Table 10. *Packing distances shorter than 4 Å*

From atom x in molecule M	to atom y	in molecule	Distance
N_3	C_1	$M_{00\bar{1}}$	3·457 Å
C_1	C_9	$B_{\bar{1}00}$	3·686
C_1	C_8	$B_{\bar{1}00}$	3·466
C_2	C_{12}	B	3·774
C_2	C_{13}	$B_{0\bar{1}0}$	3·592
C_2	C_8	$B_{\bar{1}00}$	3·635
C_2	N_2	$B_{\bar{1}00}$	3·796
N_1	N_2	$B_{\bar{1}00}$	3·890
N_1	C_4	$B_{\bar{1}00}$	3·680
N_1	C_{13}	$B_{0\bar{1}0}$	3·716
C_3	C_4	$B_{\bar{1}00}$	3·559
O_3	C_6'	M_{010}	3·617
O_3	C_6''	M_{010}	3·282
O_3	C_6'	B	3·270
O_3	C_6''	B	3·711
O_3	C_7	B	3·658
C_{13}	C_3	B	3·901
O_5	C_9	M_{010}	3·449
O_5	C_{12}	M_{010}	3·660
O_5	C_{13}	M	3·588
O_5	C_{12}	$B_{00\bar{1}}$	3·930
C_{13}	C_{12}	$B_{00\bar{1}}$	3·816

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The Crystal Structure of the Hydrazine Salt of 5-Aminotetrazole

BY JOHN H. BRYDEN

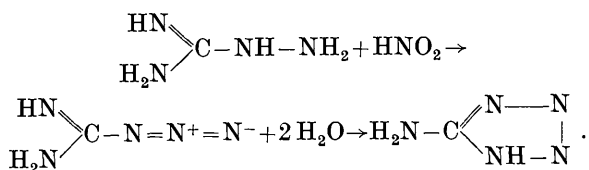*Chemistry Division, Research Department, U.S. Naval Ordnance Test Station, China Lake, California, U.S.A.*

Crystals of the hydrazine salt of 5-aminotetrazole are orthorhombic, crystallizing in the space group D_2^3–$P2_12_12$. The unit-cell dimensions are $a_0 = 13·54$, $b_0 = 9·67$, $c_0 = 3·86$ Å, and there are four molecules per unit cell. The structure was refined by Fourier methods, using the $hk0$ and $hk1$ data. The 5-aminotetrazole molecule is planar within the accuracy of the analysis. The hydrazine molecule exists as the NH_2–NH_3^+ ion, as shown by the hydrogen-bonding arrangement in the crystal.

Introduction

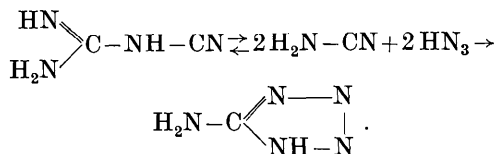5-Aminotetrazole is a valuable intermediate in the preparation of tetrazole compounds because of its varied reactions and its ease of preparation. It is obtained by the reaction of nitrous acid with aminoguanidine (Thiele, 1892; Hantzsch & Vagt, 1901) or by the reaction of hydrazoic acid with dicyandiamide (Stollé, 1929). The first reaction forms guanylazide, which rearranges to 5-aminotetrazole:

$$\begin{aligned}\text{HN} \!\!\searrow\!\!\\ \text{H}_2\text{N}\!\!\nearrow\end{aligned} \text{C}-\text{NH}-\text{NH}_2 + \text{HNO}_2 \rightarrow$$

$$\begin{aligned}\text{HN} \!\!\searrow\!\!\\ \text{H}_2\text{N}\!\!\nearrow\end{aligned} \text{C}-\text{N}=\text{N}^+=\text{N}^- + 2\,\text{H}_2\text{O} \rightarrow \text{H}_2\text{N}-\text{C} \begin{array}{c} \text{N}\!\!-\!\!\text{N} \\ | \\ \text{NH}-\text{N} \end{array} .$$

In the second reaction the dicyandiamide depolymerizes to cyanamide, which then reacts with hydrazoic acid to give 5-aminotetrazole:

$$\begin{aligned}\text{HN} \!\!\searrow\!\!\\ \text{H}_2\text{N}\!\!\nearrow\end{aligned} \text{C}-\text{NH}-\text{CN} \rightleftharpoons 2\,\text{H}_2\text{N}-\text{CN} + 2\,\text{HN}_3 \rightarrow$$

$$\text{H}_2\text{N}-\text{C} \begin{array}{c} \text{N}\!\!-\!\!\text{N} \\ | \\ \text{NH}-\text{N} \end{array} .$$

5-Aminotetrazole is a weak acid with a dissocation constant of $K_a = 10^{-6}$ (Lieber, Patinkin & Tao, 1951). As hydrazine is a weak base its salt with 5-aminotetrazole is somewhat unstable, losing hydrazine when exposed to the air. In spite of this, the hydrazine salt appeared to have the most satisfactory crystals for an analysis of the structure of 5-aminotetrazole of any derivatives that have been examined (Bryden, 1953).

Experimental

Crystals of the hydrazine salt of 5-aminotetrazole were prepared by Dr R. A. Henry (1952) by mixing equivalent quantities of anhydrous 5-aminotetrazole and anhydrous hydrazine in a minimum volume of hot absolute alcohol. Upon cooling, the salt was obtained as needles or prisms. Measurements on an optical goniometer showed that the crystals usually exhibit the forms {010}, {110}, and {032}.

X-ray photographs were taken about the c axis (the needle axis) and about the b axis, using Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). These photographs showed the crystals to be orthorhombic. The unit-cell dimensions, measured from the rotation and zero-layer Weissenberg photographs taken about the c axis, were found to be

$$a_0 = 13.54 \pm 0.03, \quad b_0 = 9.67 \pm 0.02,$$
$$c_0 = 3.86 \pm 0.01 \text{ Å}.$$

There are four molecules per unit cell (calculated density $= 1.539$ g.cm.$^{-3}$). Extinctions noted on the $hk0$ photograph were $h00$ present only with $h = 2n$ and $0k0$ present only with $k = 2n$. On the $h0l$ photograph the only extinctions found were $h00$ present only with $h = 2n$; all possible orders of $00l$ were present. The space group is therefore D_2^3–$P2_12_12$.

The intensity data for the structure determination were estimated visually from multiple-film equi-inclination Weissenberg photographs of the $hk0$ and $hk1$ reflections. In addition, very rough intensities of the $h0l$ reflections were estimated from the single photograph prepared to observe the space-group extinctions.

Determination of the structure

The x and y parameters

Because of the small size of the c axis, the molecule should project on (001) without any serious distortion. Using the $hk0$ data, a sharpened Patterson projection (Patterson, 1935) was calculated. By placing a model of the tetrazole molecule as found in earlier work (Bryden, 1955, 1956) on the peaks surrounding the origin it was possible to determine its orientation in the unit cell. The position of the amino substituent on the tetrazole ring could also be inferred with fair certainty. The tetrazole ring was oriented so that a twofold axis of the pentagon was nearly parallel to the a axis. Therefore, interatomic vectors between pentagons related by the screw axes parallel to the a axis should produce a large peak along the line $u = \frac{1}{2}$. Such a peak is found at $u = 0.500$, $v = 0.165$, placing the twofold axis of the pentagon along $y = 0.168$. The orientation of the pentagons with respect to the screw axes parallel to the b axis was found to be determined by hydrogen bonding from the amino groups between tetrazole molecules related by these screw axes. This arrangement left large holes between the chains of 5-aminotetrazole molecules where the hydrazine must be located. The hydrazine was found by calculating the contribution of the 5-aminotetrazole molecule to the $hk0$ reflections and preparing a Fourier projection with the 60 terms whose signs were fixed with reasonable certainty by this contribution. Two peaks of about half the height of the other nitrogen peaks appeared on this projection in the region where the hydrazine was expected. With these initial para-

Table 1. *Parameters*

Atom	$hk0$ parameters		$hk1$ parameters			Average parameters		
	x	y	x	y	z	x	y	z
N_1	0.4222	0.1611	0.4224	0.1620	0.445	0.4223	0.1616	0.445
N_2	0.3685	0.0554	0.3687	0.0553	0.576	0.3686	0.0554	0.576
N_3	0.2812	0.0984	0.2809	0.0990	0.657	0.2811	0.0987	0.657
N_4	0.2746	0.2350	0.2744	0.2339	0.583	0.2745	0.2344	0.583
N_5	0.3890	0.3997	0.3889	0.3995	0.349	0.3890	0.3996	0.349
C	0.3612	0.2682	0.3611	0.2667	0.462	0.3611	0.2674	0.462
N_6	0.1020	0.3259	0.1013	0.3252	0.963	0.1016	0.3256	0.963
N_7	0.0803	0.1850	0.0809	0.1858	0.057	0.0806	0.1854	0.057

meters the projected structure refined rapidly by Fourier methods. The final parameters obtained from the $hk0$ data and corrected for series-termination errors by the backshift method (Booth, 1946) are listed in Table 1. The final Fourier projection is shown in Fig. 1.
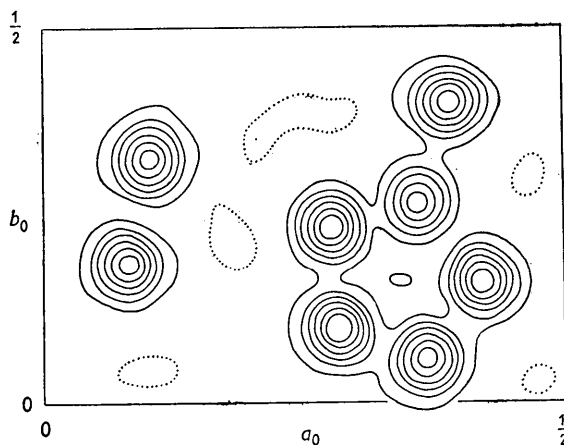

Fig. 1. Fourier projection of the hydrazine salt of 5-amino-tetrazole on (001). The zero contour is dotted.

The z parameters

A trial-and-error method was used to obtain rough values of the z parameters. The great intensity and the spacing of the (211) reflection $(d = 3\cdot17$ Å) suggested that the 5-aminotetrazole molecule might be nearly parallel to this plane. Using the x and y parameters already obtained, the molecule was moved along the c axis so as to always be parallel to the (211) plane. The hydrazine molecule was placed approximately $\frac{1}{2}c_0$ above the tetrazole molecule. Values of the structure amplitudes of the $h0l$ reflections were calculated at increments in z of $0\cdot05$ $(0\cdot193$ Å) and the results were compared with the observed values. The set of parameters which gave the best agreement was then improved by least-squares refinement. For this purpose very rough intensities of the $h0l$ reflections were estimated. The refinements were carried out on an IBM Type 701 computer, using a program which solves the complete normal equations to obtain the parameter corrections. After eight cycles of refinement the value of $\Sigma(F_o - F_c)^2$ had dropped from 5568 to 978. Considering the quality of the data, all possible information had probably been obtained from them.

From this point the refinements were continued by means of generalized projections, using the $hk1$ data. Cochran & Dyer (1952) have shown that a generalized Fourier projection is given by

$$\varrho_l(x, y) = C_l(x, y) + iS_l(x, y) , \quad (1)$$

where $C_l(x, y)$ and $S_l(x, y)$ are the component projections. Fridrichsons & Mathieson (1955) have used the component projections to obtain the z parameters of atoms from the equation

$$2\pi l z = \tan^{-1}\frac{S_l(x, y)}{C_l(x, y)} , \quad (2)$$

and the x and y parameters from the modulus projection,

$$|\varrho_l(x, y)| = [C_l^2(x, y) + S_l^2(x, y)]^{\frac{1}{2}} . \quad (3)$$

In the space group $P2_12_12$ and for the $hk1$ reflections, the component projections reduce to

$$C_1(x, y) = \frac{4}{A} \sum_h \sum_k \overset{h+k=2n}{[A(hk1)]} \cos 2\pi hx \cos 2\pi ky$$
$$\overset{h+k=2n+1}{- A(hk1) \sin 2\pi hx \sin 2\pi ky] ,} \quad (4)$$

$$S_1(x, y) = \frac{4}{A} \sum_h \sum_k \overset{h+k=2n+1}{[B(hk1)]} \cos 2\pi hx \cos 2\pi ky$$
$$\overset{h+k=2n}{- B(hk1) \sin 2\pi hx \sin 2\pi ky] .} \quad (5)$$

Two refinements of the z parameters were first calculated, using equations (4), (5), and (2). The heights and coordinates of the peaks were calculated by a nine-point, least-squares Gaussian method (Shoemaker, Donohue, Schomaker & Corey, 1950). At this stage no attempt was made to refine the x and y parameters; those obtained with the $hk0$ data were retained. Using these x and y parameters and the twice-refined z parameters, a least-squares plane was calculated for the 5-aminotetrazole molecule. It was found that the average deviation of the atoms from this plane was $0\cdot045$ Å. The z parameters for atoms in the least-squares plane were calculated and these were used for the next stages of refinement. These consisted of calculating both $|F_o|$ and $|F_c|$ component projections by equations (4) and (5), obtaining the z parameters with equation (2) and the x and y parameters with equation (3), and then making backshift corrections. This refinement process was carried out twice. The final parameters obtained from the $hk1$ data are listed in Table 1 along with the average of the x and y parameters obtained from both the $hk0$ and $hk1$ data. The final $|F_o|$ component projections $_5C_1$ and $_5S_1$, are shown in Figs. 2(a) and 2(b).

Accuracy

The final structure amplitudes were calculated with the scattering factors of Hoerni & Ibers (1954) from the average parameters listed in Table 1, and were multiplied by an isotropic temperature correction of the form $\exp[-B(\sin^2\theta/\lambda^2)]$. For the $hk0$ data $B = 1\cdot872$ Å² and for the $hk1$ data $B = 2\cdot055$ Å². The percentage discrepancy was $11\cdot2$ for the $hk0$ data and $10\cdot3$ for the $hk1$ data. The reflections (001) and (101), which could not be observed because of the experimental arrangement, and (011), (211), and (031) were used in the refinements at their calculated values and were omitted from the calculation of the percentage discrepancy. The final values of the observed and
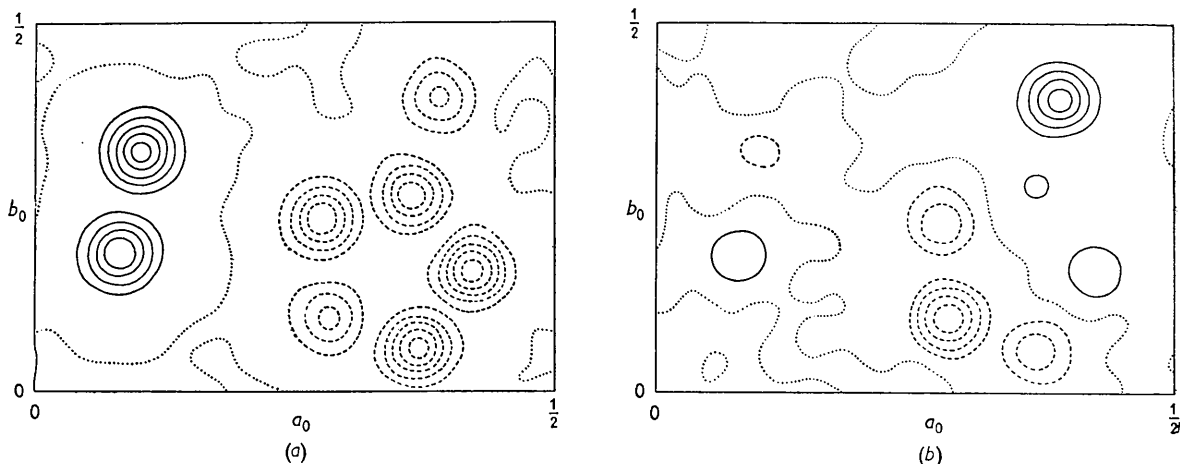
Fig. 2. Component projections of the hydrazine salt of 5-aminotetrazole: (a) the cosine function, $_5C_1$, and (b) the sine function, $_5S_1$. The zero contour is dotted, and the negative contours are broken.

calculated $hk0$ and $hk1$ structure amplitudes are listed in Tables 3 and 4, respectively.

The standard deviations of the x and y atomic coordinates were estimated by the method of Cruickshank (1949). Very little variation was found among the different atoms, the average values being $\sigma(x) = \sigma(y) = 0\cdot003$ Å for the $hk0$ data, and $\sigma(x) = \sigma(y) = 0\cdot004$ Å for the $hk1$ data. The standard deviations of the electron density are $\sigma(\varrho) = 0\cdot183$ e.Å^{-2} for the $hk0$ data and $\sigma(\varrho) = 0\cdot115$ e.Å^{-2} for the $hk1$ data. The difference in these values is undoubtedly due to the seven hydrogen atoms per molecule of salt which were not included in the calculation of the structure amplitudes. This omission would affect the $hk0$ reflections more seriously than the $hk1$ reflections.

The standard deviations of the z atomic coordinates were estimated from the standard deviation of the electron density, since these parameters are a function of peak heights on the component projections. This was done with the equation

$$\sigma(z) = \frac{c_0}{2\pi l}\left[\frac{\sigma(\varrho)}{\sqrt{(C_l^2+S_l^2)}}\right]. \quad (6)$$

Again, little variation was found from atom to atom. The average value is $\sigma(z) = 0\cdot008$ Å.

The standard deviation of the bond lengths were calculated using $\sigma(x) = \sigma(y) = 0\cdot004$ Å and $\sigma(z) = 0\cdot008$ Å for the standard deviations of all atomic coordinates. The results of these calculations are given in Table 2.

Discussion

The 5-aminotetrazole molecule

A least-squares plane was calculated for the atomic coordinates of the 5-aminotetrazole molecule. The equation of this plane in the normal form is

Table 2. *Interatomic distances and bond angles*

Bond lengths		σ	Bond angles	
N_1–N_2	1·356 Å	0·008 Å	C–N_1–N_2	103·4°
N_2–N_3	1·295	0·007	N_1–N_2–N_3	109·6
N_3–N_4	1·346	0·006	N_2–N_3–N_4	109·0
N_4–C	1·302	0·008	N_3–N_4–C	104·8
N_1–C	1·318	0·006	N_4–C–N_1	113·2
N_5–C	1·403	0·007	N_4–C–N_5	125·3
N_6–N_7	1·432	0·007	N_1–C–N_5	121·5

Hydrogen bonds		Hydrogen-bonding angles	
$N_5 \cdots N_3'$	3·002 Å	C–N_5'–N_3'	112·4°
$N_6 \cdots N_4$	2·900	C''–N_5'–N_7	98·0
$N_6 \cdots N_1''$	2·896	N_7–N_6–N_4	90·0
$N_6 \cdots N_2^{(')}$	2·875	N_7–N_6–N_1''	90·7
$N_5'' \cdots N_7$	3·140	N_7–N_6–$N_2^{(')}$	127·1
		N_4–N_6–N_1''	114·5
		N_4–N_6–$N_2^{(')}$	115·8
		N_1''–N_6–$N_2^{(')}$	114·9

Non-bonded distances	
$N_6 \cdots N_2'$	3·071 Å
$N_7 \cdots N_5''$	3·204
$N_7 \cdots N_3$	3·234
$N_7 \cdots N_4$	3·235
$N_7 \cdots N_1''$	3·246
$N_1' \cdots N_2''$	3·560

$$0\cdot3209X+0\cdot2154Y+0\cdot9223Z = 3\cdot764 \,.$$

The average deviation of the atoms from the plane is 0·005 Å and the largest deviation is 0·008 Å. Therefore, the 5-aminotetrazole molecule is planar within the limits of accuracy of the structure determination.

Table 2 lists the bond lengths found in the 5-aminotetrazole molecule. All are shorter than the usual values for carbon–nitrogen and nitrogen–nitrogen single bonds. The following resonance structures probably represent the most important forms contributing to the structure of the molecule:

Table 3. *Observed and calculated structure amplitudes for the hk0 reflections*

A negative structure amplitude in the 'observed' list indicates the minimum observable value for an unobservably weak reflection

h	k	l	Obs.	Calc.
0	0	0	---.--	220.0•
2	0	0	9.8	14.2-
4	0	0	51.6	58.2-
6	0	0	50.2	55.8-
8	0	0	19.8	18.9
10	0	0	10.4	13.0
12	0	0	4.3	4.2-
14	0	0	11.9	11.8
16	0	0	5.9	5.6-
1	1	0	15.1	16.3-
2	1	0	26.0	33.1
3	1	0	19.2	19.9
4	1	0	31.8	33.2-
5	1	0	7.9	8.4-
6	1	0	8.2	7.1
7	1	0	8.4	6.9
8	1	0	5.5	3.8-
9	1	0	9.0	7.1-
10	1	0	20.9	21.3
11	1	0	7.9	9.3
12	1	0	16.4	16.6-
13	1	0	4.7	5.1-
14	1	0	1.7-	1.6-
15	1	0	2.2	2.9-
16	1	0	2.2	1.7
17	1	0	1.6	1.8
0	2	0	35.6	50.4-
1	2	0	22.3	26.7-
2	2	0	2.6	0.4-
3	2	0	17.0	13.0
4	2	0	1.0-	1.0
5	2	0	27.6	26.6-
6	2	0	25.7	23.6
7	2	0	7.4	7.7-
8	2	0	4.9	5.9
9	2	0	7.8	7.7
10	2	0	1.7-	1.5-
11	2	0	11.2	12.4
12	2	0	7.9	9.0-
13	2	0	9.2	10.6
14	2	0	5.5	5.7-
15	2	0	14.0	12.7-
16	2	0	5.2	5.2
17	2	0	4.9	6.5-
1	3	0	5.4	4.1
2	3	0	30.2	31.3
3	3	0	3.5	3.7
4	3	0	14.8	12.7
5	3	0	2.6	1.7
6	3	0	10.9	11.9-
7	3	0	19.8	17.5-
8	3	0	12.5	12.7-
9	3	0	5.3	5.9
10	3	0	1.7	3.0
11	3	0	6.0	4.9
12	3	0	7.3	7.6
13	3	0	3.1	2.0
14	3	0	3.2	3.4-
15	3	0	6.6	5.9-
16	3	0	1.2-	1.2-
17	3	0	0.5-	0.2
0	4	0	17.0	13.0-
1	4	0	9.1	8.7-
2	4	0	18.0	13.9-
3	4	0	15.7	11.7
4	4	0	10.9	8.7
5	4	0	26.0	24.2
6	4	0	16.4	15.6
7	4	0	2.6	2.0
8	4	0	7.0	6.3
9	4	0	16.9	17.1-
10	4	0	13.3	13.3-
11	4	0	11.6	10.9-
12	4	0	2.5	2.6-
13	4	0	5.8	6.1
14	4	0	4.3	4.6
15	4	0	3.7	3.3
16	4	0	1.3	1.4
1	5	0	5.3	4.7-
2	5	0	30.8	27.4-
3	5	0	1.3-	0.9-
4	5	0	13.2	11.0-
5	5	0	15.1	14.6
6	5	0	13.8	12.8-
7	5	0	2.8	4.0-
8	5	0	1.7-	3.5-
9	5	0	6.4	6.8-
10	5	0	15.6	16.7
11	5	0	6.1	6.3-
12	5	0	4.9	4.7-
13	5	0	7.1	8.3
14	5	0	1.3-	0.6-
15	5	0	6.8	6.5
16	5	0	0.8	0.6-
0	6	0	9.4	9.1-
1	6	0	6.1	7.5-
2	6	0	27.8	28.2
3	6	0	10.3	9.3-
4	6	0	9.1	8.5-
5	6	0	1.6-	1.0
6	6	0	11.8	12.8-
7	6	0	6.2	7.0
8	6	0	15.8	17.1-
9	6	0	1.8-	0.9-
10	6	0	5.2	6.2
11	6	0	1.7-	1.3-
12	6	0	17.0	16.1
13	6	0	1.4-	0.1-
14	6	0	2.9	3.1-
15	6	0	1.9	1.9
1	7	0	8.0	7.5-
2	7	0	22.2	21.0-
3	7	0	4.8	3.7-
4	7	0	1.7-	1.1
5	7	0	11.6	12.1
6	7	0	1.8	0.5-
7	7	0	1.7-	0.6
8	7	0	16.6	17.8
9	7	0	6.0	5.5
10	7	0	10.0	9.1-
11	7	0	7.4	7.8-
12	7	0	1.4-	0.9-
13	7	0	1.4	0.8-
14	7	0	5.3	5.5-
0	8	0	7.9	7.9-
1	8	0	1.7-	1.0
2	8	0	11.2	11.6-
3	8	0	21.1	20.9-
4	8	0	12.2	12.5
5	8	0	8.8	9.1
6	8	0	5.2	6.7
7	8	0	2.5	2.0
8	8	0	2.0	2.5
9	8	0	1.7	1.5-
10	8	0	3.6	3.7-
11	8	0	4.0	3.4
12	8	0	4.0	4.6-
13	8	0	0.8-	0.1
1	9	0	14.2	14.5
2	9	0	6.2	6.7
3	9	0	5.9	6.8-
4	9	0	4.2	5.1
5	9	0	19.3	19.4-
6	9	0	1.7-	0.7-
7	9	0	10.6	10.8
8	9	0	2.2	2.2-
9	9	0	1.4-	1.0
10	9	0	3.0	3.7-
11	9	0	1.9	2.4
12	9	0	2.0	2.9-
0	10	0	1.7-	0.4-
1	10	0	1.7	1.0
2	10	0	1.7-	0.8-
3	10	0	7.9	8.0
4	10	0	2.3	2.9
5	10	0	3.5	2.7-
6	10	0	3.0	3.3-
7	10	0	2.4	2.0
8	10	0	1.3	1.7-
9	10	0	1.1-	0.2
10	10	0	5.8	5.8
1	11	0	1.7	2.1
2	11	0	3.8	3.2-
3	11	0	1.3-	0.5
4	11	0	1.8	1.9-
5	11	0	2.5	2.7-
6	11	0	1.2-	0.2-
7	11	0	1.3	1.5-
0	12	0	8.4	8.7
1	12	0	2.4	1.9
2	12	0	1.0-	0.5
3	12	0	3.4	2.3

NH₂ / C / N N⁻ / N═N **(A)**
NH₂ / C / ⁻N N / N═N **(B)**
NH₂ / C / N N / ⁻N—N **(C)**
NH₂ / C / N N / N—N⁻ **(D)**
⁺NH₂ / C / ⁻N N⁻ / N═N **(E)**

Forms (A), (B), (C), and (D) are of about equal importance since they represent essentially equivalent forms of the ionized acid. Form (E) is somewhat less important. By weighting the first four forms at 22%

each and the last form at 12% and applying Pauling's bond-character relation,

$$r = r_1 - (r_1 - r_2)(3x)/(2x+1) \qquad \text{(Pauling, 1940)},$$

the following bond lengths are calculated:

Bond	Double-bond character	Length Calc.	Length Obs.
C–N₁	0.44	1.327 Å	1.318 Å
C–N₄	0.44	1.327	1.302
C–N₅	0.12	1.413	1.402
N₁–N₂	0.22	1.365	1.356
N₂–N₃	0.56	1.288	1.295
N₃–N₄	0.22	1.365	1.346

For the carbon–nitrogen bonds, the bond-character curve suggested by Donohue, Lavine & Rollett (1956) was used. For the nitrogen–nitrogen bonds, values of 1·47 Å for the single-bond length and 1·24 Å for the double-bond length were used. The agreement between observed and calculated bond lengths is sufficiently

3*

Table 4. *Observed and calculated structure amplitudes for the hk1 reflections*

Phase angles are not given. A negative structure amplitude in the 'observed' list indicates the minimum observable value for an unobservably weak reflection

h	k	l	Obs	Calc
0	0	1	---.---	59.8
1	0	1	---.---	8.0
2	0	1	34.8	34.9
3	0	1	7.6	8.1
4	0	1	2.5	3.0
5	0	1	22.3	27.2
6	0	1	1.9	4.2
7	0	1	13.5	12.6
8	0	1	17.1	16.4
9	0	1	7.0	4.6
10	0	1	10.2	10.5
11	0	1	9.0	10.5
12	0	1	11.1	12.7
13	0	1	6.4	7.5
14	0	1	12.3	11.3
15	0	1	1.5-	1.0
16	0	1	2.4	2.2
17	0	1	0.7-	1.1
0	1	1	22.4	30.4
1	1	1	16.9	16.9
2	1	1	54.7	81.7
3	1	1	30.3	31.9
4	1	1	19.5	18.9
5	1	1	8.0	7.2
6	1	1	8.9	7.2
7	1	1	8.1	7.3
8	1	1	26.4	28.8
9	1	1	3.1	4.0
10	1	1	6.1	5.4
11	1	1	7.1	6.8
12	1	1	9.4	10.6
13	1	1	7.2	7.9
14	1	1	6.6	6.7
15	1	1	5.5	6.0
16	1	1	3.4	3.8
17	1	1	4.0	4.0
0	2	1	7.1	4.4
1	2	1	23.1	22.2
2	2	1	33.6	34.2
3	2	1	6.7	5.1
4	2	1	22.4	20.8
5	2	1	8.5	6.0
6	2	1	5.5	7.4
7	2	1	10.5	9.4
8	2	1	11.3	12.8
9	2	1	2.7	2.6
10	2	1	13.3	14.5
11	2	1	1.8	2.5
12	2	1	1.8-	1.1
13	2	1	2.6	2.5
14	2	1	6.2	5.2
15	2	1	4.7	4.2
16	2	1	1.9	2.6

h	k	l	Obs	Calc
0	3	1	18.4	7.0
1	3	1	6.5	6.5
2	3	1	16.1	12.1
3	3	1	16.0	15.6
4	3	1	12.5	9.3
5	3	1	4.6	4.1
6	3	1	9.9	9.3
7	3	1	22.9	24.5
8	3	1	3.8	3.6
9	3	1	8.5	9.0
10	3	1	2.3	2.8
11	3	1	3.9	4.8
12	3	1	7.0	6.9
13	3	1	11.9	12.9
14	3	1	4.9	5.0
15	3	1	4.4	5.0
16	3	1	1.7	1.7
0	4	1	9.7	7.0
1	4	1	10.3	9.0
2	4	1	12.5	13.8
3	4	1	5.9	3.4
4	4	1	6.7	3.8
5	4	1	14.9	14.2
6	4	1	7.1	6.1
7	4	1	6.2	5.7
8	4	1	8.8	8.4
9	4	1	9.4	9.0
10	4	1	8.0	8.0
11	4	1	2.7	4.0
12	4	1	3.2	2.9
13	4	1	8.2	8.5
14	4	1	3.2	3.2
15	4	1	3.1	3.2
16	4	1	0.7-	0.8
0	5	1	27.0	22.5
1	5	1	10.9	11.0
2	5	1	1.9	1.3
3	5	1	6.8	6.2
4	5	1	23.4	23.9
5	5	1	7.6	7.7
6	5	1	11.5	10.5
7	5	1	9.8	9.2
8	5	1	9.8	10.5
9	5	1	2.1	2.5
10	5	1	16.3	18.2
11	5	1	5.0	5.1
12	5	1	7.9	8.8
13	5	1	3.2	3.7
14	5	1	5.4	4.8
15	5	1	1.7	1.7

h	k	l	Obs	Calc
0	6	1	31.2	31.1
1	6	1	4.0	3.6
2	6	1	11.6	9.4
3	6	1	4.7	3.2
4	6	1	10.7	10.3
5	6	1	8.8	9.6
6	6	1	6.2	6.8
7	6	1	8.7	9.2
8	6	1	12.8	12.3
9	6	1	5.5	6.0
10	6	1	3.7	4.1
11	6	1	6.1	7.0
12	6	1	5.7	6.0
13	6	1	3.5	4.2
14	6	1	1.1	0.5
15	6	1	0.5-	-4.0
0	7	1	11.5	11.1
1	7	1	4.2	3.5
2	7	1	9.2	10.1
3	7	1	11.4	11.2
4	7	1	15.9	17.5
5	7	1	11.7	11.4
6	7	1	5.1	6.0
7	7	1	3.9	3.8
8	7	1	3.3	5.0
9	7	1	5.7	6.7
10	7	1	12.5	11.6
11	7	1	4.8	4.7
12	7	1	4.4	4.9
13	7	1	2.2	2.2
14	7	1	1.9	2.4
0	8	1	11.0	12.6
1	8	1	5.7	5.3
2	8	1	6.6	7.5
3	8	1	18.0	19.1
4	8	1	2.1	2.2
5	8	1	8.0	8.4
6	8	1	8.6	8.8
7	8	1	6.3	6.8
8	8	1	6.5	7.0
9	8	1	1.9	1.2
10	8	1	5.9	6.0
11	8	1	1.3-	0.4
12	8	1	3.9	3.3
13	8	1	0.5-	1.8

h	k	l	Obs	Calc
0	9	1	11.3	10.4
1	9	1	9.4	8.5
2	9	1	3.6	4.2
3	9	1	4.5	4.1
4	9	1	4.9	4.9
5	9	1	10.2	9.6
6	9	1	7.7	6.2
7	9	1	7.3	6.1
8	9	1	5.4	4.4
9	9	1	4.5	4.5
10	9	1	3.9	4.2
11	9	1	1.1	0.6
0	10	1	9.1	7.5
1	10	1	3.3	3.0
2	10	1	2.3	2.0
3	10	1	8.5	8.0
4	10	1	5.5	4.6
5	10	1	6.9	7.0
6	10	1	2.4	2.5
7	10	1	6.0	5.4
8	10	1	1.2-	0.2
9	10	1	1.9	2.3
0	11	1	1.6	0.8
1	11	1	1.9	0.8
2	11	1	5.8	5.4
3	11	1	3.0	2.5
4	11	1	2.4	2.2
5	11	1	3.4	2.1
6	11	1	1.0	1.7
7	11	1	1.9	2.3
0	12	1	2.1	1.2
1	12	1	2.8	3.0
2	12	1	2.2	2.5
3	12	1	1.9	2.7

good to show that the above resonance forms are a simple representation of the structure of ionized 5-aminotetrazole.

The hydrazine molecule

The nitrogen–nitrogen distance in the hydrazine molecule is 1·432 Å, intermediate in length between 1·42 Å found in $N_2H_6Cl_2$ (Donohue & Lipscomb, 1947) and 1·46 Å found in crystalline hydrazine (Collin & Lipscomb, 1951). Sakurai & Tomiie (1952) also found an intermediate value of 1·45 Å in N_2H_5Cl. From the hydrogen-bonding arrangement in the crystal, the hydrazine molecule appears to exist largely as the NH_2–NH_3^+ ion. The decrease in the nitrogen–nitrogen interatomic distance is presumably due to the effect of the positive charge on the covalent radius of nitrogen (Pauling, 1940).

Hydrogen bonding

There appear to be five well defined hydrogen bonds per molecule of salt in the crystal. These are shown schematically in Fig. 3. The 5-aminotetrazole molecules related by the screw axes parallel to the b axis are formed into chains by hydrogen bonding from the amino groups. The hydrazine molecules are in holes between these chains, holding the chains together through hydrogen bonding to three surrounding 5-aminotetrazole molecules. Only atom N_6 of the hydrazine appears to be involved, forming three hydrogen bonds to N_4, N_1'', and $N_2^{()'}$. The hydrazine molecule is tipped so that the bond angles are 90·0°, 90·7°, and 127·1°; however, when viewed along the N_6–N_7 bond, the atoms N_4, N_1'', and $N_2^{()'}$ are equally spaced around N_6. The distances of these atoms from N_6 and their configuration strongly indicate that the hydrazine
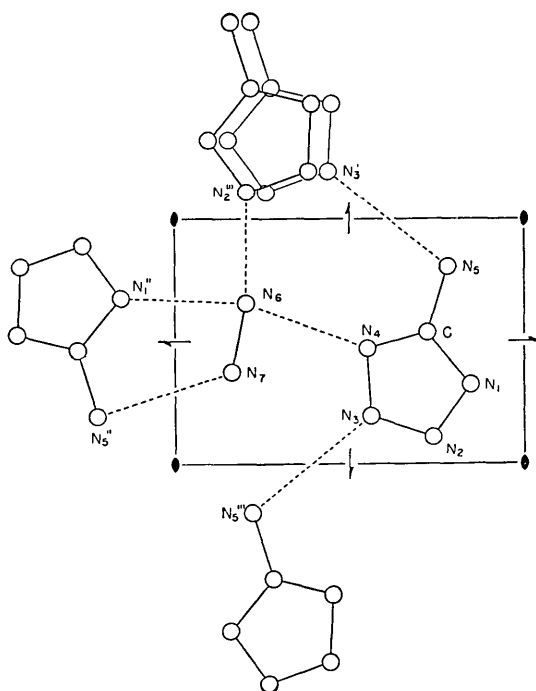
Fig. 3. Schematic drawing of the hydrogen bonding system in the crystal of the hydrazine salt of 5-aminotetrazole. At the top of the drawing two 5-aminotetrazole molecules separated by a unit translation along the c axis are offset for clearness.

molecule exists as the NH_2–NH_3^+ ion. These hydrogen bonds of length 2·900, 2·896, and 2·875 Å are somewhat shorter than the $NH \cdots N$ bond usually found (Donohue, 1952). A weaker hydrogen bond of length 3·140 Å is formed from the amino group, N_5'', to N_7. The two hydrogen atoms on N_7 are not involved in hydrogen bonding as all interatomic distances from N_7 are greater than 3·20 Å, with the exception of that to N_5''. An identical situation is to be found in N_2H_5Cl (Sakurai & Tomiie, 1952), where the positively charged hydrazine nitrogen is hydrogen-bonded to two chloride ions and to the uncharged nitrogen of a surrounding NH_2–NH_3^+ ion.

The interatomic distance of 3·071 Å between N_6 and N_2' represents a particularily short non-bonded approach of two atoms. The line through N_6 and N_2' makes an angle of 28° with the line through N_6 and N_7 and lies between the two hydrogen atoms forming bonds to N_4 and N_1''. A similar close approach of 3·11 Å has been found between a nitrogen atom and a methyl group in 2-methyl-5-aminotetrazole (Bryden, 1956).

The use of generalized projections

Fridrichsons & Mathieson (1955) have discussed some of the advantages of using generalized projections, particularily in connection with structures containing heavy atoms. The component projections have also been used to obtain atomic coordinates perpendicular to the plane of projection by White & Clews (1956) in 4,5-diamino-2-chloropyrimidine, by Phillips (1956) in refining the structure of acridine, and by Dyer (Cochran & Dyer, 1952; Lipson & Cochran, 1953) for diglycylglycine ethyl ester hydrobromide. Dyer (1951) has also used upper-layer-line Patterson projections to obtain atomic coordinates in a structure containing heavy atoms. Clews & Cochran (1949) have used the modulus projection to refine parameters in the projection plane. As another possible advantage, Phillips (1954, 1956) has found increased atomic resolution on modulus projections. All the examples cited above, with the exception of the Patterson application, have been centrosymmetric structures; however, the present work shows that the method may be applied to non-centrosymmetric structures with equally satisfactory results. It appears to be particularly advantageous when used with structures having only one well-resolved projection, and for which the accuracy desired is no greater than ordinarily obtained by two-dimensional methods.

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