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Nitroguanidine-Fused Bicyclic Guanidinium Salts: A Family of High-Density Energetic Materials

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Abstract: A series of nitroguanidine-fused bicyclic guanidinium energetic salts paired with inorganic energetic anions, mono- and di-tetrazolate anions were synthesized through simple metathesis reactions of 2-iminium-5-nitriminooctahydroimidazo[4,5-*d*]imidazole chloride and sulfate with the corresponding silver and barium salts, respectively, in aqueous solution. Key physical properties, such as melting point, thermal stability, and density were measured. The relationship between the structures of the salts and these properties was determined. The salts exhibit thermal stability and density ($>1.60\,g\,cm^{-3}$) that are comparable to currently used explosives The structures of the nitrate salt **1** and the dinitrocyanomethanide salt **4** were confirmed by single-crystal X-ray analysis. Densities, heats of formation, detonation pressures and velocities, and specific impulses were calculated. All of the salts possess positive calculated heats of formation and most of them exhibit promising energetic performance that is comparable with those of 1,3,5-trinitrobenzene (TNT), 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), and cyclotrimethylenetrinitramine (RDX). The effect of the fused bicycle 2-iminium-5-nitriminooctahydroimidazo[4,5-d]imidazole on these physicochemical properties was examined and discussed.

Keywords: ab initio calculations · energetic salts · explosives · heats of formation · thermodynamics

Introduction

During the past decades, considerable effort has been focused on the development of nitrogen-rich high-energy density materials (HEDM) with high performance and/or decreased sensitivity as well as environmental compatibility.[1–6] Higher energetic performance has always been a primary requirement for the research and development of explosives and propellants,[2–4] however, these types of materials often exhibit poorer thermal stability and higher sensitivity to thermal shock, friction, and electrostatic discharge, and vice versa. In principle, combination of these positive properties is desirable.

The performance of an energetic compound is a function of its density, oxygen balance, and heat of formation.[5] Density is one of the most important factors because the detonation pressure is dependent on the square of the density and the detonation velocity is proportional to the density according to an empirical equation proposed by Kamlet.[6] It was well known that the presence of strong hydrogen bonds has a special effect on the physical and chemical properties of energetic compounds. Such hydrogen-bonding interactions (especially between the NH_2 and NO_2 groups) not only help to stabilize the compounds substantially, decrease their toxicities and solubility in common solvents,[4e] but also can markedly increase the density of energetic compounds.[7] A typical example is 1,3,5-triamino-2,4,6-trinitrobenzene (TATB): six bifurcated hydrogen bonds in this molecule result in high density ($1.937\,g\,cm^{-3}$), high thermal stability (350 °C), and low solubility in all solvents except concentrated H_2SO_4. In sharp comparison, the density and the degradation temperature of 1,3,5-trinitrobenzene are $1.76\,g\,cm^{-3}$ and 315 °C, respectively. Although strong hydrogen bonds decrease the heat of formation slightly, an increase in density tends to outweigh this concomitant adverse effect, as the performance of an energetic compound is most heavily dependent on density.[3c]

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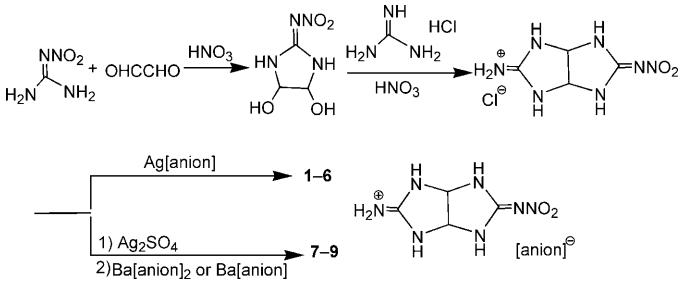
One of the most recent and exciting developments in the field of HEDM are heterocyclic energetic salts with high nitrogen content.[4,7–16] Salt-based energetic materials often possess advantages over nonionic molecules, as these salts tend to exhibit lower vapor pressures and higher thermal stability than their atomically similar nonionic analogues. In addition, their properties are readily improved and optimized through judicious combination of different anions and cations, as well as a result of independent modification of cationic and anionic components. The approach significantly increases the number of energetic compounds available. Various energetic cations or anions derived from imidazole,[8–10] triazole,[10–12] and tetrazole[4,7,13–16] in which each cation or anion pairs with a family of its counterparts through metathetical or protonation reactions have been well-documented.

In our previous studies on nitrogen-containing heterocyclic energetic salts, we have synthesized a series of guanidinium-based energetic salts paired with heterocyclic anions.[4a,9a,15] The strong hydrogen bonds between cations and anions result in remarkable stability and considerable insensitivity to physical stimuli as well as good explosive performances. With the continuation of our program to search for more dense, less sensitive, eco-friendly explosives and propellants, we have found that the fused bicyclic compounds usually are more rigid than their monocyclic analogues,[9c,15b] which should result in higher density and more superior performance. However, the fused bicyclic energetic salts were seldom studied to an extent comparable with monocyclic salts.[9c,15b,16] Herein, we report the syntheses and characterization of a series of nitroguanidine-fused bicyclic guanidinium energetic salts. The choice of inorganic as well as nitrogen-rich heterocyclic mono- and dianions was made in order to establish the broad relative potential to comprehensively evaluate their performance.

Results and Discussion

Some of the primary requirements of an energetic compound for practical application are that its synthesis should be simple and safe, and that the starting materials should be inexpensive. As shown in Scheme 1, the 2-iminium-5-nitriminooctahydroimidazo[4,5-*d*]imidazole chloride (INI-Cl) was easily synthesized by the condensation reaction of commercially available nitroguanidine and glyoxal followed by the reaction with guanidinium chloride.[17] It is well known that the metathesis reaction of silver and barium salts with halides and sulfates, respectively, is one of the most straightforward and widely-used methods for the synthesis of energetic salts.[9–16] The impetus of the reactions is the formation of silver halide and barium sulfate, and because each has a very low solubility in water, the products can be easily separated by simple filtration. Thus, the straightforward metathesis reactions of INI-Cl with silver salts or INI_2-SO_4, formed in situ by reaction of INI-Cl and Ag_2SO_4, with barium(II) salts in H_2O gave rise to the corresponding energetic salts **1**–**9**.



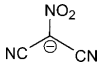
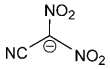
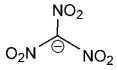
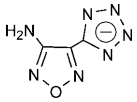
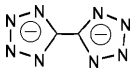
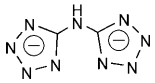
Scheme 1. Synthesis of the energetic salts **1**–**9**. For the definition of the corresponding anions see Table 1 (INI-Cl = 2-iminium-5-nitriminooctahydroimidazo[4,5-*d*]imidazole chloride).

All of the energetic salts are stable in air and may be stored for long periods. The structures of these energetic salts were confirmed by infrared spectroscopy, ^1H and ^{13}C NMR spectra, and elemental analyses. The chemical shifts of the cyanide carbon in the ^{13}C NMR spectra of the nitrodicyanomethanide salt **3** and the dinitrocyanomethanide salt **4** are $\delta = 116.2$ and 114.3 ppm, respectively. The strong absorption bands of cyanide in the IR spectra of the nitrodicyanomethanide and dinitrocyanomethanide salts were observed at $\tilde{\nu} = 2214$ and 2222 cm^{-1}, respectively. All of the values are similar to those of their mono-heterocyclic analogues.[16b]

Phase transition temperatures (midpoints of melting points) and thermal stabilities of **1**–**9** were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. In Table 1, the melting point of salt **6** is $T_m = 117\,^\circ C$ whereas the other salts decomposed before melting. It is not surprising that the nitroform salt **5** has the lowest thermal stability ($T_d = 104\,^\circ C$), which is comparable with other nitroformate salts.[18] The decomposition temperatures of the remaining salts fall in the range from 191 to 282 °C. As expected, the 5,5′-bistetrazolate salt **8** ($T_d = 282\,^\circ C$) is more stable than the imino-bis(5-tetrazolate) salt **9** ($T_d = 198\,^\circ C$) owing to higher aromatic conjugation of anions and lower nitrogen content.

The measured densities of the salts **1**–**9** are in the range of 1.64–1.84 $g\,cm^{-3}$, which is comparable with currently used explosives (1.6–1.8 $g\,cm^{-3}$[7b,15b]). Noteworthy, the density of salts **1** and **2** fall in the range for new high-performance energetic materials (1.8–2.0 $g\,cm^{-3}$[7b,15b]), which is close to that of cyclotrimethylenetrinitramine (RDX) (1.82 $g\,cm^{-3}$[5a]). It should be mentioned that their density is higher than those of analogous mono-heterocyclic salts based on guanidinium derivatives.[9d,13,15,18] The higher density can be most likely ascribed to the fusion of bicycles and the extensive hydrogen-bonding interactions. The effect of non-heterocyclic anions on density of INI salts is in the following order: nitrodicyanomethanide < dinitrocyanomethanide < nitroform < nitrate < dinitramide, because the nitro group usually makes a positive contribution to density. The densities were also calculated according to our tabulated volume parameters.[4e,19] The calculated densities agreed reasonably well with the experimental values (within 5% deviation). As

Table 1. Properties of energetic salts .

Compd	Anion	T_m[a] [°C]	T_d[b] [°C]	d_{calcd}[c] [g cm^{-3}]	d_{expl}[d] [g cm^{-3}]	Oxygen balance[e]	$\Delta_f H_{anion}$[f] [kJ mol^{-1}]	$\Delta_f H_{lat}$[g] [kJ mol^{-1}]	$\Delta_f H_{salt}$[h] [kJ mol^{-1}]	$\Delta_f H_{salt}$[h] [kJ g^{-1}]	P[i] [GPa]	^vD[j] [m s^{-1}]	I_{sp}[k] [s]
1	NO_3^-	decomp	191	1.82[l]	1.81	−45.1	−307.9	493.0	4.4	0.02	30.47	8644	217
2		decomp	193	1.86[l]	1.84	−32.9	−156.2	474.6	174.5	0.60	34.38	8916	240
3		decomp	243	1.64	1.64	−75.6	32.2	459.2	378.3	1.28	21.04	7271	209
4		decomp	195	1.72	1.73	−50.6	−127.7	457.9	219.8	0.70	25.12	7975	218
5		decomp	104	1.79	1.77	−28.6	−287.0	453.4	64.9	0.19	29.94	8409	244
6		117	224	–	1.74 (1.79)[n]	−53.3	9.8	462.2	352.9	1.12	28.31	8619	209
7		decomp	252	1.71[l]	1.73	−75.7	306.7	450.1	661.9	1.96	23.86	8124	212
8		decomp	282	1.69 (1.72)[m]	1.67 (1.70)[n]	−75.5	594.9	1078.4	1127.1	2.21	24.06	8177	217
9		decomp	198	1.67 (1.71)[m]	1.64 (1.68)[n]	−74.9	630.0	1061.5	1179.2	2.25	23.86	8159	218

[a] Melting point. [b] Thermal degradation. [c] Calculated density (ref. [4e,19]). [d] Measured density (gas pycnometer). [e] Oxygen balance (OB) is an index of the deficiency or excess of oxygen in a compound required to convert all C into CO_2 and all H into H_2O. For a compound with the molecular formula of $C_aH_bN_cO_d$, OB [%] = $1600[(d-2a-b/2)/M_W]$. [f] Calculated molar enthalpy of formation of cation. [g] Calculated molar lattice energy. [h] Calculated molar enthalpy of formation of salts. [i] Detonation pressure. [j] Detonation velocity. [k] Specific impulse. [l] Volume of the salts was corrected by −8 Å^3 for strong hydrogen bonds. [m] Calculated density without water molecule. [n] Density was corrected by subtracting the volume of water molecule, $V(H_2O) = 25$ Å^3.

shown in Table 2, the measured densities of **1** and **4** are the same as those obtained from X-ray crystal structures (vide infra).

Oxygen balance (OB) is used to indicate the degree to which a compound can be oxidized.[5] All salts possess negative OB (see Table 1). The OB falls in the range from −28.6 to −75.7, which is comparable with that of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB, OB = −55.8) and 1,3,5-trinitrobenzene (TNT, OB = −74.0). The nitroform salt **5** possesses the least negative oxygen balance (−28.6), slightly lower than that of RDX and cyclotetramethylenetetranitramine (HMX) (−21.6).

Heat of formation is another important parameter in order to evaluate the performance of energetic salts. A nitro substituent usually decreases heat of formation, while a cyano group tends to increase it, thus, the calculated heats of formation of the non-heterocyclic anions are in the following order: nitrodicyanomethanide > dinitrocyanomethanide > nitroform > nitrate (Table 1). The calculated heat of formation of the aminofurazan-functionalized tetrazolate anion in **7** is much higher than that of nitroamino-functionalized tetrazolate anion in **6**, since the furazan group exhibits a much higher heat of formation.[15a] All of the salts possess positive calculated heats of formation (Table 1). With the exception of the nitrate salt **1** and the nitroformate salt **5**, the calculated heats of formation of the other salts are in range 0.60 to 2.25 kJ g^{-1}, which are higher than that of RDX (0.42 kJ g^{-1}) and HMX (0.35 kJ g^{-1}).[15b,20]

The detonation pressure (P), the detonation velocity (^vD), and the specific impulse (I_{sp}) were calculated by using CHEETAH 5.0 (Table 1).[21] The detonation pressures lie in the range 23.86–34.38 GPa, which are higher than that of TNT (19.5 GPa[5a,21]) and are comparable with that of TATB (31.2 GPa[5a,21]). The detonation velocities are found in the range from 7271 to 8916 m s^{-1}, which are higher than that of TNT (6881 m s^{-1}[5a,21]) and are comparable to TATB (8114 m s^{-1}[5a,21]) and RDX (8977 m s^{-1}[5a,21]). The salts have specific impulse values ranging between 209 and 244 s. This promising performance suggests potential application of the fused bicyclic salts as ingredients of explosives and propellants. Especially in the case of the dinitramide salt **2**, the energetic performance is much superior to the traditional explosives TNT and TATB, and slightly lower than that of RDX.

Crystal structures of 1 and 4: Single-crystal X-ray diffraction analysis revealed that compounds **1** and **4** crystallize in the monoclinic space group $P2_1/n$ and $C2/c$, respectively (Table 2). As shown in Figure 1a and Figure 2, their asymmetric unit consists of a crystallographically independent INI cation and an energetic anion. In the INI cations of **1** and **4**, the fused five-membered rings are in a V shape with

Table 2. Crystallographic data for compounds **1** and **4**.

	1	**3**
empirical formula	$C_4H_8N_8O_5$	$C_6H_8N_{10}O_6$
M_w	248.18	316.22
crystal size [mm]	0.50×0.20×0.20	0.20×0.20×0.20
crystal system	monoclinic	monoclinic
space group	*P*2(1)/*n*	*C*2/*c*
a [Å]	11.098(6)	25.041(11)
b [Å]	8.328(4)	8.330(3)
c [Å]	11.103(6)	13.653(6)
β [°]	117.303(7)	121.360(7)
V [Å^3]	911.9(8)	2432.0(18)
Z	4	8
T [K]	173(2)	173(2)
ρ_{calcd} [g cm^{-3}]	1.808	1.727
μ [mm^{-1}]	0.162	0.153
λ ($Mo_{K\alpha}$) [Å]	0.71073	0.71073
F(000)	512	1296
reflns collected	6846	9239
independent reflns	2079	2748
R_{int}	0.0227	0.0334
parameters	186	232
S on F^2	1.083	1.095
R_1 [$I>2\sigma(I)$][a]	0.0365	0.0489
$_wR_2$ (all data)[b]	0.0990	0.1410
Largest diff. peak and hole [e Å^{-3}]	0.213 and −0.180	0.251 and −0.274

[a] $R=\Sigma||F_0|-|F_c||/\Sigma|F_0|$. [b] $_wR=[\Sigma w(F_0^2-F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$.

the twisting angle between them at 59.7 and 58.4°, respectively. The atoms in the ring [C(1), C(2), C(4), N(2), and N(5)] with the exocyclic iminium [N(1)] are approximately coplanar with the mean deviation from the basic plane being 0.048 and 0.0208 Å, respectively. The exocyclic iminium nitrogen atom [N(1)] is out of the plane (0.1538 and 0.1056 Å, respectively). The mean deviation of the atoms in the other five-membered ring [C(2), C(3), C(4), N(3), and N(4)] from their basic plane is 0.042 and 0.0286 Å, respectively. The exocyclic nitrimino group is twisted out of the plane of the ring with the dihedral angle between their planes being 10.1 and 15.1°, respectively. The mean deviation of the nitrimino atoms from their respective plane [N(6), N(7), O(1) and O(2)] is 0.0028 and 0.0033 Å, respectively. The bond lengths and bond angles of the INI cation in **1** and **4** are similar. The nitrate and dinitrocyanomethanide anions are also planar with mean deviations from the respective plane being 0.0002 and 0.0297 Å, respectively. These slight differences may be ascribed to different packing effects and the extensive hydrogen-bonding interaction in the crystals of **1** and **4**. Strong intramolecular interactions were formed in the INI cation [N(4)−H(3)···O(1) 2.5952(17) Å in **1**; N(3)−H(6)···O(2) 2.611(2) Å in **4**]. As shown in Figure 1b, the discrete INI and NO_3 in **1** are linked into a 2D network by extensive hydrogen-bonding interactions between the INI cations [N(4)−H(3)···O(2)^{i} 2.996(2), N(5)−H(8)···O(1)^{i} 2.953(2) Å; symmetry code: i = $-x+1/2$, $y-1/2$, $-z+1/2$] as well as between INI and NO_3 [N(3)−H(9)···O(5)^{ii} 2.918(2), N(2)−H(5)···O(4)^{ii} 2.939(2), N(1)−H(6)···O(3)^{iii} 2.913(2) Å; symmetry codes: ii = $-x+3/2$, $y-1/2$, $-z+1/2$; iii = $x+1/2$, $-y-1/2$, $z+1/2$]. There is no

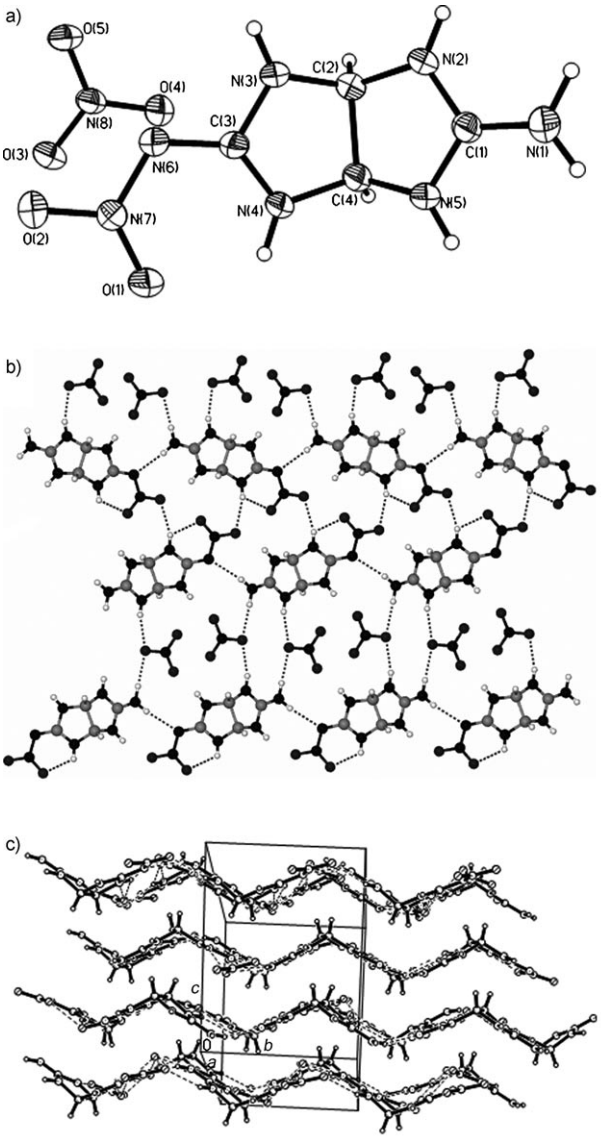


Figure 1. a) Molecular structure of **1** with thermal ellipsoids at 50% probability. b) View of the 2D layer formed by hydrogen-bonding interactions. c) Packing diagram of **1** along the *a* axis.

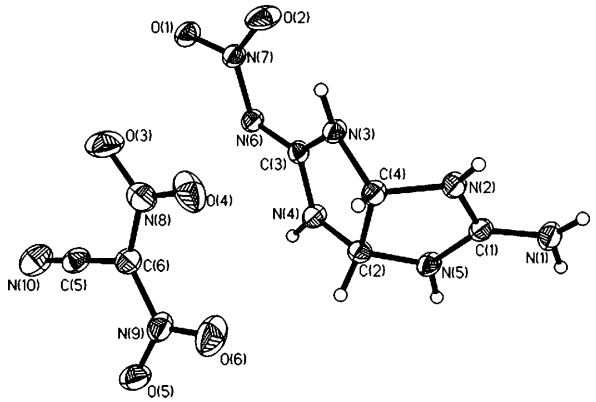


Figure 2. Molecular structure of **4** with thermal ellipsoids at 50% probability.

significant interaction among the adjacent layers (Figure 1c). In **4**, the extensive hydrogen bonds between the INI cations [N(3)–H(6)···O(1)^{i} 3.005(2) Å; symmetry code: i = $-x+1/2$, $y+1/2$, $-z+1/2$] as well as INI and dinitrocyanomethanide [N(4)–H(5)···O(5)^{ii} 2.843(2), N(1)–H(2)···O(3)^{iii} 2.973(2), N(5)–H(3)···O(4)^{iii} 3.008(2) Å; symmetry codes: ii = $-x$, y, $-z+1/2$; iii = x, $-y+1$, $z+1/2$] link the discrete INI and dinitrocyanomethanide into a 3D network (Figure S1 in the Supporting Information).

In order to obtain a better understanding on the fused bicyclic cation INI, the natural bond orbital (NBO) and the molecular orbital analyses based on the optimized structure of the isolated cation (B3LYP/6-31G(d,p)) were carried out by using Gaussian 03.[22] As shown in Figure 3, the NBO

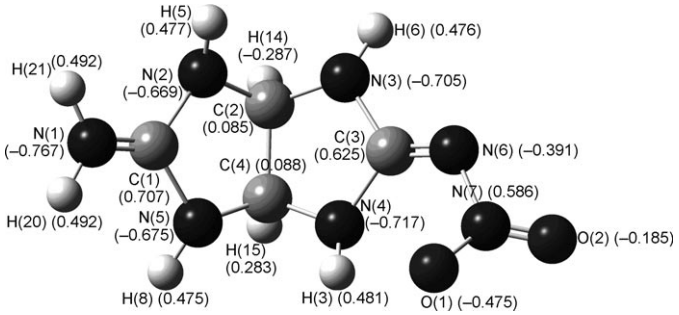


Figure 3. Charge distribution in the INI cation as found with a natural bond orbital (NBO) analysis (B3LYP/6-31+G(d,p)).

analysis indicates that the positive charge is delocalized over the guanidinium group in which the positive charge of H(20) and H(21) (0.492 e) is much higher than to the other hydrogen atoms, and N(1) and C(1) carry the highest negative (–0.767 e) and positive charge (0.707 e), respectively. The negative charges of N(3) and N(4) are lower than that of N(2) and N(5) of the nitroguanidine group. Interestingly, the charges are not delocalized over the INI cation, and the fused atoms [C(2) and C(4)] have the lowest positive charge. The negative charge of O(1) and the positive charge of H(3) as well as the steric effect suggest an intramolecular hydrogen bond. The highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of INI further reveal that the guanidinium and nitroguanidine groups occupy the LUMO and HOMO, respectively; the cation is not delocalized over the fused bicycle (Figure 4).

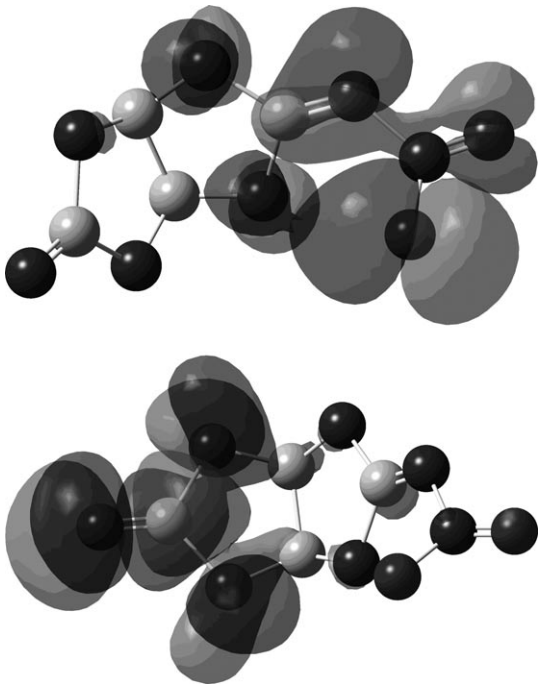


Figure 4. HOMO (top) and LUMO (bottom) of INI cation.

Conclusion

A series of nitroguanidine-fused bicyclic guanidinium energetic salts were synthesized and characterized. Because 2-iminium-5-nitriminooctahydroimidazo[4,5-*d*]imidazole (INI) is a fused bicycle and the nitroguanidine and guanidinium groups in the cation can form extensive hydrogen bonds, its salts paired with inorganic and tetrazolate anions show excellent thermal stability, positive calculated heats of formation, and high densities. The densities of salts **1** and **2** approach that of RDX (1.82 g cm^{-3}[5a]) and fall in the range of new high-performance energetic materials (1.8–2.0 g cm^{-3}[7b,15b]); the others are in the range of currently used explosives (1.6–1.8 g cm^{-3}[7b,15b]). Most of the energetic properties are superior to or comparable with those of the mono-heterocyclic analogues.[13,15] The calculated detonation velocity and detonation pressure of the dinitramide salt **2** are higher than those of conventional explosives, such as 1,3,5-trinitrobenzene (TNT) and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), whereas the other salts are comparable with them. In conclusion, this research has demonstrated that the fused bicyclic iminooctahydroimidazo[4,5-*d*]imidazole salts are a type of promising high-energy density materials with high performance.

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: IR spectra were recorded by using KBr plates on a BIORAD model 3000 FTS spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on spectrometers at 300 and 75 MHz, respectively, by using [D$_6$]DMSO as a locking solvent. Chemical shifts were reported in ppm relative to TMS. Densities were measured at 25 °C by using a Micromeritics Accupyc 1330 gas pycnometer. Differential scanning calorimetry (DSC) measurements were performed by using a calorimeter equipped with an auto-cool accessory and calibrated by using indium. The samples were heated from 40 to 300 or 400 °C with 10 °C min^{-1}. The transition temperature, T_m, was taken as peak maximum. Thermogravimetric analysis (TGA) measurements were carried out by heating samples with

10 °C min^{-1} from 25 to 500 °C in a dynamic nitrogen atmosphere (flow rate = 70 mL min^{-1}). Elemental analyses were performed on a CE-440 Elemental Analyzer.

Theoretical study: Calculations were carried out by using the Gaussian 03 (Revision D.01) suite of programs.[22] The geometric optimization of the structures and frequency analyses were carried out by using B3-LYP functional with the 6-31+G** basis set, single-point energy was calculated at the MP_2(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 a Born–Haber energy cycle (Scheme 2), the heat of formation of a salt can be simplified by the formula:

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

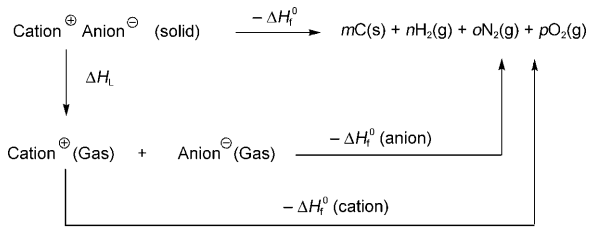
where ΔH_L is the lattice energy of the salt that could be predicted by the formula suggested by Jenkins et al.[23] as:

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

where n_M and n_X depend on the nature of the ions M^{p+} and X^{q-}, respectively, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for lattice potential energy U_{POT} [Eq. (3)] has the form:

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

where ρ_m is the density in [g cm^{-3}], M_m is the chemical formula mass of the ionic material in [g], and the coefficients γ in [kJ mol^{-1} cm] and δ in [kJ mol^{-1}] are assigned literature values.[21]



Scheme 2. Born–Haber cycle for the formation of energetic salts.

X-ray crystallography: Data collection for **1** and **4** was performed on Mercury CCD and Saturn 724 CCD diffractometer, respectively, by using graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Intensity data set was collected by using a ω scan technique and corrected for *Lp* effects. The primitive structures were solved with direct methods and refined on F^2 with full matrix least-squares methods by using the SHELXS-97 and SHELXL-97 programs, respectively.[24] The hydrogen atoms were generated geometrically, non-hydrogen atoms were refined anisotropically. Details of the crystal data are summarized in Table 2. CCDC-756118 (**1**) and 756119 (**4**) 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

General procedures for preparation of the energetic compounds 1–6: To a stirred solution of 2-iminium-5-nitriminooctahydroimidazo[4,5-*d*]imidazole chloride (0.222 g, 1.0 mmol) in H_2O (20 mL) was added dropwise a solution of silver salts (1.0 mmol) in MeCN (10 mL). The resulting solution was stirred at 25 °C for 1 h. After removal of AgCl by filtration, the slow evaporation of filtrate in air gave rise to the desirable products, which were subsequently washed with Et_2O (2×5 mL).

2-Iminium-5-nitriminooctahydroimidazo[4,5-*d*]imidazole nitrate (1): Yield: 0.21 g (85 %); ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 9.46$ (s, 2H), 9.06 (s, 2H), 8.04 (s, 2H), 5.82 ppm (s, 2H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 161.7$, 159.3, 70.4 ppm; IR (KBr): $\tilde{\nu} = 3366$ (w), 3295 (w), 3175 (w), 2856 (vw), 2234 (vw), 1703 (s), 1574 (s), 1536 (w), 1452 (w), 1407 (vw), 1389 (vw), 1350 (vw), 1292 (s), 1249 (s), 1113 (vw), 1082 (m), 1045 (w), 1006 (w), 964 (w), 887 (w), 858 (vw), 827 (w), 785 (w), 733 (vw), 706 (vw), 633 (m), 530 (w), 505 (vw), 438 cm^{-1} (vw); elemental analysis calcd (%) for $C_4H_8N_8O_5$ (248.16): C 19.36, H 3.25, N, 45.15; found: C 19.36, H 3.24, N 45.00.

2-Iminium-5-nitriminooctahydroimidazo[4,5-*d*]imidazole dinitramide (2): Yield: 0.25 g (86 %); ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 9.41$ (s, 2H), 9.02 (s, 2H), 7.98 (s, 2H), 5.80 ppm (s, 2H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 161.5$, 159.1, 70.4 ppm; IR (KBr): $\tilde{\nu} = 3385$ (w), 3349 (w), 3268 (w), 3181 (w), 2832 (vw), 1694 (s), 1579 (s), 1541 (vw), 1498 (w), 1452 (m), 1426 (w), 1354 (w), 1275 (s), 1253 (s), 1163 (w), 1088 (m), 1049 (w), 996 (m), 885 (w), 856 (vw), 786 (vw), 756 (w), 716 (vw), 626 (m), 550 (w), 490 cm^{-1} (vw); elemental analysis calcd (%) for $C_4H_8N_{10}O_6$ (292.17): C 16.44, H 2.76, N 47.94; found: C 16.23, H 2.63, N 47.44.

2-Iminium-5-nitriminooctahydroimidazo[4,5-*d*]imidazole dicyanonitromethanide (3): Yield: 0.23 g (78 %); ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta =$ 9.45 (s, 2H), 9.03 (s, 2H), 7.97 (s, 2H), 5.80 ppm (s, 2H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 161.7$, 159.3, 116.2, 70.4 ppm; IR (KBr): $\tilde{\nu} =$ 3456 (vw), 3349 (w), 3291 (vw), 3193 (w), 2214 (s), 2206 (s), 1699 (s), 1589 (s), 1527 (w), 1450 (m), 1413 (m), 1366 (s), 1322 (w), 1296 (w), 1157 (w), 1107 (m), 1049 (m), 1007 (vw), 970 (w), 892 (m), 859 (w), 829 (vw), 783 (vw), 745 (w), 718 (w), 644 (m), 565 (w), 527 (w), 480 cm^{-1} (w); elemental analysis calcd for $C_7H_8N_{10}O_4$ (296.20): C 28.38, H 2.72, N, 47.29; found: C 28.31, H 2.65, N 47.23.

2-Iminium-5-nitriminooctahydroimidazo[4,5-*d*]imidazole dinitrocyanomethanide (4): Yield: 0.29 g (92 %); ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta =$ 9.46 (s, 2H), 9.03 (s, 2H), 7.97 (s, 2H), 5.80 ppm (s, 2H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 161.7$, 159.3, 114.3 70.4 ppm; IR (KBr): $\tilde{\nu} =$ 3365 (w), 3184 (w), 2777 (vw), 2222 (s), 1703 (s), 1579 (s), 1543 (w), 1503 (s), 1452 (m), 1409 (vw), 1391 (vw), 1345 (vw), 1286 (s), 1238 (s), 1143 (w), 1099 (w), 1042 (w), 1002 (w), 972 (w), 890 (m), 847 (w), 785 (w), 762 (w), 742 (m), 674 (vw), 615 (w), 556 (w), 498 cm^{-1} (vw); elemental analysis calcd for $C_6H_8N_{10}O_6$ (316.19): C 22.79, H 2.55, N 44.30; found: C 22.89, H 2.48, N 44.18.

2-Iminium-5-nitriminooctahydroimidazo[4,5-*d*]imidazole nitroform (5): Yield: 0.26 g (77 %); ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 9.46$ (s, 2H), 9.09 (s, 2H), 8.03 (s, 2H), 5.82 ppm (s, 2H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 161.7$, 159.4, 70.6 ppm; IR (KBr): $\tilde{\nu} = 3363$ (w), 3308 (w), 3254 (vw), 3176 (w), 1700 (s), 1574 (s), 1533 (w), 1487 (w), 1456 (w), 1410 (w), 1383 (w), 1292 (br, s), 1250 (s), 1158 (m), 1116 (w), 1084 (m), 1006 (vw), 968 (m), 858 (vw), 827 (vw), 789 (m), 735 (w), 667 (vw), 637 (vw), 550 cm^{-1} (w); elemental analysis calcd for $C_5H_8N_{10}O_8$ (336.18): C 17.86, H 2.40, N 41.66; found: C 18.19, H 2.59, N 42.15.

2-Iminium-5-nitriminooctahydroimidazo[4,5-*d*]imidazole 5-nitraminotetrazolate hydrate (6): ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 9.47$ (s, 2H), 9.08 (s, 2H), 8.03 (s, 2H), 5.83 ppm (s, 2H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 161.7$, 159.3, 158.3, 70.4 ppm; IR (KBr): $\tilde{\nu} = 3482$ (w), 3349 (w), 3274 (vw), 3179 (w), 1696 (s), 1585 (s), 1532 (s), 1451 (w), 1423 (m), 1343 (w), 1294 (w), 1254 (w), 1222 (w), 1102 (m), 1059 (m), 1044 (w), 1028 (w), 1013 (vw), 969 (w), 897 (m), 859 (w), 824 (w), 774 (w), 747 (w), 692 (w), 632 (vw), 551 (w), 525 (vw), 493 cm^{-1} (w); elemental analysis calcd for $C_5H_9N_{13}O_4 \cdot H_2O$ (333.22): C 18.02, H 3.33, N 54.64; found: C 17.96, H 3.26, N 54.53.

General procedures for preparation of the energetic compounds 7–9: To a stirred solution of 2-iminium-5-nitriminooctahydroimidazo[4,5-*d*]imidazole chloride (0.222 g, 1.0 mmol) in H_2O (50 mL) was added silver sulfate (0.156 g , 0.5 mmol). The mixture was stirred for 0.5 h at 25 °C. Then barium salts (1.0 mmol for **7**, 0.5 mmol for **8** and **9**) in H_2O (10 mL) were added, and the resulting mixture was stirred for an additional 1 h at 25 °C. After filtration, slow evaporation of the filtrate gave rise to desirable products. These were washed with Et_2O (2×5 mL).

2-Iminium-5-nitriminooctahydroimidazo[4,5-*d*]imidazole 4-amino-3-(5-tetrazolate)furazan (7): Yield: 0.28 g (83 %); ^{1}H NMR (300 MHz,

[D$_6$]DMSO): $\delta = 9.29$ (s, 4H), 8.06 (s, 2H), 6.51 (s, 2H), 5.81 ppm (s, 2H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 161.7$, 159.3, 155.9, 150.8, 140.4, 70.4. IR: $\tilde{\nu} = 3399$ (w), 3337 (w), 2977 (w), 1700 (s), 1634 (w), 1583 (s), 1534 (vw), 1452 (w), 1414 (w), 1360 (w), 1276 (s), 1254 (s), 1152 (w), 1115 (w), 1084 (m), 1045 (w), 976 (w), 888 (w), 866 (w), 779 (w), 727 (w), 694 (vw), 553 (vw), 530 cm^{-1} (w); elemental analysis calcd for $C_7H_{10}N_{14}O_3$ (338.25): C 24.86, H 2.98, N 57.97; found: C 24.52, H 2.83, N 57.78.

Bis(2-iminium-5-nitriminooctahydroimidazo[4,5-*d*]imidazole) 5,5′-bistetrazolate hydrate (8): Yield: 0.20 g (76%); ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 9.22$ (br s, 5H), 5.90 ppm (s); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 161.7$, 160.0, 153.9, 70.8. IR: $\tilde{\nu} = 3412$ (w), 3367 (w), 3248 (w), 3055 (vw), 2849 (w), 2203 (vw), 1709 (m), 1615 (s), 1586 (s), 1533 (vw), 1483 (w), 1377 (w), 1329 (m), 1259 (s), 1186 (w), 1148 (vw), 1109 (s), 1077 (vw), 1043 (m), 1020 (vw), 961 (w), 897 (w), 851 (w), 814 (vw), 779 (w), 741 (w), 687 (w), 631 (vw), 548 (w), 442 cm^{-1} (vw); elemental analysis calcd for $C_{10}H_{16}N_{22}O_4 \cdot H_2O$ (526.39): C 22.82, H 3.45, N 58.54; found: C 23.09, H 3.45, N 58.77.

Bis(2-iminium-5-nitriminooctahydroimidazo[4,5-*d*]imidazole) iminobis(5-tetrazolate) dihydrate (9): Yield: 0.22 g (79%); ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 5.76$ pm (s); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 161.6$, 160.2, 158.6, 71.9 ppm; IR (KBr): $\tilde{\nu} = 3358$ (w), 3258 (w), 3188 (w), 2756 (vw), 2232 (vw), 1700 (s), 1584 (s), 1497 (w), 1458 (w), 1350 (vw), 1288 (vw), 1252 (s), 1153 (vw), 1115 (vw), 1086 (m), 1046 (w), 967 (vw), 890 (w), 849 (w), 783 (w), 743 (vw), 712 (vw), 635 (vw), 548 (w), 486 cm^{-1} (vw); elemental analysis calcd for $C_{10}H_{17}N_{23}O_4 \cdot 2H_2O$ (559.52): C 21.47, H 3.78, N 57.59; found: C 21.12, H 3.78, N 56.58.

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