

Table 9. *A comparison of bond lengths (Å) in molecules having N—S—N or N—S—S bonds*

	N(1)—S(6a)	S(6a)—N(6)	S(6a)—C(3a)	Reference
(III)	1.983	1.833	1.717	(a)
(VIII)	1.901	1.948	1.742	(b)
	S(1)—S(6a)			
(IX)	2.493	1.779	1.742	(c)
(X)	2.364	1.887	1.744	(d)
(XI)	2.396	1.871	1.752	(e)
(XII)	2.435	1.849	1.735	(f)
(XIII)	2.447	1.863	1.746	(g)

References: (a) Present work. (b) Hordvik & Julshamn (1972). (c) Darro & Hansen (1977). (d) Leung & Nyburg (1971). (e) Leung & Nyburg (1972). (f) Hansen & Tomren (1977). (g) Hansen (1977).

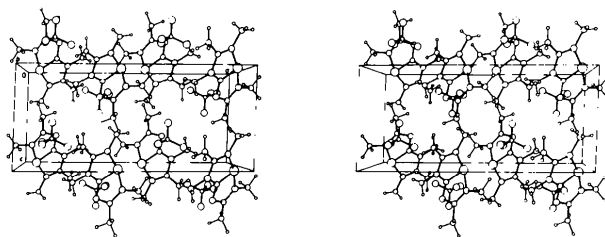


Fig. 4. Stereoscopic view of the packing of (III).

π -hypervalent S atom during these reactions. An intermediate state should be of the thiathiophene type. It is interesting that (III) has a molecular structure of the thiathiophene type in the crystalline state.

The crystal structure of (III) is shown in Fig. 4. There are no contacts less than the sum of the van der Waals radii.

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The Structure of 5-[(1-Aminoethylidene)amino]-3-chloromethyl-1,2,4-thiadiazole

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Abstract

$C_5H_7ClN_4S$, $M_r = 190.60$, monoclinic, $P2_1/a$, $a = 9.667$ (2), $b = 9.736$ (3), $c = 9.543$ (2) Å, $\beta =$

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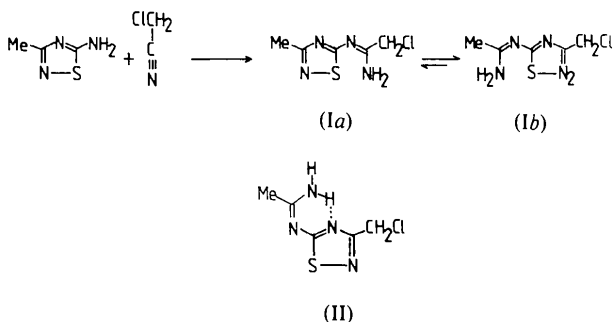
110.15 (2)°, $U = 843.1$ (3) Å³, $Z = 4$, $D_x = 1.502$ Mg m⁻³, $F(000) = 392$. Final $R = 0.049$ for 1371 observed reflexions. The constitution of the 1:1 adduct of 5-amino-3-methyl-1,2,4-thiadiazole and chloroacetonitrile is 5-[(1-aminoethylidene)amino]-3-chloromethyl-1,2,4-thiadiazole. A bond switch at the π -hypervalent

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sulfur is observed in the formation of the adduct. The amino group is linked to N(4) in the thiadiazole ring forming an intramolecular $\text{NH}\cdots\text{N}$ hydrogen bond [$\text{N}\cdots\text{N}$ 2.691 (5), $\text{N}\cdots\text{H}$ 2.04 (4) Å, \angle NHN 131 (3)°]. There is a weak intermolecular hydrogen bond between the amino group and the imino N atom forming a chain elongated along \mathbf{a} [$\text{N}\cdots\text{N}$ 2.968 (5), $\text{H}\cdots\text{N}$ 2.10 (4) Å, \angle NHN 167 (4)°].

Introduction

5-Amino-3-methyl-1,2,4-thiadiazole forms a 1:1 adduct with chloroacetonitrile. In solution, the NMR spectrum shows this compound to be an equilibrium mixture of (Ia) and (Ib) (Akiba, Kobayashi & Arai, 1979). The X-ray analysis reported here shows that the constitution of the adduct is 5-[(1-aminoethylidene)-amino]-3-chloromethyl-1,2,4-thiadiazole (II) in the crystals.



The adduct was recrystallized from benzene-hexane solution as colorless prisms. Intensities were collected

Table 1. Positional parameters ($\times 10^4$, for H $\times 10^3$) and isotropic thermal parameters (Å^2), with *e.s.d.*'s in parentheses

For nonhydrogen atoms $B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}/B
Cl	1025 (1)	4571 (1)	-1353 (1)	5.5
S	5809 (1)	4825 (1)	2463 (1)	4.0
N(2)	4677 (4)	3816 (3)	1163 (4)	4.1
N(4)	3102 (3)	5028 (3)	2072 (3)	3.2
N(5)	4693 (3)	6556 (3)	3975 (3)	2.9
N(6)	2200 (3)	6840 (3)	3707 (4)	3.6
C(3)	3340 (4)	4081 (3)	1136 (4)	3.5
C(5)	4383 (4)	5558 (3)	2914 (4)	2.9
C(31)	2062 (5)	3352 (4)	28 (5)	4.9
C(6)	3618 (4)	7159 (3)	4294 (4)	3.0
C(7)	4030 (5)	8284 (4)	5425 (5)	4.3
H(31)	247 (4)	260 (4)	-68 (4)	6.2 (10)
H(32)	137 (4)	299 (4)	56 (4)	5.3 (10)
H(61)	192 (4)	623 (3)	300 (4)	5.3 (10)
H(62)	155 (4)	738 (3)	392 (4)	5.9 (10)
H(71)	413 (4)	905 (4)	493 (5)	7.2 (11)
H(72)	506 (4)	834 (4)	603 (4)	6.3 (10)
H(73)	374 (4)	822 (4)	608 (5)	7.2 (11)

on a Rigaku automatic diffractometer with graphite-monochromatized $\text{Mo } K\alpha$ radiation from a crystal $0.2 \times 0.2 \times 0.1$ mm. Reflexions in the range $2\theta \leq 55^\circ$ were measured by the ω - 2θ scan technique with a scan width of $\Delta\omega = 1.2^\circ + 0.5^\circ \tan \theta$ and a scanning speed of 4° min^{-1} in 2θ . At both ends of the scan range 10s background counts were taken for each reflexion. Reflexions with $|F_o| \geq 3\sigma(F_o)$ were considered as observed. No absorption corrections were applied.

The positions of the S and Cl atoms were determined from a sharpened Patterson map. A Fourier synthesis made it possible to locate all the non-hydrogen atoms. The structure was refined by block-diagonal least squares. When R was 0.064, a difference synthesis revealed the positions of all H atoms. All atoms were refined by block-diagonal least squares with anisotropic temperature factors for non-hydrogen atoms and isotropic for H. The quantity minimized was $\sum w(|F_o| - k^{-1}|F_c|)^2$ where $w = 1/\sigma^2(F_o)$ was derived from counting statistics. The final R was 0.049 for all observed reflexions. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All computations were performed on the Hitac 8800/8700 computer of the Computer Center of the University of Tokyo, with a local version of *UNICS* (Sakurai, 1967). The final atomic parameters are given in Table 1.*

Discussion

Fig. 1 shows the structure of the molecule with the atom numbering. Bond lengths and angles are listed in Table 2.

The analysis shows that in the solid state the constitution of the adduct is 5-[(1-aminoethylidene)-amino]-3-chloromethyl-1,2,4-thiadiazole (II). One of the amino H atoms forms an intramolecular hydrogen

* Lists of structure factors and anisotropic temperature factors for non-hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35637 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

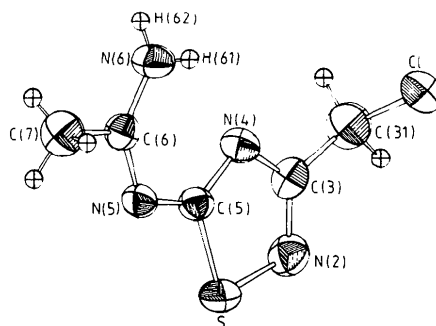


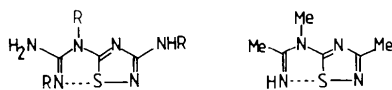
Fig. 1. Perspective drawing of the molecule showing the thermal ellipsoids with a probability of 50% (ORTEP, Johnson, 1965).

Table 2. Bond lengths (Å) and angles (°) with their e.s.d.'s

S—N(2)	1.663 (4)	C(31)—H(31)	1.16 (4)
S—C(5)	1.732 (4)	C(31)—H(32)	1.04 (4)
N(2)—C(3)	1.310 (6)	C(7)—H(71)	0.91 (4)
N(4)—C(3)	1.357 (5)	C(7)—H(72)	0.97 (4)
N(4)—C(5)	1.327 (5)	C(7)—H(73)	0.78 (4)
C(3)—C(31)	1.500 (7)	N(6)—H(61)	0.87 (4)
C(5)—N(5)	1.361 (5)	N(6)—H(62)	0.89 (4)
N(5)—C(6)	1.317 (5)	N(4)···N(6)	2.691 (5)
C(6)—N(6)	1.327 (5)	N(4)···H(61)	2.04 (4)
C(6)—C(7)	1.493 (6)		
C(31)—Cl	1.800 (5)		
N(2)SC(5)	93.1 (2)	C(3)C(31)H(31)	110 (2)
SN(2)C(3)	106.8 (3)	C(3)C(31)H(32)	109 (2)
N(2)C(3)N(4)	120.7 (4)	C1C(31)H(31)	102 (2)
N(2)C(3)C(31)	119.2 (4)	C1C(31)H(32)	107 (2)
N(4)C(3)C(31)	120.0 (4)	H(31)C(31)H(32)	119 (2)
C(3)N(4)C(5)	109.2 (3)	C(6)C(7)H(71)	106 (3)
SC(5)N(4)	110.2 (3)	C(6)C(7)H(72)	116 (2)
SC(5)N(5)	119.3 (3)	C(6)C(7)H(73)	116 (3)
N(4)C(5)N(5)	130.4 (4)	H(71)C(7)H(72)	89 (4)
C(5)N(5)C(6)	120.1 (3)	H(71)C(7)H(73)	129 (4)
N(5)C(6)N(6)	125.5 (4)	H(72)C(7)H(73)	96 (4)
N(5)C(6)C(7)	117.3 (4)	C(6)N(6)H(61)	119 (3)
N(6)C(6)C(7)	117.2 (4)	C(6)N(6)H(62)	118 (3)
C(3)C(31)Cl	108.7 (3)	H(61)N(6)H(62)	121 (4)
		N(6)H(61)N(4)	131 (3)

bond to N(4) in the thiadiazole ring. The N(6)···N(4) and H(61)···N(4) lengths are 2.691 and 2.04 Å, respectively. The angle N(4)H(61)N(6) is 131°. The thiadiazole ring is planar within 0.002 Å. The maximum deviation of the exocyclic C and N atoms from this plane is 0.16 Å for C(7).

The dimensions of the thiadiazole ring are similar to those of other 1,2,4-thiadiazoles, such as (III) (Akiba, Tsuchiya, Inamoto, Onuma, Nagashima & Nakamura, 1976) and (IV) (Iwasaki & Akiba, 1981).

(III) (R = *p*-bromophenyl)

(IV)

The S—N distance is 1.663(4) Å, as in 1,2,4-thiadiazole but slightly shorter than the S—N lengths in 1,2,4-thiadiazoline (Butler, Glidewell & Liles, 1978; L'Abbé, Verhelst, Toppet, King & Briers, 1976). The S—C length is 1.732 (4) Å. N(2)—C(3), 1.310 (6) Å, is slightly longer than the normal C—N double-bond length and the corresponding N—C distances in

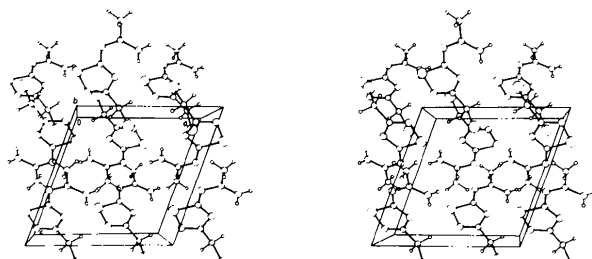


Fig. 2. Stereoscopic view of the crystal structure.

thiadiazolines but is normal for 1,2,4-thiadiazole. C(3)—N(4) is, however, somewhat shorter and N(4)—C(5) longer than the corresponding C—N distances in other 1,2,4-thiadiazoles, owing to the difference of the conformations of the 5-exocyclic chains. N(2)SC(5) [93.1 (2)°] and SC(5)N(4) [110.2(3)°] are also slightly different from the corresponding angles in (III) (91.3 and 112.7°) and (IV) (91.4 and 112.4°). The lengths of the exocyclic C—C bonds, 1.500(7) and 1.493(6) Å for C(3)—C(31) and C(6)—C(7) respectively, are normal for such a single bond. C(31)—Cl [1.800(5) Å] is significantly longer than the normal C—Cl distance (1.78 Å).

The crystal structure viewed along **b** is shown in Fig. 2. There is a weak intermolecular interaction between the amino group [N(6)—H(62)] and the imino N(5') of the molecule at $\frac{1}{2} + x, -y, z$. N(6)···N(5') and H(62)···N(5') are 2.968(5) and 2.10(4) Å respectively. N(6)H(62)N(5') is 167(4)°. The hydrogen-bonded chain is elongated along **a**.

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