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Nitrogen-rich energetic compounds of

4-carboxamide-5-(1H-tetrazol-5-yl)-1H-1,2,3-triazole and its

1D sodium complex: synthesis and properties

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Abstract

The nitrogen-rich energetic compound of new 4-carboxamide-5-(1H-tetrazol-5-yl)-1H-1,2,3-triazole (2) and its sodium complex (3) had been synthesized by using diaminomaleodinitrile as the starting material in a three step synthesis. Both of them were comprehensively characterized by using the Fourier transform-infrared spectroscopy (FT-IR), Mass spectrometry (MS) and elemental analysis (EA). Sodium complex of 4-carboxamide-5-(1H-tetrazol-5-yl)-1H-1,2,3-triazole confirmed by single-crystal X-ray diffraction for the first time. The thermal stability of two compounds had been measured by differential scanning calorimetry (DSC), which indicated that the decomposition peak temperature were 332.6 °C (2) and 374.1 °C (3) respectively. The density and enthalpy of formation of **2** were calculated with Gaussian 09 and detonation pressure (21.9 GPa) and detonation velocity (7182 m s⁻¹) were predicted by Kamlet-Jacobs equations. Compound 2 was insensitive towards impact (>40J) and friction (>360N).

Keywords: Synthesis; 1,2,3-triazoles; nitrogen-rich compounds

1. Introduction

Nitrogen-rich compounds have been world-wide working in the field of energetic materials in the recent years. The high nitrogen content of compounds results high potential as explosive due to the large number of inherent N–N, N=N and C–N bonds.¹⁻³ Recently, lots of studies of new high energy density materials (HEDM) continues to focus on the derivatives of furazan⁴⁻⁶, triazole⁷⁻¹⁰ and tetrazole¹¹⁻¹⁴. Furthermore, the nitrogen-rich compounds are green and environmental protection which mainly release nontoxic N₂ upon decompositions.¹⁵ In general, tetrazole is more energetic but also more sensitive towards external stimuli, whereas triazoles (1,2,3-triazole and 1,2,4-triazole) are less sensitive.¹⁶ In regard to the requirements of detonation performance and safety, the triazole are the most promising backbones.

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At present, great number of studies concentrated on 1,2,4-triazoles¹⁷⁻²² and salts²³⁻²⁵, but only few reports for derivatives of 1,2,3-triazoles and derivatives are known. In 1992, it is first report on 4-amino-5-nitro-1,2,3-2H-triazole (ANTZ)²⁶ with nitrogen content being 54%. ANTZ is a high energy candidate and also an important intermediates of energy material. Surprisingly, ANTZ (T_d , 297 °C) is more thermally stable than 3-amino-5-nitro-1,2,4-triazole (T_d , 243 °C). The single-crystal structure of 4-nitramino-5-nitro-1,2,3-2H-triazole²⁷ with high density (1.919 g cm⁻³) is obtained in 2003. So, the nitrogen-rich derivatives of 1,2,3-triazole is a very promising research direction. Here, the goal of this study has therefore been the synthesis of nitrogen-rich 4,5-substituted 1,2,3-triazole compounds: 4-carboxamide-5-cyano-2H-1,2,3-triazole 51%), (1, nitrogen content: 4-carboxamide-5-(1H-tetrazol-5-yl)-1H-1,2,3-triazole (2, nitrogen content: 62%), and its Sodium complex (3). All of compounds are comprehensive characterized and the decomposition temperature and kinetics parameters of 2 and 3 are obtained.

Results and discussion

Synthesis

There was a possible route to synthesize the new nitrogen-rich compound 4-carboxamide-5-(1H-tetrazol-5-yl)-1H-1,2,3-triazole (2). The synthesis route was described in Scheme 1. 4,5-Dicyano-2H-1,2,3-triazole²⁸ was prepared by one step reactions from diaminomaleodinitrile according to literature method. 4,5-Dicyano-2H-triazole could be hydrolysed with 1M HCl and 1M acetic acid to obtain 4-carboxamide-5-cyano-2H-1,2,3-triazole (1) in 67% yield. The compound 1 could be recrystallized with hot water. The reaction of compound 1 with sodium azide and zinc chloride 1,3-dipolar cycloaddition achieved in а 4-carboxamide-5-(1H-tetrazol-5-yl)-1H-1,2,3-triazole (2) in 78% yield. The sodium complex of 4-carboxamide-5-(1H-tetrazol-5-yl)-1H-1,2,3-triazole (3) was synthesized by metathesis reaction of compound 2 and sodium hydroxide. The complex 3 was stable and could be stored for extended periods in air.



Scheme 1. synthesis route toward 4-carboxamide-5-cyano-2H-1,2,3-triazole (1), 4-carboxamide-5-(1H-tetrazol-5-yl)-1H-1,2,3-triazole (2), Sodium complex of 4-carboxamide-5-(1H-tetrazol-5-yl)-1H-1,2,3-triazole (3).

Single-crystal X-ray structure analysis

The X-ray crystallographic data of compounds **1** hydrate and **3** were obtained with A Rigaku AFC-10/Saturn 724+ CCD diffractometer with graphite mono-chromated Mo-K_{α} radiation. The structures were solved by direct methods using SHELXS97²⁹ and refined anisotropically on F2 by the full-matrix least-squares technique using the SHELXL97³⁰ programs. Crystallographic data and structure refinements are summarized in **Table 1** and can be obtained free of charge on quoting the depository numbers CCDC-1497228 (**1**) and CCDC-1497227 (**3**),

	1 H ₂ O	3
Empirical formula	$C_4H_5N_5O_2$	$C_8H_{14}N_{16}Na_2O_6$
$MW (g mol^{-1})$	155.13	476.33
Temperature (K)	298(2)	298(2)
Crystal System	Monoclinic	Triclinic
Space Group	P2(1)/c	P-1
<i>a</i> (Å)	3.6672(3)	6.7660(6)
<i>b</i> (Å)	16.3613(14)	7.2849(7)
<i>c</i> (Å)	11.3345(8)	10.7541(9)
α (°)	90.00	109.069(2)
β (°)	97.7600(10)	98.9320(10)
γ (°)	90.00	103.404(2)
$V(\text{\AA})^3$	673.84(9)	471.70(7)
Z	4	1
$\rho_{\rm calcd} ({\rm g \ cm}^{-3})$	1.529	1.677
$\mu (\text{mm}^{-1})$	0.126	0.178
F (000)	320	244
Crystal size (mm)	0.40 x 0.10 x 0.07	0.21 x 0.14 x 0.06
heta (°)	3.08-25.01	3.01-25.02
Reflections collected	3230	1631
Unique reflections	1183	1631

Table 1. Crystallographic data and structure refinements for 1 H₂O and 3

R _{int}	0.0809	0.0000
Data/restraints/parameters	1183 / 0 / 100	1631 / 0 / 147
GOF on F^2	1.018	1.042
$R_1, wR_2 [I > 2\sigma(I)]$	R_1 =0.0556, wR_2 =0.1325	$R_1 = 0.0676, wR_2 = 0.1680$
R_1 , wR_2 (all data)	$R_1 = 0.0894, wR_2 = 0.1491$	$R_1 = 0.0901, wR_2 = 0.1811$
CCDC	1497228	1497227

The 4-carboxamide-5-cyano-2H-1,2,3-triazole hydrate (1) crystallized in the monoclinic space group P21/c with four formula units per unit cell and a calculated density of 1.529 g cm⁻³ at 298 K. As shown in Figure 1, The bond lengths in the 4,5-substituted 1,2,3-triazole are between the length of the corresponding single and double bonds. N1–N2 bond (1.320(3) Å) is almost the same as N2–N3 bond (1.323(3))Å), and then triazole ring is symmetrical. Amide C1-N4 bond (1.318(4) Å) is shorter than single bonds, because amide group is almost planar and effect of unshared pair electron of the nitrogen atom. C4–N5 bond of cyano (1.139(4) Å) is corresponding triple bond. The intermolecular hydrogen bond is formed N5-H4...O1 between the amide group and oxygen atom of neighboring amide (D···A: 2.173 Å; D-H···A: 167°). Between the amide group and a nitrogen atom of a neighboring triazole ring which is also formed hydrogen bond N4-H4···N1 (D···A: 2.396 Å; D-H···A: 162°). Moreover, the 4-carboxamide-5-cyano-2H-1,2,3-triazole crystallizes with one molecule water to form its monohydrate. Molecule features intermolecular hydrogen bond N2-H2···O2 (D···A: 2.661 Å; D-H···A: 169°), O2-H2···O1 (D···A: 1.962 Å; D-H···A: 156°), and O2-H2···N5 (D···A: 2.125 Å; D-H···A: 156°). Furthermore, the detail information of the crystal structure determination has been compiled is in the Supplementary information (Table S1&S2).





Figure 1. Molecular structure of 1 $H_2O(a)$, Hydrogen bonds and Unit cell packing of 1 $H_2O(b)$.

The title nitrogen-rich sodium complex of 4-carboxamide-5-(1H-tetrazol-5-yl)-1H-1,2,3-triazole (3) crystallized in the Triclinic space group P-1 with one formula units per unit cell. The molecular unit is depicted in Figure 2. The bond lengths of triazole and tetrazole are also between formal single and double bonds. Furthermore, the bond lengths of triazole ring is different from that of 1 H₂O with N2–N3 and N3–N4 bond lengths of 1.310(5) and 1.341(4) Å respectively. It has been found that sodium form a chelated structure with the triazole ring. The sodium ion displays an octahedral hexa-coordinate complex which is coordinated by the nitrogen atoms N2, N3 of two triazole rings, oxygen atom O1 of amide group and oxygen atom O2, O2, O3 of the coordinated water molecules. The complex 3 forms a 1D chain-like structure constructed by coordination bonds. The struc-

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ture is dominated by an extensive hydrogen bonding network involving three nitrogen atoms and four oxygen atoms of the coordinated water molecules. The intermolecular hydrogen bond is formed N1–H1····N8 (D····A: 2.027 Å; D–H···A: 176°) and N1–H1····N5 (D····A: 1.964 Å; D–H···A: 164°) between the amide group and nitrogen atom of neighboring tetrazole (D····A: 2.173 Å; D–H···A: 167°). Between the nitrogen atom of triazole ring and oxygen atoms of neighboring amide group which is also formed hydrogen bond N4–H4····O1 (D···A: 2.013 Å; D–H···A: 160°). Moreover, intermolecular hydrogen bonds between the coordinated water molecules and nitrogen atom of tetrazole are O2–H2····N6 (D···A: 2.085 Å; D–H···A: 166°) and O3–H3···N7 (D···A: 2.061 Å; D–H···A: 158°). At last, there is the detail information of the crystal structure determination h in the Supplementary information (**Table S3&S4**).

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(a)



(b)



Figure 2. Molecular structure of 3 (a), 1D chain-like structure of 3 (b),Hydrogen bonds and Unit cell packing of 3 (c).

Thermal analyses

The differential scanning calorimetry (DSC) shows the thermal behaviors of **2** and **3** in the temperature range of 20-500 °C at the heating rate of 5 °C min⁻¹ (see Figure **3**). Phase transition processes of **2** start at 200 °C with the peak temperature of 223.3 °C, which ends at 241 °C. It is a sharp exothermic process with the peak temperature at 332.6 °C. For **3**, it is found in the DSC curve that two exothermic stages

appear. Two sharp exothermic process with the peak temperature appear at 374.1 °C and 410.4 °C respectively. Both of them have the advantages of good thermal stability. Furthermore, **3** performs higher thermal stability than 2 in the high temperature conditions.



Figure 3. DSC curves with a heating rate of 5°C min⁻¹

Non-Isothermal kinetics analysis

Kissinger's method³¹ and Ozawa-Doyle's method³² are employed to determine the apparent activation energy (*E*) and the pre-exponential factor (*A*). The Kissinger (1) and Ozawa-Doyle (2) equations are as follows (T_p is peak temperature, °C; *R* is the gas constant, 8.314 J mol⁻¹ °C ⁻¹; β is the linear heating rate, °C min⁻¹ and *C* is a constant):

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{A_k R}{E_k}\right) - \frac{E_k}{RT_k} \tag{1}$$

$$\log\beta + \frac{0.4567E_a}{RT_p} = C \tag{2}$$

Based on the exothermic peak temperatures measured at four different heating

rates of 5, 10, 15 and 20 °C min⁻¹, the kinetic parameters of **2** and **3** are calculated. The apparent activation energy E_k and E_o , pre-exponential factor A and linear correlation coefficients R_k and R_o are shown in **Table 2**.

The calculated results using both methods are quite close, which are all in the normal range of kinetic parameters for the thermal decomposition reaction of solid materials.³³ Using the obtained E_a (the average of E_k and E_o) and $\ln A_k$ value, the Arrhenius equations of 2 and 3 can be expressed as $\ln k = 20.29-257.9 \times 10^3/RT$ (2) and $\ln k = 20.19-275.1 \times 10^3/RT$ (2) for the exothermic processes, which can be used to estimate the rate constants of the initial thermal decomposition processes .

	2	3	
$\beta(^{\circ}C \min^{-1})$	Peak temperatures T_p (°C)		
5	332.6	374.1	
10	336.8	380.6	
15	342.4	385.3	
20	348.1	391.5	
Kissinger's method			
$E_{\rm k}~({\rm kJ~mol}^{-1})$	259.4	276.7	
$\ln[A_k(s^{1-})]$	20.29	20.19	
$R_{ m k}$	-0.9636	-0.9831	
Ozawa's method			
Eo (kJ mol ⁻¹)	256.4	273.5	
Ro	-0.9662	-0.9844	

Table 2. Peak temperatures and kinetics parameters for 2 and 3

Theoretical calculations and properties

The density and enthalpy of formation are two important parameters in energetic materials. In this work, the enthalpy of formation was computed using the method of atomization energy and density also was computed by the Gaussian 09 suite of programs. The geometric optimization of the structure and frequency analyze carried out using B3LYP functional with the 6-311++G** basis set. The optimized structure was characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

The detonation pressure and detonation velocity of energetic compound can be calculated by using empirical Kamlet-Jacobs equations³⁴ with the value of enthalpy

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of formation and density. Where each term in equations 3 and 4 is defined as follows: D, detonation velocity (m s⁻¹); P, detonation pressure (GPa); N, moles of detonation gases per gram explosive (mol g⁻¹); \overline{M} , average molecular weight of these gases (g mol⁻¹); Q, heat of detonation (cal g⁻¹); and ρ , the loaded density of explosives (g cm⁻³). **Table 3** listed all the calculated results. The title compound **2** had a high nitrogen content (62.2%) and the calculated density, calculated detonation pressure and detonation velocity were 1.67 g cm⁻³, 21.9 GPa and 7182 m s⁻¹ respectively.

$$D = 1.01 \left(N \overline{M}^{1/2} Q^{1/2} \right)^{1/2} (1 + 1.30\rho)$$
(3)

$$P = 1.558\rho^2 N \bar{M}^{1/2} Q^{1/2} \tag{4}$$

For a further analysis, the HOMO-LUMO orbital was calculated to reveal the potential sensitivity of compound **2**. As show in **Figure 4**, red part relates to the positive area and green part relates to the negative area. In the HOMO orbital, electron distributes uniformly in the whole molecular, but in the LUMO orbital, it concentrates on the triazole part and the amide group part without the tetrazole part. The energy level difference between the HOMO-LUMO orbital is 5.99 eV, which can indicate the sensitivity of the energetic material. Therefore, compound **2** can be considered as a kind of high-energy material with low sensitivity.



Figure 4. HOMO-LUMO orbital

For initial safety testing, the impact and friction sensitivities of **2** were measured by following BAM standard methods. The results also showed **in Table 3**. It is not surprising that compound **2** is insensitive towards impact (>40J) and friction (>360N).

	2	TNT ³⁵	RDX ³⁶
Formula	$C_4H_4O_1N_8$	$C_7H_5O_6N_3$	$C_3H_6N_6O_6$
$FW/g mol^{-1}$	180.05	227.13	222.12
N ^a /%	62.2	18.5	37.8
IS ^b /J	>40	15	7.5
FS ^c /N	>360	>353	120
$T_m^{d/\circ}C$	223.3	80.1	204.1
T _d ^e /°C	332.6	295.0	230.0
$\Omega_{ m CO}^{ m f}$ /%	-44.4	-24.7	0
$\Omega_{ m CO2}$ g/%	-79.9	-74	-21.6
$\rho^{\rm h}/{\rm g~cm^{-3}}$	1.67	1.654	1.82
$\Delta_{\rm f} { m H}^{\circ}$ ⁱ /kJ mol ⁻¹	537.77	-67	80
P ^j /GPa	21.9	21.3	34.9
$D^k/m s^{-1}$	7182	6881	8748

Table 3. Energetic properties and detonation parameters of 2 compared with TNT and RDX

[a] Nitrogen content. [b] Impact sensitivity. [c] Friction sensitivity. [d] Melting point. [e] Decomposition temperature. [f] Oxygen balance assuming the formation of CO respectively. [g] CO₂. [h] Calculated density. [i] Calculated enthalpy of formation. [j] Calculated detonation pressure. [k] Calculated detonation velocity.

Experimental section

Material and instruments

All chemical reagents and solvents of analytical grade were obtained from commercial sources. Elemental analyses were performed on a Flash EA 1112 fully automatic trace element analyzer. The FT-IR spectra were recorder as KBr pellets on a Bruker Equinox 55. Mass spectra were recorded on an Agilent 500-MS.Differential scanning calorimetry (DSC) was carried out on a model Pyris-1 differential scanning calorimeter in static air. The single-crystal X-ray diffraction analysis was carried out by on Bruker CCD area-detector diffractometer.

4,5-Dicyano-2*H*-1,2,3-triazole

4,5-Dicyano-2*H*-1,2,3-triazole has been synthesized according to the reference method.²⁸

4-carboxamide-5-cyano-2H-1,2,3-triazole (1)

4,5-Dicyano-2*H*-1,2,3-triazole (2.38 g, 20 mmol) was refluxed in an aqueous solution of AcOH (1 M 25mL) and HCl (1 M 25mL) for 30 min. The solution was cooled to 0 °C, whereby the precipitate formed was filtered off and recrystallized from hot water to afford **1** hydrate colourless needles (1.84 g, 67%). IR (KBr, cm⁻¹): 3545, 3481, 3397, 3305, 3242, 2918, 2850, 2606, 2263, 2151, 1942, 1705, 1612, 1521, 1434, 1366, 1215, 1145, 990, 953, 795, 720, 640. MS (ESI-): m/z = 136.10 ([M]⁻). EA for C₄H₃N₅O₁ (%): calcd: C 35.04, H 2.21; N 51.08; found: C 35.12, H 2.16, N 51.15.

4-carboxamide-5-(1*H*-tetrazol-5-yl)-1*H*-1,2,3-triazole (2)

Compound 1 (1.37g 10 mmol) was dissolved in water (50 mL) and sodium azide (0.78 g, 12 mmol) and zinc chloride (1.5 g, 11 mmol) were added. The reaction mixture was stirred and heated under reflux for 4 h. The solution was then cooled to ambient temperature and concentrated hydrochloric acid (10 mL) was added while cooling to 0 °C. The precipitate was removed by filtration under suction and the product was washed with cold water and ethanol to obtain the compound 2 (1.4g 78%). IR (KBr, cm⁻¹): 3348, 3223, 3092, 2921, 2858, 27801, 1685, 1587, 1469, 1309, 1217, 1175, 1125, 1048, 992, 858, 714, 666. MS (ESI-): m/z = 179.10 ([M]⁻). EA for C₄H₄N₈O₁ (%): calcd: C 26.67, H 2.24; N 62.21; found: C 26.73, H 2.28, N 62.17.

Sodium complex of 4-carboxamide-5-(1H-tetrazol-5-yl)-1H-1,2,3-triazole (3)

Sodium hydroxide (0.08 g, 2 mmol) was added to a suspension of (2) (0.36 g, 2 mmol) and water (10 mL), the mixture was stirred at 50 °C for 1 h, the clear solution was slowly evaporated and single crystals of **3** was obtained. IR (KBr, cm⁻¹): 3569, 3408, 3181, 3052, 2917, 2849, 2693, 1696, 1632, 1580, 1510, 1416, 1310, 1267,

1171, 1124, 1054, 1029, 999, 898, 795, 728, 654. MS (ESI-): m/z = 179.10 ([M]⁻). EA for C₄H₃N₈O₁ (%): calcd: C 23.77, H 1.50; N55.44; found: C 23.85, H 1.57, N 55.42.

Conclusion

In this work. synthetic routes. structures properties of the and 4-carboxamide-5-(1H-tetrazol-5-yl)-1H-1,2,3-triazole (2) and its sodium complex (3) were report. Single-crystal structures of 3 was obtained for the first time and it showed a 1D chain-like structure that sodium ions form a chelated structure with the triazole. Compound 2 (332.6 °C) and complex 3 (374.1 °C) had the advantage of good thermal stability. The kinetic parameters of exothermal process of 2 and 3 were calculated with Kissinger's and Ozawa-Doyel's methods. The Arrhenius equation of 2 and 3 were obtained. The compound 2 had the high nitrogen contents (62%) and the detonation pressure (21.9 GPa) and detonation velocity (7182 m s⁻¹) were calculated by using Kamlet-Jacobs equations. The impact sensitive (>40J) and friction sensitive (>360N) of **2** were measured. Based on detonation properties and stabilities, 4-carboxamide-5-(1H-tetrazol-5-yl)-1H-1,2,3-triazole was an insensitive energetic material.

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