moléculaire est $\bar{1}$, de deux positions pour les fragments de molécule appartenant au groupe ponctuel $2/m$ et, bien entendu, se réduiraient à une position unique pour les fragments répondant à la symétrie *mmm*.

A en juger d'après les tenseurs d'agitation thermique, ce dernier cas semble bien réalisé par les carbones des carbonyles et les atomes des cycles benzéniques. Par contre, c'est probablement une séparation trop importante des positions à superposer qui masque l'observation des hydrogènes éthyliquement exocycliques.

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The Structures of 3,5-Dichloro-1,1-diisopropylamino-1H-1λ^4,2,4,6-thiatriazine (I) and 3,5-Bis(phenylthio)-1,1-diisopropylamino-1H-1λ^4,2,4,6-thiatriazine (II)*

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(*Received* 12 *October* 1978; *accepted* 2 *January* 1979)

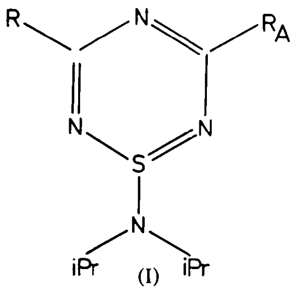
Abstract

The structures of compounds (I) and (II) have been established by X-ray crystallography from diffractometer data. Crystals of (I) ($C_8H_{14}Cl_2N_4S$) are orthorhombic, space group *Pnam*, with $a = 13 \cdot 170$ (7), $b = 7 \cdot 537$ (3), $c = 13 \cdot 137$ (4) Å, $Z = 4$ (*i.e.* the molecule has mirror symmetry). Crystals of (II) ($C_{20}H_{24}N_4S_3$) are monoclinic, space group $P2_1/c$, with $a = 8 \cdot 225$ (1), $b = 16 \cdot 684$ (4), $c = 16 \cdot 411$ (7) Å, $\beta = 93 \cdot 84$ (2)°, $Z = 4$. The structures were refined to $R = 0 \cdot 039$ for 668 reflexions of (I) and to $R = 0 \cdot 067$ for 1714 reflexions of (II). The thia(IV)triazine ring in both (I) and (II) is non-planar. The S(IV) atom situated at the top of a distorted trigonal pyramid has in both compounds different S—N bond lengths. Nevertheless, their means (1·633 and 1·631 Å) agree with each other and with values reported in the literature.

* This paper is part VI of the series: Stereochemical Investigations of Heterocyclic Compounds.

Introduction

The 1-amino-substituted 1H-1λ^4,2,4,6-thiatriazines form a new class of heterocyclic molecules (Schramm, Voss, Rembarz & Fischer, 1974), which can be characterized by a tri-nitrogen-coordinated sulphur centre. This moiety raises questions in the field of chemical bonding and molecular conformation. In order to shed light on these questions X-ray analysis of three related compounds depicted by a general formula



(I)

(I) $R = R_A = Cl$
(II) $R = R_A = S—C_6H_5$
(III) $R = Cl$, $R_A = NH—C_6H_{11}$

0567-7408/79/040860-07$01.00

has been performed. The structure of 3-chloro-5-cyclohexylamino-1,1-diisopropylamino-1H-λ^4,2,4,6-thiatriazine (III), where $R \neq R_A$ (Kálmán, Argay, Fischer, Rembarz & Voss, 1977), has been published. Now we report the structures of (I) and (II).

Experimental

Compound (I)

3,5-Dichloro-1,1-diisopropylamino-1H-1λ^4,2,4,6-thiatriazine. Crystals (m.p. 387–389 K) were obtained as described by Schramm, Voss, Michalik, Rembarz & Fischer (1975).

Crystal data

$C_8H_{14}Cl_2N_4S$, M_r = 269·45, orthorhombic, a = 13·170 (7), b = 7·537 (3), c = 13·137 (4) Å, V = 1304 Å^3, D_c = 1·371 Mg m^{-3}, Z = 4, $F(000)$ = 560, $\mu[\lambda$(Mo $K\bar{\alpha}$) = 0·7107 Å] = 0·574 mm^{-1}, space group *Pnam* (from systematic absences and refinement).

Intensities of 668 independent reflexions were collected on a Syntex $P2_1$ computer-controlled four-circle diffractometer equipped with a graphite monochromator. Cell constants were determined by least-squares refinement from the setting angles of 15 reflexions. A slow decomposition of the specimen was indicated by the need for frequent recentring. A similar correction to that applied for (III) (Kálmán *et al.*, 1977) was made after data reduction had been carried out. No absorption correction was applied.

The structure was solved in the non-centrosymmetric space group $Pna2_1$. 30 out of 145 normalized structure factors having $E \geq 1·1$ with highest products $E_o \times E_c$ were phased on the basis of a partial structure defined by the parameters of three peaks assigned as Cl and C atoms (1 : 2) from a Patterson map. In the E map calculated after recyclization of these phases in *SHELX* (Sheldrick, 1976), eight atoms were located and the subsequent structure factor calculation (R = 0·38) and Fourier synthesis gave the positions of the missing seven non-hydrogen atoms. The symmetry of the Fourier map indicated that the molecule lies on a mirror plane. Therefore, the space group was changed to *Pnam*. Before refinement the positions of eight H atoms were generated assuming regular tetrahedral C atoms with C—H = 1·08 Å. These moieties were treated as rigid groups. Full-matrix least-squares refinement of atomic coordinates of the ten non-hydrogen atoms in the asymmetric unit for the centrosymmetric space group with anisotropic vibrational parameters resulted in somewhat better residuals with a weighting scheme $w = k/[\sigma^2(F_o) + gF_o^2]$ (final k = 2·3343 and g = 0·000747) than those for the non-centrosymmetric space group $Pna2_1$:

Residual	*Pnam*	$Pna2_1$
$R = \sum \Delta/\sum \lvert F_o\rvert$	0·039	0·043
$R_w = \sum w^{1/2}\Delta/\sum w^{1/2}\lvert F_o\rvert$	0·041	0·046
$R_G = (\sum w\Delta^2/\sum w\lvert F_o\rvert^2)^{1/2}$	0·055	0·056.

Compound (II)

3,5-Bis(phenylthio)-1,1-diisopropylamino-1H-1λ^4,-2,4,6-thiatriazine was prepared by dropwise addition of Na thiophenolate (5·3 g in dry methanol) to a solution of (I) (5·5 g in 200 ml dry methanol) with intensive stirring. After one day the separated NaCl was removed and a small amount of water added. The product (m.p. 425–427 K) was crystallized from a water–ethanol mixture with a yield of 81%.

Table 1. *Fractional coordinates* (× 10^4) *for* (I)

E.s.d.'s are given in parentheses.

	x	y	z
S(1)	1799 (2)	2310 (2)	2500
N(2)	2145 (3)	1129 (5)	1497 (3)
C(3)	2366 (3)	−529 (6)	1653 (3)
N(4)	2461 (4)	−1478 (6)	2500
N(5)	591 (4)	2305 (6)	2500
C(6)	−18 (6)	634 (7)	2500
C(7)	64 (6)	4056 (7)	2500
C(8)	−643 (5)	516 (8)	1535 (5)
C(9)	298 (5)	5097 (8)	1544 (5)
Cl(10)	2570 (1)	−1750 (2)	548 (1)

Table 2. *Fractional coordinates* (× 10^4) *for* (II)

E.s.d.'s are given in parentheses.

	x	y	z
S(1)	−1536 (2)	1538 (1)	3388 (1)
S(10)	2317 (2)	−90 (1)	3654 (1)
S(10A)	−2324 (2)	−73 (1)	1461 (1)
N(4)	−159 (6)	96 (2)	2632 (3)
N(2)	56 (5)	1027 (2)	3756 (3)
N(2A)	−2419 (5)	1010 (2)	2643 (3)
N(5)	−821 (5)	2315 (2)	2953 (3)
C(3)	518 (6)	417 (3)	3316 (4)
C(3A)	−1587 (7)	419 (3)	2355 (3)
C(6)	336 (7)	2253 (3)	2312 (3)
C(7)	−1367 (7)	3124 (3)	3233 (3)
C(8)	1992 (9)	2602 (4)	2597 (5)
C(9)	−782 (10)	3267 (4)	4110 (4)
C(8A)	−357 (10)	2621 (4)	1522 (4)
C(9A)	−3183 (10)	3188 (5)	3115 (5)
C(11)	3104 (7)	505 (3)	4470 (4)
C(12)	4338 (7)	1031 (3)	4343 (4)
C(13)	4966 (8)	1489 (4)	4985 (5)
C(14)	4410 (10)	1424 (4)	5756 (5)
C(15)	3211 (10)	889 (5)	5867 (4)
C(16)	2528 (8)	419 (4)	5236 (5)
C(11A)	−4156 (7)	427 (3)	1182 (4)
C(12A)	−4225 (9)	899 (4)	499 (4)
C(13A)	−5690 (14)	1250 (4)	231 (5)
C(14A)	−7028 (12)	1119 (5)	659 (6)
C(15A)	−6946 (10)	645 (5)	1337 (6)
C(16A)	−5506 (10)	307 (3)	1611 (4)

Crystal data

$C_{20}H_{24}N_4S_3$, M_r = 416·63, monoclinic, a = 8·225 (1), b = 16·684 (4), c = 16·411 (7) Å, β = 93·84°, V = 2247 Å^3, D_c = 1·232 Mg m^{-3}, Z = 4, $F(000)$ = 880, $\mu[\lambda(\text{Cu } K\bar{\alpha})$ = 1·5418 Å] = 2·97 mm^{-1}, space group $P2_1/c$ (from systematic absences).

Intensities of 2566 independent reflexions were collected on a Stoe two-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation (Kálmán, Simon, Schawartz & Horváth, 1974). After data reduction 852 reflexions with $|F_o| - 5\sigma(F) > 0$ were taken as unobserved. No absorption correction was applied. Cell constants were refined from precession photographs. The phases for 464 reflexions having $E \geq 1{\cdot}2$ were obtained with *SHELX* (Sheldrick, 1976) giving R = 0·31 for the non-hydrogen atoms. Prior to the refinement all H atoms were generated from assumed geometries with C—H = 1·08 Å. These moieties were refined as rigid groups. Two cycles of blocked full-matrix refinement for non-hydrogen atoms with isotropic vibrational parameters reduced R to 0·138. At this stage, in order to increase the ratio between the number of reflexions and the atomic parameters refined in an anisotropic cycle, atoms were arranged in three overlapping groups.

Table 3. *Fractional coordinates* ($\times 10^4$) *for hydrogen atoms of* (I) *with e.s.d.'s in parentheses*

	x	y	z
H(6)	547 (35)	−405 (65)	2500
H(7)	−710 (22)	3569 (78)	2500
H(81)	−1170 (5)	1612 (8)	1507 (5)
H(82)	−1058 (5)	−719 (8)	1532 (5)
H(83)	−148 (5)	567 (8)	880 (5)
H(91)	895 (5)	6038 (8)	1706 (5)
H(92)	−373 (5)	5798 (8)	1297 (5)
H(93)	544 (5)	4203 (8)	951 (5)

Table 4. *Fractional coordinates* ($\times 10^4$) *for* H *atoms of* (II) *with e.s.d.'s in parentheses*

	x	y	z
H(6)	55 (1)	163 (1)	219 (1)
H(7)	−82 (1)	357 (1)	286 (1)
H(81)	290 (1)	244 (1)	218 (1)
H(82)	226 (1)	230 (1)	317 (1)
H(83)	201 (1)	324 (1)	269 (1)
H(91)	53 (1)	323 (1)	412 (1)
H(92)	−122 (1)	284 (1)	453 (1)
H(93)	−112 (1)	386 (1)	429 (1)
H(81*A*)	49 (1)	258 (1)	105 (1)
H(82*A*)	−68 (1)	324 (1)	160 (1)
H(83*A*)	−142 (1)	227 (1)	135 (1)
H(91*A*)	−350 (1)	381 (1)	321 (1)
H(92*A*)	−395 (1)	280 (1)	345 (1)
H(93*A*)	−333 (1)	305 (1)	247 (1)
H(12)	481 (1)	108 (1)	375 (1)
H(13)	594 (1)	191 (1)	489 (1)
H(14)	491 (1)	179 (1)	625 (1)
H(15)	276 (1)	82 (1)	647 (1)
H(16)	158 (1)	−0 (1)	534 (1)
H(12*A*)	−313 (1)	100 (1)	18 (1)
H(13*A*)	−575 (1)	162 (1)	−30 (1)
H(14*A*)	−816 (1)	140 (1)	46 (1)
H(15*A*)	−802 (1)	54 (1)	166 (1)
H(16*A*)	−542 (1)	−4 (1)	216 (1)

Table 5. *Interatomic distances* (Å) *with their e.s.d.'s in parentheses for* (I) *and* (II)

The symmetry-equivalent distances for (I) can be seen in Fig. 1, the second column for (II) represents part *A* of the molecule.

	(I)	(II)	
S(1)—N(2)	1·655 (3)	1·644 (4)	1·638 (4)
N(2)—C(3)	1·300 (4)	1·318 (7)	1·306 (7)
C(3)—N(4)	1·329 (4)	1·331 (7)	1·343 (7)
S(1)—N(5)	1·590 (4)	1·610 (4)	
N(5)—C(6)	1·494 (6)	1·470 (7)	
N(5)—C(7)	1·491 (6)	1·503 (6)	
C(6)—C(8)	1·513 (5)	1·525 (9)	1·512 (9)
C(7)—C(9)	1·512 (5)	1·506 (9)	1·497 (10)
C(3)—Cl(10)	1·739 (3)	–	–
C(3)—S(10)	–	1·762 (5)	1·754 (5)
S(10)—C(11)	–	1·756 (6)	1·757 (6)
C(11)—C(12)	–	1·368 (8)	1·367 (9)
C(12)—C(13)	–	1·375 (10)	1·385 (13)
C(13)—C(14)	–	1·377 (12)	1·362 (15)
C(14)—C(15)	–	1·352 (11)	1·363 (13)
C(15)—C(16)	–	1·387 (10)	1·361 (11)
C(16)—C(11)	–	1·380 (9)	1·369 (10)

Table 6. *Bond angles* (°) *with their e.s.d.'s in parentheses for* (I) *and* (II)

Symmetry-equivalent bond angles for (I) can be seen in Fig. 1, the second column for (II) represents part *A* of the molecule.

	(I)	(II)	
N(2)—S(1)—N(2*A*)	105·6 (2)	107·3 (2)	
S(1)—N(2)—C(3)	117·0 (2)	116·8 (4)	117·4 (4)
N(2)—C(3)—N(4)	132·2 (3)	130·7 (5)	130·4 (5)
N(2)—C(3)—S(10)	–	117·7 (4)	119·7 (4)
N(2)—C(3)—Cl(10)	114·3 (2)	–	–
N(4)—C(3)—S(10)	–	111·6 (4)	109·9 (4)
N(4)—C(3)—Cl(10)	113·6 (2)	–	–
C(3)—N(4)—C(3*A*)	113·8 (4)	115·6 (4)	
C(3)—S(10)—C(11)	–	103·1 (3)	103·7 (3)
N(2)—S(1)—N(5)	105·9 (1)	105·9 (2)	105·0 (2)
S(1)—N(5)—C(6)	122·7 (3)	122·3 (3)	
S(1)—N(5)—C(7)	117·6 (3)	117·5 (4)	
C(6)—N(5)—C(7)	119·7 (4)	120·2 (4)	
N(5)—C(6)—C(8)	110·0 (3)	111·2 (5)	111·1 (5)
C(8)—C(6)—C(8*A*)	113·7 (5)	112·7 (5)	
N(5)—C(7)—C(9)	111·4 (3)	110·6 (5)	110·0 (5)
C(9)—C(7)—C(9*A*)	112·2 (5)	111·3 (6)	
S(10)—C(11)—C(12)	–	119·1 (5)	118·4 (5)
S(10)—C(11)—C(16)	–	120·3 (4)	120·5 (5)
C(11)—C(12)—C(13)	–	119·0 (6)	119·5 (7)
C(12)—C(13)—C(14)	–	121·9 (6)	119·0 (7)
C(13)—C(14)—C(15)	–	117·8 (7)	121·0 (9)
C(14)—C(15)—C(16)	–	122·3 (7)	120·3 (8)
C(15)—C(16)—C(11)	–	118·3 (6)	119·2 (6)
C(16)—C(11)—C(12)	–	120·6 (5)	121·0 (6)

Refinement with anisotropic vibrational parameters reduced R to 0·067 ($R_w = 0{\cdot}070$, $R_G = 0{\cdot}083$ and $R_{\text{total}} = 0{\cdot}096$). The k and g parameters in the weighting scheme, similar to that described above, refined to 1·000 and 0·0008, respectively. Each layer of reflexions from $h0l$ to $h16l$ was refined with its own scale factor.

In both analyses a bonded H-atom scattering factor was employed (Stewart, Davidson & Simpson, 1965) with complex neutral scattering factors for the remaining atoms (Cromer & Mann, 1968; Cromer & Liberman, 1970). All calculations were performed with *SHELX* (Sheldrick, 1976) adapted on a CDC 3300 computer in Budapest. The final coordinates for the non-hydrogen atoms are given in Tables 1 and 2, the parameters for H atoms in Tables 3 and 4 and the bond distances and angles in Tables 5 and 6.* A common atomic numbering for both structures is shown in Fig. 1.

Discussion

The conformation of the molecules (Figs. 2 and 3) can be described best in terms of the torsion angles (Table 7), Newman projections (Fig. 4) and the least-squares

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34118 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

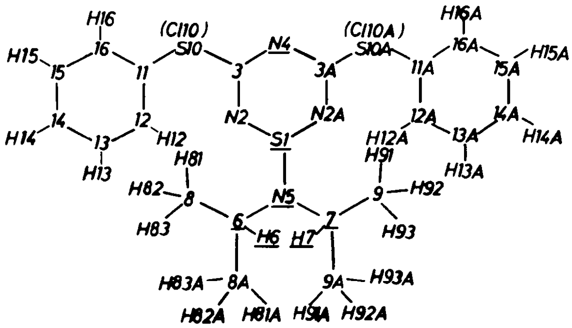


Fig. 1. Atomic numbering for (I) and (II). Atoms are carbon unless indicated otherwise. In (I), $R = R_A$ is represented by Cl(10) and Cl(10A) in parentheses and the atoms sitting on the mirror plane are underlined.

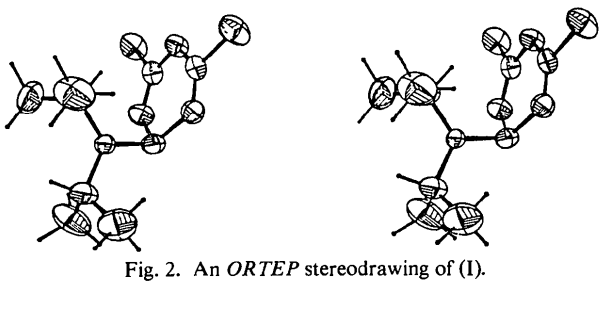


Fig. 2. An *ORTEP* stereodrawing of (I).

Table 7. *Endocyclic and some relevant exocyclic torsion angles (°) for* (I) (X = Cl) *and* (II) (X = S)

	(I)	(II)
S(1)–N(2A)–C(3A)–N(4)	7·2	9·0
N(2A)–C(3A)–N(4)–C(3)	4·2	1·1
C(3A)–N(4)–C(3)–N(2)	−4·2	−3·3
N(4)–C(3)–N(2)–S(1)	−7·2	−5·3
C(3)–N(2)–S(1)–N(2A)	15·6	13·2
N(2)–S(1)–N(2A)–C(3A)	−15·6	−14·9
X(10A)–C(3A)–N(2A)–S(1)	−172·4	−170·3
X(10A)–C(3A)–N(4)–C(3)	−176·2	180·0
N(5)–S(1)–N(2A)–C(3A)	96·5	97·5
N(5)–S(1)–N(2)–C(3)	−96·5	−98·5
X(10)–C(3)–N(4)–C(3A)	176·2	176·5
X(10)–C(3)–N(2)–S(1)	172·4	175·0

Estimated standard deviations vary between 0·7 and 1·5°.

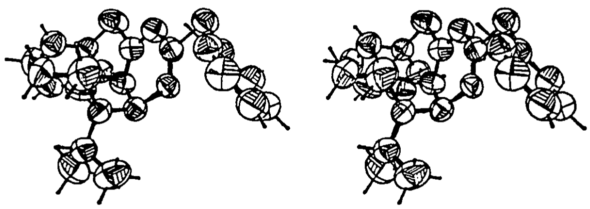


Fig. 3. An *ORTEP* stereodrawing of (II).

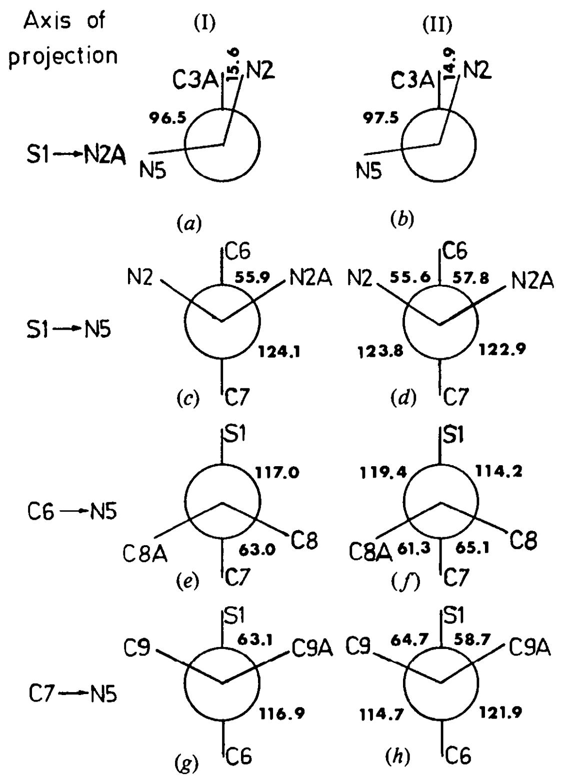


Fig. 4. Newman projections showing the conformations of the characteristic moieties for (I) and (II).

planes (Table 8). Comparison of the corresponding parameters of (I), (II) and (III) (Kálmán *et al.*, 1977) shows that the thia(IV)triazine rings are non-planar. In each ring the S atom is significantly out of the best plane for the remaining five atoms:

	ΔS	$\bar{\Delta}$ for the other five atoms
(I)	0·26 Å	0·011 Å
(II)	0·22	0·008
(III*a*)	0·36	0·036
(III*b*)	0·27	0·017.

To each thia(IV)triazine ring of quasi-sofa conformation, as opposed to $S_3N_4PPh_3$ and $S_3N_4AsPh_3$ (Holt & Holt, 1974; Holt, Holt & Watson, 1977), the exocyclic N(5) atom is linked pseudo-axially. In (I), the two isopropyl groups together with the endocyclic SN_2 moiety are related by a pseudo-threefold symmetry axis at N(5) perpendicular to the crystallographic mirror plane. In (II) this pseudo-threefold axis makes an angle <90° with the pseudo mirror plane bisecting S(1), N(4) and N(5). This deviation from 90° is even more pronounced in (III*a*) and (*b*). The angles between further relevant planes [*e.g.* phenyl rings of (II)] are given also in Table 8.

Table 8. *Equations of planes in the form AX + BY + CZ = D, where X, Y and Z are orthogonal coordinates* (Å) *related to the axes a*, b, c*

Deviations (Å × 10^3) of relevant atoms from the planes are given in square brackets; values for (I) precede those for (II). *X* = Cl for (I) and S for (II).

Plane (1) N(2), C(3), N(4), C(3*A*), N(2*A*)

$0·9770X + 0·2131Y = 2·9466$

$0·4897X + 0·6417Y - 0·5903Z = -2·5250$

[S(1) 260, 221; N(2) −5, 10; C(3) 13, −16; N(4) −17, 9; C(3*A*) 13, 2; N(2*A*) −5, −5; *X*(10) 79, −106; *X*(10*A*) 79, 21]

Plane (2) S(1), N(2), N(2*A*)

$0·8900X + 0·4560Y = 2·9026$

$0·5665X + 0·4526Y - 0·6886Z = -3·4408$

[C(3) −311, 269; N(4) −525, 459; C(3*A*) −311, 297; N(5) −1417, 1438]

Plane (3) S(1), N(5), C(6), C(7)

$Z = 3·2840$

$0·7646X + 0·0243Y + 0·6441Z = 2·7324$

[S(1) 0, 1; N(2) −1318, 1312; C(3) −1113, 1096; N(4) 0, −41; C(3*A*) 1113, −1166; N(2*A*) 1318, −1331; N(5) 0, −4; C(6) 0, 1; C(7) 0, 1]

Planes (4), (4*A*) for phenyl rings in (II)

$0·6807X - 0·7105Y + 0·1783Z = 2·4211$

$0·2271X + 0·8040Y + 0·5495Z = 0·9957$

[C(11) −8, −6; C(12) 8, 0; C(13) −2, 1; C(14) 5, 3; C(15) 5, −9; C(16) 2, 10]

Angles (°) between planes: (1)–(2) 14·8, 13·0; (1)–(3) 90·0, 89·4; (2)–(3) 90·0, 90·0; in (II): (1)–(4) 103·2, 72·4; (2)–(4) 93·4, 83·4; (3)–(4) 51·8, 56·8; (4)–(4*A*) 108·6

The hetero ring in both structures is, owing to its six π-electron system, formed by S–N and C–N multiple bonds (Table 5). The C(sp^3)–N(sp^2) lengths vary between 1·300 and 1·343 Å [theoretical C–N single-bond length 1·47 Å (Pauling, 1960)]. As in (III), in both (I) and (II) the S atom situated at the top of a distorted trigonal pyramid makes three S–N multiple bonds. In (I) the two endocyclic S–N lengths, apparently influenced by the symmetrical electron-withdrawing effect of the Cl atoms at C(3), are equal [1·655 (3) Å] and similar to those in *S,S*-diethyl-*N*-dichloroacetyl [1·673 (10) Å] and *S,S*-dimethyl-*N*-trichloroacetyl [1·667 (7) Å] sulphilimines (Kálmán, Sasvári & Kucsman, 1971, 1973). In (II) the endocyclic S–N bonds are also of equal length [1·638 (4), 1·644 (4) Å] but somewhat shorter than in (I) due to the diminished electron-withdrawing effect of the S-phenyl moieties. In both (I) and (II) the exocyclic S–N length [(I) 1·590 (4), (II) 1·610 (4) Å] is shorter than was expected by comparison with *N*-acyl sulphilimines, sulphurdiimides and related compounds (Kálmán, Sasvári & Kucsman, 1973; Gieren & Pertlik, 1976; Cameron, Duncanson & Morris, 1976; Eliel, Koskimies, McPhail & Swern, 1976; and references therein).* An explanation may be found in the observation (Kálmán *et al.*, 1977) that the mean values of the three S(IV)–N lengths belonging to the same S(IV)N_3 pyramid agree with each other within experimental error [(I), 1·633; (II), 1·631; (III), 1·643 Å] and with those of similar systems (Table 9). The grand mean of the S(IV)–N lengths for 13 compounds (Table 9) which possess one or two (symmetry-independent) S(IV)N_3 groups is 1·647 ± 0·011 Å. This suggests that we assume that any S(IV)N_3 pyramid has a certain capacity to buffer the electron-withdrawing or -releasing effect of the ligands bound to the N atoms in order to maintain the valence number around the S atom as near to four as possible. Therefore, rather than studying mean S–N lengths further, an analysis of the double-bond order *p* of these bonds has been performed.

The *p* values were calculated from Coulson's (1939) formula modified by Liquori & Vaciago (1956):

$$B = S - \frac{S - D}{1 + 0·6625(1 - p)/p}, \qquad (1)$$

* Kálmán (1976), classifying more than 80 S(IV)–N and S(VI)–N lengths, suggested the following distances as the most probable values for S(IV)–N bonds:

Bond character	π-Bond order	Bond polarization (δ)	Coordination of nitrogen	Bond length
Double bond	~1		2	1·53 Å
Strong multiple bonds	<1	weak	2	1·63
	<1	weak	3	1·64
Weak multiple bonds	≪1	strong	2	1·67
	≪1	strong	3	1·68.

Table 9. *Comparison of bond lengths and their double-bond order* (p_i), *valence number* (V) *and mean bond angles for trigonal pyramidal* S(IV)N_3 *moieties in* 13 *compounds*

Δ	d_1	d_2	d_3	d_{mean}	p_1	p_2	p_3	V	Δ	ρ_{mean}
(*a*)	1·590 (4)	1·655 (3)	1·655 (3)	1·633 Å	0·540	0·285	0·285	4·12	3·0%	105·8°
(*b*)	1·610 (4)	1·638 (4)	1·644 (4)	1·631	0·475	0·345	0·320	4·14	3·5	106·1
(*c*)	1·645 (5)	1·621 (6)	1·668 (6)	1·645	0·325	0·415	0·245	3·99	0·3	107·2
	1·634 (6)	1·620 (6)	1·670 (5)	1·641	0·365	0·420	0·240	4·03	0·7	106·1
(*d*)	1·513 (4)	1·740 (4)	1·744 (4)	1·666	0·925	0·025	0·020	3·97	0·7	103·8
(*e*)	1·582	1·682	1·689	1·651	0·575	0·195	0·175	3·95	1·3	101·3
(*f*)	1·546	1·691	1·693	1·643	0·740	0·170	0·160	4·07	1·8	105·2
(*g*)	1·554 (5)	1·669 (4)	1·686 (3)	1·636	0·705	0·240	0·185	4·13	3·2	106·3
(*h*)	1·602 (10)	1·667 (10)	1·693 (10)	1·654	0·490	0·245	0·165	3·90	2·5	106·2
(*i*)	1·594 (7)	1·662 (6)	1·692 (8)	1·636	0·525	0·410	0·165	4·10	2·5	106·4
(*j*)	1·620 (5)	1·689 (4)	1·689 (4)	1·666	0·420	0·175	0·175	3·77	5·7	–
	1·638 (5)	1·674 (4)	1·674 (4)	1·662	0·350	0·226	0·226	3·80	5·0	–
(*k*)	1·702 (3)	1·621 (3)	1·623 (3)	1·649	0·140	0·415	0·410	3·97	0·7	107·8
(*l*)	1·64	1·62	1·65	1·637	0·365	0·420	0·307	4·09	2·2	107·3
	1·68	1·63	1·66	1·656	0·205	0·380	0·275	3·86	3·5	106·3
(*m*)	1·643	1·643	1·643	1·643	0·333	0·333	0·333	4·00	–	101·7

(*a*) Compound (I); (*b*) compound (II) (present work); (*c*) compound (III) (Kálmán *et al.*, 1977); (*d*) 1-phenylimino-2,5-diphenyl-1λ^4,2,5-thiadiazolidine-3,4-dione (Neidlein *et al.*, 1977); (*e*) 1-ethyl-1-phenyliminium-2,5-diphenyl-1λ^4,2,5-thiadiazolidine-3,4-dione.BF_4; (*f*) 1-tosylimino-2,5-di-*tert*-butyl-1λ^4,2,5-thiadiazolidine-3,4-dione (Gieren *et al.*, 1978); (*g*) $S_3N_4AsPh_3$ (Holt *et al.*, 1977); (*h*) $S_3N_4PPh_3$ (Holt & Holt, 1974); (*i*) $S_3N_3PF_2$ (Weiss *et al.*, 1974); (*j*) S_4N_5Cl (Chivers & Fielding, 1978); (*k*) S_5N_6 (Chivers & Proctor, 1978); (*l*) $[R_4N][S_4N_5]$ (Flues *et al.*, 1976); (*m*) $K_2[S(NTs)_3]$ (Gieren & Narayanan, 1975).

where B is an observed bond length, S is the pure S(IV)—N single and D the pure double-bond distance. S = 1·75 Å was calculated with the equation of Schomaker & Stevenson (1941) from atomic radii and electronegativities given by Pauling (1960) for N and Truter (1962) for S(IV), while D = 1·50 Å was deduced as follows. The trigonal pyramidal S(IV)N_3 groups can be characterized by two extreme arrangements of bonding: (1) One double bond ($p = 1$) is accompanied by two single bonds ($p = 0$). (2) S(IV) is surrounded by three multiple bonds of the same double-bond order $p = \frac{1}{3}$. The first arrangement is represented approximately by 1-phenylimino-2,5-diphenyl-1λ^4,2,5-thiadiazolidine-3,4-dione (Neidlein, Leinberger, Gieren & Dederer, 1977) while the second was found in $K_2[S(N{-}SO_2{-}C_6H_4CH_3)_3]$ (Gieren & Narayanan, 1975). Both are depicted in Fig. 5. As can be seen the bond distances in $K_2[S(NTs)_3]$ agree well with the grand mean of S(IV)—N distances (1·647 Å). This prompted us to attach $p = \frac{1}{3}$ to the bond distance 1·643 Å and introduce it with S = 1·75 Å into (1) in order to deduce D.

With p assigned to each experimental S(IV)—N distance in Table 9, a study of valence number $V = \sum (s_i + p_i) \simeq 4{\cdot}0$ (where s_i is the single-bond order, $\simeq 1$) for 16 independent S(IV)N_3 groups has shown the following:

(*a*) The e.s.d. from V = 4·0 is 2·0–2·5% which is within the range of experimental error.

(*b*) Apart from S_4N_5Cl (Chivers & Fielding, 1978), in which there is strong competition between the sulphurdiimide and S(IV)N_3 moieties, deviation from 4·0 does not exceed 5%.

Fig. 5. Two characteristic arrangements of S—N lengths for a trigonal pyramidal S(IV)N_3 moiety as found in (*a*) 1-phenylimino-2,5-diphenyl-1λ^4,2,5-thiadiazolidine-3,4-dione (Neidlein *et al.*, 1977) and (*b*) $K_2[S(NTs)_3]$ (Gieren & Narayanan, 1975).

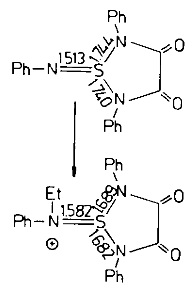


Fig. 6. The effect of alkylation (R = Et) of the exocyclic N atom on the bonding of the S(IV)N_3 moiety in 1-phenylimino-2,5-diphenyl-1λ^4,2,5-thiadiazolidine-3,4-dione (Gieren *et al.*, 1978).

(*c*) Thus the trend of the trigonal pyramidal S(IV)N_3 moieties to maintain an equilibrium of the bonding around S atoms can be described best in terms of the sum of bond orders. As can be seen in Fig. 6 the alkylation (R = ethyl) of 1-phenylimino-2,5-diphenyl-1λ^4,2,5-thiadiazolidine-3,4-dione (Gieren, Dederer & Abelein, 1978) alters significantly the S—N distances in the derivative obtained, but the valence number (V = 3·95) remains almost identical with that of the parent

(a)

(b)

(c)

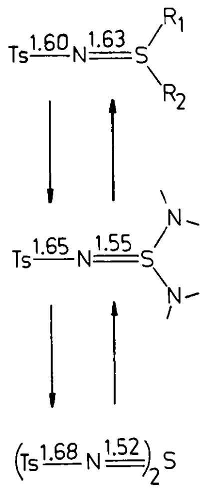


Fig. 7. A comparison of the S—N lengths found to be characteristic of the Ts—N=S< moiety (*a*) in *N*-tosylsulphilimines (mean values for three molecule structures), (*b*) in 1-tosylimino-2,5-di-*tert*-butyl-1λ^4,2,5-thiadiazolidine-3,4-dione and (*c*) in ditosyl-sulphuridiimide (Gieren & Pertlik, 1974).

compound (V = 3·97). A similar phenomenon is observed if the bond lengths and valence numbers of (I) and (II) are compared.

Accordingly, the rule revealed may give an answer to the question why the Ts—N=S< bonding (Fig. 7) observed in 1-tosylimino-2,5-di-*tert*-butyl-1λ^4,2,5-thiadiazolidine-3,4-dione (Gieren, Dederer & Abelein, 1978) differs significantly from those found in the corresponding *S*,*S*-diphenyl-, *S*,*S*-dimethyl- and *S*-phenyl-*S*-propyl-*N*-tosyl sulphilimines (Kálmán, Duffin & Kucsman, 1971; Cameron, Hair & Morris, 1973; Kálmán & Sasvári, 1972). If we accept the fact, as indicated by V = 4·07, that S—N distances in the S(IV)N_3 group of 1-tosylamino-2,5-di-*tert*-butyl-1λ^4,2,5-thiadiazolidine-3,4-dione are governed by the rule discussed above and the endocyclic S—N bonds cannot gain more multiple-bond character than they have, then the short exocyclic double bond is explained. This short S=N double bond, similar to that in ditosyl-sulphurdiimide (Gieren & Pertlik, 1974) is accompanied by a considerably weakened S(VI)—N bond.

The valence numbers for (I) and (II), which are slightly greater than 4·0, and that observed for (III) have raised further questions on the substituent effect. These are to be studied by further structure determinations of 1*H*-1λ^4,2,4,6-thiatriazine derivatives.

We thank Dr Alfred Gieren for continuous information about his own work and his invaluable comment and criticism on the study of S(IV)N_3 groups.

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