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Polyamino-Substituted Guanyl-Triazole Dinitramide Salts with Extensive Hydrogen Bonding: Synthesis and Properties as New Energetic Materials

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A series of new energetic salts based on the polyamino-1-guanyl-triazole cation with three to five amino groups and the dinitramide anion were synthesized. These new nitrogen-rich salts tend to have extensive hydrogen bonding and exhibit high densities and thermal stabilities. The impact of multiple amino groups in the cation of the dinitramide salts was investigated. Their properties were modified by varying the guanyl substituents and/or the amino substituents on the triazole ring. On the basis of theoretical calculations, 3,5-diamino-1-guanyl-1,2,4-triazole dinitramide, **8**, has higher detonation pressure and velocity values than the dinitramide energetic materials such as ammonium dinitramide (ADN), and *N*-guanylurea-dinitramide (FOX-12). The structures of salts **7**−**10** (where **7** is 3-amino-1-guanyl-1,2,4-triazole dinitramide, **8** is 3,5-diamino-1-guanyl-1,2,4-triazole dinitramide, **9** is 5-amino-*N*-amidino-1-guanyl-1,2,4-triazole dinitramide, and **10** is 3,5-diamino-*N*-amidino-1-guanyl-1,2,4-triazole dinitramide) were investigated using single-crystal X-ray diffraction analysis.

Introduction

The interest in the development of new solid energetic materials continues at a very high level, particularly for propellants with good oxygen balance. Since it offers significant advantages over currently used oxidizers, such as ammonium perchlorate, especially based on environmental considerations, $NH_4^+N(NO_2)_2^-$ (ADN) is of special interest.[1] Highly dense and stable nitrogen-rich salts of dinitramide (DN) anion with a variety of cations make it a promising candidate in the development of new energetic materials.[2] There are reports of many metal and organic ion salts, e.g., NH_4^+,[3] K^+,[3] $Ag(NCCH_3)^+$,[4] $Cu(NH_3)_4^+$,[4] and methylurotropinium,[5] guanidinium,[6] bisguanidinium,[7] *N*-guanylurea (FOX-12),[8] 1,2,4-triazolium,[9] and 1,5-diamino-4-methyltetrazolium[10] as cations. Many of these salts are either highly hygroscopic, sensitive, or of low thermal stability. The decomposition of ADN is an acid-catalyzed process, initiated by the formation of ammonia and free dinitramide acid which immediately is converted into N_2O and HNO_3.[11]

Reports of a large number of energetic nitrogen-rich salts and high-energy density materials continue to grow at a rapid rate.[12] 3,5-Diamino-1-guanyl-triazole is a polyamino heterocycle which is moderately basic and which forms a variety

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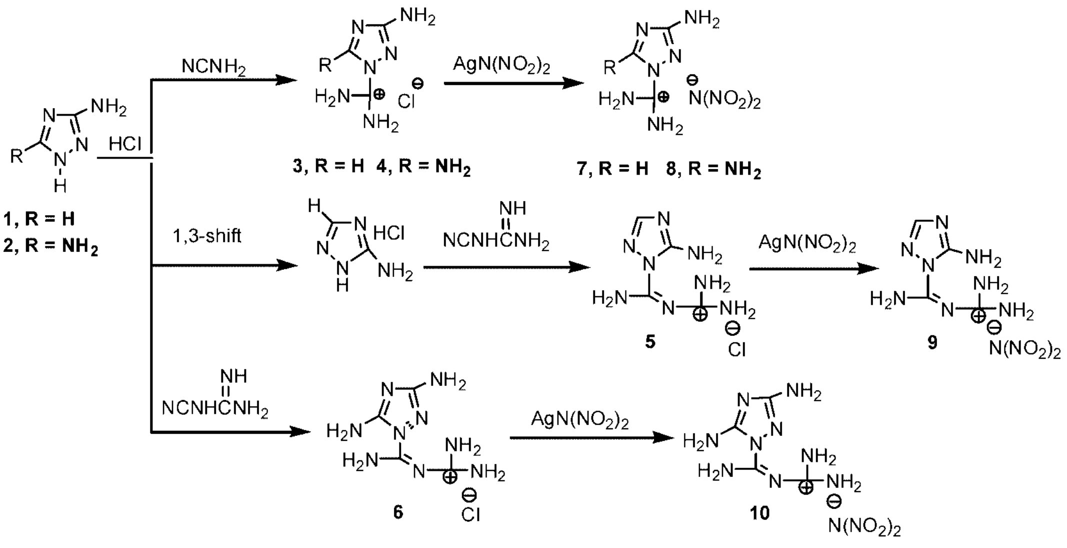
Scheme 1. Synthesis of Polyamino-1-guanyl-triazole Dinitramides



of salts readily.[13] Its cationic form has a calculated positive heat of formation of $\Delta H_f = 796$ kJ/mol (see below). In 3,5-diamino-1-guanyl-triazolium dinitramide, the opportunity for the formation of extensive intramolecular hydrogen bonding between the four amino groups of the cation and the four oxygen atoms of dinitramide should improve the energetic performance characteristics since the density, and as a consequence, the detonation pressure and velocity, will be enhanced. Varying the substrate from 3,5-diamino-1-guanyl-triazole to 3-diamino-1-guanyl-triazole and further to the *N*-amidino-guanyl triazole should markedly influence the properties of these dinitramide salts.

In this work, we report the synthesis and properties of the latter dinitramide salts in an effort to establish the impact on energetic properties of the presence of multiple amino groups contained in a single cation.

Results and Discussion

Synthetic routes to energetic 3-amino-1-guanyl-triazole, 3,5-diamino-1-guanyl-triazole, 3-amino-*N*-amidino-1-guanyl-triazole, and 3,5-diamino-*N*-amidino-1-guanyl triazole dinitramide salts, **7**−**10**, are depicted in Scheme 1. The amino- and diamino-substituted 1,2,4-triazole hydrochlorides, **1** and **2**, were reacted with cyanamide in ethanol at reflux for 6 h to form 3-amino-1-guanyl-1,2,4-triazole hydrochloride, **3**, and 3,5-diamino-1-guanyl-1,2,4-triazole hydrochloride, **4**, respectively. When **1** was reacted with cyanoguanidine in a similar manner, the product 5-amino-*N*-amidino-1-guanyl-1,2,4-triazole hydrochloride, **5**, was obtained in 70% yield. A possible mechanism is for 3-amino-1,2,4-triazole hydrochloride, **1**, to undergo a 1,3-shift followed by reaction with cyanoguanidine to yield **5**. In a previous report, when 3-amino-1,2,4-triazole was reacted with alkyl isothiocyanates, a similar 1,3-shift addition product, 5-amino-1-[alkylamino(thiocarbonyl)]-1*H*-1,2,4-triazole, was obtained.[14] 3,5-Diamino-*N*-amidino-1-guanyl-1,2,4-triazole hydrochloride, **6**, was formed when **2** was reacted with cyanoguanidine analogously. Subsequent metathetical reactions of **3**−**6** with a solution of silver dinitramide gave energetic salts, **7**−**10**.

X-ray Structures. The single-crystal X-ray structures of **7**−**10** were determined on crystals obtained from slow concentration of aqueous solutions of the respective salts (Figure 1).

The triazole rings display the same bonding pattern with similar defined double-bond localizations. The cationic positions (C1, C8, and C11) have delocalized bonding to both terminal amino groups with C−N bonds of ca. 1.31−1.32 Å and with planar geometry at these sites. The dihedral angle of the cationic site to the triazole ring changes from coplanar in **7**, to ca. 25° in **8**, ca. 55° in **9**, and ca. 40° in **10**. The dinitramide anions have asymmetric bonding around the central nitrogen as well as in each nitro group with N−N differences of **7**, 0.0291, **8**, 0.0135, **9**, 0.023, and **10**, 0.0105 Å. The N−O bonds facing the cation which are involved in strong hydrogen bonding are ca. 0.02 Å shorter than the other N−O bonds and are relatively close to each other with interatomic distances of ca. 2.5 Å, which has been described previously.[7a,10a,15] Each dinitramide has a twist with dihedral angles of **7**, ca. 23°, **8**, ca. 11°, **9**, ca. 17°, and **10**, ca. 8°, between each NO_2 plane around the central nitrogen atom. The structural flexibility seen in the anion can be seen in other complexes such as 3,3-dinitroazetidinium dinitramide,[16] 5-amino-1-methyltetrazolium dinitramide,[17] and 1-isopropyl-3,3-dinitroazetidinium dinitramide.[16]

Each compound has complex hydrogen bonding motifs. In **7**, the extended structure generated by H-bonding leads

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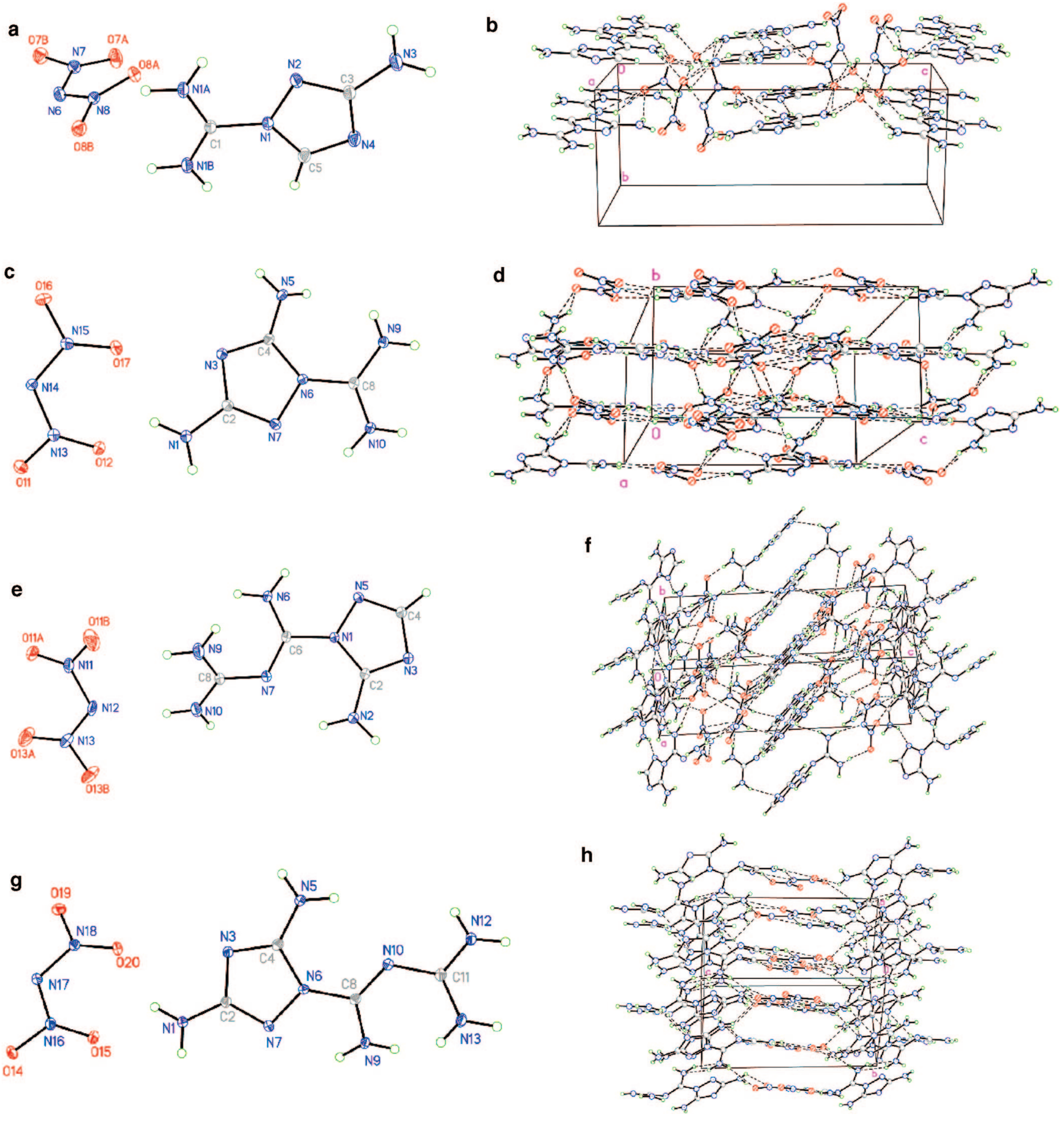

Figure 1. (a) Molecular structure of **7** (thermal displacement at 30% probability). Hydrogen atoms are shown as spheres of arbitrary size. Water molecules are not shown for clarity. (b) Packing diagram of one hydrogen-bonded sheet of **7**. Dashed lines indicate hydrogen bonding. (c) Molecular structure of **8** (thermal displacement at 30% probability). Hydrogen atoms are shown as spheres of arbitrary radius. (d) Packing diagram of **8** with dashed lines indicating hydrogen bonding. (e) Molecular structure of **9** (thermal displacement at 30% probability). Hydrogen atoms are shown as spheres of arbitrary radius. (f) Packing diagram of **9** with dashed lines indicating hydrogen bonding. (g) Molecular structure of **10** (thermal displacement at 30% probability). Hydrogen atoms are shown as spheres of arbitrary radius. (h) Packing diagram of **10** with dashed lines indicating hydrogen bonding.

to a bilayer shown in Figure 1b which is oriented parallel to the *ab* face. The cations in **7** form single hydrogen bonds to different dinitramides unlike the other complexes. Bifurcated H-bonds are formed in **8**, **9**, and **10** by the cation to the dinitramide anion (**8**, N1···O12, 3.088(1), N1···O17, 3.044(1) Å; **10**, N1···O15, 2.903(1), N1···O20, 3.095(2) Å) albeit in **9** these are very weak (C4···O11a, 3.004(3), C4···O13a, 3.287(5) Å). Different architectures are seen in the latter three complexes, and all have a common ladder/rung motif with voids of ca. 3 Å diameter between rungs (see Figure 1, parts d, f, and h).

Despite the extensive hydrogen bonding, the densities of the complexes vary widely (Table 1). However, the density can be correlated to the twist and asymmetry seen above: more nonplanarity of the cation and anion leads to lower density. Hence, complex **9** has the lowest density with some of the weaker intermolecular hydrogen bonding, in spite of the similarity in packing to **8** and **10**.

Table 1. Crystallographic Data and Structure Refinement Parameters

	7	8	9	10
formula	$C_3H_8N_9O_{4.50}$	$C_3H_8N_{10}O_4$	$C_4H_9N_{11}O_4$	$C_4H_{10}N_{12}O_4$
fw	242.18	248.19	275.22	290.24
space group	$P2/c$	$P2(1)/n$	$P2(1)/n$	$P\bar{1}$
exposure (s)		5		5
a (Å)	7.4650(6)	11.8028(7)	6.1940(2)	6.8858(6)
b (Å)	7.0171(6)	6.4019(4)	9.4341(3)	7.1705(7)
c (Å)	17.5443(15)	12.5397(7)	18.8610(5)	12.4774(12)
α (deg)				90.933(2)
β (deg)	93.009(1)	101.356(1)	93.548(1)	92.849(2)
γ (deg)				117.2470(17)
V (Å^3)	917.75(13)	928.95(10)	1100.03(6	546.50(9)
Z	4	4	4	2
T (K)	173(2)	90(2)	173(2)	90(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
D_{calcd} (Mg/m^3)	1.753	1.775	1.662	1.764
μ (mm^{-1})	0.158	0.157	0.144	0.153
index ranges	$-9 \le h \le 9$, $-8 \le k \le 7$, $-21 \le l \le 21$	$-15 \le h \le 15$, $-8 \le k \le 8$, $-16 \le l \le 16$	$-8 \le h \le 5$, $-4 \le k \le 12$, $-22 \le l \le 23$	$-8 \le h \le 8$, $-9 \le k \le 9$, $0 \le l \le 16$
data/restraints/params	1899/0/155	2135/0/178	2525/91/237	2503/0/212
GOF	1.038	1.038	1.095	1.063
R_1 [$I > 2\sigma(I)$][a]	0.0310	0.0389	0.0370	0.0345
wR_2 [$I > 2\sigma(I)$][a]	0.0883	0.0987	0.1007	0.0840

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

Table 2. Properties of New Dinitramide Energetic Salts 7−10

salt	D^a	Td^b	OB^c	$\Delta H_f^{d1\ d}$	$\Delta H_f^{d2\ d}$	P^e	vD^f	$I_{sp}{}^g$
7	1.76	188.1	−38	186.3	0.80	29.9	8568	227.7
8	1.78	196.8	−45	148.8	0.60	31.0	8775	219.3
9	1.66	174.7	−49	217.8	0.79	23.9	8040	209.9
10	1.76	183.2	−50	171.5	0.59	28.5	8651	204.0
$[C_2H_4N_3^+][N(NO_2)_2^-]$	1.64	146.0	−55	153.2	0.87	26.8	8164	262.4
$[C_2H_5N_4^+][N(NO_2)_2^-]$	1.66	120.0	−54	263.8	1.38	28.4	8381	268.1
ADN	1.81	145.0	25.8	−149.7	−1.21	30.6	8635	202.2
FOX-12	1.75	215.0	−19	−355.0	−1.65	29.6	8436	213.0

[a] Density (g/cm^3). [b] Decomposition temperature (°C). [c] Oxygen balance (OB): 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 (%) = $1600[(d - 2a - b/2)/M_w]$. [d] Heat of formation (d1, kJ/mol; d2, kJ/g). [e] Detonation pressure (GPa). [f] Detonation velocity (m s^{-1}). [g] I_{sp}: specific impulse, s.

Physical characteristics and some key properties of these energetic materials, such as density, heat of formation, oxygen balance, and detonation velocity and pressure, are given in Table 2. To assess the potential of the newly prepared dinitramide salts, their energetic characteristics are compared with contemporary materials, 1,2,4-triazolium dinitramide ($[C_2H_4N_3^+][N(NO_2)_2^-]$), 4-amino-1,2,4-triazolium dinitramide ($[C_2H_5N_4^+][N(NO_2)_2^-]$), ammonium dinitramide (ADN), and *N*-guanylurea-dinitramide (FOX-12). The detonation pressure and velocity (based on the traditional Chapman−Jouget thermodynamic detonation theory) and I_{sp} for all compounds in Table 2 were obtained by using Cheetah 4.0.[18]

Thermal Stability. The thermal stabilities of these salts, ranging from 175 to 197 °C, for **7**−**10** are superior to that of ADN (145 °C) by nearly 30 °C. In general, the new salts with 3-amino-triazole as cation are thermally less stable, compared to the analogous 3,5-diamino-triazole cation salts, e.g., **7** and **8**, at 186.1 and 196.8 °C, respectively. The substituent also influences the thermal stability, for example, changing from guanyl to *N*-amidino-guanyl gives rise to a decrease in thermal stability, e.g., **8** at 196.8 °C and **10** at 183.2 °C. The 3,5-diamino-1-guanyl-triazole dinitramide **8** has the highest decomposition temperature which likely arises from the extensive hydrogen bonding interactions between the four amino groups of the cation and four oxygen atoms of dinitramide.

Energetic Properties. The heats of formation for **7**−**10** were calculated using the Gaussian 03 suite of programs (see below) and are summarized in Table 1. The heats of formation exhibited by these energetic salts fall between 149 and 218 kJ/mol. The heats of formation of the *N*-amidino-1-guanyl-triazole dinitramide salts are higher than those of the 1-guanyl-triazole dinitramides, e.g., **9**, **10** (ΔH_f = 217.8, 171.5 kJ/mol) and **7**, **8** (ΔH_f = 186.3, 148.8 kJ/mol), respectively. These values are also higher than the calculated heat of formation for ADN (−122.7 kJ/mol). Calculation of detonation properties and specific impulse I_{sp} values using Cheetah 4.0 shows that **8** has the highest detonation pressure (P = 31.0 GPa) and velocity (vD = 8775 m s^{-1}). In general, the new salts with 3-amino-1-guanyl-triazole as cation have lower detonation properties, in comparison with the analogous 3,5-diamino-1-guanyl-triaozle cation salts, e.g., **7** and **8**, at P = 29.9 GPa, vD = 8568 m s^{-1} and P = 31.0 GPa, vD = 8775 m s^{-1}. Longer guanyl substituents result in lower detonation properties, e.g., changing the guanyl to *N*-amidino-guanyl, the detonation pressure decreases, e.g., **10**, P = 28.5 GPa, vD = 8651 m s^{-1}, **8**, P = 31.0 GPa, vD = 8775 m s^{-1}. All of the salts, except **9**, have higher detonation

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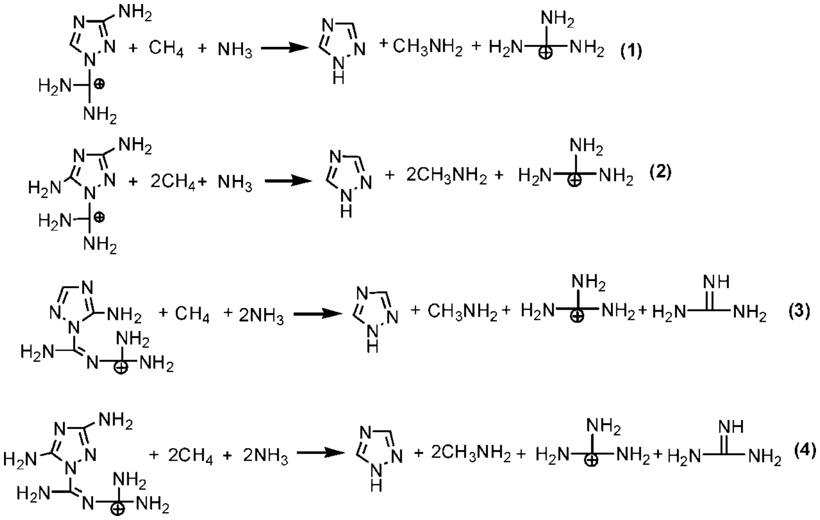
Scheme 2. Isodesmic Reactions for the Polyamino-1-guanyl-triazole Cations



pressures and velocities than other dinitramide energetic materials such as 1,2,4-triazoloium dinitramide ($[C_2H_4N_3^+][N(NO_2)_2^-]$), and 4-amino-1,2,4-triazolium dinitramide ($[C_2H_5N_4^+][N(NO_2)_2^-]$). Salt **8** exhibits higher detonation pressure and velocity than ADN and FOX-12. All the salts have specific impulse values ranging between 204.0 and 227.7 s. The impact sensitivities were measured using a BAM Fallhammer apparatus with a 10 kg drop weight and were found to be more than 60 J. This places them in the insensitive class, whereas ADN is at 6.2 J (sensitive).[8] The new salts are nonhygroscopic and exhibit good thermal stabilities, low sensitivities, and rather high detonation properties that makes them encouraging as energetic materials.

Theoretical Study. Computations were performed with the Gaussian03 (revision D.01) suite of programs.[19] The geometric optimization of the structures and frequency analyses are carried out using B3-LYP functional with 6-31+G** basis set,[20] and single-energy points were calculated at the MP2/6-311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

On the basis of the Born−Haber energy cycles, the heat of formation of a salt can be simplified by the formula

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

where ΔH_L is the lattice energy of the salt, which could be predicted by the formula suggested by Jenkins et al.[21] as given in eq A:

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

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 B) has the form

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

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 mol^{-1} cm) and δ (kJ mol^{-1}) are assigned literature values.[22]

The remaining task is to determine the heats of formation of the cations and anions which are computed using the method of isodesmic reactions (Scheme 2). The energies of the parent ions in the isodesmic reactions were calculated from protonation reactions (heat of formation of H^+ is 1530 kJ/mol) (Scheme 2).[22,23] The enthalpy of isodesmic reaction ($\Delta H_r^\circ{}_{298}$) is obtained by combining the MP2/6-311++G** energy difference for the reaction, the scaled zero-point energies (B3LYP/6-31+G**), and other thermal factors (B3LYP/6-31+G**). The protonation reactions were calculated at G2 level. The heats of formation of 1,2,4-triazole, guanidine, and the guanidinium cation were used directly from the literature (190.3, 26.0, and 579.8 kJ mol^{-1})[24] The heat of formation of the dinitramide anion was calculated based on the calculated value for dinitramide acid and its protonation affinity.[25]

Conclusion

New energetic dinitramide salts that employ polyamino heterocyclic cations, i.e., 3-amino-1-guanyl-triazole, 3,5-diamino-1-guanyl-triazole, 5-amino-*N*-amidino-1-guanyl-triazole, and 3,5-diamino-*N*-amidino-1-guanyl-triazole, were synthesized in good yields. These salts tend to have extensive hydrogen bonding between the polyamino heterocyclic cation and the dinitramide anion. The properties of the new salts can be adjusted by varying the guanyl substituents and/or

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the amino substituents on the triazole ring. Theoretical calculations show that these dinitramide salts exhibit promising energetic properties.

Experimental Section

Caution: No problems were encountered while handling these compounds. The impact sensitivities of **7**−**10** were measured to be >60 J (BAM Fallhammer), and they are not sensitive to scraping with a spatula. However, they should be synthesized only in millimole amounts and handled with extreme care.

General Considerations. All the reagents were analytical grade purchased from commercial sources and used as received. Silver dinitramide was synthesized by literature methods.[4] ^{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 DMSO-d_6 unless otherwise specified. The melting and decomposition points were recorded on a differential scanning calorimeter (DSC) and a thermogravimetric analyzer (TGA) at a scan rate of 10 °C/min, respectively. Infrared spectra were recorded using KBr pellets. The densities of energetic salts were measured at room temperature using a Micromeritics Accupyc 1330 gas pycnometer. Elemental analyses were obtained on an Exeter CE-440 elemental analyzer.

X-Ray Crystallography. A thick colorless plate of **7** and a colorless prism crystal of **9** (with dimensions 0.56 × 0.48 × 0.19 and 1.131 × 0.491 × 0.479 mm^3, respectively) were mounted on a glass fiber using a small amount of Cargille immersion oil. Crystals of **8** and **10** 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.[26] Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD (**7**, **9**) and a SMART APEX (**8**, **10**) detector. The crystals were irradiated using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). MSC X-Stream and Cryocool NeverIce low-temperature devices were used to keep the crystals at a constant 173(2) and 90(2) °K for **7**, **9** and **8**, **10**, respectively, during data collection.

Data collection was performed and the unit cell was initially refined using SMART.[27] Data reduction was performed using SAINTPlus[28] and XPREP.[29] Corrections were applied for Lorentz, polarization, and absorption effects using SADABS.[30]

Structures were solved by direct methods and refined by least-squares method on F^2 using the SHELXTL program package.[31] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. H atoms were included using a riding model. No decomposition was observed during data collection. In **7**, the water molecule lies on a twofold rotation axis. In **9**, the dinitramide is disordered over two positions with relative populations of 82:18. Data for **10** were rotationally twinned and were deconvoluted using CELLNOW[32] giving a two-component twin relationship: 179.5° rotation about the reciprocal axis 0.003, −0.001, 1.000, with a refined twinning ratio of 0.457(1). The matrix used to relate the second orientation to the first domain is (−1.004, −0.009, 0.006, 0.010, −0.996, −0.003, 0.254, 0.170, 0.999). Each cell component was refined using SAINTPlus[28] on all observed reflections. Absorption corrections were applied using TWINABS.[33] Details of the data collection and refinement for **7**−**10** are given in Table 1. Further details are provided in the Supporting Information.

General Procedure for Preparation of 3-Amino-1-guanyl-1,2,4-triazozle Hydrochloride (3) **or 3,5-Diamino-1-guanyl-1,2,4-triazole Hydrochloride** (4)**.** To a round-bottomed flask fitted with a reflux condenser is added 3 mmol each of 3-amino-1,2,4-triazole hydrochloride or 3,5-diamino-1,2,4-triazole hydrochloride and cyanamide in 30 mL of EtOH. This is heated at reflux for 6 h. The mixture was filtered and washed with 15 mL of EtOH, and the white solid was recrystallized from methanol to give **3** or **4**.

*3-Amino-1-guanyl-1,2,4-triazole Hydrochloride (***3***).* Yield 60%; white solid; mp (DSC) 211 °C (decomposition); ^{1}H NMR δ 9.37 (s, 4H), 9.31 (s, 1H), 6.35 (s, 2H); ^{13}C NMR δ 166.1, 151.3, 147.3. Anal. Calcd (%) for $C_3H_7ClN_6$ (162.04): C 22.16, H 4.34, N 51.69. Found: C 22.29, H 4.23, N 51.65.

*3,5-Diamino-1-guanyl-1,2,4-triazole Hydrochloride (***4***).* Yield 65%; white solid; mp (DSC) 220 °C (decomposition); ^{1}H NMR δ 8.77 (s, 4H), 7.38 (s, 2H), 5.83 (s, 2H); ^{13}C NMR δ 164.3, 157.6, 152.7. Anal. Calcd (%) for $C_3H_8ClN_7$ (177.05): C 20.29, H 4.54, N 55.21. Found: C 20.39, H 4.47, N 54.79.

General Procedure for Preparation of 3-Amino-*N*-amidino-1-guanyl-1,2,4-triaozle Hydrochloride (5) **or 3,5-Diamino-*N*-amidino-1-guanyl-1,2,4-triazole Hydrochloride** (6)**.** To a round-bottomed flask fitted with a reflux condenser is added 3 mmol each of 3-amino-1,2,4-triazole hydrochloride or 3,5-diamino-1,2,4-triazole hydrochloride and cyanoguanidine in 30 mL of EtOH. The mixture is heated at reflux for 6 h. The mixture was filtered and washed with 15 mL of EtOH, and the white solid was recrystallized from methanol to give **5** or **6**.

*5-Amino-*N*-amidino-1-guanyl-1,2,4-triazole Hydrochloride (***5***).* Yield 70%; white solid; mp (DSC) 186 °C (decomposition); ^{1}H NMR δ 8.25 (s, 4H), 8.16 (s, 2H), 7.62 (s, 1H), 7.49 (s, 2H); ^{13}C NMR δ 163.3, 157.5, 151.7, 150.7. Anal. Calcd (%) for $C_4H_9ClN_8$ (204.06): C 23.48, H 4.43, N 54.70. Found: C 23.87, H 4.22, N 54.77.

*3,5-Diamino-*N*-amidino-1-guanyl-1,2,4-triazole Hydrochloride (***6***).* Yield 70%; white solid; mp (DSC) 215 °C (decomposition); ^{1}H NMR δ 7.96 (s, 4H), 7.73 (s, 2H), 7.39 (s, 2H), 5.59 (s, 2H); ^{13}C NMR δ 162.9, 162.6, 157.2, 151.1. Anal. Calcd (%) for $C_3H_8ClN_7$ (177.05): C 21.77, H 5.07, N 57.13. Found: C 22.40, H 4.52, N 56.92.

General Procedure for Preparation of Salts 7−10. Amino-1-guanyl-1,2,4-triazole hydrochloride, **3**−**6** (1 mmol) was dissolved in water, and an aqueous solution of silver dinitramide (1 mmol) was added. After 2 h, the solid was filtered, the solvent was removed slowly, and the product, **7**−**10**, was isolated as a yellow crystalline solid.

*3-Amino-1-guanyl-1,2,4-triazole Dinitramide (***7***).* Yield 65%; yellow crystal; mp (DSC) 186 °C (decomposition); IR (KBr) 3351, 3237, 1703, 1630, 1437, 1177, 1023, 445 cm^{-1}; ^{1}H NMR δ 9.05 (s, 4H), 8.88 (s, 1H), 6.35 (s, 2H); ^{13}C NMR δ 166.2, 150.9, 146.8. Anal. Calcd (%) for $C_3H_7N_9O_4 \cdot H_2O$ (251.07): C 14.35, H 3.61, N 50.19. Found: C 13.95, H 3.03, N 49.91.

*3,5-Diamino-1-guanyl-1,2,4-triazole Dinitramide (***8***).* Yield 65%; yellow crystal; mp (DSC) 197 °C (decomposition); IR (KBr) 3490, 3367, 1695, 1626, 1569, 1512, 1201, 1026 cm^{-1}; ^{1}H NMR δ 8.49 (s, 4H), 7.21 (s, 2H), 5.85 (s, 2H); ^{13}C NMR δ 162.6, 155.9, 150.9. Anal. Calcd (%) for $C_3H_8N_{10}O_4$ (248.07): C 14.52, H 3.25, N 56.44. Found: C 14.55, H 3.25, N 55.81.

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*5-Amino-*N*-amidino-1-guanyl-1,2,4-triazole Dinitramide* (**9**). Yield 60%; yellow crystal; mp (DSC) 175 °C (decomposition); IR (KBr) 3401, 3318, 1654, 1593, 1521, 1193, 1025, 690 cm^{-1}; ^{1}H NMR δ 8.17 (s, 4H), 7.98 (s, 4H), 7.65 (s, 1H), 7.48 (s, 2H); ^{13}C NMR δ 163.1, 157.5, 151.7, 150.8. Anal. Calcd (%) for $C_4H_9N_{11}O_4$ (275.08): C 17.40, H 3.26, N 55.99. Found: C 17.43, H 3.21, N 55.73.

*3,5-Diamino-*N*-amidino-1-guanyl-1,2,4-triazole Dinitramide* (**10**). Yield 60%; yellow crystal; mp (DSC) 183 °C (decomposition); IR (KBr) 3491, 3396, 1639, 1522, 1440, 1195, 1019, 756 cm^{-1}; ^{1}H NMR δ 7.75 (s, 6H), 7.38 (s, 2H), 5.60 (s, 2H); ^{13}C NMR δ 161.3, 161.2, 155.8, 149.7. Anal. Calcd (%) for $C_4H_{10}N_{12}O_4$ (290.09): C 16.56, H 3.47, N 57.92. Found C 16.50, H 3.42, N 57.26.

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Supporting Information Available: Differential scanning calorimeter (DSC) figures for new dinitramide salts **7**−**10**, properties of new dinitramide salts **7**−**10**, and various atomic parameters for **7**−**10** (PDF); crystallographic data for **7**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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