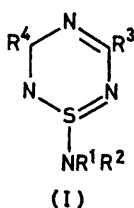


Stereochemical Investigations of Heterocyclic Compounds. Part 4.† Crystal and Molecular Structure of 3-Chloro-5-cyclohexylamino-1-di- isopropylamino-1*H*-1,2,4,6-thia(IV)triazine

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The structure of the title compound has been established by X-ray crystallography from diffractometer data. Crystals are monoclinic, space group $P2_1$, cell dimensions $a = 12.730(3)$, $b = 12.085(3)$, $c = 13.369(4)$, $\beta = 115.91(2)^\circ$, $Z = 4$ (i.e. two molecules in the asymmetric unit). The structure was solved by direct methods and refined by least-squares calculations to R 0.050 for the total 2 363 reflections. The thia(IV)triazine ring in both symmetry-independent molecules (A) and (B) is clearly nonplanar. The S^{IV} atom situated at the top of a distorted trigonal pyramid makes three different S–N bonds (mean for each type: 1.669, 1.640, and 1.621 Å). Their mean (1.643 Å) agrees with the means of reported values.

THE 1-amino-substituted 1*H*-1,2,4,6-thia(IV)triazines have been described¹ as a new class of heterocyclic compounds which contain a tri-nitrogen co-ordinated sulphur centre. The triazines are known to possess significant biological activities (e.g. they are potential herbicides²), so that their new derivatives also deserve manifold structural investigations. It was of primary importance to unravel the conformation of the six-membered thia(IV)triazine ring (I) with different substituents: R¹, R², R³, and R⁴.



As six π electron systems containing sulphur are not necessarily planar,³⁻⁵ we decided to examine these compounds by X-ray diffraction. Also only a few S^{IV}–N bonds^{6,7} linked to carbon through nitrogen have been studied by X-ray diffraction, even taking into account some of the sulphur di-imides.⁸ We describe here the structure of the title compound, with three

† Part III, ref. 3.

¹ W. Schramm, G. Voss, G. Rembarz, and E. Fischer, *Z. Chem.*, 1974, **14**, 471.

² E. Knüsli, *Chem. and Ind.*, 1968, 1666.

³ Part III, M. Michalik, E. Fischer, G. Rembarz, G. Voss, and W. Storek, *J. prakt. Chem.*, 1977, in the press.

⁴ G. A. Wieggers and A. Voss, *Proc. Roy. Soc.*, 1962, 387.

⁵ O. Glemser, *Angew. Chem.*, 1963, **75**, 697.

different substituents [(I); R¹ = R² = CH(Me)₂, R³ = Cl, R⁴ = C₆H₁₁NH].

EXPERIMENTAL

Preparation.—The title compound was prepared by the addition of cyclohexylamine (12 g) to a solution of 3,5-dichloro-1-di-isopropylamino-1*H*-1,2,4,6-thia(IV)triazine⁹ (16.2 g) in diethyl ether (200 ml). The solution obtained was evaporated after filtration from the resulting hydrochloride, and ethanol added. The product (m.p. 118–120 °C) was crystallized by dropwise addition of water and kept under argon until X-ray measurements were made.

Crystal Data.—C₁₄H₂₆ClN₅S, $M = 331.91$. Monoclinic, $a = 12.730(3)$, $b = 12.085(3)$, $c = 13.369(4)$ Å, $\beta = 115.91(2)^\circ$, $U = 1\ 849.98$ Å³, $D_c = 1.191$, $Z = 4$ (two molecules in the asymmetric unit), $D_m = 1.18$ g cm⁻³, $F(000) = 712$. Space group $P2_1$ (from systematic absences and Wilson's statistics confirmed by the structure determination and refinement). Mo- K_{α} radiation, $\lambda = 0.710\ 69$ Å; $\mu(\text{Mo-}K_{\alpha}) = 2.78$ cm⁻¹. A crystal of maximum dimension 0.4 mm was mounted on a Syntex $P2_1$ computer-controlled four-circle diffractometer equipped with graphite monochromator. Cell constants were determined during alignment procedures by least-squares refinement of the setting angles of 15 carefully centred reflections. A slow decomposition of the specimen was indicated by the fre-

⁶ (a) A. Kálmán, K. Sasvári, and Á. Kucsman, *Chem. Comm.*, 1971, 1447; (b) *Acta Cryst.*, 1973, **B29**, 1241; (c) A. F. Cameron, F. D. Duncanson, and D. G. Morris, *Acta Cryst.*, 1976, **B32**, 1998.

⁷ S. Sato, T. Yoshioka, and C. Tamura, *Acta Cryst.*, 1975, **B31**, 1385.

⁸ G. Leandri, V. Busetti, G. Valle, and M. Mammi, *Chem. Comm.*, 1970, 413; R. T. Kops, E. van Aken, and H. Schenk, *Acta Cryst.*, 1973, **B29**, 913.

⁹ W. Schramm, G. Voss, M. Michalik, G. Rembarz, and E. Fischer, *Z. Chem.*, 1975, **15**, 19.

quent automatic recentering procedures. A correction was made for this, after the Lorentz and polarization corrections had been made, by the aid of a linear function, deduced from the monotonic decrease of the intensities of three check reflections (100, 020, and 001) according to $|F_o|_{\text{corr.}} = |F_o|_m[1 + 0.22(n/N)]$, where n is the serial number of the n^{th} reflections to be corrected, N the total number of intensity measurements (2 642), and 0.22 the mean of the three scale factors obtained for each check reflection by regression analysis. After this correction had been made 70 of the 2 363 independent reflections collected with $F - 5\sigma(F) < 0$ were considered unobserved. No absorption correction was applied.

0.064 for the total 2 363 reflections). Weights were $w = k/[\sigma^2(F_o) + gF_o^2]$ where k and g refined to 1.0 and 0.001 107, respectively. A bonded hydrogen atom scattering factor¹¹ was employed with complex neutral atom scattering factors^{12,13} for the remaining atoms. All calculations were performed with the program SHELX.¹⁰ Final co-ordinates for non-hydrogen atoms are given in Table 1, and for hydrogen atoms in Table 2. Structure factors calculated with final atomic parameters and anisotropic thermal parameters for non-hydrogen atoms are listed in Supplementary Publication No. SUP 22020 (16 pp., 1 microfiche)* Bond distances, angles, and torsion angles are listed in Tables 3–5.

TABLE 1

Final fractional co-ordinates ($\times 10^4$) for non-hydrogen atoms with estimated standard deviations in parentheses

	Molecule (A)			Molecule (B)		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
Cl	7 307(2)	−1 096(1)	−951(2)	−412(2)	7 925(2)	1 952(1)
S	6 924(1)	1 424(2)	944(1)	1 460(1)	6 400	4 979(1)
N(1)	7 000(5)	188(4)	425(4)	495(5)	7 160(5)	3 941(4)
N(2)	7 409(4)	1 034(4)	−997(4)	1 553(5)	6 888(4)	2 855(4)
N(3)	7 559(4)	2 297(4)	465(4)	2 594(4)	6 241(4)	4 741(3)
N(4)	7 871(4)	2 839(4)	−1 037(4)	3 343(5)	6 089(5)	3 466(4)
N(5)	5 518(4)	1 692(5)	428(4)	786(5)	5 214(5)	4 806(4)
C(1)	7 225(5)	232(5)	−420(5)	705(6)	7 231(5)	3 082(5)
C(2)	7 588(5)	2 061(5)	−491(5)	2 476(5)	6 394(5)	3 717(4)
C(3)	8 140(5)	3 990(5)	−661(5)	4 461(6)	5 650(6)	4 264(6)
C(4)	7 883(6)	4 727(5)	−1 648(6)	4 502(7)	4 411(8)	4 270(8)
C(5)	8 192(7)	5 924(6)	−1 302(7)	5 708(8)	3 981(9)	5 081(9)
C(6)	9 459(7)	6 038(7)	−419(7)	6 681(8)	4 470(10)	4 894(8)
C(7)	9 672(6)	5 302(6)	561(6)	6 627(7)	5 701(10)	4 875(9)
C(8)	9 396(5)	4 104(6)	221(5)	5 432(7)	6 122(9)	4 014(8)
C(9)	4 809(6)	1 767(6)	−758(6)	339(6)	4 615(6)	3 763(6)
C(10)	3 621(7)	1 239(10)	−1 123(8)	−951(7)	4 373(9)	3 305(7)
C(11)	4 702(8)	2 972(9)	−1 208(7)	989(8)	3 543(8)	3 852(7)
C(12)	5 123(6)	2 222(7)	1 207(6)	814(6)	4 701(6)	5 837(5)
C(13)	5 118(8)	1 394(11)	2 036(8)	266(8)	5 469(8)	6 389(7)
C(14)	5 798(8)	3 229(10)	1 734(10)	2 030(6)	4 355(7)	6 643(6)

Structure Determination and Refinement.—The structure was solved by direct methods with the program system SHELX,¹⁰ by use of 322 normalized structure factors having $E \geq 1.3$. Four E maps were computed, of which one with the best consistency gave the positions of 23 of the 42 non-hydrogen atoms (R 0.32). One successive cycle of structure-factor and Fourier calculations allowed the location of the missing 19 non-hydrogen atoms (R 0.19). Before refinement the positions of the hydrogen atoms were generated assuming regular tetrahedra for carbon atoms and sp^2 hybridization for N(4) with distances constrained to 1.08 Å. These moieties were treated throughout the refinement as rigid groups.

Owing to the large number of atomic parameters to be refined on a CDC 3300 computer with limited memory, 1 757 reflections were selected ($\sin\theta_{\text{max.}} 0.35$) for the refinement and the atomic positions of the two symmetry-independent molecules were refined separately by blocked full-matrix least-squares methods with isotropic thermal parameters (R 0.085). Similarly, in the anisotropic procedure there were the 42 non-hydrogen atoms arranged in four groups and refined separately. The refinement was terminated at R 0.041 [$R' = (\sum w\Delta^2/\sum w|F_o|^2)^{1/2} = 0.055$] for the reflections applied in the refinement (R 0.050, and R'

* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1976, Index issue.

¹⁰ SHELX, Crystal Structure Calculation Program, 1975, G. M. Sheldrick, University of Cambridge.

DISCUSSION

Conformation.—The thia(IV)triazine ring in both symmetry-independent molecules (A) and (B) is visibly non-planar. Each has, as shown by the torsion angles (Table 5), a twisted half-boat conformation (atom numbering is shown in Figure 1). The heterocyclic ring is more nearly flat than is the N_3S_3 ring in triphenylphosphine trisulphur tetranitride,¹⁴ but, in the title compound, the two molecules have the hetero-ring unequally flattened. Thus, molecule (A) shows a mean deviation from planarity of 0.035 Å, with the S atom 0.36 Å from the best plane [plane (1)] through the five atoms, while for molecule (B) corresponding values are 0.020 Å, with the S atom 0.27 Å out of the plane (*cf.* Table 6). The dihedral angles between the normals to plane (1) and to the planes formed by N(1), S, and N(3) moieties are 159.0 [molecule (A)] and 163.8° [molecule (B)] *vs.* 139.0° in the S_3N_3 -NPPH₃ molecule. The S atoms are linked to three atoms and, as pointed out in ref. 14, 'would not be expected to employ the same bonding

¹¹ R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

¹² D. T. Cromer and D. Lieberman, *J. Chem. Phys.*, 1970, **53**, 1891.

¹³ D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

¹⁴ E. M. Holt and S. L. Holt, *J.C.S. Dalton*, 1974, 1990.

TABLE 2

Fractional co-ordinates ($\times 10^4$) and isotropic thermal parameters (U_i) for hydrogen atoms of molecules (*A*) and (*B*)

Atom	Molecule (<i>A</i>)				Molecule (<i>B</i>)			
	<i>x</i>	<i>y</i>	<i>z</i>	$U/\text{\AA}^2$	<i>x</i>	<i>y</i>	<i>z</i>	$U/\text{\AA}^2$
H(N4)	7 907(4)	2 608(4)	-1 801(4)	111(12)	3 203(5)	6 173(5)	2 612(4)	111(16)
H(3)	7 591(5)	4 243(5)	-274(5)	111(12)	4 582(6)	5 897(6)	5 084(6)	111(16)
H(41)	8 387(6)	4 447(5)	-2 073(6)	86(11)	3 857(7)	4 098(8)	4 518(8)	86(8)
H(42)	6 964(6)	4 676(5)	-2 205(6)	86(11)	4 304(7)	4 121(8)	3 443(8)	86(8)
H(51)	8 083(7)	6 404(6)	-2 023(7)	86(11)	5 720(8)	3 095(9)	4 982(9)	86(8)
H(52)	7 615(7)	6 236(6)	-970(7)	86(11)	5 846(8)	4 171(9)	5 919(9)	86(8)
H(61)	9 622(7)	6 888(7)	-142(7)	86(11)	7 502(8)	4 210(10)	5 557(8)	86(8)
H(62)	10 042(7)	5 804(7)	-774(7)	86(11)	6 623(8)	4 179(10)	4 108(8)	86(8)
H(71)	10 580(6)	5 366(6)	1 151(6)	86(11)	6 776(7)	5 995(10)	5 689(9)	86(8)
H(72)	9 129(6)	5 575(6)	947(6)	86(11)	7 300(7)	6 018(10)	4 667(9)	86(8)
H(81)	9 979(5)	3 810(6)	-114(5)	86(11)	5 299(7)	5 871(9)	3 191(8)	86(8)
H(82)	9 515(5)	3 617(6)	939(5)	86(11)	5 415(7)	7 014(9)	4 054(8)	86(8)
H(9)	5 257(6)	1 290(6)	-1 137(6)	111(16)	481(6)	5 161(6)	3 195(6)	111(13)
H(101)	3 142(7)	1 281(10)	-2 017(8)	133(8)	-1 330(7)	3 987(9)	2 495(7)	133(7)
H(102)	3 091(7)	1 573(10)	-747(8)	133(8)	-1 101(7)	3 857(9)	3 889(7)	133(7)
H(103)	3 834(7)	388(10)	-871(8)	133(8)	-1 351(7)	5 172(9)	3 255(7)	133(7)
H(111)	4 166(8)	3 042(9)	-2 093(7)	133(8)	872(8)	2 905(8)	4 360(7)	133(7)
H(112)	5 547(8)	3 336(9)	-998(7)	133(8)	692(8)	3 243(8)	3 011(7)	133(7)
H(113)	4 285(8)	3 401(9)	-769(7)	133(8)	1 902(8)	3 759(8)	4 184(7)	133(7)
H(12)	4 238(6)	2 510(7)	735(6)	111(16)	292(6)	3 957(6)	5 586(5)	111(13)
H(131)	4 626(8)	710(11)	1 528(8)	133(8)	191(8)	5 119(8)	7 099(7)	133(7)
H(132)	4 622(8)	1 784(11)	2 419(8)	133(8)	752(8)	6 234(8)	6 629(7)	133(7)
H(133)	5 936(8)	1 094(11)	2 674(8)	133(8)	-595(8)	5 630(8)	5 735(7)	133(7)
H(141)	5 781(8)	3 809(10)	1 112(10)	133(8)	2 104(6)	3 998(7)	7 412(6)	133(7)
H(142)	6 690(8)	3 101(10)	2 341(10)	133(8)	2 264(6)	3 743(7)	6 186(6)	133(7)
H(143)	5 296(8)	3 557(10)	2 141(10)	133(8)	2 610(6)	5 057(7)	6 823(6)	133(7)

orbital arrangement as a sulphur bonded to only two other atoms. Thus it is not surprising that it is not a part of the planar system'. The orientation of the 1-di-isopropylamino-group with respect to the thia(IV)-triazine ring, in both molecules, is axial as shown by the Newman projections [Figure 2 (a) and (b)]. (The orienta-

described by the Newman projections [Figure 2(c)—(h)]. The best plane [plane (4)] of the S, N(5), C(9),

TABLE 4

Bond angles ($^\circ$), with estimated standard deviations in parentheses

TABLE 3

Bond lengths (\AA), with estimated standard deviations in parentheses

	Molecule (<i>A</i>)	Molecule (<i>B</i>)
S-N(1)	1.668 (6)	1.670 (5)
N(1)-C(1)	1.281 (10)	1.289 (10)
C(1)-N(2)	1.322 (9)	1.310 (10)
N(2)-C(2)	1.384 (8)	1.372 (7)
C(2)-N(3)	1.325 (9)	1.323 (8)
N(3)-S	1.621 (6)	1.620 (6)
C(1)-C(1)	1.777 (7)	1.769 (6)
C(2)-N(4)	1.333 (9)	1.339 (10)
S-N(5)	1.645 (5)	1.634 (6)
N(4)-C(3)	1.467 (8)	1.456 (8)
C(3)-C(4)	1.506 (10)	1.498 (12)
C(4)-C(5)	1.517 (10)	1.533 (12)
C(5)-C(6)	1.533 (10)	1.488 (17)
C(6)-C(7)	1.507 (12)	1.490 (17)
C(7)-C(8)	1.512 (10)	1.539 (11)
C(8)-C(3)	1.522 (8)	1.526 (14)
N(5)-C(9)	1.444 (8)	1.449 (9)
C(9)-C(10)	1.513 (12)	1.509 (11)
C(9)-C(11)	1.559 (13)	1.513 (12)
N(5)-C(12)	1.485 (11)	1.497 (10)
C(12)-C(13)	1.496 (15)	1.531 (13)
C(12)-C(14)	1.479 (13)	1.508 (9)

tion of the triphenylphosphinylimino-moiety in S_3N_3 -NPPH₃ molecule is equatorial.) The S-N(5) bonds in both molecules are almost perpendicular to the corresponding planes. The dihedral angle between plane (1) and that of the N(2), S, and N(5) atoms [plane (3) in Table 6] is 91.7 for molecule (*A*) and 93.2° in molecule (*B*). The conformations of the 1-di-isopropylamino-groups are

	Molecule (<i>A</i>)	Molecule (<i>B</i>)
N(3)-S-N(1)	106.8(3)	107.2(3)
S-N(1)-C(1)	113.9(5)	114.4(5)
N(1)-C(1)-N(2)	135.3(6)	134.2(5)
C(1)-N(2)-C(2)	113.9(6)	115.6(6)
N(2)-C(2)-N(3)	126.6(6)	126.8(7)
C(2)-N(3)-S	118.0(4)	118.6(4)
N(1)-C(1)-Cl	112.9(5)	113.0(5)
N(2)-C(1)-Cl	111.9(5)	112.8(5)
N(2)-C(2)-N(4)	113.0(6)	113.9(6)
N(3)-C(2)-N(4)	120.3(6)	119.2(5)
C(2)-N(4)-C(3)	124.0(6)	124.4(6)
N(4)-C(3)-C(4)	109.4(5)	112.9(5)
N(4)-C(3)-C(8)	111.1(5)	109.2(6)
C(3)-C(4)-C(5)	111.6(6)	111.4(7)
C(4)-C(5)-C(6)	111.5(6)	113.4(9)
C(5)-C(6)-C(7)	110.2(7)	111.3(10)
C(6)-C(7)-C(8)	111.9(6)	111.5(8)
C(7)-C(8)-C(3)	110.4(5)	110.1(8)
C(8)-C(3)-C(4)	112.2(6)	112.2(8)
N(1)-S-N(5)	104.6(3)	102.4(3)
N(3)-S-N(5)	110.2(3)	109.0(3)
S-N(5)-C(9)	121.1(6)	122.4(5)
S-N(5)-C(12)	115.5(4)	115.7(4)
C(9)-N(5)-C(12)	120.1(6)	121.3(6)
N(5)-C(9)-C(10)	112.6(8)	112.8(8)
N(5)-C(9)-C(11)	112.9(6)	112.4(5)
C(10)-C(9)-C(11)	111.3(7)	109.1(7)
N(5)-C(12)-C(13)	110.1(8)	111.1(6)
N(5)-C(12)-C(14)	112.6(8)	112.1(7)
C(13)-C(12)-C(14)	112.8(8)	111.4(6)

C(12) moiety is also nearly perpendicular to the heteroring in both molecules (87.5 and 92.0°). The chlorine atoms are, opposite to S atoms, 0.40 [molecule (*A*)] and 0.13 \AA [molecule (*B*)] from plane (1) in accordance with the fairly coplanar Cl-C(1)-N(1)-S moieties (torsion angles are 180.0 and 174.1°).

TABLE 5
Torsion angles

	(A)	(B)
(a) In the thia(iv)triazine rings		
S-N(1)-C(1)-N(2)	0.0	-4.6
N(1)-C(1)-N(2)-C(2)	12.6	-4.6
C(1)-N(2)-C(2)-N(3)	-1.9	0.0
N(2)-C(2)-N(3)-S	-17.9	14.0
C(2)-N(3)-S-N(1)	25.9	-19.9
N(3)-S-N(1)-C(1)	-17.6	15.4
(b) Exocyclic torsion angles		
Cl-C(1)-N(1)-S	180.0	174.1
Cl-C(1)-N(2)-C(2)	-167.7	176.7
N(5)-S-N(1)-C(1)	99.2	-99.3
N(5)-S-N(3)-C(2)	-87.2	90.3
N(4)-C(2)-N(2)-C(1)	174.6	-177.8
N(4)-C(2)-N(3)-S	165.8	-168.9
N(2)-C(2)-N(4)-C(3)	-178.1	173.7
N(3)-C(2)-N(4)-C(3)	-1.4	-3.8
N(4)-C(3)-C(4)-C(5)	-177.7	177.4
N(4)-C(3)-C(8)-C(7)	177.5	178.0
(c) Torsion angles in cyclohexyl rings		
C(8)-C(3)-C(4)-C(5)	-54.0	55.0
C(3)-C(4)-C(5)-C(6)	53.9	-53.2
C(4)-C(5)-C(6)-C(7)	-55.1	52.6
C(5)-C(6)-C(7)-C(8)	56.9	-54.8
C(6)-C(7)-C(8)-C(3)	-56.6	57.7
C(7)-C(8)-C(3)-C(4)	54.7	-57.5

Further torsion angles are shown by the corresponding Newman projections (Figure 2).

TABLE 6

Equations of atomic planes in the form $AX + BY + CZ = D$, where X , Y , and Z are orthogonal (\AA) co-ordinates related to the axes a^* , b , c . Deviations ($\text{\AA} \times 10^3$) of relevant atoms from the planes are given in square brackets; values for molecule (A) precede those for molecule (B)

Plane (1): C(1), C(2), N(1)-(3)

$$0.972 7X - 0.206 2Y + 0.106 7Z = 7.437 6$$

$$0.432 9X + 0.895 2Y + 0.106 2Z = 8.541 5$$

[N(1) -43, -20; C(1) 63, 27; N(2) -26, -7; C(2) -21, -16; N(3) 27, 16; S -357, -274; Cl 404, 129; N(4) 6, -3; N(5) -1 980, -1 876; C(3) 57, 124; C(4) -539, -1 198; C(8) 1 478, 1 023]

Plane (2): N(1), N(3), S

$$0.873 4X - 0.173 4Y + 0.455 1Z = 5.448 0$$

$$0.400 8X + 0.833 8Y + 0.379 6Z = 9.337 6$$

[C(1) -355, -312; N(2) -737, -563; C(2) -511, -395; Cl -339, -463; N(4) -794, -615; N(5) -1 420, -1 450]

Plane (3): N(2), S, N(5)

$$0.188 9X + 0.974 2Y - 0.123 7Z = 3.494 3$$

$$0.875 9X - 0.478 1Y - 0.065 3Z = -2.615 4$$

[N(1) -1 348, -1 351; C(1) -1 092, -1 099; C(2) 1 176, 1 169; N(3) 1 288, 1 291; Cl -2 544, -2 562; N(4) 2 263, 2 269; C(9) 82, -27; C(12) 383, 236]

Plane (4): S, N(5), C(9), C(12)

$$0.269 5X + 0.930 1Y - 0.249 5Z = 4.347 0$$

$$0.879 1X - 0.444 2Y - 0.172 9Z = -2.991 8$$

[N(1) -1 146, -1 217; C(1) -714, -824; N(2) 462, 347; C(2) 1 528, 1 431; N(3) 1 461, 1 407; S 36, 16; Cl -1 993, -2 168; N(5) -119, -51; C(9) 43, 19; C(12) 40, 17]

Dihedral angles ($^\circ$) between planes: (1)-(2) 20.9, 16.2; (1)-(3) 91.7, 93.2; (1)-(4) 87.5, 92.0; (2)-(3) 93.5, 94.2; (2)-(4) 92.3, 94.8; (3)-(4) 8.9, 6.5.

The exocyclic N(4) atom of the guanidine moiety lies in plane (1) of both molecules. The C(3) atoms of the cyclohexyl rings are in a nearly eclipsed conformation

with N(3) atoms, as shown by the torsion angles (-1.4 and -3.8°). Apart from the cyclohexyl groups, the two molecules of the asymmetric unit are nearly mirror image as revealed by the Newman projections and

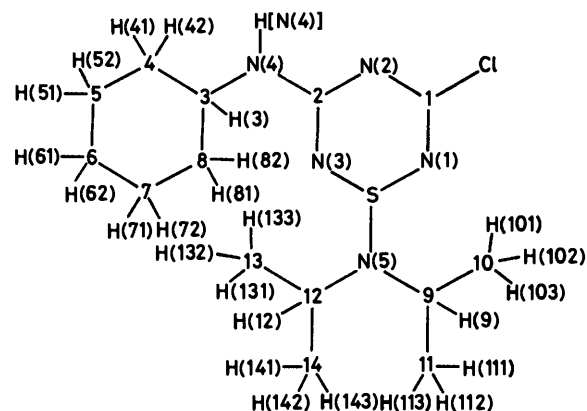


FIGURE 1 Atom numbering system used for the title compound; atoms are carbon unless otherwise indicated

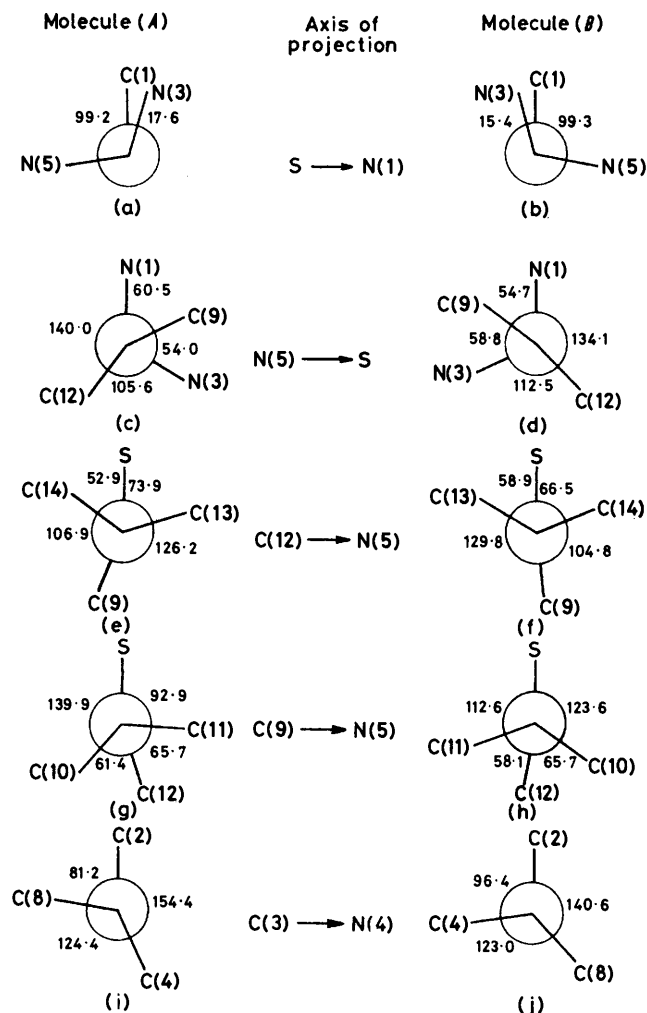


FIGURE 2 Newman projections showing the conformations of the characteristic moieties for both molecules (A) and (B)

torsion angles. The cyclohexyl ring in molecule (*B*) is twisted by *ca.* 75° around the equatorial N(4)–C(3) bond relative to the same moiety in molecule (*A*) [Figure 2(i) and (j)]. Both cyclohexyl rings have almost perfect chair conformations (mean torsion angle for both rings 55.2°) and are bonded to the guanidine moieties equatorially [corresponding N(4)–C–C torsion angles are nearly 180° (Table 5)].

Bonding.—The corresponding bond lengths and angles (Tables 3 and 4) of the symmetry-independent molecules

effect of the coplanar N(1)–C(1)–Cl moiety. Similar S–N multiple bonds were found in the *N*-acylsulphimides⁶ (Table 7). The length of the N(1)–C(1) bond is shorter, while that of the C(1)–Cl bond is similar to those found in *N*-acylsulphimides. The shortness of the N(1)–C(1) bond length is presumably due to the replacement of the oxygen atom by N(2) relative to the *N*-acylsulphimides. The other endocyclic S–N bond is visibly stronger and shares p_π orbitals with the guanidine moiety. This bond length is comparable with the

TABLE 7

A comparison of S^{IV}–N and N–X [where X = S^{VI}, C(*sp*²), C(*sp*³)] bond lengths (Å) and angles (°) for the R¹R²S^{IV}N moieties [where R¹, R² = C(*sp*²), C(*sp*³), N, and O atoms]

S ^{IV} –N	S ^{VI} –N	C–N	C–S–C	C–S–N	N–S–N	Mean X–S–Y
1.673 (10) ^a		1.344 (10)	99.3(5)	103.8(5) 99.2(5)		100.8
1.670 (5) ^b					109.0(3)	106.1 ^d
1.668 (6)					110.2(3) ^e	107.3
1.667 (7) ^c		1.320 (10)	99.9(5)	104.7(5) 98.5(4)		101.0
1.659 (2) ^f		1.344 (3)	101.0(2)	104.2(1) 99.5(1)		101.6
1.667 ^g						
1.652 (9) ^h		1.530 (9) 1.471 (10)	104.2(4) (C–S=O)	101.8(4)	114.6(5) (N–S=O)	106.9
1.644 (5) ⁱ	1.681 (5)	1.541 (8)	100.6(5)	105.9(5) 107.9(5)		104.8 <i>d</i>
1.645 (5) ^b					106.8(3)	
1.634 (6)					107.2(2) ^e	
1.644 ^j						
1.643 ^k	1.570				101.7	101.7
(3×)	(3×)				(3×)	
1.636 (8) ^l	1.591 (8)		98.4(5)	104.3(5) 106.9(5)		103.2
1.626 (2) ^m	1.603 (2)		98.2(2)	105.1(2) 101.2(1)		101.5
1.628 (7) ⁿ	1.598 (8)		101.0(4)	103.7(4) 103.8(4)		102.8
1.620 (7) ^o	1.618 (7)		97.4(4)	103.6(4) 103.6(4)		101.5
1.621 (6) ^b					102.4(3)	<i>d</i>
1.620 (6)					104.6(3) ^e	
1.631 ^p						

^a *N*-Dichloroacetyl-SS-diethylsulphimide (ref. 6a). ^b Title compound. ^c To each S–N bond in the molecules of the title compound is given the opposite N–S–N bond angle. ^d Mean of the N–S–N bond angles given only once for molecules (*A*) and (*B*). ^e SS-Dimethyl-*N*-trichloroacetyl sulphimide (DMTAS) (ref. 6b). ^f *N*-Benzyl-SS-dimethylsulphimide (DMBES) (ref. 6c). ^g Mean for fairly polarized S^{IV}–N (two-co-ordinate) multiple bonds. ^h 2,2,6,6-Tetramethyl-1-phenylsulphonylpiperidin-4-one (TMPSO) (ref. 7). ⁱ *trans*-1-(*N*-Ethyltosylamino)-4-*t*-butyl-1-thioniacyclohexane tetrafluoroborate (ref. 18). ^j Mean for S^{IV}–N (three-co-ordinate) multiple bonds. ^k Potassium [sulphur tris-(tosylimide)] (ref. 20). ^l SS-Dimethyl-*N*-tosylsulphimide (DMTSS) (ref. 16c). ^m *N*-Mesityl-SS-dimethylsulphimide (DMMSS) (ref. 16a, e). ⁿ SS-Diphenyl-*N*-tosylsulphimide (DPTSS) (ref. 16b). ^o *S*-Phenyl-*S*-propyl-*N*-tosylsulphimide (PPTSS) (ref. 16d). ^p S^{IV}–N (two-co-ordinate) multiple bonds.

are similar (except for terminal C–C bonds), so only one of the molecules will be discussed. The hetero-ring is, owing to its six π electron system, formed by S–N and C–N multiple bonds. The C(*sp*²)–N(*sp*²) bond lengths vary between 1.281 and 1.384 Å (theoretical C–N single-bond length¹⁵ 1.47 Å). The sulphur situated at the top of a distorted trigonal pyramid (*cf.* N–S–N angles in Table 4) makes three different S–N bonds. The endocyclic nitrogen atoms are bonded to two atoms, while the exocyclic one is three-co-ordinate. The S–N(1) bond, as might be expected, is the longest [1.668(6) and 1.670(5) Å] owing to the electron-withdrawing

S^{IV}–N bond length found in the *N*-sulphonylsulphimide: PPTSS^{16d} (see Table 7).*

The configuration of the exocyclic three-co-ordinate N(5) atom which holds two isopropyl groups through a C–N single bond (mean bond length 1.469 Å) as shown by the bond angles and Newman projections [Figure 2(c)–(d)], is nearly *sp*². The co-ordination about N(5) is consistent with delocalization of the non-bonding pair toward the S atom thus forming a d_π – p_π multiple

¹⁵ L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 1960, 3rd edn.

¹⁶ (a) A. Kálmán, *Acta Cryst.*, 1967, **22**, 501; (b) A. Kálmán, B. Duffin, and Á. Kucsman, *Acta Cryst.*, 1971, **B27**, 586; (c) A. F. Cameron, N. J. Hair, and D. G. Morris, *J.C.S. Perkin II*, 1973, 1951; (d) A. Kálmán and K. Sasvári, *Cryst. Struct. Comm.*, 1972, **1**, 243; (e) A. Kálmán and L. Párkányi, unpublished work.

¹⁷ A. Kálmán, D.Sc. Thesis, MTA Budapest, 1974.

* The S^{IV}–N bond in PPTSS, is unlike those in the other *N*-sulphonylsulphimides (Table 7) owing to an intramolecular non-bonded interaction,¹⁷ and seems to be strengthened at the expense of the weakened S^{VI}–N(*sp*²) multiple bond [1.618 (7) Å].

bond [1.645(5) and 1.634(6) Å] which is similar to those observed in the *N*-alkylated *N*-sulphonylsulphimide¹⁸ and in TMPSO (Table 7).⁷ The fact that the mean S^{IV}-N (three-co-ordinate) bond length (1.644 Å) is scarcely longer than that of S^{IV}-N (two-co-ordinate)

is comparable to those found in sulphaguanidine monohydrate and a related compound.²²

The symmetry-independent molecules (*A*) and (*B*) are separated. Their relative positions can be given by the dihedral angle (75.5°) between plane (1) for each

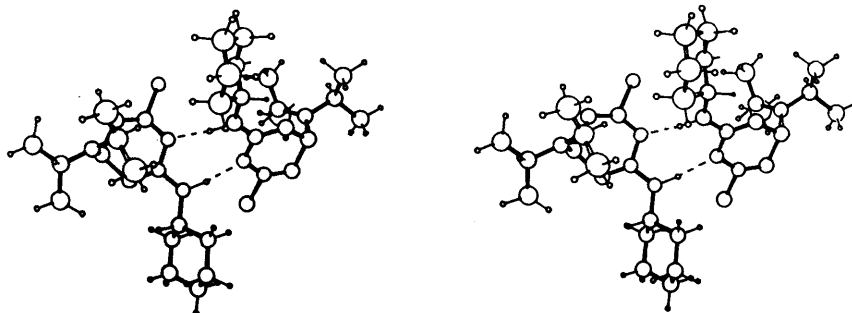


FIGURE 3 An ORTEP stereodrawing of molecule (*A*) at x, y, z and (*B*) at $1 - x, -\frac{1}{2} + y, -z$, showing their linkage through a pair of hydrogen bonds

(1.632 Å) suggests that they are less dependent than the S^{VI}-N bond lengths on the state of co-ordination of nitrogen.^{16e}

The mean of the three S-N bond lengths (1.643 Å) agrees well with mean (1.644 Å) for such bonds in the S^{IV}N₃ groups of S₃N₃-NPPPh₃,¹⁴ S₃N₅PF₂,¹⁹ and K₂[sulphur tris-(*p*-tolylsulphonylimide)].²⁰ This means that the trigonal pyramidal S^{IV}N₃ groups [like, for example, the tetrahedral oxyanions, XO₄ⁿ⁻ (cf. ref. 21)] can perhaps be characterized by an equilibrium distance of 1.64 ± 0.01 Å. This observation needs, however, further corroboration. The bonding of the guanidine moiety

¹⁸ R. E. Cook, M. D. Glick, J. J. Rigau, and C. R. Johnson, *J. Amer. Chem. Soc.*, 1971, **93**, 924.

¹⁹ J. Weiss, I. Ruppert, and R. Appel, *Z. anorg. Chem.*, 1974, **406**, 329.

molecule. They form, however, dimers with symmetry-equivalent molecules at $(1 - x, y - 1/2, -z)$ through hydrogen-bonded pairs as depicted in Figure 3.

	N(4) ··· N(2)	H ··· N(2)	N(4)-H ··· N(2)
N ··· N, (<i>A</i>) ··· (<i>B</i>)	3.01	1.96 Å	163.5°
N ··· N, (<i>B</i>) ··· (<i>A</i>)	3.05	2.02	160.4

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²⁰ A. Gieren and P. Narayanan, *Acta Cryst.*, 1975, **A31**, S, 120.

²¹ A. Kálmán, *J. Chem. Soc. (A)*, 1971, 1857.

²² M. Alléaume, A. Gulko, F. H. Herbstein, M. Kapon, and R.E. Marsh, *Acta Cryst.*, 1976, **B32**, 669.