

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ARTICLE

Synthesis and Characterization of New Energetic Derivatives Containing High Nitrogen Content Moiety and Picryl Group: A New Strategy for Incorporating the Picryl Functionality

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Bo Wu,^a Hongwei Yang,^{*a} Zhixin Wang,^a Qiuhan Lin,^{a,b} Xuehai Ju,^a Chunxu Lu,^a and Guangbin Cheng^{*a}

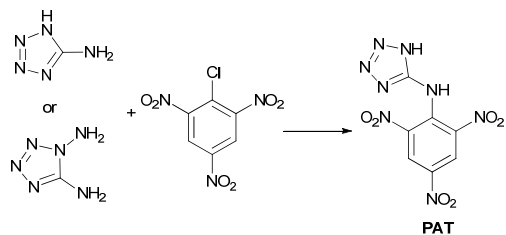
New energetic picryl derivatives were synthesized via the reactions of 2,4,6-trinitrobenzaldehyde with high nitrogen content compounds (above 70%) containing hydrazine group. The resulting compounds **1-3** and **5-7** were well characterized by IR spectroscopy, multinuclear NMR spectroscopy, DSC measurements as well as elemental analysis. Additionally, the structures of compounds **1**, **2** and **5** were confirmed by single crystal X-ray diffraction analysis. Except for the compound **2**, all the remaining products exhibit good thermal stabilities with decomposition onset temperatures above 180 °C. All products possess high heats of formation ranging from 128.62 to 989.52 kJ mol⁻¹. The calculated detonation velocities lie in the range between 7417 and 8271 m s⁻¹. The detonation pressures range between 21.8 and 31.1 GPa.

Introduction

The development of energetic materials continues to focus on these compounds with high densities, high heats of formation and good detonation properties.¹ The novel energetic compounds possessing excellent performance and low sensitivity are extremely desirable. Recently, a new group of energetic materials containing high nitrogen content moieties has been studied.² In contrast with traditional explosives, whose energy is derived from the overall heat of combustion, the most energy of these energetic compounds containing high nitrogen fragment derives from their very high heats of formation. The high heat of formation is directly attributed to large numbers of N—N and C—N bonds within their structures.³ Additionally, energetic compounds with high nitrogen, but low hydrogen and carbon content allow a good oxygen balance to be achieved more easily. Nitrogen-rich parent compounds such as guanidines,⁴ tetrazoles^{2c, 5} and tetrazines⁶ are essential units to synthesize energetic compounds containing high nitrogen content moieties. Generally, oxygen-containing energetic substituents such as nitro (NO₂),^{1c-1e, 2b, 7} nitrate (ONO₂),⁸ and nitramine (NHNO₂)^{1g, 2c, 6e, 9} functionalities are introduced into nitrogen-rich parent compounds to produce novel energetic derivatives with excellent detonation performance.

2,4,6-trinitrophenyl moiety (picryl moiety) has been used as an energetic unit in the field of energetic materials.¹⁰ As known, the nitro group is helpful to enhance the oxygen balance and density of the energetic materials, which improves the detonation performances. Therefore, picryl moiety plays a remarkable role in preparation of new energetic materials. Incorporation of a picryl group into the nitrogen heterocyclic compounds such as triazoles^{10c, 10e} furazans,^{10b} trizines^{10a} and tetrazoles^{10h} has been investigated. Among these energetic picryl derivatives, typical picryl derivatives with high nitrogen moiety (nitrogen contents above 70%) are the following: 5-picrylamino-1,2,3,4-tetrazole (**PAT**) and (2,4,6-trinitrophenyl)guanidine. In contrast to (2,4,6-trinitrophenyl)guanidine, 5-picrylamino-1,2,3,4-tetrazole (**PAT**) has been fully investigated. It can be synthesized from the reactions of picryl chloride with 5-amino-1,2,3,4-tetrazole or 1,5-diaminotetrazole (Scheme 1).^{10h} It also has been further characterized for structural aspects, thermal behaviour and explosive properties. Usually, picryl halogen (halogen = F, Cl) is used as the starting materials for synthesizing energetic picryl derivatives. In the present work, 2,4,6-trinitrobenzaldehyde was used as new starting material for the preparation of new energetic picryl derivatives. These new picryl derivatives containing high nitrogen content moieties were synthesized via the condensation reactions of 2,4,6-trinitrobenzaldehyde with high nitrogen content parent compounds

containing hydrazine group such as aminoguanidine derivatives, 5-hydrazinotetrazolium chloride and 3,6-dihydrazine-1,2,4,5-tetrazine dihydrochloride. These new energetic picryl derivatives were characterized for structural aspects, thermal behaviour and explosive properties by experimental and theoretical methods.



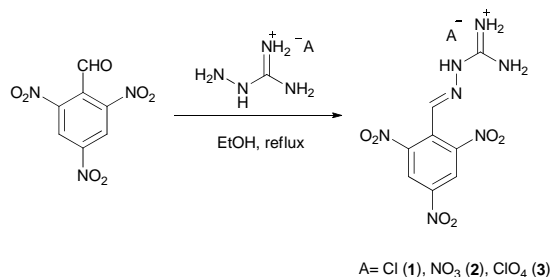
Scheme 1 Synthesis of 5-picrylamino-1,2,3,4-tetrazole (PAT)

Results and discussion

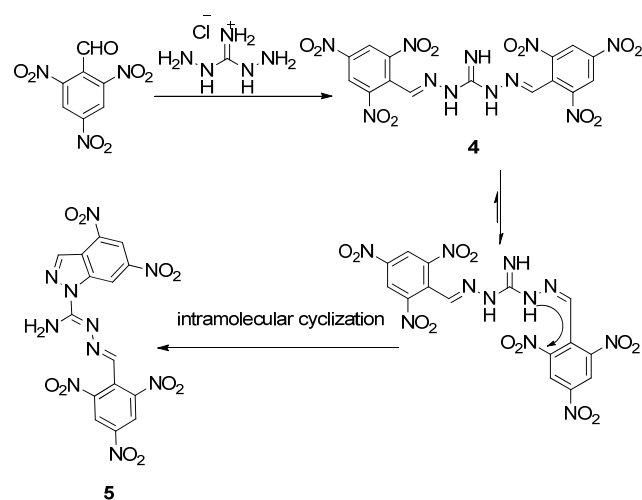
Synthesis

It is known that aromatic aldehyde can readily react with amines and hydrazines to generate Schiff bases and hydrazones with the elimination of water molecules. However, 2,4,6-trinitrobenzaldehyde possesses lower reactivity than common aldehydes owing to the strong electron-withdrawing inductive effect of the three nitro groups attached to the benzene ring. In the beginning, the attempts of reactions between the amino derivatives of tetrazole (e.g., 5-aminotetrazole and 1,5-diaminotetrazole) and 2,4,6-trinitrobenzaldehyde did not result in the desired picryl derivatives. It was probably due to the fact that the reactivity of the amino group is poorer than that of the hydrazine group in nitrogen-rich compounds. Then, the commercially available aminoguanidine hydrochloride reacted with 2,4,6-trinitrobenzaldehyde to yield *N*-(2,4,6-trinitrobenzylideneamino) guanidinium chloride (**1**). The corresponding picryl derivatives **2** and **3** were also synthesized from the reactions of 2,4,6-trinitrobenzaldehyde with aminoguanidinium nitrate and aminoguanidinium perchlorate (Scheme 2). Surprisingly, the desired 1,3-bis(2,4,6-trinitrobenzylideneamino) guanidine (**4**) was not obtained from the reaction of 1,3-diaminoguanidium monohydrochloride with 2,4,6-trinitrobenzaldehyde.

4,6-Dinitro-*N*-(2,4,6-trinitrobenzylidene)-1*H*-indazole-1-carbohydrazonamide (**5**) was the only ultimate product. It was probably caused by the intramolecular cyclization of **4**. As reported, the *o*-nitro group in picryl moiety could be replaced by nucleophiles (Scheme 3).¹¹

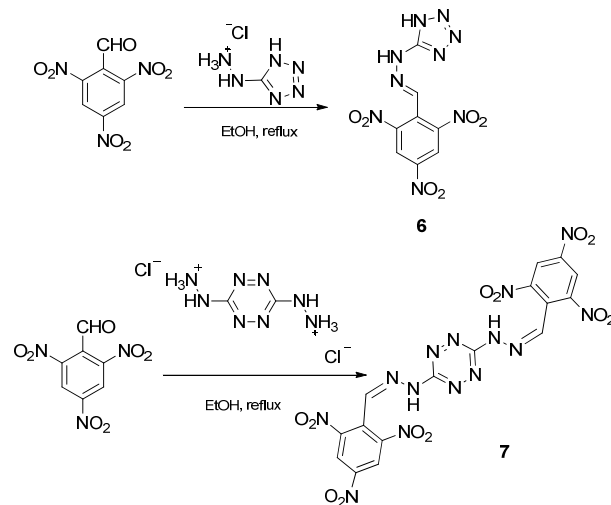


Scheme 2 Synthesis of picryl derivatives **1-3**.



Scheme 3 The process for the formation of **5**

After preparation of these picryl-functionalized guanidine derivatives, we turned our attention to synthesize picryl-functionalized tetrazole and 1,2,4,5-tetrazine derivatives. 5-(2-(2,4,6-trinitrobenzylidene)hydrazinyl)-1*H*-tetrazole (**6**) and 3,6-bis-(2-(2,4,6-trinitrobenzylidene)hydrazinyl)-1,2,4,5-tetrazine (**7**) were prepared from the reactions of 2,4,6-trinitrobenzaldehyde with 5-hydrazinotetrazolium chloride and 3,6-dihydrazine-1,2,4,5-tetrazine dihydrochloride in the yield of 80% and 60%, respectively (Scheme 4).



Scheme 4 Synthesis of picryl derivatives **6** and **7**

Single-Crystal X-ray Analysis

Three compounds described herein (**1**, **2** and **5**) were characterized by single-crystal X-ray diffraction analysis. Selected data and parameters of the measurements and refinements were gathered in Table 1.

Table 1. Crystal data and structure refinement details of **1**, **2** and **5**

Crystal	1	2	5
---------	----------	----------	----------

formula	C ₈ H ₈ ClN ₇ O ₆	C ₈ H ₈ N ₈ O ₉	C ₁₅ H ₈ N ₁₀ O ₁₀
λ [Å]	0.71073	0.71073	0.71075
crystal system	orthorhombic	monoclinic	orthorhombic
space group	<i>Pbca</i>	<i>P21/c</i>	<i>Aba2</i>
<i>a</i> [Å]	12.387(3)	17.6205(13)	24.962(3)
<i>b</i> [Å]	11.618(2)	10.4858(7)	16.401(2)
<i>c</i> [Å]	18.866(4)	15.8252(10)	9.4116(10)
α [°]	90	90	90
β [°]	90	111.333(3)	90
γ [°]	90	90	90
<i>V</i> [Å ³]	2715.0(9)	2723.6(3)	3853.2(8)
<i>Z</i>	4	8	8
ρ_{calc}	1.633	1.757	1.683
[g cm ⁻³]			
GOF on <i>F</i> ²	1.041	1.015	0.963
Final <i>R</i> indexes [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0566, <i>wR</i> 2 = 0.1394	<i>R</i> 1 = 0.0477, <i>wR</i> 2 = 0.0880	<i>R</i> 1 = 0.0673, <i>wR</i> 2 = 0.1507
Final <i>R</i> indexes (all data)	<i>R</i> 1 = 0.0810, <i>wR</i> 2 = 0.1549	<i>R</i> 1 = 0.1057, <i>wR</i> 2 = 0.1072	<i>R</i> 1 = 0.1149, <i>wR</i> 2 = 0.1815
CCDC	996727	996728	996729

N-(2,4,6-trinitrobenzylideneamino)guanidinium chloride (**1**) crystallizes in the orthorhombic space group *Pbca* with a cell volume of 2715.0(9) Å³ and four molecules in the unit cell. The density is 1.633 g cm⁻³. As shown in Figure 1, the molecules are in an *E* configuration. In the *N*-(2,4,6-trinitrobenzylideneamino) guanidium cation, the atoms in either benzene ring or guanyl moiety are planar with mean deviations from their respective plane of 0.0238 and 0.0289 Å, respectively. The benzene ring and guanidinium moiety are twisted with the dihedral angle between them of 63.0°. The 4-NO₂ group in the picryl group lies in the plane of the benzene ring, whereas both nitro groups in the ortho positions are substantially twisted out of the plane of the aromatic system with angles of 10.8° (1-NO₂ group) and 4.9° (3-NO₂ group) due

to the steric effect of the -C=N- group. The C7-N4 bond length of 1.277(6) Å, shows typical C-N double bond values.¹² The C-N bond lengths of the protonated guanidine moiety differ in a range of 1.311(3) Å to 1.346(3) Å, which are longer than C=N double bonds (1.277(6) Å) but shorter than the C-N single bond (1.460(2) Å).^{12, 13} It indicates that the conjugation system exists in the protonated guanidine moiety. Classical N6—H6A•••N4 hydrogen bond was found (Figure 1). Further investigation on hydrogen bonds within the crystal structure of compound **1** shows the infinite chains (Figure 2). The hydrogen atoms of the protonated guanidine structure together with chlorine atoms add many intra- and intermolecular hydrogen-bond interactions to form two dimensional network in the *bc*-plane. These hydrogen-bond interactions are helpful to increase the thermal stability of **1**. The details of all hydrogen bonds are gathered in Supporting Information (see Table S7)

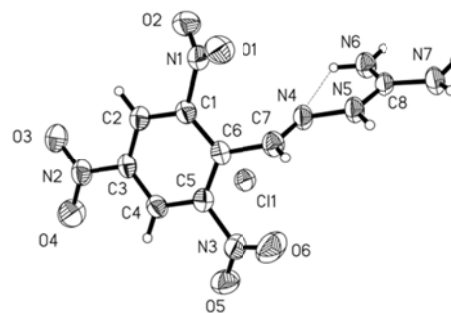


Figure 1 Molecular structure of **1** and its labeling scheme. Ellipsoids are drawn at the 50% probability level. Dashed lines indicate intramolecular hydrogen bond.

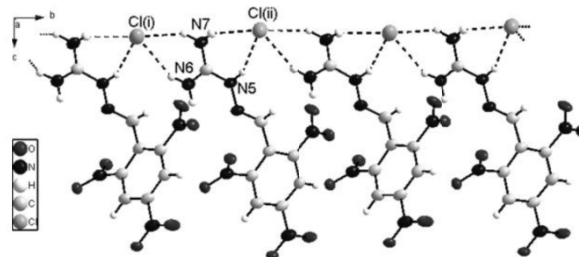


Figure 2 Hydrogen bonds viewed on the chains along the *b* axis in the structure of **1**.

N-(2,4,6-trinitrobenzylideneamino)guanidinium nitrate (**2**) crystallizes in the monoclinic space group *P21/c* as a racemic twin (Figure 3). There are eight molecules in the unit cell and the density is 1.757 g cm⁻³. The molecules are also in an *E* configuration. In two independent *N*-(2,4,6-trinitrobenzylideneamino) guanidinium cations, the atoms in either benzene ring or guanidinium moiety are planar with mean deviations from their respective plane of 0.0048, 0.0083, 0.0059 and 0.0589 Å, respectively. The benzene ring and guanidinium moiety are slightly twisted with the dihedral angles between them of 3.6° and 0.6°, respectively. They are much smaller than that of compound **1**, which is attributed to the lack of strong hydrogen bonds involving the chlorine atoms with the bulky guanidinium moiety in the *bc*-plane within the

crystal structure of compound **2**. As shown in Figure 3, non-classical C7—H7...O2 and C15—H15...O7 hydrogen bonds were observed. In addition, classical N4—H4B...O4, N4—H4B...N2 and N12—H12B...N9 hydrogen bonds were observed. In the packing diagram of **2**, as depicted in Figure 4, classical intermolecular hydrogen bonds are found between the protons in guanidinium fragment and the oxygen atoms of nitro groups and nitrate anions. Nonclassical intermolecular hydrogen bonds are also observed between the imine protons and the oxygen atoms of nitrate anions. The details of hydrogen bonds are summarized in Supporting Information (see Table S8). These interactions build up a 3D network which consists of "rhombic shape" unit along *c* direction.

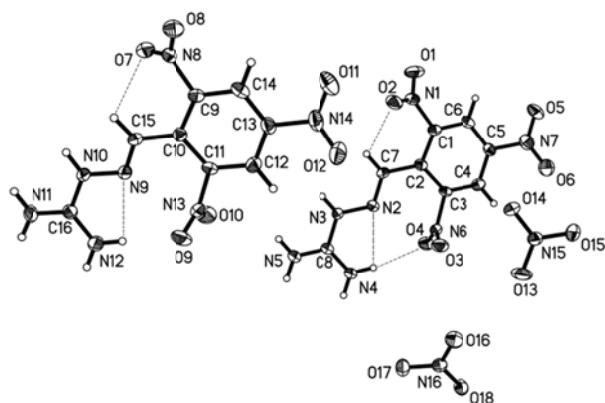


Figure 3 Molecular structure of **2**. Ellipsoids are drawn at the 50% probability level. Dashed lines indicate intramolecular hydrogen bonds.

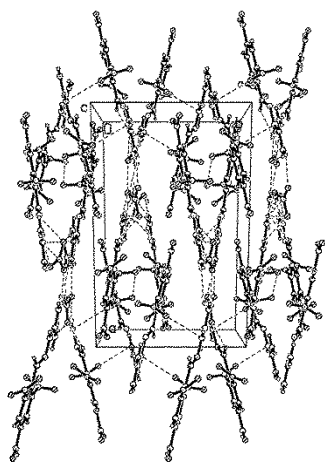


Figure 4 Ball and stick packing diagram of **2** viewed down the *c* axis. Dashed lines indicate strong hydrogen bonds.

4,6-dinitro-*N'*-(2,4,6-trinitrobenzylidene)-1*H*-indazole-1-carbohydrazonamide (**5**) crystallizes in the orthorhombic space group *Aba2* with a cell volume of 3853.2(8) Å³ and eight molecules in the unit cell. A density of 1.683 g cm⁻³ was determined from the X-ray crystal structure. As shown in Figure 6, the molecules are in *E* configuration. The atoms in the 2,4,6-trinitrobenzene ring, benzopyrazole ring and guanidine moiety are planar with mean

deviations from their respective plane of 0.0090, 0.0245 and 0.0151 Å, respectively. The dihedral angle between the guanidine moiety and benzene ring is 15.3 ° while that between the guanidine moiety and benzopyrazole ring is 10.7 °. The bond lengths of C8-N6 and C9-N7 are 1.302(7) and 1.281(7) Å, respectively. In the entire molecule, a large conjugation system is formed between the 2,4,6-trinitrobenzene ring and benzopyrazole ring through two double bonds (C8-N6 and C9-N7). All the protons possess acidity due to the electron-withdrawing inductive effect of five nitro groups attached to the conjugation system. As depicted in Figure 5, nonclassical C1—H1...O3, C4—H4...N6 and C9—H9...O10 intramolecular hydrogen bonds were found. Additionally, intermolecular nonclassical interactions were observed between CH protons and the oxygen atoms of the nitro groups. The details of all hydrogen bonds are gathered in Supporting Information (see Table S9). In the packing diagram of **5**, as shown in Figure 7, the rows show a zigzag type pattern and present an angle of 95.72 ° within the rows.

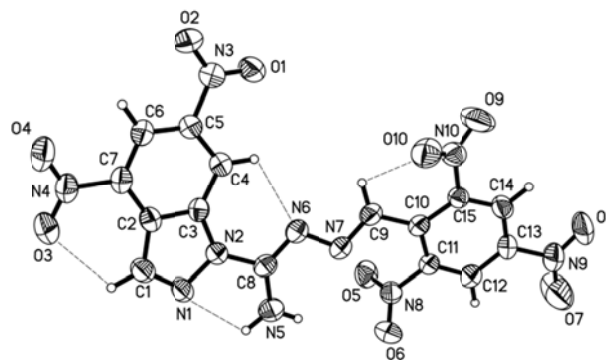


Figure 5 Molecular structure of **5** and its labeling scheme. Ellipsoids are drawn at the 50% probability level. Dashed lines indicate intramolecular hydrogen bonds.

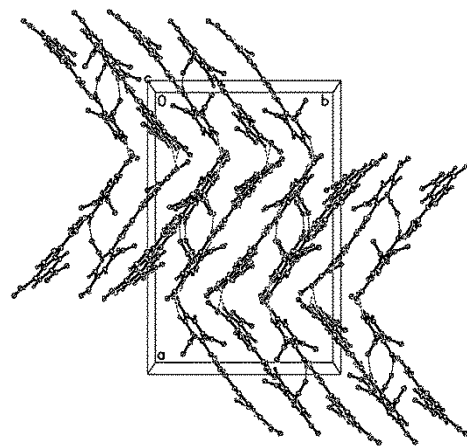


Figure 6 Ball and stick packing diagram of **5** viewed down the *c* axis. Dashed lines indicate strong hydrogen bonds.

Spectroscopy

In the IR spectrum of compounds **1-3** and **5-7**, the characteristic asymmetric stretching vibrations ν_{as} NO₂ are found in the range of 1638–1539 cm⁻¹ and the symmetric stretching vibrations ν_s NO₂ at 1310–1295 cm⁻¹. The signals lie in the range of 1678–1600 cm⁻¹

representing the stretching vibrations of C=N. The vibration around 3200 cm⁻¹ can be interpreted as the stretching vibrations of C–H in the –CH=N– group as well as signals for valence vibrations of C–H in the trinitrobenzene ring around 3100 cm⁻¹. For all new picryl derivatives, the signals lying in the range of 3551–3409 cm⁻¹ representing N–H vibrations are observable.

All products were investigated using ¹H NMR and ¹³C NMR. Additionally, the ¹⁵N NMR spectra were recorded for compounds **2** and **3**. The multinuclear NMR spectra were measured in [D6]DMSO and the chemical shifts were given with respect to DMSO or CH₃NO₂ as external standard. The ¹H and ¹³C NMR spectra of all compounds were given in the Supporting Information (Figures S3–S14). For compounds **1–3** and **6–7**, in the ¹H NMR spectra, the proton signals of picryl group appear between $\delta = 9.06$ and 9.14 ppm, which are at a little higher field than that of 2,4,6-trinitrobenzaldehyde ($\delta = 9.16$ ppm). The proton signals of the –CH=N– groups range from $\delta = 8.39$ to 8.59 ppm, which are significantly at higher field than that of –CH=O group appearing at $\delta = 10.54$ ppm in 2,4,6-trinitrobenzaldehyde. In the ¹³C NMR spectra, for all compounds, the carbon signals of picryl moiety are identified around $\delta = 150$, 148, 130 and 125 ppm. The carbon signals of the C=N double bonds connecting the picryl group to nitrogen-rich moieties of **1–3** and **5** locate at the lower field ranging from 140.78 to 143.32 ppm than that of **6–7** appearing at 136.2 and 135.53 ppm. It can be attributed to the fact that the electron-withdrawing inductive effect of guanidine moiety is stronger than nitrogen-rich heterocycles.

The ¹⁵N NMR spectra for compound **2** shows six singlet resonances. And five well-resolved resonances are detected in the ¹⁵N NMR of compound **3**. The assignments of the nitrogen signals were determined based on the literature values of compounds with similar structures.^{4a, 14} As depicted in Figure 7, in the spectra of **2**, the signals of nitrate anion locate at the lowest field with $\delta = -4.37$ ppm. In the same *N*-(2,4,6-trinitrobenzylideneamino) guanidinium fragment of **2** and **3**, the strong nitrogen signals of the nitro groups in benzene ring appear around -16.78 (N1/N3) and -20.00 (N2) ppm. The nitrogen signals of –CH=N– group connecting the guanidine structure to the benzene ring are found around $\delta = -59.91$ ppm while the nitrogen signals of the –NH– group (N5) are observed at a relatively higher field (around -231.65 ppm). In addition, for compounds **2** and **3**, the signals at highest field are attributed to protonated semi-guanidine moieties, which appearing at $\delta = -304.2$ ppm.

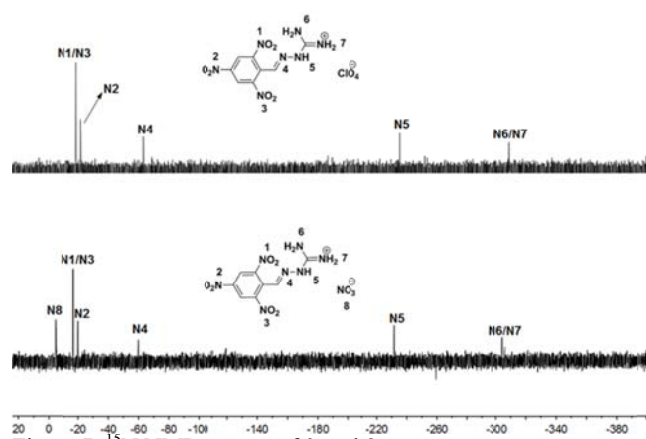


Figure 7 ¹⁵N NMR spectra of **2** and **3**.

Thermal Behavior and Sensitivities

Thermal stability is one of the most important physicochemical properties of energetic materials. The thermal behaviour of all products was investigated by differential scanning calorimetry (DSC) at a heating rate of 10 °C min⁻¹. The plots were shown in the Supporting Information (Figures S15–S20). As summarized in Table 2, compounds **1**, **3**, **6** have melting process, whereas the other compounds decompose directly. Generally, the decomposition onset temperatures of presented energetic picryl derivatives are higher than 180 °C. A thermal stability above 180 °C is an essential requirement for energetic compounds to adaptation for practical use. The only exception is **2**, whose decomposition onset temperature is 146.3 °C. This lower stability may be due to the lack of the hydrogen bonding network in the structure. For compounds **1**, **3**, **5**, **6**, **7**, their decomposition onset temperatures are higher than that of 5-picrylamino-1,2,3,4-tetrazole (PAT) ($T_{dec,onset} = 183$ °C),^{10h} which probably due to the existence of the large conjugation system within their structures. The most stable compound is **7**, which decomposed at almost 230 °C. Its decomposition onset temperature is higher than that of RDX (1,3,5-trinitro-1,3,5-triazinane; $T_d = 205$ °C).¹⁵ The sensitivities of the resulting compounds **1–3** and **5–7** towards impact, friction, and electrostatic discharge were tested by using standard procedures.¹⁶ As depicted in Table 2, the impact sensitivity values are found to be in the range from 6 (**3**) to 35 J (**6**). The friction sensitivity values differ in the range from 120 (**3**) to 360 N (**6**). Based on the classification standard of sensitivities,¹⁷ the ionic picryl derivatives **1–3** are classified as sensitive due to their impact sensitivities of 25, 11 and 6 J and friction sensitivities of 192, 168 and 120 N, respectively. The compounds **5** and **7** are less sensitive to impact and friction than RDX (7.5 J, 120 N) due to their impact sensitivities of 32 and 30 J and friction sensitivities of 320 and 288 N, respectively. The impact and friction sensitivity values of **6** are 35 J and 360 N, respectively, placing it in the insensitive class. These picryl derivatives **1–3** and **5–7** differ strongly in their electrostatic sensitivities. As shown in Table 2, compounds **1**, **5–7** are significantly less sensitive to electrostatic discharge than RDX. The nitrate **2** is slightly less sensitive than RDX, whereas perchlorate **3** is more sensitive than RDX.

Heats of Formation and Detonation Parameters

The heat of formation (HOF) plays an important role in evaluating the performance of energetic materials. The heats of formation of the resulting compounds **1-3** and **5-7** were calculated based on appropriate isodesmic reactions (Scheme S1, Supporting Information). Calculations were carried out using the Gaussian 09 program suite.¹⁸ The geometry optimization of the structures and frequency analyses were carried out using the B3LYP functional with the 6-311+G** basis set.¹⁹ All of the optimized structures were characterized by true local energy minima on the potential energy surface without imaginary frequencies. For ionic energetic compounds **1-3**, the positive heats of formation were calculated using the Born–Haber energy cycle. As summarized in Table 2, the

resulting compounds **1-3** and **5-7** exhibit positive heats of formation. The calculated values fall in the range from 128.62 (**3**) to 989.52 (**7**) kJ mol⁻¹, which are highly positive due to the feature of high nitrogen content.

The detonation velocity (D) and detonation pressure (P), which are used to measure the performance of a high explosive, were calculated by using the EXPLO5 program (Version 6.01).²⁰ As summarized in Table 2, for these new energetic picryl derivatives **1-3** and **5-7**, the calculated detonation velocities lie in the range between 7417 and 8271 m s⁻¹, most of which are remarkably higher than that of **PAT** (7770 m s⁻¹).^{10h} The detonation pressures range between 21.8 and 31.1 GPa, in which the highest detonation pressure value of **3** (31.1 GPa) is slightly lower than that of RDX (35.2 GPa).

Table 2. The physicochemical properties of **1-3** and **5-7** compared with 5-picrylamino-1,2,3,4-tetrazole (**PAT**) and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX).

Compound	T_m^a [°C]	T_d^b [°C]	OB ^c	N ^d [%]	ρ (g cm ⁻³)	$\Delta_f H_m^e$ (kJ/mol)	D^h (m/s)	P^i (GPa)	IS^j [J]	FS^k [N]	ESD ^l [J]
1	205.7	207.7	-67.14	29.39	1.633 ^e	214.18	7417	21.8	25	192	0.887
2	-	146.3	-48.86	31.11	1.757 ^e	134.76	8256	29.6	11	168	0.321
3	211.1	211.1	-40.24	24.66	1.853 ^f	128.62	8271	31.1	6	120	0.119
5	-	189.1	-78.64	28.69	1.683 ^e	525.42	7782	24.8	32	320	1.1
6	182.2	184.2	-61.89	39.01	1.765 ^f	652.06	8234	28.4	35	360	0.714
7	-	229.5	-65.27	33.33	1.795 ^f	989.52	8188	28.4	30	288	0.821
PAT ^m	-	183	-50.02	37.84	1.552	452.23	7770	26.4	>60	>360	1.0
RDX ⁿ	-	205	-21.6	37.84	1.80	70	8795	35.2 ^o	7.5	120	0.2

^a Melting point. ^b Thermal decomposition temperature under nitrogen gas. ^c Oxygen balance (%) for C_aH_bN_cO_d: OB (%) = 1600 × (d-2a-b/2)/ Mw (based on carbon dioxide). ^d Nitrogen content. ^e Density from X-ray structure. ^f Density from theoretical calculation. ^g Molar enthalpy of the formation. ^h Detonation velocity. ⁱ Detonation pressure. ^j Impact sensitivity measured with a 2.0 kg hammer. ^k Friction sensitivity. ^l Sensitivity against electrostatic discharge. ^m Data from ref [10h]. ⁿ Data from ref [15]. ^o Data from ref [2e].

Experimental

Caution: Although we experienced no difficulties in handling these energetic materials, small scale and best safety practices (leather gloves, face shield) are strongly encouraged.

General Methods

All chemical reagents and solvents were obtained by purchase and were used as supplied without further purification. 2,4,6-trinitrobenzaldehyde,²¹ aminoguanidinium perchlorate,^{4a} 5-hydrazinotetrazolium chloride,⁵ⁱ 3,6-dihydrazino-1,2,4,5-tetrazine dihydrochloride²² were prepared according to published procedures. The ¹H spectra were recorded on a

Bruker Avance III 500 instrument at 25 °C. The ¹³C and ¹⁵N NMR spectra were recorded on a Bruker Avance III 300 instrument at 25 °C. The chemical shifts were given relative to dimethyl sulfoxide (¹H, ¹³C) or nitromethane (¹⁵N) as external standards. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 °C. DSC studies were performed at a heating rate of 10 °C min⁻¹ in closed Al containers with a nitrogen flow of 30 mL min⁻¹ on an STD-Q600 instrument. Analyses of C/H/N were performed with a Vario EL III Analyzer. The electrostatic sensitivity tests were carried out with an Electric Spark Tester ESD JGY-50 III. The sensitivities towards impact and friction

were determined by using a HGZ-1 drophammer and a BAM friction tester.

X-ray Crystallography: The X-ray diffraction measurements for **1**, **2** and **5** were performed with a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The data collection and the initial unit cell refinement was performed by using APEX2 (v2010.3-0). Data Reduction was performed by using SAINT (v7.68A) and XPREP (v2008/2). Corrections were applied for Lorentz, polarization, and absorption effects by using SADABS (v2008/1). The structure was solved and refined with the aid of the programs in the SHELXTL-plus (v2008/4) system of programs. The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included in a riding model. The structure was solved by direct methods with SHELXS-97 and expanded by using the Fourier technique. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located and refined.

Preparation of 2,4,6-trinitrobenzaldehyde

Several crystals of I_2 were added to a suspension of 2,4,6-trinitrotoluene (10 g, 0.044 mol) and *N,N*-dimethylp-nitrosoaniline (7 g, 0.047 mol) in pyridine (15 mL). The reaction mixture was stirred at 30 °C for 48 h. The resulting precipitate was filtered off, washed with cold acetone and dried in air to yield 11.07 g *N,N*-dimethyl-*N'*-(2,4,6-trinitrobenzylidene)benzene-1,4-diamine in a yield of 70%. A suspension of *N,N*-dimethyl-*N'*-(2,4,6-trinitrobenzylidene)benzene-1,4-diamine (10 g, 0.027 mol) in 80 mL concentrated HCl was stirred at 60 °C for 3 h. The precipitate was filtered off, washed with water and dried in air to obtain 4.36 g of 2,4,6-trinitrobenzaldehyde in a yield of 65%. 1H NMR (500M, DMSO): δ (ppm) 10.54 (s, 1H, -CHO), 9.16 (s, 2H, -CH). ^{13}C NMR (75M, DMSO): δ (ppm) 189.7, 149.6, 149.2, 135.7, 126.2.

General procedures for preparation of energetic compounds 1-3

A solution of aminoguanidium salts (2 mmol) and 2,4,6-trinitrobenzaldehyde (0.7233g, 0.003 mol) in 30 mL ethanol was refluxed for 24 h. Then, the reaction mixture was cooled to room temperature. The residue was purified on a silica gel column chromatography employed by a solvent mixture of ethyl acetate: methanol = 8 : 1 to afford the desired product.

N-(2,4,6-trinitrobenzylideneamino) guanidinium chloride (**1**)

0.5672 g of **1** was obtained as reddish solid in a yield of 85%. DSC: T_{dec} = 207.7 °C. 1H NMR (500 MHz, DMSO): δ (ppm) 12.88 (br, 1H, -NH-), 9.12(s, 2H, -CH), 8.61(s, 1H, -CH=N-), 7.86 (s, 4H, -NH₂). ^{13}C NMR (75 MHz, DMSO): δ (ppm) 157.0, 150.5, 148.9, 140.8, 129.6, 125.0. IR (KBr): 3409, 3250, 3175, 3108, 3012, 2965, 2361, 2336, 1678, 1606, 1537, 1468, 1401, 1347, 1224, 1176, 1141, 1079,1018, 910, 725, 675, 583, 559, 503 cm^{-1} . C, H, N analysis (%): C₈H₈ClN₇O₆ (333.65), calculated result: C 28.80, H 2.42, N 29.39; found: C 29.12, H 2.56, N 28.78.

N-(2,4,6-trinitrobenzylideneamino) guanidinium nitrate (**2**)

0.6484 g of **2** was obtained as white solid in a yield of 90%. DSC: T_{dec} = 146.3 °C. 1H NMR (500 MHz, DMSO): δ (ppm) 12.34 (s, 1H, -NH-), 9.14 (s, 2H, -CH), 8.58 (s, 1H, -CH=N-), 7.73 (s, 4H, -NH₂). ^{13}C NMR (75 MHz, DMSO): δ (ppm) 156.4, 150.5, 149.0, 141.3, 129.6, 125.1. ^{15}N NMR (30 MHz, DMSO) δ (ppm) -4.37, -16.78, -20.00, -59.91, -231.65, -304.61. IR (KBr): 3423, 3166, 3104, 2886, 1683, 1631, 1612, 1547, 1400, 1385, 1348, 1303, 1226, 1149, 1081, 1037, 914, 825, 726 cm^{-1} . C, H, N analysis (%): C₈H₈N₈O₉ (360.20), calculated result: C 26.68, H 2.24, N 31.11; found: C 27.32, H 2.44, N 30.98.

N-(2,4,6-trinitrobenzylideneamino) guanidinium perchlorate (**3**)

0.7316 g of **3** was obtained as white solid in a yield of 92%. DSC: T_{dec} = 211.1 °C. 1H NMR (500 MHz, DMSO): δ (ppm) 12.30 (s, 1H, -NH-), 9.13 (s, 2H, -CH), 8.59 (s, 1H, -CH=N-), 7.70 (s, 4H, -NH₂). ^{13}C NMR (75 MHz, DMSO): δ (ppm) 156.4, 150.5, 149.0, 141.4, 129.6, 125.1. ^{15}N NMR (30 MHz, DMSO) δ (ppm) -16.78, -20.00, -59.91, -231.65, -304.61. IR (KBr): 3551, 3472, 3417, 3245, 3106, 1688, 1638, 1617, 1539, 1465, 1401, 1349, 1231, 1146, 1115, 1086, 917, 847, 827, 723, 628, 500 cm^{-1} . C, H, N analysis (%): C₈H₈ClN₇O₁₀ (397.64), calculated result: C 24.16, H 2.03, N 24.66; found: C 25.07, H 2.11, N 23.12.

Synthesis of 5

A solution of 1,3-diaminoguanidine monohydrochloride (0.2512 g, 0.002 mol) and 2,4,6-trinitrobenzaldehyde (1.2056 g, 0.005 mol) in 30 mL ethanol was refluxed for 48 h. Then, the reaction mixture was cooled to room temperature and the precipitate was collected by filtration. 0.72 g **5** as yellow solid was obtained in a yield of 74%. DSC: T_{dec} = 189.1 °C. 1H NMR (500 MHz, DMSO): δ (ppm) 9.10 (s, 6H, -CH), 8.51 (br, -NH₂). ^{13}C NMR (75 MHz, DMSO): δ (ppm) 156.8, 155.1, 150.5, 148.9, 147.4, 143.3, 141.2, 139.9, 138.1, 129.9, 125.1, 124.5, 119.5, 116.4. IR (KBr): 3478, 3422, 3367, 3150, 3119, 3092, 1638, 1594, 1537, 1462, 1445, 1401, 1347, 1300, 1189, 1081, 1034, 916, 787, 719, 474 cm^{-1} . C, H, N analysis (%): C₁₅H₈N₁₀O₁₀ (488.29), calculated result: C 36.90, H 1.65, N 28.69; found: C 37.54, H 1.77, N 28.01.

Synthesis of 6

A solution of 5-hydrazinotetrazolium chloride (0.2731 g, 0.002 mol) and 2,4,6-trinitrobenzaldehyde (0.7233 g, 0.003 mol) in 30 mL ethanol was refluxed for 24 h. Then the reaction mixture was cooled to room temperature. The mixture was purified on a silica gel column chromatography employed by a solvent mixture of ethyl acetate : methanol = 4 : 1 to afford 0.52 g **6** as reddish solid in a yield of 80%. DSC: T_{dec} = 184.2 °C. 1H NMR (500 MHz, DMSO): δ (ppm) 15.56 (br, NH), 12.52 (s, 1H, -NH-), 9.08 (s, 2H, -CH), 8.39 (s, 1H, -CH=N-). ^{13}C NMR (75 MHz, DMSO): δ (ppm) 157.7, 150.4, 149.3, 136.2, 130.2, 124.9. IR (KBr): 3418, 3094, 2956, 2888, 1643, 1605, 1543, 1402, 1346, 1264, 1150, 1122, 1079, 1059, 920, 742, 721 cm^{-1} . C, H, N analysis (%): C₈H₅N₉O₆ (323.18), calculated result: C 29.73, H 1.56, N 39.01; found: C 30.24, H 1.67, N 38.52.

Synthesis of 7

A solution of 2,4,6-trinitrobenzaldehyde (0.7233 g, 0.003 mol), 3,6-dihydrazine-1,2,4,5-tetrazine dihydrochloride (0.2150 g,

0.001 mol) in 20 mL ethanol was stirred at 80 °C for 18 h. The resulting precipitate in reaction mixture was filtered off. Then washed with cold ethanol (50 mL) and dried to afford 0.35 g **7** as red powder in a yield of 60%. DSC: $T_{\text{dec}} = 229.5$ °C. ^1H NMR (500 MHz, DMSO): δ (ppm) 12.75 (s, 2H, -NH-), 9.06 (s, 4H, -CH), 8.54 (s, 2H, -CH=N-). ^{13}C NMR (75 MHz, DMSO): δ (ppm) 161.3, 150.2, 147.9, 135.5, 129.9, 124.1. IR (KBr): 3422, 3215, 3093, 2989, 2880, 2361, 2338, 1600, 1539, 1450, 1348, 1303, 1178, 1084, 1055, 968, 923, 738, 722, 569 cm^{-1} . C, H, N analysis (%): $\text{C}_{16}\text{H}_8\text{N}_{14}\text{O}_{12}$ (588.32), calculated result: C 32.66, H 1.37, N 33.33; found: C 33.15, H 1.41, N 32.94.

Conclusions

The new energetic picryl derivatives **1-3** and **5-7** were synthesized via the condensation reactions of 2,4,6-trinitrobenzaldehyde with high nitrogen content (above 70%) compounds containing hydrazine group. All products were well characterized by means of IR spectroscopy, multinuclear NMR spectroscopy, DSC measurements as well as elemental analysis. Single crystal X-ray measurements were accomplished for compounds **1**, **2** and **5**. According to the DSC results, Except for the compound **2** ($T_{\text{d, onset}} = 146.3$ °C), the decomposition onset temperatures ($T_{\text{d, onset}}$) of the remaining energetic picryl derivatives are higher than 180 °C, which indicates that these new energetic picryl compounds possess good thermal stabilities in contrast with 5-picrylamino-1,2,3,4-tetrazole (PAT). In particular, the most stable compound is **7**, which decomposed at almost 230 °C. Its decomposition onset temperature is higher than that of RDX ($T_{\text{d}} = 205$ °C). The calculated detonation velocities lie in the range between 7417 and 8271 m s^{-1} . The detonation pressures range from 21.8 to 31.1 GPa. Ionic picryl derivative **3** has a detonation pressure and velocity of 31.1 GPa and 8271 m s^{-1} , respectively, which is significantly higher than those of PAT (26.4 GPa and 7770 m s^{-1}). Except **3**, most new picryl derivatives are less sensitive to impact, friction and electrostatic discharge than RDX. In conclusion, the way to synthesize new picryl derivatives starting from 2,4,6-trinitrobenzaldehyde enriches the methodology for development of new energetic picryl compounds.

Acknowledgements

This work was supported by the Natural Science Foundation of Jiangsu Province (BK2011696) and the National Natural Science Foundation of China (No. 21376121).

Notes and references

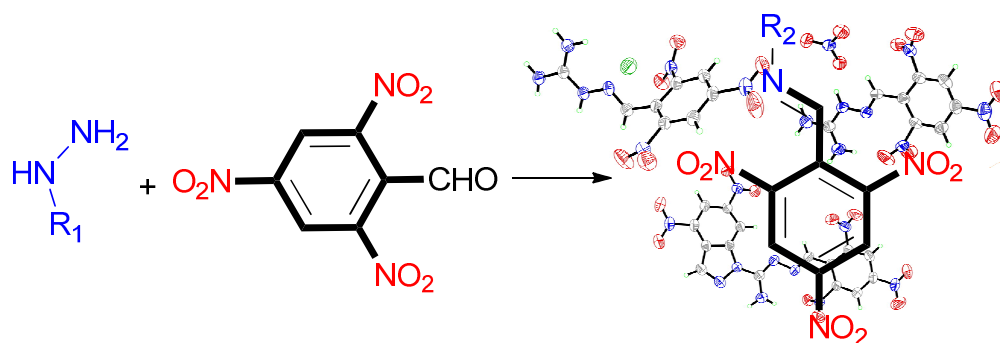
^a School of Chemical Engineering, Nanjing University of Science and Technology, Xiaolingwei 200, Nanjing, P. R. China, E-mail: hyang@mail.njust.edu.cn (H. Yang); gcheng@mail.njust.edu.cn (G. Cheng).

^b School of Materials Science & Engineering, Beijing Institute of Technology, 5 South Zhongguancun Street, Beijing, P. R. China.

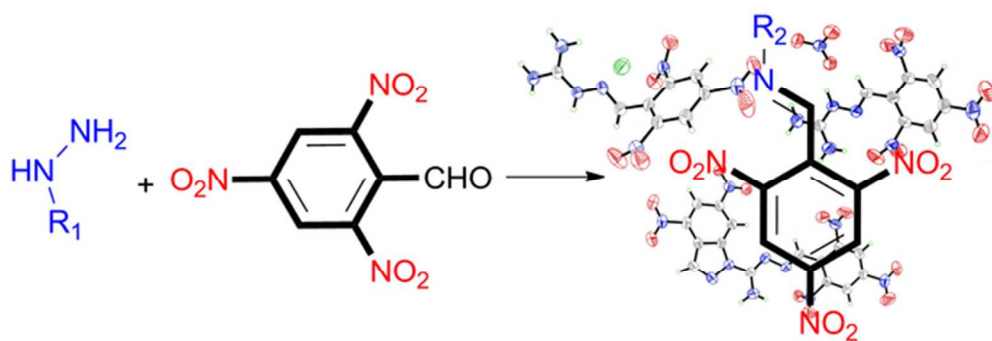
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

- (a) J. P. Agrawal, R. D. Hodgson, *Organic Chemistry of Explosives*, Wiley, New York, **2007**; (b) T. M. Klapötke, J. Stierstorfer and A. U. Wallek, *Chem. Mater.*, 2008, **20**, 4519; (c) M. Göbel and T. M. Klapötke, *Adv. Funct. Mater.*, 2009, **19**, 347; (d) V. Thottempudi, H. Gao and J. M. Shreeve, *J. Am. Chem. Soc.*, 2011, **133**, 6464; (e) V. Thottempudi and J. M. Shreeve, *J. Am. Chem. Soc.*, 2011, **133**, 19982; (f) A. A. Dippold and T. M. Klapötke, *J. Am. Chem. Soc.*, 2013, **135**, 9931; (g) J. Zhang and J. M. Shreeve, *J. Am. Chem. Soc.*, 2014, **136**, 4437.
- (a) H. Gao and J. M. Shreeve, *Chem. Rev.*, 2011, **111**, 7377; (b) V. Thottempudi, F. Forohor, D. A. Parrish and J. M. Shreeve, *Angew. Chem.* 2012, **124**, 10019; *Angew. Chem. Int. Ed.* 2012, **51**, 9881; (c) T. M. Klapötke, F. A. Martin, and J. Stierstorfer, *Chem. Eur. J.*, 2012, **18**, 1487; (d) Q. Zhang, C. He, P. Yin, and J. M. Shreeve, *Chem. Asian J.*, 2014, **9**, 212.
- (a) M. V. Huynh, M. A. Hiskey, E. L. Hartline, D. P. Montoya, R. Gilardi, *Angew. Chem.*, 2004, **116**, 5032; (b) D. E. Chavez, M. A. Hiskey and R. D. Gilardi, *Angew. Chem.* 2000, **112**, 1861; *Angew. Chem. Int. Ed.*, 2000, **39**, 1791; (c) K. O. Christe, W. W. Wilson, J. A. Sheehy, J. A. Boatz, *Angew. Chem.* 1999, **111**, 2112; (d) A. Hammerl, T. M. Klapötke, H. Nöth, M. Warchhold, *Propellants Explos. Pyrotech.*, 2003, **28**, 165; (e) J. Neutz, O. Grosshardt, S. Schäufele, H. Schuppler, W. Schweikert, *Propellants Explos. Pyrotech.*, 2003, **28**, 181.
- (a) T. M. Klapötke and J. Stierstorfer, *Cent. Eur. J. Energ. Mater.*, 2008, **5**, 13; (b) R. Wang, Y. Guo, Z. Zeng and J. M. Shreeve, *Chem. Commun.*, 2009, 2697; (c) R. Wang, Y. Guo, Z. Zeng, B. Twamley and J. M. Shreeve, *Chem. Eur. J.*, 2009, **15**, 2625; (d) Y. Huang, Y. Zhang and J. M. Shreeve, *Chem. Eur. J.*, 2010, **17**, 1538.
- (a) T. M. Klapötke, P. Mayer, A. Schulz and J. J. Weigand, *J. Am. Chem. Soc.*, 2005, **127**, 2032; (b) T. Abe, G. H. Tao, Y. H. Joo, Y. Huang, B. Twamley and J. M. Shreeve, *Angew. Chem.*, 2008, **120**, 7195; *Angew. Chem., Int. Ed.*, 2008, **47**, 7087; (c) T. M. Klapötke and J. Stierstorfer, *J. Am. Chem. Soc.*, 2008, 131, 1122; (d) Y. -H. Joo, J. M. Shreeve, *Angew. Chem.* 2009, **121**, 572; *Angew. Chem., Int. Ed.*, 2009, **48**, 564; (e) T. M. Klapötke, F. A. Martin and J. Stierstorfer, *Angew. Chem.*, 2011, **123**, 4313; *Angew. Chem., Int. Ed.*, 2011, **50**, 4227; (f) T. M. Klapötke, D. G. Piercey and J. Stierstorfer, *Dalton Trans.*, 2012, **41**, 9451; (g) Q. Zhang, J. Zhang, D. A. Parrish and J. M. Shreeve, *Chem. Eur. J.* 2013, **19**, 11000; (h) Q. Lin, Y. Li, C. Qi, W. Liu, Y. Wang and S. Pang, *J. Mater. Chem. A* 2013, **1**, 6776; (i) D. Chand, D. A. Parrish and J. M. Shreeve, *J. Mater. Chem. A*, 2013, **1**, 15383.
- (a) M. H. V. Huynh, M. A. Hiskey, J. G. Archuleta, E. L. Roemer and R. Gilardi, *Angew. Chem.*, 2004, **116**, 5776; *Angew. Chem. Int. Ed.* 2004, **43**, 5658; (b) D. E. Chavez, M. A. Hiskey and R. D. Gilardi, *Org. Lett.*, 2004, **6**, 2889; (c) M. H. V. Huynh, M. A. Hiskey, D. E. Chavez, D. L. Naud and R. D. Gilard, *J. Am. Chem. Soc.*, 2005, **127**, 12537; (d) H. Gao, R. Wang, B. Twamley, M. A. Hiskey and J. M. Shreeve, *Chem. Commun.*, 2006, 4007; (e) Z. Fu, C. He and F. Chen, *J. Mater. Chem.* 2012, **22**, 60; (f) D. E. Chavez, S. K. Hanson, J. M. Veauthier and D. A. Parrish, *Angew. Chem.*, 2013, **125**, 7014; *Angew. Chem. Int. Ed.*, 2013, **52**, 6876.
- (a) G. Herve, C. Roussel and H. Graindorge, *Angew. Chem.* 2010, **122**, 3245; *Angew. Chem. Int. Ed.*, 2010, **49**, 3177; (b) A. A. Dippold, T. M. Klapötke and N. Winter, *Eur. J. Inorg. Chem.*, 2012, **2012**,

- 3474; (c) T. T. Vo, J. Zhang, D. A. Parrish, B. Twamley and J. M. Shreeve, *J. Am. Chem. Soc.*, 2013, **135**, 11787.
- 8 (a) T. M. Klapötke, B. Krumm, F. X. Steemann and K. Umland, *Z. Anorg. Allg. Chem.* 2010, **636**, 2343; (b) N. Fischer, T. M. Klapötke, J. Stierstorfer and C. Wiedemann, *Polyhedron*, 2011, **30**, 2374; (c) Y. Li, W. Liu, S. Pang, *Molecules*, 2012, **17**, 5040.
- 9 (a) T. Fendt, N. Fischer, T. M. Klapötke and J. Stierstorfer, *Inorg. Chem.*, 2011, **50**, 1447; (b) T. M. Klapötke, C. Petermayer, D. G. Piercey and J. Stierstorfer, *J. Am. Chem. Soc.*, 2012, **134**, 20827; (c) D. Fischer, T. M. Klapötke, M. Reymann, and J. Stierstorfer, *Chem. Eur. J.*, 2014, **20**, 1.
- 10 (a) M. D. Coburn, *J. Heterocycl. Chem.*, 1966, **3**, 365; (b) M. D. Coburn, *J. Heterocycl. Chem.*, 1968, **5**, 83; (c) M. D. Coburn and T. E. Jackson, *J. Heterocycl. Chem.*, 1968, **5**, 199; (d) M. D. Coburn and J. L. Singleton, *J. Heterocycl. Chem.*, 1972, **9**, 1039; (e) M. E. Sitzmann, *J. Org. Chem.*, 1978, **43**, 3389; (f) H. S. Jadhav, M. B. Talawar, R. Sivabalan, D. D. Dhavale, S. N. Asthana and V. N. Krishnamurthy, *J. Hazard. Mater.*, 2007, **143**, 192; (g) K. Hou, C. Ma, Z. Liu, *New J. Chem.*, 2013, **37**, 2837; (h) Y. Tang, H. Yang, X. Ju, H. Huang, C. Lu, G. Cheng, *J. Mater. Chem. A*, 2014, **2**, 4127.
- 11 (a) F. Benedetti, D. R. Marshall and C. J. M. Stirling, *J. Chem. Soc., Chem. Commun.*, 1982, 918; (b) O. V. Serushkina, M. D. Dutov and S. A. Shevelev, *Russ. Chem. Bull.*, 2001, **50**, 261; (c) O. V. Serushkina, M. D. Dutov, V. N. Solkan and S. A. Shevelev, *Russ. Chem. Bull.*, 2001, **50**, 2406; (d) V. M. Vinogradov, A. M. Starosotnikov and S. A. Shevelev, *Mendeleev Commun.*, 2002, **12**, 198.
- 12 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.
- 13 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans.*, 1987, **2**, S1.
- 14 (a) G. A. Olah, A. Burcher, G. Rasul, M. Hachoumy and G. S. Prakash, *J. Am. Chem. Soc.*, 1997, **119**, 12929; (b) R. Marek, A. Lyka, *Curr. Org. Chem.*, 2002, **6**, 35; (c) T. C. Martins, T. C. Ramalho, J. D. Figueroa-Villar, A. C. Flores, C. P. Pereira, *Magn. Reson. Chem.*, 2003, **41**, 983; (d) A. Lyka, R. Mareka, *Curr. Org. Chem.*, 2007, **11**, 1154.
- 15 T. M. Klapötke, A. Penger, C. Pflüger, J. Stierstorfer and M. Sućeska, *Eur. J. Inorg. Chem.*, 2013, **2013**, 4667.
- 16 (a) C. M. Sabaté, H. Delalu and E. Jeanneau, *Chem. Asian J.*, **7**, 1085; (b) C. M. Sabaté, H. Delalu and E. Jeanneau, *Chem. Asian J.*, 2012, **7**, 2080.
- 17 Impact: insensitive > 40 J, less sensitive \geq 35 J, sensitive \geq 4 J, very sensitive \leq 3 J. Friction: insensitive > 360 N, less sensitive: 360 N, sensitive < 360 N and > 80 N, very sensitive \leq 80 N, extremely sensitive \leq 10 N; according to the UN Recommendations on the Transport of Dangerous Goods.
- 18 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Gaussian, Inc., Wallingford, CT, 2009.
- 19 P. C. Hariharan and J. A. Pople, *Theoretica Chimica Acta.*, 1973, **28**, 213.
- 20 M. Sućeska, 6.01 ed., Zagreb, Croatia, 2013.
- 21 A. M. Starosotnikov, A. V. Lobach, V. V. Kachala and S. A. Shevelev, *Russ. Chem. Bull.*, 2004, **53**, 584.
- 22 J. Pan, J. He, Y. Tao, *Chin. J. Energ. Mater.*, 2006, **14**, 116.



Synthesis of new picryl derivatives containing high nitrogen content moiety from new starting materials are now reported.



29x10mm (600 x 600 DPI)