The Crystal Structure of Tetrathiazylfluoride, (NSF)₄

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(NSF)$_4$ belongs to the space group $P\bar{4}2_1c$; the two molecules in the unit cell are located at special positions with symmetry $\bar{4}$. Approximate coordinates were found from Patterson projections, and refined by successive two-dimensional Fourier syntheses. The (NSF)$_4$ molecule is a puckered ring of alternating sulphur and nitrogen atoms; the fluorine atoms are linked to the sulphur atoms. The N–S bond lengths are 1·65 (s.d. 0·02) Å and 1·55 (s.d. 0·02) Å indicating alternating 'single' and 'double' N–S bonds in the molecule. The S–F bond length is 1·64 (s.d. 0·02) Å. The valence angles are: S–N–S 123°, N–S–N 112°, F–S–N 91° and F–S=N 106°.

Introduction

A large number of compounds, obtained from N_4S_4 and hydrogen, halogen or halogenating agents, have been described recently (Becke–Goehring, 1959; Glemser, Schröder & Wyszomirski, 1959; Schröder & Glemser, 1959). In (NSH)$_4$ molecules, which contain an eight-membered ring of alternating sulphur and nitrogen atoms, the hydrogen atoms are linked to the nitrogen atoms (Sass & Donohue, 1958; Lund & Svendsen, 1957). For the thiazylhalides $(NSX)_n$, however, chemical evidence suggests that the halogen atoms are linked to the sulphur atoms.

In analogy to $(PNCl_2)_3$ and $(PNCl_2)_4$, an aromatic character may be expected for the six- and eight-membered rings in thiazylhalides with $n=3$ or 4. A theoretical discussion of this aromaticity was given by Craig (1959).

In order to obtain direct experimental information on the above points, we investigated the crystal structure of tetrathiazylfluoride, which is described in this paper, and that of trithiazylchloride. The approximate determination of the latter structure showed that $(NSCl)_3$ molecules contain a six-membered ring of alternating sulphur and nitrogen atoms, with the chlorine atoms linked to the sulphur atoms. After a three-dimensional refinement of this crystal structure with low temperature data, the results will be published. In addition, the crystal structures of (NSF)$_3$ (Schröder & Glemser, 1959), $N_2S_3F_2$ (Glemser, Schröder & Wyszomirski, 1959), and $(NSOCl)_3$ (Becke–Goehring, 1959) will be examined in our laboratory.

Experimental

Crystals of (NSF)$_4$ were kindly provided by Prof. Glemser, University of Göttingen, who was the first to prepare this compound (Glemser, 1955). For the X-ray work crystals were used with diameters varying from 0·06 to 0·10 mm. perpendicular to the crystal axis about which the photographs were taken. The crystals were sealed in pyrex capillaries.

Unit cell and space group

A preliminary X-ray study had already been carried out by Glemser (1955) with the following results:

$$a = 9\cdot2, \quad c = 4\cdot3 \text{ Å}; \quad \text{space group } P\bar{4}2_1c .$$

The crystals are needles along the tetragonal axis. There are two molecules of (NSF)$_4$ per unit cell at special positions with symmetry $\bar{4}$. The calculated density, 2·37 g.cm.$^{-3}$, agrees with the experimental value, 2·33 g.cm.$^{-3}$.

During our investigation the lattice constants were determined accurately from back-reflexion photographs. With $\lambda(\text{Cu }K\alpha_2) = 1\cdot54433$ Å and $\lambda(\text{Cu }K\alpha_1) = 1\cdot54051$ Å, the following values were found:

$$a = 9\cdot193 \pm 0\cdot005, \quad c = 4\cdot299 \pm 0\cdot003 \text{ Å} .$$

Structure factors

The intensities of the reflexions $hk0$, $hk1$, $hk2$ and $h0l$ were measured with a densitometer (Smits & Wiebenga, 1953) on integrated equi-inclination Weissenberg photographs (Wiebenga & Smits, 1950), taken with nickel-filtered copper radiation. Use was made of the multiple-film technique.

Assuming a cylindrical shape for the crystals, an approximate correction for absorption was calculated (Bond, 1959). The reflexions were obtained from different crystals with μR values from 0·4 to 0·6. Intensities were put on an approximate absolute scale by using Wilson's statistical method for the $hk0$ data.

Determination of the coordinates

Approximate coordinates for the three independent atoms, namely one sulphur, one nitrogen and one fluorine atom, could be obtained from the Patterson syntheses of the [001] projection, the first generalized [001] projection and the [010] projection. The coordinates were refined by successive Fourier syntheses and difference Fourier syntheses of the [001] and [010]

projection. Because of overlap, the z-coordinate of the nitrogen atom could not be obtained accurately from the [010] projection. Therefore this coordinate was refined further by trial and error with the $hk2$ reflexions, the remaining parameters being kept constant.

For the calculation of the structure factors, use was made of Viervoll & Øgrim's (1949) f curve for sulphur and of Freeman's (1959) f curves for nitrogen and fluorine. After each calculation of the structure factors, the temperature factor, which was assumed to be equal for the different atoms, and the scale factor were determined by comparison of the calculated and observed structure factors.

Table 1. *Final atomic coordinates*

	x	y	z
S	0·0258	0·2073	0·0868
N	0·1258	0·1173	−0·1660
F	0·3281	0·0165	0·1781

The final disagreement indices R for the observed reflexions $hk0$, (omitting the reflexion 220 which showed strong extinction) and for the reflexions $h0l$, were 0·070 and 0·082 respectively. In Table 3 the calculated structure factors based on the final coordinates in Table 1 are compared with those observed. The temperature factor is

$$\exp\left(-2{\cdot}70 - 0{\cdot}80 \cos^2 \varphi\right) \sin^2 \theta / \lambda^2,$$

where φ is the angle between the normal of the reflecting plane and the z-axis. The final electron-density maps of the two projections are shown in Figs. 1(a) and 2(a).

Accuracy of the coordinates

An estimate of the accuracy of the final atomic coordinates was obtained by applying Cruickshank's (1949) formula, and by comparing the x- and y-coordinates from the two projections. The standard deviations, which were assumed to be independent of direction, are:

$$\sigma(S) = 0{\cdot}005, \quad \sigma(N) = 0{\cdot}02, \quad \sigma(F) = 0{\cdot}02 \text{ Å}.$$

Discussion of the structure

The crystal structure consists of molecules $(NSF)_4$

Table 2. *Intramolecular distances and angles*

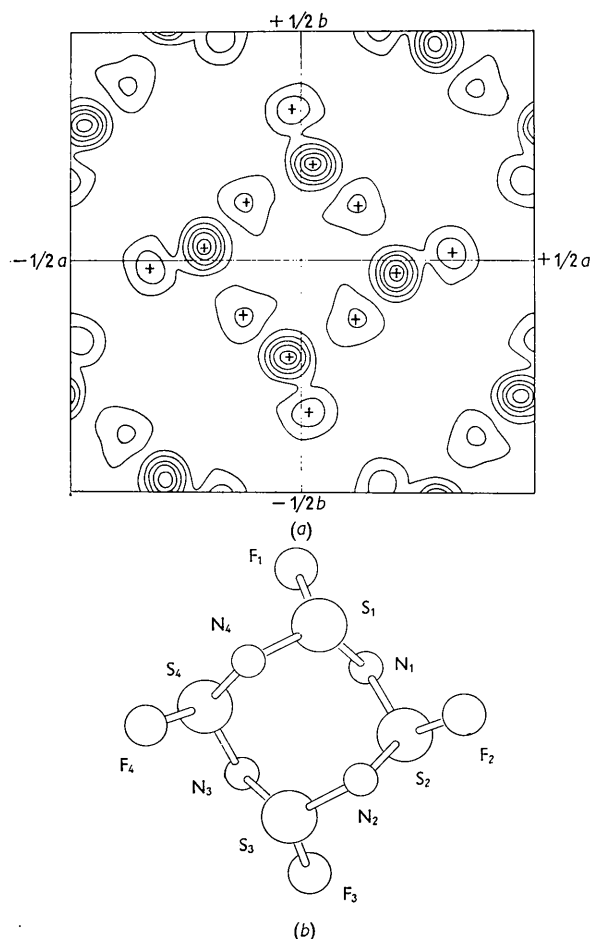|	Distance	S.d.		Angle	S.d.
N_1–S_1	1·65 Å	0·02 Å	S_1–N_1–S_2	123°	1·3°
N_1–S_2	1·55	0·02	N_1–S_2–N_2	112	1·3
S–F	1·64	0·02	F_1–S_1–N_1	91	1·0
			F_1–S_1–N_4	106	1·0
$S_1 \cdots S_2$	2·82	0·01			
$S_1 \cdots S_3$	3·84	0·01			
$N_1 \cdots N_2$	2·65	0·03			
$N_1 \cdots N_3$	3·16	0·04			
$N_1 \cdots F_1$	2·34	0·03			
$N_4 \cdots F_1$	2·55	0·03			

Fig. 1. (a) Final electron-density map of the [001] projection. Contour lines are at intervals of 5 e.Å^{-2}, starting with 3 e.Å^{-2}. Crosses indicate final atomic coordinates for one molecule. (b) Molecule of $(NSF)_4$ projected along [001].
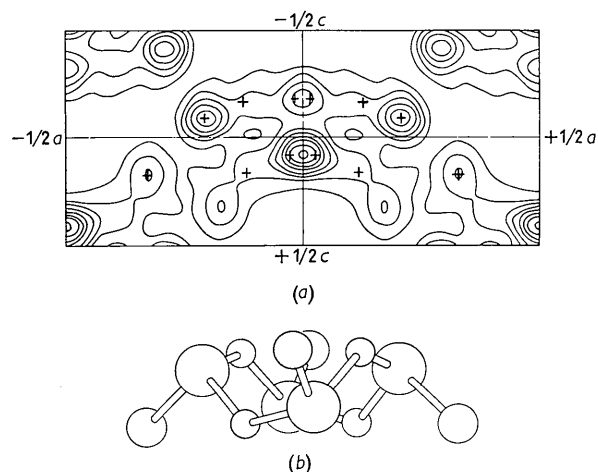

Fig. 2. (a) Final electron-density map of the [010] projection. Contour lines are at intervals of 5 e.Å^{-2}, starting with 3 e.Å^{-2}. Crosses indicate final atomic coordinates for one molecule. (b) Molecule of $(NSF)_4$ projected along [010].

Table 3. *Observed and calculated structure amplitudes, and calculated phases of the hk0, hk1, hk2 and h0l reflections*

hkl	F_o	F_c	α_c^0	hkl	F_o	F_c	α_c^0	hkl	F_o	F_c	α_c^0
200	17·4	19·9	0	901	16·5	16·0	0	712	20·9	22·2	256·0
400	27·0	26·8	0	10,0,1	6·6	6·7	270	812	10·0	10·1	146·9
600	33·5	37·2	0	11,0,1	5·6	4·7	180	912	8·3	8·6	270·6
800	<5·9	5·0	0	211	31·5	34·2	159·9	10,1,2	7·6	8·1	231·2
10,0,0	13·4	12·9	0	311	45·3	50·8	105·5	222	16·8	18·2	124·3
110	26·3	24·8	0	411	12·9	13·7	127·9	322	16·3	16·2	104·0
210	<2·8	2·0	180	511	20·0	18·6	232·6	422	<5·5	5·1	24·6
310	22·7	23·2	180	611	24·6	26·6	283·3	522	30·2	28·8	266·0
410	18·3	17·3	180	711	16·0	16·1	141·2	622	18·2	19·2	250·2
510	5·4	3·0	0	811	12·4	13·2	241·0	722	8·7	7·8	83·7
610	8·8	8·9	180	911	11·6	11·6	170·1	822	<6·8	1·5	206·5
710	18·7	18·3	180	10,1,1	9·7	9·7	324·5	922	<6·5	3·6	244·1
810	15·1	14·9	180	11,1,1	4·7	4·5	182·5	10,2,2	<5·5	4·7	1·4
910	18·5	18·7	0	321	41·7	44·7	128·4	332	36·3	39·8	145·5
10,1,0	9·0	7·7	180	421	21·9	22·8	219·0	432	29·5	30·0	273·1
11,1,0	7·0	7·3	180	521	9·6	8·7	271·3	532	<6·5	4·1	110·6
220	82·9	102·0	180	621	7·8	9·0	116·5	632	9·9	9·3	328·4
320	20·2	21·3	180	721	26·2	25·5	204·8	732	10·2	8·1	172·0
420	23·8	26·4	180	821	12·1	12·8	180·0	832	<6·9	2·9	306·5
520	9·9	10·2	180	921	9·7	9·0	33·4	932	12·1	12·1	88·2
620	5·2	4·4	180	10,2,1	7·0	6·5	218·9	10,3,2	8·1	9·3	298·4
720	14·5	16·1	180	11,2,1	<3·0	2·8	121·2	442	15·7	14·8	68·0
820	19·2	20·2	180	431	13·3	11·7	54·3	542	9·8	8·0	286·7
920	14·1	15·5	180	531	33·3	35·4	294·3	642	<7·1	1·6	241·9
10,2,0	9·9	8·1	0	631	6·2	6·5	284·9	742	15·1	13·9	75·5
11,2,0	<3·9	2·9	180	731	10·6	10·6	350·8	842	13·3	13·2	73·1
330	7·3	9·1	0	831	14·5	14·7	141·8	942	<5·5	1·7	279·5
430	4·3	3·7	180	931	5·6	4·9	309·0	10,4,2	3·8	4·1	28·9
530	21·9	22·8	0	10,3,1	9·3	8·9	36·0	552	12·3	12·2	10·8
630	25·8	24·4	0	11,3,1	7·3	8·3	345·6	652	15·1	14·5	72·3
730	22·9	22·4	180	541	23·4	22·4	8·9	752	<6·9	2·8	328·0
830	<5·8	4·0	0	641	29·0	28·5	28·6	852	8·8	7·2	147·0
930	10·9	10·5	0	741	13·5	12·6	186·8	952	4·9	4·0	45·0
10,3,0	7·6	7·6	0	841	7·0	6·8	20·3	662	14·7	12·8	249·0
11,3,0	<3·6	0·4	0	941	9·5	7·3	53·1	762	<6·3	3·4	142·8
440	29·7	29·2	0	10,4,1	10·0	10·6	333·9	862	<5·5	1·1	180·0
540	29·0	28·9	0	651	10·8	10·2	4·3	962	5·9	6·3	195·7
640	14·4	13·6	0	751	11·7	10·9	99·4	772	6·5	6·0	236·0
740	20·5	19·9	0	851	8·8	9·5	129·5	872	5·5	6·2	183·5
840	16·6	18·0	180	951	8·1	7·7	164·3				
940	7·2	8·7	0	10,5,1	5·7	5·3	306·6	103	17·7	17·4	180
10,4,0	5·9	4·4	0	761	9·3	7·1	223·9	203	41·6	40·0	90
11,4,0	13·0	14·1	0	861	15·8	14·8	187·3	303	7·0	9·6	180
550	26·5	25·2	0	961	5·9	5·7	326·3	403	5·9	7·8	90
650	11·0	8·0	0	871	4·3	4·3	150·4	503	<6·0	3·9	0
750	12·6	13·0	180	971	5·6	5·2	164·6	603	6·0	7·1	90
850	12·0	11·2	180					703	<5·6	5·5	180
950	5·6	4·4	0	002	<5·0	8·3	180	803	9·4	9·3	90
660	9·4	11·5	0	102	<5·0	1·9	270	903	6·4	8·7	180
760	12·2	12·1	180	202	<5·0	4·0	180				
860	<5·6	4·0	180	302	42·6	40·8	90	004	21·8	22·1	180
960	14·6	14·8	180	402	19·2	18·9	0	104	11·7	15·6	90
770	11·6	9·7	180	502	19·0	19·7	270	204	<5·9	1·3	180
870	6·5	5·6	180	602	<6·0	4·0	180	304	15·3	15·4	90
970	4·9	5·4	0	702	14·3	13·2	90	404	<5·8	5·5	180
				802	<5·9	5·4	180	504	<5·4	3·6	90
101	73·3	73·5	0	902	<5·3	3·6	270	604	<4·8	4·1	180
201	8·1	4·2	90	10,0,2	<5·0	2·5	0	704	10·3	12·1	90
301	14·3	14·4	0	112	9·5	12·0	357·2	804	<2·6	0·8	180
401	13·7	17·2	270	212	28·3	29·0	102·2				
501	33·1	32·6	0	312	7·9	6·5	197·1	105	6·0	6·8	180
601	6·8	6·0	90	412	13·1	12·0	204·1	205	6·5	7·7	90
701	6·4	3·6	180	512	29·9	31·6	314·9	305	<3·9	1·5	0
801	<4·0	2·1	270	612	13·5	13·2	140·1	405	<3·5	2·7	90

with symmetry $\bar{4}$. The molecules are shown in Figs. 1(b) and 2(b); the intramolecular distances and valence angles and their estimated standard deviations are listed in Table 2. In estimating these standard devia-

tions, errors due to the inaccuracies in the cell constants could be neglected.

The atoms F_1, S_1, N_1 and S_2 (Fig..1(b)) are approx-imately located in the plane:

$$+0.8017x+0.5388y+0.2587z=1.3115;$$

the distance of any atom from this plane did not exceed 0.012 Å.

The fluorine atoms, which are linked to the sulphur atoms, are located so as to give the most compact molecule. The length, 1.64 Å, of the S–F bond is equal to the value, 1.63 Å, predicted from atomic radii and electronegativity differences (Schomaker & Stevensen, 1941), but is larger than the values found in other compounds, which range from 1.56 to 1.58 Å (Sutton, 1958).

The difference of 0.10 Å between the lengths of the two crystallographically non-equivalent N–S bonds was tested for significance in two ways.

(a) The standard deviation σ in the difference was calculated.

$$\sigma=[2\sigma^2(S)+2\sigma^2(N)-2\sigma^2(S)\cos(N\text{-}S\text{-}N)$$
$$-2\sigma^2(N)\cos(S\text{-}N\text{-}S)]^{\frac{1}{2}}=0.036\text{ Å}.$$

(b) The lengths of the N–S bonds were made equal to each other by shifting the nitrogen atom. The minimum changes in the coordinates are:

$$\Delta x(N)=-0.042,\ \Delta y(N)=+0.030,\ \Delta z(N)=+0.026\text{ Å}.$$

Due to these changes in the final coordinates, the residuals R for the reflexions $hk0$, $hk1$ and $h0l$ increased from 0.070 to 0.080; 0.076 to 0.085 and 0.082 to 0.094 respectively. It should be noted that the reflexions $hk1$ were not used during the refinement of the structure.

From a and b it may be concluded that the N–S bonds have unequal lengths, so that the N–S bonds in the eight-membered ring are alternatingly different.

In $(NSF)_4$ molecules, therefore, delocalization of the binding electrons, as discussed by Craig (1959) for six- and eight-membered rings with alternating single and $p\pi$–$d\pi$ double bonds, does not occur to an appreciable extent.

It is not certain whether this delocalization exists in the eight-membered ring of $(PNCl_2)_4$, as the coordinates of the one independent nitrogen atom have not been determined very accurately during the crystal-structure investigation by Ketelaar & De Vries (1939). The latter structure is being refined with three-dimensional data in our laboratory.

The length 1.55 Å, of the shorter N–S bond is equal to the double-bond length, about 1.56 Å, predicted from conventional radii (Pauling, 1940). The double-bond character suggests promotion of an electron into the $3d$ orbitals of sulphur and overlap of a sulphur $d\pi$ orbital with the nitrogen $p\pi$ orbital. According to Craig (1958) this promotion and overlap · is possible if the sulphur atom has exocyclic bonds to electronegative atoms.

The N–S distance of 1.65 Å may be compared with the N–S bond lengths in sulphamide and related

molecules, which range from 1.57 to 1.73 Å (Trueblood & Mayer, 1956) and with the N–S distance in $(NSH)_4$, which amounts to 1.674 Å (Sass & Donohue, 1958; Lund & Svendsen, 1957). Most of these bond lengths are smaller than the value, 1.73 Å, predicted for a single bond from atomic radii and electronegativity differences (Schomaker & Stevensen, 1941). A conclusive explanation of the relative N–S bond lengths has not yet been given.

Shortest intermolecular distances—between fluorine atoms 2.95 Å, and between sulphur and fluorine atoms 3.26 to 3.37 Å—indicate that neighbouring molecules have Van der Waals interaction only.

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