Synthesis, single crystal structure and characterization of pentanitromonoformylhexaazaisowurtzitane

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ABSTRACT

Pentanitromonoformylhexaazaisowurtzitane (PNMFIW) was synthesized by the nitrolysis of tetraacetyldiformylhexaazaisowurtzitane (TADFIW) in mixed nitric and sulfuric acids and structurally characterized by element analysis, FT-IR, MS and ^{1}H NMR. Single crystals of PNMFIW were grown from aqueous solution employing the technique of controlled evaporation. PNMFIW belongs to the orthorhombic system having four molecules in the unit cell, with space group $P2(1)2(1)2(1)$ and the lattice parameters $a = 8.8000(18)$ Å, $b = 12.534(2)$ Å, and $c = 12.829(3)$ Å. The calculated density reaches $1.977\,g/cm^3$ at 93 K, while the experimental density is $1.946\,g/cm^3$ at 20 °C. The calculated detonation velocity and pressure of PNMFIW according to the experimental density are 9195.76 m/s and 39.68 GPa, respectively. PNMFIW is insensitive compared with ε-HNIW through drop hammer impact sensitivity test.

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1. Introduction

Nitramines are potentially a class of high energy density compounds (HEDCs). Caged nitramines became a hot subject-matter due to their high energy density at the end of last century [1,2]. Hexanitrohexaazaisowurtzitane (HNIW) is a new nitramine explosive with 20% more energy than octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine [3]. The discovery of HNIW was a breakthrough in energetic materials with higher performance, minimum signature, and reduced hazard characteristics. The studies carried out on HNIW indicated that it has numerous military and commercial applications [1,4]. The method of HNIW synthesis involves the preparation of hexabenzylhexaazaisowurtizitane followed by debenzylation, acetylation and nitration [5]. A novel process for the 2-stage synthesis of HNIW has been developed. The process comprises a first stage of reaction of an α,β-dicarbonyl derivative with a primary amine which makes it possible to form a hexasubstituted hexaazaisowurtzitane derivative. And at the second stage, HNIW is subsequently obtained by nitration of the hexaazaisowurtzitane derivative obtained at the first stage [6].

The synthesis of mono-amine and di-amine derivatives of HNIW has been patented, which is effected by the novel use of fluoroacylating compounds to protect the secondary amine groups of acylated precursors of HNIW against nitrolysis [7]. Wardle and Hinshaw provided methods of synthesis of HNIW and related energetic compounds, which are improvement from the standpoint of cost and environment impact. In the same time, they disclosed several novel hexaazaisowurtzitane derivatives which can be converted to HNIW and related high energy caged nitrogen compounds [8]. Bellamy and Cuish used N- and O-trifluoroacetylation to protect secondary amine groups and hydroxyl groups, respectively under nitrolysis/nitration and subsequently removed the trifluoroacetyl protecting group from the nitrated products by solvolysis under mild condition to produce hexaazaisowurtzitane derivatives including 2,6,8,12-tetranitro- and 2,4,6,8,12-pentanitro-2,4,6,8,10,12-hexaazaisowurtzitane, 2-hydroxymethyl-2-methyl-1,3-dinitratopropane [2,2-bis-(nitratomethyl)-propan1-ol] and N-nitroazetidin-3-ol [9].

Recently, insensitive explosives have been much needed for safety and new military weapons, thus high energetic compounds with lower sensitivity become promising explosives of future [10–12]. Slightly high sensitivity of HNIW retards its wider application in insensitive munitions [13]. Sensitivity characteristics of HEDCs can be related to their chemical as well as physical characteristics [14]. The physical characteristics of explosives such as crystal size, morphology, purity, internal and surface defects have been modified through a re-crystallization process to lower the sensitivity of such explosives [15–17]. However, the effect of

chemical characteristics of polynitrohexaazaisowurtzitane derivatives on the sensitivity has not been studied theoretically, and the sensitivities of such derivatives have not been reported in series and systemically. Slight variation of the structure of polynitrohexaazaisowurtzitane derivative of molecule may result in much decreasing of sensitivity but little loss of energy density according to the initiation mechanism.

Pentanitromonoformylhexaazaisowurtzitane (PNMFIW) was even known as a by-product in the synthesis of HNIW [18–20]. The polymorphs and sensitivity of PNMFIW was theoretically studied by AM1 and PM3 semi-empirical methods in our laboratory, and the result shows that the shock sensitivities of individual morphologies are lower than that of HNIW [21]. Further, we theoretically studied PNMFIW with quantum calculation and found that PNMFIW has a density about $2.0\,g/cm^3$ which is very near the density of ε-HNIW. Accordingly, PNMFIW may be a novel high energy density compound with lower sensitivity than HNIW. Crystal structure of an energetic compound is very important, because detonation performance such as detonation velocity and pressure, depends largely on density which is identified by its crystal structure, and the sensitivity closely correlates with the crystal structure [22,23]. Therefore, it is very interesting to synthesize PNMFIW and characterize its crystal structure as well as to predict its detonation performances. To now, the crystal structure and properties of PNMFIW have not been reported.

In this study, we report the synthesis, the determination of single crystal structure of PNMFIW and predict its detonation properties, so as to enrich the existing data on HNIW and its derivates and facilitate the energetic materials application of PNMFIW.

2. Experimental

2.1. Caution

The titled compound and related derivatives are energetic materials and tend to explode under certain conditions. Proper protective measures (safety glasses, face shields, leather coat, ear plugs and earthening equipment and person) should be taken during the synthesis, test and measurement processes, especially when these compounds are prepared on a larger scale.

2.2. Materials and analytic instrument

All the reagents and chemicals were of AR grade in the present study. Tetraacetyldiformylhexaazaisowurtzitane (TADFIW) was prepared in laboratory by us, and the purity of self-prepared TADFIW was 98.5% measured by high performance liquid chromatography of waters. The IR spectra were recorded on PerkinElmer FT-IR-1600 spectrophotometer in KBr matrix and ^{1}H NMR spectra were scanned on a 500 MHz Varian instrument in deuterated solvents at 25 °C with TMS as internal standard. Mass spectra (CI) and element analysis were done on a Managa 560 mass spectra instrument and ARX400 element analysis instrument, respectively. The particle apparent density measurements were performed on an Ultrapycno Meter 1000 pycnometer.

2.3. Synthesis of PNMFIW

Fuming sulfuric acid was slowly added into fuming nitric acid in a three-neck flask with stirring. After the solution of mixed acids was heated to 60 °C, TADFIW (10 g) was added, and then the temperature was elevated to 65 °C. The solution was maintained at 65 °C for 12 h; thereafter the solution was poured into ice-water. The precipitated solid was filtered off, washed with water and then dried. The obtained solid was a mixture of polynitrohexaazaisowurtzitane derivatives with different number of nitro
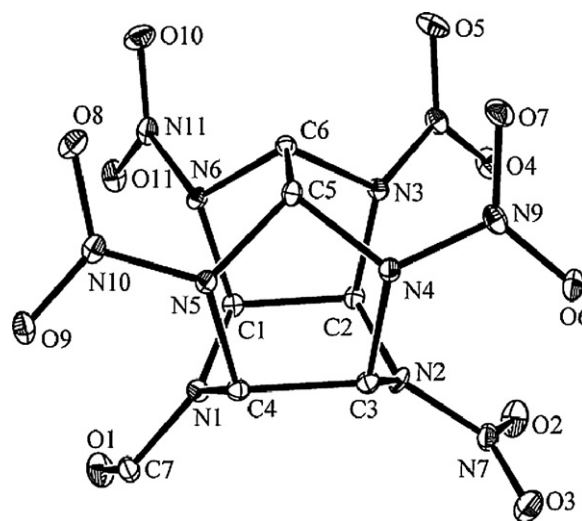

Fig. 1. Molecular structure of PNMFIW.

substitutes. Pure PNMFIW was obtained through a silica column chromatography with hexane/acetyl acetate (6/4 by volume) as mobile phase at room temperature (25 °C).

2.4. Determination of molecular structure of PNMFIW

Element analysis: calculated for $C_7H_7N_{11}O_{11}$ (%): C 19.95, H 1.66, N 36.58; Found (%): C 20.17, H 1.65, N 36.48. Mass spectra: m/z 422 (M+1)$^+$, 375 (M-NO$_2$+1)$^+$, 299 (M-2NO$_2$-CHO)$^+$, 253 (M-3NO$_2$-CHO)$^+$. IR (KBr pellets, 4000–400 cm^{-1}): ν C-H on rings 3037 s, ν OC-H 2917, ν C=O 1720 s, ν_{as} NO$_2$ 1591 s, ν N-CHO 1326 s, ν_s NO$_2$ 1277. ^{1}H NMR (COCD$_3$, 400 MHz) δ (ppm): 8.468 (s, –OCH, 1H), 7.02 (d, five-membered ring-CH, 1H), 7.81–8.02 (multi, six-membered ring-CH, 4H). According to above data of MS, IR, element analysis and ^{1}H NMR, the molecular structure of PNMFIW was confirmed as shown in Fig. 1.

2.5. Preparation and determination of PNMFW single crystal

Pure PNMFIW was dissolved in mixed solvents of acetone and n-hexane, and then the resulted solution was placed in ambient condition (15–20 °C). A week later, single crystal was obtained by controlling the evaporation of solvent. The crystal structure of PNMFIW was determined by single crystal X-ray diffraction. The data collection was performed on Rigaku Maxis Rapid IP Diffractometer with highly oriented graphite crystal monochromated Mo Kα radiation (λ = 0.071073 nm) at 93 K in 2θ–ω scans mode. The crystal structure was re-determined by direct methods and refined by full-matrix least-squares techniques based on F^2 using the SHELXTL program package (SHELXTL, 1998). All non-hydrogen atoms were obtained from the difference Fourier map and refined with atomic anisotropic thermal parameters. The hydrogen atom were placed geometrically and treated by a constrained refinement. The details of data collection and refinement are given in Table 1.

2.6. Impact sensitivity test and apparent density measurement

An HGZ-1 impact instrument was used to test the impact sensitivity of the explosive samples. Each sample (50 mg) was tested 25 times to obtain a H_{50}. The H_{50} value represents the height from which dropping a 5 kg weight will result in an explosive event in 50% of the trials. With four replicate tests, an average value of H_{50} was calculated.

Table 1
Crystal data and structure refinement parameters for PNMFIW.

Empirical formula	$C_7H_7N_{11}O_{11}$
Molar mass (g/mol)	421.24
Temperature (K)	93(2)
Crystal system	Orthorhombic
Space group	$P2(1)2(1)2(1)$
Crystal size (mm)	$0.33 \times 0.30 \times 0.20$
a (Å)	8.8000(18)
b (Å)	12.534(2)
c (Å)	12.829(3)
V (Å^3)	1419.6(4)
Z	4
Dc	1.977
λ (nm)	0.071073
Data collection	
θ_{min}, θ_{max} (°)	2.27, 27.48
h_{min}, h_{max}	−11, 10
k_{min}, k_{max}	−16, 14,
l_{min}, l_{max}	−16, 16
Reflections independent, observed	12763, 1873
R_{int}	0.0279
Refinement	
Goodness-of-fit on F^2 (observed reflections)	1.003
R_1, wR_2 (observed reflections)	0.0331, 0.0809
R_1, wR_2 (independent reflections)	0.0371, 0.0837
Extinction coefficient	0.0021(10)
Largest diff. peak and hole	0.693, −0.265 e Å^{-3}

The particle apparent density measurement was performed on a ULTRAPYCNO METER 1000 Pycnometer, with the test conditions: temperature of 20 °C, pressure of 14 psi, and pure N_2 gas. Ultrapycno Meter 1000 pycnometer bases on the displacement principle to measure the apparent density of sample [24]. After air was displaced from the entire empty space within the pycnometer by pure N_2 gas, volume of tested PNMFIW sample in the pycnometer was determined according to the amount of the volume of displaced pure N_2 gas by tested PNMFIW crystals. And the weight of tested PNMFIW sample could be known through an electronic balance before the determination of volume. The apparent density can be obtained through the calculation using the measured weight and volume of the sample.

3. Results and discussion

3.1. Synthesis of PNMFIW

The nitrolysis of TADFIW was carried out using mixed fuming nitric acid and sulfuric acid as nitrolysis agent (please see Scheme 1). In the nitrolysis of TADFIW, nitronium undergoes electrophilic attack to N atom of acylamide to form nitramine. The nitrolysis activities for acylamides were generally propanamide > acetylamide > formylamide > benzoylamide. Due to higher electronic density of five-membered ring than six-membered ring, N atoms on 2, 6, 8, 12-positions of five-membered rings are more reactive than N atoms on 4 and 10-positions of six-membered ring. Therefore, the four acetyls on five-membered rings are firstly cleaved and replaced by nitro groups in a stepwise process. In the nitrolysis reaction, with the increasing of nitro electron-withdrawing groups on caged structure, the electron densities of N atoms of formylamide become more and more low, thus the cleavage of formyl on six-membered ring becomes very difficult. Therefore, PNMFIW can be obtained through controlling the nitrolysis stage of TADFIW in mixed nitric and sulfuric acids.

In order to obtain PNMFIW as main product, the nitrolysis temperature, volume ratio of fuming nitric acid to sulfuric acid and reaction time were optimized to control nitrolysis on the stage of PNMFIW. After reacting for preset reaction time under such conditions, the nitrolysis mixture was poured into ice-water to terminate nitrolysis reaction. Then, the precipitated solid product was filtered off, washed with water and then dried. The compositions of nitrolysis product were quantificationally analyzed by HPLC according to areas of individual peaks. The results were summarized in Table 2.

Referring to entries 1–5 together with entries 6–8, it was observed that due to the relative higher PNMFIW contents (51.77% of entry 3, 47.29% of entry 7) in the nitrolysis product, the temperature of 60 °C was preferred nitrolysis temperature under the reaction conditions. According to above description for nitrolysis activities of acylamides in mixed nitric and sulfuric acids, it is well known that with the increasing of nitro groups on caged structure, the cleave of acyl becomes more and more difficult. High temperature is valuable to the nitrolysis of polynitrohexaazaisowurtzitane (such as PNMFIW), while low temperature facilitates the nitrolysis of less-nitro hexaazaisowurtzitane (such as TNMADFIW). When the appropriate temperature was selected, the nitrolysis of TADFIW was performed in a stepwise manner, and the nitrolysis was thus controlled on the stage of PNMFIW.

When the ratio of nitric acid to sulfuric acid was 1:1, PNMFIW content in nitrolysis product achieved 51.77% which was much higher than the content under the ratio of 3:2 (47.29%). The reason was that sulfuric acid of high concentration could produce more NO_2^+ which was a good nitrolysis agent. However, too high concentration of sulfuric acid would result in lower yield. The reason was that sulfuric acid of too high concentration made the cyclic structure cleaved in the nitrolysis reaction. Accordingly, the radio of nitric/sulfuric acid of 1:1 was preferred radio. Furthermore, the reaction time was optimized through a series of experiments. Referring to entries 9–12 and 3, the content of PNMFIW in nitrolysis product had the highest value of 53.92% for reaction time of 14 h.

Therefore, nitric/sulfuric acid ratio of 1:1, temperature of 60 °C and reaction time for 14 h were the most preferred reaction conditions in the synthesis of PNMFIW. Pure PNMFIW was obtained
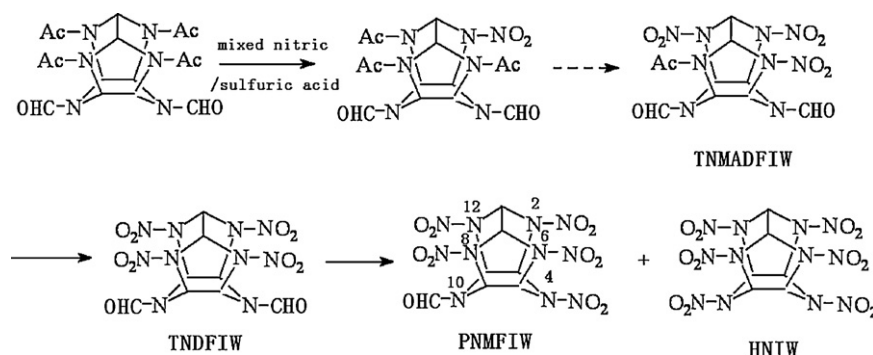
Scheme 1. Nitrolysis of TADFIW in the mixed nitric and sulfuric acids.

Table 2
Compositions of nitrolysis product under different reaction conditions.

Entry	T (°C)	Reaction time (h)	Ratio of acids[a]	TNMADFIW[b] (%)	TNDFIW[b] (%)	PNMFIW[b] (%)	HNIW[b] (%)
1	50	12	1:1	0.27	42.98	44.37	12.38
2	55	12	1:1	0.18	39.60	45.79	14.43
3	60	12	1:1	0	8.93	51.77	39.30
4	65	12	1:1	0	1.49	31.85	66.67
5	70	12	1:1	0	0.94	20.44	78.62
6	55	12	3:2	0.11	38.54	47.18	14.17
7	60	12	3:2	0	15.16	47.29	37.55
8	65	12	3:2	0	1.84	29.40	68.16
9	60	10	1:1	0.90	22.07	39.80	37.23
10	60	14	1:1	0.00	5.42	53.92	40.66
11	60	17	1:1	0.00	0.20	30.17	69.63
12	60	19	1:1	0.00	0.00	19.25	80.75

[a] Volume ratio of fuming nitric acid to sulfuric acid.
[b] Contents calculated on the basis of results of HPLC analysis, wherein TNMADFIW is trinitromonoacetyldiformylhexaazaisowurtzitane, TNDFIW is tetronitrodiformylhexaaza-isowurtzitane, PNMFIW is pentanitromonoformylhexaazaisowurtzitane, HNIW is hexanitrohexaazaisowurtzitane.

by a silica column chromatography using hexane/acetyl acetate as mobile phase. The final yield of PNMFIW was 41.2% based on the moles of TADFIW used. The molecular structure of PNMFIW was confirmed using FT-IR, MS, ¹H NMR and element analysis (please see Section 2).

3.2. Crystal structure description of PNMFIW

A perspective view of PNMFIW molecule is shown in Fig. 1, and the three-dimensional packing diagram of PNMFIW crystal cell is shown in Fig. 2. The atomic coordinates and displacement parameters, selected bond distances and angles are listed in Tables 3–5, respectively. The caged structure of hexaazaisowurtzitane is constructed from one six-membered and two five-membered rings which are closed by the C5–C6 bond, thus creating two seven-membered rings. The more stable conformation of six-membered ring is chair form; however, the six-membered pyrazine ring in PNMFIW molecule is shaped like a boat. The two five-membered rings are also non-planar, being characterized by the torsion angles of two five-membered rings. Four nitro groups are appended to the four nitrogen atoms of the two five-membered rings, while a nitro group and a formyl are attached to the two nitrogen atoms of the six-membered ring, respectively. Due to caged structure of PNMFIW, the bond length of N–N (1.369–1.436 Å) is much

longer than common nitramine (1.360 Å). The bond length of C–C (1.561–1.587 Å) of PNMFIW is also much longer than common C–C bond (0.154 nm) (see Table 4). Bond angles of N(4)–C(5)–C(6) (112.7°), C(7)–N(1)–C(1) (122.2°) and C(2)–N(2)–C(3) (117.5°) on caged structure are much bigger than normal angle of sp3 hybrid bond (see Table 5). From the molecular structure analysis above, it is known that PNMFIW molecule has high tensile force and energy.
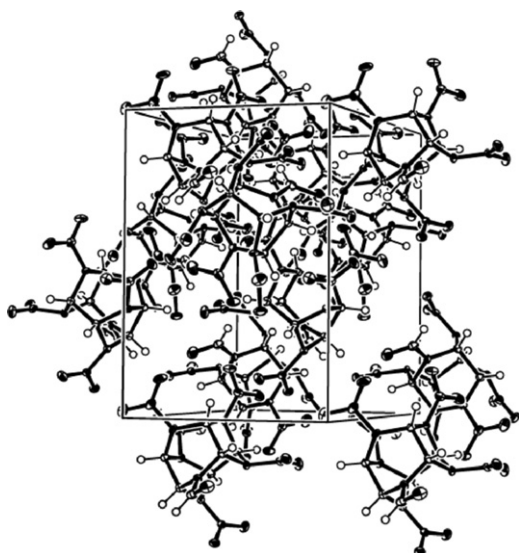
Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^5 \text{ nm}^2$) for PNMFIW.

Atom	x	y	z	U (equiv.)
C(1)	1030(3)	8839(2)	6700(2)	12(1)
C(2)	2005(3)	9815(2)	7048(2)	11(1)
C(3)	4239(3)	8641(2)	7211(2)	12(1)
C(4)	3243(3)	7671(2)	6861(2)	12(1)
C(5)	2702(3)	8051(2)	8666(2)	12(1)
C(6)	1270(3)	8807(2)	8546(2)	12(1)
C(7)	1668(3)	7590(2)	5290(2)	16(1)
N(1)	1974(3)	8029(2)	6246(2)	12(1)
N(2)	3567(3)	9603(2)	6794(2)	13(1)
N(3)	1812(3)	9845(2)	8180(2)	11(1)
N(4)	4119(3)	8571(2)	8364(2)	12(1)
N(5)	2765(3)	7224(2)	7875(2)	11(1)
N(6)	344(3)	8432(2)	7676(2)	11(1)
N(7)	4484(3)	10415(2)	6401(2)	17(1)
N(8)	1323(3)	10777(2)	8662(2)	15(1)
N(9)	4565(3)	9438(2)	8954(2)	15(1)
N(10)	1707(3)	6426(2)	7896(2)	14(1)
N(11)	−1263(3)	8569(2)	7806(2)	16(1)
O(1)	621(3)	7886(2)	4754(2)	25(1)
O(2)	3882(3)	11267(2)	6202(2)	25(1)
O(3)	5806(2)	10201(2)	6246(2)	26(1)
O(4)	1518(3)	11597(2)	8183(2)	21(1)
O(5)	823(3)	10690(2)	9544(2)	23(1)
O(6)	5497(2)	10036(2)	8564(2)	20(1)
O(7)	3993(2)	9507(2)	9825(2)	19(1)
O(8)	996(2)	6304(2)	8706(2)	20(1)
O(9)	1596(2)	5882(2)	7105(2)	18(1)
O(10)	−1739(2)	8453(2)	8680(2)	23(1)
O(11)	−1992(2)	8717(2)	7014(2)	20(1)

Fig. 2. Packing diagram of PNMFIW.

Table 4
Selected bond lengths (Å) of PNMFIW.

C(1)–N(1)	0.1437(3)	C(7)–N(1)	0.1373(4)
C(1)–N(6)	0.1482(3)	C(5)–N(5)	0.1453(4)
C(1)–C(2)	0.1561(4)	C(5)–N(4)	0.1461(3)
C(2)–N(2)	0.1439(4)	C(5)–C(6)	0.1587(4)
C(2)–N(3)	0.1464(3)	C(6)–N(6)	0.1462(3)
C(3)–N(2)	0.1447(4)	C(6)–N(3)	0.1465(3)
C(3)–N(4)	0.1486(3)	C(4)–N(1)	0.1440(4)
C(3)–C(4)	0.1567(4)	C(4)–N(5)	0.1478(3)

Table 5
Selected angles (°) of PNMFIW.

N(3)–C(6)–C(5)	107.7(2)	N(2)–C(3)–N(4)	112.9(2)
N(1)–C(1)–C(2)	110.6(2)	N(2)–C(3)–C(4)	108.2(2)
N(6)–C(1)–C(2)	104.7(2)	N(4)–C(3)–C(4)	101.5(2)
N(2)–C(2)–N(3)	109.9(2)	N(1)–C(4)–N(5)	112.3(2)
N(2)–C(2)–C(1)	108.4(2)	N(1)–C(4)–C(3)	110.5(2)
N(3)–C(2)–C(1)	103.9(2)	N(5)–C(4)–C(3)	101.6(2)
N(6)–C(6)–C(5)	109.0(2)	C(5)–N(5)–C(4)	110.8(2)
N(5)–C(5)–C(6)	112.9(2)	C(1)–N(1)–C(4)	116.6(2)
N(4)–C(5)–C(6)	112.7(2)	C(6)–N(6)–C(1)	107.9(2)
C(7)–N(1)–C(1)	122.2(2)	C(5)–N(4)–C(3)	110.6(2)
C(2)–N(3)–C(6)	109.5(2)	C(2)–N(2)–C(3)	117.5(2)

Crystal data and details of the data collection for the crystal structure determination are listed in Table 1. The crystal structure of HNIW is reported for the first time in the literature. The crystal structure of PNMFIW belongs to the orthorhombic system with space group $P2(1)2(1)2(1)$ and the lattice parameters $a = 8.8000(18)$ Å, $b = 12.534(2)$ Å, $c = 12.829(3)$ Å. There are four molecules in the unit cell of PNMFIW with the cell volume of $1415.1(5)$ Å^3 and the molar mass 421.24 g/mol, thus the density calculated with single crystal data reaches 1.977 g/cm^3 at the temperature of 93 K. There are four structural isomers (α, β, γ and ε-forms) of HNIW crystals. The α and β,-forms of crystals have the space groups of $Pbca$ and $Pb21a$, respectively, and γ and ε-HNIW crystals are same in the space group of $P21/n$. The ε-HNIW with the lattice parameters $a = 8.791(2)$ Å, $b = 12.481(3)$ Å, $c = 13.185(3)$ Å, $\beta = 106.55(3)$ at 100 K is thermodynamically and mechanically the most stable due to its highly symmetric molecular configuration. At the temperature of 100 K, the calculated density of ε-HNIW is 2.083 g/cm^3, while the calculated density of γ-HNIW is 1.954 g/cm^3 [25]. Apparently, the space group of PNMFIW has more highly symmetric molecular configuration than that of γ-HNIW, and the calculated density of PNMFIW is higher than γ-HNIW at the same temperature.

3.3. Characterization of impact sensitivity, detonation velocity and pressure

Impact sensitivity of PNMFIW was tested using a 5 kg drop hammer, and calculated value of H_{50} represented the drop height of 50% initiation probability. The impact sensitivity values (H_{50}) of PNMFIW was 26.8 cm. Under the same test conditions, the impact sensitivities (H_{50}) of ε-HNIW, β-HMX and RDX were 21.1 cm, 29.1 cm and 26.5 cm, respectively, which were consistent with the values of Ref. [26]. Therefore, the impact sensitivity of PNMFIW is much lower than that of ε-HNIW. The particle apparent density measurement was performed on a ULTRAPYCNO METER 1000 Pycnometer, under the test conditions: temperature of 20 °C, pressure of 14 psi, pure N_2 gas. The apparent density of PNMFIW determined by a pycnometer was 1.946 g/cm^3 at the temperature of 20 °C, which is very near the calculated density using the single crystal data.

Detonation velocity (D) and detonation pressure (P) are the most important targets of scaling the detonation characteristics of energetic materials. The detonation velocity and pressure of an explosive can be predicted with the nitrogen equivalent equation (NE equation) shown as formulas (1)–(3) [27].

$$V_D = (690 + 1160\rho_0)\Sigma N \tag{1}$$

$$P = 1.092(\rho_0 \Sigma N)^2 - 0.574 \tag{2}$$

$$\Sigma N = \frac{100}{M \Sigma x_i N_i} \tag{3}$$

in which V_D represents detonation velocity of an explosive, ρ_0 represents density of an explosive, ΣN represents nitrogen equivalent of the detonation products, N_i is nitrogen equivalent index of certain detonation product, x_i is the mole number of certain detonation product produced by a mole explosive.

The detonation products produced by general explosives together with their nitrogen equivalent indexes are listed in Table 6. According to the order of H_2O–CO–CO_2 in forming detonation products, the detonation products of PNMFIM are calculated as follows:

$$C_7H_7N_{11}O_{11} = (3.5)H_2O + (6.5)CO + (0.5)CO_2 + (5.5)N_2.$$
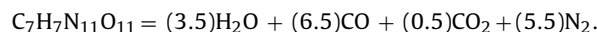
According to Eq. (3), in which $M = 421.24$, $\rho_0 = 1.946$ g/cm^3, total nitrogen equivalents of PNMFIW are obtained through the nitrogen equivalent indexes of the detonation products in Table 6:

$$\Sigma N = \frac{100}{421.24 \times (3.5 \times 0.54 + 6.5 \times 0.78 + 0.5 \times 1.35 + 5.5 \times 1)}$$

$$= 3.120.$$

According to Eqs. (1) and (2), detonation velocity and pressure can be obtained as follows:

$$V_D = (690 + 1160\rho_0)\Sigma N = (690 + 1160 \times 1.946) \times 3.120$$

$$= 9195.76 \text{ m/s},$$

$$P = 1.092(\rho_0 \Sigma N)^2 - 0.574 = 1.092(1.946 \times 3.120)^2 - 0.574$$

$$= 39.68 \text{ GPa}.$$

As indicated above, PNMFIW has a measured density of 1.946 g/cm^3, an impact sensitivity values (H_{50}) of 26.8 cm, and the calculated detonation velocity and pressure of PNMFIW are 9195.76 m/s and 39.68 GPa, respectively.

4. Conclusions

In summary, a hexaazaisowurtzitane derivative of PNMFIW can be synthesized through the nitrolysis of TADFIW in mixed nitric and sulfuric acids. Its crystal structure belongs to the orthorhombic system having four molecules in the unit cell, with space group $P2(1)2(1)2(1)$ and the lattice parameters $a = 8.8000(18)$ Å, $b = 12.534(2)$ Å, and $c = 12.829(3)$ Å. The single crystal structure is reported for the first time in the literature. The density calculated with single crystal data reaches 1.977 g/cm^3 at 93 K, while the experimental density is 1.946 g/cm^3 at 20 °C. The calculated detonation velocity and pressure of PNMFIW according to the experimental density reach 9195.76 m/s and 39.68 GPa, respectively. PNMFIW is insensitive compared with ε-HNIW through drop hammer impact sensitivity test.

Table 6
Nitrogen equivalents of different detonation products.

Detonation product	N_2	H_2O	CO	CO_2	O_2	C	HF	CF_4	H_2	Cl_2
Nitrogen equivalent index	1	0.54	0.78	1.35	0.5	0.15	0.577	1.507	0.290	0.876

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