similar packing in the unit cell and this bond is involved in a close contact between molecules at (000) and ($\frac{1}{2}-x$, $\bar{y}$, $\frac{1}{2}+z$) in dipara-anthracene and between molecules at (000) and (001) in the photo-isomer.

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# The Crystal Structures of Two Sulphur-Nitrogen Compounds with (S–N)$_3$ Rings
## I. α-Sulphanuric Chloride, α (NSOCl)$_3$

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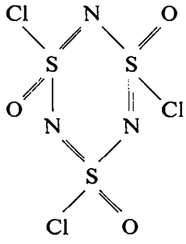
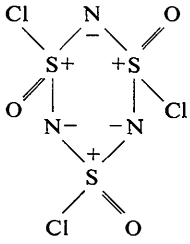
α-Sulphanuric chloride, α(NSOCl)$_3$ is orthorhombic with $a=7{\cdot}552$, $b=11{\cdot}540$, and $c=10{\cdot}078$ Å; the space group is $Pnma$ ($D_{2h}^{16}$) and there are 4 molecules in the unit cell. Independent three-dimensional investigations have shown that the molecule exists as the chair form with the chlorine atoms in the axial positions. The mean bond lengths, with e.s.d. are: S–N 1·571 (0·004), S–Cl 2·003 (0·003) and S–O 1·407 (0·007) Å; and the bond angles: N–S–N 112·8 (0·4), S–N–S 122·0 (0·4), N–S–O 111·9 (0·3$_5$), N–S–Cl 106·3 (0·3); and O–S–Cl 107·9° (0·3$_5$). The fact that the S–N bonds are all short, and equal, indicates the presence of delocalized $p_\pi$–$d_\pi$ bonds.

### Introduction

The potential aromatic character of the cyclic phosphonitrilic halides and the thiazyl halides has been recognized for some time and has been discussed in detail (Craig, 1959; Dewar, Lucken & Whitehead, 1960; Cruickshank, 1961*a*; Davies, 1962; Craig & Paddock, 1962). Recent X-ray studies on several trimeric and tetrameric phosphonitrilic compounds have shown that in each case the P–N bonds are equal, and short. However, in the case of the thiazyl halides, an X-ray investigation of (NSF)$_4$ showed the molecule to have alternate long and short S–N bonds (Wiegers & Vos, 1962). It therefore seemed worth while to investigate other potentially aromatic (NS$^{\text{IV}}$)$_n$ and (NS$^{\text{VI}}$)$_n$ systems.

Several modifications of sulphanuric chloride, (NSOCl)$_3$, are known. Chemical evidence suggests that both the α and the β forms contain an (NS)$_3$ ring (Kirsanov, 1952; Goehring, 1957). Kirsanov (1952) proposed the structures I and II,


(I)


(II)

and on the basis of their physical properties suggested that the α was the *trans* and the β the *cis* compound.

The structure of the α form has been determined simultaneously in two laboratories, and has been briefly reported by both groups: Banister & Hazell (1962), and Wiegers & Vos (1962). In both cases three-dimensional anisotropic refinements were carried out. Hazell, with 590 visually estimated intensities, refined by the method of least-squares to a discrepancy index of $R=0{\cdot}11$; Wiegers & Vos, with 503 photometrically measured intensities, refined by Fourier methods to $R=0{\cdot}047$. The two structure determinations are described, and results are discussed in terms of the more accurate determination, *i.e.* that of Wiegers & Vos; a compari-

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son of the two sets of results is also given. The abbreviations H for Hazell, and W for Wiegers & Vos will be used in the remainder of paper.

The results confirm that α-sulphanuric chloride is trimeric with an $(NS)_3$ ring, but in contradiction to Kirsanov's supposition all the chlorine atoms are on the same side of the ring. The molecule is in fact a chair form with all the chlorine atoms in axial positions and with all S–N distances equal within the limits of experimental error.

In this structure determination, as is the case with many of the phosphonitrilic compounds, there is the possibility that the equality of bond lengths may arise from the wrong choice of the possible two space groups (here *Pnma* and $Pn2_1a$). Wiegers & Vos (1963) have demonstrated that the equality in bond lengths is almost certainly real and not due to space group ambiguities.

## Experimental

### *Preparation and crystal data*

α-Sulphanuric chloride was prepared by Goehring's (1957) method (W) and by Banister's (unpublished) modification of Kirsanov's (1952) method (H). In both cases the crystals were sublimed under high vacuum to obtain crystals suitable for X-ray work. The melting point, 142–3°C (W), was in good agreement with the values quoted by Kirsanov (1952), and Goehring (1957).

The compound, which is colourless, crystallizes in the orthorhombic system with space group *Pnma* ($D_{2h}^{16}$) or $Pn2_1a$ ($C_{2v}^{9}$), and has cell dimensions (Å):

| | *a* | *b* | *c* |
|---|---|---|---|
| H | 7·60 | 11·46 | 10·10 |
| W | 7·552 s.d. 0·003 | 11·540 s.d. 0·003 | 10·078 s.d. 0·004 |

The values of W were determined from powder data obtained with a Philips diffractometer, PW1050/30, with Cu $K\alpha_1$ radiation ($\lambda = 1{\cdot}54051$ Å) and are more accurate than H's values, which were determined from oscillation and Weissenberg photographs. The measured density (2·22 $g.cm^{-3}$, W) shows that there are 4 molecules in the unit cell (calculated density 2·21 g. $cm^{-3}$); for *Pnma* the implied molecular symmetry is *m* or $\bar{1}$. The crystals are tabular on (010) bounded by {101}. No piezoelectric effect could be observed (W and H).

### *Intensity data*

In both cases the intensities were measured from Weissenberg films by the multiple-film technique. H, using Cu *Kα* radiation, measured 590 independent non-zero reflexions (*0kl*–*6kl*, *h0l*, and *hk0*–*hk2*); these were estimated visually by means of a calibration strip. Although the crystals were of radius approximately $2/\mu$ ($\mu = 156$ $cm^{-1}$ for Cu *Kα*) no absorption corrections were made. W, using Mo *Kα* radiation, recorded 558 independent non-zero reflexions (*0kl*–*7kl*, *h0l*, and *hk0*–*hk3*) with an integrating Weissenberg camera (Wiebenga & Smits, 1950) and measured the intensities with a densitometer (Smits & Wiebenga, 1953). Crystals were chosen such that the mean value of $\mu R$ perpendicular to the rotation axis was 0·17 ($\mu = 16{\cdot}85$ $cm^{-1}$ for Mo *Kα*). Scaling of intensities was done by comparing the intensities of reflexions common to photographs taken about different axes. W found the errors of the scaling factors, for an individual layer line, to be from 2 to 4%. The accuracy of the intensity measurements (W) 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 the individual and mean values respectively. For the 184 common reflexions this discrepancy factor was 0·054.

## Determination of the structure

The distribution of vectors in a three-dimensional Patterson function shows that the space group is probably *Pnma*, and so the molecule, if an $(NS)_3$ ring, must lie on the mirror plane. W found the positions of all the atoms from the Patterson function whereas H merely found the sulphur atoms and used the 'heavy atom technique' to find the positions of the other atoms. The approximate structures were refined anisotropically, by the method of least-squares (H) and by difference Fourier syntheses (W).

### *Least-squares refinement* (H)

The function minimized was $r = \Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2$, where the weighting factor, $w$, was $(a + |F| + b|F|^2)^{-1}$. The values of $a$ and $b$ were chosen so that the mean values of the weighted differences, $w(|F_o| - |F_c|)^2$, were approximately independent of the magnitude of $F_o$; in the early stages of refinement $a = b = 0$ was used, for the final cycle the values used were $a = 8$, $b = 0{\cdot}02$ (*cf.* $2F_{\min} = 14$, $2/F_{\max} = 0{\cdot}015$). All 590 reflexions were used.

During 5 cycles of isotropic refinement the value of $R$ dropped from 0·42 to 0·21, and $r$ from 0·327 to 0·082. One oxygen atom which had been incorrectly placed shifted ~0·4 Å. A further four cycles of anisotropic refinement reduced $R$ to 0·16 and $r$ to 0·060. At this stage it was clear that the scale factors for the individual layer lines were incorrect; after rescaling, a further four cycles reduced $R$ to 0·11 and $r$ to 0·023. Refinement was terminated when the maximum coordinate shift was less than a half standard deviation, and maximum thermal parameter shift less than one standard deviation.

The final coordinates and anisotropic thermal parameters are listed in Tables 1 and 2, together with their standard deviations as estimated from the least-squares residuals (Cruickshank & Robertson, 1953). The atomic scattering factors used were those of Tomiie & Stam (1958) for chlorine and sulphur and those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for oxygen and nitrogen. The calculations were performed on Durham University's Ferranti Pegasus computer with programs written by Cruickshank *et al.* (1961).

*Difference-Fourier refinement* (W)

Preliminary two-dimensional refinement reduced the value of $R$ to 0·13 for the $hkl$ reflexions. The parameters were then refined by successive difference-Fourier syntheses. During refinement those reflexions thought likely to suffer from extinction, and also some very weak ones, were omitted (these are marked with an asterisk in Table 3).

The first three-dimensional difference synthesis was calculated with isotropic temperature factors and indicated, just as the three-dimensional electron density distribution, a strong libration of the molecule (Fig. 1) The directions of the principal axes of the thermal-vibration tensors were determined, for each atom, from this first difference synthesis and the $F_o$ synthesis. These directions were used in the further cycles of anisotropic refinement. For the first few cycles the temperature factor shifts were obtained by the method of Cochran (1951, formula 4·7), but in the later stages the shifts were estimated by comparing successive syntheses.

Before calculating the final cycles the scale factors $K_h$ for the individual $h$ layer-lines were adjusted so that $K_h\Sigma|F_o|=\Sigma|F_c|$, for $h=1$–6 the changes in $K_h$ were $<3\%$, but for $h=7$ the correction was 10%.

After five cycles of refinement the atomic coordinate shifts were small compared with the standard deviations, and the value of $R$ was 0·047 and $r=0{\cdot}00307$ for the reflexions used in the refinement ($R=0{\cdot}049$ for all non-zero reflexions). The observed and calculated structure factors are compared in Table 3; the final

Table 1. *Fractional atomic coordinates, and estimated standard deviations* (Å × 10³)

| | | $x$ | $y$ | $z$ | $(\sigma^2)^{\frac{1}{2}}$ | $\sigma(x)$ | $\sigma(y)$ | $\sigma(z)$ |
|---|---|---|---|---|---|---|---|---|
| S(1) | W | −0·1324 | 0·1313 | −0·1350 | 3 | | | |
| | H | −0·1324 | 0·1317 | −0·1351 | | 3 | 4 | 5 |
| S(2) | W | 0·1026 | 0·2500 | 0·0207 | 3 | | | |
| | H | 0·1029 | 0·2500 | 0·0209 | | 4 | 0 | 5 |
| Cl(1) | W | −0·3251 | 0·0968 | −0·0061 | 3 | | | |
| | H | −0·3246 | 0·0967 | −0·0068 | | 4 | 5 | 5 |
| Cl(2) | W | −0·0163 | 0·2500 | 0·1979 | 3 | | | |
| | H | −0·0163 | 0·2500 | 0·1979 | | 5 | 0 | 5 |
| N(1) | W | 0·0434 | 0·1380 | −0·0508 | 10 | | | |
| | H | 0·0426 | 0·1349 | −0·0514 | | 10 | 13 | 11 |
| N(2) | W | −0·1805 | 0·2500 | −0·2015 | 10 | | | |
| | H | −0·1875 | 0·2500 | −0·2016 | | 17 | 0 | 18 |
| O(1) | W | −0·1300 | 0·0406 | −0·2274 | 10 | | | |
| | H | −0·1264 | 0·0400 | −0·2187 | | 11 | 12 | 12 |
| O(2) | W | 0·2860 | 0·2500 | 0·0448 | 10 | | | |
| | H | 0·2904 | 0·2500 | 0·0424 | | 13 | 0 | 16 |

Table 2. *Anisotropic thermal parameters* (Å² × 10⁴)

The arrangement is: (1) H's value with the e.s.d. in brackets, (2) W's observed value, (3) W's calculated value.

| Atom | | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{23}$ | $U_{13}$ |
|---|---|---|---|---|---|---|---|
| S(1) | H | 404 (16) | 510 (17) | 442 (16) | −2 (29) | 90 (32) | −100 (28) |
| | $W_o$ | 351 | 380 | 354 | −34 | −39 | −59 |
| | $W_c$ | 366 | 441 | 380 | −45 | −36 | −57 |
| S(2) | H | 269 (21) | 603 (28) | 379 (22) | 0 | 0 | −35 (36) |
| | $W_o$ | 283 | 481 | 248 | 0 | 0 | −19 |
| | $W_c$ | 323 | 476 | 316 | 0 | 0 | −12 |
| Cl(1) | H | 410 (19) | 742 (26) | 812 (27) | 244 (38) | −135 (46) | 175 (37) |
| | $W_o$ | 502 | 531 | 671 | 117 | −20 | 100 |
| | $W_c$ | 458 | 517 | 473 | 142 | −62 | 46 |
| Cl(2) | H | 492 (29) | 845 (37) | 408 (22) | 0 | 0 | 85 (43) |
| | $W_o$ | 368 | 653 | 476 | 0 | 0 | −36 |
| | $W_c$ | 381 | 622 | 368 | 0 | 0 | −14 |
| O(1) | H | 753 (81) | 663 (70) | 723 (79) | −75 (123) | 530 (124) | −35 (116) |
| | $W_o$ | 654 | 537 | 555 | −136 | −90 | −197 |
| | $W_c$ | 646 | 528 | 556 | −178 | −111 | −101 |
| O(2) | H | 276 (65) | 1005 (127) | 631 (87) | 0 | 0 | −192 (134) |
| | $W_o$ | 519 | 704 | 346 | 0 | 0 | −12 |
| | $W_c$ | 502 | 731 | 349 | 0 | 0 | 77 |
| N(1) | H | 300 (51) | 661 (71) | 512 (60) | 20 (108) | 186 (112) | −307 (100) |
| | $W_o$ | 465 | 360 | 360 | 2 | 44 | −5 |
| | $W_c$ | 471 | 429 | 384 | −59 | 34 | −21 |
| N(2) | H | 505 (100) | 534 (92) | 494 (85) | 0 | 0 | −195 (158) |
| | $W_o$ | 433 | 506 | 314 | 0 | 0 | −91 |
| | $W_c$ | 312 | 480 | 326 | 0 | 0 | −80 |

coordinates and anisotropic temperature factors are listed in Tables 1 and 2.

The standard deviations of the coordinates were estimated using Cruickshank's (1949) formula. For the heavy atoms (S and Cl) standard deviations of about 0·0015 Å were calculated; for the light atoms (N and O) the standard deviations were about 0·005 Å. The final difference map shows some systematic deviations, probably due to the fact that the refinement was carried out with fixed directions of the principal axes of the vibration-ellipsoids. The errors in the coordinates may therefore be larger than the s.d. estimated by Cruickshank's formula. We think values of 0·003 Å for the heavy atoms and 0·01 Å for the light atoms to be a reasonable estimate of the 'standard deviations' in the coordinates.

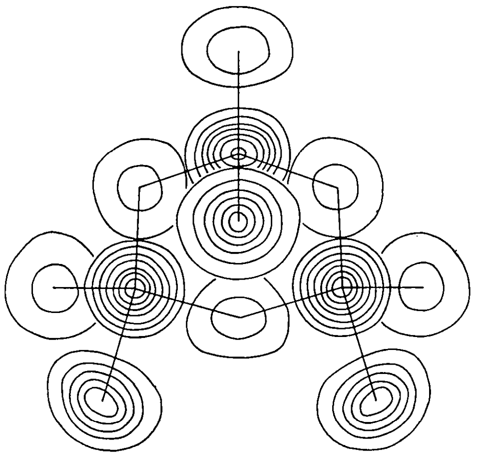

Fig. 1. Superposition of sections through the three-dimensional $F_o$ synthesis .The sections are parallel to (001) through the atomic positions of the atoms. Contour lines are drawn at intervals of 5 e.Å$^{-3}$ starting at 2 e.Å$^{-3}$.

Table 3. *Observed and calculated structure factors* (W)

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

| h k l | $\|F_o\|$ | $F_c$ | h k l | $\|F_o\|$ | $F_c$ | h k l | $\|F_o\|$ | $F_c$ | h k l | $\|F_o\|$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| •0,2,0 | 96.3 | 95.0- | 1,7,1 | 28.5 | 28.5- | 1,1,12 | 27.8 | 27.6- | 2,7,6 | 15.9 | 16.4 |
| 4 | 41.7 | 42.7- | 8 | 48.3 | 48.0 | | | | 2,0,7 | 23.9 | 23.3 |
| • 6 | 106.2 | 108.9- | 9 | 18.9 | 18.8- | 2,1,0 | 7.7 | 7.6 | 1 | 11.8 | 9.8- |
| • 8 | 103.4 | 110.9 | 10 | 39.3 | 40.4- | 2 | 53.2 | 54.3- | 2 | 21.7 | 22.1 |
| 10 | 36.7 | 37.0- | 11 | 23.0 | 22.4 | 3 | 9.2 | 11.0 | 3 | 18.9 | 17.8 |
| 14 | 9.9 | 8.8- | •1,0,2 | 115.3 | 117.5- | 4 | 31.1 | 34.2 | 4 | 33.8 | 32.3- |
| 0,1,1 | 48.1 | 44.7 | 1 | 33.9 | 33.4 | 5 | 27.5 | 27.0- | 5 | 25.6 | 22.5- |
| • 3 | 126.2 | 131.6 | 2 | 18.7 | 19.4 | 6 | 20.2 | 19.2 | 2,0,8 | 33.9 | 32.9- |
| 5 | 46.8 | 49.3- | 3 | 73.9 | 76.9 | 7 | 38.1 | 37.4 | 3 | 27.2 | 26.9 |
| 7 | 18.8 | 18.2 | 4 | 27.4 | 28.0 | 8 | 19.4 | 16.9 | 4 | 13.6 | 12.3 |
| 9 | 29.1 | 28.3 | 5 | 66.1 | 68.0- | 9 | 46.1 | 48.2 | 5 | 37.0 | 37.9- |
| 11 | 19.2 | 17.8 | • 6 | 8.8 | 7.6 | 10 | 27.0 | 27.7- | 6 | 12.0 | 11.7 |
| 13 | 21.4 | 23.0- | 8 | 36.5 | 36.9- | • 11 | 12.0 | 11.1 | 9 | 17.2 | 17.5 |
| •0,0,2 | 96.4 | 97.0 | 9 | 26.8 | 24.2 | 13 | 32.3 | 33.6- | 13 | 19.8 | 19.8- |
| 2 | 18.6 | 19.7- | 10 | 16.2 | 13.8 | •2,0,1 | 114.4 | 117.0- | 2,0,9 | 43.4 | 43.1- |
| 4 | 85.6 | 87.0- | • 11 | 12.4 | 14.4 | 1 | 53.7 | 52.4- | 1 | 17.9 | 15.6 |
| 6 | 48.9 | 50.8- | 12 | 12.9 | 12.7 | 2 | 23.5 | 23.3- | 2 | 17.4 | 17.8 |
| 8 | 25.7 | 23.4 | 13 | 21.6 | 21.3- | 3 | 46.3 | 43.5 | 3 | 17.4 | 18.9- |
| 10 | 25.6 | 26.7 | •1,0,3 | 98.4 | 99.7- | 4 | 23.0 | 24.0 | • 4 | 11.4 | 11.6 |
| 12 | 17.5 | 17.5 | 1 | 58.3 | 59.2- | 5 | 37.9 | 36.9- | • 5 | 10.7 | 12.4 |
| 0,1,3 | 40.4 | 38.0 | 3 | 74.3 | 75.0 | 7 | 22.6 | 21.8 | 8 | 25.9 | 26.5- |
| 3 | 48.1 | 42.9 | 4 | 29.4 | 31.1 | 8 | 26.6 | 26.3- | 10 | 15.9 | 16.3 |
| 5 | 81.1 | 81.0- | 6 | 18.7 | 20.6 | 9 | 16.1 | 14.2- | 2,1,10 | 16.8 | 15.9- |
| 7 | 30.6 | 30.2- | 8 | 21.7 | 22.3- | 10 | 18.1 | 19.1 | 2 | 16.4 | 18.2- |
| 9 | 14.8 | 12.2 | 1,9,3 | 60.9 | 61.9- | • 11 | 12.0 | 8.8 | 3 | 17.2 | 18.2- |
| 13 | 15.7 | 14.7- | 13 | 16.6 | 17.4 | 12 | 18.8 | 20.3 | 4 | 21.7 | 22.4 |
| •0,0,4 | 98.0 | 102.7 | 1,1,4 | 29.4 | 27.2 | 2,0,2 | 58.8 | 57.1- | 2,1,11 | 18.9 | 19.4- |
| 4 | 64.8 | 67.0 | 2 | 21.7 | 22.5 | • 1 | 113.6 | 124.7- | • 2 | 12.6 | 13.2 |
| 6 | 79.2 | 80.6- | 3 | 26.1 | 24.0- | 2 | 8.9 | 8.6 | • 3 | 13.9 | 12.4 |
| 8 | 14.1 | 12.4- | 4 | 16.6 | 19.5- | 3 | 51.7 | 51.1- | • 4 | 10.7 | 11.0- |
| 12 | 32.9 | 33.5 | 6 | 24.3 | 23.7 | 4 | 12.4 | 10.1- | • 5 | 12.6 | 13.1- |
| 0,1,5 | 42.7 | 44.6- | • 7 | 11.3 | 12.2- | 5 | 45.5 | 45.2- | 2,1,12 | 15.4 | 15.9- |
| 3 | 32.9 | 32.0 | 1,0,5 | 29.3 | 27.3 | 6 | 47.5 | 47.6 | 2,4,13 | 17.4 | 19.5- |
| 5 | 21.0 | 18.8 | 1 | 10.6 | 13.2 | 7 | 44.6 | 43.6 | | | |
| 7 | 35.1 | 36.6 | 2 | 53.6 | 53.3- | 9 | 19.7 | 18.5- | •3,0,1 | 66.1 | 60.3 |
| 9 | 29.0 | 30.8- | 3 | 39.5 | 41.1 | 10 | 14.0 | 14.0- | 1 | 18.9 | 20.0- |
| 0,0,6 | 75.1 | 78.1 | 4 | 84.1 | 86.6 | 12 | 11.5 | 11.5- | 2 | 18.8 | 17.3 |
| 2 | 33.7 | 31.6- | 5 | 22.8 | 21.9 | 13 | 13.2 | 12.9- | 3 | 16.2 | 16.0 |
| 4 | 12.2 | 18.0- | 6 | 25.5 | 23.1- | 2,0,3 | 11.8 | 7.4 | 4 | 29.2 | 27.1- |
| 6 | 42.7 | 42.0- | • 8 | 12.5 | 10.9 | 1 | 50.9 | 49.9 | 5 | 27.2 | 23.0- |
| 8 | 32.7 | 33.8 | 9 | 24.7 | 22.5- | 2 | 36.8 | 36.2 | 6 | 41.0 | 41.9- |
| 12 | 9.9 | 11.5 | 10 | 25.9 | 26.7- | 3 | 27.0 | 25.8- | 7 | 11.1 | 11.2 |
| 0,1,7 | 41.6 | 41.7- | • 12 | 15.2 | 14.1 | 4 | 27.9 | 28.7 | • 8 | 9.0 | 8.4- |
| 3 | 34.4 | 33.6 | 1,1,6 | 51.1 | 48.8- | 5 | 9.7 | 11.5 | 10 | 25.4 | 26.4 |
| 5 | 32.2 | 33.4- | • 2 | 10.3 | 9.7 | 7 | 14.3 | 14.6- | 11 | 15.8 | 14.0 |
| 7 | 25.4 | 21.6 | 3 | 21.9 | 21.6 | 8 | 29.0 | 28.7- | 12 | 16.1 | 15.9 |
| 9 | 22.3 | 24.7- | 4 | 62.1 | 61.7- | 9 | 17.7 | 16.9 | 3,0,2 | 28.5 | 28.3- |
| 0,0,8 | 38.8 | 41.2 | 6 | 29.8 | 29.9 | 2,0,4 | 16.4 | 17.3- | 1 | 61.1 | 62.3- |
| 2 | 28.1 | 28.8 | 7 | 40.1 | 39.6 | 1 | 89.5 | 94.3- | 2 | 11.6 | 10.5- |
| 4 | 54.9 | 55.2- | 8 | 14.1 | 14.6 | 2 | 24.3 | 24.0- | 4 | 30.1 | 29.2 |
| 0,1,9 | 27.2 | 25.8 | 9 | 18.3 | 18.9- | 3 | 47.0 | 47.1- | 7 | 21.6 | 23.5 |
| 3 | 33.7 | 37.0 | 1,0,7 | 14.0 | 12.7- | 4 | 18.7 | 19.0 | 8 | 16.9 | 17.1- |
| 5 | 26.3 | 27.7- | 1 | 27.8 | 27.5 | 5 | 42.8 | 42.1 | 9 | 31.2 | 34.2- |
| • 9 | 9.9 | 12.0 | 3 | 52.7 | 53.1 | 6 | 17.7 | 17.7 | • 12 | 11.8 | 11.3 |
| •0,0,10 | 10.3 | 9.3 | 4 | 22.0 | 21.2- | 7 | 67.3 | 69.8 | 3,0,3 | 106.5 | 105.1 |
| 2 | 14.0 | 13.2- | 5 | 43.6 | 40.8- | • 8 | 9.7 | 9.2 | 1 | 64.1 | 66.1- |
| 4 | 31.4 | 31.0 | 6 | 15.7 | 16.2 | 9 | 21.3 | 22.4- | 2 | 42.3 | 43.5 |
| 6 | 27.2 | 30.0- | 7 | 24.5 | 25.0- | 10 | 17.3 | 17.9- | 3 | 10.2 | 10.1- |
| 0,1,11 | 22.3 | 21.0- | 1,0,8 | 23.7 | 24.7- | 2,0,5 | 43.2 | 40.6 | 4 | 92.3 | 94.1- |
| 3 | 25.4 | 26.1 | 2 | 17.0 | 18.9 | 1 | 24.4 | 23.7 | 7 | 27.0 | 28.3 |
| 5 | 15.7 | 16.0- | 5 | 25.6 | 25.8- | 4 | 75.0 | 76.1- | 8 | 20.6 | 20.0 |
| 0,0,12 | 25.6 | 25.3- | • 8 | 12.7 | 14.4- | 5 | 13.6 | 12.9- | 9 | 27.5 | 29.0- |
| 2 | 15.7 | 15.3 | 1,1,9 | 18.0 | 18.9 | 6 | 18.9 | 18.4 | 10 | 17.6 | 16.0 |
| | | | 3 | 23.2 | 23.8 | 8 | 27.4 | 28.6 | • 12 | 11.5 | 12.8- |
| •1,0,1 | 106.8 | 109.7 | 4 | 22.4 | 21.1 | 9 | 10.7 | 12.8 | 3,0,4 | 15.5 | 13.4 |
| 1 | 41.6 | 41.1 | 1,0,10 | 37.6 | 39.9- | 2,0,6 | 14.4 | 15.7- | 1 | 60.9 | 61.0 |
| • 2 | 74.7 | 78.3- | 3 | 19.7 | 18.8 | 1 | 20.6 | 20.2- | 2 | 18.4 | 18.6 |
| • 3 | 134.4 | 152.2 | • 5 | 14.8 | 15.7- | 2 | 22.1 | 21.6- | 4 | 28.9 | 28.2- |
| 4 | 8.0 | 8.9 | 8 | 17.2 | 15.5- | 3 | 11.4 | 12.1- | 5 | 18.8 | 16.5 |
| 5 | 40.7 | 41.3- | 1,0,11 | 22.8 | 21.8- | 4 | 30.7 | 32.0 | 6 | 20.5 | 20.6 |
| 6 | 7.6 | 9.2 | 4 | 28.5 | 27.6 | 5 | 37.7 | 38.0- | 7 | 21.6 | 21.6- |

Table 3 (*cont.*)

| h k l | $\|F_o\|$ | $F_c$ | h k l | $\|F_o\|$ | $F_c$ | h k l | $\|F_o\|$ | $F_c$ | h k l | $\|F_o\|$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3,9,4 | 23.4 | 24.0 | 4,3,4 | 54.5 | 54.5 | 5,5,4 | 15.3 | 15.9 | 6,1,5 | 9.6 | 7.5 |
| 3,0,5 | 62.6 | 62.4 | 4 | 46.3 | 49.8- | 7 | 17.0 | 16.8- | 4 | 28.5 | 29.3 |
| 1 | 27.3 | 26.0- | 5 | 12.7 | 13.0- | 9 | 17.8 | 18.5 | 5 | 16.3 | 16.2 |
| 4 | 40.1 | 41.7- | 6 | 25.2 | 25.2 | 5,0,5 | 17.9 | 14.8- | 6 | 11.6 | 9.6- |
| 6 | 29.6 | 30.0- | 7 | 14.2 | 15.4- | 2 | 13.5 | 11.4- | 6,0,6 | 18.6 | 17.0 |
| 7 | 19.3 | 21.5 | 8 | 18.3 | 20.6 | 3 | 18.7 | 18.1- | 2 | 11.2 | 9.7 |
| 8 | 21.6 | 20.6 | 9 | 18.4 | 18.3- | 6 | 14.5 | 14.9 | 3 | 18.6 | 19.2- |
| • 10 | 11.5 | 13.0 | 11 | 8.8 | 10.7 | 9 | 13.8 | 13.8 | 4 | 18.6 | 19.1- |
| 3,0,6 | 26.5 | 25.9 | 12 | 16.0 | 17.0- | • 10 | 8.5 | 7.4- | 5 | 16.3 | 16.0 |
| 3 | 50.8 | 51.3 | 4,0,5 | 16.8 | 15.9- | 5,1,6 | 22.0 | 22.1 | 6 | 7.6 | 6.6- |
| 4 | 33.1 | 35.0- | 1 | 34.8 | 35.8 | 4 | 21.8 | 22.9 | 6,2,7 | 16.5 | 17.1- |
| 5 | 49.6 | 52.7- | 2 | 9.0 | 11.5 | 6 | 14.5 | 11.1- | 4 | 15.6 | 16.3 |
| 6 | 11.0 | 10.0 | 4 | 16.5 | 14.0- | 7 | 15.3 | 14.8- | 6,1,8 | 16.2 | 16.1- |
| 8 | 15.2 | 16.5 | 5 | 32.8 | 33.5- | 5,0,7 | 47.5 | 50.1- | 2 | 12.7 | 14.8 |
| 3,0,7 | 17.5 | 15.8- | 6 | 17.5 | 17.0 | 1 | 21.0 | 21.0- | 4 | 27.0 | 24.5- |
| 2 | 32.0 | 34.7 | 7 | 20.2 | 22.0- | 2 | 18.1 | 19.5 | 6,0,9 | 22.2 | 23.9 |
| 3 | 26.2 | 24.5 | 9 | 26.5 | 27.8 | 3 | 20.7 | 20.8- | 1 | 18.7 | 19.0 |
| 5 | 39.1 | 40.1- | 4,0,6 | 28.3 | 25.6- | 5 | 15.7 | 17.7 | 6,0,10 | 14.8 | 11.9 |
| 6 | 12.7 | 12.6- | 1 | 14.2 | 11.4 | 6 | 21.6 | 22.6 | 1 | 15.3 | 14.1 |
| 8 | 25.1 | 26.7- | 2 | 13.7 | 13.9 | 7 | 19.8 | 18.3 | | | |
| 10 | 23.7 | 22.1 | 3 | 31.3 | 32.0 | 8 | 22.0 | 22.0- | 7,0,1 | 16.0 | 15.4 |
| 3,0,8 | 20.7 | 18.4- | 4 | 17.6 | 16.3 | 5,0,8 | 13.5 | 11.8 | 1 | 21.7 | 24.9 |
| 1 | 13.0 | 13.1 | 7 | 12.5 | 12.5- | 1 | 15.3 | 16.0 | 5 | 30.5 | 32.1 |
| 2 | 19.9 | 19.8 | 8 | 19.7 | 19.4- | 3 | 26.1 | 22.5- | 7 | 24.6 | 24.8- |
| • 3 | 10.4 | 8.4- | • 9 | 10.7 | 12.6- | 4 | 18.9 | 20.9- | 7,0,2 | 19.5 | 24.3 |
| 5 | 26.0 | 26.5 | 4,0,8 | 59.9 | 60.3- | 5 | 20.8 | 21.1 | 3 | 17.8 | 19.8 |
| • 6 | 11.0 | 11.0 | 2 | 18.8 | 19.6 | 5,0,9 | 14.7 | 14.8- | 5 | 20.3 | 21.2- |
| 8 | 14.3 | 15.0- | 3 | 20.4 | 20.9 | 3 | 13.0 | 11.0- | 8 | 14.0 | 14.9 |
| 3,3,9 | 13.3 | 13.1 | 6 | 15.1 | 13.5 | 5,0,10 | 24.5 | 20.0 | 9 | 14.8 | 11.4 |
| 5 | 12.8 | 11.0- | 8 | 30.5 | 29.8- | 3 | 19.7 | 19.3- | 7,0,3 | 30.8 | 34.5- |
| 3,0,10 | 31.6 | 31.5- | 4,0,9 | 18.6 | 17.2- | • 4 | 12.8 | 12.8- | 1 | 22.2 | 25.0 |
| 3 | 14.2 | 13.0- | 2 | 13.9 | 14.4 | • 5 | 11.7 | 13.0 | 3 | 18.1 | 18.2 |
| 5 | 14.7 | 13.7 | 3 | 39.5 | 41.2- | 5,1,11 | 16.6 | 14.6 | 4 | 16.9 | 16.4 |
| 3,0,11 | 27.0 | 27.4 | 4 | 17.9 | 19.6- | | | | 7 | 20.7 | 21.0- |
| 4 | 16.6 | 15.3- | 5 | 32.3 | 34.1 | 6,0,0 | 46.7 | 44.9 | 8 | 21.1 | 19.7- |
| | | | 6 | 17.1 | 18.0 | 2 | 12.0 | 12.8 | 7,3,4 | 12.7 | 13.9- |
| 4,0,0 | 82.6 | 86.2- | 4,0,10 | 15.1 | 14.0 | 3 | 68.4 | 74.4- | 7,1,5 | 33.7 | 34.6 |
| 1 | 20.4 | 19.7- | • 1 | 11.2 | 12.9 | 4 | 32.1 | 32.0- | 4 | 20.9 | 17.3 |
| 2 | 26.3 | 26.4- | 4,1,13 | 18.8 | 18.0 | 5 | 45.5 | 50.6 | 5 | 17.4 | 14.9 |
| 3 | 61.2 | 57.6 | | | | 6 | 20.4 | 17.1- | 7 | 25.7 | 26.7- |
| 4 | 51.4 | 49.7 | 5,0,1 | 72.7 | 74.8 | 10 | 13.2 | 12.6 | 7,1,6 | 25.4 | 23.5- |
| 8 | 31.9 | 30.9- | 1 | 50.0 | 50.2- | 11 | 13.9 | 14.2- | 2 | 13.2 | 13.1- |
| 9 | 40.0 | 41.3- | 2 | 15.4 | 14.6 | 13 | 19.0 | 17.8 | 4 | 16.8 | 16.4 |
| 12 | 17.9 | 17.7 | 3 | 51.9 | 52.4- | 6,0,1 | 51.2 | 50.2 | 5 | 14.2 | 10.7 |
| 4,0,1 | 30.0 | 31.9 | 5 | 29.3 | 28.5 | 3 | 10.5 | 11.5 | 7 | 15.6 | 14.4 |
| 1 | 64.1 | 62.8- | 6 | 37.1 | 36.9 | 4 | 14.8 | 15.1- | 7,4,7 | 19.5 | 21.3- |
| 2 | 17.4 | 15.3- | 7 | 28.3 | 27.8 | 8 | 20.3 | 21.1 | 7,0,8 | 15.0 | 12.1 |
| 3 | 16.0 | 15.7- | 8 | 19.5 | 22.4- | 10 | 13.2 | 12.3- | 7,0,11 | 13.6 | 10.1- |
| 7 | 16.1 | 16.7 | • 9 | 9.8 | 11.1- | 6,2,2 | 39.3 | 39.4 | | | |
| 8 | 13.6 | 13.3 | 5,0,2 | 59.3 | 62.7 | 3 | 17.4 | 16.5- | 8,3,0 | 24.7 | 24.4- |
| 9 | 31.0 | 32.8- | 1 | 10.7 | 13.5- | 4 | 46.7 | 47.1- | 8,3,1 | 15.5 | 18.4 |
| 4,0,2 | 21.4 | 19.2- | 3 | 17.5 | 18.5- | 5 | 11.7 | 13.6 | 5 | 14.8 | 15.1- |
| 1 | 6.9 | 5.1- | 4 | 35.6 | 36.2- | 8 | 12.7 | 12.9- | 8,0,2 | 20.5 | 20.2- |
| 2 | 47.2 | 46.4 | 5 | 16.1 | 16.0 | 9 | 14.0 | 11.1 | 3 | 17.7 | 17.6- |
| 3 | 64.1 | 63.5 | 8 | 28.4 | 29.9 | 10 | 25.5 | 24.9 | • 4 | 14.2 | 15.5 |
| 4 | 23.1 | 22.7- | 12 | 14.3 | 12.2- | 6,0,3 | 24.8 | 26.0 | 8,0,4 | 20.5 | 23.6- |
| 6 | 37.5 | 37.9 | 5,0,3 | 50.0 | 52.0- | 1 | 17.8 | 17.5 | 8,0,5 | 17.0 | 17.1 |
| 7 | 11.0 | 10.6- | • 1 | 5.7 | 4.0- | 2 | 13.6 | 14.7- | 8,0,7 | 15.7 | 17.8 |
| 8 | 23.6 | 20.8- | 2 | 33.8 | 35.5 | 4 | 18.3 | 20.5- | | | |
| 9 | 29.9 | 30.9- | 4 | 40.2 | 39.0- | 7 | 12.8 | 12.0- | 9,0,1 | 23.1 | 23.2 |
| • 11 | 12.2 | 12.6 | 5 | 16.0 | 17.1- | 8 | 17.1 | 19.9 | 6 | 17.5 | 15.6- |
| 12 | 15.9 | 15.4- | 6 | 51.9 | 54.1 | 6,0,4 | 10.9 | 9.3 | •9,4,2 | 15.4 | 17.3 |
| 4,0,3 | 9.6 | 10.4- | 7 | 13.9 | 12.5 | 1 | 29.7 | 30.9 | 9,3,3 | 18.3 | 16.7- |
| 2 | 17.2 | 16.0 | • 8 | 9.3 | 11.2- | 2 | 16.8 | 17.7 | 9,0,5 | 19.5 | 16.5 |
| 3 | 24.4 | 23.7- | 9 | 18.2 | 19.9 | 3 | 10.0 | 9.9- | 9,0,6 | 19.9 | 19.5 |
| 4 | 32.7 | 33.1- | 12 | 27.0 | 22.7- | 4 | 17.0 | 16.6- | 9,0,7 | 16.6 | 15.3 |
| 5 | 38.7 | 39.8 | 5,0,4 | 9.3 | 10.7- | 5 | 14.7 | 14.3- | | | |
| 6 | 22.5 | 22.7 | 1 | 35.6 | 34.6 | 6 | 10.9 | 11.4- | •10,1,0 | 13.3 | 14.2 |
| • 11 | 11.0 | 10.2- | 2 | 11.2 | 11.0 | 7 | 19.1 | 20.4- | • 2 | 13.6 | 11.9- |
| 4,0,4 | 10.8 | 9.7 | 3 | 21.0 | 21.7- | 9 | 26.2 | 25.1 | • 3 | 13.6 | 13.4 |
| 1 | 10.3 | 9.4 | 4 | 21.6 | 20.1- | 10 | 19.5 | 15.8 | 4 | 19.6 | 20.0 |

The atomic scattering factors used were those of Tomiie & Stam (1958) for sulphur and chlorine, of Berghuis *et al.* (1955) for oxygen and those of Freeman (1959) for nitrogen. The Fourier syntheses and structure factors were calculated on a Stantec ZEBRA computer with programs written by Dr D.W. Smits. Since only a machine program was available for calculating structure factors with isotropic temperature factors, the anisotropic calculations were made by the 'fractional atom' method introduced by Kartha & Ahmed (1960) and extended by Vos & Smits (1961).

### *Analysis of the thermal motion* (W)

The assumption was made that the molecule could be treated as a rigid body and Cruickshank's (1956) method was used to calculate the molecular librations and translations from the individual atomic vibrations.

The molecular axes chosen were (1) coincident with the approximate threefold axis of the molecule, (2) parallel to the *b* axis, (3) perpendicular to 1 and 2;

the origin was the centre of mass of the molecule. The tensors $U_{ij}$ (Cruickshank's (1956) notation is used throughout) were then transposed to these axes. The values for nitrogen were not used in any further calculations on account of their low accuracy.

Since the molecule lies on a mirror plane the tensor elements $T_{12}$, $T_{23}$, and $\omega_{12}$, $\omega_{23}$ are zero. The remaining $T_{ij}$'s and $\omega_{ij}$'s were determined from 40 observational equations (*cf.* Cruickshank's equation 2·3). The equations were solved on Groningen University's ZEBRA computer with the least-squares program Gron-A3. The values of $T_{ij}$ and $\omega_{ij}$ together with their standard deviations are given in Table 4.

Table 4. *Elements of the translational* (Å$^2$ × 100) *and vibrational* (deg$^2$) *tensors and their standard deviations*

| $ij$ | $T_{ij}$ | $\sigma(T_{ij})$ | $\omega_{ij}$ | $\sigma(\omega_{ij})$ |
|---|---|---|---|---|
| 11 | 2·39 | 0·47 | 11·1 | 2·6 |
| 22 | 3·72 | 0·39 | 11·0 | 3·0 |
| 33 | 3·06 | 0·33 | 19·3 | 3·5 |
| 13 | −0·41 | 0·30 | −0·1 | 0·8 |

Since $T_{13}$ and $\omega_{13}$ are zero within experimental error the principal axes of the tensors coincide with the molecular axes. The calculated librational parameters were used to correct the coordinates and hence the bond lengths and angles (Cruickshank, 1961*b*). The corrected and uncorrected values are shown in Table 5. It may be noted that the S–Cl bond lengths both changed by 0·008 Å, *i.e.* 2 standard deviations; the bond angles remained almost unchanged.

### Discussion (W's results)

The trimeric molecule exists in the chair form with all the chlorine atoms in axial positions (Fig. 2). The distances from the plane through the sulphur atoms are given in Table 6.

Table 6. *Distances of the atoms from the plane through the sulphur atoms*

| | | | |
|---|---|---|---|
| N(1) and N(1′) | −0·244 Å | N(2) | −0·262 Å |
| O(1) and O(1′) | −0·710 | O(2) | −0·736 |
| Cl(1) and Cl(1′) | 1·993 | Cl(2) | 1·937 |

The N–S bond lengths obtained by refining in the space group *Pnma* are equal within experimental error. Wiegers & Vos (1963) have shown that this equality of bond lengths is probably genuine and not merely the result of refining in the wrong space group.

The symmetry of the molecule is higher than the *m* required by the space group, and in fact there are only slight deviations from $C_{3v}$ which one would infer from the equality of the bond lengths and angles (Table 5). The deviation is between the Cl(1) ··· Cl(1′)(3·536 Å) and the Cl(1) ··· Cl(2)(3·576 Å) distances, for which the s.d. in the difference is about 0·008 Å. This difference may be due to the different environments of the two chlorine atoms; comparison of intermolecular distances (Fig. 3) with the sums of the van der Waals radii, which are 1·80, 1·85, and 1·40 Å (Pauling, 1960) for Cl, S and O respectively, shows the following short distances: Cl(1) ··· Cl(1)(3·46 Å), Cl(2) ··· S(2)(3·59 Å), and Cl(2) ··· O(2)(2·99 Å). Charge transfer may account for the short Cl ··· O distances, and as would be expected (Hassel & Rømming, 1962) the three atoms S(2)–Cl(2) ··· O(2) are almost collinear.

The N–S bonds are all equal; their length 1·57 Å is 0·19 Å shorter than the N–S$^{\mathrm{VI}}$ bond in $SO_3NH_3$ (Sass, 1960) in which no $\pi$-bonding occurs. The shortness of the bonds cannot be attributed to charge separation [*cf.* formula (II)] (Craig & Paddock, 1962). The results are thus in agreement with the assumed presence of delocalized $p_\pi - d_\pi$ bonding.

The S–Cl and S–O bond lengths agree well with the values 1·99 ± 0·02 Å and 1·43 ± 0·02 Å respectively, observed in $SO_2Cl_2$ (Martz & Lagemann, 1954).

Table 5. *Molecular dimensions*

The values $W_b$ are corrected for the thermal motion of the molecule; the uncorrected values, $W_a$, are also shown.

| Bond | H | s.d. | $W_a$ | $W_b$ | s.d. |
|---|---|---|---|---|---|
| S(1)–N(1) | 1·576 Å | 11 × 10$^{-3}$ Å | 1·578 Å | 1·582 Å | 10 × 10$^{-3}$ Å |
| S(2)–N(1) | 1·576 | 13 | 1·546 | 1·552 | 10 |
| S(1)–N(2) | 1·570 | 10 | 1·568 | 1·573 | 5 |
| S(1)–Cl(1) | 1·996 | 5 | 1·991 | 1·999 | 4 |
| S(2)–Cl(2) | 2·004 | 7 | 1·999 | 2·007 | 4 |
| S(1)–O(1) | 1·349 | 12 | 1·401 | 1·405 | 10 |
| S(2)–O(2) | 1·442 | 16 | 1·406 | 1·410 | 10 |
| Angle | | | | | |
| S(1)–N(1)–S(2) | 120·9° | 0·6° | 122·3° | 122·3° | 0·6° |
| S(1)–N(2)–S(1′) | 119·5 | 1·5 | 121·8 | 121·8 | 0·6 |
| N(1)–S(1)–N(1′) | 113·7 | 0·6 | 113·5 | 113·5 | 0·7 |
| N(1)–S(1)–N(2) | 111·7 | 0·9 | 112·5 | 112·5 | 0·5 |
| Cl(1)–S(1)–O(1) | 107·8 | 0·5 | 107·1 | 107·1 | 0·5 |
| Cl(2)–S(2)–O(2) | 108·3 | 0·7 | 106·8 | 106·8 | 0·5 |
| N(2)–S(1)–Cl(1) | 104·8 | 0·7 | 106·5 | 106·5 | 0·5 |
| N(1)–S(1)–Cl(1) | 106·0 | 0·5 | 105·9 | 105·9 | 0·5 |
| N(1)–S(2)–Cl(2) | 106·4 | 0·5 | 106·7 | 106·6 | 0·5 |
| N(1)–S(1)–O(1) | 110·3 | 0·7 | 112·5 | 112·5 | 0·6 |
| N(2)–S(1)–O(1) | 111·7 | 0·7 | 111·7 | 111·8 | 0·6 |
| N(1)–S(2)–O(2) | 110·9 | 0·6 | 111·4 | 111·4 | 0·6 |

The sulphur atoms have coordination number 4; the bonds are pointing to the corners of a tetrahedron. The angles N–S–N (113°) and O–S–Cl (107°) are more nearly equal than is the case with the angles in the phosphonitrilics. For $(NPCl_2)_3$ the observed values are N–P–N = 120°, Cl–P–Cl = 102° (Wilson & Carroll, 1960). The small difference between the endo- and exocyclic angles in $\alpha(NSOCl)_3$ may be due to the double bond character of the S = O exocyclic bond. For a free molecule such as $SO_2F_2$ (Lide, Mann & Fristrom, 1957) the repulsion between two double bonds is greater than that between a double and a single bond, which in turn is greater than the repulsion between two single bonds, and so $\widehat{\mathrm{OSO}} > \widehat{\mathrm{OSF}} > \widehat{\mathrm{FSF}}$. Assuming that the same holds for the ring systems one would then expect $\widehat{\mathrm{NSN}} \simeq \widehat{\mathrm{NSO}} > \widehat{\mathrm{ClSO}} \simeq \widehat{\mathrm{NSCl}}$ and for the nitrilics $\widehat{\mathrm{NPN}} > \widehat{\mathrm{NPX}} > \widehat{\mathrm{XPX}}$, which would result in a greater discrepancy between the endocyclic and exocyclic angles.

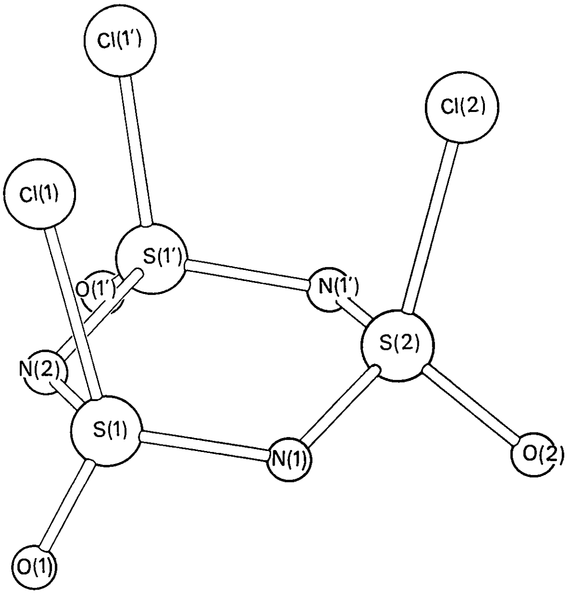

Fig. 2. Molecule of $\alpha(NSOCl)_3$. The atoms S(2), N(2), O(2), and Cl(2) are on the mirror plane.

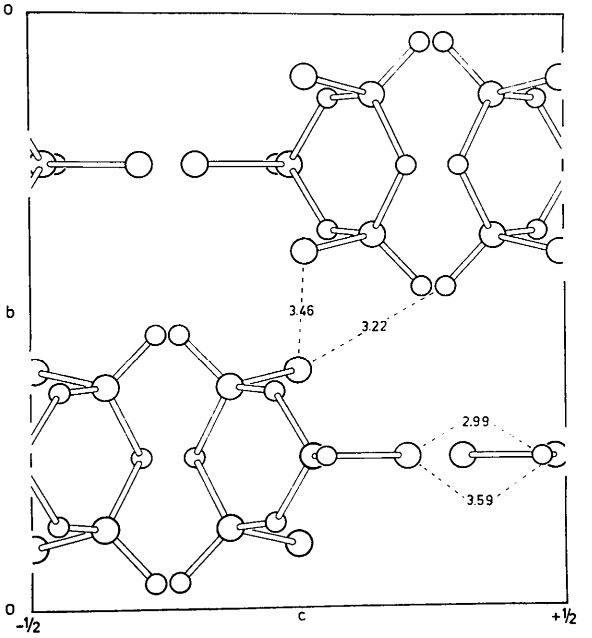

Fig. 3. $\alpha(NSOCl)_3$: projection along [100] on the (100) plane.

Unlike the tetrameric phosphonitrilics, in which the angle at the nitrogen atom varies from 132 to 147°, the angle at the nitrogen atom in $\alpha(NSOCl)_3$ appears to have no great tendency to deviate from the value of 120° to be expected from $sp^2$ hybridization, although a small increase, from 122° to 127°, would result in a planar molecule. The small value of the angle S–N–S may be associated with the small contribution of the nitrogen lone pair electrons to the bonding (Craig & Paddock, 1962). Delocalization of the lone pairs may be prevented as there are extra electrons on the S atom from the sulphur to oxygen $p\pi - d\pi$ bond. In the case of $(NPCl_2)_3$ and $(NPF_2)_3$ (Dougill, 1963) for a planar ring 120° is required at the nitrogen as the angle at P is as large as 120°.

## Comparison of the two structure determinations

### *Observed structure factors*

The intensities were obtained from crystals with diameters of approximately $4\mu^{-1}$ (H) and $0{\cdot}35\mu^{-1}$ (W); the final values of $R$ are 0·11 and 0·049 respectively. The discrepancy index between the two sets of data is 0·142. Examination of the two sets of $F_o$ values indicated systematic deviations, and so an attempt was made to eliminate these by 'temperature factor type' corrections. An isotropic scale and temperature factor were chosen so that $F_H = kF_W \exp(-B \sin^2\theta/\lambda^2)$ (by Wilson's (1949) method). Application of this correction function, with $k = 1{\cdot}13$ and $B = 1{\cdot}07$ Å², reduced the discrepancy factor to 0·128. An anisotropic correction function

$$C = k \exp(-2\pi^2 a^{*2} h^2 U_{11} - 2\pi^2 b^{*2} k^2 U_{22} - 2\pi^2 c^{*2} l^2 U_{33})$$

was calculated such that $\Sigma(F_H - CF_W)^2$ is minimal. The values obtained for the parameters are $k = 1{\cdot}11$ and $U_{11} = 0{\cdot}0001$, $U_{22} = 0{\cdot}0107$ and $U_{33} = 0{\cdot}0067$ Å²; multiplication of $F_W$ by $C$ reduced the discrepancy factor to 0·116. It may be noted that this discrepancy is only slightly larger than H's final $R$ value.

### *Atomic coordinates*

From the final coordinates listed in Table 1 r.m.s. differences of 0·0030 Å for the coordinates of the heavy atoms and 0·0375 Å for the coordinates of the light atoms were calculated. In Table 7 these r.m.s. differences are compared with the s.d. estimated by Cruickshank's (1949) formula (W) or from the least-squares residuals (H).

For the heavy atoms the observed discrepancy agrees well with the e.s.d.; for the light atoms, however, the observed deviations are much larger than the expected

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 $\omega_{ij}$ 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 $n$th 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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# 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 $a=5·49$, $b=11·14$, $c=6·05$ Å; $\beta=98·7°$ (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 $p_\pi$–$d_\pi$ bonds.

## Introduction

After the $S^{VI}$ compound $\alpha(NSOCl)_3$ described in the previous paper (Hazell, Wiegers & Vos, 1966), the $S^{IV}$ 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: