



Table 1. *Optical properties*

Bisectrix	Crystal axis	Refractive index for NaD line	Angle $2V$ obtuse bisectrix
$bX_0$	$a = 12.37 \pm 0.02 \text{ \AA}$	$\gamma = 1.620 \pm 0.001$	Red light = $97.3 \pm 0.3 (3_\sigma)$
$bX_a$	$b = 24.36 \pm 0.02$	$\alpha = 1.612 \pm 0.001$	Na D line = $100.0 \pm 0.2 (7_\sigma)$
	$c = 11.94 \pm 0.02$	$\beta = 1.616 \pm 0.001$	Blue light = $102.9 \pm 0.3 (3_\sigma)$

& Stuart (1960)), and the calculated molecular refractivity using the Lorenz-Lorentz equation is  $94.27 \pm 0.12$  for the  $\gamma$  index as compared with 94.6 and 90.9 obtained by the additivity rule for the hypothesis of ionic and covalent bonds respectively.

Several attempts to estimate the diamagnetic anisotropy of PMI were carried out with crystals floating freely in a liquid mixture of 1-bromonaphthalene and methyl iodide placed in a homogeneous magnetic field ( $H \sim 7000$  Ørsted). The magnetic anisotropy was too small to be detected.

The observed mean molecular diamagnetic susceptibility as determined by the Gouy method is  $\chi_M = -215.4 \times 10^{-6}$  c.g.s.e.m. units and, as expected from other polyhalogenated compounds (Gray & Dakers, 1931; Pascal, 1943), is lower than the calculated  $\chi_M = -249 \times 10^{-6}$  c.g.s.e.m. units using the Pascal constants from Trew (1941).

### X-ray data

The Laue symmetry is *mmm*. A complete series of oscillation photographs about the *b* axis of a crystal of rhomboidal section, diagonals *a'*, *b'* and thickness *c'*  $0.066 \times 0.167 \times 0.13$  mm. (Cu *K* $\alpha$  radiation) gave 803 *hkl* reflexions, 35% of the 2322 possible reflexions.

Equi-inclination Weissenberg methods were used to photograph the *hk0*, *hk1*, *hk2*, *hk3*, *hk4*, *hk5* layers together with the *h0l* and *0kl* data of crystals of dimensions *a'b'c'* =  $0.083 \times 0.083 \times 0.20$ ,  $0.05 \times 0.08 \times 0.11$  and  $0.065 \times 0.065 \times 0.08$  mm<sup>3</sup> respectively. The observed (*hk0*), (*h0l*) and (*0kl*) data represent some 20%, 33% and 12.5% respectively of the theoretically available data. The oscillation and Weissenberg data have  $\sin \theta / \lambda \text{ max} \sim 0.5$ .

The axial measurements gave (with e.s.d.)

$$a = 12.37 \pm 0.02, \quad b = 24.36 \pm 0.02,$$

$$c = 11.94 \pm 0.02 \text{ \AA},$$

$$a:b:c = 0.508:1:0.490.$$

$$\text{Volume } abc = 3599.4 \pm 10.7 \text{ \AA}^3.$$

The calculated density for 8 molecules of anhydrous PMI in the unit cell is  $1.632 \text{ g.cm.}^{-3}$  and for 8 molecules of PMI with 2 molecules of water of crystallization is  $1.648 \text{ g.cm.}^{-3}$ ; the observed density is  $1.644 \pm 0.002 \text{ g.cm.}^{-3}$  (5 observations) and the calculated molecular weight is 446.7.

All intensities were estimated visually, the total intensity range, using multiple-exposure and multiple-film techniques, being 1700 to 1. The systematic absences *0kl* if (*k+l*) odd and *h0l* if *h* odd, suggest

two possible space groups: *Pna2*<sub>1</sub> and *Pnam* (non-standard setting of *Pnma*). The pyroelectric and piezoelectric tests gave no results and the positions of the iodine atoms shown by the Patterson projection were insufficiently random to apply Wilson's method to *0kl* and *h0l*, or to apply statistical tests for centrosymmetry.

The 81 observed *hk0* reflexions were used to determine values of the absolute scale and temperature factor; the intensities had previously been corrected for absorption in an approximate way using the Albrecht method. Attempts to minimize absorption effects by grinding small spherical crystals were not successful because of the platy habit of the crystals and the frequent cracks and cleavage splits.

After 240 hours' irradiation and subsequent storage of crystals for one year, a Weissenberg photograph showed some evidence of incipient disorder, with the formation of a new phase having *b* nearly three times as long as previously. Even 40 hours' irradiation gave very weak row-line streaking on oscillation photographs taken about [010].

### Structure determination

The Patterson projections (010) and (100) showed alternate layers of iodine-iodine and iodine-carbon vectors parallel to (001) and separated by  $z = \frac{1}{4}c \approx 2.96 \text{ \AA}$ .

The iodine positions could not be determined from the two-dimensional Patterson projections. Three-dimensional Patterson sections synthesized from the 803 reflexions of the oscillation photographic data gave, after lengthy trials, unique trial positions for the 16 iodine atoms in the unit cell. These positions do not imply hemimorphy.

Although the optical and magnetic measurements failed to indicate the orientation of the chains in the unit cell of PMI, the iodine-carbon vector distribution in the Patterson projections along *a* and *b* and in the three-dimensional sections shows that the planes of the chains are running nearly parallel to the (160) planes. The length of the chain is closely parallel to (001).

The presence of a centre of symmetry has not been shown conclusively, but it was tentatively concluded that the space group of PMI is *Pnam* and that the asymmetric unit consists of one methonium chain and four independent half-iodine atoms.

The trial coordinates of the four independent iodine atoms were refined by least-squares and three-dimensional Fourier and difference-Fourier syntheses. These

Table 2. *Observed and calculated structure factors for pentamethonium iodide*

<i>h k l</i>	$ F_o $	$F_c$	<i>h k l</i>	$ F_o $	$F_c$	<i>h k l</i>	$ F_o $	$F_c$
0 4 0	116	133	2 3 1	90	82	3 2 3	50	-51
0 1 0 0	37	27	2 4 1	126	-114	3 3 3	57	44
0 1 2 0	109	-128	2 5 1	37	-36	3 4 3	47	44
0 1 6 0	63	-61	2 9 1	48	52	3 5 3	98	-100
0 5 1	79	-82	2 10 1	54	64	3 6 3	45	-46
0 9 1	37	-32	2 13 1	68	76	3 8 3	59	63
0 11 1	63	63	2 0 2	113	-103	3 9 3	139	-150
0 15 1	60	60	2 2 2	119	-120	3 13 3	55	-60
0 17 1	56	67	2 3 0	56	-61	3 1 4	44	-43
0 8 2	38	28	2 4 2	57	-56	3 2 4	41	-40
0 12 2	110	119	2 5 2	118	113	3 3 4	89	-97
0 14 2	41	-35	2 6 2	30	-24	3 4 4	97	-97
0 16 2	64	66	2 8 2	34	-25	3 5 4	44	42
0 5 3	32	40	2 9 2	40	-41	3 6 4	84	-77
0 11 3	100	-102	2 10 2	45	40	3 7 4	56	-61
0 15 3	66	-62	2 13 2	79	-83	3 8 4	86	-105
0 17 3	58	-58	2 17 2	62	-73	3 9 4	49	51
0 4 4	162	184	2 1 3	102	107	3 12 4	46	-35
0 12 4	75	-85	2 2 3	105	107	3 3 5	37	-29
0 16 4	58	-56	2 3 3	81	-83	3 5 5	106	101
0 5 5	49	-54	2 4 3	111	112	3 6 5	58	51
1 3 0	36	47	2 10 3	66	-65	3 9 5	91	101
1 4 0	54	-52	2 11 3	46	38	3 13 5	59	53
1 6 0	71	65	2 12 3	57	-51	4 0 0	128	-117
1 7 0	43	39	2 13 3	62	-60	4 4 0	66	-56
1 8 0	181	-186	2 0 4	45	37	4 7 0	50	47
1 9 0	124	-119	2 1 4	115	-127	4 8 0	40	30
1 10 0	43	34	2 2 4	85	86	4 10 0	50	41
1 13 0	60	-60	2 3 4	50	59	4 11 0	62	63
1 4 1	120	-115	2 4 4	41	38	4 0 1	225	-261
1 6 1	102	-106	2 5 4	86	-84	4 1 1	93	89
1 7 1	100	98	2 8 4	46	51	4 4 1	189	-181
1 8 1	145	-146	2 13 4	73	86	4 5 1	82	93
1 12 1	55	-61	2 14 4	48	-25	4 7 1	41	42
1 5 2	100	101	2 17 4	65	65	4 12 1	68	71
1 6 2	34	-30	2 0 5	91	-107	4 13 1	49	-47
1 8 2	124	126	2 1 5	55	-65	4 16 1	50	48
1 9 2	139	154	2 2 5	62	-71	4 0 2	96	99
1 10 2	39	-37	2 3 5	51	59	4 2 2	30	28
1 12 2	49	41	2 4 5	66	-73	4 4 2	54	54
1 13 2	56	60	2 13 5	62	56	4 6 2	56	-54
1 3 3	38	-40	3 1 0	39	-42	4 7 2	53	-52
1 4 3	101	121	3 2 0	121	-105	4 8 2	41	-27
1 5 3	33	31	3 3 0	171	-150	4 10 2	48	-42
1 6 3	33	39	3 4 0	145	-135	4 11 2	57	-66
1 8 3	90	91	3 5 0	43	43	4 12 2	54	-52
1 10 3	40	43	3 6 0	98	-85	4 15 2	54	-51
1 12 3	50	57	3 7 0	84	-87	4 1 3	72	-69
1 4 4	107	-119	3 8 0	127	-128	4 4 3	122	110
1 5 4	95	-108	3 9 0	57	72	4 5 3	97	-92
1 6 4	36	37	3 12 0	57	-68	4 12 3	64	-64
1 8 4	115	-134	3 1 1	31	24	4 0 4	85	-90
1 9 4	103	-113	3 2 1	34	31	4 4 4	47	-42
1 13 4	52	-52	3 3 1	62	-47	4 10 4	54	49
1 4 5	64	-84	3 5 1	158	151	4 11 4	62	68
1 6 5	67	-70	3 6 1	80	68	4 0 5	157	-183
1 7 5	65	71	3 7 1	37	-41	4 1 5	60	59
1 8 5	91	-100	3 9 1	124	144	4 4 5	122	-125
2 0 0	24	-18	3 13 1	56	66	4 5 5	67	72
2 1 0	110	-113	3 14 1	45	-42	4 12 5	64	56
2 2 0	100	88	3 1 2	46	46	5 1 0	48	-42
2 3 0	98	80	3 3 2	83	78	5 6 0	41	-34
2 4 0	57	53	3 4 2	108	102	5 7 0	42	40
2 5 0	122	-117	3 5 2	53	-44	5 9 0	58	62
2 6 0	51	38	3 6 2	74	76	5 12 0	50	-48
2 8 0	60	58	3 7 2	73	67	5 1 1	102	101
2 13 0	105	130	3 8 2	111	118	5 4 1	127	154
2 17 0	67	74	3 9 2	57	-54	5 5 1	59	61
2 0 1	147	-171	3 10 2	37	29	5 8 1	143	149
2 1 1	97	-91	3 12 2	57	58	5 10 1	49	-46
2 2 1	118	-104	3 1 3	46	-33	5 1 2	59	53

Table 2 (cont.)

<i>h k l</i>	$ F_o $	$F_c$	<i>h k l</i>	$ F_o $	$F_c$	<i>h k l</i>	$ F_o $	$F_c$
5 2 2	41	38	6 2 2	37	41	7 6 2	43	-38
5 8 2	39	32	6 3 2	51	-60	7 1 3	51	-51
5 9 2	52	-56	6 4 2	83	81	7 3 3	78	-88
5 1 3	44	-50	6 5 2	45	-53	7 7 3	55	-51
5 3 3	73	-72	6 9 2	53	-59	7 9 3	64	73
5 4 3	151	-160	6 1 3	90	-92	7 5 4	62	64
5 5 3	75	-78	6 2 3	74	72	7 9 4	51	53
5 8 3	143	-150	6 3 3	58	61	7 3 5	76	82
5 2 4	45	28	6 6 3	39	39	8 0 0	69	-74
5 9 4	49	47	6 8 3	52	48	8 1 0	66	76
5 1 5	64	60	6 12 3	54	59	8 4 0	64	-68
5 4 5	104	112	6 13 3	59	58	8 5 0	57	65
5 8 5	96	105	6 0 4	72	-77	8 0 1	60	67
6 0 0	101	-101	6 2 4	55	-47	8 0 2	61	64
6 2 0	45	-46	6 3 4	68	77	8 1 2	55	-62
6 3 0	55	58	6 4 4	67	-71	8 5 2	60	-67
6 4 0	56	-62	6 5 4	55	52	8 0 3	59	-59
6 5 0	57	62	6 9 4	49	54	8 5 3	50	54
6 7 0	59	61	6 0 5	53	51	8 7 3	59	53
6 9 0	49	63	6 1 5	69	67	8 0 4	50	-50
6 0 1	66	70	7 1 0	53	58	8 1 4	50	56
6 1 1	78	89	7 4 0	48	43	9 1 0	55	62
6 2 1	58	-68	7 5 0	68	82	9 3 0	60	68
6 3 1	52	-52	7 9 0	57	57	9 4 0	73	68
6 5 1	52	62	7 1 1	54	54	9 1 2	52	-68
6 6 1	50	-54	7 3 1	92	105	9 3 2	49	-61
6 8 1	58	-60	7 7 1	62	67	9 4 2	49	-59
6 12 1	56	-66	7 9 1	61	-78	9 8 2	66	-77
6 13 1	61	-60	7 1 2	56	-58	9 4 4	58	58
6 0 2	115	115	7 5 2	65	-76	9 8 4	55	57

Table 3

Atomic parameters derived from Weissenberg data ( $R=0.084$ )  
 Positional coordinates for all atoms. Thermal parameters only for iodine

	<i>x</i>	<i>y</i>	<i>z</i>	$b_{11}$	$b_{22}$	$b_{33}$	$b_{23}$	$b_{13}$	$b_{12}$
I(1)	0.1059	0.0454	0.25	0.0123	0.0040	0.0160	0	0	0.0041
I(2)	0.0933	0.2770	0.25	0.0107	0.0048	0.0184	0	0	0.0018
I(3)	0.0604	0.5192	0.25	0.0104	0.0065	0.0187	0	0	0.0033
I(4)	0.3069	0.7896	0.25	0.0128	0.0045	0.0144	0	0	0.0012
C(1)	0.064	0.681	0.095						
C(2)	0.178	0.711	0.924						
C(3)	0.121	0.618	0.933						
C(4)	0.234	0.647	0.080						
C(5)	0.355	0.654	0.013						
C(6)	0.437	0.628	0.095						
C(7)	0.543	0.616	0.002						
C(8)	0.650	0.598	0.089						
C(9)	0.681	0.521	0.941						
C(10)	0.809	0.558	0.086						
C(11)	0.767	0.614	0.937						
N(2)	0.150	0.670	0.006						
N(4)	0.724	0.577	0.004						

Iodine atomic parameters derived from independent oscillation data ( $R=0.129$ ) using another crystal

	<i>x</i>	<i>y</i>	<i>z</i>	$b_{11}$	$b_{22}$	$b_{33}$	$b_{23}$	$b_{13}$	$b_{12}$
I(1)	0.1047	0.0450	0.25	0.0140	0.0053	0.0125	0	0	0.0050
I(2)	0.0923	0.2775	0.25	0.0120	0.0060	0.0150	0	0	0.0020
I(3)	0.0616	0.5188	0.25	0.0120	0.0075	0.0140	0	0	0.0044
I(4)	0.3064	0.7890	0.25	0.0140	0.0055	0.0122	0	0	0.0017



placements. They may also be affected by possible extinction effects, which have been neglected because of the small crystal size. This table, however, gives a relative measure of the displacements in different directions for the various iodine atoms, and the  $b_{ij}$  may be compared with the similar data obtained independently from the oscillation data and given in Table 3.

Disorder could be due to the presence of water of crystallization in a quantity smaller than the four molecules required by the minimum symmetry of  $Pn\bar{3}m$  in the unit cell.

The two molecules of water of crystallization do not appear on the mirror-plane sections of the Fourier and difference-Fourier synthesis; they may be disguised by the secondary diffraction maxima of the iodine atoms whose van der Waals sections occupy about  $\frac{2}{3}$  of the areas of the mirror planes.

The three-dimensional difference-Fourier synthesis confirms that the structure is correct. The differences range from  $-0.8$  to  $-1.6$  electrons in the iodine atom layers and  $0.0$  to  $\pm 0.6$  electrons in the chain layers. The oscillation data gave differences of the same order.

Although the 303 Weissenberg data were refined

by least squares to give  $R=0.084$ , yet the methonium chains shown in the corresponding electron-density diagram, although resolved, have C and N peak heights only about one-half or less of those in the electron-density diagram which corresponded to the 803 oscillational data,  $R=0.22$ .

In the case of other substances, such as tetramethyl ammonium penta-iodide, (Hach & Rundle, 1951 and Brockema, Havinga & Wiebenga, 1957), and tetramethyl ammonium enneiodide (James, Hach, French & Rundle, 1955), no evidence of the positions of the nitrogen atoms was found, but our experience indicates that this may have been the consequence of the smaller number of reflections observed in these cases.

### Accuracy and implications of the structure determination

The estimated standard deviation (e.s.d.) of I, C and N atomic coordinates is approximately  $0.015$ ,  $0.17$  and  $0.14$  Å respectively. Table 5 contains the bond lengths and their s.d.

Within s.d. the chains are plane as in acetylcholine bromide (Sörum, 1959) and not gauche as in choline

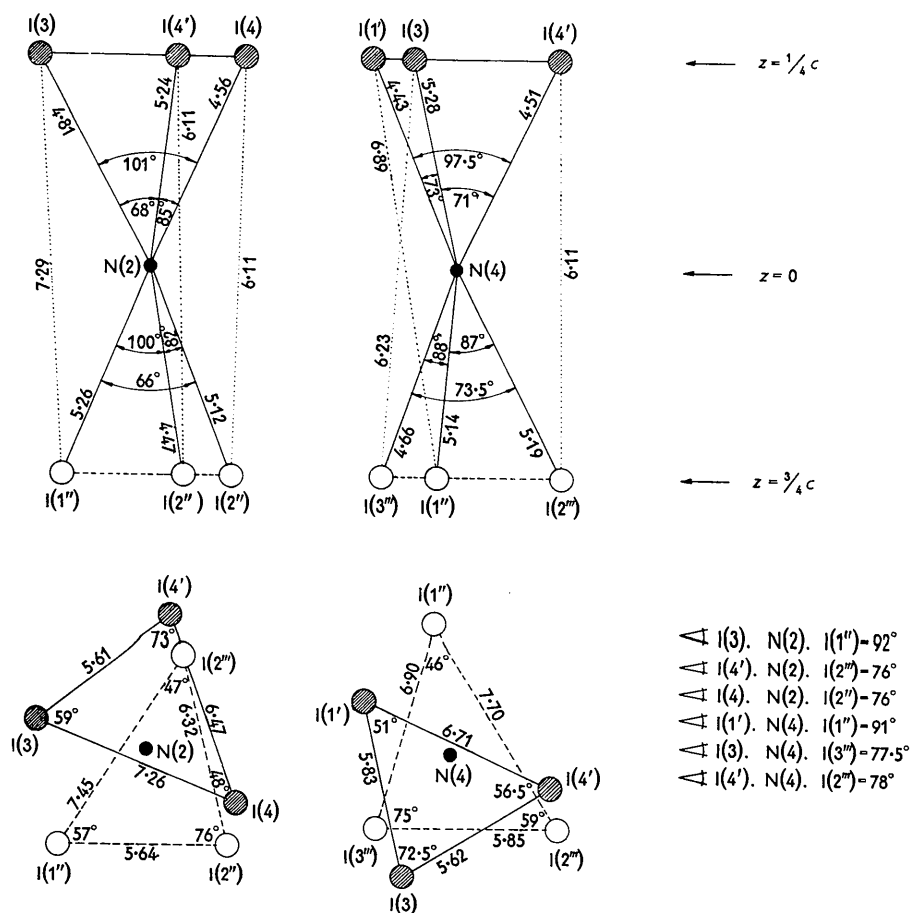


Fig. 2. Iodine coordination of nitrogen atoms of the chain. All distances in Å.

Table 5. *Bond lengths and e.s.d.*

(See description in Fig. 2)

N-I sixfold coordination +e.s.d. of the position of N in the chain			
N(2)-I(1'')	5.26 ± 0.14 Å	N(4)-I(1')	4.43 ± 0.14 Å
N(2)-I(2'')	5.12 ± 0.14	N(4)-I(1'')	5.14 ± 0.14
N(2)-I(2''')	4.47 ± 0.14	N(4)-I(2'')	5.19 ± 0.14
N(2)-I(3)	4.81 ± 0.14	N(4)-I(3)	5.28 ± 0.14
N(2)-I(4')	5.24 ± 0.14	N(4)-I(3''')	4.66 ± 0.14
N(2)-I(4)	4.56 ± 0.14	N(4)-I(4')	4.51 ± 0.14
I-I distances on the mirror planes of the iodine atoms coordinating nitrogen			
I(1'')-I(2'')	5.64 ± 0.02 Å	I(1'')-I(2''')	7.70 ± 0.02 Å
I(2'')-I(2''')	6.32 ± 0.02	I(2'')-I(3''')	5.85 ± 0.02
I(2''')-I(1)	7.45 ± 0.02	I(3''')-I(1'')	6.90 ± 0.02
I(3)-I(4)	7.26 ± 0.02	I(1')-I(3)	5.83 ± 0.02
I(4)-I(4')	6.47 ± 0.02	I(3)-I(4')	5.62 ± 0.02
I(4')-I(3)	5.61 ± 0.02	I(4')-I(1')	6.71 ± 0.02

chloride (Shenko & Templeton, 1960) and choline reineckate (Takeuchi & Saito, 1957), and their planes are approximately in (160) and (160) with their lengths in (001). The expected N-N distance is 7.5 Å and the observed value is  $7.47 \pm 0.19$  Å. Similarly the expected distance between the methyl groups  $C_1-C_{10}$  is  $\sim 10$  Å and the observed is  $9.75 \pm 0.24$  Å. These two facts confirm that the structure of the chain, despite the large standard deviation, is broadly satisfactory, although it is not profitable to discuss the significance of the different bond lengths within the chain.

The structure represents an equilibrium between anionic layers of iodines and layers of biscationic methonium chains. Both the I and N ions possess a distorted sixfold coordination built up by two triangles situated in parallel planes separated by a distance of  $\frac{1}{2}c = 5.98 \pm 0.01$  Å. The coordination of the nitrogen atoms by the iodine atoms can be seen in Fig. 2. The N coordination of I ions, since the latter are on a mirror plane, is trigonal prismatic (See Fig. 1).

In Fig. 2 it is of interest to see that although the triangular areas determined by the I ions coordinating the N ions are different, their sum for a given nitrogen is nearly constant and about 34.6 Å. Hence, even if the I-N bond lengths are different (see Table 5), yet because the inter-layer distance is a constant =  $\frac{1}{2}c$ , the bipyramid volume determined by the I-coordination of N<sup>+</sup> is nearly constant.

The shorter I-N<sup>+</sup> bond lengths (see Table 5) are in agreement with those of N<sup>+</sup>-Cl<sup>-</sup> in choline chloride (*loc. cit.*), if we add to the latter  $0.34$  Å =  $r(I^-) - r(Cl^-)$ . Both types of bond-length are among the I-N<sup>+</sup> bond lengths present in D-L isocryptopleurine methiodide (Fridrichsons & Mathieson, 1955), a layer structure with highly distorted sixfold coordination of I<sup>-</sup> and N<sup>+</sup> with bond lengths of 4.36, 5.86, 6.32, 8.18, 8.68 and 8.79 Å, which will be discussed elsewhere. Because the electric dipole of this latter substance is unknown, the ionic bond-lengths 8.18, 8.68 and 8.79 Å may only be accepted with some reservations.

## Conclusions

The Fourier synthesis obtained from oscillation data (using phases from I atoms only) has shown that the methonium chain is nearly planar and that the three CH<sub>3</sub> groups are not rotating about the N-CH<sub>2</sub> bonds. This result is in agreement with a wide-line nuclear-magnetic-resonance analysis of P.M.I. which again provides no evidence of hindered rotation. The importance of the I-N<sup>+</sup> bonds of P.M.I. in their electrolytic behaviour (Chu & Fuoss (1951), Brody & Fuoss (1957)) and in the mechanism of ganglionic nervous transmission will be discussed elsewhere (Canepa (1962)). The optical measurements are consistent with the ionic description of the structure. A more distorted sixfold coordination of the iodine anions by the quaternary nitrogen cations than that of PMI exists in DL-isocryptopleurine methiodide (Fridrichsons & Mathieson, 1955) and in muscarine iodide (Jellinek, 1957).

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## Short Communications

*Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

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**Refinement of the structure of tetrathiazylfluoride (NSF)<sub>4</sub>.** By G. A. WIEGERS and AAFJE VOS, *Laboratorium voor Structuurchemie, Rijksuniversiteit, Groningen, The Netherlands*

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Several phosphonitrilic molecules containing (PN)<sub>3</sub> or (PN)<sub>4</sub> rings have been studied by X-ray diffraction recently: (PNCl<sub>2</sub>)<sub>3</sub> (Wilson & Carrol, 1960), (PNF<sub>2</sub>)<sub>4</sub> (McGeachin & Tromans, 1961), [PN(NMe<sub>2</sub>)<sub>2</sub>]<sub>4</sub> (Bullen, 1962), (PNMe<sub>2</sub>)<sub>4</sub> (Dougill, 1961) and (PNCl<sub>2</sub>)<sub>4</sub> (Hazekamp, Migchelsen & Vos, 1962). In each of these molecules the P-N bonds in the ring have equal lengths. During our two-dimensional structure determination of the analogous compound (NSF)<sub>4</sub>, the molecules of which have symmetry  $\bar{4}$ , the N-S bond lengths were found to alternate; values of 1.55 and 1.65 Å with e.s.d. 0.02 Å were observed (Wiegiers & Vos, 1961).

As the difference in length was only just significant, we decided to determine the bond lengths more accurately from difference Fourier syntheses. The reflections *hk0*, *hk1*, *hk2* and *hk3* were used. The intensity measurements and the methods used in the refinement of the structure are as described in our paper on the two-dimensional work. The temperature factors of the atoms were assumed to be isotropic. The scaling factors for the reflections from different *l* levels, which had been recorded on different photographs, were obtained by comparing observed and calculated structure factors.

Table 1. *Final coordinates*

Two-dimensional refinement				
	<i>x</i>	<i>y</i>	<i>z</i>	$\sigma$
S	0.0258	0.2073	0.0868	0.005 Å
N	0.1258	0.1173	-0.1660	0.02
F	0.3281	0.0165	0.1781	0.02
Three-dimensional refinement				
	<i>x</i>	<i>y</i>	<i>z</i>	$\sigma$
S	0.0257	0.2078	0.0871	0.002 Å
N	0.1265	0.1160	-0.1659	0.009
F	0.3263	0.0162	0.1711	0.006

At the end of the refinement the reliability index *R* for the observed reflections except 220 which showed strong extinction, was 5.6%. The standard deviations in the coordinates, obtained by applying Cruickshank's formula (Cruickshank, 1949) are 0.002, 0.009 and 0.006 Å for S, N and F respectively. The final coordinates are listed in Table 1. The temperature factor parameters for S, N and F are 2.55, 3.31 and 3.47 Å<sup>2</sup> respectively.

Table 2. *Bond lengths and valence angles from the two dimensional (a) and three dimensional (b) refinement*

	<i>a</i>		<i>b</i>	
	Å	s.d.	Å	s.d.
N-S	1.65	0.02	1.660	0.01
N=S	1.55	0.02	1.540	0.01
S-F	1.64	0.02	1.602	0.006
S-N-S	123°	1.3°	123.9°	0.6°
N-S-N	112	1.3	111.7	0.6
F-S-N	91	1.0	91.5	0.4
F-S=N	106	1.0	106.2	0.4

The bond lengths and valence angles are compared with those from the two-dimensional refinement in Table 2. The table shows that the length of the S-F bond has changed considerably (-0.04 Å). The N-S bond lengths which changed only little, are now significantly different.

The Fourier syntheses and structure factors were calculated on the computer ZEBRA with programs devised by Dr D. W. Smits. We wish to thank Mr H. Schurer for operating ZEBRA. The Netherlands Organization for the Advancement of Pure Research (ZWO) supported this work indirectly.

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