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The Crystal Structure of the Hydrochloride and Hydrobromide Salts of 1,3-Dimethyl-5-Iminotetrazole

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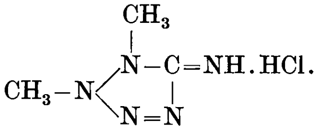
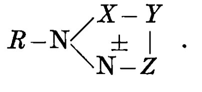
The crystal structure of the hydrochloride and hydrobromide salts of 1,3-dimethyl-5-iminotetrazole has been determined by direct methods. Crystals of these substances show the symmetry of the orthorhombic space group *Pbnm*. The planar molecules lie in the mirror planes of this space group. The results of elemental chemical analysis and the X-ray analysis show that these compounds are the cyclic meso-ionic type. The dimensions of the molecule, obtained by a modified three-dimensional Fourier synthesis, are interpreted in terms of a number of resonating ionic structures.

Introduction

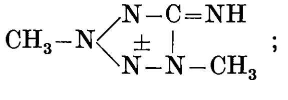
The product of the methylation of 2-methyl-5-aminotetrazole with methyl benzenesulfonate is a strongly basic material which forms neutral salts with strong acids. The hydrochloride salt has an elemental analysis corresponding to the formula $C_3H_8N_5Cl$ (Henry, Finnegan & Lieber, 1954). The expected reaction product was 1,2-dimethyl-5-iminotetrazole hydrochloride,



However, the preliminary X-ray analysis of crystals of the hydrobromide salt of the base showed that the tetrazole ring was substituted in the 1,3-positions.* No conventional covalent structure can be written for this compound. It appears to belong to a group of substances which have been called cyclic 'meso-ionic' compounds (Baker, Ollis, Poole, Barltrop, Hill & Sutton, 1947; Baker, Ollis & Poole, 1949), and which have the general formula



Substituting N for X, NR.C(:NH) for $Y-Z$ and CH_3 for R, gives 1,3-dimethyl-5-iminotetrazole,



this is one of the types that has been predicted (Baker *et al.*, 1947, 1949). A complete analysis of the crystal structure of the hydrochloride salt of 1,3-dimethyl-5-iminotetrazole has been made. Since the hydrobromide and hydrochloride salts are isomorphous it was possible to perform this analysis without making any assumptions as to the structure of the molecule.

Experimental measurements

Crystals of the hydrochloride and hydrobromide salts of 1,3-dimethyl-5-iminotetrazole were obtained by recrystallization from isopropyl alcohol. They were usually obtained as slender needles showing the forms {110} and {001}. Cleavage occurred with great ease along (001).

The unit-cell dimensions were determined from rotation and Weissenberg photographs taken about the b and c axes. The following results were obtained (λ of Cu $K\alpha$ = 1·5418 Å):

	a_0 (Å)	b_0 (Å)	c_0 (Å)	Density (g.cm.$^{-3}$) Obs.	Density (g.cm.$^{-3}$) Calc.
HCl salt:	10·90	9·60	6·58	1·43	1·443
HBr salt:	11·21	9·82	6·71	1·69	1·745

There are four molecules per unit cell. The following extinctions were noted: hkl present in all orders; $hk0$ present in all orders; $h0l$ present only with $h+l = 2n$; and $0kl$ present only with $k = 2n$. These extinctions are permitted by the space groups *Pbn* and *Pbnm*. The latter was indicated by rotation photographs taken about the c axis on which all the even layer lines showed the same sequence of intensities and similarly for the odd layer lines. This can occur only if all the atoms lie in planes $\frac{1}{2}c_0$ Å apart. A layer structure was also suggested by the great intensity of all orders of $00l$. That the crystals of the two salts were isomorphous was indicated by the general similarity of intensity of corresponding reflections.

Intensities of the $hk0$ and $hk1$ reflections from the hydrochloride salt and the $hk0$ reflections from the hydrobromide salt were estimated visually from Weis-

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* The 2-methyl-5-aminotetrazole was actually methylated in the 4-position; the tetrazole ring in the product was renumbered to give the smaller numbers.

senberg photographs. The intensities were corrected for the Lorentz and polarization factors by the expression

$$|F(hkl)|^2 = I(hkl)[\xi \cos\theta/(1+\cos^2 2\theta)]\,.$$

No allowance was made for absorption or extinction, although the agreement between the observed and calculated structure amplitudes of some intense reflections would have been improved by making these corrections.

Determination of the structure

Using the relative values of $|F(hk0)|^2$, Patterson projections were calculated; plots of this function for crystals of the two compounds are shown in Fig. 1. The positions in *Pbnm* with the symmetry *m* are

$$x, y, \tfrac{1}{4};\ \bar{x}, \bar{y}, \tfrac{3}{4};\ \tfrac{1}{2}+x, \tfrac{1}{2}-y, \tfrac{3}{4};\ \tfrac{1}{2}-x, \tfrac{1}{2}+y, \tfrac{1}{4}\,.$$

Therefore, in these Patterson projections there will be three halogen–halogen vector peaks at $(2x, 2y)$, $(\frac{1}{2}, \frac{1}{2}-2y)$ and $(\frac{1}{2}-2x, \frac{1}{2})$. These peaks are not easily identified on the Patterson projection of the hydrochloride salt, but are easily seen on that of the hydrobromide salt. In this manner the coordinates of the bromide ion were found to be $x = 0{\cdot}124$, $y = 0{\cdot}138$.

The contribution of the bromide ion to the structure amplitudes was then calculated for this position. Because the x coordinate was nearly $\frac{1}{8}$, the bromide ion contribution was essentially zero for a number of reflections; however, the phases of a sufficient number of structure amplitudes were determined to permit the calculation of a preliminary Fourier projection. In spite

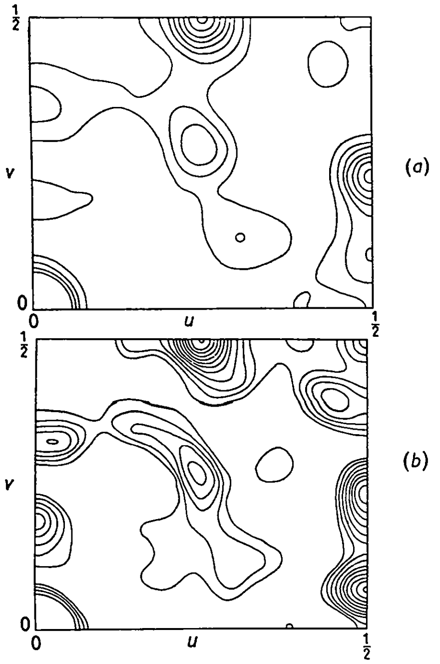


Fig. 1. Patterson projections of (*a*) the hydrobromide salt and (*b*) the hydrochloride salt of 1,3-dimethyl-5-iminotetrazole.

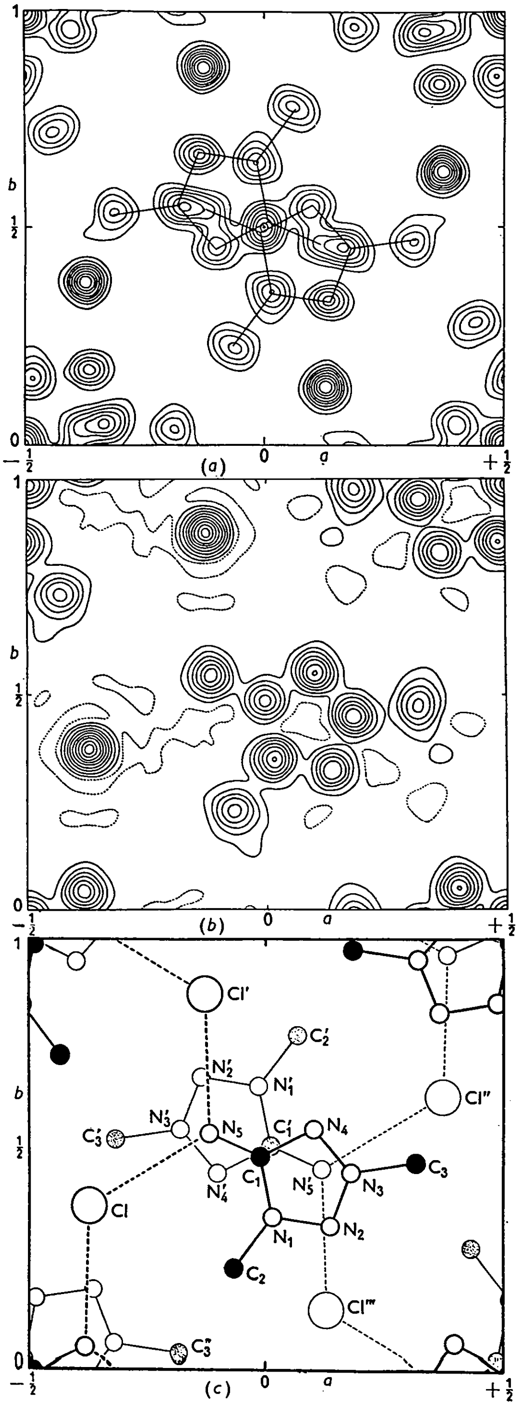


Fig. 2. (*a*) Fourier projection of 1,3-dimethyl-5-iminotetrazole hydrochloride on (001). Contour interval of the chloride ion is twice that of the light atoms.

(*b*) Fourier section at $z = \frac{1}{4}$ through the crystal of 1,3-dimethyl-5-iminotetrazole hydrochloride. Contour interval of the chloride ion is twice that of the light atoms. Negative regions are enclosed by broken lines.

(*c*) Arrangement of the molecules in one unit cell of 1,3-dimethyl-5-iminotetrazole hydrochloride. Heavy lines are molecules at $z = +\frac{1}{4}$; light lines molecules at $z = -\frac{1}{4}$. Broken lines are hydrogen bonds.

of the rather extensive overlapping of some atoms the resolution was sufficiently good to determine that the compound was either 1,3- or 2,3-substituted instead of the expected 1,2-substituted compound. An atom position that was approximately 3·4 Å from two bromide ions was taken as the imino nitrogen, thus making the compound 1,3-substituted. This choice was soon found to be correct.

It was now possible to determine reasonably accurate parameters for all the atoms, and so to continue the refinement. After two more Fourier projections and structure-amplitude calculations had been made, the reliability index was 0·144. The calculated structure amplitudes were corrected by an isotropic temperature factor, exp $[-3{\cdot}4\ (\sin\theta/\lambda)^2]$. The final Fourier projection was essentially identical with that subsequently obtained for the hydrochloride salt (Fig. 2(*a*)).

The phases of the zero-layer structure amplitudes of the hydrochloride salt were now determined by subtracting out the bromide ion contribution to the structure amplitudes of the hydrobromide salt and adding in that of the chloride ion. This gave the phases of most of the reflections. The Fourier projection calculated with these phases gave atomic parameters which were considered good enough to use in the calculation of the phases of the first-layer reflections as well as those of the zero layer.

Two Fourier projections were now calculated: the first, using the *hk*0 structure amplitudes, is shown in Fig. 2(*a*); the second, calculated with the *hk*1 structure amplitudes, was added point by point to the first projection. The resulting summation, which was essentially equivalent to a half-cell projection, removed the overlapping molecule and permitted the atomic coordinates to be determined much more accurately.

The structure amplitudes for the *hk*0 and *hk*1 reflections were again calculated. Temperature and scale factors were determined by plotting the logarithm of the ratio $[\Sigma|F_o|]\div[\Sigma|F_c|]$ against $\sin^2\theta$. The summations were taken over increments of 0·2 in $\sin^2\theta$. The plots for the two layer lines were nearly parallel lines, the slope of which gave the temperature factor, and the intercept at $\sin^2\theta = 0$ gave the scale factor. The average temperature factor used in subsequent calculations was exp $[-2{\cdot}735\ (\sin\theta/\lambda)^2]$.

Since the zero and first layer lines contain all diffraction data for the entire reciprocal lattice, the higher layer lines merely repeating this information with smaller scattering factors, it seemed feasible to use these data to calculate a three-dimensional Fourier section at $z = \frac{1}{4}$. A modification of the method employed by Brasseur & Pauling (1938) in the determination of the structure of NH_4CdCl_3 was used. It was assumed that the scattering-factor curve for the chloride ion was representative of all the atoms in the structure. Correction factors for reflections on layer lines other than the zero or first were calculated by the expressions

$$K_0=m_0+m_2f_2/f_0+m_4f_4/f_0+\ldots,\quad h_0=h_i,\quad k_0=k_i,\quad l=2n;$$

and

$$K_1=m_1+m_3f_3/f_1+m_5f_5/f_1+\ldots, h_1=h_i,\ k_1=k_i,\ l=2n+1,$$

where m_i is the multiplicity and f_i is the scattering factor of the chloride ion for the particular reflection on the *i*th layer line. After multiplying the observed structure amplitudes (with the proper phases) by these factors the Fourier section was calculated (Fig. 2(*b*)). The relative heights of light-atom peaks clearly distinguish between the carbon and nitrogen atoms. The same procedure was applied to the calculated structure amplitudes which had been corrected by the temperature factor. This second section was used with the first section to make back-shift corrections (Booth, 1946). The peak centers on the two sections were calculated by a nine-point Gaussian method (Shoemaker, Donohue, Schomaker & Corey, 1950). The maximum error in the positions of the atoms was estimated from these corrections to be ±0·02 Å for the chloride ion and ±0·04 Å for the light atoms. The final parameters are listed in Table 1. The structure amplitudes calculated with these parameters are listed with the observed structure amplitudes in Table 2. The reliability index is 0·161 for the zero-layer data and 0·136 for the first-layer data, if all non-zero reflections are included. By not including the six most intense reflections for which absorption corrections are appreciable the reliability indices become 0·126 and 0·118 respectively. (These reflections are (020), (110), (210) and (400) on the zero layer and (021) and (211) on the first layer.)

Table 1. *Final parameters*

Atom	*x*	*y*	*z*
Cl	−0·3722	0·3718	0·2500
N_1	0·0145	0·3460	0·2500
N_2	0·1370	0·3243	0·2500
N_3	0·1810	0·4498	0·2500
N_4	0·1009	0·5515	0·2500
C_1	−0·0103	0·4865	0·2500
N_5	−0·1184	0·5419	0·2500
C_2	−0·0666	0·2268	0·2500
C_3	0·3147	0·4726	0·2500

Discussion

Table 3 and Fig. 2(*c*) show the dimensions of the molecule. The interatomic distances in the ring indicate that considerable resonance is occurring. This was expected since the diffraction symmetry shows that the molecules lie in mirror planes. As no simple covalent structure can be written for the compound it can be classified as a cyclic meso-ionic compound along with the sydnones and a number of others (Baker, Ollis & Poole, 1950). The structure of the molecule is the result of a number of resonating ionic forms of which the following are probably the most important:

Table 2. *Comparison of calculated and observed structure amplitudes*

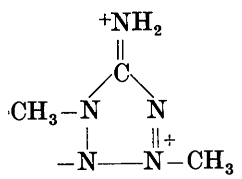
The left hand column is the *k* index, the middle column the calculated structure amplitude, and the right hand column the observed structure amplitude.

	0*k*0	
0	284·0	—
2	48·8	33·4
4	−12·9	11·9
6	18·2	21·6
8	9·6	12·8
10	−14·7	18·6
12	−11·2	12·2
	1*k*0	
1	−47·1	27·9
2	7·1	4·3
3	−30·7	28·2
4	−6·9	7·3
5	−22·8	24·4
6	−37·0	34·5
7	4·7	5·5
8	−7·1	7·1
9	20·1	21·6
10	6·8	9·2
11	−6·1	6·4
12	−2·6	2·1
	2*k*0	
0	29·0	22·0
1	53·2	31·3
2	−13·6	18·9
3	39·2	33·5
4	0·5	2·1
5	−33·9	30·6
6	7·2	9·8
7	−2·9	2·9
8	5·8	7·0
9	10·6	13·4
10	0·0	< 2·9
11	2·9	5·0
12	3·1	3·4
	3*k*0	
1	−20·7	23·3
2	22·9	18·8
3	20·6	17·5
4	18·6	23·5
5	10·7	12·3
6	−16·4	17·5
7	−30·3	30·4
8	4·7	3·2
9	−14·6	17·0
10	7·1	8·3
11	2·9	4·0
12	−0·2	< 1·3
	4*k*0	
0	−66·0	51·1
1	−18·2	20·4
2	−8·0	7·6
3	−2·3	2·1
4	24·6	26·5
5	−12·4	15·4
6	4·1	7·5
7	0·2	< 3·2
8	−3·5	5·5
9	1·4	< 3·2
10	6·9	8·4
11	2·3	2·2
	5*k*0	
1	−9·3	8·1
2	−15·8	17·5
3	27·6	27·1
4	10·9	13·8
5	8·9	9·7
6	25·5	25·2
7	−15·4	18·1
8	7·1	5·4
9	−10·0	12·1
10	−10·2	12·6
11	3·3	4·2
	6*k*0	
0	21·6	27·9
1	−30·3	29·7
2	9·9	13·9
3	−12·7	14·7
4	−4·1	4·8
5	13·2	16·1
6	14·7	16·9
7	4·9	5·5
8	2·6	3·7
9	−11·8	12·0
10	−0·3	< 2·3
11	−7·8	8·7
	7*k*0	
1	−2·1	2·7
2	−25·9	25·4
3	−6·5	6·6
4	−6·8	6·5
5	−22·9	22·6
6	4·5	6·7
7	5·7	5·7
8	−5·3	5·0
9	4·6	5·0
10	−6·3	5·9
	8*k*0	
0	29·9	28·9
1	12·1	12·0
2	0·9	< 2·9
3	5·2	5·3
4	−25·2	24·4
5	−2·8	3·9
6	11·6	12·1
7	2·7	3·1
8	9·8	11·4
9	0·7	2·3
10	−1·7	2·1
	9*k*0	
1	−6·8	7·8
2	9·4	7·9
3	−11·3	11·2
4	6·1	7·2
5	−12·8	12·7
6	−6·9	7·3
7	4·2	5·3
8	−0·8	2·4
9	2·9	3·9
	10,*k*,0	
0	8·4	8·9
1	21·1	18·6
2	14·2	14·4
3	7·6	9·0
4	6·3	7·6
5	−11·5	12·8
6	1·8	< 2·8
7	−3·0	4·0
8	−1·9	2·2
	11,*k*,0	
1	−11·9	12·5
2	5·7	5·3
3	4·2	4·3
4	−0·9	< 2·8
5	7·6	7·6
6	−3·0	3·9
7	−4·6	4·3
	12,*k*,0	
0	−9·2	8·9
1	0·7	< 2·8
2	2·0	3·2
3	−3·8	2·6
4	11·4	10·9
5	0·7	< 2·1
6	−0·7	< 1·6
	13,*k*,0	
1	−2·9	3·2
2	−7·2	7·2
3	3·9	3·8
4	−0·5	< 1·6
	14,*k*,0	
0	0·8	< 1·2
1	−4·8	3·7
	0*k*1	
2	−81·3	56·4
4	21·8	25·5
6	32·4	33·7
8	−18·4	16·7
10	−9·5	9·6
12	−3·6	2·9
	1*k*1	
0	4·1	5·3
1	11·2	14·4
2	21·6	27·6
3	−41·5	41·6
4	27·3	25·8
5	−3·9	4·1
6	4·4	4·7
7	8·6	10·3
8	−21·6	24·0
9	−8·0	7·2
10	−1·7	< 2·6
11	−5·8	6·9
12	5·2	6·5
	2*k*1	
1	−49·9	37·5
2	1·7	5·8
3	56·1	49·2
4	15·9	18·4
5	15·4	16·8
6	14·5	15·4
7	−8·9	9·6
8	−3·8	5·1
9	−3·0	3·3
10	2·5	< 2·5
11	9·5	11·3
12	−1·3	2·4

Table 2 (*cont.*)

	$3kl$	
0	−39·6	37·8
1	32·1	33·0
2	− 3·0	< 1·6
3	26·9	32·4
4	5·5	4·4
5	−11·0	15·4
6	3·1	5·5
7	− 4·9	6·5
8	−17·0	18·2
9	19·8	20·3
10	0·9	2·6
11	7·4	7·2
12	7·2	< 1·0*
	$4kl$	
1	− 0·2	7·7
2	22·7	21·1
3	1·4	< 1·9
4	−21·7	24·6
5	− 6·1	8·3
6	−31·1	30·8
7	1·4	< 2·8
8	− 6·3	7·5
9	− 3·9	4·1
10	5·8	7·1
11	2·5	2·3
	$5kl$	
0	6·2	4·4
1	25·4	24·8
2	4·1	3·4
3	38·2	35·5
4	−29·2	27·1
5	− 1·2	< 2·4
6	0·3	< 2·6
7	4·0	6·2
8	13·4	15·2
9	12·0	15·3
10	− 2·6	3·2
11	0·1	1·6
	$6kl$	
1	20·1	17·8
2	−27·9	29·2
3	−20·7	18·2
4	− 7·7	9·9
5	− 9·7	9·7
6	−14·1	14·1
7	16·5	15·8
8	−10·4	10·6
9	6·5	8·7
10	− 4·9	4·1
11	− 1·6	1·4
	$7kl$	
0	27·9	28·8
1	− 8·1	7·5
2	8·9	9·8
3	− 6·3	6·2
4	−11·6	11·4
5	1·6	4·0
6	3·6	3·4
7	15·5	15·4
8	6·4	7·4
9	− 5·9	6·3
10	− 5·1	6·6
	$8kl$	
1	− 1·1	3·0
2	−22·4	19·5
3	11·9	11·6
4	22·8	20·6
5	1·3	< 2·9
6	22·8	21·7
7	− 3·9	5·3
8	2·9	< 2·4
9	2·0	2·5
10	− 6·0	6·7
	$9kl$	
0	−19·2	15·8
1	−11·2	10·6
2	−19·2	15·2
3	−10·2	10·3
4	4·3	5·2
5	− 5·2	3·9
6	1·5	3·1
7	2·9	2·9
8	− 7·5	6·0
9	− 3·6	3·4
	$10,k,l$	
1	− 7·2	8·0
2	3·2	3·4
3	19·8	17·3
4	1·2	< 2·7
5	8·4	7·3
6	− 1·2	< 2·4
7	−13·1	12·1
8	− 0·2	< 1·5
	$11,k,l$	
0	− 4·2	4·6
1	6·4	5·5
2	− 6·2	4·5
3	8·6	8·9
4	4·8	4·9
5	− 6·3	5·4
6	− 2·0	< 1·9
7	− 5·6	5·3
	$12,k,l$	
1	2·5	< 2·4
2	9·2	7·6
3	− 0·3	< 2·2
4	− 5·1	4·8
5	4·6	3·5
6	− 9·7	8·8
	$13,k,l$	
0	14·1	13·1
1	7·1	5·9
2	1·8	2·2
3	4·2	4·1
4	− 5·7	5·1

* This reflection is probably too far in the back-reflection region ($\sin\theta = 0·994$) to be recorded on the film.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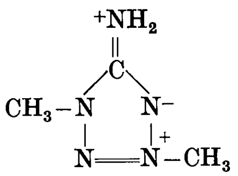
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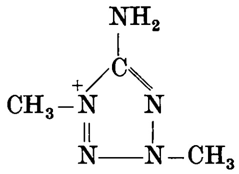
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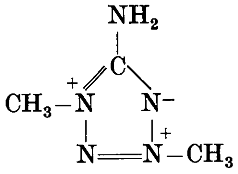
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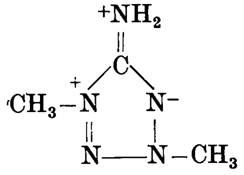
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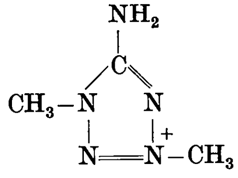
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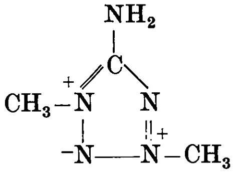
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Table 3. *Molecular dimensions and interatomic distances*

Dimensions of the molecule

N_1–N_2	1·35 Å	N_1–N_2–N_3	103°
N_2–N_3	1·30	N_2–N_3–N_4	117
N_3–N_4	1·31	N_3–N_4–C_1	104
N_4–C_1	1·36	N_4–C_1–N_1	106
C_1–N_1	1·38	C_1–N_1–N_2	110
C_1–N_5	1·29	C_1–N_1–C_2	131
N_1–C_2	1·45	N_2–N_1–C_2	119
N_3–C_3	1·47	N_2–N_3–C_3	120
		N_4–N_3–C_3	123
		N_1–C_1–N_5	126
		N_4–C_1–N_5	128

Hydrogen bonds

N_5–Cl	3·21 Å	C_1–N_5–Cl	125°
N_5–Cl′	3·17	C_1–N_5–Cl′	116
		Cl–N_5–Cl′	119

Non-bonded interatomic distances

C_2–N_5	3·08 Å	
C_2–C_3''	4·02	
C_2–Cl	3·61	
C_2–Cl′	3·47	(Cl′ in adjacent unit cell)
C_2–Cl‴	4·03	
C_3–Cl	3·55	(Cl in adjacent unit cell)
C_3–Cl″	3·67	
N_2–Cl‴	3·79	
C_1–C_1'	3·31	
N_5–N_3'	3·36	
N_5–N_4'	3·42	
N_4–C_1'	3·45	

From the short length of the C_1–N_5, N_2–N_3, and N_3–N_4 bonds it can be inferred that structures I and II make the larger contributions to the overall structure, while the others make smaller contributions. There is no truly single or double bond in the molecule with the exception of the nitrogen–carbon bonds to the methyl groups which show the normal single-bond distance.

The tetrazole ring appears as a slightly irregular planar pentagon. Whether this is typical of tetrazole compounds in general will only be determined from the crystal structures of compounds containing 'normal' tetrazole rings. However, there is some indication from the X-ray data obtained previously in this laboratory that the planar ring is the rule.

The molecule is ideally situated with respect to chloride ions in the same plane to form $N \cdots Cl^-$ hydrogen bonds with the imino nitrogen. The nitrogen–chloride ion distances are 3·17 and 3·21 Å, agreeing well with those found in crystals of other hydrochloride salts (Donohue, 1952). The hydrogen atoms of the $=NH_2^+$ group, therefore, also lie in the plane with the heavier atoms of the molecule.

There is evidence of steric repulsion between the imino nitrogen and the methyl group bonded to N_1 as a result of their close approach (3·08 Å). This is shown by the C_1–N_1–C_2 and N_2–N_1–C_2 bond angles of 131 and 119°, respectively; these angles have a greater divergence than the other ring-substituent bond angles (126 and 128° for the imino nitrogen and 120 and 123° for the other methyl group). The only apparent effect of this repulsion is to bend the N_1–C_2 bond slightly.

A number of the distances between methyl groups and chloride ions are appreciably shorter than the predicted value of 3·8 Å, based on a van der Waals radius of 2·0 Å for a methyl group and 1·81 Å for the ionic radius of a chloride ion (Pauling, 1940). These distances range from 3·47 Å to 3·67 Å with an average of 3·59 Å, 0·2 Å shorter than predicted. This suggests that the methyl groups cannot rotate freely, but are either entirely prevented from rotating or must rotate against a rather high potential barrier. On the other hand the one methyl–methyl contact that occurs is 4·02 Å, agreeing well with the predicted value.

The most important structural feature of the crystal is the columns of molecules along 2_1 axes with the chloride ions fitting into holes between the columns. The planes of the molecules in these columns are 3·29 Å apart. There are four interatomic distances which represent the closest approaches of adjacent molecules in the columns: 3·31 Å between ring carbon atoms; 3·36 and 3·42 Å between the imino nitrogen and two ring nitrogens, N_3 and N_4; and 3·45 Å between the ring carbon and ring nitrogen N_4. The extent of overlapping of the molecules is rather small so that the principal interactions between them probably occur through the imino nitrogen and ring nitrogens N_3 and N_4. This interaction is probably similar to the polarization bonding which has been suggested for aromatic nitro compounds in which there are a number of close approaches of nitro oxygens and carbon atoms in adjacent molecules (Abrahams & Robertson, 1948). The intermolecular forces along the columns are of primary importance in determining the structure of the crystal, for the feature of molecules lying in mirror planes has been found in crystals of two closely related substances which are not salts. These compounds are 2-methyl-5-aminotetrazole, crystallizing in the space group *Pbnm*, and 1,4-dimethyltetrazolone, crystallizing in the space group *Pbcm*.

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The Crystal Structures of P_4S_{10} and P_4S_7

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P_4S_{10} and P_4S_7 belong to the space groups $P\bar{1}$ and $P2_1/n$ with 2 and 4 molecules per unit cell respectively. Approximate coordinates were found from three-dimensional Patterson syntheses; the coordinates were refined by computing Fourier syntheses of projections. The structures consist of molecules of P_4S_{10} and P_4S_7. The intermolecular distances are approximately 3·4 Å. In both molecules two types of P–S bonds may be distinguished with bond lengths of 2·08 and 1·95 Å respectively. The e.s.d. is approximately 0·01 Å for the former and $0{\cdot}01_5$ Å for the latter. The symmetry of the P_4S_{10} molecule is $\bar{4}3m$; the S–P–S and P–S–P angles show no significant deviation from 109·5°. In P_4S_7 some S–P–S bond angles are significantly different from 109·5°; the molecule has the symmetry $mm2$ and contains a remarkably long P–P bond (2·37 Å with an e.s.d. of 0·04 Å).

Introduction

Phosphorus and sulfur form the compounds P_4S_3, P_4S_5, P_4S_7 and P_4S_{10} (Stock, 1910*a*, *b*, *c*; Treadwell & Beeli, 1935; Pernert & Brown, 1949). The only direct information available on the structures of these compounds was an electron-diffraction study of P_4S_3 (Hassel & Pettersen, 1941). For P_4S_{10} molecules in solution a structure was postulated (Pernert & Brown, 1949) analogous to that of P_4O_{10} molecules, as determined by Hampson & Stosick (1938) by electron diffraction. Though this structure for the molecule in solution is very probable, this does not imply that solid P_4S_{10} should also consist of these molecules. For P_4O_{10}, for example, three solid modifications were reported, only one form containing molecules of P_4O_{10} (de Decker & MacGillavry, 1941; de Decker, 1941; MacGillavry, de Decker & Nijland, 1949). The structures proposed for P_4S_7 and P_4S_5 (Pernert & Brown, 1949) are far less certain than that suggested for P_4S_{10} and did not find general acceptance.

Our X-ray examination of crystalline P_4S_{10} and P_4S_7 shows these compounds to consist of molecules of P_4S_{10} and P_4S_7. The structure reported for the P_4S_{10} molecule confirms that proposed by Pernert & Brown; that observed for P_4S_7 is different from all structures postulated previously for this compound.

The crystal structures of P_4S_5 and P_4S_3 are now being investigated in our laboratory.

Materials

P_4S_{10} and P_4S_7 were prepared by melting a mixture of phosphorus and sulfur (*Organic Synth.*, 1932). After solidification of the melt, crystals could be obtained by a slow continuous extraction with CS_2. As the crystals are not stable in moist air, they were transferred into a boron silicate glass capillary in which they could be kept for a long time. Perpendicular to the crystal axis, about which the X-ray photographs were made, their diameter was approximately 0·1 mm.

P_4S_{10}

Unit cell and space group

Optical goniometric measurements and a construction of the reciprocal lattice from oscillation, rotation and Weissenberg photographs about the *a* axis showed the crystals to be triclinic. With $\lambda(\text{Cu}\,K\alpha) = 1{\cdot}5418$ Å the following lattice constants were obtained:

$$a = 9{\cdot}07,\ b = 9{\cdot}18,\ c = 9{\cdot}19\ \text{Å};$$
$$\alpha = 92{\cdot}4,\ \beta = 101{\cdot}2,\ \gamma = 110{\cdot}5^\circ.$$

With a density of 2·09 g.cm.$^{-3}$ (Stock, 1910*c*) the number of molecules per cell was calculated to be 1·98. Wilson's statistical method (Wilson, 1949) and the absence of piezoelectricity indicated the space group $P\bar{1}$, which was confirmed during the structure analysis.