Acta Cryst. (1956). 9, 874

The Crystal Structure of 2-Methyl-5-Aminotetrazole

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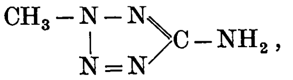
(*Received* 19 *March* 1956)

2-Methyl-5-aminotetrazole crystallizes in the orthorhombic space group *Pbnm* with four molecules per unit cell. The unit cell dimensions are $a_0 = 9{\cdot}22$, $b_0 = 8{\cdot}04$, and $c_0 = 6{\cdot}62$ Å. The crystal structure was derived from a sharpened Patterson projection and from possibilities of hydrogen bonding, and was refined by least-squares and Fourier methods. The dimensions of the molecule indicate that ionic resonance forms make major contributions to the structure of the molecule.

Introduction

The X-ray structure analysis of the halide salts of 1,3-dimethyl-5-iminotetrazole (Bryden, 1955) showed that this substance is an example of a group of compounds that has been called 'meso-ionic' (Baker, Ollis & Poole, 1949). Subsequently the examination of crystals of 2-methyl-5-aminotetrazole showed that this compound probably had a similar structure, although a conventional covalent structure,



$$\begin{array}{l} CH_3-N-N\diagdown \\ \qquad\;\; | \qquad\;\; \rangle C-NH_2\,, \\ \qquad\; N=N\diagup \end{array}$$

can be written, and it is therefore not a meso-ionic compound in the strict sense of the definition*. An investigation of the crystal structure has been undertaken to determine its relation to the 1,3-dimethyl-5-iminotetrazole salts.

Experimental measurements

The material used in this investigation was prepared by Drs R. A. Henry and W. G. Finnegan (1954). The crystals were grown by slow evaporation of a chloroform solution. They were obtained as clear, colorless orthorhombic prisms showing the forms {110} and {101}, and usually elongated in the direction of [001]. They cleaved with such ease along (001) that great care had to be exercised in their handling.

Crystals of 2-methyl-5-aminotetrazole have an appreciable vapor pressure near room temperature so that satisfactory crystals can also be grown by sublimation. In order to retain the crystals unchanged during the required exposure times on the Weissenberg camera it was necessary to enclose them in thin-walled glass capillaries. Dr H. W. Pitman (private communication) has measured the vapor pressure in the range 10–45° C. with a piston manometer (Ernsberger & Pitman, 1955), and has obtained the equation

$$\log_{10} P_\mu = 15{,}685-(4{,}611/T)\,,$$

where P_μ is the vapor pressure in microns and T is the absolute temperature.

The unit-cell dimensions were obtained from the rotation and zero layer Weissenberg photographs about [001], and are

$$a_0 = 9{\cdot}22,\; b_0 = 8{\cdot}04, \text{ and } c_0 = 6{\cdot}62 \text{ Å, all } \pm 0{\cdot}03 \text{ Å}\,.$$

The density, calculated for four molecules per unit cell, is 1·342 g.cm.$^{-3}$. The following extinctions were noted on the zero, first and second layers: (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 rotation photograph about [001] showed that the even layer lines have the same sequence of intensities and similarly for the odd layer lines. This will occur only if all the atoms are in planes $\frac{1}{2}c_0$ apart along [001], and therefore the molecules are in the mirror planes at $z = \frac{1}{4}$ and $\frac{3}{4}$ of the space group *Pbnm*.

Determination of the structure

The intensity data required for the structure determination were estimated visually from equi-inclination Weissenberg photographs of the ($hk0$) and ($hk1$) reflections. After correction of the intensities for the Lorentz and polarization factors, the ($hk0$) data were used to calculate a sharpened Patterson projection (Patterson, 1935). The Fourier coefficients for this

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* Baker *et al.* (1949) defined meso-ionic compounds as '... compounds exhibiting aromatic characteristics, which can be represented only as resonance hybrids of a large number of contributing ionic forms. It is impossible to represent them, even approximately, by any one covalent formula, or as a hybrid of a number of covalent formulae, and their case is therefore fundamentally different from that of most organic compounds which can be satisfactorily represented either by a single covalent form, or as a hybrid of a few covalent forms, ..., or as a hybrid of covalent and ionic forms, ...'. 1,3-Dimethyl-5-iminotetrazole fits this definition exactly. Though 2-methyl-5-aminotetrazole does not formally fit this definition the resonance forms making the major contribution to the structure of the molecule have charge separations, and it is therefore quite analogous to the true meso-ionic compounds. Also, the ultraviolet absorption spectrum of 2-methyl-5-aminotetrazole shows similarities to that of the 1,3-dimethyl compound (Henry, Finnegan & Lieber, 1954), indicating a close relationship between the two compounds.

projection were obtained by dividing the relative values of $|F(hk0)|^2$ by f_N^2, where f_N is the scattering factor of nitrogen for the reflection $(hk0)$. The peak at the origin was not removed. A model of the molecule on the same scale as the vector map was then prepared. This model was a regular pentagon, 1·30 Å on a side, with the amino group 1·35 Å and the methyl group 1·45 Å from the ring atoms to which they are bonded. The orientation of the molecule in the unit cell was found by placing this model on the peaks about the origin. It was immediately apparent that the bond to one of the substituents on the ring was orientated parallel to the *a* axis. It seemed probable that this would be the amino group, as such an arrangement would allow intermolecular hydrogen bonding along the *b* axis. Ignoring the methyl group, the molecule in this position will have a twofold axis parallel to the *a* axis. Two such molecules related by the *n* glide should produce a large vector peak on the line $u = \frac{1}{2}$ of the Patterson projection. Such a peak is indeed found at $u = 0{\cdot}500$, $v = 0{\cdot}418$. This interpretation of the peak placed the twofold axis of the molecule along the line $y = 0{\cdot}041$. Models of the molecule were then adjusted so that molecules a unit translation apart along the *b* axis were connected through hydrogen bonds to molecules related to the others by the *b* glide. This placed the center of the pentagon at $x = 0{\cdot}050$. With the center located the initial parameters of the atoms were quickly obtained. These are listed in Table 1.

Table 1

	Initial parameters		Final parameters		
	x	*y*	*x*	*y*	*z*
N_1	0·084	0·172	0·0846	0·1827	0·2500
N_2	−0·047	0·122	−0·0490	0·1166	0·2500
N_3	−0·047	−0·041	−0·0506	−0·0441	0·2500
N_4	0·088	−0·088	0·0856	−0·0933	0·2500
N_5*	0·312	0·042	0·3128	0·0469	0·2500
C_1	0·172	0·042	0·1655	0·0476	0·2500
C_2†	−0·178	0·227	−0·1806	0·2215	0·2500

* Amino. † Methyl.

The trial structure was first refined by means of Fourier projections. All but two of the atoms (N_2 and N_4) were well resolved on these projections. The final Fourier projection is shown in Fig. 1(*a*). In order to improve the parameters of the overlapping atoms a series of least-squares refinements of the $(hk0)$ data were made, using the complete normal equations. These calculations were made automatically on the IBM 701 calculator in the Mathematics Division. A series of five or six refinements could be made in about 15 min. with this machine. The final refinements were made by the procedure of calculating Fourier sections at $z = \frac{1}{4}$, using the $(hk0)$ and (hkl) data, and making back-shift corrections as was done earlier with 1,3-dimethyl-5-iminotetrazole hydrochloride (Bryden, 1955). The final parameters are also listed in Table 1. The final Fourier section is shown in Fig. 1(*b*).

Accuracy

The observed and calculated structure amplitudes are compared in Table 5. Isotropic temperature corrections of the form $\exp[-B(\sin\theta/\lambda)^2$ were used in these calculations, even though anisotropic corrections would be more accurate. This is indicated by the fact that $B = 2{\cdot}81$ Å^2 for the $(hk0)$ reflections while $B = 4{\cdot}33$ Å^2 for the (hkl) reflections. The value of $R = [\Sigma||F_o|-|F_c||\div\Sigma|F_o|]$ is 0·143 for the $(hk0)$ reflections and 0·139 for the (hkl) reflections. The non-observed reflections and the low-order reflections (110), (020), (200) and (101) were not included in the calculation of R.

The standard deviations in the atomic positions were calculated by Cruickshank's equations (Cruickshank, 1949; Ahmed & Cruickshank, 1953). The data were treated as though two-dimensional methods were used to obtain the structure. The average values of

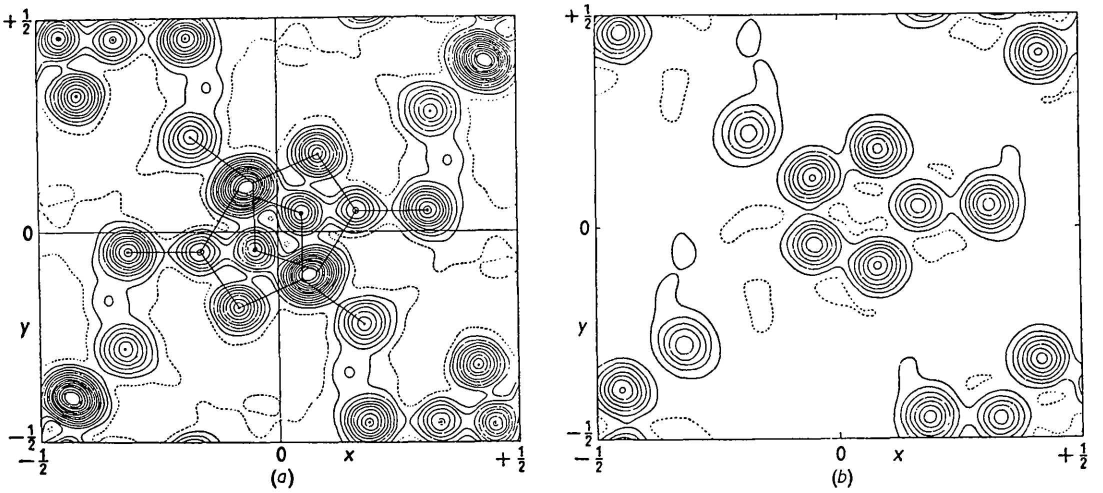


Fig. 1. (*a*) Fourier projection of 2-methyl-5-aminotetrazole on (001). (*b*) Fourier section at $z = \frac{1}{4}$ through the crystal of 2-methyl-5-aminotetrazole. Negative regions are enclosed with broken lines.

Table 2

Atom	$\varrho_{\max.}$ (e.Å^{-2})	$\lvert\partial^2\varrho/\partial x^2\rvert$ (e.Å^{-4})	$\lvert\partial^2\varrho/\partial y^2\rvert$ (e.Å^{-4})	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\bar{\sigma}(x)$ (Å)	$\bar{\sigma}(y)$ (Å)
N_1	9·2	34·9	38·1	0·0132	0·0120	0·0122	0·0119
N_3	10·5	42·8	37·6	0·0108	0·0122		
N_5	8·8	36·9	39·9	0·0125	0·0115		
C_1	7·7	28·2	32·4	0·0163	0·0141	0·0178	0·0168
C_2	6·6	23·8	23·3	0·0194	0·0196		

$\sigma(\partial\varrho/\partial x)$ and of $\sigma(\partial\varrho/\partial y)$ for the ($hk0$) and (hkl) reflections were used in the calculation. The curvatures were obtained from the unobscured atomic peaks on the final Fourier projection (Fig. 1(*a*)). This procedure probably leads to slightly larger standard deviations than would otherwise be expected. The average values were $\sigma(x) = \sigma(y) = 0{\cdot}012$ Å for the nitrogen atoms, and $\sigma(x) = 0{\cdot}018$ Å and $\sigma(y) = 0{\cdot}017$ Å for the carbon atoms. These values give standard deviations of 0·017 Å for nitrogen–nitrogen bonds and 0·020 Å for carbon–nitrogen bonds. The calculations are summarized in Table 2.

Discussion

Table 3 lists the interatomic distances and angles, and Fig. 2 gives the numbering of the atoms in the molecule. The bond lengths indicate that considerable resonance is occurring in the ring. The N_2–C_2 distance, however, is the expected single-bond carbon–nitrogen distance. The per cent double-bond character was estimated using the expression given by Pauling (1940) relating bond length and double-bond character. Using 1·47 Å for the single bond N–N and C–N distances, 1·23 Å for the N–N double-bond distance, and 1·25 Å for the C–N double-bond distance, the following results were obtained:

Table 3. *Interatomic distances and angles*

Bond lengths and bond angles

N_1–N_2	1·34 Å	N_1–N_2–N_3	114°
N_2–N_3	1·29	N_2–N_3–N_4	107
N_3–N_4	1·32	N_3–N_4–C_1	106
N_4–C_1	1·35	N_4–C_1–N_1	112
C_1–N_1	1·32	C_1–N_1–N_2	101
C_1–N_5	1·36	N_1–N_2–C_2	122
N_2–C_2	1·48	N_3–N_2–C_2	124
		N_1–C_1–N_5	125
		N_4–C_1–N_5	123

Hydrogen bonds

N_5–N_1'	3·08 Å	C_1–N_5–N_1'	108°
N_5–N_4''	3·04	C_1–N_5–N_4''	108
		N_1–N_5–N_4''	144

Methyl group–ring nitrogen van der Waals contact

C_2–N_3'''	3·11 Å	N_2–C_2–N_3'''	178°

Interatomic distances between molecules in adjacent mirror planes

N_2–N_4'	3·33 Å	N_3–N_4'	3·50 Å
N_3–C_1'	3·48	N_3–N_1'	3·51
N_3–N_2'	3·48	N_3–N_3'	3·51

Table 4. *Comparison of bond lengths in 2-methyl-5-aminotetrazole and 1,3-dimethyl-5-iminotetrazole hydrochloride*

Bond	2-Methyl	1,3-Dimethyl
N_1–N_2	1·34 Å	1·35 Å
N_2–N_3	1·29	1·30
N_3–N_4	1·32	1·31
N_4–C_1	1·35	1·36
C_1–N_1	1·32	1·38
C_1–N_5	1·36	1·29
N_2–C_2	1·48	—
N_1–C_2	—	1·45
N_3–C_3	—	1·47

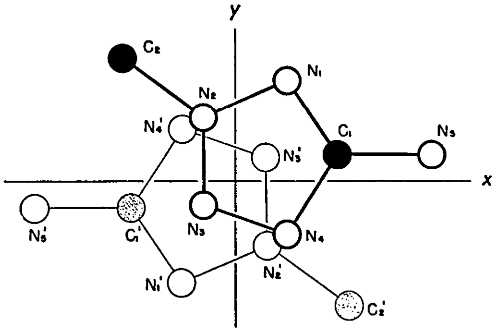
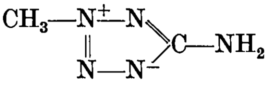
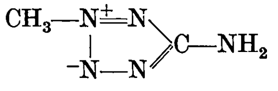


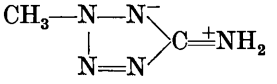
Fig. 2. Arrangement of the molecules of 2-methyl-5-aminotetrazole along the twofold screw axes. Filled circles are carbon atoms, and the open circles are nitrogen atoms. The heavy lines indicate molecules at $z = +\frac{1}{4}$ and light lines molecules at $z = -\frac{1}{4}$.

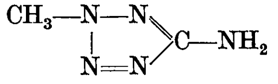
Bond	Double-bond character	Calculated bond length	Observed bond length
N_1–N_2	0·25	1·35 Å	1·34 Å
N_2–N_3	0·50	1·29	1·29
N_3–N_4	0·35	1·32	1·32
N_4–C_1	0·25	1·36	1·35
C_1–N_1	0·40	1·32	1·32
C_1–N_5	0·25	1·36	1·36

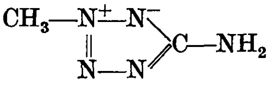
The total corresponds to two double bonds resonating among the six positions. The following resonance structures are probably the most important ones contributing to the overall structure of the molecule:

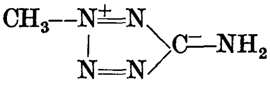

(*A*)


(*B*)


(*C*)


(*D*)


(*E*)


(*F*)

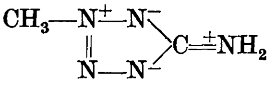

(*G*)

Table 5. *Observed and calculated structure amplitudes*

The structure amplitudes have been multiplied by ten. The left column is the *h* index, the middle column is the observed structure amplitude, and the right column is the calculated structure amplitude.

	*h*00	
0	—	1880
2	117	217
4	152	−131
6	36	−36
8	171	−232
10	20	−9
	*h*10	
1	312	668
2	143	103
3	178	169
4	130	−99
5	166	−160
6	73	77
7	75	−77
8	29	31
9	68	−79
10	<11	−15
11	18	−18
	*h*20	
0	181	292
1	81	−79
2	48	33
3	84	97
4	25	25
5	110	89
6	40	42
7	23	−20
8	47	−48
9	<12	10
10	26	−36
11	< 9	4
	*h*30	
1	152	−162
2	91	101
3	51	66
4	156	144
5	22	23
6	29	13
7	77	74
8	74	−82
9	<12	−6
10	<10	−2
11	32	−41
	*h*40	
0	37	−19
1	145	−138
2	158	−167
3	179	150
4	<11	0
5	82	95
6	102	115
7	132	−165
8	12	−18
9	13	−19
10	<10	8
11	< 3	3
	*h*50	
1	55	−44
2	<11	13
3	69	−68
4	89	−102
5	30	31
6	16	−20
7	<13	18
8	62	−68
9	12	0
10	18	−22
	*h*60	
0	72	−84
1	139	−130
2	<12	6
3	122	−132
4	<13	7
5	73	−74
6	15	−19
7	66	−62
8	17	28
9	16	12
	*h*70	
1	49	−48
2	131	−136
3	31	37
4	132	−127
5	17	7
6	23	−35
7	<10	6
8	10	−7
	*h*80	
0	90	−72
1	113	−111
2	25	18
3	67	−57
4	24	30
5	15	−10
6	<10	−4
7	47	−52
	*h*90	
1	<11	11
2	12	−8
3	11	−20
4	<10	−10
5	19	28
6	< 3	2
	h,10,0	
0	19	−17
1	10	19
2	33	27
3	16	12
	*h*01	
1	180	−294
3	66	−33
5	145	153
7	85	95
9	71	75
11	6	8
	*h*11	
1	195	−212
2	20	10
3	66	59
4	7	8
5	19	−13
6	147	159
7	15	16
8	47	51
9	29	28
10	16	16
11	6	−10
	*h*21	
0	226	−279
1	222	−261
2	83	69
3	181	192
4	24	−2
5	163	182
6	56	−68
7	62	−66
8	44	44
9	26	32
10	8	7
11	< 6	1
	*h*31	
1	169	173
2	98	99
3	84	−87
4	101	97
5	17	−12
6	14	13
7	68	−68
8	50	−47
9	< 9	—
10	12	−7
11	29	28
	*h*41	
0	128	128
1	13	17
2	183	182
3	43	30
4	28	−26
5	12	−5
6	123	−121
7	31	−28
8	12	−13
9	20	−22
10	< 6	5
	*h*51	
1	136	127
2	8	14
3	85	69
4	58	−60
5	12	−22
6	11	−8
7	51	−59
8	14	−8
9	< 7	−5
10	9	−10
	*h*61	
0	70	−76
1	10	−3
2	163	124
3	18	−7
4	61	61
5	13	−11
6	44	−49
7	10	−10
8	23	17
9	7	−1
	*h*71	
1	−9	9
2	15	2
3	39	24
4	49	42
5	58	52
6	16	−15
7	< 7	−7
8	7	−6
	*h*81	
0	37	−11
1	58	47
2	23	14
3	31	20
4	25	22
5	< 7	−3
6	< 7	7
7	18	12
	*h*91	
1	< 7	3
2	19	15
3	< 7	2
4	< 6	−9
5	< 5	4
	h,10,1	
0	17	−15
1	21	13
2	< 4	7
3	< 2	−21

If we weight (*A*) at 30%, (*B*) and (*C*) at 15% each, and the other four at 10% each the resulting double-bond character of each bond will be as given in the above table. The tautomeric structure having an imino group at the 5-position and a hydrogen at the 4-position was not considered since the Fourier projection (Fig. 1(*a*)) suggests that there are two hydrogen atoms bonded to N_5, and also because this structure seems unlikely chemically.

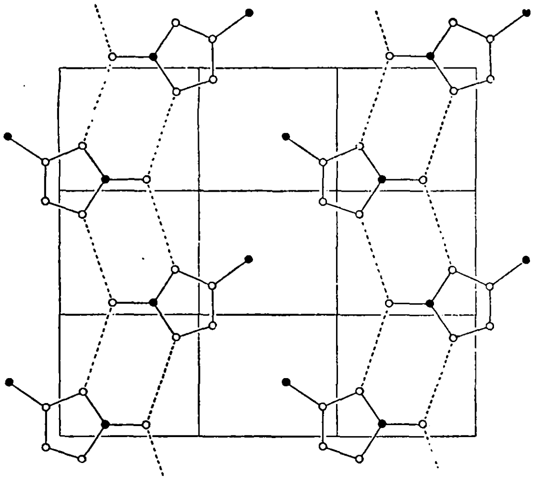


Fig. 3. Arrangement of molecules of 2-methyl-5-aminotetrazole in the mirror planes. Broken lines indicate hydrogen bonds.

Table 4 compares the bond lengths found in 2-methyl-5-aminotetrazole with those found in 1,3-dimethyl-5-iminotetrazole hydrochloride. It is seen that within the experimental error the bond lengths are the same, with the exception of the C_1–N_1 and C_1–N_5 bonds. The 1,3-dimethyl compound shows greater double-bond character in the C_1–N_5 bond than does the 2-methyl compound, as would be expected from the imino character of the first substance. The total double-bond character in the C_1–N_1 and C_1–N_5 bonds is about the same in the two compounds, however.

The molecule of 2-methyl-5-aminotetrazole is ideally suited by size and shape to form a compact hydrogen bonding system along the *b* axis. The nitrogen–nitrogen hydrogen bond lengths of 3·04 and 3·08 Å agree in general with those found in other compounds (Donohue, 1952) and in particular with those found in melamine (Hughes, 1941). The hydrogen bonding arrangement is shown in Fig. 3. The ribbons of molecules have only one important van der Waals contact with the adjacent ribbons in the same mirror plane. This is between the methyl groups of one ribbon and the nitrogen, N_3, of adjacent ribbons. The three atoms N_2, C_2 and N_3''' are nearly linear, forming an angle of 178° at C_2. This short contact of 3·11 Å apparently occurs because the nitrogen atom fits into the 'crown' of hydrogen atoms of the methyl group.

Table 3 also lists the shorter interatomic distances between molecules related by the 2_1-axis. The two atoms which overlap on the Fourier projection, N_2 and N_4', are closest at 3·33 Å. This is about the same as the closest distances found in 1,3-dimethyl-5-iminotetrazole hydrochloride. Atom N_3 is nearly equidistant from all atoms in the rings of the molecules above and below, with distances ranging from 3·48 to 3·51 Å.

I wish to express my appreciation to Drs R. A. Henry and W. G. Finnegan for supplying the material used in this investigation, for many helpful discussions, and for reviewing the manuscript.

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