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The Synthesis of Di(aminoguanidine) 5-Nitroiminotetrazolate: Some Diprotic or Monoprotic Acids as Precursors of Energetic Salts

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Abstract: Syntheses of salts with 4,6-bis(nitroimino)-1,3,5-triazinan-2-one (DNAM), 3,5-dinitro-1,2,4-cyclopentanetrione (DDCP), 3-nitroiminotriazolate, and 5-nitroiminotetrazolate as anions yielded moderately dense nitro-containing energetic salts that are thermally stable to >200 °C (measured by thermogravimetric analysis). Di(aminoguanidine) 5-nitroiminotetrazolate (**8**) crystallizes in the monoclinic space group *P*2(1)/*c* with an essentially planar 5-nitroiminotetrazolate dianion. Based on experimental and calculated densities, and theoretical calculations carried out by using the Gaussian 03 suite of programs, all of the salts have calculated detonation pressures and velocities that exceed those of 2,4,6-trinitrotoluene (TNT) and a few have values that approach those of triaminotrinitrobenzene (TATB).

Keywords: ab initio calculations · energetic compounds · heats of formation · nitrogen · salt formation

Introduction

Nitro compounds have long been the focal point of useful energetic compounds.[1] The energy of traditional nitro compounds results primarily from the combustion of the carbon backbone, which consumes the oxygen provided by the nitro groups. Commercially important examples are 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazine (RDX), and nitroglycerine (NG), in which nitro groups are bonded to carbon, nitrogen, or oxygen atoms to form nitro, nitroamino, and nitrate ester compounds, respectively. The presence of nitro groups tends to decrease the heat of formation but contributes markedly to the overall energetic performance. The search for new and improved energetic materials, suitable for use as explosives, propellants, or pyrotechnics, is a continuing challenge. The synthesis of energetic salts as a special class of highly energetic materials has received increased interest over the past decade.[2–4] Energetic materials that are salt based often possess advantages over nonionic molecules because these salts tend to exhibit lower vapor pressures and higher densities than their atomically similar nonionic analogues. The present search for energetic salts is mainly directed toward the modification of cations or the synthesis of organic anions. The further development of energetic salts requires new anions that exhibit high safety, performance, density, and stability.[4s] 4,6-Bis(nitroimino)-1,3,5-triazinan-2-one (DNAM)[5] and 3,5-dinitro-1,2,4-cyclopentanetrione (DDCP)[6] are compounds that contain two nitro groups and can be used as energetic materials. DNAM was first synthesized in 1951.[5a] It exhibits good thermal stability over a wide temperature range[5b] and has relatively high density (1.95 $g\,cm^{-3}$),[5e] low sensitivity to impact and friction, etc. It has been used as a new ingredient in propellant formulations.[5e,f]

DNAM has two nitroamino functional groups, $R_2N{-}NO_2$, which are sometimes useful in the design of energetic materials, such as the nitroamines found in the explosives cyclotetramethylenetetramine, cyclotrimethylene trinitramine, and 2,4,6-trinitrophenyl-*N*-methylnitramine (tetryl). Despite the presence of secondary amine groups, this species has little basic character due to the electron-withdrawing effect of the nitro groups. Secondary nitroamines of the structure $R{-}NH{-}NO_2$ are actually weak organic acids and they can react easily with bases to form salts. DDCP was synthesized as its potassium or ammonium salt. Studies show that the ammonium DDCP salt can be used as a promising energetic

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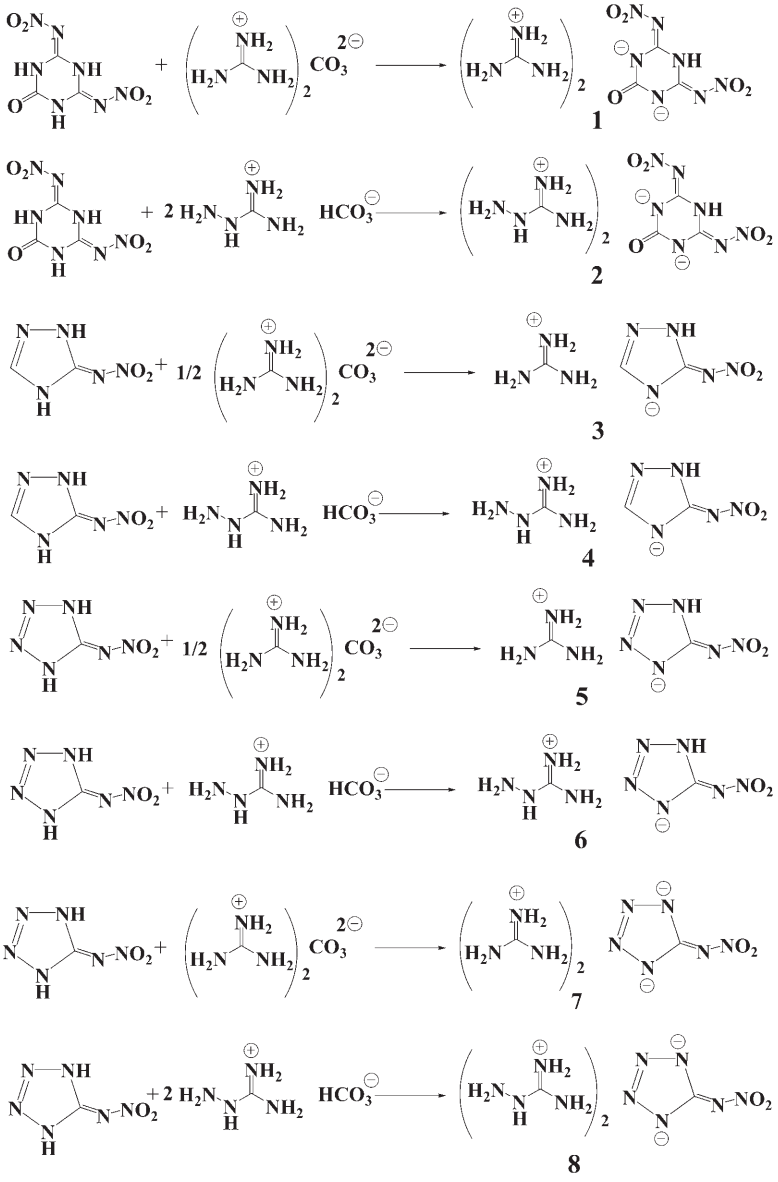
material and as a gas-generating composition.[6a] However, studies on designing energetic salts based on either DNAM or DDCP are limited.

In this work, we report the synthesis and energetic properties of a series of salts with DNAM and DDCP dianions. In addition, we have synthesized energetic salts with 3-nitroimino-1,2,4-triazolate and 5-nitroimino-1,2,3,4-tetrazolate as anions for comparison of their properties with the DNAM and DDCP salts. Guanidine and aminoguanidine are sufficiently basic to ensure reaction with these moderately strong acids. They have a high nitrogen content, which contributes positively to the heats of formation and to enhanced densities through hydrogen bonding. Additionally, DDCP was also treated with other substituted guanidines.

Results and Discussion

The key synthons, DNAM,[5a] potassium DDCP,[6b] 3-nitroimino-1,2,4-triazole,[7] and 5-nitroimino-1,2,3,4-tetrazole,[8a] were prepared by literature methods. Silver DDCP was prepared by reaction of potassium DDCP with an equal amount of silver nitrate in water. The syntheses of energetic salts **1** and **2**, and **7** and **8** were accomplished by utilizing DNAM and 5-nitroimino-1,2,3,4-tetrazole, respectively, as diprotic acids. Additionally, 3-nitroimino-1,2,4-triazole and 5-nitroimino-1,2,3,4-tetrazole were examined as monoprotic acids with guanidine carbonate (**3**, **5**) or aminoguanidine bicarbonate (**4**, **6**) directly (Scheme 1).



Scheme 1. Formation of the guanidinium and aminoguanidinium salts of DNAM (**1**, **2**), 3-nitroimino-1,2,4-triazole (**3**, **4**), and 5-nitroimino-1,2,3,4-tetrazole (**5**–**8**).

5-Nitroimino-1,2,3,4-tetrazole exhibits a very high calculated detonation pressure of 363 kbar and a detonation velocity of 9173 $m\,s^{-1}$, both of which are higher than those of TNT.[8b] Its metal complexes were synthesized and have potential applications as initiators for explosive materials.[8c] Although the guanidine and aminoguanidine salts with 5-nitroimino-1,2,3,4-tetrazolate anions (**5** and **6**) were synthesized previously,[9] only salts of it with single organic cations have been synthesized. The starting material, nitroguanylazide, is not stable and the synthesis requires several steps.[9] This methodology has been markedly improved. The impact of introducing a fourth nitrogen atom into the triazole ring and thus forming the tetrazole analogue is seen by comparing salts **3** and **5** or **4** and **6.** With a common cation, the densities and heats of formation, and thus the detonation properties, are more favorable for the tetrazolate salts. While none of these salts decomposes below 226 °C, the triazolates are more stable thermally (Table 1).

Interestingly, both hydrogen atoms on the tetrazole ring are acidic, which allows this species to react as either a monoprotic or diprotic acid. However, to date, it has only been used as a monoprotic acid in syntheses of energetic salts.[4p] In this paper, we report the successful preparation of monoanionic 5-nitroimino-1,2,3,4-tetrazolate salts in one-step re-

Table 1. Properties of the nitroimino heterocyclic and 3,5-dinitro-1,2,4-cyclopentanetrione energetic salts.

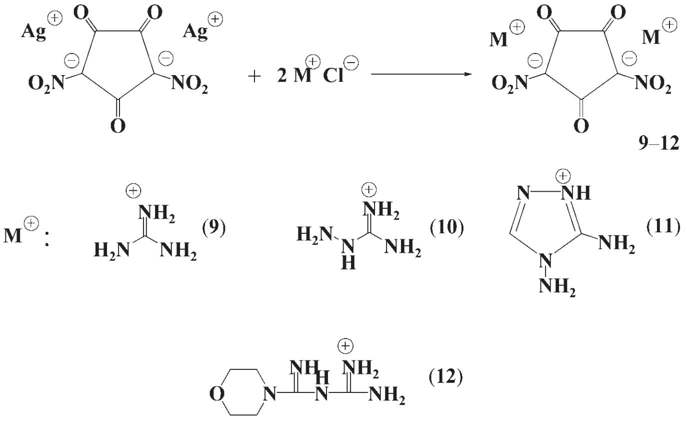
Salt	ρ[a]	OB[b]	T_d[c]	Lattice energy	ΔH_f cation	ΔH_f anion	ΔH_f salt		P[d]	v_D[e]	I_{sp}[f]	h_{50}[g]
	[g cm^{-3}]		[°C]	[kJ mol^{-1}]	[kJ mol^{-1}]	[kJ mol^{-1}]	[kJ mol^{-1}]	[kJ g^{-1}]	[GPa]	[m s^{-1}]	[s]	[cm]
1	1.63	−54.9	288.6	1247.6	575.9	214.8	119.0	0.35	22.6	7959	204.1	77
2	1.69	−54.8	211.4	1224.3	667.4	214.8	325.4	0.89	27.1	8571	214.0	77
3	1.55	−68.0	251.9	512.3	575.9	−13.5	50.0	0.27	18.2	7465	187.1	–
4[h]	1.58	−66.9	225.9	496.2	667.4	−13.5	157.6	0.78	20.8	7920	198.0	–
5	1.61	−46.5	227.6	511.6	575.9	9.8	74.0	0.39	22.1	8069	192.3	33
6	1.64	−47.0	227.0	509.5	667.4	9.8	167.7	0.82	25.0	8479	200.9	35
7	1.50	−64.5	243.6	1403.5	575.9	338.7	87.0	0.35	18.1	7617	187.0	94
8	1.55	−63.3	216.6[h]	1344.7	667.4	338.7	328.9	1.18	22.6	8312	204.3	91
9	1.62	−65.0	300.8	1266.5	575.9	−519.8	−634.6	−1.98	18.6	6920	173.2	89
10	1.61	−64.0	203.8	1221.2	667.4	−519.8	−406.3	−2.14	19.2	7224	186.4	67
11	1.65	−68.0	232.6	1171.6	901.3	−519.8	111.2	0.28	20.8	7243	198.1	57
12	1.62	−114.6	231.3	1033.3	659.2	−519.8	−234.8	−0.43	18.8	6910	182.2	–

[a] Density (calcd).[4r] [b] Oxygen balance (OB) is an index of the deficiency or excess of oxygen in a compound required to convert all of the carbon atoms into CO_2 and all of the hydrogen atoms into H_2O. For a compound with the molecular formula of $C_aH_bN_cO_d$, OB (%) $=1600[(d-2a-b/2)/M_W]$. [c] Decomposition temperature. [d] Detonation pressure. [e] Detonation velocity. [f] Specific impulse. [g] Calculated impact sensitivities taken from reference [11a] for salts **1**, **2**, and **5**–**8**, and from reference [11b] for salts **9**–**11**. [h] $T_d = 209$–$210\,°C$.[12]

actions, as well as the synthesis of dianionic 5-nitroimino-1,2,3,4-tetrazolate salts with two organic cations to prepare salts **7** and **8**. The dianionic nitroiminotetrazolate salts are less dense and have higher heats of formation but concomitantly lower detonation values than their monoanionic counterparts when a common cation is present. Salts **1**–**8** decompose at temperatures in excess of 200 °C. However, the monoanionic salts are more stable thermally. Salts **1** and **2** with the DNAM dianion exhibit densities that are considerably higher than their dianionic nitroiminotetrazolate counterparts **7** and **8**, respectively. The bis(aminoguanidinium) DNAM salt, **2**, has the most attractive energetic properties of our new series of compounds. However, as is typical, the aminoguanidinium cation salts are less thermally stable than the guanidinium cation analogues.

Salts **9**–**12** were synthesized by the reaction of various organic chloride salts with stoichiometric amounts of silver DDCP in aqueous solution (Scheme 2). The densities of these salts fall in the 1.61–1.65 $\mathrm{g\,cm^{-1-3}}$ range, with their calculated detonation properties resembling those of TNT.

Although all of the salts were studied with differential scanning calorimetry (DSC), only **4** melted (193.3 °C) prior to decomposition. The decomposition temperatures were obtained by using thermogravimetric analysis (TGA). All of the salts decomposed at >200 °C, with **9** having the highest thermal stability and being stable to 301 °C (Table 2).



Scheme 2. Formation of the substituted guanidinium salts of DDCP.

The enthalpy of formation is one of the most important parameters to be considered in the design of energetic salts. Recently, significant progress has been made in the theoretical prediction of thermal properties of energetic salts.[10] Heats of formation can be calculated for the salts with good accuracy (including the heats of formation of the cation and anion and the lattice energy of the salts).[10d] The calculated heats of formation of the DNAM, DDCP, and 3-nitroimino-1,2,4-triazolate anions and of the 3,4-diamino-triazolium and moroxydine cations were obtained based on isodesmic reactions (Scheme 3). The values for the other cations and anions were reported by us earlier.[10d] The DNAM and 5-nitroiminotetrazolate anions have positive heats of formation, as do all of their salts. The lower heat of the formation of the DDCP anion gives rise to salts that have smaller heats of formation than those found for the salts with the DNAM, 3-nitroiminotriazolate, or 5-nitroiminotetrazolate anions. The values calculated for their detonation properties are concomitantly slightly lower. Three of the DDCP salts have negative heats of formation. The highest positive heat of formation in the series is exhibited by **8** at 328.9 kJ mol^{-1} (1.18 kJ g^{-1}).

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. Although all of the salts described in this paper have negative OB values, most of them have better oxygen balance than TNT (−74 %). Salt **5** exhibits the least negative oxygen balance of −46.5 %.

The performance of energetic compounds is measured by their detonation velocity, v_D (m s^{-1}), detonation pressure, P (GPa), and specific impulse, I_{sp} (s).[13] These parameters are directly related to the density and heat of formation. The detonation pressure and velocity (based on the traditional Chapman–Jouget thermodynamic detonation theory) and the I_{sp} value were obtained by using the Cheetah 4.0 program (Table 1).[14] For compounds **1**–**12**, the calculated detonation pressures lie in the range between $P=18.1$ GPa (**7**; comparable to the value of 19.5 GPa for TNT)[14b] and $P=27.1$ GPa (**2**; comparable to the value of $P=27.07$ GPa for Composition B (60% RDX/40% TNT)).[14b] Detonation velocities are found in the range between $v_D=6920\,\mathrm{m\,s^{-1}}$ (**9**; comparable to that for TNT, $v_D=6950\,\mathrm{m\,s^{-1}}$)[14b] and $v_D=8571\,\mathrm{m\,s^{-1}}$ (**2**; comparable that for RDX, $v_D=8977\,\mathrm{m\,s^{-1}}$].[14b] Salts **6** and **8** are nearly competitive with **2** with respect to detonation velocity, and **6** is similar to **2** for detonation pressure. However, the rather low densities preclude detonation properties that would move these new salts into the RDX range. The salts have specific impulse values ranging between 173.2 and 214.0 s. The performance data for these energetic salts suggest likely applications as energetic materials. The calculated impact sensitivities **1**, **2**, and **5**–**11** are reported as h_{50} values.[11a,b] Additionally, the experimental impact sensitivities of **7** and **8** have been shown to be >60 J. All of these salts fall into the insensitive or less sensitive classification.

X-ray crystallography: X-ray quality crystals of **8** were grown by slow evaporation of an aqueous solution. The solid-state structure was confirmed by single-crystal X-ray diffraction (Figure 1). The molecule crystallizes in the monoclinic $P2(1)/c$ space group with four sets of cations and their dianions in the unit cell and with a calculated density of 1.577 $\mathrm{mg\,m^{-3}}$ (Table 2). In spite of weak diffraction, the amino-group hydrogen atoms on N12 and N17 were freely refined. All other hydrogen atoms were located and then constrained. The 5-nitroiminotetrazole dianion is essentially planar, with a bonding pattern similar to that seen in the only other congener, the rubidium salt $[\mathrm{Rb}]_3[\mathrm{CN_6O_2}]$-$[\mathrm{CN_3O_2}]\cdot\mathrm{H_2O}$.[15] The highest degree of multiple-bonding character in **8** is seen between N2 and N3, with a bond length of 1.319(3) Å (1.295(5) Å in the Rb salt). The exocyclic double-bond lengths are also similar (C5–N6 1.398(3) Å; Rb salt: 1.368(5) Å). The guanidinium cation cores are also planar, with the imino-group hydrogen atoms perpendicular to this plane. The bond lengths are very similar in each cation with strong carbocation delocalization evident around C10 and C15, with bond-length harmonization and loss of pyramidalization at the nitrogen atoms. This is commonly seen in other guanidinium cations.[41] The synergistic effect of the delocalization and planarity leads to an extended structure of planar ribbons with considerable hydrogen bonding within the layers (with donor–acceptor distances ranging from 2.8 to 3.3 Å) and weaker associations through the perpendicular amino hydrogen atoms (approximately 3.2–3.5 Å) between the layers, as shown in Figure 1 b. These ribbons are oriented along the (104) index and have an interplanar distance of approximately 3.02 Å

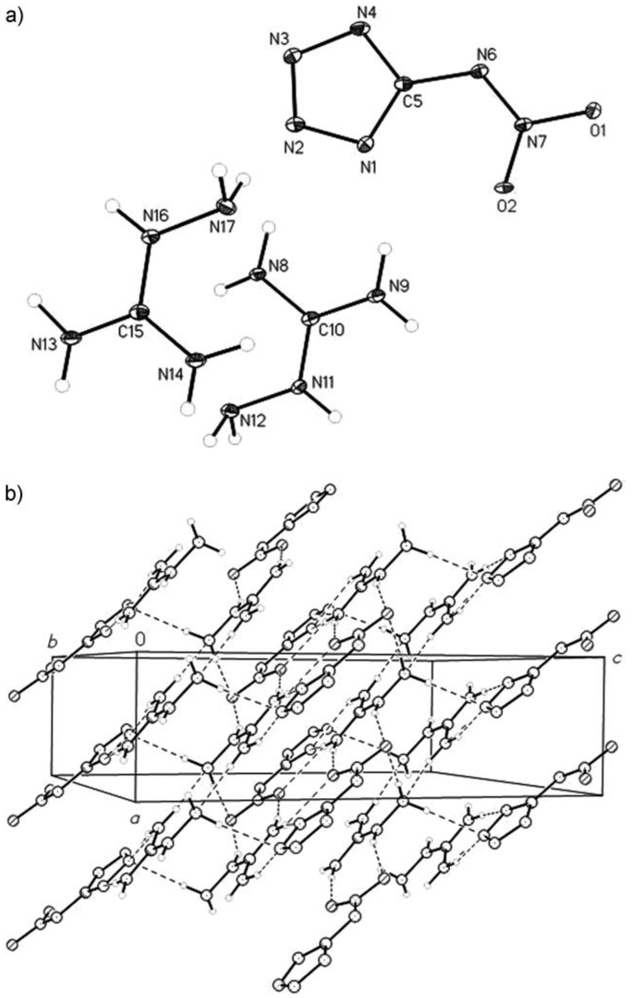


Figure 1. a) Molecular structure of **8** (30% thermal displacement) showing the numbering scheme. Hydrogen atoms are shown (arbitrary spheres) but are unlabeled for clarity. b) Packing diagram of **8** (ball-and-stick) showing the hydrogen-bonded (dashed lines) interconnected layers parallel to the (104) index.

Theoretical study: Calculations were carried out by using the Gaussian 03 (Revision D.01) suite of programs.[16] The geometric optimization of the structures and frequency analyses were carried out by using the B3LYP functional with the 6-31+G** basis set,[17] and single-point energies were calculated at the $\mathrm{MP_2(full)}$/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 (Figure 2), the heat of formation of a salt can be simplified according to Equation (1), where ΔH_L is the lattice energy of the salt.

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

The ΔH_L value could be predicted by the formula suggested by Jenkins et al [Eq. (2)],[18] where U_{POT} is the lattice poten-

Table 2. Crystallographic data and structure refinement parameters.

	8
formula	$C_3H_{14}N_{14}O_2$
M_W	278.28
crystal system	monoclinic
space group	$P2(1)/c$
a [Å]	4.6517(3)
b [Å]	15.7517(11)
c [Å]	15.9968(12)
β [°]	90.314(1)
V [Å^3]	1172.10(14)
Z	4
T [K]	90(2)
λ [Å]	0.71073
ρ_{calcd} [mg m^{-3}]	1.577
μ [mm^{-1}]	0.131
F(000)	584
crystal size [mm^3]	0.33×0.09×0.02
θ range [°]	1.81–25.24
index ranges	$-5 \leq h \leq 5$ $-18 \leq k \leq 18$ $-19 \leq l \leq 19$
reflns collected	13339
independent reflns	2122 [R(int)=0.0508]
data/restraints/parameters	2122/0/188
GOF	1.075
R_1[a] [$I > 2\sigma(I)$]	0.0551
wR_2[a] [$I > 2\sigma(I)$]	0.1303
largest diff. peak, hole [e Å^{-3}]	0.523, −0.237

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

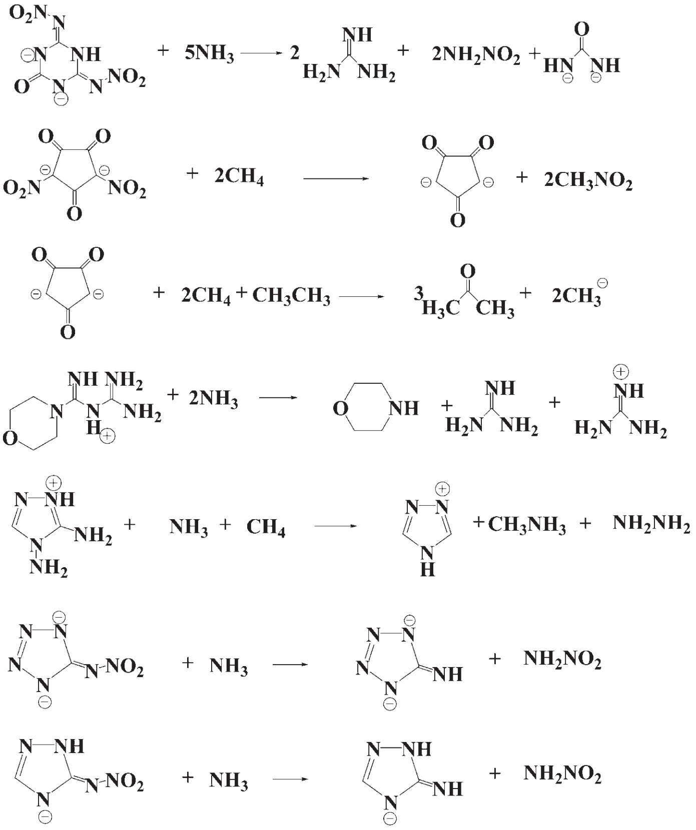
tial energy and n_M and n_X depend on the nature of the ions M^{p+} and X^{q-}, respectively, and are equal to three for monoatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions.

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

The equation for the lattice potential energy, U_{POT}, takes the form of Equation (3), where ρ_m is the density (g^{-1}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.[18]

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

The remaining task is to determine the heats of formation of the cations and anions, which are computed by using the method of isodesmic reactions (Scheme 3).The sources of the energies of the parent ions in the isodesmic reactions were calculated earlier.[10d] The enthalpy of an isodesmic reaction ($\Delta H_{r\,298}$°) is obtained by combining the MP2(full)/6-311++G** energy difference for the reaction, the scaled zero-point energies(B3LYP/6-31+G**), and other thermal factors (B3LYP/6-31+G**). Thus, the heats of formation of the cations and anions being investigated can be extracted readily (see the Supporting Information).



Scheme 3. Isodesmic reactions for the calculation of the heats of formation of the DNAM, DDCP, and 3-nitroimino-1,2,4-triazolate anions and of the 3,4-diamino-triazolium, and moroxydine cations.

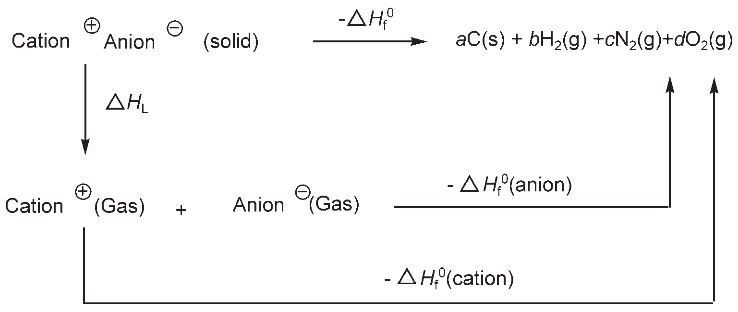


Figure 2. Born–Haber cycle for the formation of energetic salts. a, b, c, d are the number of moles of the respective products.

Conclusion

The formation of DNAM, DDCP, 3-nitroimino-1,2,4-triazolate and 5-nitroimino-1,2,3,4-tetrazolate salts provides a straightforward approach to energetic salts that exhibit acceptable physical properties. The 5-nitroiminotetrazolate dianions form salts that have higher positive heats of formation but densities and detonation properties that are lower than those of the monoanion analogues. Although the triazolates are thermally more stable, the analogous tetrazolates have more energetically attractive enthalpies, densities, and detonation properties. Of the salts studied, the dianionic DNAM salts exhibit the highest heats of formation and detonation properties. Some of these compounds show calculated detonation velocities and detonation pressures comparable to those of commonly used explosives. All of the salts have excellent thermal and hydrolytic stabilities.

Experimental Section

Caution: While we have experienced no difficulties with shock and friction sensitivity of these salts, they must be synthesized only in millimolar amounts and handled with caution.

General methods: All of the reagents were analytical reagents purchased from commercial sources and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz nuclear magnetic resonance spectrometer operating at 300.13 and 75.48 MHz, respectively. Chemical shifts are reported relative to Me_4Si. The solvent was [D$_6$]dimethyl sulfoxide ([D$_6$]DMSO) unless otherwise specified. The melting and decomposition points were recorded on a differential scanning calorimeter and a thermogravimetric analyzer at a scan rate of 10°C min^{-1}, respectively. Infrared spectra were recorded by using KBr pellets. The densities of the energetic salts were measured at room temperature by using a Micromeritics Accupyc 1330 gas pycnometer. Elemental analyses were obtained on an Exeter CE-440 elemental analyzer.

X-ray crystallography: Crystals of compound **8** were removed from the flask, a suitable crystal was selected and attached to a glass fiber, and data were collected at 90(2) K by using a Bruker/Siemens Smart Apex instrument (Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) equipped with a Cryocool NeverIce low-temperature device. Data were measured by using omega scans of 0.3° per frame for 20 s, and a full sphere of data was collected. A total of 2400 frames were collected for each structure with a final resolution of 0.83 Å. Cell parameters for **8** were retrieved by using Smart[19] software and refined by using the SaintPlus[20] software on all observed reflections. Data reduction and correction for Lorentzian polarization and decay were performed by using the SaintPlus software. Absorption corrections were applied by using the SADABS program.[21] The structure was solved by direct methods and refined by the least-squares method on F^2 by using the SHELXTL program package.[22] The structure of **8** was solved in the space group $P2(1)/c$ (no. 14) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. Although diffraction was very weak, the amino hydrogen atoms (on N12 and N17) were located and freely refined. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 2. Further details are provided in the Supporting Information.

Synthesis

General method: **bis(guanidine) DNAM (1)**: DNAM (217 mg, 1 mmol) and guanidinium carbonate (180.2 mg, 2 mmol) were mixed in hot water (5 mL). After CO_2 release was complete, the solution was cooled to room temperature, and a microcrystalline solid was isolated by filtration under vacuum and dried in air. The product (281 mg, 84 %) was a colorless powder: ^{1}H NMR: $\delta = 7.21$ ppm (s, 6H); ^{13}C NMR: $\delta = 159.5$ ppm; IR (KBr): $\tilde{\nu} = 3383$, 3130, 2820, 2250, 1706, 1655, 1614, 1550, 1446, 1391, 1332, 1290, 1234, 1121, 793, 739, 545 cm^{-1}; elemental analysis calcd (%) for $C_5H_{13}N_{13}O_5$ (335.24): C 17.91, H 3.91, N 54.32; found: C 18.12, H 3.87, N 54.13.

Bis(aminoguanidine) DNAM (2): The reaction of DNAM (217 mg, 1 mmol) and aminoguanidinium bicarbonate (272 mg, 2 mmol) was conducted as for **1** to give a colorless powder (295 mg, 81 %): ^{1}H NMR: $\delta =$ 8.77 (s, 2H), 6.98 (br, 8H), 4.67 ppm (s, 4H); ^{13}C NMR: $\delta = 160.2$ ppm; IR (KBr): $\tilde{\nu} = 3338$, 3099, 1682, 1573, 1524, 1382, 1331, 1287, 1124, 1012, 792, 720, 580, 520 cm^{-1}; elemental analysis calcd (%) for $C_5H_{15}N_{15}O_5$ (365.27): C 16.44, H 4.14, N 57.52; found: C 16.56, H 3.99, N 57.13.

Guanidine 3-nitroiminotriazolate (3): 3-Nitroiminotriazole (258 mg, 2 mmol) and guanidine carbonate(180 mg, 2 mmol) were subjected to the general method to give a colorless powder (338 mg, 90 %): ^{1}H NMR: $\delta =$ 7.60 (s, 1H), 7.13 ppm (s, 6H); ^{13}C NMR: $\delta = 159.3$, 157.8, 149.8 ppm; IR (KBr): $\tilde{\nu} = 3434$, 3336, 3120, 2802, 2220, 1800, 1682, 1644, 1577, 1537, 1494, 1362,1278, 1252, 1147, 1063, 1012, 975, 902, 862, 725, 524, cm^{-1}; elemental analysis calcd (%) for $C_3H_8N_8O_2$ (188.15): C 19.15, H 4.29, N 59.56; found: C 19.18, H 4.29, N 59.62.

Aminoguanidine 3-nitroiminotriazolate (4): Compound **4** was synthesized by the literature method:[10] ^{1}H NMR: $\delta = 8.94$ (s, 1H), 7.64 (s, 1H), 7.30 (br, 2H), 7.16 (br, 2H), 4.72 ppm (s, 2H); ^{13}C NMR: $\delta = 160.2$, 157.8, 149.8 ppm; IR (KBr): $\tilde{\nu} = 3410$, 3327, 3251, 3089, 2760, 2351, 2419, 2166, 2105, 1811, 1672, 1518, 1489, 1427, 1348, 1271, 1197, 1101, 1062, 997, 980, 885, 852, 795, 732, 580, 502, 468, 416 cm^{-1}; elemental analysis calcd (%) for $C_3H_9N_9O_2$ (203.16): C 17.74, H 4.47, N 62.05; found: C 17.66, H 4.30, N 61.43.

Guanidine 5-nitroiminotetrazolate (5): 5-Nitroaminotetrazole (260 mg, 1 mmol) and guanidine carbonate (180 mg, 2 mmol) were subjected to the general method to give colorless needle crystals (311 mg, 82 %): ^{1}H NMR: $\delta = 7.03$ ppm (s, 6H); ^{13}C NMR: $\delta = 159.2$, 158.9 ppm; IR (KBr): $\tilde{\nu} = 3471$, 3411, 3344, 3178, 2979, 2844, 2343, 2214, 1696, 1635, 1539, 1388, 1436, 1352, 1242, 1148, 1031, 999, 870, 742, 700, 571, 520, 497, 410 cm^{-1}; elemental analysis calcd (%) for $C_2H_7N_9O_2$ (189.14): C 12.70, H 3.73, N 66.65; found: C 12.72, H 3.59, N 66.04.

Aminoguanidine 5-nitroiminotetrazolate (6): 5-Nitroiminotetrazole (260 mg, 1 mmol) and aminoguanidinium bicarbonate (272 mg, 2 mmol) were subjected to the general method to give colorless needle crystals (303 mg, 74 %): ^{1}H NMR: $\delta = 8.60$ (s, 1H), 7.27 (br, 2H), 6.80 (br, 2H), 4.89 ppm (br, 2H); ^{13}C NMR: $\delta = 159.2$, 158.9 ppm; IR (KBr): $\tilde{\nu} = 3439$, 3170, 3016, 2887, 2748, 2627, 2012, 1672, 1533, 1327, 1248, 1155, 1097, 1060, 991, 902, 869, 748, 696, 647, 565, 497, 455, 416 cm^{-1}; elemental analysis calcd (%) for $C_2H_8N_{10}O_2$ (204.15): C 11.77, H 3.95, N 68.61; found: C 11.85, H 3.79, N 68.19.

Diguanidine 5-nitroiaminotetrazolate (7): 5-Nitroiminotetrazole (130 mg, 1 mmol) and guanidine carbonate (272 mg, 2 mmol) were subjected to the general method to give colorless needle crystals (208 mg, 84 %): ^{1}H NMR: $\delta = 7.59$ ppm (s); ^{13}C NMR: $\delta = 165.3$, 159.6 ppm; IR (KBr): $\tilde{\nu} = 3430$, 3122, 2762, 2414, 2318, 1911, 1637, 1585, 1440, 1387, 1313, 1244, 1138, 1069, 1023, 877, 763, 734, 615, 558, 487 cm^{-1}; elemental analysis calcd (%) for $C_3H_{12}N_{12}O_2$ (248.21): C 14.52, H 4.87, N 67.72; found: C 14.52, H 4.94, N 68.08.

Di(aminoguanidine) 5-nitroiminotetrazolate (8): 5-Nitroiminotetrazole (130 mg, 1 mmol) and aminoguanidinium bicarbonate (272 mg, 2 mmol) were subjected to the general method to give colorless needle crystals (220 mg, 79 %): ^{1}H NMR: $\delta = 8.59$ (s, 1H), 7.22 (br, 2H), 6.84 (br, 2H), 4.69 ppm (s, 2H); ^{13}C NMR: $\delta = 160.1$, 159.1 ppm; IR (KBr): $\tilde{\nu} = 3475$, 2895, 2787, 2415, 2198, 2015, 1672, 1450, 1408, 1290, 1219, 1126, 1066, 1005, 873, 758, 729, 695, 605, 507 cm^{-1}; elemental analysis calcd (%) for $C_3H_{14}N_{14}O_2$ (278.24.): C 12.95, H 5.07, N 70.48; found: C 12.81, H 5.01, N 68.36.

Bis(guanidine) DDCP (9): Guanidine chloride (191 mg, 2 mmol) was dissolved in water (10 mL) and the DDCP silver salt (416 mg, 1 mmol) was suspended in the solution. The mixture was stirred at room temperature for 3 h. After filteration of the silver chloride, the solution was evaporated slowly to leave yellow needle crystals (237 mg, 74 %): ^{1}H NMR: $\delta =$ 7.06 ppm (s, 12H); ^{13}C NMR: $\delta = 179.8$, 177.7, 159.3, 120.0 ppm; IR (KBr): $\tilde{\nu} = 3426$, 3189, 2234, 1665, 1644, 1562, 1418, 1358, 1274, 1139, 997, 933, 778, 694, 539, 486 cm^{-1}; elemental analysis calcd (%) for $C_7H_{12}N_8O_7 \cdot 0.5\,H_2O$ (329.23): C 25.54, H 3.98, N 34.04; found: C 25.75, H 3.69, N 34.22.

Bis(aminoguanidine) DDCP (10): The reaction of aminoguanidine chloride (221 mg, 2 mmol) and DDCP silver salt (416 mg, 1 mmol) was performed as for **9** to give yellow needle crystals (290 mg, 83 %): ^{1}H NMR: $\delta = 8.69$ (s, 1H), 7.29 (br, 2H), 6.93 (br, 2H), 4.70 ppm (s, 2H); ^{13}C NMR: $\delta = 179.6$, 177.7, 160.2, 120.2 ppm; IR (KBr): $\tilde{\nu} = 3492$, 3180, 2855, 2755, 2237, 1683, 1607, 1388, 1362, 1519, 1269, 1097, 1001, 931, 782, 838, 740, 696, 539, 514, 414 cm^{-1}; elemental analysis calcd (%) for $C_7H_{14}N_{10}O_7{\cdot}H_2O$ (368.26): C 22.83, H 4.38, N 38.03; found: C, 22.75, H 4.45, N 37.78.

3,4-Diaminotriazolium DDCP (11): The reaction of 3,4-diaminotriazolium chloride (271 mg, 2 mmol) and the DDCP silver salt (416 mg, 1 mmol) by the same method as for **9** gave yellow square crystals (280 mg, 80 %): m.p. 143.3 °C; ^{1}H NMR: $\delta = 8.42$ (s, 2H), 8.15 (s, 4H), 6.13 ppm (s, 4H); ^{13}C NMR: $\delta = 179.8$, 177.8, 152.2, 143.1, 120.2 ppm; IR (KBr): $\tilde{\nu} = 3341$, 3248, 3155, 3101, 2191, 1689, 1642, 1622, 1556, 1482, 1402, 1351, 1246, 1066, 1014, 951, 931, 846, 783, 732, 696, 644, 478 cm^{-1}; elemental analysis calcd (%) for $C_9H_{12}N_{12}O_7{\cdot}H_2O$ (418.28): C 25.84, H 3.37, N 40.18; found: C 25.56, H 3.23, N 39.89.

Moroxydine DDCP (12): The reaction of moroxydine chloride[23] (415 mg, 2 mmol) and the DDCP silver salt (416 mg, 1 mmol) was carried out as for **9** to give yellow needle crystals (424 mg, 81 %): ^{1}H NMR: $\delta = 7.32$ (s, 4H), 6.86 (s, 8H), 3.61 (t, $J = 4.2$ Hz, 8H), 3.43 (t, $J = 4.2$ Hz, 8H), 3.38 ppm (s, 8H); ^{13}C NMR: $\delta = 177.8$, 160.8, 159.1, 66.8, 46.3 ppm; IR (KBr): $\tilde{\nu} = 3426$, 3189, 2234, 1665, 1644, 1562, 1418, 1358, 1274, 1139, 997, 933, 778, 694, 539, 486 cm^{-1}; elemental analysis calcd (%) for $C_{17}H_{28}N_{12}O_9$ (544.48): C 37.50, H 5.18, N 30.87; found: C 37.09, H 5.07, N 30.81.

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