

New Energetic Ionic Derivatives of Symmetric 4,6-Dihydrazinium-1,3,5-Triazine-2-One Cation with Low Impact and Friction Sensitivities

Bo Wu,^{*[a, b]} Xiaohui Duan,^[a] Xiufang Qi,^[c] Decai Zhou,^[d] Jingshu Wei,^[d] and Chonghua Pei^{*[a]}

Abstract: A facile synthetic protocol was developed to synthesize unique energetic salts based on 4,6-dihydrazino-1,3,5-triazine-2-one in good to high yield from commercial sources. The process was found to be practical and easily scalable. The resulting energetic compounds show good to excellent thermal stability with decomposition temperatures ranging from 180 °C to 331 °C. They possess low sensitivity to impact and friction (IS > 20 J, FS > 360 N), as well

as positive enthalpy of formation (148.9~1381.7 kJ mol⁻¹). Their detonation velocity (V_D) values locate between 8301 ms⁻¹ and 9282 ms⁻¹, and detonation pressure (P) values range from 26.1 GPa to 37.2 GPa, in some cases, which are comparable to those of HMX. From the view of sensitivity and energy level, some of the energetic compounds prepared in this work exhibit potential as insensitive excellent performance energetic materials.

Keywords: Energetic compounds · Triazine · Low sensitivity · X-ray diffraction · Detonation

1 Introduction

Low sensitivity is one of key targets for the development of energetic materials [1]. Traditionally, 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), 1,1-diamino-2,2-dinitroethylene (FOX-7), 2,6-diamino-3,5-dinitropyrazine *N*-oxide (LLM-105) as well as 3,3'-diamino-4,4'-azoxyfurazan (DAAF) are considered as insensitive high explosives (IHEs). The results from their crystal structures analysis demonstrate that the presence of intra- and intermolecular hydrogen bonding interactions and layer π -stacking can enhance their high thermal stabilities and low sensitivities to impact and friction [2]. New synthetic strategies have been employed for tuning the sensitivity of energetic compounds by reinforcing intra- and intermolecular interactions in the molecular design [3]. For example, some energetic covalent molecules with the vicinal C-NH₂ and C-NO₂ functionalities, 4-amino-3,7,8-trinitropyrazolotriazine (PTX), 4-amino-3,7-dinitro-1,2,4-triazolotriazine (DPX-26), have been investigated. The development of nitrogen-rich energetic salts [4] could be another effective approach for insensitive high explosives owing to their unique properties, such as low vapor pressures, high positive enthalpy of formation, and high thermal stabilities. In addition, nitrogen-rich energetic salts were readily optimized and improved through the combination of different cations and anions. Nevertheless, these works suffer from one or more disadvantages, such as, multiple reaction steps, separation issue, poor detonation performance, and massive waste acid production. For enhancing the energetic performance of energetic salts, it is efficient to incorporate oxygen atom into cations and anions, which is useful for improving the density and oxygen balance.


On the other hand, the presence of -NH₂ and the -NH-NH₂ structures can reinforce the intra- and intermolecular hydrogen bonding interactions [5]. Amino- and hydrazino- derivatives are ideal cationic components. Moreover, the backbones connecting with functionalities also play important role for the performance of their energetic derivatives. 1,3,5-triazine is one of an interesting backbones, whose energetic derivatives have exhibited great potential in the field of energetic materials with high energy and low sensitivities [6]. Some energetic amino- and hydrazino- derivatives based on 1,3,5-triazine reported by Liu etc. and Wu etc., show good potential in the field of insensitive energetic materials [5e, 7]. Herein, we were encouraged to de-

[a] B. Wu, X. Duan, C. Pei
State Key Laboratory of Environment-friendly Energy Materials
Southwest University of Science and Technology
59 Qinglong road, Mianyang 621010 (P.R. China)
*e-mail: wubo@swust.edu.cn
peichonghua@swust.edu.cn

[b] B. Wu
Sichuan Civil-military Integration Institute
Southwest University of Science and Technology
59 Qinglong road, Mianyang 621010 (P.R. China)

[c] X. Qi
School of National Defense Science and Technology
Southwest University of Science and Technology
59 Qinglong road, Mianyang 621010 (P.R. China)

[d] D. Zhou, J. Wei
Sichuan Lanshi Technology Co. Ltd.
Mianyang, 621000, P.R. China

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sign and synthesize energetic salts with a symmetric hydrazino divalent cation, which is comprised of one oxygen atom, one triazine ring backbone and two hydrazinium cations. These energetic salts are expected to exhibit good thermal stabilities, low sensitivities, and good energetic performances.

2 Experimental Section

2.1 General Methods

Cyanuric chloride, 3,5-diamino-1,2,4-triazole and 1,3-diaminoguanidine monohydrochloride were purchased from Aladdin (Shanghai) Technology Co., LTD. Ammonium hydroxide, nitrate acid and perchlorate acid were obtained from Kelong (Chengdu) Technology Co., LTD. Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm). ^1H and ^{13}C NMR spectra were recorded on a Bruker advance III 600 spectrometer (600 MHz for ^1H and 150 MHz for ^{13}C) in d_6 -DMSO with TMS as an internal standard. IR spectra were recorded by a PerkinElmer spectrum one FTIR spectrometer. Elemental analyses were performed using a Vario EL cube instrument. The DSC measurements were carried out on a Netzsch STA449F5 simultaneous thermal analyzer at a heating rate of 5°C min^{-1} with Al pans. X-ray crystal diffraction measurements of the crystals were performed on a Bruker Smart APEX II CCD diffractometer. Sensitivity data were determined using a BAM drophammer and a BAM friction tester. The weight of drop hammer in the BAM drophammer tester is 2 kg. Scanning electron microscopy (SEM) was performed with a field emission scanning electron microanalyzer (Carl Zeiss Ultra 55).

Caution: Herein, all as-prepared compounds should be handled carefully. Although we have encountered no difficulties in synthesizing these compounds (2–6), manipulations must be carried out by using appropriate standard safety precautions. Eye protection and leather gloves should be worn.

2.2 Synthesis

4,6-dihydrazinium-1H-[1,3,5]-triazin-2-one dinitrate (2): To a suspension of **1** (0.39 g, 2.5 mmol) in hot water (20 mL), 0.5 mL dilute nitric acid was added dropwise and until the suspension was dissolved. Then 20 mL EtOH was added to the cooled resulting mixture, and stirred for 30 minutes. The precipitate was filtered and dried in vacuo to give colorless solid with a yield of 90%. $T_m = 150^\circ\text{C}$, $T_d = 229^\circ\text{C}$. ^1H NMR (600 MHz, [D6]DMSO): $\delta = 11.17$ (s), 5.92 (br); ^{13}C NMR (150 MHz, [D6]DMSO): $\delta = 150.39$, 100.00 ppm; IR (KBr): $\nu = 3452$, 3029, 1724, 1385, 1098, 964, 825, 753, 693, 536, 493 cm^{-1} ; elemental analysis calcd (%) for $\text{C}_3\text{H}_9\text{N}_7\text{O}_7$: C 12.73, H 3.20, N 44.52; found: C 13.02, H 3.10, N 46.10.

4,6-dihydrazinium-1H-[1,3,5]-triazin-2-one bis-(3,5-dinitrotriazolate) (3): To a suspension of **1** (0.39 g, 2.5 mmol) in EtOH (20 mL), excess 3,5-dinitrotriazole in 30 mL dichloromethane was added dropwise. After stirred for 1.5 h, yellowish precipitate was filtered and dried in vacuo. yellowish solid (1.09 g, 92%). $T_m = 114^\circ\text{C}$, $T_d = 180^\circ\text{C}$. ^1H NMR (600 MHz, [D6]DMSO): $\delta = 10.96$ (s), 9.65 (s); ^{13}C NMR (150 MHz, [D6]DMSO): $\delta = 163.31$, 158.88 ppm; IR (KBr): $\nu = 3386$, 3355, 3299, 3049, 1734, 1682, 1543, 1494, 1417, 1386, 1344, 1307, 1296, 1118, 1054, 935, 848, 758, 685, 587, 541, 488 cm^{-1} ; elemental analysis calcd (%) for $\text{C}_7\text{H}_9\text{N}_{17}\text{O}_9$: C 17.69, H 1.91, N 50.10; found: C 18.01, H 1.79, N 51.68.

4,6-dihydrazinium-1H-[1,3,5]-triazin-2-one 3,3'-dinitro-5,5'-bis(1H-1,2,4-triazolate) (4): The suspension of **1** (0.39 g, 2.5 mmol) and 3,3'-dinitro-5,5'-bis(1H-1,2,4-triazole) (0.61 g, 2.5 mmol) in 20 mL water was heated until boiling. After stirred for 1.5 h, the resulting clear solution was placed at room temperature for 5 h. And the precipitate was formed, and then filtered. The sample was dried in vacuo to give colorless crystalline solid (0.91 g, 95%). $T_d = 251^\circ\text{C}$; ^1H NMR (600 MHz, [D6]DMSO): $\delta = 10.06$ (s), 8.74 (br); ^{13}C NMR (150 MHz, [D6]DMSO): $\delta = 164.97$, 159.01, 151.64 ppm; IR (KBr): $\nu = 3355$, 3332, 3229, 1776, 1754, 1673, 1612, 1542, 1483, 1454, 1413, 1394, 1309, 1126, 983, 834, 759, 725, 609, 580, 490 cm^{-1} ; elemental analysis calcd (%) for $\text{C}_7\text{H}_9\text{N}_{15}\text{O}_5$: C 21.94, H 2.37, N 54.82; found: C 22.35, H 2.21, N 55.98.

4,6-dihydrazinium-1H-[1,3,5]-triazin-2-one bis[3-(5-nitroimino-1,2,4-triazolate)] (5): The suspension of **1** (0.39 g, 2.5 mmol) and bis[3-(5-nitroimino-1,2,4-triazole)] (0.64 g, 2.5 mmol) in 20 mL water was heated until boiling. After stirred for 1.5 h, the resulting clear solution was placed at room temperature for 5 h. And the precipitate was formed, and then filtered. The sample was dried in vacuo to give 1.01 g colorless crystalline solid in a yield of 98%. $T_d = 222^\circ\text{C}$. ^1H NMR (600 MHz, [D6]DMSO): $\delta = 10.05$ (s), 6.69 (br); ^{13}C NMR (150 MHz, [D6]DMSO): $\delta = 158.94$, 156.06, 146.42 ppm; IR (KBr): $\nu = 3325$, 3266, 3169, 1741, 1677, 1632, 1602, 1576, 1533, 1452, 1386, 1370, 1336, 1226, 1149, 1071, 1003, 770, 715, 644, 598, 481 cm^{-1} ; elemental analysis calcd (%) for $\text{C}_7\text{H}_{11}\text{N}_{17}\text{O}_5$: C 20.34, H 2.68, N 57.62; found: C 20.89, H 2.65, N 59.11.

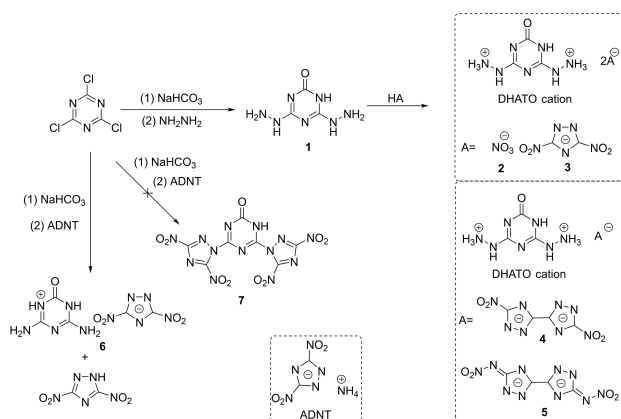
One-pot reaction for 4,6-diamino-1H-[1,3,5]-triazin-2-one 3,5-dinitrotriazolate (6). 20 mL aqueous solution of 1.1 g sodium bicarbonate was heated to 40°C , and 1.0 g of cyanuric chloride was added within 10 minutes. After stirred for one hour, ammonium 3,5-dinitrotriazolate in 5 mL water was added dropwise to the resulting solution. The temperature of the mixture was increased to 95°C and stirred for 12 h. Then, the reaction mixture was cooled to 0°C , and white crystals were formed. The precipitated crystals were collected by filtration in a yield of 65%.

Colorless crystalline solid (1.0 g, 65%). $T_m = 81^\circ\text{C}$; 310°C , $T_d = 331^\circ\text{C}$. ^1H NMR (600 MHz, [D6]DMSO): $\delta = 11.18$ (s), 7.34 (br); ^{13}C NMR (150 MHz, [D6]DMSO): $\delta = 163.28$, 150.43 ppm; IR (KBr): $\nu = 3563$, 3364, 3265, 1646, 1551, 1506, 1396, 1365, 1309, 1108, 1053, 846, 831, 648, 527 cm^{-1} ; elemental analy-

sis calcd (%) for $C_5H_6N_{10}O_5$: C 20.99, H 2.11, N 48.95; found: C 21.30, H 2.06, N 50.09.

3 Results and Discussion

Cyanuric chloride was treated with sodium bicarbonate, and then hydrazine hydrate to give known dihydrazine (1). [8] Energetic salts 2–5 were obtained via the reactions of 1 with nitric acid, 3,5-dinitrotriazole, 3,3'-dinitro-5,5'-bis-triazole and 3,3'-dinitramine-5,5'-bistriazole, respectively (see Scheme S1 in the Supporting Information). We attempted to prepare 4,6-bis(3,5-dinitro-1H-1,2,4-triazol-1-yl)-1,3,5-triazine-2-one (7) through the one-pot reaction of cyanuric chloride with sodium bicarbonate, and then ammonium 3,5-dinitrotriazolate. However, 4,6-diamino-1,3,5-triazine-2-one 3,5-dinitrotriazolate (6) were collected in a yield of 65%, rather than 7. And 3,5-dinitro-1,2,4-triazole was recovered by extraction of the residue solution with ethyl acetate. The formation of 6 is probably derived from amina-



Scheme 1. Synthetic route for energetic salts 2–6.

Table 1. Crystallographic data for $2 \cdot 2H_2O$ and $6 \cdot 2H_2O$.

Entry	$2 \cdot 2H_2O$	$6 \cdot 2H_2O$
CCDC	1848091	1848090
Formula	$C_3H_{19}N_{10}O_{14}$	$C_5H_{10}N_{10}O_7$
Crystalsystem	orthorhombic	triclinic
Space group	<i>Pccn</i>	<i>P-1</i>
$\rho/g\text{cm}^{-3}$	1.722	1.7193(4)
$a/\text{\AA}$	9.3397(9)	7.0263(9)
$b/\text{\AA}$	11.9376(10)	8.2029(10)
$c/\text{\AA}$	14.5080(15)	10.9622(13)
$\alpha/^\circ$	90	83.075(4)
$\beta/^\circ$	90	83.926(4)
$\gamma/^\circ$	90	85.668(4)
GooF	1.053	1.050
Final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0441$, $wR_2 = 0.0926$	$R_1 = 0.0453$, $wR_2 = 0.0830$
Final R indexes (all data)	$R_1 = 0.0791$, $wR_2 = 0.1079$	$R_1 = 0.0850$, $wR_2 = 0.0964$

tion reaction of C–Cl with ammonia resulting from the proton transfer of ammonium cations to 3,5-dinitro-1,2,4-triazolate anions under high temperature, which agrees with the results from previous works on the proton transfer [9]. The result provides a greener way for energetic salts based on 4,6-diamino-1,3,5-triazine-2-one cation than that of previous work reported by Pang's group [5e].

All new energetic salts were investigated using 1H , ^{13}C spectroscopy analysis, and 1H and ^{13}C NMR spectra are given in the Supporting Information (Figure S3–S12). The structures of 2 and 6 were confirmed by the X-ray diffraction analysis of $2 \cdot 2H_2O$ and $6 \cdot 2H_2O$. Their crystallographic data and structure refinement details were displayed in Table 1. The detail information about the crystal structure has been deposited with the Cambridge Crystallographic Data Centre as CCDC-1848091 (for $2 \cdot 2H_2O$) and CCDC-1848090 (for $6 \cdot 2H_2O$).

$2 \cdot 2H_2O$ crystallizes from water in the orthorhombic crystal system, and belongs to the *Pccn* space group. The molecule structure is displayed in Figure 1, in which 2,4-dihydrazinium-1,3,5-triazine-2-one cation is symmetric and nearly planar. The torsion angle of $O(1)–C(2)–N(2)–C(1)$ is $-178.21(16)^\circ$, and $N(2)–C(1)–N(1)–C(1)a$ is $1.9(3)^\circ$. The torsion angle of $N(1)–C(1)–N(3)–N(4)$ measured $-7.8(3)^\circ$. The $C2–O1$ bond lengths in $2 \cdot 2H_2O$ are 1.211 Å. The $N3–N4$ distances (1.414 Å) are longer than $N–N$ single bond (1.398 Å) owing to the protonation of hydrazine group. As is shown in Figure S1(a), layers that run parallel to an axis are formed in the packing diagram of $2 \cdot 2H_2O$ with the perpendicular distance of 5.617 Å. The periodic array of DHATO cations and nitrate anions was observed from the single layer view (Figure S1(b)) with extensive hydrogen-bonding interactions.

$6 \cdot 2H_2O$ crystallizes in the triclinic space group *P-1* (2). As is presented in Figure 2, the asymmetric unit consists of 2,4-diamino-1,3,5-triazinate-2-one cation, nitrate anion as well as two water molecules. The triazine cations and 3,5-dinitrotriazolate anions adopt a nearly planar conformation with

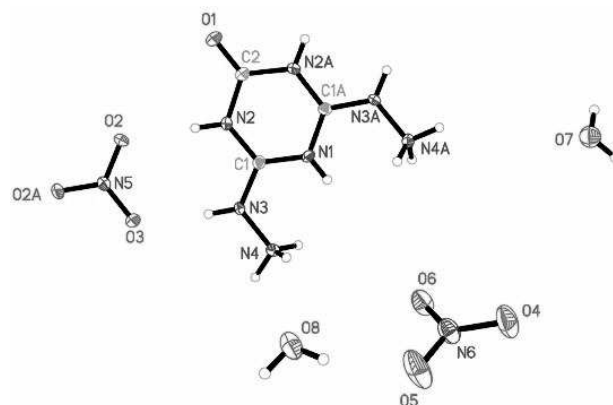


Figure 1. Molecular structure of $2 \cdot 2H_2O$ as it appears in the crystal structure. Ellipsoids are 50% probability.

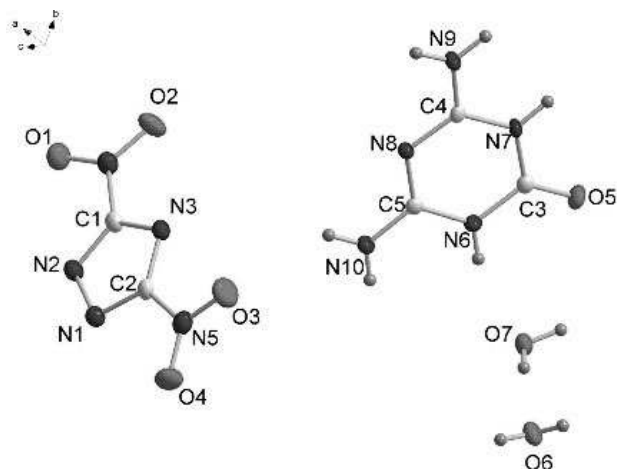


Figure 2. Molecular structure of $6 \cdot 2\text{H}_2\text{O}$ as it appears in the crystal structure. Ellipsoids are 50% probability.

mean deviations from their plane of 0.0284 Å and 0.0037 Å, respectively. The C3–O5 bond lengths in $6 \cdot 2\text{H}_2\text{O}$ are almost identical at about 1.22 Å, which agrees with that reported in previous work [5e]. It is noteworthy that two intermolecular hydrogen bonds are found involving hydrogens of the coordinating water molecules and hydrogens of amino groups attached to the triazine ring. Taking all these extensive interactions into account, the overall crystal packing can be regarded as a 3D network (Figure S2).

As potential energetic materials, the thermal behavior of 2–6 was examined. As is shown from the DSC curve (Figure 3), their onset decomposition temperatures are higher than 180 °C, which meets the requirement for practical use. Of these, the onset decomposition temperatures of 2, 4–6 are higher than that of RDX (210 °C). Especially, 6 starts to decompose at approximately 331 °C, which is higher than that of HNS, and comparable to that of TKX-55 [10]. It can be concluded that 6 is a promising candidate for heat-resistant explosives. In addition, 2, 3 and 6 were hygroscopic, while 4 and 5 were not hygroscopic.

Furthermore, as-prepared 2–6 were investigated by scanning electron microscopy (SEM). As shown in Figure S13–S17, they displayed different morphology, and their grain sizes were in the range of 1–10 μm. Sensitivities towards mechanical stimulus deserve the attention by researchers because this is closely linked with the safety of handling and applying explosives. In the present study, the impact and friction sensitivities of 2–6 were evaluated using a standard BAM fall-hammer and a BAM friction tester, respectively. Due to the promising structural feature of intermolecular hydrogen bonds, they exhibit very low sensitivity towards mechanical stimuli. As shown in Table 2, the energetic salts 2–6 ($FS > 360 \text{ N}$, $IS > 20 \text{ J}$) are much less sensitive than that of the well-known explosives RDX and HMX with the value of 7.5 J [10].

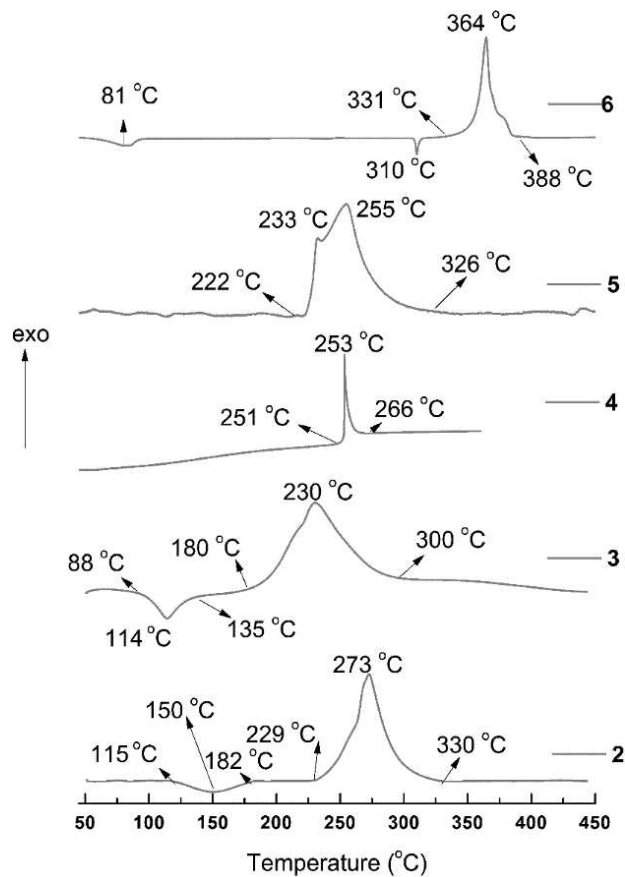


Figure 3. DSC curve of 2–6.

The enthalpy of formation is an important parameter to evaluate the energetic performance of new energetic materials. They were calculated by using the Gaussian 09 suite of a program by using the method of isodesmic reactions (Scheme S1). DFT with the B3LYP functional and 6-311+G** basis set was used to optimize the structures. The enthalpy of formation of 4,6-dihydrazinium-1,3,5-triazine-2-one cation is as high as 1830.7 kJ mol⁻¹, because of its unique dihydrazinium moiety. As results, all energetic salts exhibit positive enthalpy of formation values ranging between 148.9 and 1381.7 kJ mol⁻¹ listed in Table 2. In addition, their detonation properties were evaluated via the EXPLO5 computer code. Their predicted detonation velocities range from 8301 m s⁻¹ (6) to 9282 m s⁻¹ (3), and detonation pressures range from 26.1 GPa (6) to 37.2 GPa (2). Owing to good oxygen balance and high heats of formation, energetic salt 2 and 3 show excellent detonation performance, which are comparable to HMX ($V_D = 9221 \text{ m s}^{-1}$, $P = 39.2 \text{ GPa}$).

To evaluate the initial performance of new energetic compounds, the detonation test was carried out. The representation of the test setup was shown in Figure 4(a). The internal diameter of the tube is 7.8 mm. For lead plate, the diameter of is 30 mm and the thickness is 4 mm. 120 mg PETN (pressed)

Table 2. Properties of energetic compounds 2–6.

Entry	2	3	4	5	6	RDX ⁱ	HMX ⁱ
T _m ^[a] /°C	150	114	–	–	81; 310	–	–
T _d ^[b] /°C	229	180	251	222	331	205	280
ρ ^[c] /g cm ⁻³	1.71	1.78	1.73	1.73	1.74	1.80	1.90
IS ^[d] /J	> 20	> 20	> 20	> 20	> 20	7.4	7.4
FS ^[e] /N	> 360	> 360	> 360	> 360	> 360	120	120
ESD ^[f] /J	0.28	0.39	0.57	0.55	0.73	0.2	–
Δ _f H _m ^[g] /KJ mol ⁻¹	748.5	1381.7	855.3	942.6	148.9	86.3	116.1
ν _D ^[h] /m s ⁻¹	9260	9282	8952	8713	8301	8878	9221
P ^[i] /GPa	37.2	36.2	29.9	28.6	26.1	34.9	39.2

^[a] Melting point temperature. ^[b] Thermal decomposition temperature (onset) under nitrogen gas (DSC, 5 °C/min). ^[c] Densities measured by a gas pycnometer at 25 °C. ^[d] Impact sensitivity. ^[e] Friction sensitivity. ^[f] Sensitivity against electrostatic discharge. ^[g] Calculated enthalpy of formation. ^[h] Calculated detonation velocity. ^[i] Calculated detonation pressure. ^[j] Ref. [11].

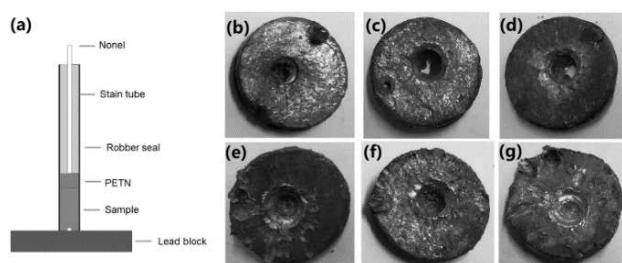


Figure 4. (a) Representation of the test setup; (b) The picture of lead blocks after the detonation of PETN; (c) The picture of lead blocks after the detonation of 2; (d) The picture of lead blocks after the detonation of 3; (e) The picture of lead blocks after the detonation of 4; (f) The picture of lead blocks after the detonation of 5; (g) The picture of lead blocks after the detonation of 6.

was used for each lead block test of new energetic compound (250 mg, pressed). The results reveal that all new compounds can be ignited by PETN, according to the evidently dent of lead blocks displayed in Figure 4 (b–g).

4 Conclusion

Five energetic compounds based on 4,6-dihydrazinium-1,3,5-triazine-2-one and 4,6-diamino-1,3,5-triazine-2-one cation were designed, and synthesized under mild condition from commercial raw materials in good to high yields. They were well characterized by IR, NMR spectroscopic analysis and elemental analysis. The structures of 2 and 6 were confirmed by single crystal X-ray diffraction analysis of 2·2H₂O and 6·2H₂O, which provided insight into structural characteristics as well as inter and intramolecular interactions. All energetic compounds exhibit good thermal stabilities with decomposition temperature above 180 °C, and possess insensitivity towards mechanical stimuli with the value of IS > 20 J and FS > 360 N. Based on EXPLO5 calculations, these salts exhibit good to high detonation performances. The high detonation properties coupled with

good thermal stability and insensitivity towards mechanical stimuli make 2 and 3 as promising insensitive high-energy materials.

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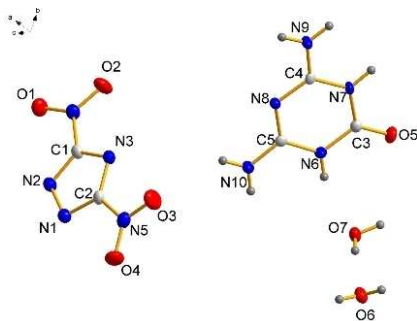
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*B. Wu**, *X. Duan*, *X. Qi*, *D. Zhou*, *J. Wei*,
*C. Pei**

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Triazine-2-One Cation with Low
Impact and Friction Sensitivities**

