Higher performing and less sensitive CN_7^- -based high-energy-density material

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ABSTRACT The highest nitrogen-containing binary C-N anion, 5-azido-tetrazolate (CN_7^-), has attracted significant attention owing to its high-energy content. Due to its relative instability and high sensitivity, it is an ongoing challenge to develop more stable and less sensitive novel materials based on CN_7^- . Towards this goal, we have stabilized the CN_7^- anion without compromising its energetic performance by formation of its NH_3OH^+ salt containing an additional NH_2OH molecule, $[\text{NH}_3\text{OH}][\text{CN}_7][\text{NH}_2\text{OH}]$ (2). It possesses the best detonation performance and the lowest mechanical sensitivity among all known CN_7^- -based materials. The structure-property relationship was elucidated through a careful investigation of the noncovalent interactions in the crystal lattice and the important role of the NH_2OH moiety. In addition, the structurally related compound $[\text{NH}_3\text{OH}][\text{CN}_7]$ (1) was also studied.

Keywords: high nitrogen, binary C-N anion, hydrogen bonds, high-energy-density material

INTRODUCTION

Retaining the energetic performance of a material while enhancing its stability and safety as well as its synthetic feasibility is an ongoing challenge in energetic materials research. In that regard, nitrogen-rich (N-rich) compounds have attracted much attention owing to their high energy density, diverse structures, challenging synthetic preparations and remarkable application potentials [1–8]. Their energy arises from the breaking of weak N–N single and N=N double bonds and the formation of the highly energetic $\text{N}\equiv\text{N}$ bonds. The best-known systems with 100% nitrogen content are N_2 , N_3^- , N_5^- , and N_5^+ (Scheme 1) [9–13]. Except for N_2 , these molecules are thermodynamically unstable and can be stabilized using metal-nitrogen or hydrogen-nitrogen noncovalent interactions [14–17].

In addition to all-N systems, binary carbon-nitrogen (C-N) anions with high nitrogen content have also garnered much attention as they possess notable energetic properties while also affording potential synthetic design strategies [18,19]. These anions are generally based on the tetrazole moiety (Scheme 1), as seen in 5,5'-bistetrazolate ($\text{C}_2\text{N}_8^{2-}$), 5,5'-azotetrazolate ($\text{C}_2\text{N}_{10}^{2-}$), and so on [20–22]. Among these, 5-azido-tetrazolate anion (CN_7^-) is expected to have the highest contribution to an energetic material due to its high heat of formation, $477.6 \text{ kJ mol}^{-1}$ (4.34 kJ g^{-1}), which results from its high nitrogen content of 89.09% [23]. The importance of the high nitrogen content is demonstrated by $[\text{N}_2\text{H}_5][\text{CN}_7]$, which, despite its low density of 1.568 g cm^{-3} , exhibits a very high detonation velocity of 9231 m s^{-1} . However, all reported CN_7^- compounds are extremely sensitive to external stimuli, with impact sensitivities lower than 1 J and friction sensitivities lower than 5 N, limiting their use in practical applications [24–26]. Therefore, reaching an ideal balance between the detonation performance and mechanical sensitivity remains a challenge in CN_7^- -based energetic materials.

Solvent molecules can sometimes generate interesting property changes in energetic materials. Crystal water plays an important role to establish hydrogen bonds, thus helping stabilize the molecule [27–29]. However, water molecules decrease the density and heat of formation, which results in lower detonation performance. Compared with water molecules, hydroxylamine possesses a high heat of formation, thus enhancing detonation performance. At the same time, mechanical sensitivity can be reduced with extensive hydrogen bonds generated by hydroxylamine [30,31]. It seems that the formation of an NH_2OH adduct can be an effective strategy to balance the detonation performance and mechanical sensitivity of CN_7^- systems.

Herein we report a novel energetic adduct, $[\text{NH}_3\text{OH}]$ -

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Scheme 1 Four all-N species and representative C-N anions.

[CN₇][NH₂OH] (**2**), which exhibits the best detonation performance and the lowest mechanical sensitivity among all CN₇[−] compounds reported to date. For comparison, the structurally related compound [NH₃OH][CN₇] (**1**) was also studied.

EXPERIMENTAL SECTION

Caution: the CN₇[−] compounds are highly powerful energetic materials. Safety protections are strongly encouraged in all operations.

Synthesis of [NH₃OH][CN₇] (**1**)

Aqueous hydroxylamine solution (50%; 0.305 mL, 5 mmol) was added to the solution of 5-azidotetrazole (0.555 g, 5 mmol) in water. After 30 min, the water was removed using a rotary evaporator to get a white solid, which was then washed with cold ether to get [NH₃OH][CN₇] (0.40 g, 55.0% yield). Crystals suitable for X-ray diffraction were obtained by slow evaporation in tetrahydrofuran. ¹H NMR (DMSO-d₆, 500 MHz): δ 8.75 (s) ppm. ¹³C NMR (DMSO-d₆, 500 MHz): δ 158.3 ppm. IR (KBr): 3144, 2915, 2687, 2037, 1668, 1583, 1502, 1405, 1174, 999, 976, 787, 651, 623 cm^{−1}. Elemental analysis: calculated for CH₄N₈O (144.10): C 8.34, H 2.80, N 77.76%; found C 8.20, H 2.67, N 77.87%.

Synthesis of [NH₃OH][CN₇][NH₂OH] (**2**)

Aqueous hydroxylamine solution (50%; 0.732 mL, 12 mmol) was added to the solution of 5-azidotetrazole (0.555 g, 5 mmol) in water. After 30 min, the water was removed very slowly using a rotary evaporator to get crystalline [NH₃OH][CN₇][NH₂OH] (0.37 g, 41.8% yield). ¹H NMR (DMSO-d₆, 500 MHz): δ 8.21 (s) ppm. ¹³C NMR (DMSO-d₆, 500 MHz): δ 158.8 ppm. IR (KBr): 3001, 2955, 2141, 1560, 1471, 1447, 1346, 1198, 1112, 938, 809, 740, 603 cm^{−1}. Elemental analysis: calculated for CH₇N₉O₂ (177.13): C 6.78, H 3.98, N 71.17 %; found C 6.65, H 4.08, N 71.30 %.

RESULTS AND DISCUSSION

Preparation

The preparation of these two CN₇[−] energetic compounds is shown in **Scheme 2**. The reaction of cyanogen azide with sodium azide leads to the formation of 5-azido-1H-tetrazole (CN₇H) [32]. The addition of one equivalent of hydroxylamine (NH₂OH) yields **1**. By a simple increase to two equivalents of hydroxylamine, the hydroxylamine adduct (**2**) was obtained. Both compounds were structurally characterized by IR spectroscopy, multinuclear NMR spectroscopy, and element analysis.

Scheme 2 Syntheses of [NH₃OH][CN₇] (**1**) and [NH₃OH][CN₇][NH₂OH] (**2**).

Crystal structures

The solid-state molecular structures of **1** and **2** were investigated by using single-crystal X-ray diffraction and their structures are shown in Fig. 1a and c, respectively. The structure refinement details are given in Table 1, while the bond lengths and angles are given in Tables S1 and S2 (Supplementary information).

Both compounds crystallize in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The N–N bond lengths for **1** and **2** are comparable, in the range of 1.121–1.360 and 1.121–1.356 Å, respectively. The bond angles for **1** and **2** are also similar, which can be seen from Table 2. The azido groups and the tetrazole rings are almost coplanar, with torsion angles N1–C1–N5–N6 of 0.89° for **1** and 6.50° for **2**. Their crystal densities are 1.626 g cm^{-3} for **1** (172 K) and 1.574 g cm^{-3} for **2** (173 K). The packing and hydrogen-bonding interactions are presented in Fig. 1b and d. With the hydrogen bonds, compound **1** is shown to exhibit a 2D structure, while **2** is a 3D structure with NH_2OH molecules (highlighted in the green circles) acting as linkages. It is worth noting that this system represents the first example of dimensional transformation of hydrogen-bonded structures in the field of energetic materials.

To further investigate the role of NH_2OH in the structure, the hydrogen bonds around CN_7^- in **1** and **2** were investigated. As shown in Fig. 2a and b, there are three pairs of hydrogen bonds around CN_7^- in **1**, and no

hydrogen bonds generated by the azido group. For **2**, there are six hydrogen bonds around CN_7^- and two pairs of hydrogen bonds involving the azido group. The strength of the hydrogen bonds can be distinguished through their different colors (Fig. S1, Supplementary information). In general, the darker the color, the stronger the hydrogen bonds. The details of hydrogen bonds (bond angles and lengths) are provided in Tables S3 and S4. These azido hydrogen bonds in **2** arise from the NH_2OH molecules, indicating the importance of NH_2OH in connecting the 3D structure. In addition, the hydrogen bonds around NH_2OH were also studied (Fig. 3). There are six pairs of hydrogen bonds around NH_2OH , in which, three pairs are from CN_7^- , two pairs are from NH_2OH molecules, and one pair from NH_3OH^+ , respectively. All the details of hydrogen bonds (bond angles and lengths) are provided in Fig. 3 and Table 3.

Physical property and energetic performance

To investigate how the introduction of NH_2OH and its respective structural changes have affected the physico-chemical properties, the density, thermal stability, heat of formation, detonation performance, and mechanical sensitivity of these two compounds were studied.

Comparison with other CN_7^- -based materials

As can be seen from Table 4, owing to the CN_7^- moiety, both $[\text{NH}_3\text{OH}][\text{CN}_7^-]$ and $[\text{NH}_3\text{OH}][\text{CN}_7^-][\text{NH}_2\text{OH}]$ ex-

Figure 1 (a) and (c) Crystal structures for **1** and **2**; (b) and (d) 2D and 3D structures for **1** and **2**, both viewed down the a axis. The transformation from 2D to 3D and NH_2OH moieties in green circles are highlighted.

Table 1 Crystallographic data of compounds **1** and **2**

Compound	1	2
Formula	CH ₄ N ₈ O	CH ₇ N ₉ O ₂
Molecular weight	144.12	177.16
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> ₂ ₁ / <i>c</i>	<i>P</i> ₂ ₁ / <i>c</i>
<i>a</i> (Å)	3.6968(6)	3.8011(6)
<i>b</i> (Å)	20.973(3)	25.626(4)
<i>c</i> (Å)	7.6825(9)	7.7480(13)
α (°)	90	90
β (°)	98.731(4)	97.924(6)
γ (°)	90	90
<i>V</i> (Å ³)	588.75(14)	747.5(2)
<i>Z</i>	4	4
<i>T</i> (K)	172	173
ρ_{calcd} (g cm ⁻³)	1.626	1.574
μ (mm ⁻¹)	0.138	0.138
<i>F</i> (000)	296	368
θ range (°)	3.31–24.64	3.09–24.92
Data/restraints/parameters	6499/718/715	1384/6/130
GOF on <i>F</i> ²	1.054	1.030
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.0516	0.0617
<i>wR</i> (<i>F</i> ²)	0.1069	0.1461

Table 2 N–N bond lengths and selected bond angles of compounds **1** and **2**

Compound	1	2
Bond lengths (Å)		
N1–N2	1.360(3)	1.356(4)
N2–N3	1.308(3)	1.318(4)
N3–N4	1.353(3)	1.349(4)
N5–N6	1.255(4)	1.282(4)
N6–N7	1.121(4)	1.121(5)
Bond angles (°)		
N1–C1–N5	126.8(3)	126.7(3)
C1–N5–N6	113.9(2)	112.0(3)
N5–N6–N7	172.5(3)	174.6(4)

hibit very high nitrogen contents of 77.8% and 71.2%, respectively. Due to the introduction of NH₂OH, the nitrogen content of compound **2** is not very high when compared with other CN₇[−]-based materials; however, NH₂OH affords this adduct with the highest oxygen content in all CN₇[−] materials, with the value of 18.1%, which holds the promise to yield better detonation per-

Figure 2 Hydrogen bonds (NCI analysis) around CN₇[−] for compounds **1** (a) and **2** (b). The NH₂OH molecules are highlighted in the green circles.

formance. The densities of **1** and **2** measured by a gas pycnometer at room temperature are 1.60 and 1.55 g cm^{−3}, respectively. The introduction of NH₂OH leads to the decrease of density, the main reason is the low density of hydroxylamine. Although compound **2** has a lower density, this value is still higher than that of [CN₄H₇][CN₇] and [N₂H₅][CN₇]. Owing to the high enthalpy of the CN₇[−] unit (4.34 kJ mol^{−1}), the heats of formation for these two compounds, calculated by Gaussian 09 [33], are very high with values of 4.16 and 4.14 kJ g^{−1}, respectively (the calculation details are given in Schemes S1 and S2, Supplementary information). They are in the range of other CN₇[−] organic salts having values ranging from 3.47 kJ g^{−1} for [CN₄H₇][CN₇] to 4.92 kJ g^{−1} for [N₂H₅][CN₇]. The thermal stability of compounds **1** and **2** was evaluated by differential scanning calorimetry (DSC), and their onset decomposition temperatures are 93 and 150°C (Fig. S2), respectively. It must be noted that the introduction of NH₂OH causes a dramatic improvement of 57°C in thermal stability, which may result from the formation of the 3D structure.

With the values of density, heats of formation, and molecular formula, the detonation performance of [NH₃OH][CN₇] and [NH₃OH][CN₇][NH₂OH] were evaluated by using EXPLO 5 [34]. The results indicate that **2** has a detonation velocity of 9307 m s^{−1} and a detonation pressure of 32.5 GPa, which ranks it the best among all the energetic CN₇[−] compounds (Fig. 4). The excellent energetic performance of [NH₃OH][CN₇][NH₂OH] can be explained by its high heats of formation and its highest

Figure 3 Hydrogen bonds around NH_2OH .

Table 3 Details about the hydrogen bonds around NH_2OH

D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)
O1–H1...N1''	0.811	2.012	2.823	178.10
N8–H8A...N5'	0.858	2.612	3.464	171.92
N8–H8B...N7	0.857	2.637	3.384	146.42
N9–H9C...N8	0.913	1.940	2.835	166.18
N8–H8B...O1''	0.857	2.494	3.214	142.13
N8'–H8B'...O1	0.857	2.494	3.214	142.13

Table 4 The physical properties of compounds **1** and **2** compared with other CN_7^- salts

Compound	N ^a (%)	O ^b (%)	d^c (g cm ⁻³)	ΔH_f^d (kJ g ⁻¹)	T_d^e (°C)
1	77.8	11.1	1.60/1.63	4.16	93
2	71.2	18.1	1.55/1.57	4.14	150
$[\text{N}_2\text{H}_5][\text{CN}_7]^f$	88.1	0	1.52/1.57	4.92	136
$[\text{NH}_4][\text{CN}_7]^f$	87.5	0	1.58/1.61	4.22	157
$[\text{CN}_4\text{H}_7][\text{CN}_7]^f$	79.6	0	1.50/1.52	3.47	159

a) Content of nitrogen. b) Content of oxygen. c) Left: density measured by a gas pycnometer at 298 K; right: crystal density at tested temperatures. Attention: Compounds **1** and **2** were tested at 172 and 173 K, respectively. $[\text{N}_2\text{H}_5][\text{CN}_7]$ was tested at 100 K, while $[\text{NH}_4][\text{CN}_7]$ and $[\text{CN}_4\text{H}_7][\text{CN}_7]$ were tested at 200 K. d) Calculated heats of formation. e) Thermal decomposition temperature (DSC, onset, 5°C min⁻¹). f) Ref. [23].

oxygen content in all CN_7^- -based materials. Compared with oxygen-free CN_7^- energetic materials reported, the oxygen atoms in this adduct play an important role in improving the detonation performance. The extra NH_2OH molecule provides an additional oxygen atom to badly under-oxidized molecules, which results in its best energetic performance among all CN_7^- energetic materials.

The mechanical sensitivity of these compounds was determined by standard BAM methods (Tests were conducted according to Ref. [35]). It should be noted that the mechanical sensitivity of salts $[\text{N}_2\text{H}_5][\text{CN}_7]$, $[\text{NH}_4][\text{CN}_7]$, and $[\text{CN}_4\text{H}_7][\text{CN}_7]$ were retested, because this kind of data can vary strongly depending on the apparatus and operator. Compound **2** exhibits an impact sensitivity of

10 J and friction sensitivity of 140 N, which indicates that this adduct possesses the lowest mechanical sensitivity among all CN_7^- energetic compounds (Fig. 4). All the energetic properties of these compounds are summarized in Table S5.

Comparison with the state-of-art RDX and HMX

Due to the impressive energetic performance of $[\text{NH}_3\text{OH}][\text{CN}_7][\text{NH}_2\text{OH}]$, the detonation performance and mechanical sensitivity of this compound were also compared with the state-of-art hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). As can be seen from Table 5, **2** exhibits higher detonation velocity (D : 9307 m s^{-1}) than RDX (D : 8795 m s^{-1}) and HMX (D : 9144 m s^{-1}). However, its detonation pressure is lower than those of RDX and HMX. The values of mechanical sensitivities also indicate that this adduct (impact sensitivity (IS): 10 J;

friction sensitivity (FS): 140 N) is less sensitive than RDX (IS: 7.4 J; FS: 120 N) and HMX (IS: 7.4 J; FS: 120 N).

Hirshfeld surface analysis

Since compound $[\text{NH}_3\text{OH}][\text{CN}_7][\text{NH}_2\text{OH}]$ displays greater stability (higher thermal stability and lower mechanical sensitivity) than $[\text{NH}_3\text{OH}][\text{CN}_7]$, the 2D fingerprints of these two compounds and the associated Hirshfeld surfaces were analyzed in order to better understand the differences in stability. As shown in Fig. 5a and b, compound **2** possesses stronger close interactions than **1**, with the majority being hydrogen-bonding interactions. Quantifying this in Fig. 5e and f, 64.0% of interactions in **2** are $\text{N}\cdots\text{H}$ and $\text{O}\cdots\text{H}$ bonds, while for **1** this value is 57.6%, which is 6.4% lower than that of **2**. Based on the study of crystal structures and noncovalent interactions, we propose that the introduction of NH_2OH and the associated increase in hydrogen-bonding inter-

Figure 4 Comparison of energetic performance (detonation velocity, detonation pressure, impact sensitivity, and friction sensitivity) of compounds **1** and **2** with N_2H_5^+ , NH_4^+ , and CH_4H_7^+ salts.

Table 5 Energetic properties of $[\text{NH}_3\text{OH}][\text{CN}_7][\text{NH}_2\text{OH}]$ compared with RDX and HMX

Compound	D^a (m s^{-1})	P^b (GPa)	IS ^c (J)	FS ^d [N]
2	9307	32.5	10	140
RDX ^e	8795	34.9	7.4	120
HMX ^e	9144	39.2	7.4	120

a) Detonation velocity. b) Detonation pressure. c) Impact sensitivity. d) Friction sensitivity. e) Ref. [31].

Figure 5 Hirshfeld surfaces of **1** (a) and **2** (b); fingerprint plots for **1** (c) and **2** (d); individual atomic contact percentage contribution to the Hirshfeld surfaces of **1** (e) and **2** (f).

actions are responsible for the improvement of the thermal stability and mechanical sensitivity.

CONCLUSIONS

In summary, for the formation of energetic adducts, an effective strategy to improve the overall performance of the material, was used to stabilize the CN_7^- anion. By applying this method, a promising high-energy-density material, $[\text{NH}_3\text{OH}][\text{CN}_7][\text{NH}_2\text{OH}]$ (**2**), was prepared and structurally characterized by single-crystal X-ray diffraction. The introduction of NH_2OH into the $[\text{NH}_3\text{OH}][\text{CN}_7]$ framework (**1**) extends the 2D structure (**1**) to 3D (**2**), increases the thermal stability greatly from 93 to 150° C, and improves the mechanical sensitivity from 1 J and 5 N to 10 J and 140 N due to the increase in hydrogen-bonding interactions. This is supported by the non-covalent intermolecular interactions (NCI) and a Hirsh-

feld surfaces analysis. It should be noted that **2** exhibits the highest oxygen content, the best detonation performance, and the lowest mechanical sensitivity among all studied CN_7^- materials. Furthermore, **2** also shows better detonation velocity and lower mechanical sensitivity than the powerful explosive HMX and RDX. This work, therefore, gives insight into binary C-N anions, hydrogen-bonding interactions, and energetic materials (e.g., energetic adducts).

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting information are available in the online version of the paper.

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更加高能低感的 CN_7^- 高能量密度材料

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摘要 具有最高氮含量的二元C-N阴离子, 叠氮四唑离子 —CN_7^- , 因其极高的能量密度受到广泛关注, 但由于 CN_7^- 的不稳定性, 以此合成新型低感的高能量密度材料存在极大难度. 本文制备出一种新型高能加合物 $[\text{NH}_3\text{OH}][\text{CN}_7][\text{NH}_2\text{OH}]$, 该化合物在所有已知的 CN_7^- 化合物中表现出最好的爆轰性能与最低的机械感度. 为了探索 NH_2OH 分子对含能化合物性质的影响, 我们合成了另一种含能盐 $[\text{NH}_3\text{OH}][\text{CN}_7]$, 并对其与加合物 $[\text{NH}_3\text{OH}][\text{CN}_7][\text{NH}_2\text{OH}]$ 的结构与性能进行了比较. 结果表明 NH_2OH 及其氢键作用对于改善 CN_7^- 的热稳定性和机械感度起到了重要作用.