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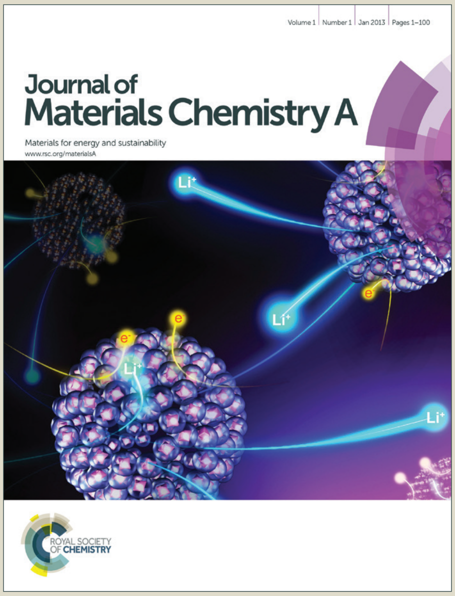

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ARTICLE TYPE

The Unique Synthesis and Energetic Properties of Novel Fused Heterocycle: 7-Nitro-4-oxo-4,8-dihydro-[1,2,4]triazolo[5,1-d][1,2,3,5]tetrazine 2-oxide and Its Energetic Salts

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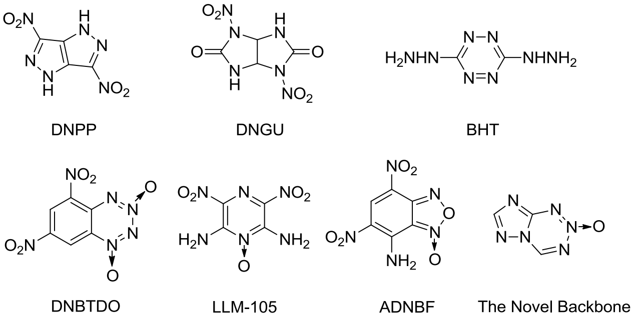
The unique and facile synthesis of 7-nitro-4-oxo-4,8-dihydro-[1,2,4]triazolo[5,1-d][1,2,3,5]tetrazine 2-oxide (HBCM) and a proposed mechanism for its formation are described. The hygroscopicity of HBCM was overcome by transforming it into salts. The energetic salts of HBCM were characterized by ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy, infrared spectroscopy, differential scanning calorimetry (DSC) and elemental analysis. The crystal structures of the sodium and guanidinium salts were determined by single-crystal X-ray diffraction. The densities of the salts range from 1.77 to 1.97 g cm^{-3}. Most of the energetic salts decompose above 230 ℃ and tend to be insensitive to impact, friction and electrostatic discharge. Theoretical performance calculations (Gaussian 03 and EXPLO5) for the energetic salts provide detonation pressures and velocities within the ranges 25.2–39.5 GPa and 7856–9069 m s^{-1}, respectively. The hydroxylammonium salt shows high density (1.97 g cm^{-3}), acceptable decomposition temperature (T_d = 197 ℃), low sensitivities, and excellent detonation velocity (9069 m s^{-1}) and pressure (39.5 GPa), which suggests that it has the potential to be used as a High-energy-density material.

Introduction

High-energy-density materials (HEDMs) with high thermal and mechanical stabilities attract considerable research attention.[1] The contradictory relationship between high performance and low sensitivity is the main challenge in this research.[2] Modern HEDMs are designed to be nitrogen-rich or to have ring or cage strain; they may also contain a combination of these design features.[3] Hence, fused heterocyclic compounds, such as 3,6-dinitro-1,4-dihydropyrazolo[4,3-c]pyrazole (DNPP)[4] and 1,4-dinitroglycoluril (DNGU),[5] are promising materials that fulfill many requirements in this challenging field. Fused cyclic compounds with ring strain energy can be used as HEDMs when nitro groups and other energetic groups are present in the ring, since fused compounds are usually more rigid than their single-ring analogues. This should result in a higher density and a superior performance. For example, DNPP is thermally stable (T_d = 330 ℃) and relatively insensitive to impact ($H_{50\%}$ = 68 cm), has a high density (1.865 g cm^{-3}),[6] and has a predicted performance (Cheetah calculation) which is 85% that of 1,3,5,7-tetranitrotetraazacyclooctane (HMX).[7]

Derivatives of 1,2,4,5-tetrazine and 1,2,3,4-tetrazine, such as 3,6-dihydrazinyl-1,2,4,5-tetrazine (BHT)[8] and 5,7-dinitrobenzo-1,2,3,4-tetrazine-1,3-dioxide (DNBTDO),[9] respectively, are well studied.[10] However, 1,2,3,5-tetrazine compounds haven not been investigated for their application in explosives.[11] To the best of our knowledge and belief, 1,2,3,5-tetrazine 2-oxide has not yet been reported in the literature.



Scheme 1 Structures of mentioned compounds.

In a continuing effort to seek more powerful and less sensitive HEDMs, we directed our attention to the new molecule [1,2,4]triazolo[5,1-d][1,2,3,5]tetrazine 2-oxide. Its backbone consists of a 1,2,4-triazole ring fused with a 1,2,3,5-tetrazine 2-oxide ring through a shared C-N bond. The three catenated

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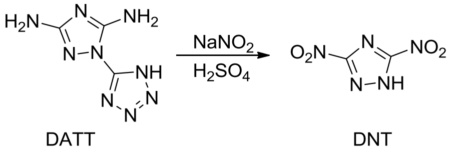
Electronic Supplementary Information (ESI) available: the methodology and details for the heat of formation. CCDC reference number 1032297 (**3**·$3H_2O$) and 1032298 (**7**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

nitrogen atoms in the tetrazine unit and the bridgehead nitrogen enhance the ring strain and introduce additional energy. The *N*-oxide moiety not only leads to a higher density and a better oxygen balance (thus resulting in improved energetic performance[12]), but also changes the charge distribution and increases the aromaticity of the fused heterocyclic system, thus stabilizing it.[13] The utility of *N*-oxides is illustrated by the variety of energetic materials that possess this functionality, such as 2,6-diamino-3,5-dinitropyrazine 1-oxide (LLM-105)[14] and 7-amino-4,6-dinitrobenzofuroxan (ADNBF).[15]

In this paper, we report a unique and facile synthetic route to 7-nitro-4-oxo-4,8-dihydro-[1,2,4]triazolo[5,1-d][1,2,3,5]tetrazine 2-oxide (henceforth denoted as HBCM). HBCM and its energetic salts were fully characterized, and their detonation properties were calculated. Furthermore, the crystal structures of HBCM's sodium and guanidinium salts were determined by single-crystal X-ray diffraction.

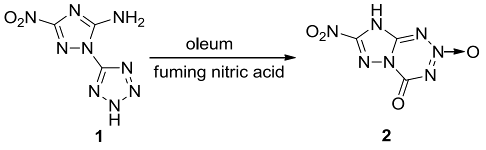
Results and Discussion

Synthesis of HBCM. We recently reported that diazotization of 3,5-diamino-1-(1*H*-tetrazol-5-yl)-1*H*-1,2,4-triazole (DATT)[16] with excess sodium nitrite in dilute sulfuric acid followed by denitrification and nitration, affords 3,5-dinitro-1*H*-1,2,4-triazole (DNT) as the main product.[17] The expulsion of the tetrazole ring, to generate DNT, was explained by the low electron density of the N1 atom in the triazole ring due to the strong electron-withdrawing inductive effect of the two nitro groups.



Scheme 2 The inspiring reaction.

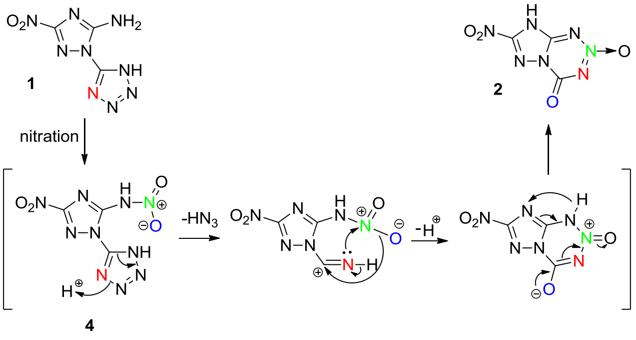
Further study focused on the nitration of 3-nitro-1-(2*H*-tetrazol-5-yl)-1*H*-1,2,4-triazol-5-amine (HANTT)[17] to check whether the tetrazole ring can sustain the electron-withdrawing inductive effect of one nitro group and one nitramine group; the combined electron-withdrawing inductive effect of these two groups is weaker than that of two nitro groups. The product 7-nitro-4-oxo-4,8-dihydro-[1,2,4]triazolo[5,1-d][1,2,3,5]tetrazine 2-oxide (**2**, Scheme 3) was synthesized successfully. HANTT (**1**) was dissolved in oleum/fuming nitric acid below 20 ℃, and then stirred for 2 h at room temperature. The reaction mixture was quenched with crushed ice, and the resulting solution was extracted with ethyl acetate.



Scheme 3 Synthesis of HBCM.

It is worth noting that treatment of the organic phase with brine, followed by drying with anhydrous Na_2SO_4, affords light yellow Na(BCM) (**3**) as the final product. This could be ascribed to the poor solubility of the sodium salt in ethyl acetate. Alternatively, evaporation of the organic phase under vacuum without further treatment affords yellow, hygroscopic HBCM (**2**); it rapidly becomes viscous when exposed to air. We failed to get the melting point of pure **2** because the flow of protective N_2 gas was not strong enough to avoid absorption of water by **2** when DSC was performed.

Mechanism. A proposed mechanism for the formation of **2** is shown in Scheme 4. HANTT first reacts with the mixed nitric/sulfuric acid to generate unstable intermediate **4**, a nitramine compound. Expulsion of HN_3 from the tetrazole unit precedes the ring closure between the nitrogen atom of the remaining activated C=N moiety and the nitrogen atom of the nitro group. A nucleophilic attack of the nitro group's oxygen atom on the carbocation of the former C=N moiety then occurs, giving rise to the 1,2,3,5-tetrazine 2-oxide ring, which is the first example prepared from a connected 1,2,4-triazole and tetrazole system. The final product HBCM is then obtained through proton and electron transfer. In other words, the tetrazole structure protects, and then affords, the crucial C=N double bond. Ring closure occurs when the nitramine group (rather than the nitro group) is introduced into the ortho position of the tetrazole. The nitramine group contains one more nitrogen atom in the chain than the nitro group. Therefore, less ring strain is built up during the cyclization process of the nitramine derivative, which enables the cyclization. We confirmed that HN_3 gas was released by its reaction with aqueous $AgNO_3$ to afford the white precipitate AgN_3. A strong infrared band of HBCM at 1787 cm^{-1}, and the absence of any obvious absorption in the 3600–2500 cm^{-1} region, support the presence of a carbanyl rather than a hydroxyl group.



Scheme 4 Proposed mechanism for the formation of HBCM.

Synthesis of Energetic Salts. In sharp contrast to HBCM, Na(BCM) is not hygroscopic nor deliquescent. Thus transformation into salts would be a reasonable and simple approach to overcome the hygroscopicity of HBCM. Moreover, salt formation is usually an efficient method for improving the thermal stability.

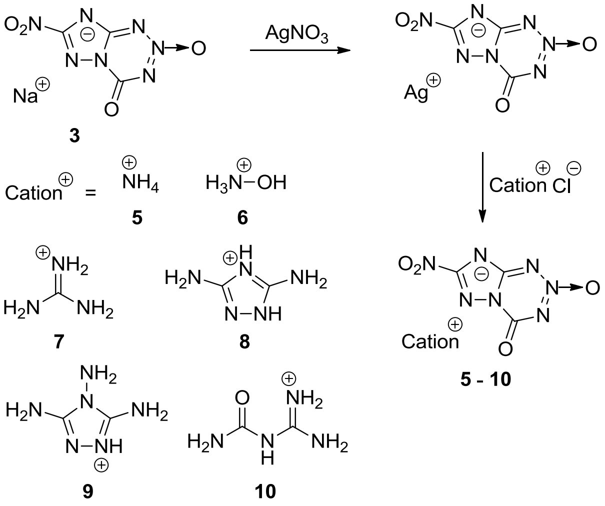
The synthetic pathways to the energetic salts are depicted in Scheme 5. Compounds **5-10** were prepared from the reaction of $AgNO_3$ with Na(BCM) (**3**) to give brown Ag(BCM), followed by cation exchange of Ag(BCM) with the corresponding hydrochloride in hot water. All of the energetic salts are stable in air and could be stored for extended periods of time. Salts **3** and **5-10** were dried at 70 ℃ under vacuum for 2 h before characterization by IR spectroscopy, DSC, ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. The data are listed in the Experimental Section.

Spectroscopy. As no protons are present in BCM anion, all of the signals in the ^{1}H NMR spectra are assignable to the cations. The NMR chemical shifts of the cations in this study were consistent with previously published ones.[18] The ^{13}C NMR resonances for the BCM anion are located at δ = 163.4, 158.7, and 148.9 ppm.

Table 1 Physiochemical properties and detonation parameters of energetic salts based on HBCM.

Comp.	**3**	**5**	**6**	**7**	**8**	**9**	**10**	TATB	RDX
$T_m{}^a$ (℃)	dec	dec	dec	266	dec	213	208	350	dec
$T_d{}^b$ (℃)	296	249	197	269	252	237	241	~360	230
ρ^c (g cm^{-3})	2.02	1.77	1.97	1.78^m	1.89	1.81	1.80	1.93	1.82
$\Delta_f H_L{}^d$ (kJ mol^{-1})	-	507.8	512.9	486.1	475.2	464.1	468.2	-	-
$\Delta_f H_{sal}{}^e$ (kJ mol^{-1})	-	180.6	218.6	151.8	350.8	475.6	-55.6	-154.2	92.6
$\Delta_{Ex} U^o{}_{sal}{}^f$ (kJ kg^{-1})	-	927.4	1032.7	683.9	1268.0	1613.4	-90.1	-511	617.3
$P_{cj}{}^g$ (GPa)	-	29.0	39.5	27.1	30.7	29.2	25.2	31.2	34.9
$v_D{}^h$ (m s^{-1})	-	8252	9069	8113	8463	8374	7856	8114	8748
IS^i (J)	> 40	> 40	> 40	> 40	> 40	> 40	> 40	50	7
FS^j (N)	> 360	324	324	324	360	324	> 360	> 360	120
ESD^k	–	–	–	–	–	+	–	–	0.2
OB^l (%)	-39.8	-29.6	-20.6	-43.3	-48.2	-48.5	-45.1	-55.8	-21.6

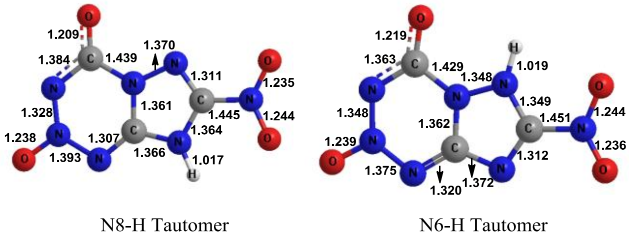
[a] Melting point. [b] Thermal decomposition temperature. [c] Measured density (gas pynometer). [d] Calculated molar lattice energy. [e] Calculated molar enthalpy of formation of salts ($\Delta_f H$ anion = 62.1 kJ mol^{-1} calculated from Gaussian 03). [f] Energy of formation. [g] Detonation pressure. [h] Detonation velocity. [i] Impact sensitivity. [j] Friction sensitivity (BAM friction apparatus). [k] Rough sensitivity to the electrostatic discharge (+/–): + = sensitive; – = insensitive. [l] Oxygen balance. [m] single crystal density (163 K).



Scheme 5 Synthesis of energetic salts based on HBCM.

Thermal Behavior. The melting points (T_m, onset) and decomposition temperatures (T_d, onset) of the energetic salts were determined by DSC at a heating rate of 5 ℃ min^{-1}. As shown in Table 1, the guanidinium (**7**), 3,4,5-triamino-1,2,4-triazolium (**9**), and *N*-carbamoylguanidinium (**10**) salts melt prior to decomposition, having T_m = 266, 213, and 208 ℃, respectively. With the exception of hydroxylammonium salt (**6**), decomposition temperatures of most salts are higher than 237 ℃ which are superior to that of 1,3,5-trinitro-1,3,5-triazinane (RDX , T_d = 230 ℃).

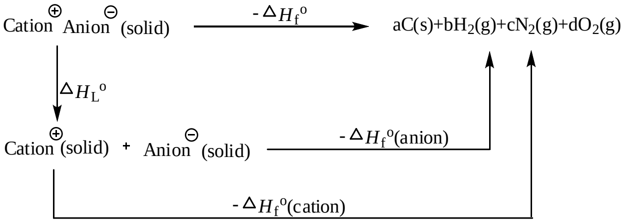
Heat of Formation. The standard enthalpies of formation for neutral compound HBCM and BCM anion were calculated by the Gaussian-3 (G3)[19] method using the Gaussian 03 package.[20] All of the optimized structures were predicted to be genuine minima with all real vibrational frequencies.



N8-H Tautomer N6-H Tautomer

Figure 1 The optimized geometries for the neutral compound HBCM.

There are two different tautomers for HBCM with the only hydrogen atom bonded to N6 or N8 position (Figure 1). N8-H tautomer is more stable, whose calculated total energy lies below N6-H tautomer by 33.2 kJ mol^{-1}. The gas-phase heats of formation of BCM anion is 62.1 kJ mol^{-1}. The gas-phase heats of formation of cations are provided in the literature.[4a,21] The solid-phase heats of formation of energetic salts **5-10** are calculated on the basis of Born-Haber energy cycles (Supporting Information for details).



Scheme 6 Born-Haber cycle for the formation for energetic salts.

Usually, the presence of nitro group, carbonyl group, and *N*-oxide moiety tend to decrease the heat of formation of a compound.[22] However, most of our energetic salts show highly endothermic heats of formation, ranging from 151.8 (**7**) to 475.6 kJ mol^{-1} (**9**). Because $\Delta_f H$ of the cation is much lower than its lattice energy, *N*-carbamoylguanidinium salt (**10**) possesses a negative heat of formation (Δ_fH = -55.6 kJ mol^{-1}). The most positive value is for 3,4,5-triamino-1,2,4-triazolium salt (**9**), which has the largest number of C-N, N-N and C=N bonds; this is followed by the 3,5-diamino-1,2,4-triazolium salt (**8**) (Δ_fH = 350.8 kJ mol^{-1}).

Sensitivities. (Impact sensitivity = IS; Friction sensitivity = FS; Sensitivity to the electrostatic discharge = ESD) The sensitivities of the salts to impact, friction, and electrostatic discharge were tested by standard procedures.[23] Salts **3** and **10** are classed as impact and friction insensitive energetic materials(IS > 40 J, FS > 360N). Salts **5-9** are insensitive toward impact and tend to be insensitive toward friction. Most of the salts are insensitive to electrostatic discharge of approximately 20 kV, except for 3,4,5-triamino-1,2,4-triazolium salt **9**. All of the energetic salts are much less sensitive than RDX, which may be due to the abundance of intra- and intermolecular hydrogen bonds. Moreover, the sensitivities of *N*-carbamoylguanidinium salts **10** even could be comparable to those of triaminotrinitrobenzene (TATB).

Detonation Parameters. Density is one of the most important properties contributing to the performance of an explosive. As shown in Table 1, Na(BCM) (**3**) has a density of 2.02 g cm^{-3}, while the densities of salts **5-10** range from 1.77 (**5**) to 1.97 g cm^{-3} (**6**) (measured using a gas pycnometer at 25 ℃). It is noteworthy that the densities of compounds **6** and **8-10** fall in the range designated for new HEDMs (1.8−2.0 g cm^{-3}).[1a] Moreover, the high density of **6** (1.97 g cm$^{−3}$) is even comparable with those of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclododecane (CL-20) (1.94−2.04 g cm$^{−3}$) and HMX (1.91 g cm$^{−3}$).

Oxygen balance (OB) is used to indicate the degree to which an explosive can be oxidized. All of the energetic salts possess a negative OB, ranging from -48.5%(**9**) to -20.6%(**6**). The hydroxylammonium salt (**6**) possesses the least negative OB (-20.6%), which is slightly higher than that of RDX.

The detonation pressures (*P*) and velocities (v_D) of the new energetic salts were determined using **EXPLO5** program (version 5.05) according to the measured densities and the calculated Δ_fH.[24] The calculated detonation velocities fall between 7856 (**10**) and 9069 m s^{-1} (**6**), and the calculated detonation pressures range from 25.2 (**10**) to 39.5 GPa (**6**). Most of the energetic salts show detonation properties better than those of TATB (*P* = 8114 m s^{-1}, v_D = 31.2 GPa), except for the guanidinium (**7**) and *N*-carbamoylguanidinium (**10**) salts. 3,5-Diamino-1,2,4-triazolium salt (**8**) possesses a high heat of formation (Δ_fH = 350.8 kJ mol^{-1}) and a high density (ρ = 1.89 g cm^{-3}), thus confirming its good detonation performance (v_D = 8463 m s^{-1}, *P* = 30.7 GPa). Hydroxylammonium salt (**6**) displays the best performance, having a calculated detonation velocity of 9069 m s^{-1} and a calculated detonation pressures of 39.5 GPa, because it has the highest density (ρ = 1.97 g cm^{-3}) and the highest oxygen balance (OB = -20.6%). Taking the detonation parameters, sensitivities and thermal stability into account, hydroxylammonium salt (**6**) outperforms RDX, as it shows much lower sensitivities and a higher density.

X-ray Crystallography. Colorless crystals of **3**·$3H_2O$ suitable for single-crystal X-ray analysis were obtained by slow evaporation of water from an aqueous solution of **3** at room temperature. Compound **3**·$3H_2O$ crystallizes in the orthorhombic space group *Pnma* with a calculated density of 1.807 g cm^{-3}. Crystallographic data and refinement details can be found in the Supporting Information.

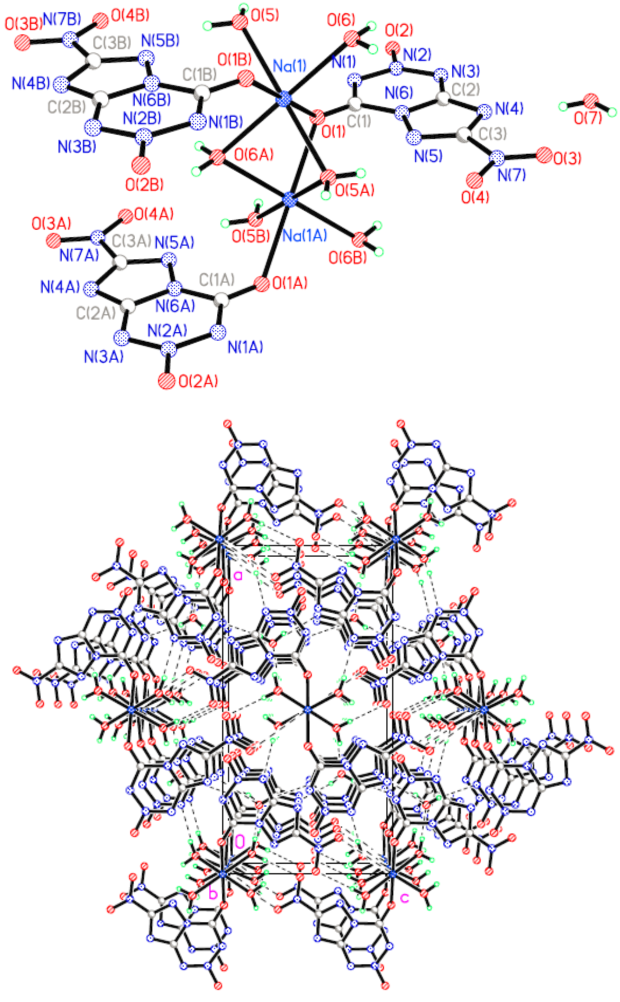


Figure 2 a) Displacement ellipsoid plot (50%) of **3**·$3H_2O$. The hydrogen atoms are included but unlabeled for clarity. b) Ball and stick packing diagram of **3**·$3H_2O$ viewed down the b axis. The dashed lines indicate hydrogen bonding.

As shown in Figure 2a, the deprotonation of the NH functionality of the 1,2,4-triazole moiety is confirmed. The unit cell consists of one BCM anion, one sodium cation and three H_2O molecules. Each sodium cation is six-coordinated by two water oxygen atoms and by an O1 atom of a BCM anion that bridges between two sodium cations. The Na–O1 distance is 2.4079(9) Å. Three BCM anions are coplanar, just like all atoms of each BCM anion. The C–N bond lengths in the fused ring range from 1.3163(18) (C3–N5) to 1.3951(17) Å (C1–N6). The C=O bond length is 1.2209(16) Å, which is a little shorter than that of 6-amino-4-oxo-2-phenyl-4*H*-1,2,3,5-tetrazin-2-ium-1-ide (1.223 Å),[25] but longer than that of 6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1,2,4,5-tetrazin-3(2*H*)-one (1.215 Å).[26] The N2–O2 bond length is 1.2466(15) Å which is longer than those of DNBTDO (1.229(7) Å and 1.240(6) Å),[10] ADNBF (1.224 Å)[15c] and 1,2,3-triazolo4,5-efurazano3,4-bpyrazine 6-oxide (1.220 Å),[3e] but much shorter than that of LLM-105 (1.320(3) Å).[27] The packing structure of **3**·3H_2O consists of 2D layers that are held together by various hydrogen bonds, and a view along the *b* axis is depicted in Figure 2b.

A crystal of **7** suitable for X-ray diffraction analysis was obtained by slow evaporation of water at room temperature from an aqueous solution of **7**. Compound **7** crystallizes in the monoclinic space group $P2_1/c$ with a calculated density of 1.785 g cm^{-3}. The unit cell contains one BCM anion and one guanidinium cation, in which proton transfer from HBCM to guanidine is confirmed. All atoms of the BCM anion are nearly coplanar with the largest torsion angle of -177.84(12)° between C3–N5–N6–C1. The C=O bond length is 1.2207(16) Å. The N2–O2 bond length is 1.2535(15) Å which is longer than that of **3**·3H_2O. The lengths of C–N bonds in the ring range from 1.3189(17) (C3–N5) to 1.3962(16) Å (C1–N6), a range similar to that found for **3**·3H_2O. The guanidinium cation and BCM anion are nearly coplanar with a dihedral angle between them of 6.08°. Viewed along the *b* axis, the packing structure of **7** shows a variety of hydrogen bonds.

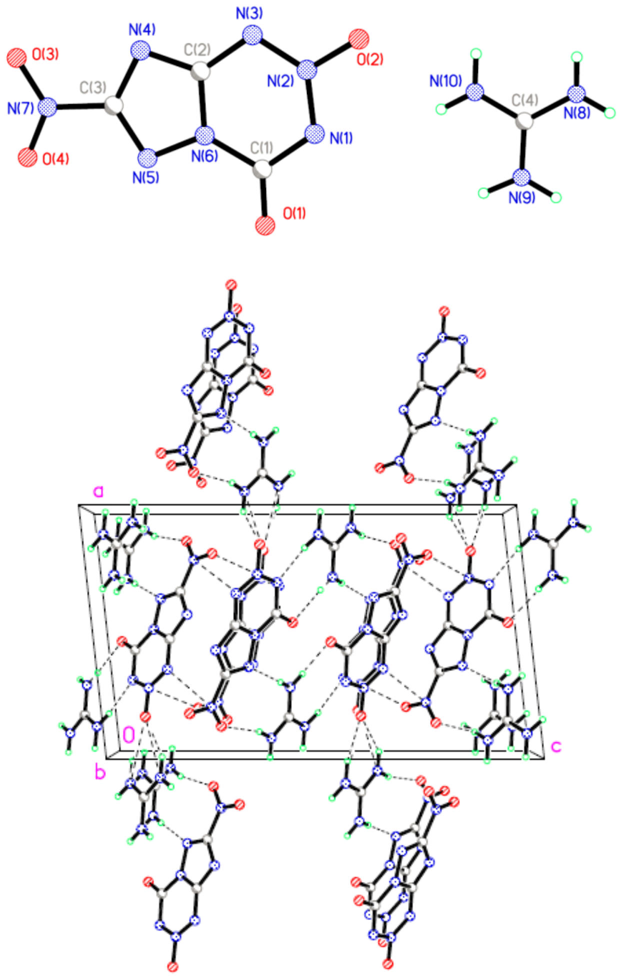


Figure 3 a) Displacement ellipsoid plot (50%) of **7**. The hydrogen atoms are included but unlabeled for clarity. b) Ball and stick packing diagram of **7** viewed down the b axis. The dashed lines indicate hydrogen bonding.

Conclusions

A unique and facile approach to 7-nitro-4-oxo-4,8-dihydro-[1,2,4]triazolo[5,1-d][1,2,3,5]tetrazine 2-oxide (HBCM) has been described. The mechaninsm for its formation presumably involves cleavage of a tetrazole ring, followed by cyclization of a C=N bond with a nitro group. This fused heterocycle proved to be a promising family of thermally stable High-energy-density materials with low sensitivity. The prominent hydroxylammonium salt based on HBCM shows high density (ρ = 1.97 g cm^{-3}), acceptable decomposition temperature (T_d = 197 ℃), low sensitivities (IS >40 J, FS = 324 N, negative ESD), and excellent detonation velocity (9069 m s^{-1}) and pressure (39.5 GPa). In particular, the combination of the high performance (superior to that of RDX) and low sensitivity to mechanical stimuli highlights the potential for hydroxylammonium salt **6** to be used as as a high-energy-density material. This attractive discovery would provide an efficient approach to a wide variety of fused heterocycles based on 1,2,3,5-tetrazine 2-oxide. Further explorations will be reported in due course.

EXPERIMENTAL SECTION

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: ^{1}H, ^{13}C NMR spectra were recorded on a 500 MHz nuclear magnetic resonance spectrometer operating at 500 and 100 MHz, respectively. Chemical shifts are reported relative to TMS for ^{1}H and ^{13}C NMR spectra. The solvent was [D$_6$] dimethyl sulfoxide ([D$_6$]DMSO) unless otherwise specified. The melting and decomposition points (onset) were recorded on a differential scanning calorimetry (DSC) at a scan rate of 5 ℃ min^{-1} in a dynamic nitrogen atmosphere (flow rate = 50 mL min^{-1}). Infrared spectra were recorded using a Bruker Alpha with a ATR-Ge device. Densities were measured at 25 ℃ using a Micromeritics Accupyc Ⅱ 1340 gas pycnometer. Elemental analyses were obtained on an Elementar Vario MICRO CUBE (Germany) elemental analyzer.

For initial safety testing, the impact sensitivity were measured using a BAM Fall Hammer BFH-10; the friction sensitivity were measured using BAM Friction Apparatus FSKM-10; the electrostatic sensitivity were measured using EST806F electrostatic discharge generator.

X-ray crystallography

Crystals of **3**·3H_2O and **7** were removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was then selected, attached to a glass fiber, and placed in the low-temperature nitrogen stream. Data for **3**·3H_2O and **7** were collected at 163(2) K using a Rigaku Saturn724 CCD (AFC10/Saturn724+ for 7) diffractometer equipped with a graphite-monochromatized MoKα radiation (λ = 0.71073 Å) using omega scans. Data collection and reduction were performed and the unit cell was initially refined by using CrystalClear -SM Expert 2.0 r2 software.[28] The reflection data were also corrected for Lp factors. The structure was solved by direct methods and refined by the least squares method on F^2 using the SHELXTL-97 system of programs.[29] Structure were solved in the space group *Pnma* for **3**·3H_2O and $P2_1/c$ for **7**, by analysis of systematic absences. In this all-light-atom structure the value of the Flack parameter did not allow the direction of polar axis to be determined and Friedel reflections were then merged for the final refinement. CCDC-1032297 (**3**·3H_2O) and CCDC-1032298 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk./data_request/cif.

Na(BCM) (**3**) HANTT were prepared according to the literature.[17] 4.4 g (22.3 mmol) HANTT was added in portions to a mixture of oleum (11 mL) and fuming nitric acid (11 mL) below 20 ℃. The system was stirred for 10 min and then warmed to room temperature. After 2 h, the reaction mixture was poured into crushed ice, and extracted with ethyl acetate. The organic phase was washed with brine and dried with anhydrous Na_2SO_4, then concentrated in vacuum and filtrated to give yellow Na(BCM) (yield 81%). ^{13}C NMR ([D$_6$]DMSO, 100 MHz, 25 ℃): δ= 163.4, 158.7, 148.9

ppm. IR (neat): 1795, 1695, 1556, 1481, 1443, 1379, 1308, 1142, 1051, 869, 840, 751, 733, 626, 565, 536 cm^{-1}. MS (ESI): 198 (M-H)$^{-}$. Anal. calcd. for $NaC_3N_7O_4$: C 16.30, H 0.00, N 44.35%; found C 16.28, H 0.03, N 44.32%.

7-nitro-4-oxo-4,8-dihydro-[1,2,4]triazolo[5,1-d][1,2,3,5]tetrazine 2-oxide (**HBCM**, **2**) HBCM was synthesized from 2 mmol HANTT in the similar way of NaBCM. But the ethyl acetate phase evaporated directly in vacuum without further treatment and resulted in viscous solid which was then washed with dichloromethane and dried under vacuum to give yellow HBCM (yield 89%). ^{13}C NMR ([D$_6$]DMSO, 100 MHz, 25 ℃): δ= 163.4, 158.7, 148.9 ppm. IR (neat): 1787, 1702, 1551, 1470, 1377, 1304, 1196, 1165, 1031, 994, 837, 732, 683, 526 cm^{-1}. Anal. calcd. for $C_3HN_7O_4$: C 18.10, H 0.51, N 49.25%; found C 18.04, H 0.60, N 49.18%.

Ag(BCM): A solution of $AgNO_3$ (1.70 g, 10 mmol) in H_2O (20 mL) was added dropwise to the solution of Na(BCM) (2.21 g, 10 mmol) in H_2O (20 mL) under stirring. After half an hour, the precipitate was removed by filtration, and dried in air to leave brown solid (yield 97%); Anal. calcd. for $AgC_3N_7O_4$: C 11.78, H 0.00, N 32.05%; found: C 11.80, H 0.04, N 32.01%. IS > 40 J, FS > 360 N.

General Procedures for the Preparation of Energetic salts 5-10: Ag(BCM) (306 mg, 1 mmol) was added to a solution of the corresponding hydrochloride (1 mmol) in H_2O (10 mL) and the resulting mixture was stirred at 80 ℃ for 4 h. The hot solution was filtered and evaporated in vacuo and the residue was recrystallized from H_2O to give the target product.

Ammonium BCM (5)
Pale yellow solid (183 mg, 85%). ^{1}H NMR ([D$_6$]DMSO, 500 MHz, 25 ℃, TMS): δ= 7.08 (t, 4H) ppm. ^{13}C NMR ([D$_6$]DMSO, 500 MHz, 25 ℃): δ= 163.4, 158.7, 148.9 ppm. IR (neat): 3554, 3402, 3198, 3007, 1712, 1673, 1550, 1480, 1436, 1409, 1366, 1299, 1227, 1196, 1139, 1047, 870, 839, 750, 735, 627, 538 cm^{-1}. Anal. calcd. for $C_3H_4N_8O_4$: C 16.67, H 1.87, N 51.85%; found C 16.66, H 1.89, N 51.83%.

Hydroxylammonium BCM (6)
Pale yellow solid (190 mg, 82%). ^{1}H NMR ([D$_6$]DMSO, 500 MHz, 25 ℃, TMS): δ= 10.09 (s, 3H), 9.90 (s, H) ppm. ^{13}C NMR ([D$_6$]DMSO, 500 MHz, 25 ℃): δ= 163.4, 158.7, 148.9 ppm. IR (neat): 2981, 2712, 1691, 1660, 1559, 1482, 1376, 1333, 1309, 1233, 1199, 1129, 999, 871, 837, 771, 751, 733, 690, 630, 547 cm^{-1}. Anal. calcd. for $C_3H_4N_8O_5$: C 15.52, H 1.74, N 48.28%; found C 15.55, H 1.73, N 48.26%.

Guanidinium BCM (7)
Yellow solid (227 mg, 88%). ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 ℃, TMS): δ= 6.91 (s, 6H) ppm. ^{13}C NMR ([D$_6$]DMSO, 100 MHz, 25 ℃): δ= 163.4, 158.7, 158.3, 148.9 ppm. IR (neat): 3461, 3374, 3182, 1646, 1550, 1476, 1439, 1416, 1375, 1327, 1307, 1237, 1198, 1133, 1052, 871, 840, 748, 617, 417 cm^{-1}. Anal. calcd. for $C_4H_6N_{10}O_4$: C 18.61, H 2.34, N 54.26%; found C 18.60, H 2.35, N 54.29%.

3,5-Diamino-1,2,4-triazolium BCM (8)
Bright yellow solid (274 mg, 92%). ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 ℃, TMS): δ= 6.99 (br s) ppm. ^{13}C NMR ([D$_6$]DMSO, 100 MHz, 25 ℃): δ= 163.4, 158.7, 151.9, 148.9 ppm. IR (neat): 3406, 3327, 2663, 1686, 1656, 1604, 1544, 1476, 1440, 1369, 1308, 1196, 1152, 1008, 876, 841, 771, 748, 731, 630, 476 cm^{-1}. Anal. calcd. for $C_5H_6N_{12}O_4$: C 20.14, H 2.03, N 56.37%; found C 20.17, H 2.05, N 56.36%.

3,4,5-Triamino-1,2,4-triazolium BCM (9)
Bright yellow solid (281 mg, 90%). ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 ℃, TMS): δ= 7.09 (s, 4H), 5.58 (s, 2H) ppm. ^{13}C NMR ([D$_6$]DMSO, 100 MHz, 25 ℃): δ= 163.4, 158.7, 150.4, 148.9 ppm. IR (neat): 3456, 3335, 3204, 2945, 2726, 1710, 1689, 1659, 1573, 1547, 1487, 1433, 1373, 1306, 1196, 1149, 867, 795, 751, 735, 625, 565 cm^{-1}. Anal. calcd. for $C_5H_7N_{13}O_4$: C 19.17, H 2.25, N 58.14%; found C 19.20, H 2.28, N 58.15%.

N-Carbamoylguanidinium BCM (10)
Pale yellow solid (250 mg, 83%). ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 ℃, TMS): δ= 9.65 (br s, H), 8.05 (br s, 4H), 7.15 (br s, 2H) ppm. ^{13}C NMR ([D$_6$]DMSO, 100 MHz, 25 ℃): δ= 163.4, 158.7, 155.8, 154.8, 148.9 ppm. IR (neat): 3429, 3392, 3307, 3138, 1731, 1688, 1561, 1484, 1381, 1343, 1314, 1239, 1200, 1130, 1048, 870, 750, 708, 658, 568, 511, 443 cm^{-1}. Anal. calcd. for $C_5H_7N_{11}O_5$: C 19.94, H 2.34, N 51.16%; found C 19.93, H 2.33, N 51.18%.

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References

1 a) J. Zhang and J. M. Shreeve, *J. Am. Chem. Soc.*, 2014, **136**, 4437−4445; b) D. Chand, D. A. Parrish, J. M. Shreeve, *J. Mater. Chem. A*, 2013, **1**, 15383–15389; c) A. A. Dippold and T. M. Klapötke, *J. Am. Chem. Soc.*, 2013, **135**, 9931−9938; d) D. Fischer, T. M. Klapötke, M. Reymann, J. Stierstorfer, *Chem. Eur. J.*, 2014, **20**, 6401−6411; e) N. Fischer, D. Fischer, T. M. Klapötke, D. G. Piercey, J. Stierstorfer, *J. Mater. Chem.*, 2012, **22**, 20418–20422; f) Y. Tang, H. Yang, B. Wu, X. Ju, C. Lu, G. Cheng, *Angew. Chem., Int. Ed.* 2013, **52**, 4875–4877.

2 a) J. Zhang, C. He, D. A. Parrish, J. M. Shreeve, *Chem. Eur. J.*, 2013, **19**, 8929−8936; b) D. Fischer, T. M. Klapötke, D. G. Piercey, J. Stierstorfer, *Chem. Eur. J.*, 2013, **19**, 4602-4613; c) J. Song, Z. Zhou, X. Dong, H. Huang, D. Cao, L. Liang, K. Wang, J. Zhang, F. Chen, Y. Wu, *J. Mater. Chem.*, 2012, **22**, 3201–3209; d) V. Thottempudi, H. Gao, J. M. Shreeve, *J. Am. Chem. Soc.*, 2011, **133**, 6464−6470; e) R. Wang, H. Xu, Y. Guo, R. Sa and J. M. Shreeve, *J. Am. Chem. Soc.*, 2010, **132**, 11904–11905.

3 a) H. Abou-Rachid, Y. Song, A. Hu, S. Dudiy, S. V. Zybin, W. A. Goddard, *J. Phys. Chem. A*, 2008, **112**, 11914–11920; b) A. A. Dippold, T. M. Klapötke, M. Oswald, *Dalton Trans.*, 2013, **42**, 11136–11145; c) C. Ye, H. Gao, J. A. Boatz, G. W. Drake, B. Twamley, J. M. Shreeve, *Angew. Chem., Int. Ed.*, 2006, **45**, 7262−7265; d) Y. H. Joo and J. M. Shreeve, *Angew. Chem., Int. Ed.*, 2010, **49**, 7320−7323; e) V. Thottemudi, P. Yin, J. Zhang, D. A. Parrish, and J. M. Shreeve, *Chem. Eur. J.*, 2014, **20**, 542-548; f) G. Tao, B. Twamley, J. M. Shreeve, *J. Mater. Chem.*, 2009, **19**, 5850-5854; g) Y. Zhang, Y. Huang, D. A. Parrish, J. M. Shreeve. J. Mater. Chem., 2011, **21**, 6891-6897; h) H. Huang, Z. Zhou, L. Liang, J. Song, K. Wang, D. Cao, W. Sun, C. Bian, M. Xue, *Chem. Asian J.*, 2012, **7**, 707-714; i) A. A. Dippold, T. M. Klapötke, *Chem. Asian J.*, 2013, **8**, 1463-1471.

4 a) J. Zhang, D. A. Parrish, and J. M. Shreeve, *Chem. Asian J.*, 2014, **9**, 2953-2960; b) S. A. Shevelev, I. L. Dalinger, T. K. Shkineva, B. I. Ugrak, V. I. Gulevskaya, M. I. Kanishchev, *Russ. Chem. Bull.*, 1993, **42**, 1063-1068; c) P. F. Pagoria, A. R. Mitchell, R. D. Schmidt, R. L. Simpson, F. Garcia, J. Forbes, J. Cutting, R. Lee, R. Swansiger, D. M. Hoffman, *Insensitive Munitions and Energetic Materials Technology Symposium*, San Diego, CA, **1998**, 956.

5 a) J. Boileau, E. Wimmer, R. Gilardi, M. M. Stinecipher, R. Gallo, M. Pierrot, *Acta Cryst.*, 1988, **44**, 696-969; b) J. Boileau, M. Carail, E. Wimmer, R. Gallo, M. Pierrot, *Propellants Explos. Pyrotech.*, 1985, **10**, 118-120; c) J. P. Agrawal, *Prog. Energy Cobust. Sci.*, 1998, **24**, 1-30.

6 R. Gilardi, *X-ray Crystallographic Determination*, Naval Research Laboratory, Washington , DC.

7 P. F. Pagoria, G. S. Lee, A. R. Mitchell, R. D. Schmidt. *Thermochimica Acta*, 2002, **384**, 181-204.

8 a) D. E. Chavez, M. A. Hiskey, *J. Energ. Mater.*, 1999, **17**, 357–377; b) T. M. Klapötke, A. Preimesser, S. Schedlbauer, J. Stierstorfer, *Cent. Eur. J. Energ. Mater.*, 2013, **10**, 151-170.

9 T. M. Klapötke, D. G. Piercey, J. Stierstorfer, M. Weyrauther, *Propellants, Explos., Pyrotech.*, 2012, **37**, 527−535.

10 a) A. M. Churakov, V. A. Tartakovsky, *Chem. Rev.*, 2004, **104**, 2601−2616; b) M. H. V. Huynh, M. A. Hiskey, D. E. Chavez. D. L. Naud, and R. D. Gilardi, *J. Am. Chem. Soc.*, 2005, **127**, 12537-12543; c) A. M. Churakov, S. L. Ioffe and V. A. Tartakovsky, *Mendeleev Commun.*, 1995, **5**, 227–228; d) D. B. Lempert, G. N. Nechiporenko, S. I. Soglasnova, *Khim. Fiz.*, 2004, **23**, 75–81; e) D. E. Chavez, M. A. Hiskey, N. Darrenl, *Org. Lett.*, 2004, **6**, 2889-2891; f) D. E. Chavez, M. A. Hiskey, B. C. Tappan, *Propellants, Explos., Pyrotech.*, 2005, **30**, 412-417; g) D. E. Chavez, M. A. Hiskey, D. L. Naud, *Propellants, Explos., Pyrotech.*, 2004, **29**, 209-

215; h) V. A. Tartakovsky, I. E. Filatov, A. M. Churakov, S. L. Ioffe, Y. A. Strelenko, V. S. Kuzmin, G. L. Rusinov, K. I. Pashkevich, *Izvest. Akad. Nauk. Ser. Khim.*, 2004, **11**, 2471-2477; i) H. Licht, H. Ritter, *J. Energ. Mater.*, 1994, **12**, 223-235; j) N. V. Palysaeva, K. P. Kumpan, M. I. Struchkova, I. L. Dalinger, A. V. Kormanov, N. S. Aleksandrova, V. M. Chernyshev, D. F. Pyreu, K.Y. Suponitsky, and A. B. Sheremetev, *Org. Lett.*, 2014, **16**, 406-409; k) Q. Zhang, C. He, P. Yin, and J. M. Shreeve, *Chem. Asian J.*, 2014, **9**, 212-217.

11 a) D. Pletsas, E. A. E. Garelnabi, L. Li, R. M. Phillips, R. T. Wheelhouse, *J. Med. Chem.*, 2013, **56**, 7120−7132; b) C. K. Moseley, S. M. Carlin, R. Neelamegam, J. M. Hooker, *Org. Lett.*, 2012, **14**, 5872−5875.

12 a) N. Fischer, T. M. Klapötke, M. Reymann, and J. Stierstorfer, *Eur. J. Inorg. Chem.*, **2013**, 2167-2180; b) H. Singh, U. Mukherjee, R. S. Saini, *J. Energ. Mater.*, 2012, **30**, 265-281.

13 a) F. Boneberg, A. Kirchner, T. M. Klapötke, D. G. Piercey, M. J. Poller and J. Stierstorfer, *Chem. Asian J.*, 2013, **8**, 148-159; b) M. Göbel, K. Karaghiosoff, T. M. Klapötke, D. G. Piercey, J. Stierstorfer, *J. Am. Chem. Soc.*, 2010, **132**, 17216-17226; c) T. M. Klapötke, D. G. Piercey, J. Stierstorfer, *Chem. Eur. J.*, 2011, **17**, 13068-13077; d) M. Noyman, S. Zilberg, Y. Haas, *J. Phys. Chem. A*, 2009, **113**, 7376−7382; e) M. N. Glukhovtsev, B. Y. Simkin, V. I. Minkin, *Zh. Organicheskoi Khim.*, 1988, **24**, 2486-2488; f) L. E. Fried, M. R. Manaa, P. F. Pagoria, R. L. Simpson, *Annu. Rev. Mater. Res.*, 2001, **31**,291-321.

14 a) J. Kerth and W. Kuglstatter, *International Annual Conference of ICT*, 2001, **166**, 1-11; b) T. D. Tran, P. F. Pagoria, D. M. Hoffman, J. L. Cutting, R. S. Lee, R. L. Simpson, *International Annual Conference of ICT*, 2002, **45**, 1-16.

15 a) W. P. Norris, R. J. Spear and R. W. Read, *Aust. J. Chem.*, 1983, **36**, 297-309; b) W. P. Norris and A. Chafin, *Heterocycles*, 1984, **22**, 271-274. c) J-W. Kim, J-K. Kim, E. J. Kim, H-S. Kim, and K-K Koo, *Korean J. Chem. Eng.*, 2010, **27**, 666-671.

16 Y-H. Joo and J. M. Shreeve, *Eur. J. Org. Chem.*, **2009**, 3573–3578.

17 C. Bian, M. Zhang, C. Li and Z. Zhou, *J. Mater. Chem. A*, **2014**, DOI: 10.1039/C4TA04107K.

18 a) L. Liang, K. Wang, C. Bian, L. Ling and Z. Zhou, *Chem. Eur. J.*, 2013, **19**, 14902–14910; b) C. Bian, K. Wang, L. Liang, M. Zhang, C. Li, Z. Zhou, *Eur. J. Inorg. Chem.*, **2014**, DOI: 10.1002/ejic.201402692.

19 a) L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, J. A. Pople, *J. Chem. Phys.* **1998**, 109, 7764–7776; b) L. A. Curtiss, C. Redfern, P. V. Rassolov, G. Kedziora, J. A. Pople, *J. Chem. Phys.* **2001**, 114, 9287–9295.

20 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, 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, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian 03, Revision D.02*, Gaussian, Inc., Wallingford CT, **2004**.

21 Y. Guo, G. Tao, Z. Zeng, H. Gao, D. A. Parrish, and J. M. Shreeve, *Chem. Eur. J.*, 2010, **16**, 3753-3762.

22 a) J. Akhavan, *The Chemistry of Explosives*, Royal Society of Chemistry, Cambridge, **2004**; b) A. T. Nielsen, *Nitrocarbons, 1st ed.*; Wiley-VCH: Weinheim, **1995**.

23 a) C. M. Sabate, H. Delalu, E. Jeanneau, *Chem. Asian J.*, 2012, **7**, 1085-1095; b) C. M. Sabate, H. Delalu, E. Jeanneau, *Chem. Asian J.*, 2012, 7, 2080-2089; c) Impact: insensitive >40 J, less sensitive ≥35 J, sensitive ≥4 J, very sensitive ≤3 J; Friction: insensitive >360 N, less sensitive = 360 N, sensitive <360 N to >80 N, very sensitive ≤80 N, extremely sensitive ≤10 N. According to the UN Recommendations on the Transport of Dangerous Goods, + indicates not safe for transport.

24 M. Suceska, *EXPLO5.05 program*, Zagreb, Croatia, **2011**.

25 K. Yamaguchi, A. Ohsawa, T. Itoh and C. Kawabata, *Acta. Cryst.*, 1990, **C46**, 261-263.

26 K. Y. Suponitsky, V. M. Chernyshev, A. G. Mazharova, N. V. Palysaeva and A. B. Sheremetev, *Acta. Cryst.*, 2013, **E69**, 1630-1631.

27 H. Ma, J. Song, F. Zhao, H. Gao, R. Hu, *Chin. J. of Chem.*, 2008, **26**, 1997-2002.

28 CrystalClear: SM Expert 2.0 r2, *An Integrated Program for the Collection and Processing of Area Detector Data*, Rigaku Corporation, **2009**.

29 G. M. Sheldrick, SHELXTL–97, *Structure Determination Software Suite*. Bruker AXS, Madison WI, **2008**.

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