

The Structures of 5-(1-Imino-*N*-methylethylamino)-3-methyl-1,2,4-thiadiazole, 3,4-Dimethyl-5-[1-(*N*-methyliminio)ethylimino]-1,2,4-thiadiazoline Tetrafluoroborate and 1,2,3,5,6-Pentamethyl-1,3,4,6-tetraaza-6a λ^4 -thiapentalenium Tetrafluoroborate

BY FUJIKO IWASAKI*

Department of Materials Science, The University of Electro-Communications, Chofu-shi, Tokyo 182, Japan

AND KIN-YA AKIBA

Department of Chemistry, Faculty of Science, Hiroshima University, Higashisendamachi, Hiroshima 730, Japan

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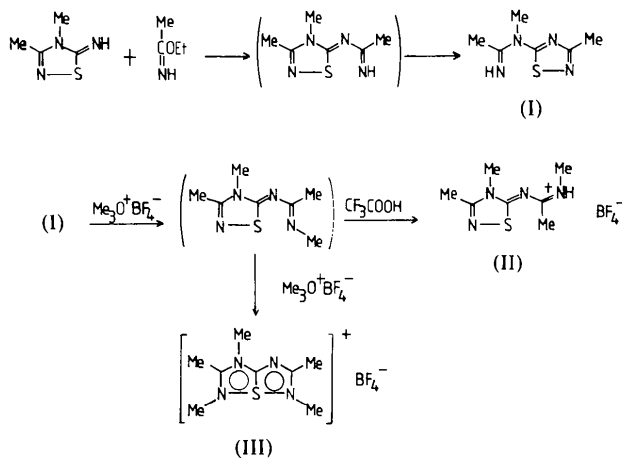
Abstract

The 1:1 adduct, C₆H₁₀N₄S (I), of 5-imino-3,4-dimethyl- Δ^2 -1,2,4-thiadiazoline and ethyl acetimidate crystallizes in the orthorhombic space group *Pcab*, with $a = 13.516$ (1), $b = 13.601$ (1), $c = 8.874$ (1) Å, $V = 1631.2$ (3) Å³, $Z = 8$. Alkylation of (I) and subsequent protonation gave the compound C₇H₁₃N₄S⁺.BF₄⁻ (II). (II) is triclinic, *P* $\bar{1}$, with $a = 9.880$ (3), $b = 8.911$ (4), $c = 7.334$ (4) Å, $\alpha = 97.62$ (9), $\beta = 89.00$ (6), $\gamma = 76.83$ (3)°, $V = 622.4$ (4) Å³, $Z = 2$. Alkylation of (I) with Meerwein reagent and further alkylation with the same reagent gave the compound C₈H₁₅N₄S⁺.BF₄⁻ (III) which is monoclinic, *P2*₁/*a*, with $a = 16.694$ (2), $b = 10.886$ (2), $c = 7.328$ (1) Å, $\beta = 91.98$ (2)°, $V = 1330.9$ (4) Å³, $Z = 4$. Final $R = 0.048$, 0.081 and 0.097 for (I), (II) and (III) respectively. (I) is revealed to be 5-(1-imino-*N*-methylethylamino)-3-methyl-1,2,4-thiadiazole in which S–N is 1.668 Å and the non-bonding short contact S...N is 2.499 Å. A bond switch at the π -hypervalent S atom takes place in the formation of (I). (II) is a 3,4-dimethyl-5-[1-(*N*-methyliminio)ethylimino]-1,2,4-thiadiazoline salt in which N–S is 1.672 Å and the *N*-methyliminio group is *trans* to C(5) across the N–C bond. There is a short non-bonding intramolecular contact S...CH₃ (3.017 Å). (III) is a salt of the tetraaza analog of 6a-thiathiophene. The two N–S bonds are 1.984 and 1.833 Å.

Introduction

With ethyl acetimidate, 5-imino-3,4-dimethyl- Δ^2 -1,2,4-thiadiazoline formed the 1:1 adduct C₆H₁₀N₄S (I). Alkylation of (I) with Meerwein reagent and subsequent protonation gave the compound

C₇H₁₃N₄S⁺.BF₄⁻ (II). Alkylation of (I) and further alkylation with the same reagent gave the compound C₈H₁₅N₄S⁺.BF₄⁻ (III) (Akiba, Arai & Iwasaki, 1978; Akiba, Arai, Tsuchiya, Yamamoto & Iwasaki, 1979). It was considered that a bond switch took place at a π -hypervalent S atom during these reactions. To elucidate such a reaction mechanism the structures of (I), (II) and (III) have been determined by X-ray analysis.



Experimental

Each compound was recrystallized from dichloromethane. Crystals of (I) are colorless needles, those of (II) and (III) colorless flat plates. They are stable in air. Crystal data are listed in Table 1.

Intensities were collected on a Rigaku automatic diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Reflexions in the range $2\theta \leq 55^\circ$ were measured by the ω - 2θ scan technique with a scan width of $1.2^\circ + 0.5^\circ \tan \theta$ and scanning speed of 4° min^{-1} in 2θ . At both ends of the scan range 10 s background counts were taken for each reflexion. For

* To whom all correspondence should be addressed.

Table 1. *Crystal data*

	(I)	(II)	(III)
M_r	$C_6H_{10}N_4S$	$C_7H_{13}N_4S^+ \cdot BF_4^-$	$C_8H_{15}N_4S^+ \cdot BF_4^-$
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	$Pcab$	$P\bar{1}$	$P2_1/a$
a (Å)	13.516 (1)	9.880 (3)	16.694 (2)
b (Å)	13.601 (1)	8.911 (4)	10.886 (2)
c (Å)	8.874 (1)	7.334 (4)	7.328 (1)
α (°)		97.62 (9)	
β (°)		89.00 (6)	91.98 (2)
γ (°)		76.83 (3)	
V (Å ³)	1631.2 (3)	622.4 (4)	1330.9 (4)
Z	8	2	4
D_x (Mg m ⁻³)	1.386	1.452	1.428

Table 2. *Positional parameters* ($\times 10^4$, for H $\times 10^3$) and *isotropic thermal parameters* (Å²) for (I), with *e.s.d.'s in parentheses*

Here and elsewhere in this paper for non-hydrogen atoms $B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$.

	x	y	z	B_{eq}/B
S	1769 (0)	1068 (0)	2356 (1)	3.6
N(2)	2739 (1)	468 (1)	3067 (2)	4.0
N(4)	3475 (1)	1721 (1)	1716 (2)	3.0
N(5)	2221 (1)	2663 (1)	569 (2)	3.1
N(6)	636 (1)	2307 (1)	1192 (2)	4.5
C(3)	3547 (1)	916 (1)	2637 (2)	3.3
C(31)	4540 (1)	582 (2)	3155 (3)	4.6
C(5)	2532 (1)	1897 (1)	1458 (2)	2.7
C(6)	2976 (1)	3275 (1)	-159 (3)	4.0
C(7)	1213 (1)	2871 (1)	478 (2)	3.5
C(8)	913 (2)	3730 (2)	-459 (3)	5.1
H(31)	454 (2)	-1 (2)	371 (3)	7.3 (7)
H(32)	500 (3)	41 (2)	236 (4)	8.9 (9)
H(33)	484 (2)	103 (2)	366 (3)	7.3 (7)
H(61)	356 (2)	287 (2)	-55 (3)	7.2 (7)
H(62)	309 (2)	382 (3)	30 (4)	9.6 (10)
H(63)	273 (2)	356 (2)	-104 (4)	8.1 (8)
H(81)	122 (2)	431 (2)	-9 (3)	7.6 (7)
H(82)	20 (2)	380 (2)	-44 (2)	4.4 (5)
H(83)	104 (2)	363 (2)	-142 (3)	6.2 (7)
H(6)	2 (2)	249 (2)	114 (3)	5.2 (5)

(I), 1729 reflexions had $|F_o| \geq 3\sigma(F_o)$ and were considered observed. For (II) and (III) 1369 and 2290 reflexions, respectively, were obtained with $|F_o| \geq 3\sigma(F_o)$. Approximate dimensions of the crystals were $0.4 \times 0.3 \times 0.4$, $0.5 \times 0.1 \times 0.3$ and $0.4 \times 0.4 \times 0.2$ mm for (I), (II) and (III) respectively. No absorption corrections were applied.

For each compound the position of the S atom was determined from a sharpened Patterson map. A Fourier synthesis then made it possible to locate all the non-hydrogen atoms. The structures were refined by block-diagonal least squares. A difference synthesis revealed the positions of all the H atoms.

For (II), four other peaks were found round the B atom in the difference map, suggesting that BF_4^- was disordered. These peaks were assigned as F atoms with an occupancy factor of 0.3 estimated from the peak

heights in the difference map. The anisotropic temperature factors of F atoms for (III) became abnormally large. The BF_4^- anion in this structure was considered to have almost free rotation.

For (I) and (III), all atoms were refined by block-diagonal least squares with anisotropic temperature factors for non-hydrogen atoms and isotropic for H. For (II), all atoms were refined by block-diagonal least squares with isotropic temperature factors for H and for F atoms with the fixed occupancy factor 0.3, and with anisotropic temperature factors for F atoms with the occupancy factor 0.7 and the other non-hydrogen atoms. The final R was 0.048, 0.081 and 0.097 for (I), (II) and (III) respectively. The quantity minimized was $\sum w(|F_o| - k^{-1}|F_c|)^2$. For (I) and (III) $w = 0.5$ if $|F_o| < 5$, $w = 1.0$ if $5 \leq |F_o| \leq 20$ and $w = (20/|F_o|)^2$ if $|F_o| > 20$. For (II) $w = 0.5$ if $|F_o| < 4$, $w = 1.0$ if $4 \leq |F_o| \leq 16$ and $w = (16/|F_o|)^2$ if $|F_o| > 16$. Neutral-atom 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

Table 3. *Positional parameters* ($\times 10^4$, for H $\times 10^3$) and *isotropic thermal parameters* (Å²) for (II), with *e.s.d.'s in parentheses*

	x	y	z	B_{eq}/B
S	4164 (2)	3473 (2)	2607 (3)	6.7
N(2)	5060 (5)	4848 (6)	2532 (9)	7.8
N(4)	2809 (4)	6174 (5)	2619 (6)	4.1
N(5)	1274 (4)	4586 (4)	2642 (6)	3.9
N(6)	-376 (5)	3237 (6)	2541 (7)	5.8
C(3)	4199 (6)	6169 (7)	2539 (9)	5.8
C(5)	2560 (5)	4743 (5)	2652 (7)	3.8
C(6)	927 (5)	3251 (6)	2742 (7)	4.6
C(7)	1892 (7)	1789 (7)	3136 (10)	7.2
C(8)	-1429 (6)	4556 (8)	2213 (9)	6.5
C(31)	4671 (6)	7659 (8)	2526 (10)	7.3
C(41)	1685 (6)	7580 (6)	2593 (9)	5.7
B	-2253 (8)	16 (9)	2195 (11)	6.2
F(1)	-1088 (5)	285 (6)	3005 (9)	10.0
F(2)	-2002 (6)	-1538 (6)	1607 (9)	10.3
F(3)	-3309 (6)	255 (9)	3530 (9)	12.1
F(4)	-2673 (8)	951 (8)	990 (10)	13.1
F(11)	-110 (2)	11 (3)	99 (3)	8.8 (5)
F(12)	-219 (3)	-90 (4)	329 (4)	13.8 (8)
F(13)	-337 (2)	6 (3)	101 (3)	9.6 (5)
F(14)	-266 (2)	155 (3)	314 (3)	10.4 (6)
H(31)	557 (5)	738 (6)	257 (7)	7.4 (14)
H(32)	422 (6)	843 (7)	347 (8)	7.7 (15)
H(33)	429 (7)	811 (8)	141 (9)	10.1 (18)
H(41)	187 (7)	845 (9)	281 (10)	12.0 (21)
H(42)	121 (7)	776 (8)	384 (9)	11.1 (19)
H(43)	117 (7)	750 (8)	191 (9)	11.0 (19)
H(61)	-64 (6)	249 (6)	267 (7)	7.5 (15)
H(71)	245 (5)	202 (5)	414 (6)	5.2 (11)
H(72)	259 (5)	148 (6)	211 (7)	6.1 (12)
H(73)	135 (5)	114 (6)	329 (7)	6.3 (12)
H(81)	-125 (6)	493 (7)	123 (8)	8.6 (16)
H(82)	-148 (6)	550 (6)	307 (7)	7.4 (14)
H(83)	-234 (7)	437 (8)	207 (9)	11.0 (19)

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

	x	y	z	B_{eq}/B
S(6a)	609 (1)	1755 (1)	-119 (2)	4.3
N(1)	1055 (3)	471 (4)	1545 (6)	4.8
N(3)	1891 (3)	454 (4)	-717 (6)	4.7
N(4)	1505 (3)	1845 (5)	-3009 (6)	4.8
N(6)	410 (3)	2821 (4)	-2018 (6)	4.8
C(2)	1690 (4)	-18 (5)	966 (8)	5.1
C(3a)	1401 (3)	1315 (5)	-1400 (7)	4.1
C(5)	923 (4)	2692 (5)	-3325 (8)	5.1
C(11)	682 (5)	170 (6)	3251 (7)	6.5
C(21)	2180 (5)	-970 (7)	1880 (10)	7.2
C(31)	2604 (4)	74 (7)	-1655 (11)	7.0
C(51)	915 (5)	3407 (7)	-5034 (9)	7.1
C(61)	-270 (5)	3680 (7)	-2013 (11)	7.3
B	3538 (5)	2042 (7)	2841 (10)	5.9
F(1)	2827 (4)	2056 (6)	2108 (14)	15.7
F(2)	3892 (5)	2974 (8)	2336 (23)	24.1
F(3)	3985 (5)	1071 (7)	2472 (10)	14.6
F(4)	3518 (8)	2101 (18)	4489 (12)	29.2
H(11)	18 (3)	51 (5)	339 (8)	3.3 (13)
H(12)	60 (3)	-65 (5)	333 (7)	2.2 (11)
H(13)	100 (4)	45 (7)	394 (10)	6.0 (18)
H(21)	220 (5)	-101 (7)	324 (10)	7.3 (19)
H(22)	263 (4)	-86 (7)	137 (9)	5.8 (18)
H(23)	225 (4)	-167 (6)	128 (9)	4.9 (16)
H(31)	300 (4)	12 (6)	-132 (8)	4.3 (15)
H(32)	249 (4)	27 (6)	-283 (9)	5.7 (17)
H(33)	262 (3)	-80 (6)	-185 (8)	3.6 (13)
H(51)	146 (5)	327 (8)	-548 (12)	9.3 (25)
H(52)	65 (6)	318 (9)	-634 (14)	10.8 (29)
H(53)	83 (5)	423 (8)	-466 (11)	7.8 (22)
H(61)	-65 (4)	355 (5)	-306 (8)	3.6 (13)
H(62)	-61 (4)	353 (7)	-83 (9)	5.4 (17)
H(63)	-3 (4)	449 (6)	-164 (9)	4.6 (15)

(Sakurai, 1967). The final atomic parameters are given in Tables 2, 3 and 4 for (I), (II) and (III) respectively.*

Discussion

The structure of (I) with the atom numbering is shown in Fig. 1(a). Bond distances and angles are listed in Table 5. The analysis shows that (I) is not a 1,2,4-thiadiazoline, but a 1,2,4-thiadiazole. The original S-N bond is opened, and a new five-membered ring formed, i.e. a bond switch is observed at the π -hypervalent S atom.

A comparison of the dimensions of some 1,2,4-thiadiazole and 1,2,4-thiadiazoline rings is given in Table 6. The dimensions of the heterocycle in (I) are similar to those reported for 1,2,4-thiadiazoles. The

* 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 35638 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

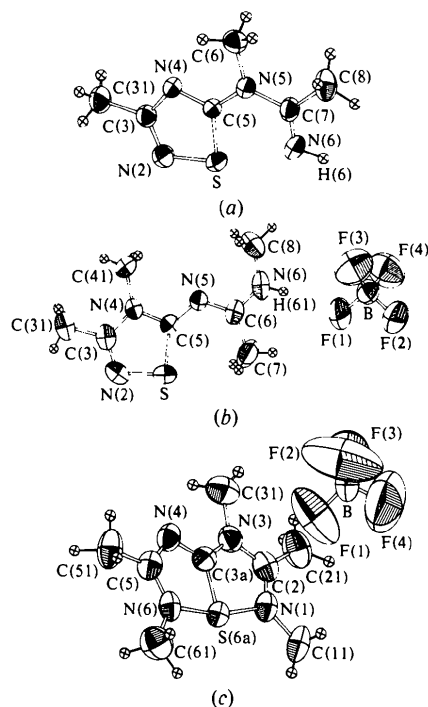


Fig. 1. Perspective drawing of the molecules showing the thermal ellipsoids with a probability of 50% (ORTEP, Johnson, 1965), with the atom numbering. (a) (I), (b) (II), (c) (III).

Table 5. Bond lengths (\AA) and angles ($^\circ$) for (I) with their e.s.d.'s

S-N(2)	1.668 (2)	C(31)-H(31)	0.94 (3)
S-C(5)	1.723 (2)	C(31)-H(32)	0.96 (4)
N(2)-C(3)	1.308 (3)	C(31)-H(33)	0.86 (3)
C(3)-N(4)	1.370 (2)	C(6)-H(61)	1.03 (3)
N(4)-C(5)	1.316 (2)	C(6)-H(62)	0.85 (4)
C(3)-C(31)	1.490 (3)	C(6)-H(63)	0.93 (4)
N(5)-C(5)	1.373 (2)	C(8)-H(81)	0.96 (3)
N(5)-C(6)	1.466 (3)	C(8)-H(82)	0.97 (2)
N(5)-C(7)	1.395 (3)	C(8)-H(83)	0.88 (3)
C(7)-N(6)	1.264 (3)	N(6)-H(6)	0.87 (3)
C(7)-C(8)	1.490 (3)		
N(2)SC(5)	91.39 (9)	C(3)C(31)H(31)	115 (2)
SN(2)C(3)	108.5 (2)	C(3)C(31)H(32)	115 (2)
N(2)C(3)N(4)	119.1 (2)	C(3)C(31)H(33)	112 (2)
C(3)N(4)C(5)	108.5 (2)	N(5)C(6)H(61)	112 (2)
SC(5)N(4)	112.4 (1)	N(5)C(6)H(62)	114 (2)
N(2)C(3)C(31)	121.3 (2)	N(5)C(6)H(63)	111 (2)
N(4)C(3)C(31)	119.5 (2)	C(7)C(8)H(81)	110 (2)
SC(5)N(6)	125.4 (1)	C(7)C(8)H(82)	109 (1)
N(4)C(5)N(6)	122.2 (2)	C(7)C(8)H(83)	112 (2)
C(5)N(5)C(6)	118.1 (2)	C(7)N(6)H(6)	113 (2)
C(5)N(5)C(7)	119.1 (2)	H(31)C(31)H(32)	100 (3)
C(6)N(5)C(7)	122.6 (2)	H(31)C(31)H(33)	110 (3)
N(5)C(7)N(6)	116.7 (2)	H(32)C(31)H(33)	104 (3)
N(5)C(7)C(8)	117.2 (2)	H(61)C(6)H(62)	119 (3)
N(6)C(7)C(8)	126.1 (2)	H(61)C(6)H(63)	103 (3)
		H(62)C(6)H(63)	96 (3)
		H(81)C(8)H(82)	110 (2)
		H(81)C(8)H(83)	112 (3)
		H(82)C(8)H(83)	103 (2)

Table 6. Comparison of 1,2,4-thiadiazole and 1,2,4-thiadiazoline rings (distances in Å, angles in deg)

	(I)	(V)	(IV)	(II)	(VI)	(VII)
S—N(2)	1.668	1.67	1.663	1.672	1.691	1.68
N(2)—C(3)	1.308	1.29	1.310	1.286	1.294	1.30
C(3)—N(4)	1.370	1.39	1.357	1.372	1.386	1.39
N(4)—C(5)	1.316	1.30	1.327	1.355	1.402	1.36
S—C(5)	1.723	1.74	1.732	1.721	1.761	1.73
N(2)SC(5)	91.4	91.3	93.1	94.6	95.3	94
SN(2)C(3)	108.5	107.7	106.8	108.9	108.9	111
N(2)C(3)N(4)	119.1	120.8	120.7	116.7	117.6	115
C(3)N(4)C(5)	108.5	107.4	109.2	113.5	113.7	114
SC(5)N(4)	112.4	112.7	110.2	106.3	104.5	107
Reference	(a)	(b)	(c)	(a)	(d)	(e)

References: (a) Present work. (b) Akiba, Tsuchiya, Inamoto, Onuma, Nagashima & Nakamura (1976). (c) Iwasaki & Akiba (1981). (d) Butler, Glidewell & Liles (1978). (e) L'Abbé, Verhelst, Toppet, King & Briers (1976).

thiadiazole ring is planar within 0.009 Å. Apart from the H atoms the maximum deviation from this plane is 0.22 Å for N(6). The dihedral angle between the thiadiazole ring and the open five-membered ring is 5.3°. The S—N(2) length is 1.668 Å. The exocyclic S...N(6) is 2.499 Å. This is significantly less than the sum of the van der Waals radii but longer than the S—N single-bond length (1.74 Å) and some N...S lengths in thiathiophene analogs such as (III) and (VIII) (Hordvik & Julshamn, 1972). The interaction between S and N(7), however, should be so weak that the S—N(1) length is not different from the corresponding distance in (IV) (Iwasaki & Akiba, 1981) in which an S...N non-bonding interaction is not found.

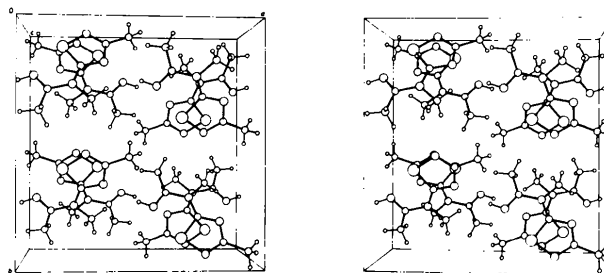
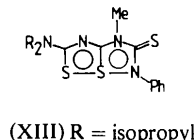
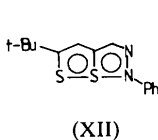
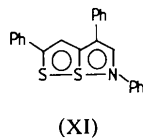
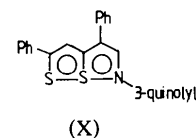
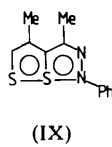
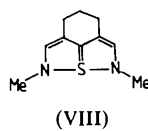
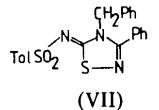
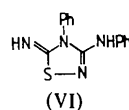
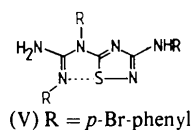
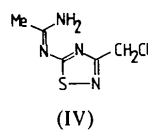


Fig. 2. Stereoscopic view of the packing of (I).

Although the C—N bonds in the thiadiazole ring lie between single and double bonds, indicating π conjugation throughout the system, N(2)—C(3) and N(4)—C(5) are significantly shorter than N(4)—C(3). The C—CH₃ and N—CH₃ lengths are normal for such single bonds.

The crystal structure of (I) is shown in Fig. 2. There is a weak intermolecular contact between N(6)—H(6)

Table 7. Bond distances (Å) and angles (°) for (II) with their *e.s.d.*'s

S—N(2)	1.672 (7)	N(6)—H(61)	0.78 (6)
S—C(5)	1.721 (5)	C(31)—H(31)	0.87 (6)
N(2)—C(3)	1.286 (9)	C(31)—H(32)	0.93 (6)
N(4)—C(3)	1.372 (8)	C(31)—H(33)	1.00 (7)
N(4)—C(5)	1.355 (7)	C(41)—H(41)	0.83 (8)
C(3)—C(31)	1.505 (10)	C(41)—H(42)	1.00 (7)
N(4)—C(41)	1.475 (8)	C(41)—H(43)	0.73 (8)
N(5)—C(5)	1.309 (6)	C(7)—H(71)	0.96 (5)
N(5)—C(6)	1.322 (7)	C(7)—H(72)	0.98 (5)
N(6)—C(6)	1.300 (7)	C(7)—H(73)	0.89 (5)
C(6)—C(7)	1.495 (9)	C(8)—H(81)	0.87 (6)
N(6)—C(8)	1.431 (9)	C(8)—H(82)	0.97 (6)
B—F(1)	1.359 (11)	C(8)—H(83)	0.96 (7)
B—F(2)	1.360 (10)		
B—F(3)	1.379 (11)	B—F(occupancy 0.3)	
B—F(4)	1.303 (11)		
			1.21–1.45 (3)
			(mean 1.39)
N(2)SC(5)	94.6 (3)	C(3)C(31)H(31)	104 (4)
SN(2)C(3)	108.9 (5)	C(3)C(31)H(32)	111 (4)
N(2)C(3)N(4)	116.7 (6)	C(3)C(31)H(33)	106 (4)
N(2)C(3)C(31)	122.4 (6)	N(4)C(41)H(41)	119 (5)
N(4)C(3)C(31)	120.9 (6)	N(4)C(41)H(42)	104 (4)
C(3)N(4)C(5)	113.5 (5)	N(4)C(41)H(43)	115 (6)
C(3)N(4)C(41)	123.7 (5)	C(6)C(7)H(71)	110 (3)
C(5)N(4)C(41)	122.7 (5)	C(6)C(7)H(72)	106 (3)
SC(5)N(4)	106.3 (4)	C(6)C(7)H(73)	105 (3)
SC(5)N(5)	134.4 (4)	N(6)C(8)H(81)	113 (4)
N(4)C(5)N(5)	119.2 (5)	N(6)C(8)H(82)	115 (3)
C(5)N(5)C(6)	123.6 (5)	N(6)C(8)H(83)	115 (4)
N(5)C(6)N(6)	116.7 (5)	C(6)N(6)H(61)	120 (4)
N(5)C(6)C(7)	125.4 (5)	C(8)N(6)H(61)	116 (4)
N(6)C(6)C(7)	117.9 (5)		
C(6)N(6)C(8)	124.3 (5)		
F(1)BF(2)	106.9 (7)	HCH(methyl group)	
F(1)BF(3)	109.0 (7)		89–118 (7)
F(1)BF(4)	112.2 (7)		(mean 108)
F(2)BF(3)	103.3 (7)		
F(2)BF(4)	117.3 (8)		
F(3)BF(4)	107.8 (7)		
		FBF(occupancy 0.3)	
			99–125 (2)
			(mean 109)

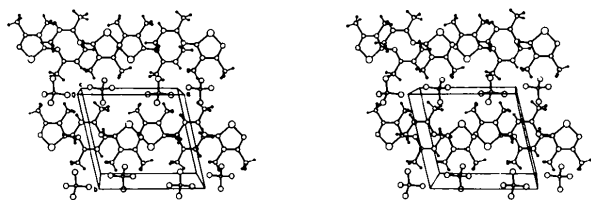


Fig. 3. Stereoscopic view of the packing of (II).

and $N(4^1)$ of the molecule at $x - \frac{1}{2}$, $-y + \frac{1}{2}$, z . $N(6) \cdots N(4^1)$ and $H(6) \cdots N(4^1)$ are 3.240(3) and 2.38(4) Å respectively. $N(6)H(6)N(4^1)$ is $163(2)^\circ$.

Bond distances and angles for (II) are listed in Table 7. The structure of (II) is shown in Fig. 1(b); it is a conjugated iminio salt of 1,2,4-thiadiazoline. The *N*-methyliminio group is *trans* to C(5) across the $N(5)-C(6)$ bond, so that a $N-S \cdots N$ linear arrangement as in (I) is not found in (II). In the formation of (II), after the bond switch at the S atom, a rotation about $N(5)-C(6)$ followed by hydrogen transfer must have occurred.

$S-N(2)$ (1.672 Å) and $S-C(5)$ (1.721 Å) are similar to the corresponding bonds in 1,2,4-thiadiazole and 1,2,4-thiadiazoline. The molecule is almost planar owing to the conjugation between the five-membered ring and the iminoethyliminio group. The exocyclic $N-C$ bonds, $C(5)-N(5)$ (1.309 Å), $N(5)-C(6)$ (1.322 Å) and $C(6)-N(6)$ (1.300 Å), are slightly shorter than the aromatic $C-N$ bond (1.34 Å). Although $N(6)$ is nominally an amino N atom, $C(6)-N(6)$ is close to the $C=N$ double-bond length. This is due to the high π -conjugation throughout the system. There is a very short intramolecular non-bonding contact between the S atom and the methyl group. The $S \cdots C(7)$ distance is 3.017(8) Å, which is significantly shorter than the sum of the van der Waals radii. $SC(5)N(5)$, $C(5)N(5)C(6)$ and $N(5)C(6)C(7)$ are larger than the corresponding angles in related compounds. This is ascribed to the planarity of the molecule and the steric hindrance between S and the methyl group.

The crystal structure viewed along **b** is shown in Fig. 3. There is a short contact between $N(6)H(61)$ and $F(1)$. $N(6) \cdots F(1)$ and $H(61) \cdots F(1)$ are 2.933(8) and 2.16(6) Å respectively. $N(6)H(61)F(1)$ is $173(6)^\circ$.

The structure of (III) with the atom numbering is shown in Fig. 1(c). Bond lengths and angles are listed in Table 8. (III) has been shown to be 1,2,3,5,6-pentamethyl-1,3,4,6-tetraaza-6a λ^4 -thiapentalenium tetrafluoroborate, a salt of the tetraaza analog of thiathiophthene. The $N-S$ distances are 1.983 and 1.833 Å. A similar example is (VIII), in which the $N-S$ distances are 1.901 and 1.948 Å (Hordvik & Julshamn, 1972). $S(6a)-N(1)$ (1.983 Å) is 14% longer than the $N-S$ single bond (1.74 Å) and $S(6a)-N(6)$ (1.833 Å) is 5% longer. The average lengthening of the $S-N$

Table 8. Bond lengths (Å) and angles ($^\circ$) for (III) with their e.s.d.'s

$S(6a)-N(1)$	1.983 (5)	$C(11)-H(11)$	0.92 (6)
$S(6a)-N(6)$	1.833 (5)	$C(11)-H(12)$	0.91 (5)
$S(6a)-C(3a)$	1.717 (6)	$C(11)-H(13)$	0.79 (8)
$N(1)-C(2)$	1.272 (8)	$C(21)-H(21)$	0.99 (8)
$C(2)-N(3)$	1.388 (8)	$C(21)-H(22)$	0.85 (8)
$N(3)-C(3a)$	1.330 (7)	$C(21)-H(23)$	0.89 (7)
$C(3a)-N(4)$	1.329 (7)	$C(31)-H(31)$	0.70 (7)
$N(4)-C(5)$	1.353 (8)	$C(31)-H(32)$	0.90 (7)
$C(5)-N(6)$	1.315 (8)	$C(31)-H(33)$	0.96 (6)
$N(1)-C(11)$	1.453 (9)	$C(51)-H(51)$	0.98 (9)
$C(2)-C(21)$	1.468 (10)	$C(51)-H(52)$	1.07 (10)
$N(3)-C(31)$	1.454 (9)	$C(51)-H(53)$	0.95 (9)
$C(5)-C(51)$	1.474 (11)	$C(61)-H(61)$	0.98 (6)
$N(6)-C(61)$	1.470 (9)	$C(61)-H(62)$	1.06 (7)
$B-F(1)$	1.29 (1)	$C(61)-H(63)$	1.00 (7)
$B-F(2)$	1.24 (2)		
$B-F(3)$	1.33 (1)		
$B-F(4)$	1.21 (2)		
$N(1)S(6a)N(6)$	165.3 (2)	$N(1)C(11)H(11)$	115 (4)
$N(1)S(6a)C(3a)$	81.9 (2)	$N(1)C(11)H(12)$	110 (3)
$N(6)S(6a)C(3a)$	83.4 (2)	$N(1)C(11)H(13)$	100 (6)
$S(6a)N(1)C(2)$	112.9 (4)	$C(2)C(21)H(21)$	119 (5)
$S(6a)N(1)C(11)$	121.6 (4)	$C(2)C(21)H(22)$	101 (5)
$C(2)N(1)C(11)$	125.4 (6)	$C(2)C(21)H(23)$	117 (4)
$N(1)C(2)N(3)$	111.8 (5)	$N(3)C(31)H(31)$	126 (5)
$N(1)C(2)C(21)$	126.9 (6)	$N(3)C(31)H(32)$	104 (5)
$N(3)C(2)C(21)$	121.2 (6)	$N(3)C(31)H(33)$	112 (4)
$C(2)N(3)C(3a)$	115.5 (5)	$C(5)C(51)H(51)$	103 (5)
$C(2)N(3)C(31)$	122.8 (5)	$C(5)C(51)H(52)$	129 (6)
$C(3a)N(3)C(31)$	121.6 (5)	$C(5)C(51)H(53)$	105 (5)
$S(6a)C(3a)N(3)$	117.8 (4)	$N(6)C(61)H(61)$	112 (4)
$S(6a)C(3a)N(4)$	119.3 (4)	$N(6)C(61)H(62)$	110 (4)
$N(3)C(3a)N(4)$	122.9 (5)	$N(6)C(61)H(63)$	105 (4)
$C(3a)N(4)C(5)$	109.5 (5)	$F(1)BF(2)$	108 (1)
$N(4)C(5)N(6)$	115.5 (6)	$F(1)BF(3)$	116 (1)
$N(4)C(5)C(51)$	119.4 (6)	$F(1)BF(4)$	111 (1)
$N(6)C(5)C(51)$	125.1 (6)	$F(2)BF(3)$	108 (1)
$S(6a)N(6)C(5)$	112.3 (4)	$F(2)BF(4)$	107 (1)
$S(6a)N(6)C(61)$	121.4 (4)	$F(3)BF(4)$	106 (1)
$C(5)N(6)C(61)$	126.3 (6)		
		HCH(methyl group)	
		77-125 (7)	
		(mean 99)	

bonds in (VIII) is 10% and that of the $S-S$ bonds in the thiathiophthenes is 12%. Such $N-S$ distances are also reported in compounds which contain an S^{IV} atom as a central atom in an $N-S-S$ chain, Table 9.

$C(3a)-S(6a)$ (1.717 Å) is shorter than the corresponding lengths in (I), (II) and (VIII). $N(1)-C(2)$ (1.272 Å) has the normal $C=N$ double-bond length and is shorter than $C(5)-N(6)$ (1.315 Å). This corresponds to the fact that $S(6a)-C(1)$ is longer than $S(6a)-N(6)$ and that $C(2)-N(3)$ (1.388 Å) is longer than $N(4)-C(5)$ (1.353 Å). The molecule is approximately planar. The dihedral angle between the two five-membered rings is 1.3° . Apart from the methyl groups the maximum deviation from the plane of the eight-membered ring is 0.026 Å.

Based on the determined structures, it can be concluded that a bond switch took place at the

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).

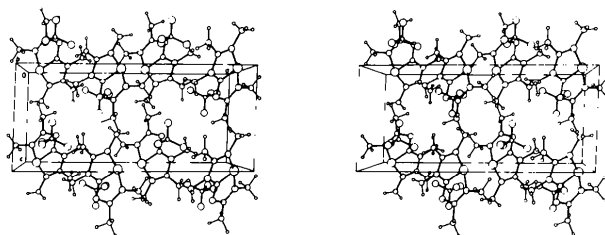


Fig. 4. Stereoscopic view of the packing of (III).

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

BY FUJIKO IWASAKI*

Department of Materials Science, The University of Electro-Communications, Chofu-shi, Tokyo 182, Japan

AND KIN-YA AKIBA

Department of Chemistry, Faculty of Science, Hiroshima University, Higashisendamachi, Hiroshima 730, Japan

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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

* To whom all correspondence should be addressed.