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## Refinement of the Structure of 5-Aminotetrazole Monohydrate

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**Abstract.**  $\text{CH}_3\text{N}_5 \cdot \text{H}_2\text{O}$ , monoclinic,  $P2_1/c$ ,  $a = 6.392$  (1),  $b = 7.277$  (2),  $c = 9.803$  (2) Å,  $\beta = 90.24$  (2)°,  $V = 456.1$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.502$  Mg m<sup>-3</sup>. The structure has been refined by block-diagonal least-squares methods, using 828 independent diffractometer-measured intensity data to  $R = 0.035$ ,  $R_w = 0.030$  (observed reflections only). The ring H atom is ordered, and the refined positions of the water-molecule H atoms give a more acceptable H–O–H bond angle than that previously given.

**Introduction.** Crystals of the title compound were obtained during an attempted recrystallization of 2,4-dimethyltetrazolo[1,5-*a*]pyrimidine from water. Complete diffractometer X-ray data had been measured before it was realized that hydrolysis had occurred, and that the compound crystallized was, in fact, one of known crystal structure (Britts & Karle, 1967). Since the earlier work had been carried out using visual intensity estimates from film, and there had been some uncertainty in the indexing, it was decided to refine the structure using our diffractometer data.

The X-ray data were measured on an Enraf–Nonius CAD-4 automated diffractometer using Ni-filtered Cu  $K\alpha$  radiation and a crystal measuring  $0.10 \times 0.18 \times 0.33$  mm. The unit-cell parameters were determined by a least-squares fit of the angular settings for 15 high-angle reflections. The  $\omega$ – $2\theta$  scanning mode was used

with  $\theta < 75^\circ$ . The intensities were corrected for Lorentz–polarization effects, but not for absorption [ $\mu(\text{Cu } K\alpha) = 1.12$  mm<sup>-1</sup>]. Of 897 possible independent reflections 828 were accepted as observed on the criterion  $I \geq 1.5\sigma(I)$ .

Refinement was carried out by block-diagonal least-squares methods starting from the non-hydrogen coordinates of Britts & Karle (1967). A difference electron density map clearly showed the positions of all the H atoms. Refinement was then continued on all positional parameters, anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the H atoms. The function minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $w$  was obtained from the counting statistics for the observed reflections, while the unobserved reflections were weighted zero. In the final cycle  $R = 0.035$ ,  $R_w = 0.030$  for observed reflections only, and  $R = 0.037$  for all reflections; the mean and maximum shift/e.s.d. were 0.08 and 0.33 respectively. The coordinates of all atoms and the isotropic thermal parameters for the H atoms are given in Table 1.† The scattering factors used for the nonhydrogen atoms are those given in *International Tables for X-ray Crystallography* (1962), and that for H is from Stewart, Davidson & Simpson (1965). All structural

† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34677 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Fractional coordinates ( $\times 10^4$  for non-hydrogen atoms,  $\times 10^3$  for hydrogen atoms)

The form of the isotropic thermal factors used was:  
 $\exp(-B \sin^2 \theta/\lambda^2)$ .

	x	y	z
N(1)	10048 (2)	2510 (2)	-1161 (2)
N(2)	11924 (2)	3151 (2)	-714 (2)
N(3)	11991 (2)	3203 (2)	591 (1)
N(4)	10117 (2)	2584 (2)	1034 (1)
C(5)	8934 (2)	2170 (2)	-48 (1)
N(6)	6979 (2)	1549 (2)	-10 (1)
O(7)	4992 (2)	5060 (2)	2495 (1)
H(4)	986 (2)	254 (3)	196 (2)
H(6,1)	637 (3)	122 (3)	-76 (2)
H(6,2)	639 (3)	125 (3)	77 (2)
H(7,1)	420 (3)	450 (3)	195 (2)
H(7,2)	583 (3)	566 (3)	196 (2)

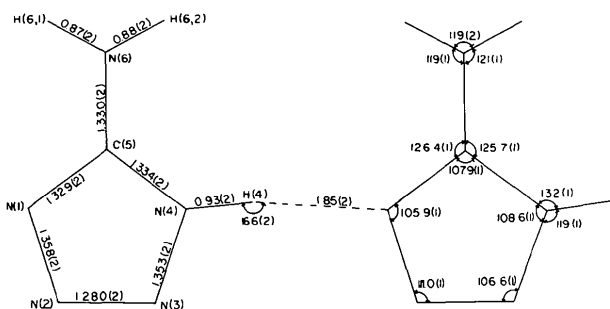


Fig. 1. Intramolecular and hydrogen-bond distances (Å) and angles ( $^\circ$ ) in the 5-aminotetrazole molecule. The molecules represented are related by  $x, y, z \rightarrow x, y, z + 1$ .

calculations were performed with the NRC system (Ahmed, Hall, Pippy & Huber, 1973).

**Discussion.** The accuracy of the structure has obviously been improved greatly by the refinement, as evidenced by the values of  $R$ , the standard deviations in coordinates (Table 1) and the bond distances and angles (Fig. 1). The following important structural differences from the previous work have emerged.

(1) The ring H atom, our H(4), is bonded to N(4) not to N(1), and there is no evidence of disorder involving this H atom.

(2) There are significant differences in the bond angles involving N(2) and N(3) shown in Fig. 1. The numerical values are close to those given in the original determination, but are interchanged.

(3) The hydrogen-bond angle N(2')-O(7)-N(3) is found to be  $105.0^\circ$ , rather than  $75.7^\circ$  as originally reported. This also reflects a much more acceptable value of  $104^\circ$  for the bond angle in the water molecule. Hydrogen-bond distances and angles involving the water molecule are shown in Fig. 2.

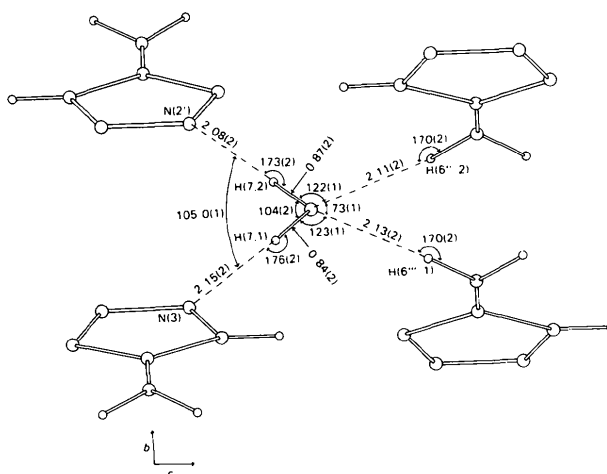
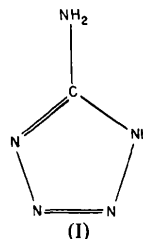
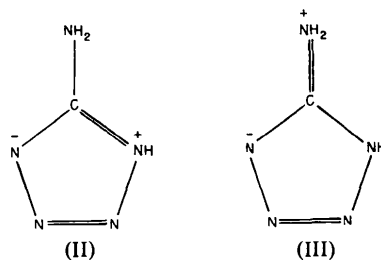


Fig. 2. Dimensions of the water molecule and its hydrogen-bonded distances (Å) and angles ( $^\circ$ ). Single, double and triple primes refer to the atoms related by  $-x, -y, -z$ ;  $-x - 1, \frac{1}{2} + y, \frac{1}{2} - z$  and  $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$ , respectively, to the coordinates of Table 1.

A least-squares mean plane of the non-hydrogen atoms of the 5-aminotetrazole molecule is represented by the equation  $-0.3499X + 0.9366Y - 0.0178Z = -0.5130$ . The maximum deviation from this plane is  $0.008(2)$  Å for N(6).



The localization of H(4) would suggest that (I) is the valence-bond description of this tautomer. However, this is an oversimplification, since the bonds from C(5) to N(1), N(4) and N(6) are almost exactly equal, while N(2)-N(3) is longer and the adjacent single bonds are shorter than standard values (Pauling, 1939). It has been shown in other meso-ionic compounds that a conventional description does not necessarily correspond to observed bond distances. In 2-methyl-5-aminotetrazole (Bryden, 1956) the N(2)-N(3) distance is only  $1.29$  Å, and is depicted as a single bond, while the 'double' bonds are  $1.32$  and  $1.35$  Å. In 5-aminotetrazole monohydrate resonance hybrids such as (II)



and (III) undoubtedly make large contributions, and species with charges on N(2) or N(3) must also be involved.

The intermolecular hydrogen bond N(4)—H(4)···N(1) is typical of a linear hydrogen bond, and the hydrogen bonding involving the water molecule is typical of distorted tetrahedral hydrogen bonding of water, as discussed in detail by Hamilton & Ibers (1968).

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## X-ray Refinement of the Structure of [N,N'-(3-Aza-1,5-pentanediy)-bis(salicylideneiminato)]dioxouranium(VI)

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**Abstract.** C<sub>18</sub>H<sub>19</sub>N<sub>3</sub>O<sub>4</sub>U, [U(C<sub>18</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub>)<sub>2</sub>], orthorhombic, *Pnma*, *a* = 10.473 (3), *b* = 21.803 (10), *c* = 8.024 (2) Å, *V* = 1832.2 Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 2.10 Mg m<sup>-3</sup>, *μ*(Mo *Kα*) = 8.48 mm<sup>-1</sup>, *λ*(Mo *Kα*) = 0.7107 Å. The structure has been refined by full-matrix least-squares methods to an *R* of 0.036 for 1272 observed reflections. Our results confirm those of an earlier structure determination but give interatomic distances and angles with greater accuracy. Anisotropic temperature factors are introduced for all non-hydrogen atoms.

**Introduction.** The structure of the title compound has previously been determined by Akhtar & Smith (1973) from visually measured film data, and showed the interesting peculiarity of having asymmetric U—O bonds in the uranyl group. The two bond distances were U—O(1) 1.72 (2) Å and U—O(2) 1.64 (3) Å, differing by 2σ from their mean of 1.68 Å. As this difference is at the limit of significance, we were interested in obtaining more accurate bond distances

and angles; also, we have studied uranyl complexes with a very similar ligand, *i.e.* [N,N'-(3-oxa-1,5-pentanediy)bis(salicylideneiminato)]dioxouranium(VI), which showed another peculiarity: a non-linear uranyl group (Brock, Cook, Fenton, Bombieri, Forsellini & Benetollo, 1978).

A single crystal of prismatic habit was used for data collection. Preliminary Weissenberg and precession photographs showed systematic absences indicating space groups *Pn2<sub>1</sub>a* or *Pnma*; *Pnma* was confirmed by the subsequent successful refinement, in agreement with the study of Akhtar & Smith (1973).

Intensities of 3216 reflections with *k*, *l* ≥ 0 were collected in the range 3 ≤ *θ* ≤ 25° with graphite-monochromated Mo *Kα* radiation and the *θ*/2*θ* scan mode on a Philips PW 1100 four-circle diffractometer. Two standard reflections registered each hour did not show any change in intensity during data collection.

The intensities of the two sets of independent reflections were corrected for absorption following the North, Phillips & Mathews (1968) method and then averaged to obtain a unique set of reflections. Of these, 1272 were considered observed according to the

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