

Synthesis and characterization of a new energetic salt 1*H*pyrazole-1-carboxamidine dinitramide and its thermal properties

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Abstract The new energetic compound 1*H*-pyrazole-1carboxamidine dinitramide (PACADN) was synthesized by the reaction of silver dinitramide with 1H-pyrazole-1-carboxamidine hydrochloride. Its structure was confirmed by single-crystal X-ray diffraction, elemental analysis and Fourier transform infrared, ultraviolet-visible and nuclear magnetic resonance spectroscopy analyses. PACADN crystallizes in the orthorhombic space group Pnna. The thermal decomposition was studied with differential scanning calorimetry, thermogravimetry analysis and thermogravimetric tandem infrared spectrum. The results indicated that PACADN exhibits good resistance to thermal decomposition up to 433 K and has 90.24 % mass loss between 433 and 523 K by undergoing exothermic decomposition. The kinetic parameters of the thermal decomposition of PACADN were also obtained from the derivative thermogravimetry analysis data using Kissinger's method, with $E_a = 143.2 \text{ kJ mol}^{-1}$. Moreover, the detonation velocity and detonation pressure of PACADN were calculated as 7.2 km s^{-1} and 21 GPa byapplying the Kamlet-Jacobs (as follows).

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$$D = 1.01 (N\overline{M}^{1/2}Q^{1/2})^{1/2} (1 + 1.3\rho)$$
$$P = 1.558\rho^2 N\overline{M}^{1/2}Q^{1/2}.$$

Keywords 1*H*-pyrazole-1-carboxamidine dinitramide (PACADN) · Single crystal · Thermal properties · Energetic properties

Introduction

Energetic materials are one of the most important functional parts in the field of science [1–3]. Typical energetic materials include explosives, pyrotechnics and propellants, which are widely used for a variety of military purposes and civilian applications. Along with growing concerns about the environment and safety issues, considerable efforts have been devoted to pursuing environmentally friendly and insensitive energetic salts [4–6]. In the development of new high-performance energetic resource, nitrogen-rich cations represent a unique class of energetic molecular frameworks, which have recently attracted significant interest in the design of energetic salts due to their high heats of formation, density and thermal stability as compared to those of their carbocyclic analogs [7].

The dinitramide anion (DN) is an inorganic member of the nitramine class of compounds and can form stable oxygen-rich salts with a variety of nitrogen-rich cations, which makes DN a promising candidate in the development of explosives and propellants [8, 9]. A number of different dinitramide salts were synthesized and actively studied, such as N-guanylurea dinitramide (FOX-12) [10]. Those salts would possess both high nitrogen and high oxygen contents;

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meanwhile, most of them have the characteristics of high energy and density. No doubt that the inherent designability of energetic salt provides great opportunities for developing new-generation ionic energetic materials, which makes both the properties and the performance of the target energetic material reasonably predictable. Pyrazole is an ideal structural unit to rich nitrogen heterocyclic compounds. Meanwhile, the number of electrons of imidazolium cation rings obeys the 4n + 2 rule, and the cation rings possess aromaticity. In this work, we presented the synthesis and characterization of this new energetic compound PACADN.

Experimental

Materials and methods

Sulfamic acid, potassium hydroxide, fuming nitric acid, sulfuric acid, silver nitrate, ethanol, acetone and isopropanol were purchased from Kelong Chemical Reagent Company (Chengdu, China). 1H-pyrazole-1-carboxamidine hydrochloride was purchased from Beijing HVSCO Technology Co. All the samples are analytically pure. FTIR spectra were recorded on Nicolet 380 FTIR spectrophotometer (Thermo Fisher Nicolet, USA) with a resolution of 4 cm^{-1} , in the wavelength range of 400–4000 cm^{-1} . The UV–Vis spectra were measured using a UV-2102 PCS spectrophotometer with H₂O as the solvent. ¹H NMR and ¹³C NMR spectra of the PACADN were carried out using a JEOL GSX 400 MHz nuclear magnetic resonance (NMR) spectrometer in (CD₃)₂CO solution using tetramethylsilane as internal standard. Single-crystal diffraction analysis was collected by a Bruker Smart APEX II CCD diffractometer. Differential scanning calorimetry (DSC) was performed by a Q200 DSC instrument at a heating rate of 10 K min⁻¹ under air flow 50 mL min⁻¹. Thermogravimetric analysis (TG) was performed with a SDT Q600 TG instrument in flowing air (flow rate 50 mL min⁻¹) at a heating rate of 5, 10, 15, 20 and 25 K min⁻¹.

Synthesis

PACADN was synthesized through four steps, as shown in Scheme 1. Sulfamic acid was reacted with potassium hydroxide to afford potassium sulfamate 1, which was nitrated and then reacted with potassium hydroxide to obtain potassium dinitramide 2. Silver dinitramide 3 was prepared through the cation exchange reaction of potassium dinitramide 2 and silver nitrate. Then, silver dinitramide 3 was allowed to react with 1*H*-pyrazole-1carboxamidine hydrochloride through anion exchange reaction to afford PACADN 4.

Synthesis of potassium sulfamate 1

In 50 mL of distilled water, 71 g sulfamic acid (HSO₃NH₂) was dissolved. Then, 46 mL potassium hydroxide (15.7 mol L^{-1}) was added slowly to the stirred mixture at room temperature. Thereafter, the reaction solution was poured into 150 mL ethanol and subsequently filtered under reduced pressure to obtain solid product. The obtained product was washed with ethanol and dried in vacuo at 50 °C to afford 85 g potassium sulfamate **1** [11], with a yield of 86 %.

Synthesis of potassium dinitramide 2

Forty-six milliliters of fuming nitric acid and 17 mL sulfuric acid were introduced into a three-necked flask equipped with a mechanical stirrer and a thermometer in a liquid nitrogen/ ethanol bath. As soon as the temperature reached -45 °C, 17 g potassium sulfamate was added in portion of 0.5-1.0 g to the reaction mixture under vigorous agitation, and the reaction temperature was maintained at -40 to -45 °C. The viscosity increased significantly as the reaction proceeded and KHSO₄ precipitated. After addition of the last portion of the salt, the vigorous stirring was continued for 30 min. Thereafter, the reaction mixture was poured into 300 g finely crushed ice and then was neutralized with cooled potassium hydroxide solution (15.7 mol L^{-1}) until the color of reaction mixture was changed to yellow-green. In the whole process of neutralization reaction, the temperature was maintained in the range -10 to 0 °C. Afterward, the reaction mixture was filtered and washed with water (30 mL). The filtrate was evaporated to dryness to obtain a mixture of potassium sulfate, potassium nitrate and potassium dinitramide. Then, the mixture salts were extracted with 300 mL acetone (3 \times 100 mL). The acetone solution was concentrated on an evaporator to about one-tenth of the volume and poured into 150 mL 2-propanol. The salt precipitated was filtered off and dried in vacuo at 50 °C to afford 9.3 g potassium dinitramide 2, with a yield of 53 %. m.p. 130.0 °C (literature data 130.5 °C) [12, 13]. FTIR (KBr) v (cm⁻¹): 1531 (v_{as} NO₂), 1369 (v_{s} NO₂). UV–Vis (H₂O), λ_{max} (nm): 284.

Synthesis of silver dinitramide 3

1.45 g (0.01 mol) potassium dinitramide 2 and 1.70 g (0.01 mol) silver nitrate were dissolved in 100 mL of boiling ethanol, respectively. Then, the two boiling solutions were mixed and reacted to precipitate the potassium nitrate. After 0.5 h, the precipitate was filtered off under reduced pressure. The filtrate was concentrated on an evaporator to about one-fifth of the volume, and the salt precipitated was filtered off. The filtrate was evaporated to

Scheme 1 Synthesis of PACADN



dryness to afford yellow crystal 1.75 g silver dinitramide 3, with a yield of 82 % [14]. m.p. 86.5 °C. FTIR (KBr) v (cm⁻¹): 1536 (v_{as} NO₂), 1360 (v_s NO₂). UV-Vis (H₂O), λ_{max} (nm): 283.

Synthesis of PACADN 4

0.21 g (1.0 mmol) silver dinitramide and 0.15 g (1.0 mmol) 1H-pyrazole-1-carboxamidine hydrochloride were dissolved in 5 mL distilled water, respectively. Then, the two solutions were mixed and reacted to precipitate the silver chloride. The precipitate was filtered off under reduced pressure. The filtrate was evaporated to dryness to afford yellow crystal 0.20 g PACADN, with a yield of 95 %. Because this salt is a typical energetic material, we do not operate it in hightemperature environment and to avoid a strong collision. Elemental analysis (EA): found (%): C, 22.15; H, 3.29; N, 45.18; calculated (%): C, 22.10; H, 3.22; N, 45.13. IR (KBr) v (cm⁻¹): 3400, 3132, 1702, 1640, 1530, 1384, 1186, 1016, 939, 775, 630. UV–Vis (H₂O) λ_{max} (nm): 284, 235. ¹H NMR ((CD₃)₂CO, 400 MHz) δ (ppm): 9.18, 8.71, 8.07, 6.83 and 3.15. ¹³C NMR ((CD₃)₂CO, 400 MHz) δ (ppm): 147.17, 131.38, 113.36.

Results and discussion

Characterization

PACADN was characterized by elemental analysis (EA) and Fourier transform infrared (FTIR), ultraviolet-visible (UV-Vis) and nuclear magnetic resonance (NMR) spectroscopies. In addition, its crystal structure was measured by X-ray diffraction. Figure 1 shows the FTIR spectrum of PACADN. As a result, the sharp bands at 1384, 1530 cm^{-1} were ascribed to the stretching vibration and asymmetrical stretching vibration of nitro group, respectively, similar to other dinitramide salts [15]. The peaks at 1702, 1640 cm^{-1} corresponded to the typical stretching modes of C=C and C=N. The main characteristic peak at about 1186 cm^{-1} was due to the C-N stretching vibration absorption, and three peaks at around 3132 cm^{-1} were the stretching vibration of



3000

2500

Wavenumbers/cm⁻¹

2000

1500

1000

500

3500

60

50

40

30

4000



Fig. 2 UV-Vis spectra of 1H-pyrazole-1-carboxamidine hydrochloride (a), silver dinitramide 3 (b) and PACADN (c)

C–H at the pyrazole. The broad band around 3400 cm^{-1} was attributed to the secondary and primary amine [16].

The UV-Vis spectra of 1H-pyrazole-1-carboxamidine hydrochloride, silver dinitramide 3 and PACADN are presented in Fig. 2. The UV-Vis spectrum of PACADN showed a strong absorption in the region about 220-260 nm with maximum absorption at 235 nm and a moderate absorption in the region about 260-320 nm with maximum



Fig. 3 1 H NMR (a) and 13 C NMR (b) spectra of PACADN

absorption at 284 nm. The absorption at 235 nm was caused by resonance of the cumulative double bond of the cation diazole ring [17], and the absorption at 284 nm was ascribed to the dinitramide ion [18].

The ¹H NMR and ¹³C NMR spectra also confirmed the correct structure of PACADN, which are shown in Fig. 3. As shown in Fig. 3a, the diazole ring protons of PACADN (denoted a–c) appeared at $\delta = 8.71$ ppm (d, J = 2.9 Hz, 1H), $\delta = 8.07$ ppm (d, J = 1.5 Hz, 1H) and $\delta = 6.83$ ppm (dd, J = 2.9 Hz, 1.5 Hz, 1H), respectively. The amino group protons of PACADN (–NH₂, denoted d–e) appeared at $\delta = 9.18$ ppm (bs, 2H) and $\delta = 3.15$ ppm (bs, 2H), respectively. In the ¹³C NMR spectrum of PACADN (Fig. 3b), the signals at $\delta = 113.36$, 131.38 and 147.17 ppm were ascribed to the *sp*² hybridized carbon of diazole ring (denoted a'–c'), and the signal at $\delta = 153.94$ ppm was ascribed to the carbon of C=N bond (denoted d').

Dissolved with ethanol and a moderate amount of the refined sample, let stand at room temperature, slow to ethanol volatilization, after 48 h, we can get a colorless single crystal for crystal structure determination. The test for the single crystal size is $0.20 \times 0.18 \times 0.12$ mm. A colorless crystal of the title compound was mounted on a glass fiber in a random orientation. The single-crystal X-ray diffraction data of PACADN are summarized in Table 1 and were collected using a Bruker Smart APEX II CCD diffractometer equipped with a graphite monochromatic Mo Ka radiation ($\lambda = 0.71073$ Å) by using an ω scan mode in the range of 2.17° $\leq \theta \leq 27.94^{\circ}$ at 293(2) K. Collected diffraction point 21,057 included the independent of the diffraction point 2173 [$R_{int} = 0.0434$]. The structure was solved by direct methods with SHELXS-97 program.

As given in Table 1, the formulas are given for the crystal $C_4H_7N_7O_4$, relative molecular weight is 217.17, the density is 1.587 g cm⁻³, and PACADN crystallizes in the orthorhombic system Pnna space group. The structure is shown in Fig. 4a. Its



 Table 1 Crystal data and structure refinement parameters of PACADN

Formula	$C_4H_7N_7O_4$		
M/g mol ⁻¹	217.17		
Crystal system	Orthorhombic		
Space group	Pnna		
a/Å	13.768(3)		
b/Å	18.759(4)		
c/Å	7.0369(14)		
α/°	90		
β/°	90		
γ/°	90		
Cell volume/Å ³	1817.5(6)		
Ζ	8		
$ ho_{ m calcd}/ m g\ m cm^{-3}$	1.587		
<i>T</i> /K	293(2)		
Absorption correction/mm ⁻¹	0.140		
R _{int}	0.0434		
Data	2173		
Restraints	6		
Parameters	149		
Final <i>R</i> indices $(I > 2\sigma(I))$	$R_1 = 0.0616, \omega R_2 = 0.1686$		
R indices (all data)	$R_1 = 0.0706, \omega R_2 = 0.1775$		
Refinement	SHELXL-97		
CCDC	1,046,164		

structure contains one crystallographically independent cation and one anion. Hydrogen bonds and selected bond lengths and angles of PACADN are presented in Tables 2 and 3, respectively. As given in Table 2, strong intramolecular interactions were formed in the crystal structure of PACADN [N(4)– H(4A)···O(4)#1, N(4)–H(4A)···N(6)#1, N(3)–H(3A)···N(6) #1, N(3)–H(3A)···O(1)#1, N(3)–H(3B)···O(4)#2, N(4)–H (4B)···N(1)#3]. Furthermore, the cations and anions are linked

Fig. 4 Molecular structure (a) and packing diagram in the unit cell (b) of PACADN



Table 2 Hydrogen bonds for the PACADN/Å, °

D–H…A	d(D–H)	$d(H{\cdots}A)$	$d(D{\cdots}A)$	<(DHA)
N(4)-H(4A)O(4)#1	0.890(9)	2.044(11)	2.914(2)	165.4(19)
N(4)-H(4A)N(6)#1	0.890(9)	2.504(14)	3.230(2)	139.1(17)
N(3)-H(3A)···N(6)#1	0.887(9)	2.221(11)	3.041(2)	153.6(19)
N(3)-H(3A)····O(1)#1	0.887(9)	2.407(15)	3.212(3)	151.1(17)
N(3)-H(3B)····O(4)#2	0.884(9)	2.094(12)	2.954(2)	164(2)
N(4)-H(4B)…N(1)#3	0.895(9)	2.243(16)	3.027(2)	146.0(18)

Table 3 Selected bond lengths/Å and torsion angles/° for PACADN

Bond	Length	Bond	Torsion angles
N(1)-N(2)	1.376(2)	C(1)-N(1)-N(2)-C(4)	177.62(17)
N(2)–C(3)	1.374(2)	C(4)-N(2)-C(3)-C(2)	-177.52(18)
C(1)–C(2)	1.399(3)	C(3)-N(2)-C(4)-N(4)	-174.99(19)
C(2)–C(3)	1.347(3)	N(1)-N(2)-C(4)-N(3)	-172.23(17)

into a complex three-dimensional network structure by these strong hydrogen bonds interactions which are shown in Fig. 4b. As given in Table 3, for the cation of PACADN, the C(2)-C(3) bond (1.347(3) Å) is slightly longer than the normal C=C bond (1.340(3) Å). The N(1)–N(2), N(2)–C(3) and C(1)–C(2) bond (1.376(2), 1.374(2) and 1.399(3) Å) are slightly shorter than the normal N–N, N–C and C–C bond (1.450(3), 1.481(3) and 1.547(3) Å), but longer than the normal N=N, N=C and C=C bond (1.250(3), 1.350(3) and 1.340(3) Å). The nitro groups and N–N–N occurred the torsion angle, and as known also from others, the metrical parameters of the dinitramide ion were easily and strongly influenced by the environment [19–21]. The [C(1)–N(1)–



Fig. 5 DSC curve of PACADN under air atmosphere

N(2)-C(4) 177.62(17), C(4)-N(2)-C(3)-C(2) -177.52(18), C(3)-N(2)-C(4)-N(4) -174.99(19), N(1)-N(2)-C(4)-N(3)-172.23(17)] torsion angles showed that the pyrazole ring is still a planar structure due to its aromaticity.

Thermal analysis

Thermal performance of energetic materials has an important effect on their preparation, storage, processing and application [22]. Therefore, the thermal stability of PACADN was investigated by thermogravimetric analysis (TG) and differential scanning calorimeter (DSC).

Figure 5 shows the DSC curve of PACADN. As could be seen from the DSC curve, PACADN exhibited good resistance to thermal decomposition up to 433 K and began to decompose rapidly above that temperature. An intense exothermic peak occurs at 463 K, and the corresponding decomposition enthalpy is 1530 J g⁻¹. Thermal characterization of PACADN



Fig. 6 TG and DTG curves of PACADN under air atmosphere



Fig. 7 FTIR spectra of gas products of PACADN during decomposition at different temperatures

was further achieved by recording their TG and derivative thermogravimetry (DTG) curves. Figure 6 shows the TG and DTG curves of PACADN, and the curves exhibited a rapid mass loss at 459 K and a mass loss of up to 90.24 %, caused by pyrazole ring and dinitramide anion almost at the same time decomposed [23, 24].

In order to well understand the thermal decomposition behavior of PACADN, thermogravimetric analysis tandem infrared spectrum was used to rapidly identify the constituents of the thermal decomposition gas. Figure 7 depicts the FTIR spectra of the gas products during decomposition at different temperatures. The results showed that the decomposed products were mainly H₂O (3540 cm^{-1}), CO₂ (2360 cm^{-1}), N₂O (2247, 1274 cm^{-1}), CO (2148 cm^{-1}) and NO₂ (1630, 1590 cm^{-1}) [25, 26]. Initially, because of the central nitrogen atom of dinitramide anion that bears two strongly electron-withdrawing groups (nitro group). As the temperature rises, dinitramide anion decomposed N₂O firstly. When the heating temperature raised to 502 K, infrared signals disappeared, which proved PACADN now completely decomposed.

Kissinger's method was employed to calculate the exothermal decomposition reaction kinetic parameters [apparent activation energy E_a (kJ mol⁻¹) and the pre-exponential constant A (s⁻¹)] of PACADN. The Kissinger's equation [27, 28] is as follows:

$$\ln\left(\frac{\beta}{T_{\rm p}^2}\right) = \ln\left(\frac{AR}{E_{\rm a}}\right) - \frac{E_{\rm a}}{RT_{\rm p}} \tag{1}$$

where β is the heating rate (K min⁻¹), T_p is the peak temperature (K), R is the ideal gas constant, E_a is the activation energy and A is the pre-exponential factor. The TG and DTG curves of PACADN under heating rates of 5, 10, 15, 20 and 25 K min⁻¹ are shown in Fig. 8 According to Eq. (1), $\ln(\beta/T_p^2)$ varies linearly with $1/T_p$, yielding the kinetic parameters of activation energy (E_a) from the slope of the straight line and pre-exponential factor from the



Fig. 8 TG (a)/DTG (b) curves of PACADN at different heating rates



Fig. 9 Dependence of $\ln(\beta/T_p^2)$ on $1/T_p$ for PACADN, scatter points are experimental data, and line denotes the linear fitting results

intercept. Figure 9 shows the experimentally measured $\ln(\beta/T_p^2)$ versus $1/T_p$. The activation energy was calculated to be 143.2 kJ mol⁻¹.

Energetic properties

Detonation velocity (D) and detonation pressure (P) are important parameters of energetic properties. The empirical Kamlet–Jacobs equations [29, 30] were employed to estimate the values of detonation velocity and detonation pressure for PACADN, as shown in the following equations:

$$D = 1.01 (N\overline{M}^{1/2}Q^{1/2})^{1/2} (1 + 1.3\rho)$$
$$P = 1.558\rho^2 N\overline{M}^{1/2}Q^{1/2}$$

where *D* is the detonation velocity (km s⁻¹), *P* is detonation pressure (GPa), *N* is for explosive detonation generated gas moles per gram (mol g⁻¹, \overline{M} is for the average molecular mass of gaseous products (g mol⁻¹), *Q* is as per gram of the explosive detonation chemical energy (kJ g⁻¹) and ρ is for the density (g cm⁻³). So as to calculate the values of *D* and *P*, we first need to calculate the value of *Q*. And *Q* is determined by $\Delta H_{\rm f}$ of the detonation reactant and product.



Fig. 11 Isodesmic and protonated reactions for the calculation of heat of formation

Table 4 Calculation of parameters in Kamlet-Jacobs equation

$M/g \text{ mol}^{-3}$	$\rho/{\rm g~cm^{-3}}$	$N/mol g^{-1}$	$\overline{M}/\text{g mol}^{-1}$	$\Delta H_{\rm f}/{\rm kJ}~{\rm mol}^{-1}$
217.17	1.587	0.033	23.724	73.3

Based on a Born–Haber [31] energy circle (Fig. 10), the heat of formation (ΔH_f) can be simplified by the formula:

$$\Delta H_{\rm f}^{\ominus}(\text{ionic salt}, 298 \, K) = \Delta H_{\rm f}^{\ominus}(\text{anion salt}, 298 \, K) + \Delta H_{\rm f}^{\ominus}(\text{cation salt}, 298 \, K) - \Delta H_{\rm f}$$

where $\Delta H_{\rm L}$ is the lattice energy of the salt and can be predicted by the formula suggested by Jenkins [32, 33]. The isodesmic reactions (Fig. 11) used to obtain the $\Delta H_{\rm f}$ of substituted PACADN anions and cations at 298 K, respectively. The accurate heats of formation of the NH⁴₄, H₂N–NO₂, cations were obtained by protonation reactions using high-precise G9 method [34]. The remaining anion was determined by isodesmic reaction, and the enthalpy of reaction was obtained at the B3LYP/6-31G* level [35]. The calculation of parameters in Kamlet–Jacobs equation is given in Table 4.

Then, the Q estimated by the $\Delta H_{\rm f}$ was 1120 kJ g⁻¹, and the theoretically computed detonation velocity (D) and



detonation pressure (P) were 7.2 km s⁻¹ and 21 GPa, respectively.

Conclusions

A new energetic salt PACADN was synthesized successfully in this study. The structure of PACADN was systematically characterized by FTIR, UV–Vis, ¹H NMR and ¹³C NMR spectroscopy analyses. X-ray diffraction study showed that PACADN crystallizes in the orthorhombic space group Pnna. In addition, the thermal stability analysis and thermal decomposition kinetics were studied, suggesting that PACADN exhibits good resistance to thermal decomposition up to 433 K and has 90.24 % mass loss between 433 and 523 K with $E_a = 143.2$ kJ mol⁻¹. Moreover, the detonation parameters of PACADN were calculated with Kamlet–Jacobs equations, and the detonation velocity and pressure of PACADN were close to those of 2-methyl-1,3,5-trinitrobenzene (TNT).

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