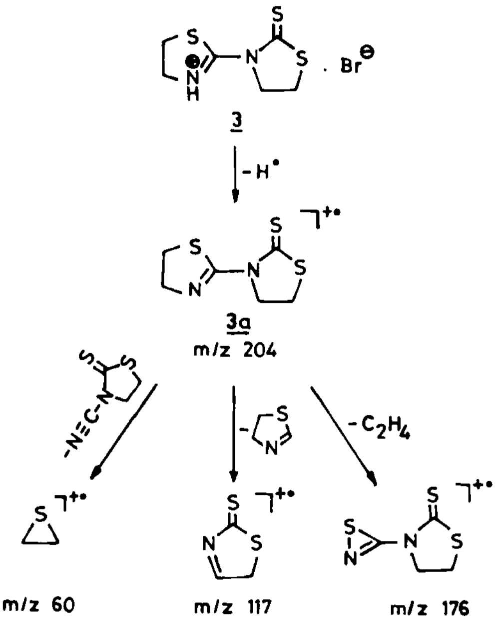
SCHEME 1

We attempted to prepare the 1,3-thiazolidine-2-thione complex of selenium(II) by the interaction of **1** with selenium(IV) in dilute acid medium. The interaction of selenium(IV) with thiols generally leads to the formation of selenotrisulfides[7] or the bisthiolatocomplex of selenium(II) in accord with the proposal of Painter.[8] However, with **1**, neither the bisthiolatoselenium(II)complex nor the disulfide, the oxidation product, could be isolated. Interaction of selenium(IV) with **1** in acid media such as HCl, $HClO_4$ and H_2SO_4 didn't yield easily isolable crystalline products. However, on employing HBr medium, long yellow crystals separated which were characterised as the title compound **3**. It is formed according to the reaction (Scheme 1), discussed later. In this paper we report the ^{1}HNMR, Mass spectral, X-PES studies and the crystal structure of the title compound.

RESULTS AND DISCUSSION

Mass spectral behaviour

The electron impact spectrum of 3 shows peaks at m/z values 206(13), 205(10), 204(100), 176(56), 117(30), 60(66). The fragmentation processes are given in Scheme 2. The Molecular ion is not observed. $[M - Br]^+$ at m/z 205 is observed.



SCHEME 2

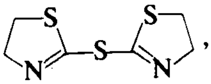
Further loss of H˙ from $[M-Br]^+$ affords the base peak in the spectrum at *m/z* 204, **3a**. Loss of an ethylene molecule from **3a** gives rise to the ion at *m/z* 176. The cleavage of the interring C-N bond with a β-hydrogen migration in **3a** yields the ion at *m/z* 117. The rupture of the 4,5-dihydro-1,3-thiazole ring in **3a** leads to the formation of the ion at *m/z* 60.

Infrared spectrum

The IR spectrum of **3** shows strong absorptions at 1580 cm^{-1} (C—N stretch), 1360 cm^{-1} (C—N stretch) and 1050 cm^{-1} (C—S stretch)

^{1}HNMR spectrum

^{1}HNMR spectrum of **3** in DMSO-D_6 shows four triplets at ∂3.25–3.45 (2H, CH_2.S.C═S), ∂3.5–3.7 (2H, CH_2.S), ∂3.85–4.10(2H, CH_2.N.C═S), ∂4.6–4.85(2H, CH_2.N). This ruled out the alternate symmetrical sulfide structure



, for which only two triplets could be expected.

X-Ray photoelectron spectrum

The photoelectron spectrum was obtained with Mg-K_α X-radiation. Figure 1 shows the sulfur electron spectrum from its 2*p*-subshell. A broad peak is obtained from the 2*p* subshell in sulfur. On deconvolution, two peaks are obtained at 161.9 and 163.2 eV of intensity ratio approximately 1:2 respectively. Each peak has a

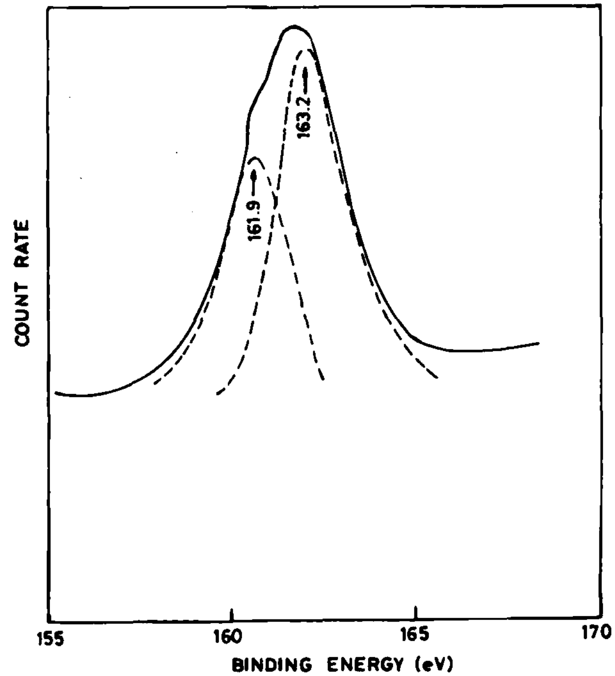


FIGURE 1 X-ray photoelectron spectrum showing S-2p emission.

full width at half maximum value of about 2.5 eV. On the basis of their intensities, the peak at 161.9 eV is assigned to the binding energy of the electron in the $2p$ subshell of the thione sulfur while that at 163.2 eV is due to the binding energy of the electron in the $2p$ subshell of heterocyclic sulfurs. These binding energy values are in agreement with those for similar sulfur types, as reported in mercaptothiazolines.[9]

Crystal structure determination

2-(2-Thioxo-1,3-thiazolidin-3-yl)-4,5-dihydro-1,3-thiazolium bromide, $C_6H_9N_2S_3Br$, $M_R = 284$. X-Ray data were collected from a single crystal in the form of yellow needle $(0.225 \times 0.375 \times 0.350)\text{mm}^3$ mounted on a glass fibre. An Enraf Nonius CAD4 diffractometer was used with graphite monochromatised Mo-K_α radiation, 0.71069 Å. The unit cell is monoclinic, $P2_1/c$, with $a = 11.236(1)$, $b = 10.138(1)$, $c = 9.571(1)$ Å, $\beta = 111.89(1)°$, determined from measurement of 2θ for 23 reflections with $41 < 2\theta < 43$, $V_c = 1011.63$ Å,^{3} $d_{X\text{-ray}} = 1.86\ \text{Mg/m}^3$ for $Z = 4$; $\mu = 4.49\ \text{mm}^{-1}$. Of 2526 unique reflections, 1498 reflections had $I > 3\sigma$ (I) and were considered observed. Correction applied for Lorentz and polarisation effects. Periodic measurements of two standard-reflections showed no appreciable change in their intensities.

Structure determination and refinement

The structure was solved by Direct methods using SHELX 76.[14] Maximum peak height in the final difference Fourier map is $1.273\ \text{e/Å}^3$ and was rejected due to its proximity to Br (0.80 Å). Refinement was terminated when the $(\text{Shif/esd})_{\max}$ in non-hydrogen parameters became less than 0.01.

Four hydrogens attached to the Carbon atoms [C(3), C(6)] adjacent to the endocyclic Sulfur atoms did not appear in the difference Fourier maps and were geometrically fixed. The remaining five hydrogens appeared in the difference Fourier maps and were refined.

The formation of the title compound can be explained by the oxidation of **1** by SeO_2 to its disulfide which in acid medium rapidly rearranges intramolecularly with the extrusion of one sulfur in analogy with the mechanism proposed by Barrett *et al.* for various disulfides.

Final atomic positional parameters and anisotropic temperature factors appear in Tables I and II. Final atomic parameters for the hydrogen atoms with isotropic temperature factors appear in Table III. Bond lengths and angles are given in Tables IV and V respectively. ORTEP[15] drawing of the molecule is given in Figure 2 and the packing diagram in Figure 3.

The C(1)—S(2), C(1)—S(1) and C(1)—N(1) bond distances in the thiazolidinethione ring suggest extensive delocalisation in the thioamide moiety. The interring C(2)—N(1) bond distance and the C(2)—S(3) and C(2)—N(2) bond distance also indicate delocalisation in the N(1)—C(2)—S(3)—N(2) moiety. The exocyclic C(1)—S(2) bond has about 75% SCF π-bond character.[10] Of the four endocyclic Carbon-Sulfur bonds, the two C_{sp2}—S bonds, C(1)—S(1) and C(2)—S(3) have about 36% SCF π-bond character while the C_{sp3}—S bonds, C(3)—S(1) and C(6)—S(3) are essentially σ in character. The C(2)—N(2) bond is almost a

TABLE I

Final atomic positional parameters

Atom	X	Y	Z
Br	0.0319 (1)	0.2461 (1)	0.0083 (1)
S1	0.3542 (2)	0.0655 (2)	0.5495 (2)
S2	0.4672 (2)	−0.1731 (2)	0.7220 (2)
C1	0.3673 (6)	−0.1043 (7)	0.5704 (7)
N1	0.2812 (5)	−0.1649 (5)	0.4429 (5)
C2	0.2670 (6)	−0.2979 (6)	0.4254 (7)
C3	0.2439 (7)	0.0599 (7)	0.3553 (8)
S3	0.3598 (2)	−0.4152 (2)	0.5513 (2)
C4	0.1870 (6)	−0.0755 (7)	0.3349 (8)
N2	0.1770 (5)	−0.3471 (5)	0.3082 (6)
C5	0.1572 (6)	−0.4912 (7)	0.3119 (9)
C6	0.2821 (7)	−0.5465 (7)	0.4173 (9)

The estimated standard deviations of the least significant digits are given in parentheses.

TABLE II

Anisotropic thermal parameters

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br	0.0422 (4)	0.0449 (4)	0.0316 (4)	−0.0051 (3)	0.0103 (3)	0.006 (3)
S1	0.0582 (12)	0.0316 (9)	0.0395 (10)	−0.0071 (7)	0.0087 (8)	−0.0026 (8)
S2	0.0392 (9)	0.0428 (10)	0.0315 (8)	0.0011 (7)	−0.0001 (6)	−0.0049 (8)
C1	0.0282 (29)	0.0362 (33)	0.0289 (31)	−0.0031 (25)	0.112 (23)	0.0007 (25)
N1	0.0281 (22)	0.0251 (24)	0.0277 (23)	−0.0015 (20)	0.0098 (18)	−0.0024 (20)
C2	0.0279 (29)	0.0298 (28)	0.0346 (32)	−0.0014 (25)	0.0115 (24)	−0.0028 (25)
C3	0.0530 (44)	0.0336 (36)	0.0340 (37)	−0.003 (28)	0.0079 (32)	0.0040 (30)
S3	0.0341 (9)	0.0310 (8)	0.0380 (9)	0.0049 (7)	0.0070 (7)	0.0000 (6)
C4	0.0357 (32)	0.0393 (36)	0.0318 (32)	0.0050 (27)	0.0089 (25)	−0.0016 (28)
N2	0.0285 (24)	0.0302 (26)	0.0342 (27)	0.0028 (22)	0.0078 (20)	0.0002 (21)
C5	0.0380 (34)	0.0272 (33)		−0.0027 (29)	0.0059 (30)	−0.0038 (26)
C6	0.0409 (36)	0.0340 (34)	0.0500 (43)	−0.0027 (30)	0.0109 (29)	−0.0040 (28)
			0.0454 (40)			

The estimated standard deviations of the least significant digits are given in parentheses.

TABLE III[#]

Hydrogen atoms positions with U_{iso}

Atom	X	Y	Z	U_{iso}
H1	0.0854	−0.5048	0.3473	0.0404
H2	0.1049	−0.0843	0.3760	0.0410
H3	0.1629	−0.0899	0.2218	0.0291
H4	0.1296	−0.5166	0.1948	0.0590
H5	0.1272	−0.3010	0.2417	0.0780
H6	0.2935	0.0753	0.2798	0.0500
H7	0.1693	0.1328	0.3346	0.0500
H8	0.2645	−0.6313	0.4761	0.0500
H9	0.3411	−0.5756	0.3563	0.0500

TABLE IV[#]

Bond lengths (Å)

S(1)—C(1)	1.737 (7)
S(1)—C(3)	1.804 (6)
S(2)—C(1)	1.619 (6)
C(1)—N(1)	1.389 (7)
N(1)—C(2)	1.366 (7)
N(1)—C(4)	1.478 (7)
C(2)—S(3)	1.731 (6)
C(2)—N(2)	1.300 (7)
C(3)—C(4)	1.498 (10)
S(3)—C(6)	1.821 (7)
N(2)—C(5)	1.489 (9)
C(5)—C(6)	1.504 (9)

The estimated standard deviations of the least significant digits are given in parentheses.

double bond. C(2)—N(1) and C(1)—N(1) bonds have approximately 30% SCF πbond character.[11] The two C_{sp3}—N bonds, C(5)—N(2) and C(4)—N(1) are σ in character. Angles within the molecule reflect the differing hybridisation states of the atoms. Those at C(3), C(4), C(5) and C(6) are close to the tetrahedral value suggesting sp^3 hybridisation while those at C(1), N(1), C(2) and N(2) are close to 120° suggesting sp^2 hybridisation. The angle at S(1) and S(3) are typical of thiazoles in that such angles are generally slightly greater than 90.0°.[12,13] The Least squares planes and the torsion angles show both the five membered rings, i.e. the thiazolidinethione ring and the dihydrothiazolyl ring adopting the halfchair[16] conformation. In the halfchair conformation, three adjacent atoms lie in a plane with the remaining two one above and one below the plane

TABLE V

Bond angles

S(1)—C(1)—S(2)	122.1 (4)
S(1)—C(1)—N(1)	109.4 (4)
C(1)—S(1)—C(3)	94.9 (3)
S(1)—C(3)—C(4)	104.9 (5)
S(2)—C(1)—N(1)	128.4 (4)
C(1)—N(1)—C(2)	123.7 (4)
C(1)—N(1)—C(4)	115.2 (4)
N(1)—C(2)—S(3)	125.4 (4)
N(1)—C(2)—N(2)	119.5 (4)
C(2)—N(1)—C(4)	120.1 (4)
N(1)—C(4)—C(3)	108.1 (5)
C(2)—S(3)—C(6)	90.2 (3)
S(3)—C(2)—N(2)	114.9 (4)
C(2)—N(2)—C(5)	115.1 (4)
S(3)—C(6)—C(5)	107.1 (5)
N(2)—C(5)—C(6)	105.6 (5)

The estimated standard deviations of the least significant digits are given in parentheses.

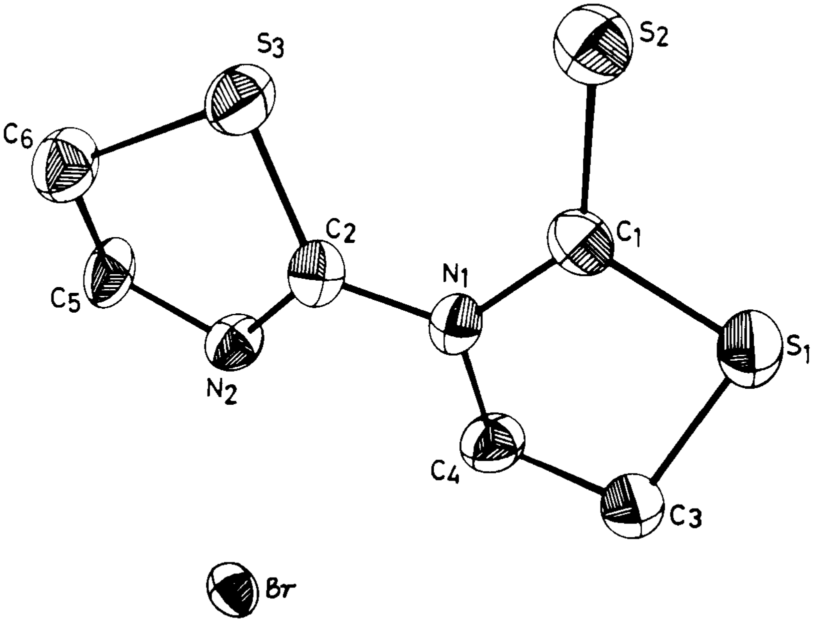


FIGURE 2 Ortep plot of the molecule.

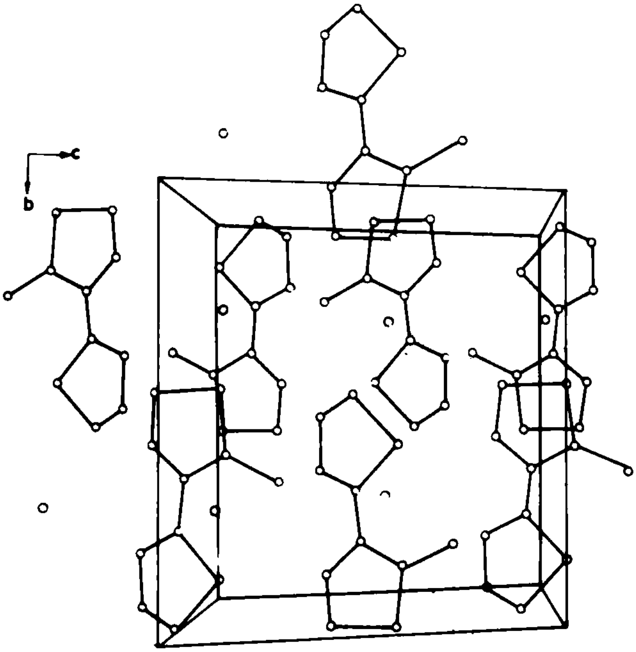


FIGURE 3 Packing diagram.

respectively. The Br is H-bonded to the dihydrothiazolyl N atom. The H . . . Br contact (2.46 Å) is significantly shorter than the sum of their corresponding Vander Waals radii (3.03 Å) and the N(2)—H(5) . . . Br angle is 157.5°. The intermolecular shortcontacts observed are Br—C′(2)^a = 3.668 Å, S(2)—S″(3)^b = 3.488 Å, $a = \bar{x}, \bar{y}, \bar{z}$; $b = \bar{x}$, $0.5 + y$, $0.5 - z$.

EXPERIMENTAL

General Data

The Mass spectrum was recorded on a Finnigan-MAT 8230 instrument, IR Spectrum on a Perkin-Elmer 983 instrument, ^{1}HNMR spectrum on a Hitachi-R 600 instrument and X-PES on an ESCALAB-MKII instrument. Microanalyses were performed at Australian Microanalytical Services, Victoria, Australia.

Preparation of 3

4 mMol of **1** was taken in 20 ml methanol and to this was addded a solution of 1 mMol of SeO_2 in 5 ml 4N HBr. After about six hours yellow needle shaped crystals of the title compound were formed along with elemental selenium. The crystals were redissolved by adding 100 ml methanol. Selenium was filtered off. The filtrate on slow evaporation to 20 ml volume gave pure crystals of the title compound m.p. 220–222°C. The yield was nearly quantitative.

#The table of atomic co-ordinates together with the tables of bond lengths and bond angles have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB21EW, U.K.

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