Table 7. *Calculated r.m.s. values for the coordinates and estimated standard deviations*

Atoms	r.m.s.	e.s.d. (H)	e.s.d. (W)
heavy	0·0030 Å	0·004 Å	0·0015 Å
light	0·0375	0·013	0·005

value. This may be due to the fact that in the calculation of the s.d. systematic effects, *e.g.* absorption, were not taken into account.

Anisotropic thermal parameters

The thermal parameters are listed in Table 2; also given are the estimated standard deviations for H's values, and the values from W's T_{ij} and ω_{ij} tensors.

Even if the standard deviations for W's U_{ij}'s were as large as those for H's, many of the differences would be very highly significant. The overall difference in the anisotropic parameters $\Delta U_{ij}=\Sigma_n p_n \Delta U_{ij,n}$ where n denotes the nth atom, with weight $p_n=Z_n^2/\Sigma_n Z_n^2$ and atomic number Z_n, are $\Delta U_{11}=4$, $\Delta U_{22}=170$, $\Delta U_{33}=79$, $\Delta U_{12}=38$, $\Delta U_{23}=35$, and $\Delta U_{13}=16\,.\,10^4$ Å^2. These values may be compared with the values from the observed structure factors.

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References

Banister, A. J. & Hazell, A. C. (1962). *Proc. Chem. Soc.* p. 282.

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A. L. (1955). *Acta Cryst.* **8**, 478.

Cochran, W. (1951). *Acta Cryst.* **4**, 408.

Craig, D. P. (1959). *J. Chem. Soc.* p. 997.

Craig, D. P. & Paddock, N. L. (1962). *J. Chem. Soc.* p. 4118.

Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 754.

Cruickshank, D. W. J. (1961*a*). *J. Chem. Soc.* p. 5486.

Cruickshank, D. W. J. (1961*b*). *Acta Cryst.* **14**, 896.

Cruickshank *et al.* (1961) in *Computing Methods and the Phase Problem in X-ray Crystal Analysis.* Oxford: Pergamon Press.

Cruickshank, D. W. J. & Robertson, A. P. (1953). *Acta Cryst.* **6**, 698.

Davies, D. W. (1962). *Nature, Lond.* **194**, 82.

Dewar, M. J. S., Lucken, E. A. C. & Whitehead, M. A. (1960). *J. Chem. Soc.* p. 2423.

Dougill, M. W. (1963). *J. Chem. Soc.* p. 3211.

Freeman, A. J. (1959). *Acta Cryst.* **12**, 261.

Goehring, M. (1957). *Ergebnisse und Probleme der Chemie der Schwefelstickstoffverbindungen.* Berlin: Akademie Verlag.

Hassel, O. & Rømming, C. (1962). *Quart. Rev. Chem. Soc. Lond.* **16**, 1.

Kartha, G. & Ahmed, F. R. (1960). *Acta Cryst.* **13**, 532.

Kirsanov, V. (1952). *J. gen. Chem.* (USSR), **22**, 93.

Lide, D. R., Mann, D. E. & Fristrom, R. M. (1957). *J. Chem. Phys.* **26**, 734.

Martz, D. E. & Lagemann, R. T. (1954). *J. Chem. Phys.* **22**, 1193.

Pauling, L. (1960). *The Nature of the Chemical Bond.* 3rd edn. Ithaca: Cornell Univ. Press.

Sass, R. L. (1960). *Acta Cryst.* **13**, 320.

Smits, D. W. & Wiebenga, E. H. (1953). *J. Sci. Instrum.* **30**, 280.

Tomiie, Y. & Stam, C. H. (1958). *Acta Cryst.* **11**, 126.

Vos, A. & Smits, D. W. (1961). *Acta Cryst.* **14**, 1299.

Wiebenga, E. H. & Smits, D. W. (1950). *Acta Cryst.* **3**, 265.

Wiegers, G. A. & Vos, A. (1962). *Proc. Chem. Soc.* p. 387.

Wiegers, G. A. & Vos, A. (1963). *Acta Cryst.* **16**, A40.

Wilson, A. & Carroll, D. F. (1960). *J. Chem. Soc.* p. 2548.

Wilson, A. J. C. (1949). *Acta Cryst.* **2**, 318.

Acta Cryst. (1966). **20**, 192

The Crystal Structures of Two Sulphur-Nitrogen Compounds with (S–N)$_3$ Rings. II. Trithiazylchloride, (NSCl)$_3$, at –130°C

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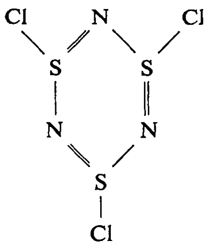
Trithiazylchloride, (NSCl)$_3$, is monoclinic with $a=5{\cdot}49$, $b=11{\cdot}14$, $c=6{\cdot}05$ Å; $\beta=98{\cdot}7°$ (at -130 °C). The space group is $P2_1/m$ and there are two molecules at special positions with symmetry m in the unit cell. The intensities of 992 independent reflexions were recorded at -130 °C on integrated equi-inclination Weissenberg photographs. Three-dimensional least-squares refinement has shown that the molecule exists as the chair form with the chlorine atoms in axial positions. The mean bond lengths, with e.s.d. are: S–N 1·605 (0·005), S–Cl 2·150 and 2·084 (0·004) Å; and the bond angles: N–S–N 113·4 (0·4), S–N–S 129·3 (0·4), N–S–Cl 113·7 (0·3)°. The fact that the S–N bonds are all short, and equal, indicates the presence of delocalized p_π–d_π bonds.

Introduction

After the S$^{\text{VI}}$ compound α(NSOCl)$_3$ described in the previous paper (Hazell, Wiegers & Vos, 1966), the S$^{\text{IV}}$ compound (NSCl)$_3$ was studied. Chemical evidence (Goehring, 1957) suggests that (NSCl)$_3$ contains an (NS)$_3$ ring with the chlorine atoms linked to the sulphur atoms:



This structure was confirmed by a preliminary X-ray investigation at room temperature. Refinement at low temperature, −130°C, was desirable to exclude space group ambiguities (in the present case $P2_1$ or $P2_1/m$ with $Z=2$), as mentioned in the paper on $\alpha(NSOCl)_3$ and discussed by Wiegers & Vos (1963*b*). Equal values for the N–S bond lengths in $(NSCl)_3$ were observed at room temperature and the present paper shows that it is very probable that the observed equality of the bond lengths is genuine.

Experimental

Preparation and crystal data

Trithiazylchloride, $(NSCl)_3$, was prepared by Goehring's (1957, p.155) method. The composition was checked by chemical analysis. The crystals are yellow monoclinic plates parallel to (010). In moist air the compound decomposes and ammonium chloride is formed on the surface of the crystals. During the X-ray work the crystals were therefore mounted in thin-walled glass capillaries. The crystallographic data are listed in Table 1. The cell dimensions were determined from zero-layer line Weissenberg photographs about the crystallographic axes. The photographs were superposed by spots of sodium chloride for calibration purposes. The experimental density, 2·09 g.cm^{-3} at 20°C (Schröder & Glemser, 1959), agrees with the calculated density, 2·15 g.cm^{-3}, for two molecules in the unit cell. From symmetry relations between reflexions and systematic absences the space group was derived to be $P2_1$ or $P2_1/m$, with two- and fourfold positions respectively. As there are only two molecules in the unit cell the molecules must lie on mirror planes if $P2_1/m$ is the correct space group.

Table 1. *Lattice constants*

	20°C	−130°C
a	5·55 ± 0·01 Å	5·49 ± 0·01 Å
b	11·23 ± 0·02	11·14 ± 0·02
c	6·13 ± 0·01	6·05 ± 0·01
β	99·2 ± 0·2°	98·7 ± 0·2°

Intensity data

All intensities were measured with a densitometer (Smits & Wiebenga, 1953) on integrated Weissenberg photographs (Wiebenga & Smits, 1950) taken with zirconium-filtered molybdenum radiation. Use was made of the multiple film technique. The crystals were cooled down to −130°C by a stream of vapour from boiling liquid nitrogen. The temperature was measured with a thermocouple and controlled by regulating the electric current in the heater placed in the boiling nitrogen. The contents of liquid nitrogen were controlled continuously by a constant level device. The technique was described in detail by Altona (1964). Small needles along the *a* or *c* axis, having cross-sections of approximately 0·2 × 0·2 mm, could be obtained by cleavage from larger crystals. This permitted the absorption correction to be neglected ($\mu \simeq 18$ cm^{-1}). 992 non-zero independent reflexions were measured (0*kl*–7*kl*, *hk*0–*hk*3). Scaling of intensities was done by comparing the intensities of reflexions common to photographs taken about different axes. The accuracy of the intensity measurements was estimated by calculating

$$\sum_{hkl}\sum_{i}|F_i^2-F_m^2| / \sum_{hkl}\sum_{i}F_i^2,$$

where i and m refer to individual and mean values respectively. For the 348 common reflexions this discrepancy factor was 0·041.

Determination of the structure

We found the approximate structure from sharpened Patterson projections calculated with room temperature data. The distribution of vectors in these syntheses could nicely be explained by assuming that molecules of $(NSCl)_3$ are lying on the mirror planes of space group $P2_1/m$. This space group was therefore adopted during refinement. During the least-squares analysis of the three-dimensional data only isotropic temperature factors could be taken into account by the available program, ZEBRA program ZK22. The function minimized was $\Sigma w(F_o-F_c)^2$; the weighting factor w was taken to be 1 for all reflexions. Reflexions thought likely to suffer from extinction, and also some very weak ones, were omitted (these are marked with an asterisk in Table 4). The scattering factors used were those of Tomiie & Stam (1958) for sulphur and chlorine and that of Freeman (1959) for nitrogen. R dropped to 0·069. The final parameters of the least-squares refinement are listed in Table 2, the observed and calculated structure factors are compared in Table 4.

Table 2. *Fractional atomic coordinates, temperature factors, and estimated standard deviations in the coordinates*

	x	y	z	B	s.d.
S(1)	−0·0450	0·1226	−0·2234	0·98 Å^2	0·0015 Å
S(2)	0·1231	0·2500	0·1744	0·90	0·0015
Cl(1)	0·2968	0·0803	−0·3382	1·58	0·0015
Cl(2)	0·5004	0·2500	0·1635	1·71	0·0015
N(1)	0·0256	0·1291	0·0430	1·19	0·006
N(2)	−0·1168	0·2500	−0·3376	1·30	0·006

After the isotropic least-squares refinement a three-dimensional F_o synthesis and a three-dimensional difference map were calculated. These syntheses show: (*a*) The atomic shifts due to changing the weighting scheme from 1 to $1/\langle f \rangle$ are very small, for nitrogen less than 0·003 Å, for sulphur and chlorine less than

Table 3. *Bond lengths and valency angles*

Bond		s.d.	Angle		s.d.
N(1)-S(1)	1·600 Å	0·007 Å	S(1)-N(1)-S(2)	123·0°	0·4°
N(1)-S(2)	1·614	0·007	S(1)-N(2)-S(1′)	124·9	0·4
N(2)-S(1)	1·602	0·007	N(1)-S(1)-N(2)	113·6	0·3
S(1)-Cl(1)	2·150	0·004	N(1)-S(2)-N(1′)	113·2	0·5
S(2)-Cl(2)	2·084	0·004	N(1)-S(1)-Cl(1)	114·1	0·3
			N(2)-S(1)-Cl(1)	113·0	0·3
			N(1)-S(2)-Cl(2)	114·0	0·3

0·0004 Å. Since these shifts are small in comparison with the estimated standard deviations the structure was not refined further. (*b*) Thermal motion of the atoms is only slightly anisotropic. For the atoms in the mirror plane the corrections ΔB in the isotropic temperature factors were estimated for the directions of the principle axes of vibration by use of Cochran's method (1951, formula 4·7). The ΔB values were small; the largest values were found for chlorine, *viz.* $-0{\cdot}3$ and $0{\cdot}0$ Å^2 for the principle axes in the mirror plane and $+0{\cdot}5$ Å^2 for the direction perpendicular to the mirror plane. (*c*) The directions of the principle axes of vibration of the atoms (Fig. 1) as well as the relatively high isotropic coefficients B of the chlorine atoms (Table 2) suggest that the deviations from spherical symmetry of the atoms may be ascribed to rigid body vibrations of the $(NSCl)_3$ molecule as a whole. In $(NSCl)_3$ the observed asymmetry in the electron density distributions of the atoms can, however, alternatively be ascribed to an incorrect choice of the space group during refinement, and might thus indicate small deviations from the assumed centrosymmetry. Attempts to fit $(NSCl)_3$ molecules, which had alternate 'single' and 'double' N–S bonds in the ring and unequal angles N–S–Cl and N=S–Cl, to the electron density distribution gave, however, higher values for the disagreement indices R than obtained for the molecules with mirror planes. It is thus very likely that in $(NSCl)_3$ all N–S bonds have the same character and that the non-spherical symmetry in the electron-density distribution

Table 4. *Observed and calculated structure factors*

The reflexions marked with an asterisk were not taken into account during the three dimensional refinement.

h k l	$\lvert F_o\rvert$	F_c
•0,4,0	34.1	28.7-
• 6	78.5	78.8-
• 8	52.0	53.4
• 10	19.4	17.5-
12	13.7	14.2
14	9.5	9.5-
16	27.0	27.3
18	16.1	15.8-
24	12.8	10.8
•0,3,1	103.6	109.4
5	28.4	29.1-
6	7.6	6.0
7	12.3	9.7-
8	33.1	33.4
9	25.5	25.6-
10	15.6	14.4-
11	20.8	22.1
12	12.8	9.2-
13	17.0	18.6-
14	11.4	10.8-
16	11.4	11.1
19	12.8	12.3
•0,0,2	86.6	79.0-
• 1	73.8	66.8-
2	15.1	14.5
3	9.5	8.8
4	7.6	7.1
5	56.3	55.1-
6	40.2	36.8
7	32.2	33.2
8	26.5	27.4-
11	33.1	35.3
13	17.0	20.7-
14	8.5	8.8
16	15.6	14.9-
17	13.2	14.6-
0,1,3	28.4	25.8-
2	49.7	47.1
3	28.9	26.6-
4	33.1	32.1-
5	27.0	26.4
7	18.9	19.2
8	40.7	42.4-
9	18.4	16.9-
10	19.4	21.4
11	18.4	18.4-
13	14.7	12.2
14	21.8	22.8
15	13.2	11.0
16	13.7	14.6-
0,0,4	6.6	5.5-
1	24.6	22.4
2	8.5	7.0
3	26.5	25.1-
4	34.1	33.5-
5	55.8	54.2
6	26.0	25.6
7	14.2	14.8-
8	17.5	17.2
9	8.5	6.9-
11	35.9	36.3-
12	30.7	30.6-
13	22.7	24.5
19	13.2	11.3-
0,0,5	24.6	25.0
1	14.2	13.0
2	18.0	16.6-
3	31.2	29.7-
7	13.2	15.4-
8	31.7	29.8
9	30.7	30.8
10	8.5	8.4-
12	11.8	8.8-
14	11.8	9.7-
15	18.0	18.7-
16	13.2	12.4
0,0,6	33.1	30.5
1	9.5	9.0
2	14.2	13.0-
3	15.1	15.1
4	27.9	25.4
• 5	8.0	7.0-
6	36.9	35.2-
7	10.9	9.2-
0,10,6	12.8	12.3-
11	11.4	7.8
12	28.4	28.9
0,0,7	26.5	24.5-
1	17.0	16.3-
2	12.3	11.0-
3	17.5	16.7
4	27.4	26.6
7	15.0	14.5
9	24.6	23.7-
0,0,8	10.9	10.9-
1	33.1	30.4-
3	12.8	12.5-
4	10.9	8.4-
6	13.2	10.0
7	25.5	24.4
• 9	10.4	9.0-
0,0,9	13.2	10.2
2	16.1	13.7
4	21.8	20.9-
0,0,10	12.8	9.2-
1	19.4	16.1
7	13.7	13.6-
0,4,11	12.3	12.3
•1,3,0	33.1	30.9-
• 4	53.0	52.5-
• 5	35.5	34.9-
• 6	9.5	9.0
7	14.2	12.7
8	42.1	40.9
9	22.2	19.7
11	23.6	23.5
12	27.9	28.4-
16	21.3	17.1
•1,1,1	38.8	37.1
• 2	55.8	54.9
• 3	42.1	37.6
4	54.4	51.3-
5	14.7	12.9-
6	11.8	10.8-
7	22.7	23.0-
8	25.1	26.4-
10	17.0	16.9
11	18.0	15.3
• 13	12.8	9.4-
14	17.0	18.7
•1,2,$\bar{1}$	34.5	31.0
• 3	33.6	30.2
4	12.3	12.0-
5	19.9	19.7
6	15.1	14.1
7	22.7	24.8
8	39.7	39.1
9	37.8	40.9-
10	11.8	11.5-
11	20.3	18.7-
12	17.5	18.9-
14	14.7	11.7-
15	22.2	23.8
16	16.6	14.2
•1,0,2	67.2	69.3-
1	15.6	15.5
2	11.8	10.1-
3	15.1	15.2
4	29.3	28.8
5	23.6	23.6
6	32.6	32.3
7	10.9	10.0-
8	17.0	16.0-
9	15.6	13.7-
11	13.7	12.7-
16	16.6	12.3-
•1,2,$\bar{2}$	17.5	16.3
3	10.9	10.4-
5	18.9	16.4
6	29.3	30.8-
8	26.0	26.1-
11	18.9	15.0-
12	29.3	30.8
• 14	13.7	10.8
1,1,3	28.4	27.8-
2	16.1	14.5-
• 3	77.6	77.8-
1,4,3	12.8	12.3
5	25.5	24.4
7	17.5	18.4
9	14.7	14.0
11	17.5	16.6-
13	17.5	16.6
1,0,$\bar{3}$	20.3	19.4-
1	22.2	21.0
2	16.6	17.1-
3	23.2	21.6-
4	26.0	25.9
5	24.1	23.5-
6	9.9	8.0
7	18.0	18.2-
9	39.3	40.8
11	17.5	16.8
15	23.2	23.0-
1,0,4	65.3	65.7
• 3	9.0	6.8-
4	29.8	28.6-
5	19.4	19.6
6	30.7	31.2-
8	20.3	18.2
11	13.7	13.7-
13	13.7	9.9
1,1,$\bar{4}$	34.5	34.8
3	44.9	44.6
4	20.8	19.5-
• 5	9.5	7.3-
6	19.4	17.9
7	25.1	25.3-
8	18.4	19.8
12	24.6	23.7-
1,2,5	18.4	18.2-
3	36.9	36.8
5	16.1	12.0-
8	27.9	26.2
• 14	14.5	11.0-
1,0,$\bar{5}$	42.6	42.6
2	22.7	21.3
4	40.3	41.6-
6	17.5	15.0-
10	12.8	11.7
1,0,6	22.7	21.4-
1	14.7	11.6-
4	16.6	15.2
5	22.7	22.2-
8	13.7	13.5-
11	19.9	18.1
•1,0,$\bar{6}$	13.5	12.1-
1	21.8	22.2-
3	26.5	26.5-
4	12.8	12.0
7	20.3	19.1
1,0,7	16.1	13.9-
2	19.4	18.2
8	28.9	27.4-
9	17.0	13.4-
1,0,$\bar{7}$	23.6	24.8-
• 1	10.8	8.9
• 2	10.8	8.1-
3	21.3	20.4
4	24.6	25.0
1,5,8	18.4	16.5
6	13.7	11.6
1,1,$\bar{8}$	18.4	16.5
7	15.7	14.6-
• 9	14.5	12.1
•2,0,0	44.0	40.9
• 1	11.8	11.6
• 2	44.5	42.7-
3	46.8	46.9
4	12.3	10.6-
5	11.4	8.7-
6	11.8	8.4
8	53.9	55.9
9	16.6	15.7-
10	13.7	14.8-
11	11.4	9.9
12	27.9	25.6-
13	11.8	8.9-
14	14.7	15.8-
16	18.0	19.6
2,0,1	18.4	18.0-
1	33.6	32.4-
2	12.3	11.9
3	11.8	10.0
4	8.5	8.7-
• 5	55.3	56.4-
6	14.7	13.6
7	12.3	12.5
8	13.7	12.5-
9	16.1	15.7
11	36.4	40.2
13	20.8	21.7-
• 15	14.2	12.1-
•2,0,$\bar{1}$	128.2	128.4
• 2	16.6	15.5-
3	9.9	9.0-
4	21.8	20.8-
5	27.9	27.8
6	52.0	53.3-
7	11.8	10.0
8	31.2	32.8
9	16.4	18.9-
10	10.9	11.2-
11	19.9	19.5-
• 12	10.9	12.4
15	14.7	13.2
16	18.0	18.5
2,0,2	14.2	11.9-
1	16.1	13.5-
2	31.2	31.6
3	14.2	13.2
5	12.8	11.9
• 7	8.5	8.5
8	41.6	44.9-
9	21.3	21.1-
10	11.8	12.5
• 11	10.9	8.4-
12	18.9	18.2
14	19.4	18.8
16	19.9	16.8-
2,0,$\bar{2}$	15.6	15.0-
1	11.8	11.3-
3	79.0	78.8-
4	12.8	11.1
5	17.0	17.5
7	9.5	7.4
9	25.1	26.7
11	13.2	13.8-
• 13	11.8	13.4
2,0,3	32.2	32.7-
3	32.6	32.0-
• 4	7.6	6.5-
5	45.4	46.9
6	30.7	30.9
• 8	8.5	6.8
9	12.8	13.0-
11	31.7	31.7-
12	20.8	20.2-
13	23.2	22.4
2,0,$\bar{3}$	65.7	63.6-
1	49.2	49.0
3	12.8	12.2
4	11.8	11.4
5	17.0	17.2
6	36.9	37.3
7	34.1	34.5-
8	15.1	17.0-
9	11.4	11.3
11	9.9	10.9-
2,0,4	31.7	32.0
3	41.2	42.6-
4	25.1	23.8-
8	23.2	23.6
9	19.4	20.0
12	14.2	12.1-
2,0,$\bar{4}$	26.0	24.3
1	19.4	18.3
2	33.1	31.9
3	40.2	41.2
4	42.1	42.3-
5	20.8	23.5-
7	15.1	15.6-
8	14.7	14.6-
10	16.1	17.5

Table 4 (*cont.*)

h k l	$\lvert F_o\rvert$	F_c
2,11,$\bar{4}$	14.2	16.3
13	14.2	12.3-
14	14.2	15.2
2,0,5	36.4	38.3
1	17.5	16.8
2	9.5	6.2-
3	23.6	24.1
6	28.9	28.1-
7	14.2	14.8-
• 8	11.3	8.3
• 12	14.0	13.6
2,0,$\bar{5}$	16.1	16.0
1	30.7	30.3-
4	29.3	32.2-
5	31.7	31.6-
6	11.8	9.4
7	22.2	23.5
8	14.2	18.1
11	18.9	20.0
12	24.1	23.0-
• 13	13.2	13.8-
2,0,6	28.9	30.2-
• 2	14.2	13.9-
3	16.6	16.0
4	31.2	29.7
2,1,$\bar{6}$	13.7	14.2-
2	20.8	20.8-
3	12.3	9.6
4	16.1	16.9
7	13.2	15.5
8	17.0	17.7
9	22.7	22.6-
2,0,7	15.1	15.7-
1	27.4	26.2-
3	15.6	17.0-
7	20.3	20.7
8	15.1	15.0-
2,0,$\bar{7}$	15.1	12.7
4	24.1	25.9
6	27.4	25.1-
• 8	11.4	9.4-
12	28.4	26.6
2,4,8	14.2	14.1-
•2,0,$\bar{8}$	11.4	9.0-
1	16.6	18.6
• 3	11.4	10.0-
• 4	11.0	8.1
7	17.0	16.9-
9	25.1	24.9
2,1,$\bar{9}$	18.9	17.4
• 7	15.1	13.9-
3,0,0	27.9	28.3
1	17.0	16.9
2	45.9	45.7
3	42.1	42.1
4	71.4	68.0-
5	7.1	7.5-
7	11.4	12.5-
8	10.4	10.2-
9	9.9	10.9-
10	23.2	23.7
12	18.4	18.7-
13	10.4	7.4-
14	14.2	17.3
• 20	14.2	13.3-
•3,0,1	68.6	69.4-
• 1	30.7	29.9
2	10.4	8.5
3	11.4	10.5
5	7.6	6.7
6	44.9	46.9
7	26.0	25.6-
8	15.6	15.9-
9	9.9	9.7
• 10	8.0	7.1
12	17.5	18.6-
16	12.3	11.5-
3,0,$\bar{1}$	49.2	49.7
1	62.4	61.5-
3	18.4	17.5-
4	34.1	35.3-
5	29.8	30.0-
6	6.6	6.5-
3,7,$\bar{1}$	41.6	43.1
8	25.5	27.1
11	16.1	18.5
12	15.1	15.7-
13	10.9	11.3-
16	15.1	13.2
17	13.6	16.7-
3,0,2	6.6	6.0-
2	12.8	5.8-
3	69.5	68.5-
4	25.1	24.5
5	25.5	24.2
6	9.0	8.8-
8	15.1	14.4-
9	25.1	26.6
11	14.2	15.0-
12	18.4	18.5
13	18.4	16.7
15	13.2	12.9-
•3,0,$\bar{2}$	10.4	9.5-
• 1	35.0	35.4-
• 2	37.8	36.8-
3	13.2	11.4
4	31.2	32.2
5	5.7	5.7
6	8.5	7.5
7	26.5	29.3
8	25.5	25.0
9	30.3	32.7-
10	20.3	21.3-
• 11	8.5	8.6-
14	13.2	14.1-
15	19.4	20.1
3,0,3	49.7	49.9
2	13.2	10.6-
3	18.9	17.4-
5	38.3	39.6
6	31.2	32.7-
8	16.6	15.8
9	17.5	18.2-
10	9.5	9.0-
11	28.4	28.4-
12	12.8	13.4
13	18.0	18.3
• 15	9.9	10.7
3,0,$\bar{3}$	27.0	24.4
1	30.3	30.1
2	8.5	8.8-
3	8.5	7.0
4	26.0	28.4
5	18.0	15.2
6	31.7	32.7-
7	19.9	21.9-
8	12.8	12.2-
10	9.5	12.1-
11	13.7	10.8-
12	30.7	33.7
• 17	11.8	9.5
• 18	11.8	12.2-
3,0,4	19.4	18.8
1	17.5	15.8-
2	26.5	26.2-
3	19.9	20.0
5	12.8	10.4-
7	11.8	11.7
8	38.8	40.4
9	15.1	16.5-
10	13.2	12.5-
12	15.6	14.7-
14	13.7	15.3-
16	15.6	15.4
3,0,$\bar{4}$	14.2	13.6
1	31.7	31.9
3	25.5	23.3-
5	12.8	11.8-
7	26.5	29.3-
9	43.5	46.0
11	12.8	11.0
15	26.5	26.4-
3,1,5	16.6	15.5-
3	15.1	12.6
5	33.1	34.1-
11	24.6	26.4
13	13.2	14.5-
3,0,$\bar{5}$	10.9	9.1-
1	18.4	17.3
2	7.6	8.5
3	10.9	8.6
4	33.6	35.5-
6	29.8	30.0
7	13.7	12.4-
8	18.4	16.2
10	10.4	10.0
12	33.1	34.7-
18	12.3	10.1
3,0,6	28.4	26.7-
2	21.3	20.9
3	14.2	14.5
8	32.2	32.3-
9	12.8	11.7-
• 10	9.9	11.3
• 14	11.8	11.2
16	14.2	13.5-
3,0,$\bar{6}$	12.3	9.4
1	13.2	12.6-
2	23.2	22.8
4	27.9	27.5-
• 5	8.5	7.3
7	14.2	13.5
8	11.4	12.2-
9	17.5	16.7-
10	13.2	12.8
• 11	9.5	8.0-
• 14	10.4	10.3
15	14.2	12.1
3,0,7	29.3	29.3-
3	16.1	16.5-
5	16.6	17.1
6	18.4	18.6
3,0,$\bar{7}$	11.8	13.0-
1	22.7	22.6-
4	18.9	17.7
5	19.9	18.0-
7	18.0	18.1
8	9.9	8.8-
• 11	9.9	10.8
• 12	10.4	10.5
• 13	10.9	8.1-
3,0,8	14.7	14.9
3	23.6	23.0-
• 5	11.4	9.5
3,0,$\bar{8}$	12.8	10.2-
1	10.4	8.8
2	15.6	13.7-
3	22.2	22.4
4	21.3	20.2
• 5	10.4	11.0-
• 7	10.9	7.2-
3,0,9	13.7	13.9
• 1	10.9	10.5
3,0,$\bar{9}$	20.8	21.1
1	18.0	15.9
6	12.8	12.4-
7	13.7	13.2-
3,3,$\overline{10}$	14.2	14.4-
3,0,$\overline{11}$	15.1	13.3-
•4,0,0	26.5	24.5
• 2	9.5	10.7
4	25.5	26.6-
5	29.3	24.4-
9	23.2	24.7
11	18.0	20.9
12	10.9	8.6-
• 13	9.5	8.4-
• 14	9.5	6.1
15	15.1	16.1-
4,1,1	10.9	13.8
3	29.8	28.9
4	10.9	11.3
6	10.9	10.2-
7	10.9	12.6-
8	18.9	20.9-
9	9.9	10.6-
12	16.6	17.2
16	10.4	8.0-
•4,0,$\bar{1}$	15.1	13.0
• 2	18.0	17.6-
4,4,$\bar{1}$	17.0	18.9-
5	8.0	9.3
6	17.5	17.9
• 9	8.0	8.2-
8	37.4	40.3
12	28.9	30.3-
16	13.7	14.1
4,0,2	35.5	35.2-
1	14.2	13.3-
2	15.1	16.8-
3	16.6	19.1-
4	24.6	27.5
5	18.0	19.5
6	18.0	18.0
7	9.5	10.9
9	9.9	9.7-
10	11.4	9.8-
11	13.2	14.6-
13	14.2	10.9
•4,0,$\bar{2}$	27.4	26.8
• 1	13.2	13.9-
4	9.0	7.6-
5	24.6	23.6
6	16.6	16.5-
7	16.1	15.3
9	26.5	28.5-
11	18.0	18.6-
12	9.5	9.0
15	18.9	18.5
4,0,3	19.4	23.2
1	25.1	28.0-
2	9.0	6.7
3	30.7	34.0-
4	19.9	18.5-
7	20.3	21.6
4,0,$\bar{3}$	14.7	14.0-
1	8.0	7.1-
2	7.1	4.8
3	27.4	26.9-
4	13.7	13.5
5	8.5	7.8-
8	18.9	19.3-
9	18.4	18.4
12	14.7	15.1
• 15	9.9	8.8-
4,0,4	25.1	27.4
• 1	7.1	5.4
3	19.4	23.5
4	20.3	20.5-
6	9.0	9.6-
8	12.8	10.0
9	11.4	13.7-
4,0,$\bar{4}$	24.1	21.4-
1	26.0	26.4
2	12.3	11.3-
3	17.5	18.7
4	9.0	8.1
5	8.5	8.1-
6	19.9	19.2
7	23.6	22.7-
8	10.5	9.5
9	12.8	12.7
• 12	9.9	10.0-
4,0,5	21.3	24.5-
1	12.3	10.4
• 3	7.6	8.3
4	10.4	11.0
6	12.8	14.9
7	11.8	10.0-
4,0,$\bar{5}$	33.6	34.5
1	12.8	11.4
2	12.3	11.5
3	24.1	24.3
4	32.2	32.2-
6	9.9	9.1-
7	9.0	8.7-
8	9.0	9.0
• 10	9.5	7.2
4,0,6	12.8	14.5-
3	12.8	15.9-
4	9.9	10.3
8	19.4	20.1-
12	12.3	10.6
4,0,$\bar{6}$	12.3	12.7

Table 4 (*cont.*)

h k l	$\lvert F_o \rvert$	F_c	h k l	$\lvert F_o \rvert$	F_c	h k l	$\lvert F_o \rvert$	F_c	h k l	$\lvert F_o \rvert$	F_c
4,1,$\bar{6}$	20.3	19.7-	5,9,3	12.3	12.7-	6,2,1	22.7	23.3-	6,4,6	15.6	14.0
• 2	7.0	5.6	10	10.9	10.0-	4	35.9	36.8	5	15.1	13.2
3	20.8	21.2-	• 12	10.9	10.3-	10	14.7	15.2-	6,0,$\bar{6}$	25.1	22.4
4	16.6	17.0-	5,0,$\bar{3}$	18.9	19.1-	12	10.9	10.5	1	9.9	7.3
7	17.0	15.4	1	12.8	13.8-	• 6,0,$\bar{1}$	27.4	29.9	4	15.6	15.0-
12	9.9	8.4-	2	28.9	28.5-	• 1	10.4	9.1	5	12.3	12.1
4,5,7	13.7	14.9	4	37.4	39.1	• 2	14.2	13.8	8	13.2	11.6
4,0,$\bar{7}$	19.9	19.4-	• 6	7.0	4.9	3	20.8	22.1-	11	13.2	9.7-
2	11.8	11.4-	7	9.0	11.9	4	28.9	33.6-	• 6,2,$\bar{7}$	9.9	7.2
4	17.5	19.4	8	10.4	9.9	• 6	6.1	5.9-	3	21.3	19.8-
• 6	8.6	8.2	9	10.9	9.3-	7	7.6	9.3-	• 8	10.9	7.5-
• 9	8.6	7.5-	10	16.6	18.4-	• 8	7.1	6.6	6,0,$\bar{8}$	23.2	20.4-
4,4,8	13.7	12.1	5,0,4	24.6	24.3	9	19.4	17.9	• 4	10.9	9.2
• 4,1,$\bar{8}$	9.9	10.6	1	16.1	15.1-	12	11.8	11.1-	6	11.8	10.1
3	17.0	15.5	3	11.4	10.2	6,0,2	9.9	11.6	6,3,$\bar{9}$	19.9	17.0
• 4	9.9	10.4	4	11.8	13.0-	1	30.3	29.8-	• 6,0,$\overline{10}$	12.3	8.3-
• 6	12.8	9.9-	5	23.6	23.6-	3	11.8	14.9-	7,2,0	7.6	6.1
12	14.7	12.7	6	12.3	11.6-	6	8.5	12.6-	6	8.0	9.3-
4,9,$\bar{9}$	17.0	14.5	7	11.4	9.8	7	24.6	24.2	7	9.9	10.0-
• 5,0,0	37.4	36.3-	11	16.6	18.1	9	12.3	11.1-	8	12.3	12.1-
• 1	18.0	19.0	5,0,$\bar{4}$	22.2	19.4	• 12	10.4	9.9	9	12.8	12.1
2	12.3	10.7	1	35.9	36.9	• 6,0,$\bar{2}$	12.3	12.8-	• 7,0,1	9.9	9.5-
4	21.8	19.9-	2	11.4	10.2-	• 1	12.3	15.0-	1	8.5	5.7
6	35.9	37.6	3	14.7	14.8	3	19.9	19.8-	4	16.6	19.5
7	19.4	18.4-	4	15.2	15.2	4	14.2	14.7-	5	16.6	15.8
9	13.2	14.5	5	12.3	9.9	5	9.9	10.7	• 11	10.4	10.5-
10	9.9	9.7	6	19.4	19.5-	6	23.2	22.2	12	12.3	11.5
• 11	8.5	7.5	7	26.5	29.7-	7	11.8	13.3	• 7,4,$\bar{1}$	16.6	18.9-
12	25.6	26.9-	• 9	8.5	9.0	8	11.8	10.9	5	7.6	4.2-
15	12.8	11.4-	12	14.2	16.0	12	21.3	20.9-	6	16.1	16.7
• 5,0,1	6.0	6.1-	5,0,5	19.9	17.9-	• 6,0,3	7.6	8.4	8	11.4	11.7
1	14.2	12.2	2	11.8	12.2	1	11.4	11.1-	• 9	9.0	9.0
2	7.6	5.4	3	21.8	22.8	2	9.5	8.6	12	19.4	19.9-
3	32.2	32.1-	8	17.0	17.9-	3	16.1	16.5	7,1,2	13.2	18.3-
4	13.7	13.5	5,0,$\bar{5}$	27.9	24.8	4	22.7	21.2-	2	9.0	7.7-
5	9.9	7.8	1	18.4	18.8	7	11.4	10.5	3	17.5	16.6-
6	8.0	9.0-	• 2	7.1	5.9	9	19.9	22.0-	• 4	6.6	5.7
7	13.7	12.8-	3	21.3	19.1-	12	11.8	11.2-	• 5	7.6	5.3
8	21.3	20.5-	4	19.9	22.5-	15	12.3	12.0	7	11.8	15.3
9	22.2	24.7	• 6	7.8	5.5-	6,0,$\bar{3}$	13.2	13.0-	7,3,$\bar{2}$	6.1	6.4
12	18.0	17.7	7	13.7	17.3-	1	11.4	12.0-	4	15.1	17.9-
15	13.2	14.4-	• 8	8.5	10.0	2	8.5	8.3	5	9.9	12.7
• 5,0,$\bar{1}$	20.5	22.7	9	26.5	27.9	3	18.0	17.6	7	8.5	7.4
• 2	21.8	22.5	15	12.8	15.6-	5	7.1	5.3	8	9.0	7.4
3	25.5	27.3	5,0,6	33.6	33.5-	7	11.8	12.2	9	17.0	18.1-
4	46.8	48.1-	• 3	9.0	11.9-	8	13.2	15.5	• 11	9.9	10.2-
• 6	6.1	5.5	6	17.5	16.8	9	23.6	24.5-	• 12	9.9	10.9-
• 7	6.0	3.8	8	14.7	13.8-	• 12	8.0	5.4	7,0,3	22.7	21.8
• 8	6.4	5.2	5,0,$\bar{6}$	17.4	15.1-	15	15.1	14.4	1	9.0	10.6-
9	19.9	22.4-	• 2	7.6	9.1	6,0,4	12.8	13.1-	4	11.4	14.7-
10	14.7	15.0	• 3	7.6	8.8-	• 1	8.5	6.1	6	9.9	9.3-
12	19.9	21.2-	4	21.3	24.4-	4	10.9	9.2-	• 7	9.9	8.2
• 15	11.4	10.5	5	10.9	8.6	6	13.7	15.2	7,0,$\bar{3}$	9.0	7.2
5,0,2	13.7	13.0	6	25.1	25.3	• 7	9.5	6.5-	1	19.4	22.2-
1	7.6	4.7	12	22.7	24.6-	9	10.4	8.1	3	6.6	7.7-
2	13.7	11.8-	5,3,7	19.9	20.2-	12	12.3	13.1-	6	9.5	9.7-
3	16.1	12.7-	5	11.8	10.8	6,0,$\bar{4}$	7.6	5.2	7	18.4	18.4
4	20.3	20.1	• 5,0,$\bar{7}$	8.0	8.2-	4	8.5	7.4	8	9.0	8.2-
5	36.9	36.4	• 1	7.6	9.1-	5	18.9	19.6-	• 9	8.5	8.3-
6	16.1	17.9-	2	13.7	12.3	6	11.4	10.3-	• 7,1,4	8.0	10.2
9	12.8	14.7-	3	12.3	9.2	8	10.9	8.3-	3	15.6	14.8
10	10.4	10.0-	• 4	9.5	5.6-	9	9.9	9.1	7,0,$\bar{4}$	15.1	14.9-
11	23.6	25.8-	• 7	9.0	9.4	11	12.8	14.5	2	12.8	11.8-
12	15.1	16.4	8	11.8	14.8-	12	13.2	12.2	4	18.0	18.5
13	15.1	16.9	9	13.2	14.8-	• 6,0,5	9.0	7.6-	5	9.5	8.3-
• 5,0,$\bar{2}$	27.9	28.1	5,1,$\bar{8}$	9.9	10.1-	1	13.2	10.7	• 6	7.6	5.9
• 1	46.8	49.7-	4	12.3	12.0	• 2	9.0	8.3	7,0,5	18.4	19.7-
3	12.3	13.1-	5	18.4	19.5-	3	11.4	9.5-	7,0,$\bar{5}$	14.7	15.0
4	7.6	8.6-	• 5,2,$\bar{9}$	11.4	10.7-	7	12.8	10.1-	1	20.8	20.8
5	14.2	15.1-	• 3	11.8	12.1	8	16.6	16.3-	3	13.7	13.9
6	11.8	14.2-	5,0,$\overline{10}$	14.7	15.6	9	11.8	12.2	7	15.6	16.8-
7	38.3	40.1	• 6,0,0	16.1	10.6	• 6,0,$\bar{5}$	7.1	9.9	8	11.4	10.4
9	12.8	15.5-	• 1	23.6	27.1	1	10.4	9.9	7,0,$\bar{6}$	20.8	20.5
• 15	10.4	11.5	2	6.6	5.3-	2	18.0	17.0-	3	13.2	10.8-
• 17	11.4	14.7-	3	19.4	20.5	5	12.3	9.7-	4	17.5	17.8-
5,0,3	14.2	11.6	4	5.7	4.8	7	12.3	9.5-	• 7,0,$\bar{7}$	14.7	12.3-
1	20.8	22.4-	5	9.0	7.1	8	25.1	24.2	3	10.9	10.6-
2	22.7	21.1-	6	10.9	8.0-	9	11.8	9.3	6	12.8	12.4
3	7.1	6.5-	7	24.6	22.9-	10	11.8	9.2-	• 7,0,$\bar{8}$	9.9	9.0-
7	18.0	18.5	6,0,1	15.6	18.7-	11	9.9	7.3	3	11.8	8.9
8	27.0	29.7	1	7.1	6.7-	12	11.8	8.3-	7,5,$\bar{9}$	12.8	11.9-

of the atoms is due to the vibrations of the molecules. In any case the deviations from centrosymmetry will be very small because of the small ΔB values in the present low temperature work [see (*b*)].

The standard deviations of the coordinates were estimated by use of Cruickshank's (1949) formula. The calculated standard deviations give only a lower limit of the errors since systematic errors (absorption, errors in the scaling factors) occur and since the anisotropy of the thermal movement was not taken into account during the refinement. The calculated values multiplied by 1·5 were therefore taken as the correct standard deviations. The root mean square value of $\sigma(x)$, $\sigma(y)$ and $\sigma(z)$ was taken as the standard deviation $\sigma(r)$ for each of the atoms. These standard deviations are given in Table 2.

Discussion of the structure

The structure consists of molecules $(NSCl)_3$ illustrated in Fig. 2. They have one mirror plane coinciding with a mirror plane in the adopted space group $P2_1/m$. As the molecules of $\alpha(NSOCl)_3$, the $(NSCl)_3$ molecules exist as the chair form with the chlorine atoms in axial positions. A similar chair configuration is observed in other six-membered inorganic ring systems, *e.g.* in $(SO_3)_3$ and in $(PO_3)_3^{3-}$. In this form, which has (approximate) symmetry $3m$, all π bonds in the ring are (almost) symmetrically equivalent and it is perhaps due to this equivalence that the chair form is realized so often.

The bond lengths and angles listed in Table 3 are calculated from the coordinates in Table 2. The N–S bond lengths are equal within experimental error. As was discussed in the previous section, it is very probable

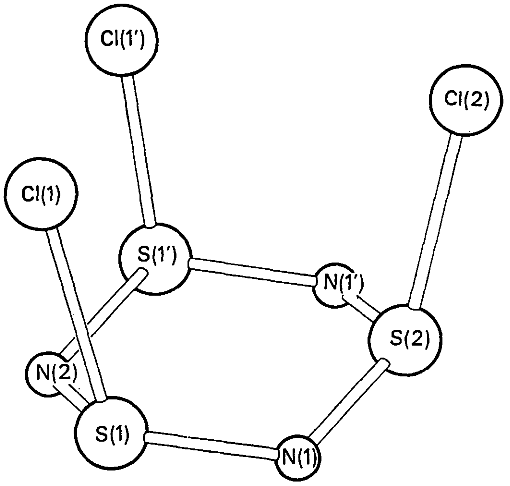


Fig. 2. Molecule of $(NSCl)_3$. The atoms S(2), N(2) and Cl(2) are on the mirror plane.

Fig. 1. Superposition of sections through the three-dimensional difference Fourier synthesis calculated after the isotropic refinement. The sections are parallel to (010) through the positions of the atoms S(1), S(2), Cl(1) and Cl(2) (left), and N(1) and N(2) (right). For the sulphur and chlorine atoms contour lines are drawn at intervals of 0·5 e.Å^{-3}, for the nitrogen atoms at intervals of 0·25 e.Å^{-3}. Positive regions are indicated by full lines, negative regions by broken lines. The zero line is indicated by.–.–.–.

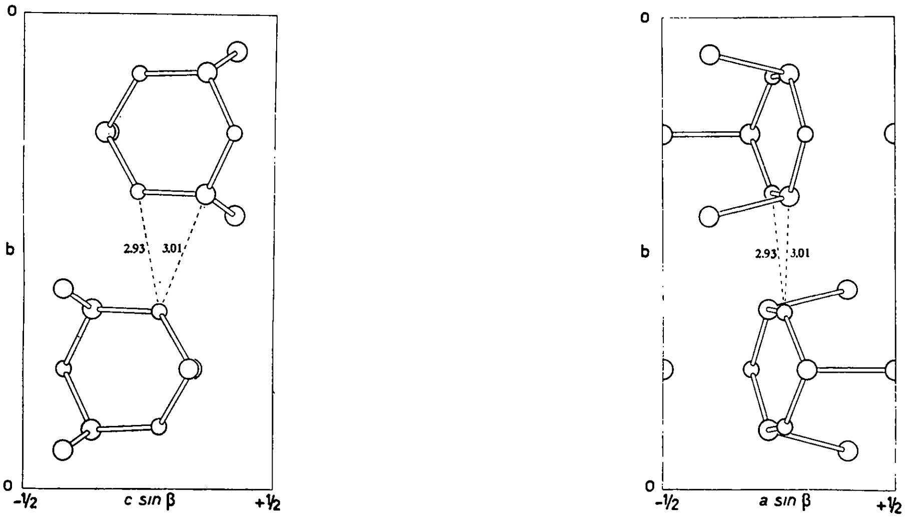


Fig. 3. $(NSCl)_3$: projections along [001] on the (001) plane (right) and along [100] on the (100) plane (left).

that this equality in bond length is genuine and not merely the result of refining in the wrong space group. The N–S bonds in $(NSCl)_3$, average length 1·605 Å, are only 0·035 Å longer than the N–S bonds in α $(NSOCl)_3$. The fact that the N–S bonds in both compounds are short and equal indicates the presence of delocalized p_π–d_π bonds. In $(NSF)_4$ also short N–S bonds are found, but in the eight-membered ring of these molecules, where the N–S bonds are not symmetrically equivalent, unequal N–S bonds with lengths 1·66 and 1·54 Å alternate. (Wiegers & Vos, 1963*a*). The elongation of the N–S bonds in $(NSCl)_3$ relative to those in α$(NSOCl)_3$ is in agreement with the experimental rule that the bonds in sulphur(IV) compounds are longer than those in sulphur(VI) compounds. A theoretical discussion of this rule was given by Truter (1962).

The lengths of the two independent S–Cl bonds in the $(NSCl)_3$ molecule are unequal, 2·084 and 2·150 Å. Both bonds are considerably longer than the S–Cl bonds in α$(NSOCl)_3$, 2·003 Å. The observed bond lengths may be compared with the S–Cl bond lengths in $SOCl_2$, 2·07 Å, and in SO_2Cl_2, 1·99 Å. The difference in length between the two independent S–Cl bonds may be due to their different environements (Fig. 3). The shorter S–Cl bond, 2·084 Å, occurs in a linear chain of S–Cl · · · S–Cl *etc.* in the mirror plane; the intermolecular S · · · Cl distance, 3·41 Å, is 0·24 Å shorter than the sum, 3·65 Å, of the van der Waals radii for sulphur and chlorine. As in other compounds where a similar intermolecular configuration with short intermolecular distances is observed (Hassel & Rømming, 1962), the short S · · · Cl distance may be explained by charge transfer. The sulphur atom of the longer S–Cl bond has strong interaction with a nitrogen atom of a neighbouring molecule; the S · · · N distance, 3·01 Å, is 0·34 Å shorter than the sum of the van der Waals radii for nitrogen and sulphur. No conclusive explanation has yet been given for the difference in length between the two S–Cl bonds in the molecule.

Owing to the strong intermolecular interaction the $(NSCl)_3$ molecule is deformed. Not only are the two independent S–Cl bonds unequal, but so are the angles between these bonds and the plane through the three sulphur atoms, *viz.* 104·0° for S(1)–Cl(1) and 101·5° for S(2)–Cl(2). The deformation is reflected also by the distances of the nitrogen atoms from the plane through the sulphur atoms, 0·225 Å for N(1) and N(1′) and 0·126 Å for N(2). The independent N–S–Cl valency angles agree rather well with each other.

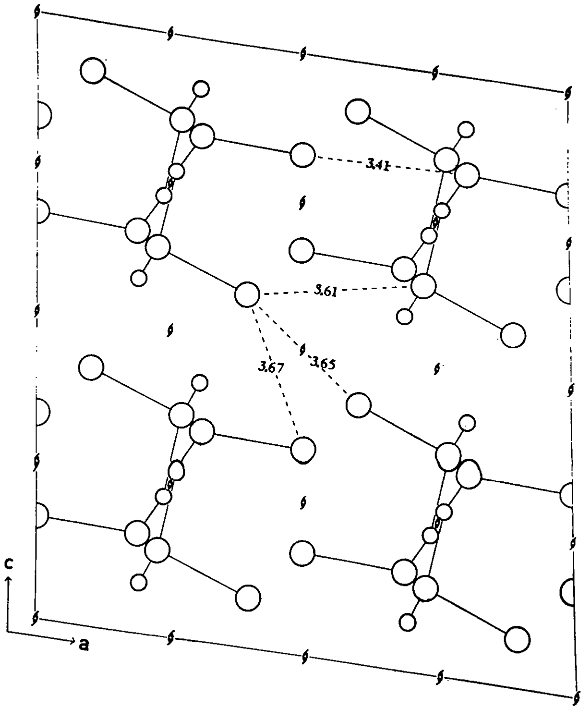


Fig. 4. $(NSCl)_3$: Projection on the plane (010). Large circles indicate sulphur or chlorine atoms, small circles correspond to nitrogen atoms.

The angles N–S–N, 113·4°, are small in comparison with the angles N–P–N (120°) in $(NPCl_2)_3$. This will be due, as in $(NSF)_4$, to the relatively great *p* character of the sulphur hybrids used for the σ bonds and to the strong repulsion of the exocyclic lone pair electrons on the sulphur atoms.

The lone pair electrons are in equatorial positions. It is noteworthy that in all cyclic N–S compounds investigated so far, $(NSF)_4$, $\alpha(NSOCl)_3$ and $(NSCl)_3$, strongly repelling groups [the lone pair electrons in the S(IV) compounds or the double bonds to the oxygen atoms in $\alpha(NSOCl)_3$] are pointing away from the mean plane of the ring.

All calculations were carried out on the digital computer ZEBRA, with programs devised by Dr D.W. Smits.

We wish to thank Professor E. H. Wiebenga for his interest throughout the course of this investigation and Mr H. Schurer for operating the ZEBRA.

References

ALTONA, C. (1964). *Acta Cryst.* **17**, 1282.
COCHRAN, W. (1951). *Acta Cryst.* **4**, 408.
CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
FREEMAN, A. J. (1959). *Acta Cryst.* **12**, 261.
GOEHRING, M. (1957). *Ergebnisse und Probleme der Chemie der Schwefelstickstoffverbindungen.* Berlin: Akademie Verlag.
HASSEL, O. & RØMMING, C. (1962). *Quart. Rev. Chem. Soc. Lond.* **16**, 1.
HAZELL, A. C., WIEGERS, G. A. & VOS, A. (1966). *Acta Cryst.* **20**, 186.
SCHRÖDER, H. & GLEMSER, O. (1959). *Z. anorg. Chem.* **298**, 78.
SMITS, D. W. & WIEBENGA, E. H. (1953). *J. Sci. Instrum.* **30**, 280.
TOMIIE, Y. & STAM, C. H. (1958). *Acta Cryst.* **11**, 126.
TRUTER, M. R. (1962). *J. Chem. Soc.* p. 3400.
WIEBENGA, E. H. & SMITS, D. W. (1950). *Acta Cryst.* **3**, 265.
WIEGERS, G. A. & VOS, A. (1963*a*). *Acta Cryst.* **16**, 152.
WIEGERS, G. A. & VOS, A. (1963*b*). *Acta Cryst.* **16**, A40.

Acta Cryst. (1966). **20**, 197

The Crystal and Molecular Structure of Acetyl-bromoacetyldihydroenmein

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The crystal structure of acetyl-bromoacetyldihydroenmein, $C_{24}H_{31}O_8Br$, has been determined in order to elucidate the molecular structure and absolute configuration of enmein, $C_{20}H_{26}O_6$, a principal bitter constituent of *Isodon trichocarpus* Kudo. The derivative was prepared through a series of reactions and it crystallized in a structure with the space group $P2_12_12_1$ and the unit-cell dimensions,

$$a=9{\cdot}78,\ b=15{\cdot}25,\ c=16{\cdot}13\ \text{Å}.$$

The crystal structure was solved by the heavy atom method and refined by the method of least squares. The final reliability index for 2237 observed reflexions was 0·10.

The present analysis, which established the structure of enmein including its absolute configuration, furnishes useful information for chemical investigations which have been carried out in parallel with the X-ray study.

Introduction

Enmein, $C_{20}H_{26}O_6$, is a diterpene bitter principle isolated from *Isodon trichocarpus* Kudo (Ikeda & Kanatomo, 1958; Takahashi, Fujita & Koyama, 1958; Naya, 1958) and its structural study by chemical methods has been carried out by several research groups (Ikeda & Kanatomo, 1958; Takahashi, Fujita & Koyama, 1958; Naya, 1958; Kanatomo, 1958; Takahashi, Fujita & Koyama, 1960; Kanatomo, 1961; Kubota, Matsuura, Tsutsui & Naya, 1961). In 1961, Kubota and his collaborators proposed the structure (I) (Fig. 1) for enmein (Kubota, Matsuura, Tsutsui & Naya, 1961), but later, they suggested that the planar structure (II) is also a probable one (Kubota, Matsuura, Tsutsui & Naya, 1963).

In order to give a crucial proof for the chemical structure and to establish the stereochemistry of enmein, the present authors have performed the X-ray study of acetyl-bromoacetyldihydroenmein (III) and determined the molecular structure of enmein including its absolute configuration as (IV), in conformity with the result of recent chemical investigations (Kubota, Matsuura, Tsutsui, Uyeo, Takahashi, Irie, Numata, Fujita, Okamoto, Natsume, Kawazoe, Shudo, Ikeda, Tomoeda, Kanatomo, Kosuge & Adachi, 1964). A preliminary short note on the present work has already appeared elsewhere (Iitaka & Natsume, 1964).