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Journal of Materials Chemistry

Cite this: J. Mater. Chem., 2012, 22, 3201

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PAPER

Super-high-energy materials based on bis(2,2-dinitroethyl)nitramine†

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Received 19th October 2011, Accepted 7th December 2011
DOI: 10.1039/c2jm15310f

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Novel super-highly energetic bis(2,2-dinitroethyl)nitramine-based salts exhibiting excellent physical and detonation properties, such as low solubility in common solvents, moderate thermal stabilities, high densities, high detonation pressures and detonation velocities, were synthesized and fully characterized. The densities of the energetic salts range between 1.77 and 2.02 g cm^{-3} as measured using a gas pycnometer. The detonation pressures and velocities as calculated by the EXPLO5 code are in the range 31.5–46.2 GPa and 8586–10 004 m s^{-1}, which make them competitive super-highly energetic materials.

Introduction

The development of high-energy-density materials (HEDMs) with improved performance has attracted considerable attention.[1–16] However, the demands of high energy and insensitivity are quite often contradictory to each other, making the development of novel HEDMs a difficult and challenging problem.[1] Up to now, there are only two compounds that possess the detonation velocities comparable to or higher than 10 000 m s^{-1}. In 1998, Ovchinnikov *et al.*[2] reported a super-highly energetic explosive—dinitrodiazenofuroxan—which exhibited the considerably high calculated detonation velocity (10 000 m s^{-1}) and density (2.02 g cm^{-3}). However, it is limited to practical application because of its high sensitivity and chemical instability. In 2000, Eaton *et al.*[3,4] reported octanitrocubane (ONC) which was predicted to possess detonation velocity 10 100 m s^{-1} based on the theoretical density of 2.1 g cm^{-3} (experimental density 1.979 g cm^{-3}).[4] However, the synthetic procedures are tedious, also, the reaction agents are expensive, the conditions are too harsh, and the overall yield is quite low.

Generally, the energy of CHNO-type high energy simple substance energetic materials can be improved by increasing the densities, nitrogen contents or nitro group contents. However, the chemical energy storage for this type of compounds is almost close to its maximum, which makes the development of novel highly energetic materials a considerably difficult problem.

Currently, energetic nitrogen-rich salts, which are among the most exciting developments, continue to attract more interest than atomically similar non-ionic analogues, due to lower vapour pressures, higher heats of formation, and enhanced thermal stabilities.[1] Salt formation of the acidic precursor by direct neutralization or metathesis reactions with alkaline nitrogen-rich cations is a very effective method to increase the nitrogen content, the heats of formation and the possibility for hydrogen bonding, as a consequence of the densities and performances.

Recently, many new energetic salts have been developed. Examples include azolate *N*-anions[1,5a–d] such as bis[3-(5-nitroimino-1,2,4-triazolate)]-based salts,[1] *N*,*N*-bis[1*H*-tetrazol-5-yl] amine-based salts,[5a,b] 5-azidotetrazole-based salts,[5f] 3,4,5-trinitropyrazole-based salts,[6a] and nitroaminodiazido[1,3,5]triazine-based salts;[6c] nitramide *N*-anions[7a,b] such as 2-methyl-5-nitraminotetrazole-based salts;[7b] dinitromethanide *C*-anions[8a–f] such as dinitromethanide salts; and oxide *O*-anions such as nitrotetrazolate-2*N*-oxides.[9] Among them, dihydrazinium *N*,*N*-bis(1*H*-tetrazolate-5-yl)-amine (BTA) salt possesses the highest calculated detonation velocity (9926 m s^{-1}) of the reported energetic salts.[5b]

Energetic materials containing trinitroethyl moieties typically have high densities and good detonation performances, moreover, they can be readily synthesized. Bis(2,2,2-trinitroethyl) nitramine (BTNENA) [detonation velocity (D) = 8661 m s^{-1}; density (d) = 1.97 g cm^{-3}] was ever used as the main ingredient in some composite explosives in China. But this type of energetic material is no longer used because of its high sensitivity and chemical instability. Recently, Shreeve, Klapötke and Jalovy[8a–f] reported several *gem*-dinitro group containing energetic salts exhibiting impressive energetic properties, such as carbohydrazidium 5-dinitromethyltetrazolate (D = 9188 m s^{-1}) and hydrazinium 1-amino-1-hydrazino-2,2-dinitroethenide (D = 9482 m s^{-1}), which drove us to design new *gem*-dinitro group containing energetic salts.

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† Electronic supplementary information (ESI) available: *Ab initio* computational data. CCDC reference number 822361. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2jm15310f

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Aiming at finding new super high-energy-density materials with detonation velocity superior to CL-20, bis(2,2-dinitroethyl) nitramine-based salts (BDNENA salts) were designed by replacing the trinitro group with a *gem*-dinitro group. A *C*-deprotonated anion could be obtained by deprotonation of BDNENA to form salts paired with nitrogen–hydrogen-rich cations. Such a design may provide the following advantages in respect of enhancing the detonation velocity: (i) attaching more NO_2 groups to the anion facilitates in improving the oxygen balance (usually negative for energetic salts), directly increases the density (group density of $C(NO_2)_2$ is 1.759 g cm^{-3}, group density of N–NO_2 is 1.745 g cm^{-3}),[17,18,23] in particular, produces more interaction sites for hydrogen bonding, therefore results in higher density. (ii) Selecting appropriate nitrogen–hydrogen-rich cations will provide more opportunities for the formation of H_2O prior to CO_2, hence more positive heats of formation.

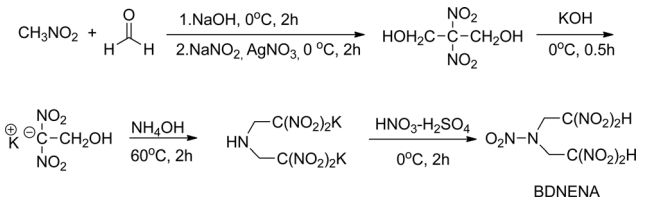
Herein, we report the synthesis and characterization of novel highly energetic BDNENA-based salts exhibiting excellent physical and detonation properties, which were synthesized by a simple and straightforward approach. The compounds prepared were fully characterized by ^{1}H and solid-state ^{13}C NMR (nuclear magnetic resonance) spectroscopy and/or with solid-state ^{15}N NMR spectroscopy, IR spectroscopy, elemental analysis and differential scanning calorimetry (DSC). Computational calculations predicting energetic performances demonstrated that modification of explosives containing trinitroethyl moieties by replacing the trinitro group with a *gem*-dinitro group to form a *gem*-dinitro group containing energetic salts is indeed an effective method of improving energetic performances.

Results and discussion

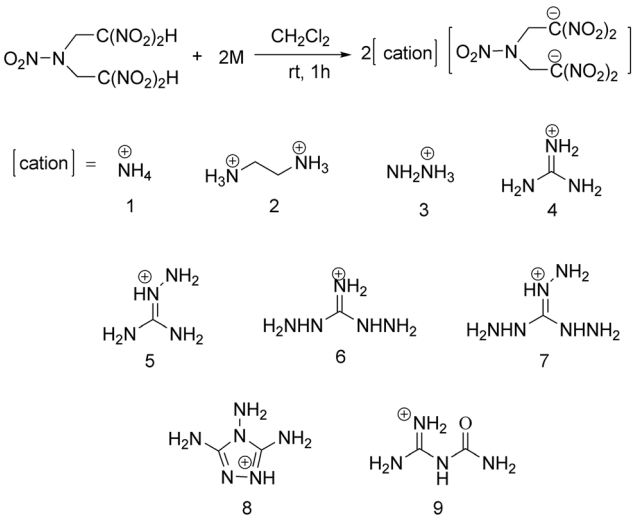
BDNENA was prepared according to literature procedures: oxidative nitration of the products of condensation of nitromethane and formaldehyde with sodium nitrite and silver nitrate gives 2,2-dinitropropane-1,3-diol, followed by reaction with KOH to form potassium 2,2-dinitroethanol, Mannich condensation with ammonia, and finally nitration with fuming nitric acid and conc. sulfuric acid. The X-ray quality single crystal of the precursor BDNENA was obtained by slow evaporation of dichloromethane (DCM) at room temperature (Scheme 1).[19–21]

Reactions of BDNENA with aqueous ammonia, ethylenediamine, hydrazine hydrate, guanidine, aminoguanidine, diaminoguanidine, triaminoguanidine, 3,4,5-triamino-1,2,4-triazole, and *N*-carbamoylguanidine in DCM resulted in the formation of salts **1–9** (Scheme 2).

All of the salts, which were isolated as powder materials in good yields (>90%), are non-hygroscopic and stable in air. Unfortunately, attempts to obtain the X-ray quality crystals of the salts were unsuccessful due to the low solubility in common



Scheme 1 Synthesis of BDNENA.



Scheme 2 Synthesis of BDNENA-based salts.

solvents or slow decomposition for long evaporation times of the dilute solution. The structures of the salts **1–9** were confirmed by ^{1}H NMR, solid-state ^{13}C NMR and solid-state ^{15}N NMR spectroscopy, IR spectroscopy, and elemental analysis. Because of decomposition in DMSO, and low solubility in $CHCl_3$, CH_3OH, CH_3CN, THF and acetone, ^{1}H NMR spectra were recorded by using D_2O as a locking solvent. Solid state ^{13}C and ^{15}N NMR spectra were used as effective techniques to determine the structure of the BDNENA salts.

In the ^{1}H NMR spectra, the proton signals of the anion were observed and easily assigned because only one signal occurred at $\delta \approx 5.3$ ppm; it was shifted downfield compared to the parent molecule ($\delta \approx 4.8$ ppm). The active proton signals of the cations were not observed because D_2O solvent was used.

In the ^{13}C NMR spectra, two signals ($\delta \approx 50$ and 133 ppm) are assigned to the anion, the other signals are associated with the cations, and the $C(NO_2)_2$ peak (133 ppm) shifted downfield compared to the parent molecule (118 ppm). These shifts suggested anionic properties of BDNENA.

In the ^{15}N NMR spectra of salts **4** and **7**, signals $\delta \approx 178$, 346 and 356 ppm are assigned to the anion and signals $\delta \approx 73$ and 115 ppm are associated with the amino group of the cations. For salts **1b** and **7b**, signals at $\delta \approx 180$, 352 and 357 ppm are assigned to the anion, signals at $\delta \approx 22$, 71, 115 ppm are associated with the amino group of cations (Fig. 1).

In the IR spectra, several main absorption bands at approximately 3020, 1610, 1490, 1460, 1360, 1334, 1280 and 1240 cm^{-1} are attributed to the C–H, N–NO_2 and C–NO_2 bonds of the anion. The intense absorption bands in the range of 3100–3500 cm^{-1} are assigned to the N–H bonds of the nitrogen-rich cations.

Properties of BDNENA salts

The thermal stabilities of the BDNENA salts were determined by differential scanning calorimetric (DSC) measurements (Table 1). All the salts decomposed without melting. Among the BDNENA salts the decomposition temperatures fall in the range from 94.2 (**1**) to 141.3 °C (**4**), which are higher than the neutral precursor BDNENA ($T_d = 103.5$ °C) and BTNENA ($T_d = 94.5$ °C)

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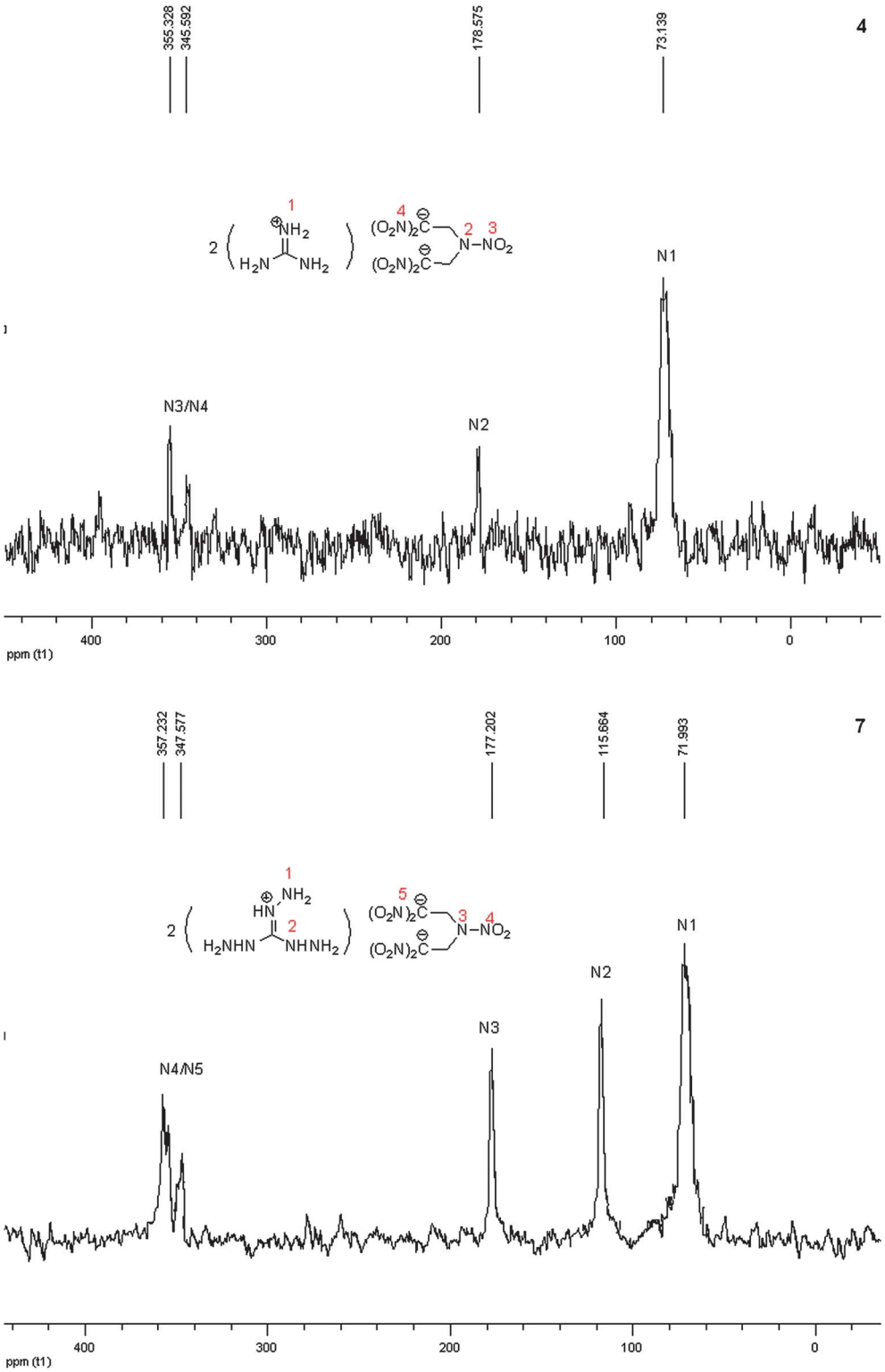


Fig. 1 ^{15}N NMR spectra of salts **4** (top) and **7** (bottom).

except for salt **1**. Explosives containing trinitroethyl moieties typically possess poor thermal stabilities. Interestingly, changing the trinitro-group to a dinitro-group and salt formation led to an increase in the thermal stability. Decomposition of explosives may be caused by the reactions in or between molecules at specific temperature. The decomposition of energetic salts composed of cations and anions is possibly related to the nucleophilic reactions of anions or electrophilic reactions of cations. As observed in Table 1, the salts paired with conjugated-ring-based cations which can delocalize the positive charge on

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Table 1 Properties of energetic salts **1–9**

Salt	T_m[a]/°C	T_d[b]/°C	d_{mean}[c]/g cm^{-3}	OB[d] (%)	H_{50}[e]/cm, kg	$\Delta H_{f\ cation}$[f]/ kJ mol^{-1}	$\Delta H_{f\ L}$[g]/ kJ mol^{-1}	$\Delta H_{f\ salt}$[h]/ kJ mol^{-1}	$\Delta U_{f\ salt}$[i]/ kJ kg^{-1}	P[j]/GPa	D[k]/m s^{-1}
1	Dec	94.2	1.78	−19.3	—	624.4	1289.5	−10.75	79.6	36.4	8982
2	Dec	131.8	1.82	−40.2	49.0, 2	1630.5	1914.3	−257.85	−609.1	33.6	8751
3	Dec	117.4	1.79	−22.1	20.9, 2	770.0	1250.5	315.48	987.7	39.0	9305
4	Dec	141.3	2.02	−38.4	30.9, 5	575.9	1237.1	59.40	209.5	42.8	9587
5	Dec	118.9	1.77	−39.4	—	660.3	1149.6	196.95	558.2	33.4	8897
6	Dec	120.5	1.88	−40.3	35.0, 5	769.0	1145.1	418.83	533.3	37.8	9314
7	Dec	135.2	1.99	−41.1	40.9, 5	871.5	1146.0	622.93	1352.7	46.2	10 004
8	Dec	122.0	1.79	−45.6	40.7, 5	877.55	1083.3	697.70	1433.9	33.7	8898
9	Dec	137.3	1.84	−41.4	23.9, 5	350.6	1114.9	−387.80	−663.4	31.5	8568
BTNENA	Dec	94.5	1.97	+16.5	44%[l]	—	—	−13.97	47.0	35.5	8661
RDX	Dec	230.0	1.82	−21.6	26.0, 5[m]	—	—	92.60[m]	417.0	34.8	8748
HMX	Dec	287.0	1.91	−21.6	32.0, 2.5[m]	—	—	104.80[m]	357.0	39.2	9059
CL-20	Dec	210.0	1.98 (β)	−11.0	18.6, 5[m]	—	—	431.00 (β)[m]	414.5	41.4	9319
			2.03 (ε)					377.40 (ε)[m]	468.2	44.6	9406

[a] Melting point. [b] Thermal degradation temperature. [c] Measured density. [d] Oxygen balance. [e] Impact sensitivity. [f] Calculated molar heat of formation of the cation. [g] Calculated molar lattice energy. [h] Calculated heat of formation for the salt. [i] Energy of formation. [j] Calculated detonation pressure (Explo 5.05). [k] Calculated detonation velocity (Explo 5.05). [l] Probability of explosio n (firing rate). [m] Ref. 1 and 29.

the cations typically possess better thermal stabilities (salts **4**, **7** and **9**). It is probable that a delocalized positive charge favors lowering the electrophilicity of the cation, consequently, resulting in higher thermal stability.

Density is one of the most important physical properties of energetic compounds. According to the Kamlet–Jacobs equations,[22] density (d) affects detonation performance. Detonation pressure (P) is dependent on the square of the density, and the detonation velocity (D) is proportional to the density. Densities for all the salts were measured with a gas pycnometer (25 °C). As shown in Table 1, the densities of BDNENA salts are in the range of 1.77 (**5**)–2.02 g cm^{-3} (**4**). Particularly, the densities of salts **2**, **4**, **6**, **7** and **9** fall in the range for new high-performance energetic materials (1.8–2.0 g cm^{-3}).[1] To the best of our knowledge, the density of the guanidinium BDNENA-based salt **4** (2.02 g cm^{-3}) is the highest of the reported energetic salts. These relatively high densities are presumably caused by the high symmetry and value of density contribution from the *gem*-dinitro group (1.759 g cm^{-3})[23] of the anion and the extensive intra- and intermolecular reticular structure through hydrogen bonds present in these salts.

Oxygen balance (OB) is an expression that is used to indicate the degree to which an explosive can be oxidized. The sensitivity, strength, and brisance of an explosive are all somewhat dependent upon oxygen balance and tend to approach their maximum values as the oxygen balance approaches zero. The oxygen balances of the BDNENA salts were calculated to fall between −45.6 (**8**) and −19.3% (**1**). They are all better than TNT (−74.0%). Salts **1** and **3** possess OBs similar to RDX and HMX.

Impact sensitivities of the synthesized salts were characterized by H_{50} for BDNENA salts and measured using Fall Hammer on an HGZ-19Z0991 apparatus (2.0 and/or 5.0 kg drop hammer; 50.0 mg sample). As shown in Table 1, the H_{50} values range from 20.9 (**3**) to 49.0 cm (**2**), most samples are less sensitive than HMX (32 cm, 2.5 kg);[29] all samples are less sensitive than CL-20 (18.6 cm, 5 kg).[29]

The heats of formation are other important parameters to be considered in the design of energetic salts. Recently, significant progress has been made in the theoretical prediction of thermodynamic properties of energetic salts.[24] Heats of formation can be calculated for the salts with good accuracy (including the heats of formation of the cations and anions and the lattice energy of the salts).[22d] The calculated heats of formation of the BDNENA anion were calculated by using the Gaussian 03 (Revision D.01)[25] suite of programs based on isodesmic reactions (Scheme 4) to be 26.0 kJ mol^{-1}. The values for the cations are available in the literature.[5a,b,6a,26,27] As shown in Table 1, most of the salts exhibit positive heats of formation. As shown in Table 1, the heats of formation of the salts are calculated using Born–Haber energy cycles (Scheme 3). The values of BDNENA salts fall in the range from −387.8 (**9**) to 697.7 kJ mol^{-1} (**8**).

The detonation pressures and velocities of the new highly energetic salts, RDX, HMX and CL-20, were calculated with the program package EXPLO5 using the version 5.05.[28] As shown in Table 1, the calculated detonation pressures lie in the range between 31.5 (**9**) and 46.2 Gpa (**7**), and the calculated detonation velocities fall in the range between 8568 (**9**) and 10 004 m s^{-1} (**7**). Salts **1**, **5** and **8** are comparable to RDX (8748 m s^{-1}, 34.8 GPa) and BTNENA (8661 m s^{-1}, 35.5 GPa), salts **3** and **6** are comparable or superior to HMX (9059 m s^{-1}, 39.2 GPa), salts **4** and **7** are comparable or even superior to CL-20 (9406 m s^{-1}, 44.6 GPa). To the best of our knowledge, salt **7** exhibits the highest detonation velocity (10 004 m s^{-1}) of the reported energetic salts,[5b] which makes it a competitive super-highly energetic material. According to the Kamlet–Jacobs equations,[22] density and heat of formation are two key factors affecting detonation performance. It appears that the differences in detonation properties for salts **4** and **7** are primarily derived from their different heats of formation but possessing approximately the same densities.

X-Ray crystallography

An X-ray quality crystal of BDNENA was obtained by slow evaporation of DCM at room temperature. The structures are shown in Fig. 2, and crystallographic data are summarized in

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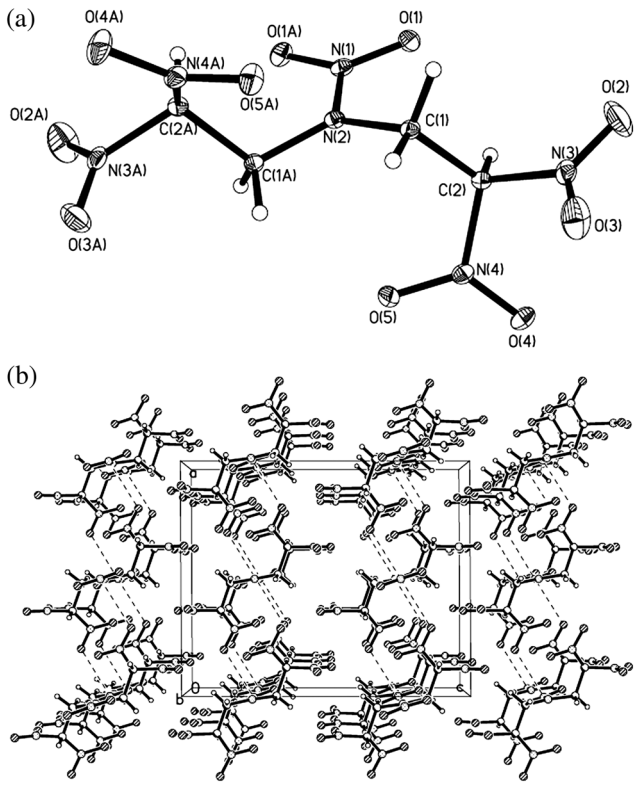


Fig. 2 (a) Thermal ellipsoid plot (30%) and labeling scheme for BDNENA. Hydrogen atoms are included but are unlabelled for clarity. (b) Ball and stick packing diagram of BDNENA viewed down the *b* axis. Dashed lines indicate strong hydrogen bonding.

Table 2. BDNENA crystallizes in monoclinic *C*2/*c* with 4 molecules in the unit cell, and with a calculated density of 1.801 g cm^{-3}. Bond lengths: [O1–N1 1.2295(18); O2–N3 1.207(2); O3–N3 1.207(2); O4–N4 1.216(2); O5–N4 1.221(2); N1–O1 1.2294(18); N1–N2 1.363(3); N2–C1 1.450(2); N2–C1 1.450(2); N3–C2 1.506 (2); N4–C2 1.510(2); C1–C2 1.525(3); C1–H1A 0.9900; C1–H1B 0.9900; C2–H2 1.0000]. Symmetry codes: (i) x, y, z; (ii) $-x, y, -z + 1/2$; (iii) $x + 1/2, y + 1/2, z$; (iv) $-x + 1/2, y + 1/2, -z + 1/2$; (v) $-x, -y, -z$; (vi) $x, -y, z - 1/2$; (vii) $-x + 1/2, -y + 1/2, -z$; (viii) $x + 1/2, -y + 1/2, z - 1/2$.

Theoretical study

Calculations were carried out by using the Gaussian 03 (Revision E.01) suite of programs.[25] The geometric optimization of the structures and frequency analyses were carried out by using the B3LYP functional with the 6-31+G** basis set,[30] and single-point energies were calculated at the MP2(full)/6-311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.

Based on the Born–Haber energy cycle (Scheme 3), the heat of formation of a salt can be simplified according to eqn (1), where ΔH_L is the lattice energy of the salt.

$$\Delta H_f^\circ(\text{ionic salt, 298 K}) = \Delta H_f^\circ(\text{cation, 298 K}) + \Delta H_f^\circ(\text{anion, 298 K}) - \Delta H_L \quad (1)$$

Table 2 Crystallographic data for BDNENA

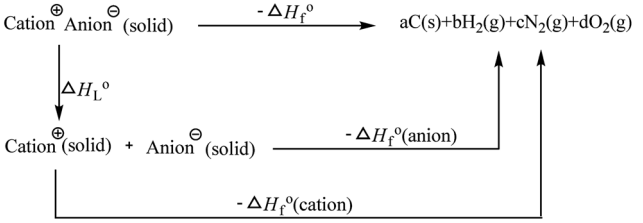
BDNENA	
Formula	$C_4H_6N_6O_{10}$
CCDC number	822361
M_r	298.15
Crystal size/mm^{-3}	0.24 × 0.20 × 0.12
Crystal color and habit	Colorless prism
Crystal system	Monoclinic
Space group	*C*2/*c*
a/Å	12.363(13)
b/Å	5.876(5)
c/Å	15.136(16)
Λ (M_o Kα)/Å	0.71073
α/°	90
β/°	90.31(8)
γ/°	90
V/Å^3	1099.6(19)
Z	4
T/K	113(2)
ρ/Mg m^{-3}	1.801
μ/mm^{-1}	0.018
F_{000}	608
θ/°	2.7 to 27.9
Index ranges	$-16 \le h \le 16$
	$-7 \le k \le 7$
	$-19 \le l \le 19$
Reflections collected	5096
Independent reflections (R_{int})	1293(0.0928)
Data/restraints/parameters	1293/0/92
GOF on F2	1.08
R_1 ($I > 2\sigma(I)$)[a]	0.0507
ωR_2 ($I > 2\sigma(I)$)[b]	0.0995
*R*1 (all data)	0.0622
w*R*2 (all data)	0.0967
Largest diff. peak and hole/e Å^{-3}	0.36 and −0.35

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $\omega R_2 = [\sum\omega(F_o^2 - F_c^2)^2/\sum\omega(F_o^2)^2]^{1/2}$.

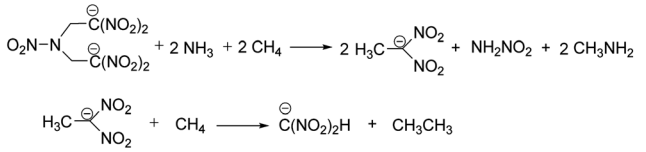
The ΔH_L value could be predicted by the formula suggested by Jenkins *et al.* (eqn (2)),[31] where U_{POT} is the lattice potential energy and n_M and n_X depend on the nature of the ions $M_p^+$and X_q^-, respectively, and are equal to three for monoatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions.

$$\Delta H_L = U_{POT} + [p((n_M/2) - 2) + q((n_X/2) - 2)]RT \quad (2)$$

The equation for the lattice potential energy, U_{POT}, takes the form of eqn (3), where ρ_m is the density (g cm^{-3}), M_m is the chemical formula mass of the ionic material (g), and the coefficients γ (kJ^{-1} mol^{-1} cm) and δ (kJ^{-1} mol^{-1}) are assigned literature values.[31]



Scheme 3 Born–Haber cycle for the formation of energetic salt.



Scheme 4 Isodesmic reactions for calculations of heats of formation.

$$U_{POT}\ (kJ^{-1}\ mol^{-1}) = \gamma(\rho_m/M_m)^{1/3} + \delta \qquad (3)$$

The remaining task was the determination of the heats of formation of the cations and anions, which were computed by using the method of isodesmic reactions (Scheme 4). The enthalpy of an isodesmic reaction ($\Delta H_f^\circ{}_{298}$) is obtained by combining the MP2(full)/6-311++G** energy difference for the reaction and the scaled zero-point energies (B3LYP/6-31+G**). The heats of formation of the cations and anions being investigated can then be extracted readily.

Detonation pressure (P) and detonation velocity (D) were calculated with the program package EXPLO5 using the version 5.05, in which several parameters have been modified. The input was made using the sum formula, energy of formation, and the experimental densities measured by a gas pycnometer. The program is based on the chemical equilibrium, steady state model of detonation. It uses the Becker–Kistiakowsky–Wilson's equation of state (BKW EOS) for gaseous detonation products and Cowan–Fickett's equation of state for solid carbon.[29,31–35] The calculation of the equilibrium composition of the detonation products is done by applying the modified White, Johnson, and Dantzig's free energy minimization technique. The program is designed to enable the calculation of detonation parameters at the CJ point. The BKW equation in the following form was used with the BKWN set of parameters ($\alpha = 0.5$, $\beta = 0.096$, $\kappa = 17.56$, $\theta = 4950$) as stated below the equations, X_i being the molar fraction of i^{th} gaseous product, and k_i being the molar covolume of the i^{th} gaseous product:

$$pV/RT = 1 + xe^{\beta x},\ x = (\kappa \sum X_i k_i)/[V(T + \theta)]^{\alpha} \qquad (4)$$

In order to obtain a better understanding of the structure of the salt, the structure optimization and natural bond orbital (NBO) and the molecular orbital analyses of salt **4** were carried out by using Gaussian 03.[25] As shown in Fig. 3, the NBO analysis indicated that the positive charge is delocalized over the guanidinium group in which the positive charges of H (19) (0.450e) and H (16, 17, 19, 20, 22, 23, 37, 38, 40, 41, 43, 44) (0.399e ≈ 0.450e) are significantly higher than those of the other hydrogen atoms H (11, 32) (0.243e) and H (12, 33) (0.254e).

In the anion, O atoms (1, 2, 3, 4, 5, 24, 25, 26, 27, 28) (−0.433e to 0.536e) carry negative charges, the charge distribution implies that the O atoms in the anion can form hydrogen bonds with the hydrogen atoms in the cation. The negative charge of O (3, 5, 26, 28) and the positive charge of H (11, 12, 32, 33), as well as the steric effect, suggest an intramolecular hydrogen bond. High symmetry in the structure and strong hydrogen bonds likely increase the density of the salt.

The highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of salt **4** (Fig. 4) further reveal that the N–NO_2 group of the anion occupies the HOMO,

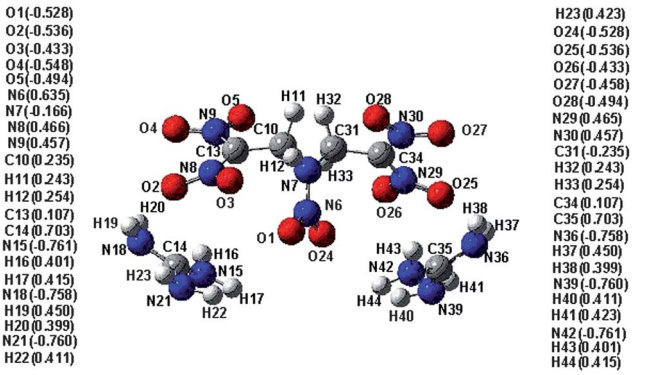


Fig. 3 Optimized structure and charge distribution in salt **4** as found with NBO analysis (B3LYP/6-311+G (d,p)).

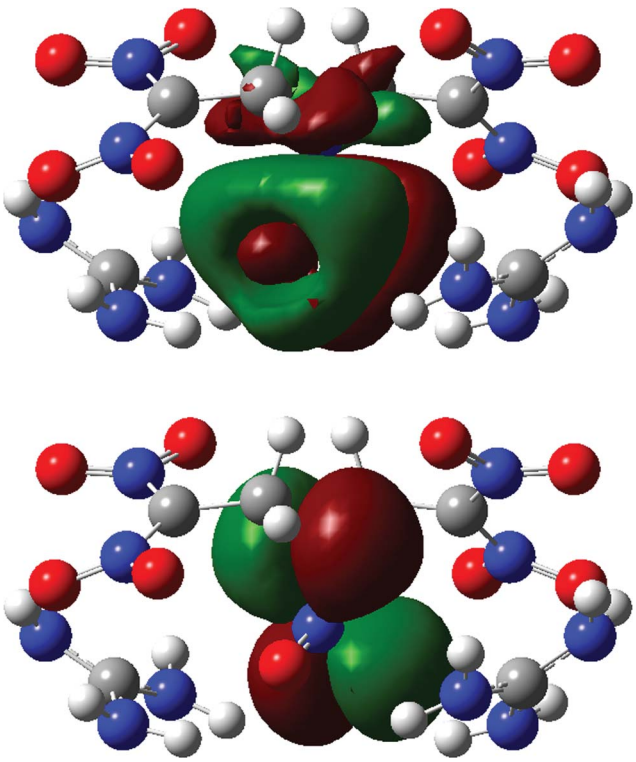


Fig. 4 HOMO (top) and LUMO (bottom) of salt **4**.

and the N7 and O24 atoms of the N–NO_2 group occupy the LUMO. The negative charge is not delocalized over the anion. The non-conjugated charge distribution likely causes the moderate thermal stabilities.

Conclusions

In summary, novel super-high-energy materials of BDNENA-based salts were successfully synthesized and fully characterized. The new salts exhibit excellent physical and detonation properties, such as low solubility in common solvents, moderate thermal stabilities, high densities, positive heats of formation, high detonation pressures and detonation velocities, and lower impact sensitivities than the parent. The comprehensive properties of most salts are better than BTNENA (see Table 1). Salt **4**

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possesses the highest density (2.02 g cm^{-3}) and salt **7** exhibits the unprecedented detonation properties (10 004 m s^{-1}, 46.2 GPa), which are better than those of the reported energetic salts. Specifically, detonation properties of salts **3** and **6** are comparable to HMX (9059 m s^{-1}, 39.2 GPa), salts **4** and **7** are comparable or even superior to CL-20 (9406 m s^{-1}, 44.6 GPa), which place these salts in the competitive super-high-energy performance class. The results also suggest the potential to serve as a series of promising alternatives to some conventional energetic materials such as HMX and CL-20.

Experimental section

Caution! Although none of the compounds described herein have exploded or detonated in the course of this research, these materials should be handled with extreme care using the best safety practices.

General methods

^{1}H, ^{13}C and ^{15}N NMR spectra were recorded on a 500 MHz nuclear magnetic resonance spectrometer operating at 400.18, 100.63 and 50.69 MHz, respectively. Chemical shifts are reported in ppm relative to TMS. The locking solvent was D_2O for ^{1}H NMR spectra. Solid state ^{13}C and ^{15}N NMR spectra were used as effective techniques to determine the structure of the salts. The melting and decomposition points were recorded on a DSC at a scan rate of 10 °C min^{-1}. IR spectra were recorded by using KBr pellets. Densities were measured at room temperature using a Micromeritics Accupyc II 1340 gas pycnometer. Elemental analyses were obtained on an Elementar Vario MICRO CUBE (Germany) elemental analyzer.

X-Ray crystallography

Crystals of bis(2,2-dinitroethyl)nitramine were removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and placed in the low-temperature nitrogen stream. Data for bis(2,2-dinitroethyl)nitramine were collected at 113(2) K using a Rigaku Saturn724 CCD 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 (ref. 36) software. The reflection data were also corrected for Lp factors. The structure was solved by direct methods and refined by least squares method on F2 using the SHELXTL-97 system of programs.[37] Structures were solved in the space group *C*2/*c* for BDNENA by analysis of systematic absences. In this all-light-atom structure the value of the Flack parameter did not allow the direction of the polar axis to be determined and Friedel reflections were then merged for the final refinement. Details of the data collection and refinement are given in Table 2.

Reactants: nitromethane, formaldehyde (37%), aqueous ammonia (28–30%), hydrazine (99%), ethylenediamine, guanidinium hydrochloride (99%), aminoguanidinium hydrochloride (98.5%), diaminoguanidinium hydrochloride (98.5%), and silver nitrate (99.95%, Salt Lake Metals) were used as received.

3,4,5-Triamino-1,2,4-triazole, triaminoguanidinium hydrochloride and *N*-carbamoylguanidinium hydrochloride were synthesized according to the literature.[38–40]

Bis(2,2-dinitroethyl)nitroamine (BDNENA)

Bis(2,2-dinitroethyl)nitroamine was synthesized according to the literature:[19–21] oxidative nitration of the condensation products from nitromethane and formaldehyde with sodium nitrite and silver nitrate; a subsequent reaction with KOH formed potassium 2,2-dinitroethanol, followed with a Mannich condensation with ammonia, and finally nitration with fuming nitric acid and conc. sulfuric acid. White solid. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 6.67 (t, 2H), 4.81 (d, 4H) ppm; ^{13}C NMR (100 MHz, CD_3CN, δ): 118.4, 53.9 ppm; IR (KBr): ν = 3217, 3035, 1487, 1422, 1356, 1322, 1240, 1151, 1111, 1078, 926, 906, 755, 733, 664, 645 cm^{-1}.

General procedure for the synthesis of the salts 1–9

To a solution of BDNENA (1 mmol) in DCM (50 mL), 2 eq. of 25% aqueous ammonia, 99% hydrazine hydrate, guanidine, aminoguanidine, diaminoguanidine, triaminoguanidine, 3,4,5-triamino-1,2,4-triazole, *N*-carbamoylguanidine, or 1 eq. ethylenediamine was added. The mixtures were stirred at room temperature for 1 h and the yellow precipitate was filtered off, washed with DCM, and dried at RT for 2 h.

Diammonium bis(2,2-dinitroethanide)nitroamine salt (1)

Yellow powder (314 mg, 96%); ^{1}H NMR (500 MHz, D_2O, δ): 5.26 (s, 1H) ppm; ^{13}C NMR (100 MHz, solid-state, δ): 132.1, 53.5 ppm; IR (KBr): ν = 3217, 3035, 1487, 1422, 1356, 1322, 1240, 1151, 1111, 1078, 926, 906, 755, 733, 664, 645 cm^{-1}; elemental analysis (%) calcd for $C_4H_{12}N_8O_{10}$: C 14.46, H 3.64, N 33.73; found: C 14.23, H 3.82, N 33.46.

Ethylenediammonium bis(2,2-dinitroethanide)nitroamine salt (2)

Yellow powder (331 mg, 94%); ^{1}H NMR (500 MHz, DMSO-d_6, δ): 7.576 (s, br, 3H), 5.242 (s, 2H), 2.978 (s, 2H) ppm; ^{13}C NMR (100 MHz, solid-state, δ): 132.1, 52.9, 37.4 ppm; IR (KBr): ν = 3145, 3024, 1610, 1495, 1462, 1367, 1334, 1288, 1247, 1203, 1160, 1129, 1069, 924, 906,779, 740, 674, 642 cm^{-1}; elemental analysis (%) calcd for $C_6H_{14}N_8O_{10}$: C 20.12, H 3.94, N 31.28; found: C 20.30, H 4.04, N 31.01.

Dihydrazinium bis(2,2-dinitroethanide)nitroamine salt (3)

Yellow powder (350 mg, 99%); ^{1}H NMR (500 MHz, D_2O, δ): 5.266 (s, 1H) ppm; ^{13}C NMR (100 MHz, solid-state, δ): 132.1, 53.5 ppm; IR (KBr): ν = 3525, 3332, 3112, 1602, 1475, 1422, 1360, 1310, 1246, 1175, 1085, 945, 906, 736, 644 cm^{-1}; elemental analysis (%) calcd for $C_4H_{14}N_{10}O_{10}$: C 13.26, H 3.90, N 38.67; found: C 12.96, H 4.12, N 38.89.

Bis(guanidinium) bis(2,2-dinitroethanide)nitroamine salt (4)

Pale yellow powder (403 mg, 98%); ^{1}H NMR (500 MHz, D_2O, δ): 5.284 (s, 1H) ppm; ^{13}C NMR (100 MHz, solid-state, δ): 159.1, 133.8, 53.3 ppm; ^{15}N NMR (50 MHz, solid-state, δ): 355.33, 345.59, 178.58, 73.14 ppm; IR (KBr): ν = 3462, 3414, 3375, 3197,

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3011, 1674, 1643, 1563, 1491,1462, 1347, 1304, 1236, 1161, 1092, 908, 738, 680, 646, 583 cm^{-1}; elemental analysis (%) calcd for $C_6H_{16}N_{12}O_{10}$: C 17.15, H 4.80, N 39.99; found: C 17.15, H 4.67, N 39.55.

Bis(aminoguanidinium) bis(2,2-dinitroethanide)nitroamine salt (5)

Orange powder (410 mg, 92%); ^1H NMR (500 MHz, D_2O, δ): 5.296 (s, 1H) ppm; ^{13}C NMR (100 MHz, solid-state, δ): 158.8, 135.3, 52.9 ppm; IR (KBr): ν = 3434, 3340, 3290, 1682, 1568, 1476, 1291, 1241, 1163, 1007, 642, 532 cm^{-1}; elemental analysis (%) calcd for $C_6H_{18}N_{14}O_{10}$: C 16.15; H 4.07; N 43.94; found: C 16.00; H 3.97; N 43.24.

Bis(diaminoguanidinium) bis(2,2-dinitroethanide)nitroamine salt (6)

Yellow powder (409 mg, 85%); ^1H NMR (500 MHz, D_2O, δ): 5.304 (s, 1H) ppm; ^{13}C NMR (100 MHz, solid-state, δ): 159.9, 135.3, 52.9 ppm; IR (KBr): ν = 3434, 3340, 3290, 1682, 1568, 1476, 1291, 1241, 1163, 1007, 642, 532 cm^{-1}; elemental analysis (%) calcd for $C_6H_{20}N_{16}O_{10}$: C 15.13, H 4.23, N 47.05; found: C 15.33, H 4.13, N 46.90.

Bis(triaminoguanidinium) bis(2,2-dinitroethanide)nitroamine salt (7)

Yellow powder (485 mg, 96%); ^1H NMR (500 MHz, D_2O, δ): 5.428 (s, 1H) ppm; ^{13}C NMR (100 MHz, solid-state, δ): 159.9, 135.3, 52.9 ppm; ^{15}N NMR (50 MHz, solid-state, δ): 357.23, 347.58, 177.20, 115.66, 71.99 ppm; IR (KBr): ν = 3434, 3340, 3290, 1682, 1568, 1476, 1291, 1241, 1163, 1007, 642, 532 cm^{-1}; elemental analysis (%) calcd for $C_6H_{22}N_{18}O_{10}$: C 14.23; H 4.38; N 49.79; found: C 13.90; H 4.17; N 49.24.

Bis(3,4,5-triamino-1,2,4-triazolium) bis(2,2-dinitroethanide) nitroamine salt (8)

Yellow powder (253 mg, 93%); ^1H NMR (500 MHz, D_2O, δ): 5.219 (s, 1H) ppm; ^{13}C NMR (100 MHz, solid-state, δ): 152.0, 133.9, 50.9 ppm; IR (KBr): ν = 3386, 3322, 3264, 3101, 1635, 1591, 1554, 1421, 1295, 1222, 1147, 1091, 1004, 954, 819, 715, 670, 619 cm^{-1}; elemental analysis (%) calcd for $C_8H_{18}N_{18}O_{10}$: C 18.26, H 3.45, N 47.90; found: C 18.36, H 3.56, N 47.56.

Bis(*N*-carbamoylguanidinium) bis(2,2-dinitroethanide) nitroamine salt (9)

Yellow powder (519 mg, 95%); ^1H NMR (500 MHz, D_2O, δ): 5.335 (s, 1H) ppm; ^{13}C NMR (100 MHz, solid-state, δ): 156.2, 155.5, 131.8, 52.7 ppm; IR (KBr): ν = 3348, 3192, 3028, 1730, 1698, 1634, 1593, 1487, 1354, 1309, 1256, 1167, 1113, 899, 851, 775, 761, 740, 677, 642 cm^{-1}; elemental analysis (%) calcd for $C_8H_{18}N_{14}O_{12}$: C 19.13, H 3.61, N 39.04; found: C 19.10, H 3.69, N 38.83.

Acknowledgements

The authors gratefully acknowledge the support of Specialized Research Fund for the Doctor Program of Higher Education (no. 20091101110033), National Defense 973 Program (no. 3100021210901) and the National Natural Science Fund Project (no. 21172020).

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