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Crystal Structure of Energetic Compound 4-Amino-1,2,4-triazolium Picrate

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Abstract: A single crystal of energetic compound 4-amino-1,2,4-triazolium picrate (4-ATPA) was cultured from methanol solvent at 25 ℃. The compound crystallized in the orthorhombic system, is space group Pcnb with a=9.177(4), b=13.279(6), c=19.855(6) Å, V=2419.5(16) Å^3, D_c=1.720 g·cm^{-3}, Z=8, μ(MoKα)=0.152 mm^{-1} and F(000)=1280. Of the 2580 total reflections, 2194 were unique(R_{int}=0.0048). The final R=0.0588 and wR=0.1370 for 2194 observed reflections with $I>2\sigma(I)$. Single X-ray diffraction reveals that the structure is composed of 4-amino-1,2,4-triazolium cation and picric anion.

Key words: physical chemistry; 4-amino-1,2,4-triazolium picrate (4-ATPA); crystal structure; ionic compound; explosive

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1 Introduction

Air Force Research Laboratory of America(AFRL) has engaged in energetic ionic compounds for over decade[1]. Recently they have investigated the feasibility of replacing TNT with an ionic liquid for use in melt castable explosives. The approach focuses on synthesizing triazolium-based salts that have the appropriate physical and safety properties, thermal stability, and theoretical performance to potentially replace TNT. Individual salts selected from several families of energetic triazolium salts recently synthesized at AFRL possess high densities, relatively high heats of formation, and pass accepted thermal stability tests[2-3].

We designed and prepared the energetic ionic compound 4-amino-1,2,4- triazolium picrate (4-ATPA)[4]. Its structure has not been reported yet. The explosive properties such as v_D and p_D have great relation to the crystal density, and the thermal properties and mechanical sensitivity also are closely linked with the crystal structure of explosive[5-7]. Therefore, we analyzed the crystal structure of 4-ATPA in the paper, and considered plenty of the hydrogen bonds and ππ bonds had much attribute to its excellent thermal stability.

2 Experimental

2.1 Materials and measurement

All chemicals from commercial sources were of reagent grade and used without further purification. 4-ATPA was synthesized by neutralization of 4-amino-1,2,4-triazolium and picric acid. X-ray diffraction was performed on a Holand ENRAF NONIUS CAD4 X-ray four-circle diffractometer equipment.

2.2 Single crystal preparation of 4-ATPA

Some 4-ATPA was added to the methanol solvent, then made them dissolved completely by heat and stirring. The solution was filtered, and the filtrate was kept at room temperature for some days, obtained colorless crystal of the title compound.

2.3 X-ray crystallography

A colorless single crystal of 4-ATPA with dimensions of 0.25 mm×0.22 mm×0.18 mm was used for X-ray data collection performed on a CAD4 four-circle diffractometer equippment with a graphite-monochromatic MoKα diffraction (λ = 0.71073 Å) at 295(2) K. A total of 2580 reflections, of which 2194 independent reflections (R_{int}=0.0048) had been collected in the range of $2.18° < \theta < 25.50°$. Corrections for Lorentz-polarization factors and empirical absorption were made. The structure was solved by direct methods and refined by full-matrix least-squares techniques based on F^2 with SHELXTL-97[8-10] program, giving the final R = 0.0588 and wR=0.1370. All non-hydrogen atoms were refined anisotropically. All H atoms were positioned geometrically with Fourier. The maximum and minimum peaks on the final difference Fourier map was 0.305 and −0.306 e/Å^3, respectively.

The Molecular framework and atomic numbering of title compound are shown in Fig.1. The crystallographic data for it are listed in Table 1, and the selected bond lengths and bond angles in Table 2 and 3.

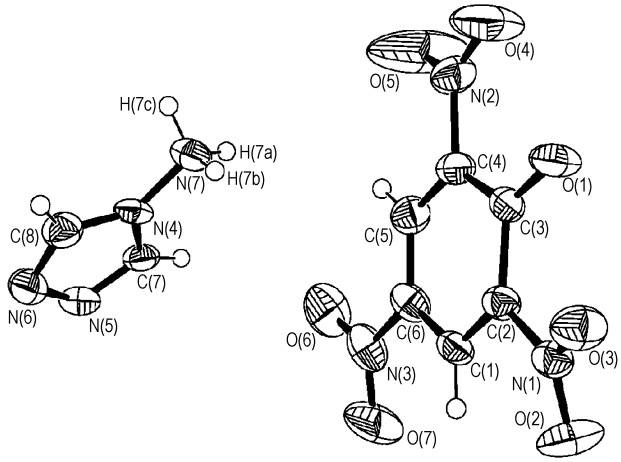

Fig.1 Molecular framework and atomic numbering

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Table 1 Selected bond lengths and bond angles

bond	length/Å	bond	length/Å	bond	length/Å
C(1)—O(2)	2.4009(13)	C(1)—O(3)	2.4349(13)	C(1)—O(4)	2.4522(13)
C(1)—O(9)	2.4069(14)	C(1)—O(10)	2.3976(17)	C(1)—O(4)^{c}	2.4975(12)
C(1)—O(7)^{a}	2.2820(16)				
bond	**angle/(°)**	**bond**	**angle/(°)**	**bond**	**angle/(°)**
O(7)^{a}—C(1)—O(10)	174.18(6)	O(3)—C(1)—O(4)	65.47(4)	O(10)—C(1)—O(3)	82.61(6)
O(10)—C(1)—O(2)	93.02(6)	O(10)—C(1)—O(4)^{c}	90.15(6)	O(9)—C(1)—O(3)	138.40(5)
O(10)—C(1)—O(9)	86.79(6)	O(9)—C(1)—O(4)^{c}	80.64(5)	O(10)—C(1)—O(4)	82.49(5)
O(7)^{a}—C(1)—O(3)	94.63(6)	O(4)—C(1)—O(4)^{c}	73.77(5)	O(9)—C(1)—O(4)	152.12(5)
O(2)—C(1)—O(3)	65.16(5)	O(7)^{a}—C(1)—O(2)	90.44(6)	O(7)^{a}—C(1)—O(4)^{c}	88.61(5)
O(7)^{a}—C(1)—O(4)	91.71(5)	O(7)^{a}—C(1)—O(9)	98.61(6)	O(2)—C(1)—O(4)^{c}	155.63(5)
O(2)—C(1)—O(4)	130.60(5)	O(2)—C(1)—O(9)	75.44(5)	O(3)—C(1)—O(4)^{c}	139.17(4)

Note: Symmetry transformation: a: x, $y+1$, z; c: $-x$, $-y+1$, $-z$.

Table 2 Hydrogen bond lengths and bond angles

D—H···A	d(D—H)/Å	d(H···A)/Å	d(D···A)/Å	∠DHA/(°)
O(9)—H(9A)···O(5)^{a}	0.868	1.868	2.728(18)	171(2)
O(9)—H(9B)···O(2)^{b}	0.873	1.936	2.796(2)	168(2)
O(10)—H(10A)···O(11)^{c}	0.857	1.993	2.795(2)	155(2)

Note: Symmetry codes: a: $-x$, $-y+1$, $-z$; b: $-x+1/2$, $-y+3/2$, $-z$; c: x, y, $z-1$.

Table 3 Bond angles of 4-ATPA

bond	angle/(°)	bond	angle/(°)	bond	angle/(°)
O(3)—N(1)—O(2)	122.5(3)	N(4)—N(7)—H(7b)	109.5	C(5)—C(4)—N(2)	115.1(3)
O(3)—N(1)—C(2)	120.4(3)	H(7a)—N(7)—H(7b)	109.5	C(3)—C(4)—N(2)	119.7(3)
O(2)—N(1)—C(2)	117.0(3)	N(4)—N(7)—H(7c)	109.5	C(4)—C(5)—C(6)	118.8(3)
O(5)—N(2)—O(4)	119.6(3)	H(7a)—N(7)—H(7c)	109.5	C(4)—C(5)—H(5)	120.6
O(5)—N(2)—C(4)	119.6(3)	H(7b)—N(7)—H(7c)	109.5	C(6)—C(5)—H(5)	120.6
O(4)—N(2)—C(4)	120.8(3)	C(2)—C(1)—C(6)	119.2(3)	C(1)—C(6)—C(5)	121.3(3)
O(6)—N(3)—O(7)	123.4(3)	C(2)—C(1)—H(1)	120.4	C(1)—C(6)—N(3)	118.6(3)
O(6)—N(3)—C(6)	118.9(3)	C(6)—C(1)—H(1)	120.4	C(5)—C(6)—N(3)	120.1(3)
O(7)—N(3)—C(6)	117.6(3)	C(1)—C(2)—N(1)	116.1(3)	N(5)—C(7)—N(4)	106.9(3)
C(7)—N(4)—C(8)	107.5(3)	C(1)—C(2)—C(3)	124.2(3)	N(5)—C(7)—H(7)	126.5
C(7)—N(4)—N(7)	124.5(3)	N(1)—C(2)—C(3)	119.8(3)	N(4)—C(7)—H(7)	126.5
C(8)—N(4)—N(7)	128.0(3)	O(1)—C(3)—C(4)	126.4(3)	N(6)—C(8)—N(4)	110.1(3)
C(7)—N(5)—N(6)	111.0(3)	O(1)—C(3)—C(2)	122.2(3)	N(6)—C(8)—H(8)	125.0
C(8)—N(6)—N(5)	104.6(3)	C(4)—C(3)—C(2)	111.4(3)	N(4)—C(8)—H(8)	125.0
N(4)—N(7)—H(7a)	109.5	C(5)—C(4)—C(3)	125.2(3)		

3 Results and discussion

The title compound contains one 4-amino-1,2,4-triazolium cation and one picric acid anion(Fig.1), and N(7) atom of the former acts as the hydrogen-bonding donors via H(7a), H(7b) and H(7c) to the neighboring hydrogen-bonding acceptors O(5) and O(4) at ($-x+1/2$, y, $z+1/2$), ($-x$, $-y+1/2$, z), ($-x+1$, $-y+1/2$, z) and ($x-1/2$, $-y+1$, $-z+3/2$) from carboxyl. There are a lots of hydrogen bonds, besides the electrovalent bonds of picric anion and 4-AT cation, which contributes to the stability of molecule structure, then increased the crystal density of 4-ATPA to 1.720 g·cm^{-3}.

By using the Four-Circle Diffractometer, packing arrangement of 4-ATPA in Cell were found as Fig. 2. The hydrogem atom of O(1) belongs to 4-AT transfered to N(7) position(Fig. 1), and it confirms the neutralization of 4-AT and picric acid.

One-dimensional chain parallel to the direction is generated by the hydrogen bonds of H(7)—O(4,5) (Fig. 1, Table 7). All the atoms of 4-AT cation are nearly in a plane with the mean deviation of 0.0048 Å, similar to the picric acid anion with the mean deviation of 0.0085 Å. The dihedral angle between them is 80.38°, suggested the hydrogen bonding interactions have little influence on the structure. The plane of 4-AT cation (Fig. 2) could be expressed as an eq.: $-6.3806x+2.4417y+13.7954z=9.6859$, the plane eq. of picric anion could be expressed as $0.0651x+13.2765y-0.3376z=1.5405$.

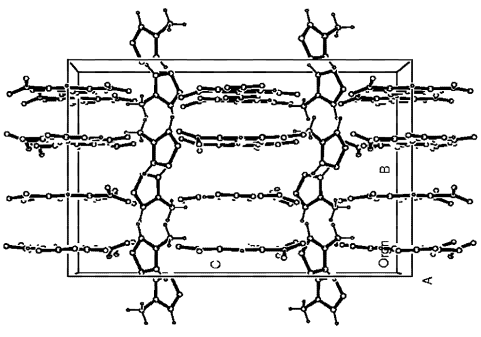

Fig. 2 Packing arrangement in crystal of 4-ATPA

Atom position and equivalent isotropic displacement parameters are shown in Table 4.

From Figure 2, we can find there are plenty of hydrogen bonds as the connections between picric ion and 5-membered ring, N(4)—C(7)—N(5)—N(6)—C(8) ion, besides static effect, that infinity extend to planar structure. In the structure of 4-ATPA, there also exist ππ effect between picric ion and 5-membered ring, that is, ππ effect among O(2), O(6) and 5-membered ring, that benefits the stability of the infinite planar structure. And the ππ bonds form infinite space three-dimensional structure between planar structure and parallel picric plane, made the structure much stable.

we analyzed the crystal structure of 4-ATPA. We considered plenty of the hydrogen bonds and ππ bonds have much attribute to its excellent thermal stability.

Table 4 Atomic coordinates ($\times10^4$) and equivalent isotropic displacement parameters ($Å^2\times10^3$)

atom	*x*	*y*	*z*	U(eq)	atom	*x*	*y*	*z*	U(eq)
O(1)	1547(2)	1229(2)	3829(1)	47(1)	C(1)	4590(3)	1255(2)	4992(2)	36(1)
O(2)	5900(3)	914(2)	3823(1)	67(1)	C(2)	3809(3)	1263(2)	4404(2)	32(1)
O(3)	4136(3)	1541(2)	3267(1)	51(1)	C(3)	2215(3)	1259(2)	4371(2)	31(1)
O(4)	−774(3)	1319(3)	4627(1)	100(1)	C(4)	1580(3)	1275(2)	5031(2)	36(1)
O(5)	−512(4)	1225(4)	5635(2)	162(3)	C(5)	2346(4)	1296(2)	5623(2)	41(1)
O(6)	4063(4)	1398(2)	6751(1)	70(1)	C(6)	3858(4)	1287(2)	5597(2)	40(1)
O(7)	6031(3)	1205(2)	6169(1)	77(1)	C(7)	3187(3)	3261(2)	7914(2)	37(1)
N(1)	4656(3)	1245(2)	3786(1)	35(1)	C(8)	2770(3)	4711(2)	7464(2)	44(1)
N(2)	−5(3)	1266(2)	5104(1)	46(1)	H(7a)	1207	2619	7186	250(2)
N(3)	4698(4)	1292(2)	6216(2)	52(1)	H(7b)	1662	3245	6624	250(2)
N(4)	2373(2)	3728(2)	7464(1)	35(1)	H(7c)	499	3581	7066	250(2)
N(5)	4030(3)	3943(2)	8188(1)	43(1)	H(1)	5603	1228	4983	45(5)
N(6)	3786(3)	4864(2)	7913(2)	48(1)	H(5)	1862	1317	6034	45(5)
N(7)	1340(3)	3249(2)	7046(1)	49(1)	H(7)	3165	2578	8017	45(5)
					H(8)	2376	5204	7185	45(5)

4 Conclusions

From the crystal structure of title compound, we presume that the 4-amino-1,2,4-triazolium cation would be willing to combine other anions, such as nitric acid anion, dipicrate anion, NTO anion and so on.

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含能化合物 4-氨基-1,2,4 −三唑苦味酸盐的晶体结构

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摘 要: 在甲醇溶液中培养了化合物 4-氨基-1,2,4 −三唑苦味酸盐的单晶。该化合物属于正交晶系, Pcnb 空间群, 晶体学参数如下: $a=9.177(4)$, $b=13.279(6)$, $c=19.855(6)$ Å, $V=2419.5(16)$ Å^3, $D_c=1.720$ g·cm^{-3}, $Z=8$, μ(MoKα) $=0.152$ mm^{-1}, $F(000)=1280$。在 2580 个点中有 2194 个独立衍射点($R_{int}=0.0048$), $R=0.0588$, $wR=0.1370$, $I>2\sigma(I)$。通过 X 射线单晶衍射得到该化合物结构中包含一个 4-氨基-1,2,4-三唑阳离子和一个苦味酸阴离子。

关键词: 物理化学; 4-氨基-1,2,4-三唑苦味酸盐(4-ATPA); 晶体结构; 离子化合物; 炸药

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