Study on the Crystal Structure and Hygroscopicity of Ammonium Dinitramide

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Ammonium dinitramide (ADN), $NH_4N(NO_2)_2$, is one of the most promising oxidizing components of future solid propellant formulations, because it is eco-friendly and more energetic and has no plume signature because there is no chlorine in its molecular structure. The hygroscopicity of the ADN crystal, which is more severe than that of ammonium perchlorate (AP), seriously affects its use. This quite different behavior is possibly associated with their structures. The X-ray single-crystal diffraction data show that vast hydrogen bonds link the ADN structure. The three-dimensional structure of ADN joined by the fourth longer hydrogen bond is an unusual two-fold three-dimensional interpropagation network structure, and the hydrogen bonds in the ADN crystal are much shorter than that in AP because of the special structure. The hydrogen bonds between ADN and water are assayed by IR spectroscopy. Differential scanning calorimetric (DSC) analysis of moisture-containing ADN and AP crystals also confirm that, because of the stronger hydrogen bond between ADN and water molecules, large amounts of bound water are present in the ADN besides some unbound water. All of this evidence suggests that the special hydrogen bonds among ADN and stronger hydrogen bonds between ADN and water molecules could possibly be the main reason of the severe hygroscopicity of ADN.

1. Introduction

Ammonium dinitramide (ADN), $NH_4N(NO_2)_2$, is a relatively newly discovered energetic ionic compound, which is of considerable interest as a potential eco-friendly oxidizing component of future solid propellant formulations. In comparison with ammonium perchlorate (AP), the work-horse oxidizer used in modern rocket propulsion systems, ADN possesses both the desirable properties of lower sensitivity of ammonium salts and the nitramine high performance characteristics. In addition ADN is halogen-free and does not produce the toxic HCl acidic plume (generated during AP combustion), an acid known to be detrimental to the earth's ozone layer. ADN has thus been considered as a replacement oxidizer for AP in propellant formulations to achieve both the elimination of hydrogen chloride from the combustion products and an increase in energy output.[1−7] According to a literature report, the space shuttle can lift 8 % more mass into orbit by using ADN in comparison to AP.[8] Furthermore, perchlorate is a known environmental contaminant, which acts pharmacologically as a competitive inhibitor of thyroidal iodide uptake in mammals and inhibits thyroid activity and alters gonadal differentiation in developing *Xenopus laevis*.[9,10]

Hygroscopicity describes the water absorption capacity of a material from the environment. The moisture in ADN which makes the ADN crystal easy to cake seriously affects its normal usage; in addition the water present in ADN can reduce the intensity and the aging properties of the propellant.[11] Badgujar[8] suggested that the smooth development of large-scale propellants based on ADN could be hampered in the USA due to its severe hygroscopicity as well as its low melting point (~ 90 °C) and decomposition temperature (123 °C). However, research on the hygroscopicity properties of ADN has seldom been reported. For this reason, we initiated the present study in which the hygroscopicity of ADN has been investigated, and the hydrogen bonds among ADN and between ADN and water are studied in detail. The main purpose of this study is to understand the relationship between hygroscopicity and the molecular structure of ADN.

2. Experimental Section

2.1. Materials. The following chemicals used in this study were synthesized in the laboratory. ADN was prepared by nitration of $NH(SO_3NH_4)_2$ followed by the neutralization of dinitramidic acid with ammonia.[12] The reaction mixture containing ADN was absorbed by active carbon in an elution column and then desorbed with acetone. The acetone solution was evaporated and ADN precipitated.

AP was synthesized from sodium perchlorate and ammonium chloride at 80 °C.[13] The coarse crystal AP was then obtained by cooling the reaction mixture. After dissolution and recrystallization of the coarse crystal, the sample was obtained.

After purification, the purities of the obtained ADN and AP were both more than 99.5 %. The purity of AP was tested by titration (MIL-A-82667/2, 1977), and the purity of AP was tested by UV spectroscopy.[12]

The melting point of ADN is 91.5 °C. It begins to pyrolyze at 127 °C and to decompose completely up to 200 °C.[14]

The sensitivity data of ADN are collected in Table 1. Obviously the sensitivity of ADN is related to its state. The needle-like crystal and aggregation are more sensitive to impact than powder and column-like crystals.[15]

2.2. Methods. The hygroscopicity of ADN and AP under different experimental conditions was determined by measuring

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Table 1. Experimental Results for ADN Sensitivity[15]

test	aggregation	needle-like crystal	powder	column-like crystal
ignition temperature, °C	194	220	202	194
drop hammer test, level	1	1	3	3
friction test, level	6	6	7	7
electrostatic spark test (E50), J	3.5	4.3	2.7	3.7

the weight change at different relative humidities (RH), time, and a temperature of 25 °C using a Mettler Toledo AB204-L electronic balance.

X-ray Single-Crystal Diffraction. Data collection was performed with a Bruker Smart Apex II CCD diffractometer equipped with a graphite monochromatic Mo Kα radiation by using a φ/ω scan technique at room temperature. The structures were solved by direct methods using the SHELXS-97 software.

Fourier Transform Infrared Spectroscopy (FTIR). FTIR spectra were recorded on a Bruker Vertex70 FTIR spectrometer employing a digital detector for improving sensitivity and veracity. To reduce the impact of moisture, we also compared different sample preparation methods.

Potassium Bromide Discs. ADN and KBr powders were ground in an agate mortar for about 10 min and pestled to get a very fine powder. This powder was then placed in a wide-mouth weighing bottle and dried at 85 °C for about 24 h. The sample was then placed in a small die and pressed mechanically until the potassium bromide disk was translucent.

Mull Technique. ADN was mixed with fluorocarbon oil and then ground in an agate mortar to give a paste. Several drops of this paste were applied between KBr flat plates for infrared scanning.

Differential Scanning Calorimetry (DSC). DSC measurements were performed using a TA DSC2010 with liquid nitrogen cooling. The measuring cell was purged with nitrogen (50 $\text{mL}\cdot\text{min}^{-1}$). The sample weight was approximately 3 mg. The temperature was adjusted using a three-point calibration with indium (China national standard, GBW (E) 130182), Sn (GBW (E) 130183), and naphthalene (GBW (E) 13232). All reported temperatures are average values of two measurements, deviating at the most by 0.4 °C.

The moisture or water content was determined by a Mettler Toledo volumetric Karl Fischer compact titrator V20. The measuring range is from 100 $\text{mg}\cdot\text{kg}^{-1}$ to 100 %.

3. Results and Discussion

3.1. Hygroscopicity of ADN and AP. The hygroscopicity of ADN and AP are presented in Figures 1 and 2. It is observed in Figure 1a that the equilibrium moisture content of ADN could not be achieved even after 1200 min when the RH values were 65 % and 80 %. Similar phenomena were also observed by Wan.[16] He reported that the saturated water adsorption content of ADN at 60 % RH and 40 °C was about 49 % (aqueous solution), which was much higher than that of AP shown in Figure 2. It also took a much longer time to reach the equilibrium water content of ADN than that of AP under the same experimental conditions. Moreover, the water content of ADN slightly decreases at 45 % RH because its critical RH is 55.2 %.[17] The conditions at RH 52 % are completely similar with those at RH 45 %, so the two lines overlap.

Figure 1b shows that, at both 65 % and 80 % RH, the water content in ADN was higher than 0.4 % in less than 20 min; in 60 min the water content reached about 1.4 % and 1.8 %, respectively. In comparison, Figure 2 shows that the water content in AP at different RH in 60 min were all below 0.12 %. Therefore, it is concluded that the moisture absorption rate of ADN was faster than that of AP. The solubility of ADN in water is also higher than that of AP (ADN 69.3 % and AP 10.7 % at 0.0 °C).[17,18] All of these indicate that, though ADN and AP are both ammonium salts, they behave quite differently in terms of their hygroscopic properties. Therefore, the following exploratory work was conducted to better understand this difference.

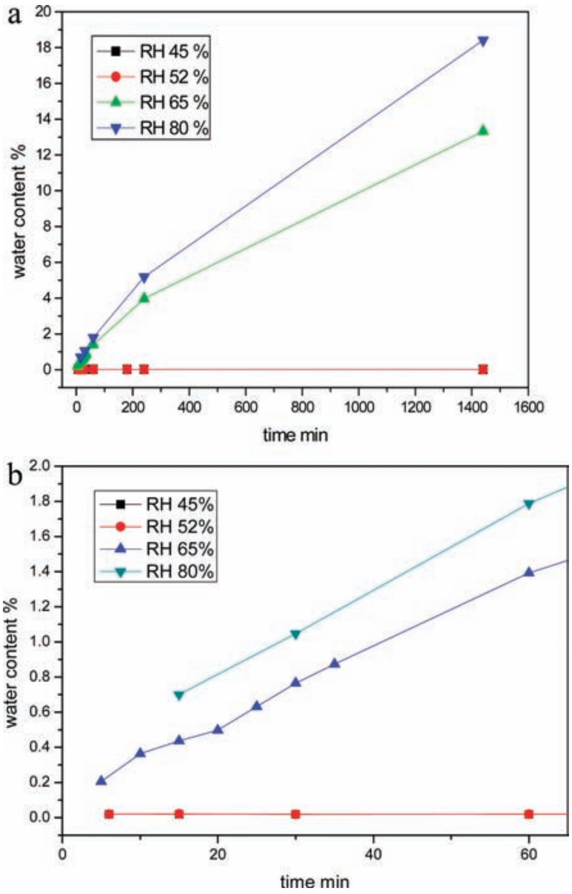


Figure 1. (a) Dependence of water content of ADN on time at different RH values and 25 °C. (b) Partial enlargement of drawing a.

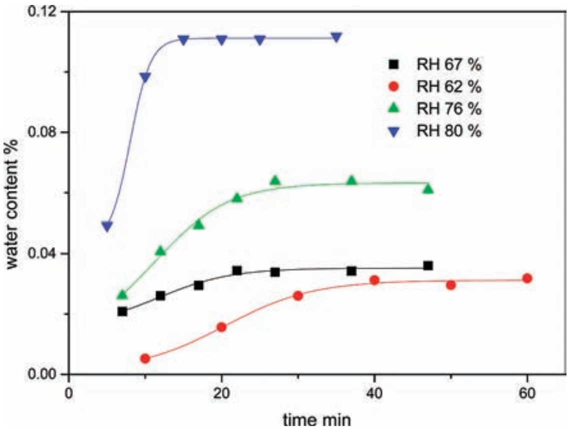


Figure 2. Dependence of water content of AP on time at different RH values and 25 °C.

3.2. Crystal Structure of ADN and AP. A crystal with dimensions of 0.38 mm × 0.23 mm × 0.12 mm was put on a Bruker Smart Apex-II CCD diffractometer equipped with a graphite-monochromatic Mo Kα radiation ($\lambda = 0.071073$ nm) by using a φ/ω scan mode at 293(2) K. Out of the total 3166 reflections collected in the range of $3.00° \leq \theta \leq 25.49°$, 850

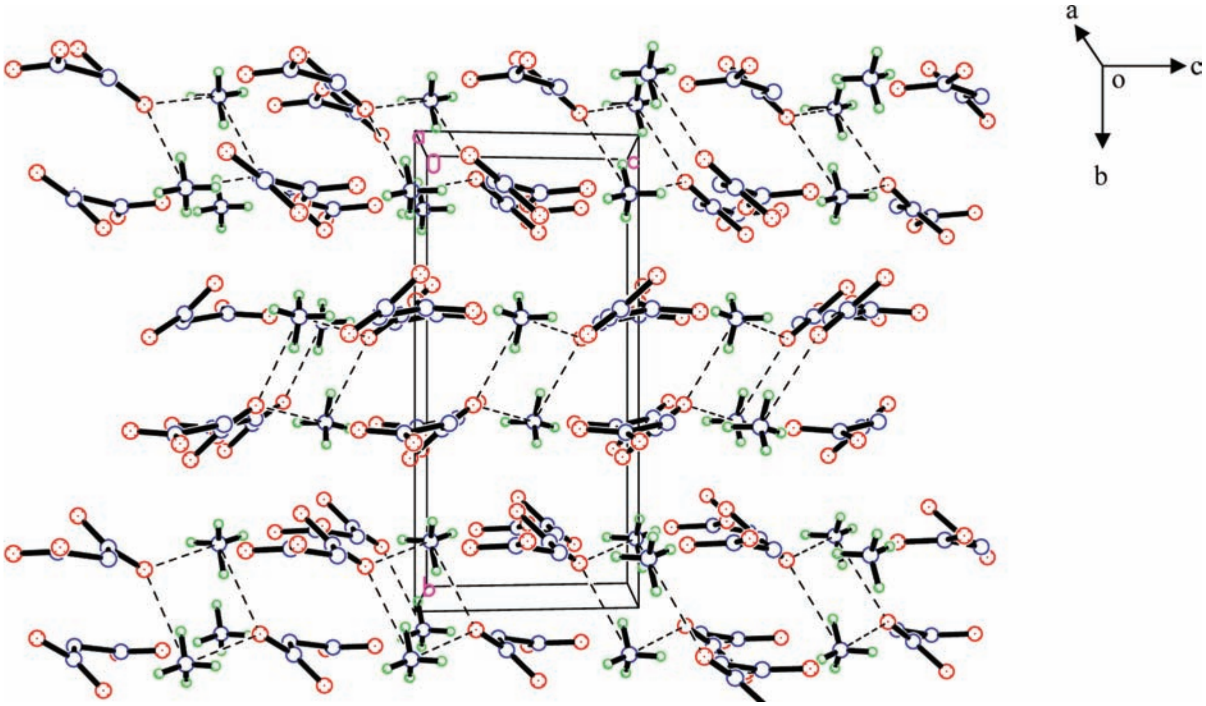


Figure 3. Hydrogen-bonding interactions among ADN, showing that the chain is formed along the *c* axis.

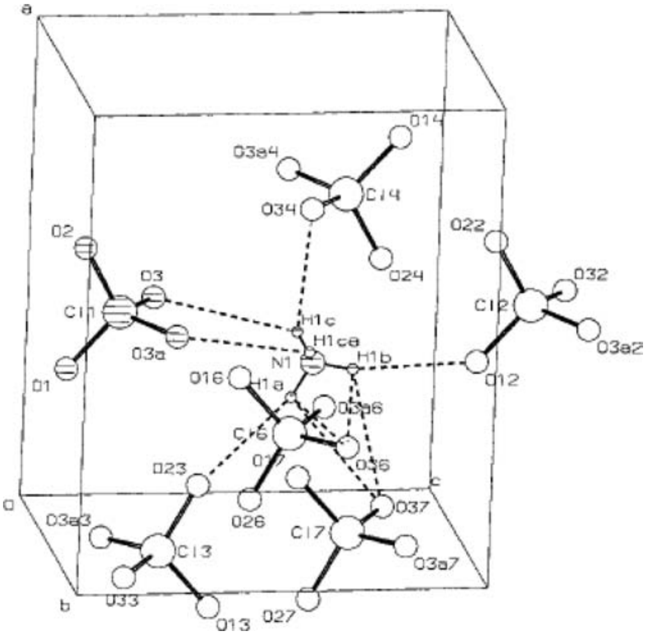


Figure 4. Perspective view of AP, showing atomic labeling (shaded atoms) and the hydrogen bonds from the ammonium ion (the symmetry equivalent H-bond of H_{1c}-O_{34} starting from H_{1ca} is omitted for clarity).[19]

Table 2. Crystal Data and Summary of Intensity Data

formula	$NH_4N_3O_4$[20]	NH_4ClO_4[19]
M	124.07	117.49
crystal system	monoclinic	orthorhombic
space group	$P2_1/c$	*Pnma* (no. 62)
a, Å	6.914(1)	9.229(1)
b, Å	11.787(3)	5.816(1)
c, Å	5.614(1)	7.461(1)
V, Å^3	450.0(2)	400.48(10)
Z	4	4
D_c, mg·m^{-3}	1.831	1.949
μ, mm^{-1}	0.187 (Mo Kα)	0.8 (Mo Kα)
T, K	496	293
crystal size	0.38 × 0.23 × 0.12	0.08 × 0.20 × 0.25
wavelength, Å	0.71073	0.71070
max, min peak, e·Å^{-3}	0.207, −0.186	−0.34, 0.31

Table 3. Hydrogen Bonds in ADN

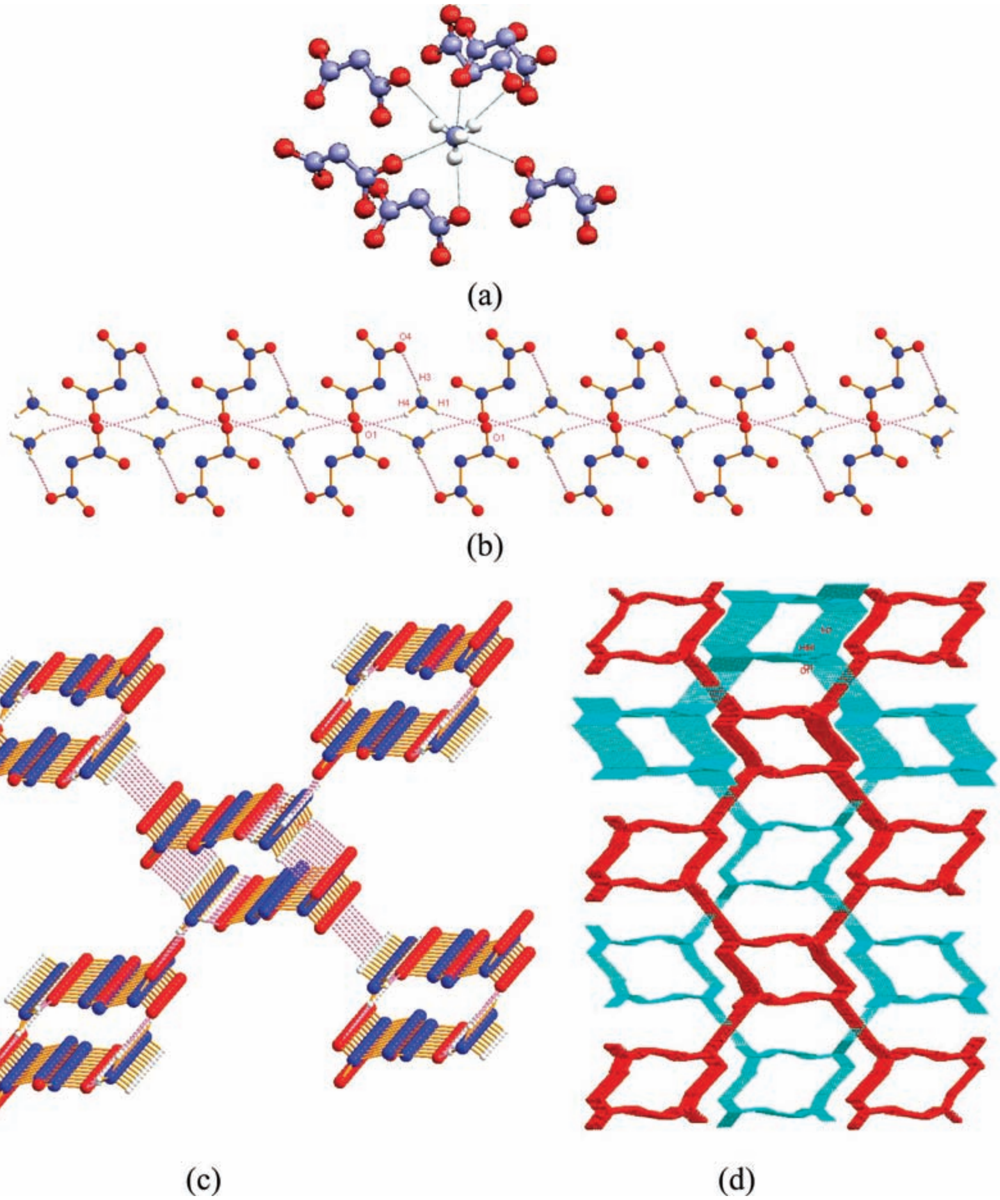
D−H···A	d(D−H)	d(H···A)	d(D···A)	<(DHA)
N(4)−H(1)···O(1)#1	0.84	2.21	3.014(2)	160.9
N(4)−H(3)···O(4)#3	0.86	2.14	2.948(2)	155.6
N(4)−H(4)···O(1)#5	0.85	2.24	3.039(2)	156.7
N(4)−H(2)···O(3)#2	0.84	2.37	3.179(2)	161.0

were independent with R_{int} = 0.0257, of which 715 were considered to be observed ($I > 2\sigma(I)$) and used in the succeeding refinement. The crystal structure was solved by a direct method using the SHELXS-97 program. Corrections for *Lp* factors and empirical adsorption adjustment were applied, and all non-hydrogen atoms were refined with anisotropic thermal parameters. The crystal structure of ADN obtained in this study is presented in Figure 3, while the crystal structure of AP given by Kótai[19] is shown in Figure 4.

Comparing Figures 3 and 4, both crystals have hydrogen bonds. However, it can be seen in Figure 4 that ClO_4 is a very disordered spherical molecule and its O atom is greatly uncertain; therefore, the hydrogen bonds associated with it also have a great uncertainty. ADN is a three-dimensional network structure linked by hydrogen bonds shown in Figure 3. The crystal data of ADN and AP from the literature are summarized in Table 2. The calculated hydrogen bonds in this study are given in Table 3.

Comparing the hydrogen bonds in ADN (Table 3) and AP,[19] the lengths of the hydrogen bonds in ADN are shorter and stronger.

The calculated molecular structure of ADN in this study is presented in Figure 5. As can be seen in Figure 5a, six anions, $N(NO_2)_2^-$, surround one cation, NH_4^+, by hydrogen bonds. Figure 5b shows that the molecules are first connected by the first three hydrogen bonds. Figure 5c demonstrates that the three-dimensional structure of ADN molecules are joined by the fourth longer hydrogen bond; it is also an unusual two-fold three-dimensional interpropagation network structure as illustrated in Figure 5d. This structure is more efficient in space filling and



(a)

(b)

(c)

(d)

Figure 5. (a) Hydrogen bonds around NH^+ among ADN, (b) one-dimensional bond along *c* axis, (c) three-dimensional molecular structure, and (d) two-fold three-dimensional interpropagation network structure of ADN (red is oxygen, blue is nitrogen, and green is hydrogen).

normally is a closely packed three-dimensional structure. Therefore, the hydrogen bonds in ADN crystal are much shorter.

From the above discussion it is concluded that plenty of strong hydrogen bonds are present in the ADN crystal. In the following sections, we studied the effects of those hydrogen bonds on the hygroscopicity of ammonium dinitamide and the conditions of the hydrogen bond between ADN and water.

3.3. FTIR Absorption Spectra. By comparing the FTIR spectrum in KBr discs of ADN without drying with that of ADN dried, it can be seen that, apart from the intra- and intermolecular hydrogen bonds among ADN, there were intermolecular hydrogen bonds between ADN and water, which brought a broader and stronger symmetric vibration absorption band and displacement to low frequencies. There was also an obvious 3500 cm^{-1} water absorption in the FTIR spectrum of ADN without drying shown in Figure 6a, due to the existence of unbound water in the sample. Figure 6b compares the impact of sample preparation methods. For the sample prepared by mull technique three obvious sharp peaks at (3134, 3022, and 2799) cm^{-1} were observed. When ADN was prepared by potassium bromide discs, only a broad strong peak appeared at 3129 cm^{-1}, and the peaks at (3025 and 2788) cm^{-1} became shoulder peaks in the infrared spectrum. ADN possibly absorbed water from its surroundings during the preparation of the potassium bromide discs; even after being dried, small amounts of water are still present. The mull technique had none of this effect because the crystal was coated by oil during sample preparation. For this reason, we studied the impact of the environment during disk scanning. Figure 6c shows that the results of the disk scanned once every 10 h on the first day. No obvious change was observed among the obtained spectra. One reason was that the water absorption of the potassium bromide disk was poor after KBr powder was pressed; another reason was that the equipment was properly sealed.

A comparison of the FTIR spectra of ADN and AP is given in Figure 7. Normally, the symmetrically stretching vibration absorption peak of N−H bond in NH_4^+ is at (3200 to 3300) cm^{-1}, such as AP at 3285 cm^{-1}, ammonium nitrate at 3265 cm^{-1}, and ammonium sulfate at 3220 cm^{-1}, and so forth. However, because of the strong intramolecular hydrogen bonds,

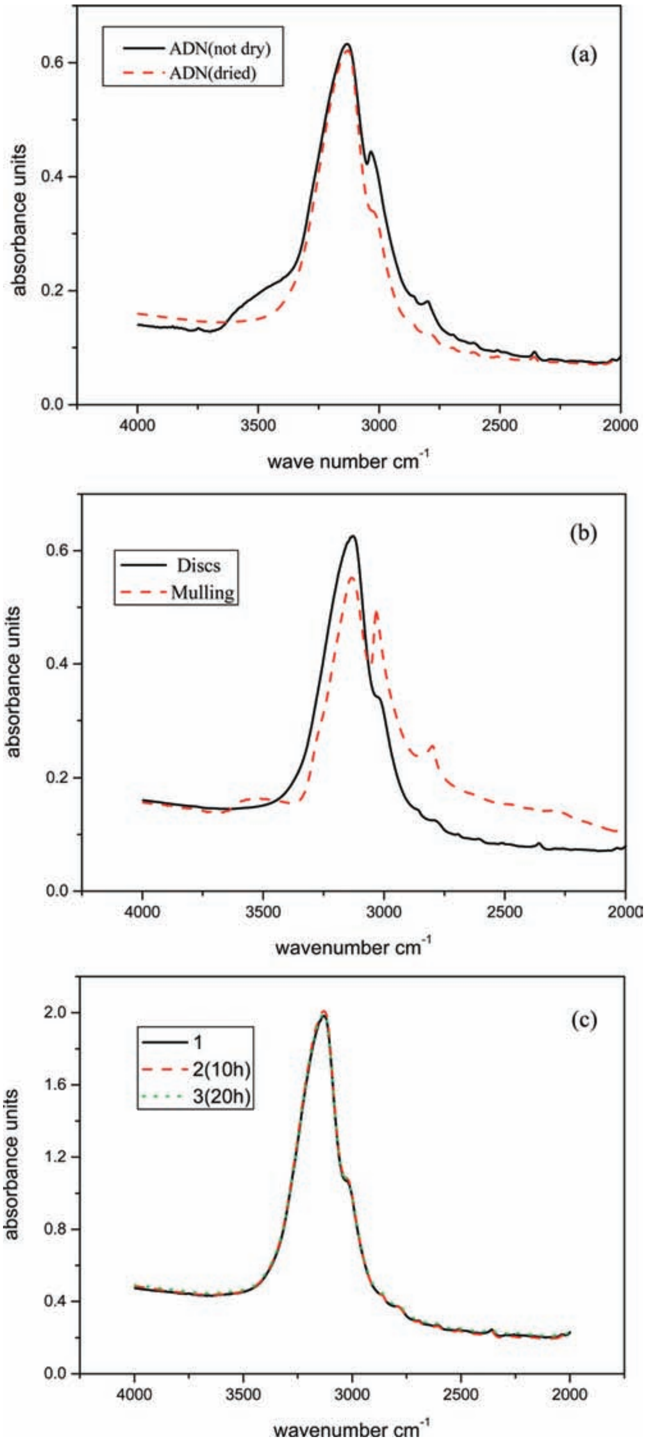


Figure 6. (a) Effect of moisture in ADN (KBr discs). (b) Comparison of the effect of different sample preparing method (KBr disk and mull technique). (c) Comparison of IR spectra scanned at different time (KBr discs).

which caused the vibration frequency of significant displacement, the stretching vibration of ADN appeared at 3120 cm^{-1}. Since the stronger the hydrogen bond is, the more displacement to low-frequency occurs, therefore the hydrogen bond in ADN is stronger than that in AP. The same conclusion drawn in this study on crystal structure verifies that it is the special hydrogen bonds among the ADN crystal that strongly affect its hygroscopicity.

3.4. DSC of 5 % Moisture Containing ADN and AP Crystals. The water on the surface of a particle is divided into two kinds: unbound (free) water and bound water. The bound water is more difficult to remove because of its association with the hydrogen bond. The hygroscopicity of a smooth (no crack and convexo-concave) particle is decided by the water-binding capacity of it, which is indicated by the heat of evaporation of a crystal containing water.

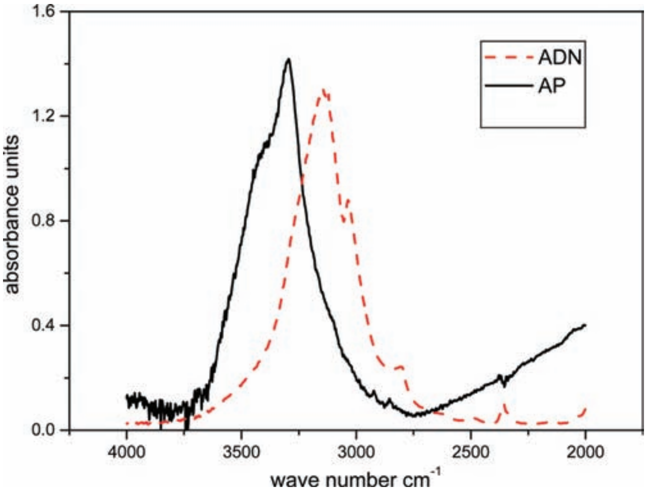


Figure 7. Comparison of the IR spectra of ADN and AP.

Figure 8 shows the heat flow during the drying of 5 % moisture containing ADN and AP crystals. The AP crystal only contained unbound water since the water in the crystal was completely dried before 40 °C. A comparison of the DSC curve of ADN and that of AP obviously shows that a large amount of bound water is present in the ADN crystal in addition to some unbound water because the DSC of dried ADN was a straight line between (0 and 85) °C, it was completely commensurate with the results given in the literature.[17,21] The bound water could not be completely removed when the ADN crystal began melting at temperatures higher than 80 °C. This could be due to the very strong hydrogen bond between ADN and water molecules, which is a possible main reason of the severe hygroscopicity of ADN.

4. Conclusions

ADN is more hygroscopic than AP, as shown by its higher saturated water absorption. The single-crystal structure of ADN obtained in this study shows that the structure of ADN molecules joined by the fourth longer hydrogen bond is a infrequent two-fold three-dimensional interpropagation network structure, and hydrogen bonds among ADN severely affect its hygroscopicity. The FTIR spectra of ADN confirms that there are intermolecular hydrogen bonds between ADN and water besides those stronger inter- and intramolecular hydrogen bonds among ADN. A comparison of the DSC of moisture-containing ADN and AP crystals also confirms the large amount of bound water present on the surface of the ADN crystal because of the stronger hydrogen bond between ADN and water molecules. Furthermore, the experimental results show that the bound water cannot be completely removed when the ADN crystal begins melting at temperatures of higher than 80 °C. All of this evidence suggests that the special hydrogen bonds in ADN and stronger hydrogen bond between ADN and water molecules are associated with its severe hygroscopicity.

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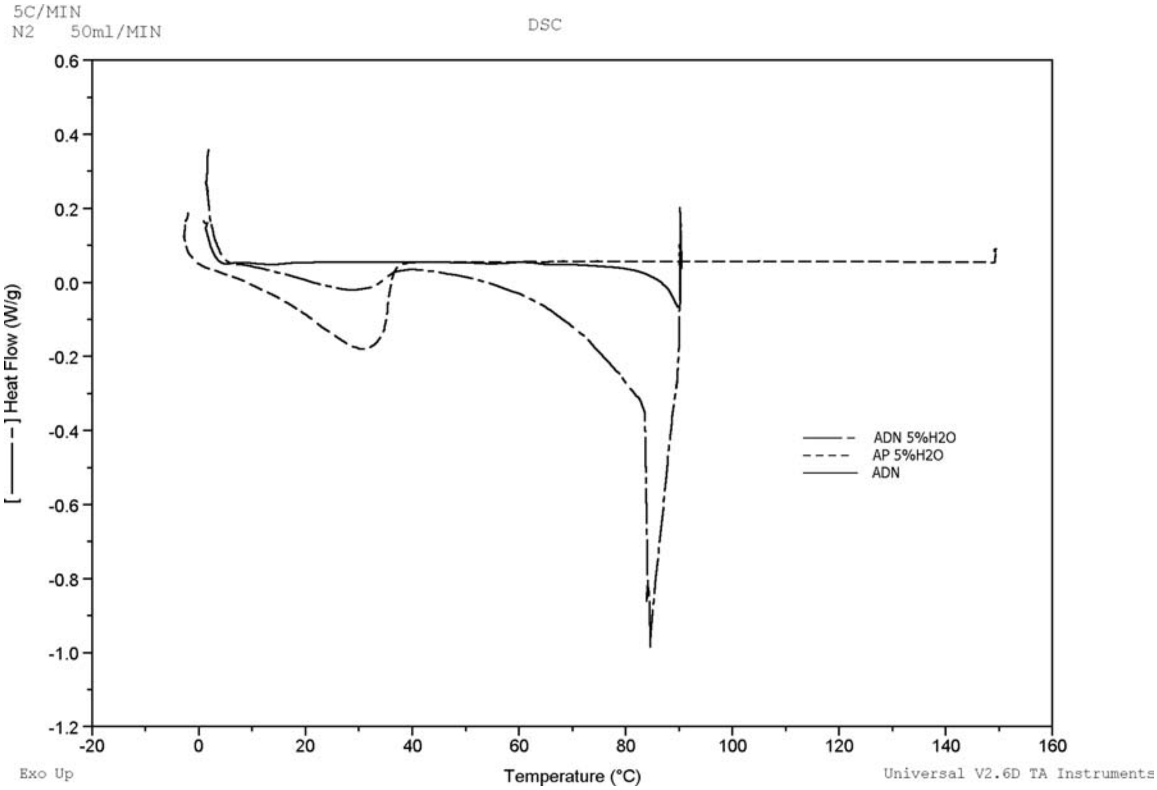

Figure 8. Comparison of DSC of 5 % moisture containing ADN and AP crystals.

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Literature Cited

(1) Talawar, M. B.; Sivabalan, R.; Mukundan, T.; Muthurajan, H.; Sikder, A. K.; Gandhe, B. R.; Subhananda Rao, A. Environmentally compatible next generation green energetic materials (GEMs). *J. Hazard. Mater.* **2009**, *161*, 589–607.
(2) Reed, R., Jr.; Ciaramitaro, D. A. High energy propellant with reduced pollution. U.S. Patent 6805760, 2004.
(3) Bottaro, J. C.; Penwell, P. E.; Schmitt, R. J. 1,1,3,3-Tetraoxy-1,2,3-triazapropene anion, a new oxy anion of nitrogen: the dinitramide anion and its salts. *J. Am. Chem. Soc.* **1997**, *119*, 9405–9410.
(4) Christe, K. O.; Wilson, W. W.; Petrie, M. A.; Michels, H. H.; Bottaro, J. C.; Gilardi, R. The dinitramide anion, $N(NO_2)_2$. *Inorg. Chem.* **1996**, *35*, 5068–5071.
(5) Östmark, H.; Bemm, U.; Langlet, A.; Sandén, R.; Wingborg, N. The properties of ammonium dinitramide (ADN): part 1, basic properties and spectroscopic data. *J. Energ. Mater.* **2000**, *18*, 123–128.
(6) Politzer, P.; Seminario, J. M.; Concha, M. C. Energetics of ammonium dinitramide decomposition steps. *J. Mol. Struct.: THEOCHEM* **1998**, *427*, 123–129.
(7) Ramaswamy, A. L. Study of the thermal initiation of ammonium dinitramide (ADN) crystals and prills. *J. Energ. Mater.* **2000**, *18*, 39–60.
(8) Badgujar, D. M.; Talawar, M. B.; Asthana, S. N.; Mahulikar, P. P. Advances in science and technology of modern energetic materials: An overview. *J. Hazard. Mater.* **2008**, *151*, 289–305.
(9) Crane, H. M.; Pickford, D. B.; Hutchinson, T. H. Effects of Ammonium Perchlorate on Thyroid Function in Developing Fathead Minnows, *Pimephales promelas*. *Environ. Health Perspect.* **2005**, *113* (4), 396–401.
(10) Wanda, L. G.; James, A. C.; Todd, A. A. Environmentally relevant concentrations of ammonium perchlorate inhibit thyroid function and alter sex ration in developing *Xenopus laevis*. *Environ. Toxicol. Chem.* **2002**, *21* (3), 590–597.
(11) Teipel, U. *Energetic Materials. Particle Processing and Characterization*, National Defense Industry Press, China; Wiley VCH: Weinheim, Germany, 2005; p 17.
(12) Foersvarets, F.; Langlet, A.; Östmark, H. Method of preparing dinitramidic acid and salts thereof. WO Patent 9706099, 1997.
(13) Udupa, H. V. K.; Narasimham, K. C.; Nagabingam, M.; Thiagarajan, N.; Subramanian, G.; Palanisamy, R.; Pushpavanam, S.; Sadagopalan, M.; Gopalakrishnan, V. Large scale preparation of perchlorates directly from sodium chloride. *J. Appl. Electrochem.* **1971**, *1* (3), 207–212.
(14) Lobbecke, S.; Krause, H. H.; Pfeil, A. Thermal analysis of ammonium dinitramide decomposition. *Propellants, Explos., Pyrotech.* **1997**, *22*, 184–188.
(15) Hatano, H.; Onda, T.; Shiino, K. New Synthesis method and physicochemical properties of Ammonium dinitramide. *Kayaku Kaggashi* **1996**, *57* (4), 160–165.
(16) Wan, D. H. Thermal decomposition and anti-hygroscopicity study of ammonium dinitramide. Master Thesis, National University of Defense Technology, Changsha, China, 2008.
(17) Wingborg, N. Ammonium dinitramide-Water: interaction and properties. *J. Chem. Eng. Data* **2006**, *51* (5), 1582–1586.
(18) *CRC Handbook of Chemistry and Physics*, 83rd ed.; CRC Press: Boca Raton, FL, 2003; pp 4−43.
(19) Kótai, L.; Argay, G.; Holly, S. Study on the existence of hydrogen bonds in ammonium permanganate. *Z. Anorg. Allg. Chem.* **2001**, *627*, 114–118.
(20) Gilardi, R.; Flippen-Anderson, J.; George, C. A new class of flexible energetic salts: The crystal structures of the ammonium, lithium, potassium, and cesium salts of dinitramide. *J. Am. Chem. Soc.* **1997**, *119*, 9411–9416.
(21) Albert, S. T. Thermal analysis of ammonium dinitramide (ADN). *Thermochim. Acta* **2000**, *357−358*, 177–193.

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