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The Crystal and Molecular Structure of 5-Aminotetrazole Monohydrate

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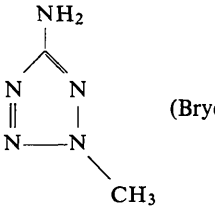
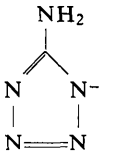
The crystal structure of 5-aminotetrazole monohydrate has been determined by obtaining the phases directly from the structure factor magnitudes by the use of the symbolic addition procedure. The space group is $P2_1/c$ and the cell parameters are: $a=6{\cdot}41$, $b=7{\cdot}29$, $c=9{\cdot}85$ Å, $\beta=90°15'$ and $Z=4$. The 5-aminotetrazole molecule is planar and exhibits a large degree of conjugation. Every atom except the carbon is involved in hydrogen bonding.

Introduction

Some years ago Bryden (1955) determined the crystal structure of 1,3-dimethyl-5-iminotetrazole hydrochloride. Since no conventional covalent formula can be written for this compound it was classified as a mesoionic compound. The bond distances indicated considerable conjugation in the ring. Subsequently the structures of several other tetrazole derivatives were determined:

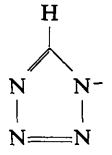


(Bryden, 1956),



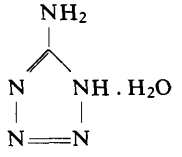
$NH_2NH_3^+$ (Bryden, 1958),

and



$Na^+ . H_2O$ (Palenik, 1963).

Even though conventional covalent structures can be written for all of these compounds, they exhibit the same sort of conjugation as was found in the imino compound. The present investigation of



shows similar effects.

Experimental

Crystals of 5-aminotetrazole monohydrate are colorless rectangular prisms elongated along the *b* axis. The material was obtained from the Aldrich Chemical Company and recrystallized from water. A set of data collected with the first crystal used indicated that all angles were 90°, that the only systematic absences occurred for the $0k0$ reflections with k odd and the $h0l$ reflections with l odd, and that $|F(hkl)|=|F(\bar{h}kl)|$. The space group $P2_1/c$ was assigned and the approximate structure was determined, in which it appeared that some disorder existed. Prof. J. Bryden* of the California State College at Fullerton, on the basis of photographs of aminotetrazole which he had taken earlier, pointed out that the crystal we had used was twinned. Subsequently, a new set of data was collected on another crystal in which $\beta>90°$ and $|F(hkl)|\neq|F(\bar{h}kl)|$, although the intensities for hkl and $\bar{h}kl$ reflections were quite similar.

Weissenberg equi-inclination, multiple-film photographs using Cu $K\alpha$ radiation were taken with the crystal mounted parallel to the *b* axis from the zero through the fifth layer. The intensities were estimated by comparison with a calibrated film strip. Unit-cell dimensions were determined from precession photographs. They are:

$$a=6{\cdot}41\pm0{\cdot}02,\ b=7{\cdot}29\pm0{\cdot}02,\ c=9{\cdot}85\pm0{\cdot}02\ \text{Å}$$
$$\beta=90°15'\pm10'\ \text{and}\ Z=4.$$

The measured density was 1·499 g.cm^{-3} while the calculated density is 1·486 g.cm^{-3}. These parameters are in reasonable agreement with those determined earlier by Bryden (1953).

The visually estimated intensities were processed on the IBM 7030 (STRETCH) computer using a program prepared by H. Norment and revised by S. Brenner of this Laboratory. Corrections were made for spot size, Lorentz and polarization factors. The data were placed on an absolute scale and corrected for thermal motion by means of a K curve (Karle & Hauptman, 1953). The output of the program consists of structure factor magnitudes, $|F|$, normalized structure factor magnitudes, $|E|$, and various statistical averages. The statistical averages, $\langle|E|\rangle=0{\cdot}79$ and $\langle|E^2-1|\rangle=1{\cdot}07$, and the distribution of the $|E|$ values

* Private communication.

where 0·4% are greater than 3·0, 5·7% are greater than 2·0, and 24·2% are greater than 1·0 are consistent with a centrosymmetric crystal.

Phase determination

The phases for 5-aminotetrazole monohydrate were obtained directly from the structure factor magnitudes by the use of the symbolic addition procedure (Karle & Karle, 1963, 1964, 1965, 1966; Karle, Britts & Gum, 1964). The origin for the crystal was fixed by assigning positive signs to three linearly independent reflections. These reflections were chosen on the basis that they had large $|E|$ values and that they entered into many combinations for the application of the Σ_2 relationship. In the present investigation it was necessary to designate the sign of only one additional reflection with an unknown symbol in order to carry out the complete sign determination. The starting set of phases is listed in Table 1.

Table 1. *Set of signs for application of the Σ_2 relationship to 5-aminotetrazole monohydrate*

hkl	$\|E\|$	Signs
12$\bar{1}$	2·82	+
410	2·67	+
52$\bar{6}$	2·32	+
240	2·73	*a*

As the phase determination progressed, many terms contributed to the sum in Σ_2 for the various $E_{\mathbf{h}}$. From relationships among these terms, it was possible to determine that the sign of the unknown symbol *a* was plus.

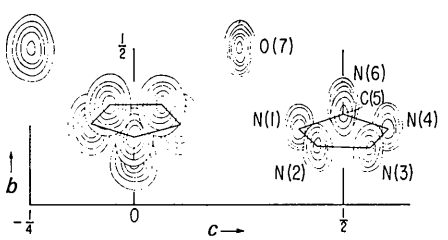


Fig. 1. Right-hand side: sections from an E map computed with 110 terms whose phases were determined by the symbolic addition procedure. The contours are at equally spaced, arbitrary levels. Left-hand side: sections from an electron density map based on the refined coordinates. The contours are spaced at 1 e.Å^{-3} beginning with the 1 e.Å^{-3} level.

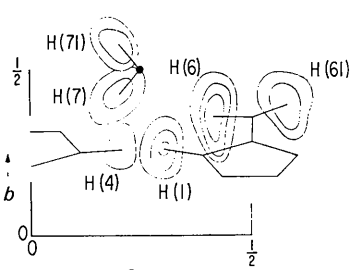


Fig. 2. Difference map showing the positions of the hydrogen atoms. The contours are spaced at 0·25 e.Å^{-3}.

From 110 signs for the largest $|E|$'s an E map (Karle, Hauptman, Karle & Wing, 1958) was computed which shows the location of the seven heavy atoms, in the asymmetric unit. Sections from the three-dimensional E map, projected along [100], are shown on the right side of Fig. 1.

The refinement

The coordinates of the seven atoms as determined from the initial E map were subjected to a least-squares refinement where the quantity $\Sigma w(F_o - F_c)^2$ was minimized with $w = 1$ for all $|F_o| > 0$. After several cycles of refinement first with isotropic temperature factors and then with anisotropic temperature factors, the R index was 14·1%. A three-dimensional difference map computed at this stage is shown in Fig. 2. It revealed the sites for the two hydrogen atoms, H(7) and H(71), of the water molecule, for the two hydrogen atoms, H(6) and H(61), of the amino group, and for H(1) attached to the ring at N(1). In addition, there is some density at site H(4). Since both the chemistry and the spatial considerations in the cell preclude the two hydrogen atoms on the ring, H(1) and H(4), existing at the same time, the structure may be somewhat disordered or the crystal used may still have some twinned regions. Further anisotropic least-squares refinement on the heavy atoms, but including the hydrogen atoms as fixed parameters, resulted in R values of 12·6% (Table 2) for the ring hydrogen in position H(1) and 12·7% for the ring hydrogen in position H(4). In both cases, the coordinates of the heavy atoms were almost identical.

Since the angle β is so close to 90°, the question arose as to whether the indices were assigned correctly. Accordingly, the reflections were relabeled from *hkl* to $HK\bar{L}$ and new structure factors were calculated. The new R value was 18% with the coordinates as listed in the manuscript. When the parameters were allowed to vary in the least-squares refinement, the R value was reduced to 13·1%, nearly the same as with the original indexing, and the coordinates of all the atoms changed so as to reflect the molecule across the *b* axis. The resulting bond distances differed by less than 0·01 Å, on an average 0·004 Å, and the bond angles differed by less than 0·5°. Diffractometer data are probably needed to resolve this ambiguity of index assignment.

The fractional coordinates and thermal parameters of the heavy atoms are listed in Table 3. Sections from an electron density map computed from the final parameters are shown on the left side of Fig. 1.

The structure

The 5-aminotetrazole molecule is essentially planar. A least-squares plane through the molecule is represented by the equation

$$-2{\cdot}2484x + 6{\cdot}8264y + 0{\cdot}1055z = -0{\cdot}5260\,,$$

where the value on the right-hand side is the origin-to-plane distance in Å (Schomaker, Waser, Marsh & Bergman, 1959). The deviations of the heavy atoms from this plane range from 0·002 to 0·013 Å. The hydrogen atoms in the molecule are within 0·03 Å of the plane.

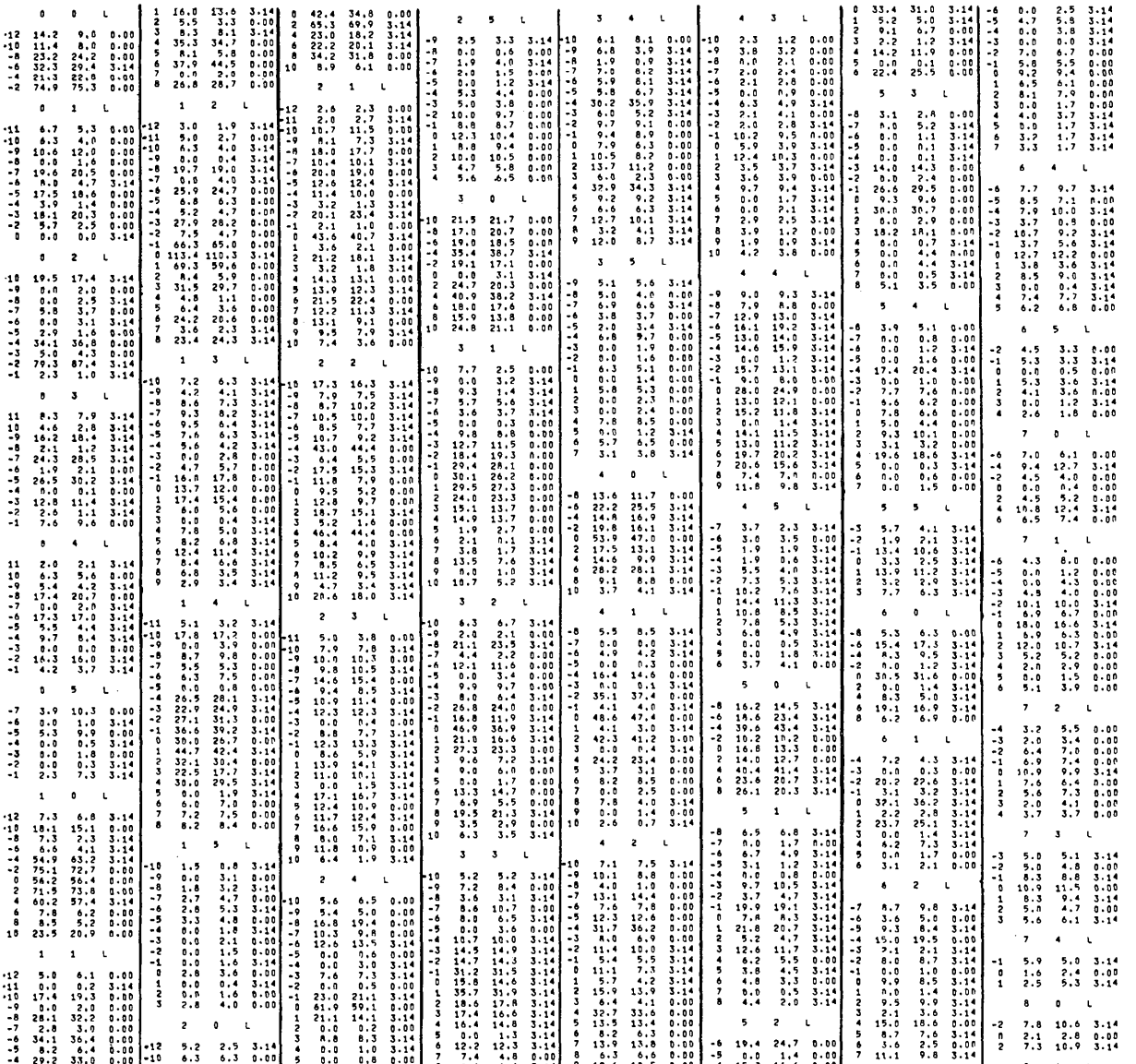
Bond lengths and angles are listed in Fig. 3. All the C–N and N–N bond values are considerably shorter than those usually found for single bonds and suggest a conjugated system of bonds similar to those found in other tetrazole derivatives. The N(2)–N(3) bond is only 1·26 Å while the N–N bonds adjacent to it are ~1·38 Å; hence a double bond must be fairly well localized between N(2) and N(3). Table 4 shows a comparison between the values found in this investigation and those found in previous investigations of various tetrazole derivatives.

It is interesting to note that a hydrogen atom does exist on the ring and does not migrate to the amino group to form a zwitterion. In the hydrazine salt of 5-aminotetrazole (Bryden, 1958), the ring is devoid of hydrogen atoms and has a net negative charge while the proton is attached to the hydrazine to form $NH_2NH_3^+$.

Fig. 4 illustrates the three-dimensional network of hydrogen bonds which exist in the crystal. Hydrogen

Table 2. *Observed and calculated structure factors*

The columns are the index l, $|F_o|$, $|F_c|$, and φ



bonding between N(1) and N(4) of adjacent 4-aminotetrazole molecules forms an infinite chain parallel to the *c*-axis. If H(1) is disordered, then the disorder cannot exist in any one chain but can occur with respect to parallel chains.

The hydrogen bonds to the water molecule are in an approximately tetrahedral configuration. The hydrogen atoms of the water molecule bond to N(2) and N(3) of different aminotetrazole molecules, and the oxygen atom of the water molecule acts as an acceptor for hydrogen bonds from the amino group of two different aminotetrazole molecules. The distances and angles involved in the hydrogen bonding are shown in Table

Table 5. *Hydrogen bond distances and angles*

Distances		Angles	
N(1)···N(4′)	2·76 Å	N(1) —N(4′)–N(3′)	108·5
		N(1) —N(4′)–C(5′)	138·2
O(7)···N(3′)	2·96	N(2‴)–O(7) –N(3′)	75·7
O(7)···N(2‴)	3·00	N(2‴)–O(7) –N(6″)	128·4
O(7)···N(6)	2·98	N(2‴)–O(7) –N(6)	111·5
O(7)···N(6″)	2·98	N(3′)—O(7) –N(6)	128·3
		N(3′)—O(7) –N(6″)	113·5
		N(6) —O(7) –N(6″)	68·5
		C(5)—N(6) –O(7)	121·2
		C(5)—N(6) –O(7″)	122·0
		O(7) —N(6) –O(7″)	111·8

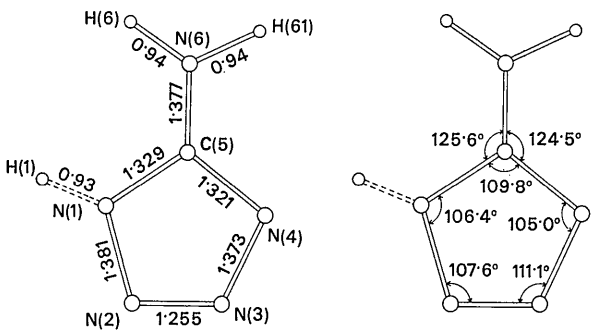


Fig. 3. Bond distances and angles in 5-aminotetrazole. For the heavy atoms, the standard deviations for bond lengths are 0·015 Å and for bond angles 0·65°.

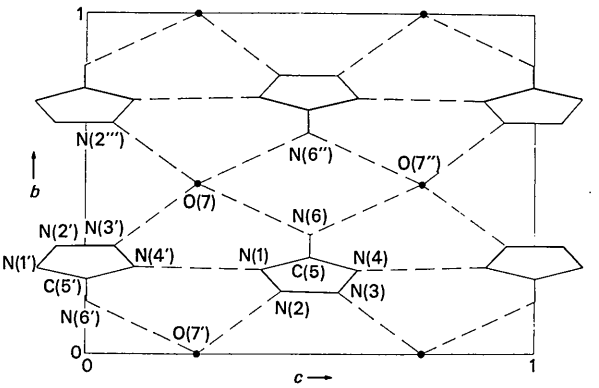


Fig. 4. Hydrogen bonding in 5-aminotetrazole monohydrate.

Table 3. *Fractional coordinates* for 5-aminotetrazole monohydrate*

The thermal parameters are of the form $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$. Each thermal parameter is multiplied by 10^4. The approximate parameters for the hydrogen atoms were obtained from the difference map.

	x	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	1·0095	0·2555	−0·1067	79	55	59	−30	19	5
N(2)	1·1994	0·3195	−0·0603	88	89	69	−41	15	−7
N(3)	1·1943	0·3163	0·0671	92	86	69	−27	19	3
N(4)	1·0065	0·2508	0·1134	94	68	41	−27	7	0
C(5)	0·8955	0·2193	0·0028	121	36	40	11	−19	−20
N(6)	0·6948	0·1522	0·0025	116	221	77	−75	−19	13
O(7)	0·5010	0·4944	0·2497	138	151	58	−63	−21	−5
H(1)	0·983	0·250	−0·200						
H(6)	0·658	0·145	−0·092						
H(61)	0·658	0·141	0·095						
H(7)	0·433	0·433	0·192						
H(71)	0·567	0·567	0·192						
Standard error									
N	0·0008	0·0011	0·0006	13	24	7	13	7	9
C	0·0009	0·0012	0·0006	16	26	6	15	8	9
O	0·0007	0·0010	0·0005	13	21	6	12	7	8

* Coordinates are so chosen that they may be substituted directly into the equation representing the least-squares plane.

Table 4. *Comparison of bond distances* (Å) *in various tetrazole derivatives*

	This study	Hydrazine salt of 5-amino-tetrazole	Sodium tetrazolate monohydrate	2-Methyl-5-amino-tetrazole	1,3-Dimethyl-5-iminotetrazole hydrochloride
C(5)–N(6)	1·377	1·403	—	1·36	1·29
N(1)–C(5)	1·329	1·302	1·329	1·32	1·38
N(4)–C(5)	1·321	1·318	1·329	1·35	1·36
N(1)–N(2)	1·381	1·346	1·348	1·34	1·35
N(2)–N(3)	1·255	1·295	1·310	1·29	1·30
N(3)–N(4)	1·373	1·356	1·348	1·32	1·31

5. The only unusual values are the N(6)–O(7)–N(6″) angle which is only 68·3° and the N(2″)–O(7)–N(3′) angle which is 75·7°. For a comparison with hydrogen bonding in other molecules, the reader is referred to Fuller (1959) and Clark (1963).

We are grateful to Dr Jerome Karle for his continuing interest and we wish to express our appreciation to Mr Stephen Brenner and Dr Donald Mitchell who performed all the calculations. We wish to thank Professor John Bryden for helpful discussions.

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Optical Determination of Water Content in Spherulitic Vaterite

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From measured indices of refraction for vaterite crystals [n_ε 1·650, n_ω 1·550; Johnston, Merwin & Williamson, *Amer. J. Sci.* **41**, 473 (1916)] and for vaterite fibers [n_e 1·625, n_o 1·538; Meyer, *Z. Kristallogr.*, **121**, 220 (1965)], Wiener's formulae give two independent values for the interstitial water content of the fibers (5·9, 5·8 vol. %). The lowering of the density from 1·645 (crystal) to 1·54 (fiber) indicates 6·4 vol. % water. The decomposition product of $CaCO_3.6H_2O$ described by Johnston *et al.* can now be identified as fibrous aggregates of vaterite and water.

Introduction

It is well known that a spherulite is a radial aggregate of fibers, in which each fiber is itself an aggregate, composed of tiny crystals separated by some interstitial medium. Such a fiber exhibits form birefringence: positive or negative, according as the constituent crystals are acicular or platy, and the indices of refraction of the fiber can be predicted by means of Wiener's (1904, 1909–10, 1912) formulae. The latter were applied to coralline algae by Baas-Becking & Galliher (1931). Chalcedony was the first mineral† in which form birefringence was thus studied (Correns & Nagelschmidt, 1933; Donnay, 1936*b*). Chalcedony fibers are composed of quartz crystals and interstitial opal. Because opal has such a variable index of refraction, chalcedony was not a particularly felicitous example. In spherulitic calcite, on the other hand, the interstitial medium is water and the application of Wiener's formulae was straightforward (Donnay, 1936*a*)‡. The water content thus determined (10·5 vol.%) agrees with the result of a chemical analysis on the same material (10·0 vol.%). This test case established the validity of the analytical method based on optical measurements. In the same paper an attempt was made to explain the indices of fibrous vaterite, but it was unsuccessful for lack of good measured values. The only conclusions that could be reached at the time were that the form birefringence is negative and that the amount of interstitial water must be very small.

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† Form birefringence was later observed in nemalite, which is fibrous brucite with interstitial magnetite (Donnay, 1945). It was also found to account for the refractive indices of layer crystal structures (where alternating structural slabs make up Wiener's *mixed body*) and in members of a solid solution in the series bastnaesite–vaterite (Donnay & Donnay, 1953, 1961).

‡ In 1936 spherulitic calcite was still called 'vaterite A', while the spherulitic form of μ-$CaCO_3$ was designated 'vaterite B'. The μ modification has now been found in nature (McConnell, 1960) and is called vaterite, whether it is spherulitic or not.