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PREPARATION AND STRUCTURE CHARACTERIZATION OF 4-AMINO-1,2,4-TRIAZOL-5-ONE HYDRATE

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4-Amino-1,2,4-triazol-5-one hydrate (ATO·H_2O) was prepared and its structure was analyzed by four-circle diffraction measurement. The obtained results show that the crystal belongs to the triclinic crystal system, space group P 1 with crystal parameters $a = 6.432(1)$, $b = 6.551(1)$, $c = 6.740(1)$ Å; $\alpha = 68.04(1)$, $\beta = 82.18(1)$, $\gamma = 81.90(1)°$; $V = 259.7(7)$ Å^3; $Z = 2$; $Dc = 1.510$ g/cm^3; $\mu = 0.131$ mm^{-1}; $F(000) = 124$. *ATO·H_2O was characterized by FT-IR analysis, X-ray diffraction analysis, and single crystal diffraction analysis.*

Keywords: 4-amino-1,2,4-triazol-5-one, molecular structure, crystal structure, structure characterization.

4-Amino-1,2,4-triazol-5-one (ATO), as a new kind of high nitrogen content material, has received much attention [1-5] since it possesses such advantages as higher nitrogen content, higher enthalpy, and lower sensitivity. The preparation, molecular structure, and thermal decomposition mechanism of its various coordination compounds have also been studied [6-9]. In order to examine the structure of ATO, we have synthesized it and tried to prepare its single crystal using different solvents and natural evaporation method. It was characterized by FT-IR analysis, X-ray diffraction analysis, and single crystal diffraction analysis.

EXPERIMENTAL

The Reagents. The commercial reagents used in the experiments were analytically pure. Carbohydrazide was produced by Zhejiang Guanghua Equipment Factory and recrystallized twice from distilled water.

The Instruments and Conditions. Infrared spectra were recorded with a Perkin-Elmer 683 FT-IR spectrometer in KBr pellets. X-Ray powder diffraction patterns were recorded by using a D/max-RB diffractometer with Cu target. In the determination of the structure with single crystal, X-ray intensities were recorded by a Siemens P4 automatic diffractometer with graphite-monochromatized Mo$K\alpha$ radiation, $\lambda = 0.70713$ Å. It scans in the form of the ω mode with the range $1.70° < \theta < 29.00°$.

Preparation of ATO·H_2O and Its Single Crystal. ATO may be prepared by the method of [10, 11]. We used triethyl orthoformate to cyclize carbohydrazide:

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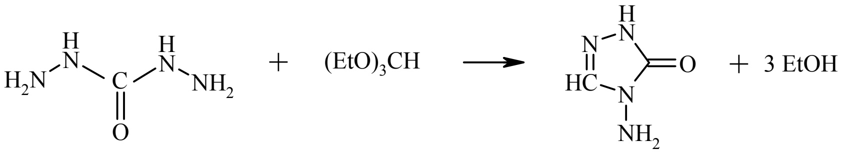

Carbohydrazide (45.00 g, 0.50 mol) was suspended in triethyl orthoformate (55.00 ml) initially introduced into a 1 liter four-neck flask with a contact thermometer, stirrer, dropping funnel, short column, and reflux condenser. While stirring, the mixture was heated at 60-95°C for 45 min and then refluxed for 3 h. At the end of the reaction a precipitate was formed. The mixture was concentrated to dryness under reduced pressure and the residue was recrystallized from alcohol (100 ml). 4-Amino-1,2,4-triazol-5-one (37 g, 77%) was obtained; mp 186.3-188.1°C.

After that, the obtained ATO (5 g) was dispersed into distilled water (50 ml), heated to 60°C, then filtered. The filtrate was deposited into a culture box at the constant temperature of 25°C. Colorless transparent single crystals for X-ray measurement appeared after about two weeks.

Determination of the Crystal Structure. The dimensions of the single crystal used for the X-ray measurement were $0.40 \times 0.40 \times 0.32$ mm^3. X-Ray intensities were recorded by a Siemens P4 automatic diffractometer with graphite-monochromatized MoK_α radiation. Cell parameters were determined from 22 reflections in the 2θ range of $3.76° < \theta < 15.43°$. At the temperature of 295(2) K, the data were collected by ω scans in the range of $3.21° < \theta < 25.99°$, h: 0~7, k: -7~7, l: -8~8, and 1238 reflections were collected which included 1238 independent reflections, among which 699 with $I > 2\sigma(I)$ were used for the determination of crystal structure and refinement.

The obtained results showed that the crystal belongs to the triclinic crystal system, space group P 1 with crystal parameters of a = 6.432(1), b =6.551(1), c = 6.740(1) Å; α = 68.04(1), β = 82.18(1), γ = 81.90(1)°; V = 259.7(7) Å^3; Z = 2; Dc = 1.510 g/cm^3; μ = 0.131 mm^{-1}; $F(000)$ = 124.

The coordinates of all of the non-hydrogen atoms in the molecule were obtained by the direct method. Refinement was performed by the block-diagonal least-square method. The hydrogen atom was obtained by the Fourier method. All calculations were carried out with the Siemens SHELXTL97 program on a personal computer. Final R indices for $I > 2\sigma(I)$ were R_1 = 0.0349, wR_2 = 0.0806, the R indices for all data were R_1 = 0.0562, wR_2 = 0.0876, and the goodness-of-fit on F^2 was 1.013 with the extinction coefficient 0.37(3),

$$\omega = 1/[s^2(F_0^2) + (0.0427P)^2 + 0.0042P],\ P = (F_0^2 + 2F_c^2)/3.$$

The largest difference peak and hole are 0.138 and -0.135 e·Å^{-3}.

RESULTS AND DISCUSSION

IR Absorption Spectra Analysis Analysis of the IR absorption curve for ATO gave the following results: $\nu^{s}_{-NH-H} = 3332$, $\nu^{as}_{-NH-H} = 3306$, $\nu^{s}_{N-H} = 3204$, $\nu^{s}_{=C-H} = 3074$, $\nu^{s}_{C=O} = 1710$, $\delta^{i}_{N-H} = 1645$, $\delta^{o.o.p}_{N-H} = 696$, $\nu^{s}_{C=N} = 1572$, $\nu^{s}_{C-N} = 1250$ cm^{-1}. The vibration absorption peaks of the triazole framework are 943, 692, and 589 cm^{-1}. The typical IR absorption curve for ATO is illustrated in Fig. 1.

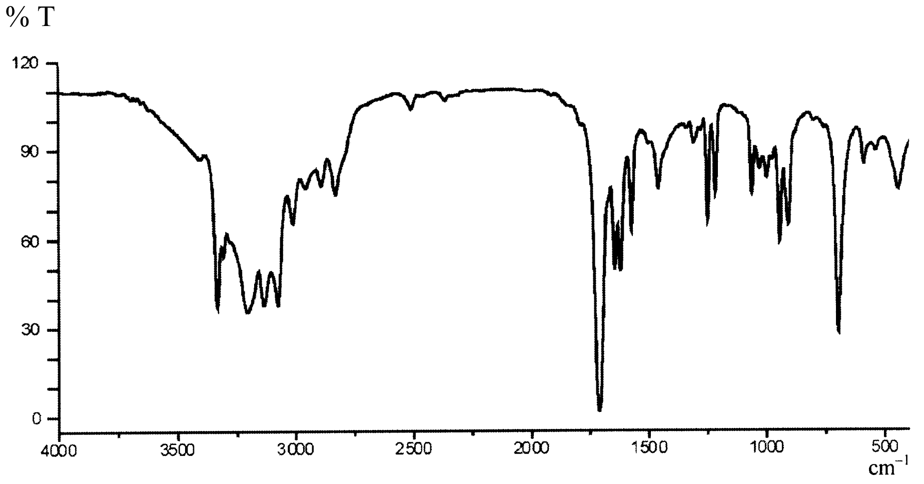

Fig. 1. Typical IR absorption curve for ATO.

X-Ray Powder Diffraction Analysis. The X-ray powder diffraction pattern of ATO was recorded by using a D/max-RB diffractometer with Cu target. The scan speed was 4°/min with collected step of 0.02° and collected range of 5-80°. The diffraction pattern of ATO is shown in Fig. 2. The positions and relative intensity of the strongest diffraction are shown in Table 1.

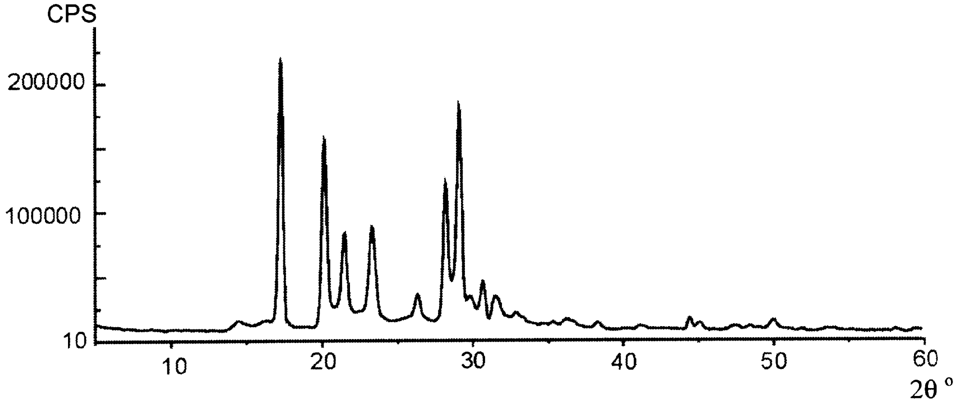

Fig. 2. X-ray powder diffraction patterns for ATO.

Determination of Structure of Single Crystal. The obtained atoms coordinates and thermal parameters are summarized in Table 2. The molecular structure and atom labels are shown in Fig. 3, and the packing of the molecule in crystal lattice is illustrated in Fig. 4.

The analytic results indicate that in the crystal one ATO molecule is combined with one water molecule. The atoms in the ATO ring are in a plane, where the least square plane equation is: $-0.0714x - 0.3111y + 0.9477z = 20.810$, the error of heavy atoms being equal to 0.0062 Å.

The obtained bond lengths and bond angles of ATO hydrate are summarized in Table 3. According to the bond length data, one can conclude that the average bond lengths of N–N and C–N are 1.382 and 1.353 Å, which are shorter than the usual lengths (1.450 and 1.470 Å). At the same time, the bond length of C=N is 1.302 Å, which is longer than the standard length (1.270 Å). Thus, the bond lengths of N–N, C–N, and C=N tend to a homogeneous value, which results from the form of the π-bonds of the ATO molecule and the

TABLE 1. The X-ray Powder Diffraction Data for ATO

Sample	Order	2θ, deg.	Width, deg.	D, g·cm^{-3}	$I \cdot I_0^{-1}$, %
ATO	1	17.420	0.390	5.0906	100
	2	20.280	0.420	4.3787	58
	3	29.260	0.420	3.0521	67

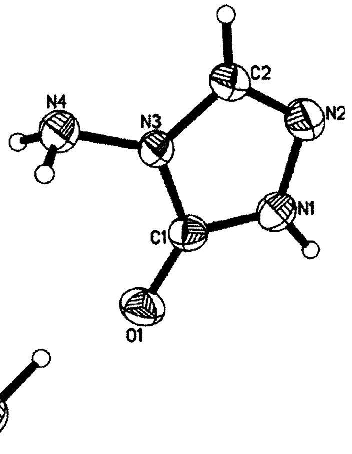

Fig. 3. The molecular structure of ATO and atom labels.

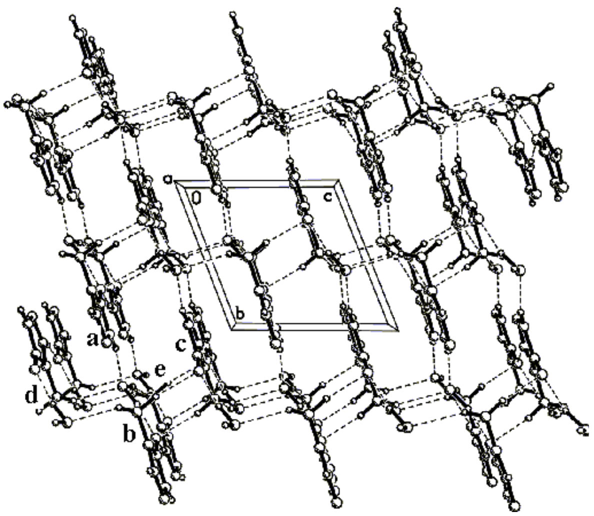

Fig. 4. The packing of the molecule in crystal lattice.

conjugation effect [12]. Based on the bond angle data of ATO, since the oxygen atom of the carbonyl and the nitrogen atom of the amino group are both involved in the conjugation, the internal angles of the ATO molecule are all close to 108.0° (the internal angles of just the pentagon), in which the biggest error is less than 4.0°.

TABLE 2. Atoms Coordinates (×10^4) and Thermal Parameters (×10^2)

Atoms	*x*	*y*	*z*	U_{eq}, Å^2
O(1)	-1045(2)	7347(2)	2807(2)	4.9(1)
O(2)	-2211(3)	4008(2)	1789(3)	5.3(1)
N(1)	750(2)	10305(2)	2528(3)	4.4(1)
N(2)	2814(3)	10711(2)	2459(3)	5.1(1)
N(3)	2614(2)	7314(2)	2682(2)	3.6(1)
N(4)	3286(3)	5136(3)	2813(3)	4.4(1)
C(1)	563(3)	8251(3)	2676(3)	3.6(1)
C(2)	3884(3)	8837(3)	2564(3)	4.3(1)
H(1)	-308	11280	2480	5.3
H(2)	5344	8580	2558	5.2
H(4A)	2880(30)	4930(30)	1770(30)	5.3(7)
H(4B)	2640(30)	4190(30)	4180(40)	7.0(7)
H(2A)	-1510(60)	5120(70)	2380(60)	7.4(5)
H(2B)	-3550(50)	4130(40)	2260(40)	8.6(9)

According to the packing of the molecule in the crystal lattice, many intramolecular and intermolecular H-bonds exist in 4-amino-1,2,4-triazol-5-one hydrate, which is showed in Table 4.

In the ATO hydrate molecule, between the oxygen atom (O(2)–H(2A)) of the crystal water molecule and carbonyl O(1) of ATO molecule, the intramolecular H-bond O(2)–H(2A)···O(1) exists. At the same time, there are two kinds of intermolecular H-bonds. The first kind formed in the same layer includes three sorts. The first one is the H-bond of N(1a)–H(1a)···O(2b), which is produced by N(1a)–H(1a) of ATO and the oxygen O(2b) of the crystal water of the next hydrate molecule lying in the same layer. The second one is the H-bond of N(4c)–H(4Bc)···O(1b), which is formed between the amino nitrogen N(4c)–H(4Bc) of the ATO molecule and the carbonyl O(1b) of the next ATO molecule.

The last one is the H-bond of N(4b)–H(4b)···O(2d) between the amino nitrogen N(4b)–H(4b) of the ATO molecule and the oxygen O(2d) of the crystal water of the next hydrate molecule lying in the same layer. The second kind of intermolecular H-bond is formed between two layers, which enhances the interactions among them. The H-bond O(2)–H(2Bb)···N(4e) exists between the oxygen atom (O(2)–H(2Bb)) of the crystal water molecule and the amino nitrogen N(4e) of the next layer ATO molecule. (Note: a, b, c, d, and e denote the different 4-amino-1,2,4-triazol-5-one hydrate molecules.)

TABLE 3. Bond Lengths and Bond Angles

Bonds	Lengths, Å	Bonds	Angles, deg.
O(1)–C(1)	1.239(2)	C(1)–N(1)–N(2)	113.22(14)
N(1)–C(1)	1.333(2)	C(2)–N(2)–N(1)	103.40(15)
N(1)–N(2)	1.382(2)	C(2)–N(3)–C(1)	108.39(14)
N(2)–C(2)	1.302(2)	C(2)–N(3)–N(4)	125.51(15)
N(3)–C(2)	1.350(2)	C(1)–N(3)–N(4)	126.10(15)
N(3)–C(1)	1.374(2)	O(1)–C(1)–N(1)	129.64(16)
N(3)–N(4)	1.405(2)	O(1)–C(1)–N(3)	127.06(16)
		N(1)–C(1)–N(3)	103.29(15)

TABLE 4. H-Bond Lengths and Bond Angles

Atom D	Atom H	Atom A	D–H, deg. Å	H···A, deg. Å	D···A, deg. Å	D–H···A, deg.
O(2)	H(2A)	O(1)	1.110(5)	1.660(5)	2.747(2)	162.2(3)
O(2)	H(2B)	N(4)	0.880(3)	2.080(3)	2.941(2)	167.1(2)
N(1)	H(1)	O(2)	0.860(1)	1.960(1)	2.795(2)	164.8(1)
N(4)	H(4B)	O(1)	0.970(2)	2.090(2)	3.058(2)	170.6(1)
N(4)	H(4A)	O(2)	0.840(2)	2.320(2)	3.096(3)	153.5(1)
C(2)	H(2)	O(1)	0.930(1)	2.360(1)	3.279(2)	171.1(1)

The hydrogen bonds between molecules are the main force forming the crystal. Lots of H-bonds exist in the three-dimensional structure of the whole crystal and enhance the stability of the compound. Otherwise, one cannot find one ATO molecule combined with one water molecule.

By determinating of the molecular and crystal structure of 4-amino-1,2,4-triazol-5-one hydrate, we confirmed its molecular formula and obtained its structural parameters, which are important for further research on this kind of energy material.

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