Crystal structure and properties of anhydrous 5-nitroaminotetrazole

Chaofeng Zhao[1], Shenghua Li[1,2,*] and Siping Pang[1,3]

[1] School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China;
[2] Yangtze Delta Region Academy, Beijing Institute of Technology, Jiaxing 314019, China;
[3] State Key Laboratory of Explosion Science and Technology, Beijing 100081, China.

Abstract. 5-Nitraminotetrazole (5-NAT) is a high-energy and green explosive material that has attracted extensive attention due to its short synthesis steps and decomposition products consisting mainly of nitrogen and water. However, the presence of a crystal water molecule in the current crystal structure of 5-nitroaminotetrazole significantly affects its detonation performance and mechanical sensitivity. In this study, we report the successful synthesis of an anhydrous crystal form of 5-NAT through slow volatilization of an ethyl acetate solution under dry conditions. The anhydrous crystal form of 5-NAT exhibited increased density and detonation velocity compared to the monohydrate crystal form. Furthermore, quantum chemical analysis showed that the anhydrous crystal form exhibited increased sensitivity to external force stimulation due to stronger oxygen-oxygen and nitrogen-oxygen repulsion. In conclusion, the anhydrous crystal form of 5-NAT shows promise as a high-energy and green primary explosive.

1. Introduction

Energetic materials belong to a class of substances that are capable of undergoing redox reactions on their own. They are primarily composed of the four elements CHNO and are widely utilized in fields such as mining, satellites, and space exploration. In recent years, there has been an increased focus on the design and synthesis of nitrogen-rich energetic materials. [1] This is not only due to the presence of multiple high-energy N-N bonds, but also because the decomposition products are primarily nitrogen, making them more environmentally friendly. 5-nitroaminotetrazole is a type of nitrogen-rich energetic material that has garnered significant attention due to its outstanding performance and simple synthesis process. It is widely employed in the creation of energetic salts, co-crystals, and MOFs. [2] However, research on 5-nitroaminotetrazole itself has been relatively limited. This is mainly due to the fact that it possesses two active hydrogens, which can readily form hydrogen bonds with water. Furthermore, reported 5-nitroaminotetrazole crystals typically contain one molecule of water, which significantly impacts its explosive properties and practical applications. [3]

In general, the presence of water in a material affects all of its properties, and the primary method for removing water is through high temperature and low pressure. This also holds true for many energetic materials. For instance, Klapotke's group removed water from H_2bta crystals by heating them to 120°C. [4] This resulted in an increase in crystal density from 1.691 g/cm^3 to 1.861 g/cm^3, and a burst speed increase from 7792 m/s to 9120 m/s. However, with 5-nitroaminotetrazole, its thermal decomposition temperature is only 122°C, making it difficult to remove water using this method. Consequently, a crystal-free body of 5-nitroaminotetrazole has not yet been reported, which makes it challenging to analyze the relationship between its physical and chemical properties and its microstructure.

To address this issue, this paper presents a method for obtaining an anhydrous crystal of 5-nitroaminotetrazole by using slow volatilization of its ethyl acetate solution in a dry environment. Additionally, quantum chemical software such as Gaussian and Multiwfn were used to analyze the reason for 5-nitroaminotetrazole's high sensitivity after water removal.

2. Results and discussion

2.1. Synthesis and characterization

As shown in Figure 1, the monohydrate of 5-nitroaminotetrazole was obtained by the reaction of 5-nitroaminotetrazole in H_2SO_4/HNO_3 for 4 h according to previous literature reports. [3] Afterwards, the resulting product was dissolved in ethyl acetate, dried by adding anhydrous sodium sulfate and placed in a dry environment with slow evaporation to obtain the crystal of anhydrous 5-nitroaminotetrazole.

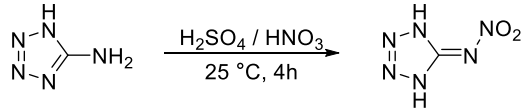

Figure 1. Synthesis of 5-nitroaminotetrazole.

*corresponding author's e-mail: lishenghua@bit.edu.cn

2.2. Physiochemical properties

2.2.1. Crystal sturcture. In order to confirm the absence of water in the prepared crystal structure, the obtained crystals were subjected to single crystal XRD tests, and the results showed that，it crystallized in the monoclinic space group, P_{21}/c, a cell contains four molecules of 5-nitroaminotetrazole with no water molecules present, as shown in the Table 1.

Table 1. Crystallographic data and parameter.

Compd	5-NAT		
Formula	$CH_2N_6O_2$	α[°]	90
Mw	130.09	β[°]	105.562
Crystal system	monoclinic	γ[°]	90
Space group	P_{21}/c	V [Å^3]	464.78(4)
a [Å]	9.3998(6)	Z	4
b [Å]	5.5105(2)	S	1.058
c [Å]	9.3144(4)	Pcalcd[g cm^{-3}]	1.859
		R(reflections)	0.0346(899)

2.2.2. Energetic properties. After confirming the absence of water molecules, we considered the differences in energetic performance between anhydrous 5-nitroimidazole and its monohydrate form. Density is the most important physical property affecting the explosive performance of energetic materials. [5] We dried the obtained crystals in a vacuum oven at 60°C overnight and conducted a true density test after confirming the basic elemental analysis. The results showed that the density of the anhydrous crystal reached 1.860 g/cm^3, which is higher than the reported density (1.80 g/cm^3) of the monohydrate form in the literature. We then used Gaussian09 to calculate the formation enthalpy of the compound and, combined with the density and formation enthalpy, [6] used EXPLO5 software to calculate the explosive performance of anhydrous 5-nitroimidazole, which was found to be significantly better than its monohydrate form (9450 m/s > 8861 m/s, 39.4 GPa > 32.3 GPa) [7]. We also obtained the friction sensitivity and impact sensitivity of the anhydrous crystal of 5-nitroimidazole through BAM standard testing, which were 10 N and 1.5 J, respectively. These values were found to be more sensitive than the monohydrate form of 5-nitroimidazole reported in the literature, as shown in Table 2.

Table 2. Sensitivities, energetic properties and detonation parameter.

Compd	d[a]	ΔH$_f$[b]	D[c]	P[d]	T[ε]	IS[f]	FS[g]
5-NAT	1.860	9450	9450	39.4	122	1.5	10
5-NAT-H_2O[h]	1.808	8849	8849	32.3	122	9	140
TNT[i]	1.648	7459	7459	23.5	290	15	353
HMX[i]	1.904	9221	9221	41.5	279	7	112

[a] Density measured by gas pycnometer (25°C), g cm^{-3}.
[b] Heats of formation, kJ mol^{-1}.
[c] Detonation velocity (calculated with EXPLO5 v6.05), m s^{-1}.
[d] Detonation pressure (calculated with EXPLO5 v6.05), GPa.
[e] Decomposition temperature under N_2, °C.
[f] Impact sensitivity, J.
[g] Friction sensitivity, N.
[h] Ref [3].
[i] Ref [8].

2.3. Theoretical Calculation Analysis

We visualized the intermolecular interactions between 5-NAT-H_2O and 5-NAT by Mutiwfn and VMD [9-10], as shown in Figure 2, where blue color indicates attraction and red color indicates repulsion, and it can be seen that the hydrogen bonding around the anhydrous 5-nitroaminotetrazole molecules is weaker compared to the crystals with water, for HB2 and HB3 in green color. according to some previous reports in the literature, hydrogen bonding can effectively improve the molecular sensitivities [11], which may be the reason for the greater sensitivity of 5-NAT.

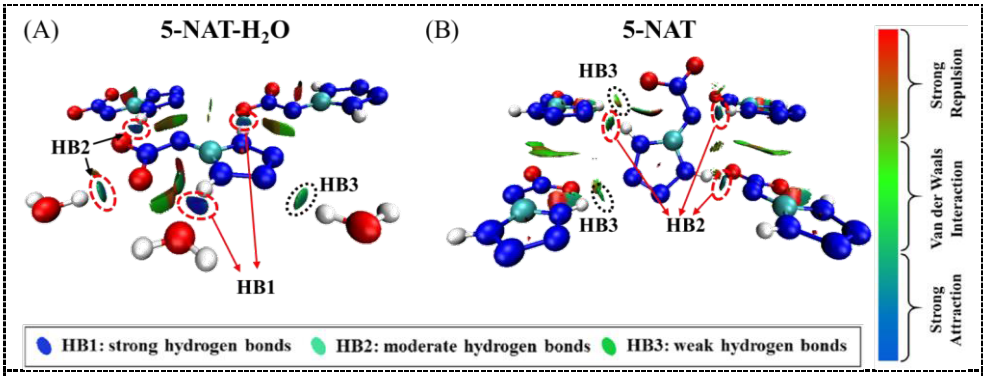

Figure 2. NCI plots of gradient iso surfaces for 5-NAT-H_2O (A) and 5-NAT (B).

To further confirm the strength of hydrogen bonding and the interaction between the elements within the two crystals, we performed Hirthfiled surface analysis, as shown in Figure 3 [12], and the results show that there are stronger N-H and O-H interactions in the monohydrate crystals and stronger O-N and N-N interactions in the anhydrous 5-NAT crystals, which further confirms the weaker hydrogen bonding in the crystal-free body of 5-NAT. Also, the bottom view shows that there are interactions between the crystal-free layers of 5-NAT, which may be another reason for its sensitivity.

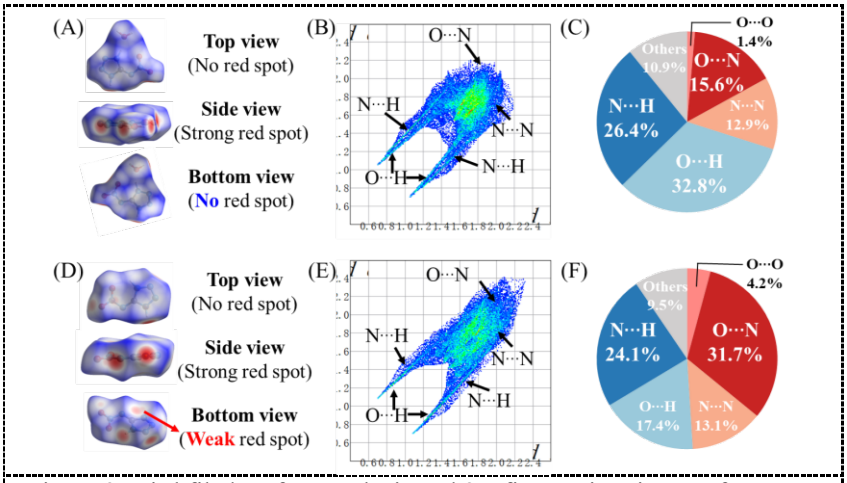

Figure 3. Hirthfiled surface analysis and 2D fingerprint picture of 5-NAT-H_2O(A-C) and 5-NAT(D-F).

3. Conclusion

In conclusion, we have successfully prepared an anhydrous crystal-free form of 5-NAT and calculated that it exhibits a higher detonation performance (D = 9450 m/s) and lower sensitivity (IS = 1.5 J) than HMX. Due to its shorter synthesis steps, lower cost, and environmentally friendly product, 5-NAT has the potential to be used as a green primary explosive.

References

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12. The program was downloaded via the following website: https://community.chocolatey.org/packages/crystalexplorer.