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Nitroamino Triazoles: Nitrogen-Rich Precursors of Stable Energetic Salts

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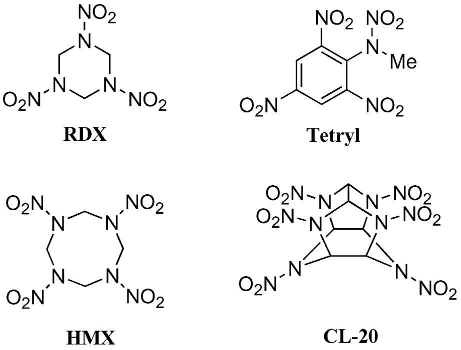
1-Nitroamino-1,2,3-triazole (**5**) was synthesized and its zwitterionic structure was established using single-crystal X-ray diffraction. The calculated detonation properties for 4-nitroamino-1,2,4-triazole (**2**) (P = 33.4 GPa, vD = 8793 m/s) and 1-nitroamino-1,2,3-triazole (**5**) (P = 33.0 GPa, vD = 8743 m/s) are comparable with RDX. A new family of energetic salts **7**–**21** based on either the 1-nitroamino-1,2,3-triazolate or the 4-nitroamino-1,2,4-triazolate anion were prepared and characterized by vibrational spectroscopy (IR), multinuclear NMR spectra, elemental analyses, density, TGA and DSC. The heats of formation ($\Delta_f H°_{298}$) and detonation properties for these stable salts were calculated using Gaussian 03 and Cheetah 4.0, respectively. Comparison of the properties of the 1,2,3- and 1,2,4-triazolate salts indicates that while the 1,2,4-derivatives are more stable thermally, the 1,2,3-analogs invariably have higher heats of formation. In contrast to its salts, 1-nitroamino-1,2,3-triazole (**5**) is extremely shock-sensitive with an impact sensitivty of <1 J.

Introduction

Energetic materials as controllable storage systems for relatively large amounts of chemical energy are widely applied in military and industrial venues. In order to meet the continuing need for improved energetic materials, the synthesis of energetic heterocyclic compounds has attracted considerable interest due to their rather large densities, good oxygen balance, and high heats of reaction. Recently, a series of energetic salts as a unique class of high energetic materials have been developed in our laboratory based on the special properties of ionic compounds such as lower vapor pressures and higher densities than their atomically similar non-ionic analogs.[1] Some of them display attractive energetic properties including high positive heats of formation and high densities, e.g., the salts of 2,4,5-trinitroimidazolate with a variety of organic cations have relatively high densities (>1.75 $g\,cm^{-3}$) and thermal stabilities (T_d >199 °C).[1h]

Compounds containing nitroamino groups as energetic materials have been intensively investigated both theoretically and experimentally because the nitramino group can offer improved oxygen balance and higher heat of formation.[2] Some of the most prominent members of these energetic materials are RDX,[3] HMX,[2e,4] CL-20,[5] nitroguanidine,[6] and tetryl.[7] RDX (d = 1.76 g/cm^3; P = 33.8 GPa, vD = 8750 m/s)[8] is widely used in military and industrial applications (Scheme 1).



Scheme 1. Traditional energetic nitroamino compounds: RDX, Tetryl, HMX and CL-20.

However, only cyclic and linear secondary nitroamines can promise reasonable sensitivities. The application of primary nitroamines as energetic materials is limited due to their relatively low thermal stability. Recently, considerable research indicated that R–$NHNO_2$ normally can act as a moderately strong acid, and that the stability of this compound can be dramatically increased by transformation of the –$NHNO_2$ moiety into –$[NNO_2]^-$ to form a salt or zwitterionic salt.[9] For example, dinitramine is a very unstable compound but the dinitramide anion is often used for preparing salts as nontoxic oxidizers.[10] Nitroaminoazoles in which the nitrogen atom of the nitroamino group is attached to a ring-carbon atom have attracted special attention for developing new energetic materials. 5-Nitroiminotetrazole is distinguished as a high-energy compound with low thermal stability. According to thermogravimetric data, its temperature of intensive (explosive) decomposition is 132 °C. As is typical of salt derivatives, salts of 5-nitroiminotetrazole are thermally more stable; the temperatures

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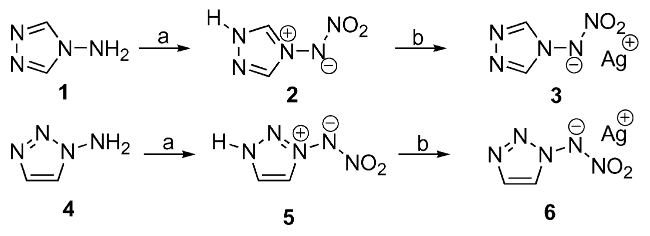
of their intense decomposition is 200–400 °C, depending on the type of cation.[1d,11] The acidity of 5-nitroiminotetrazole ($pK_a = -0.72 \pm 0.50$) makes it a useful precursor for salts with organic bases, such as pyridine, *N*-diethylaniline, ethylenediamine and guanidine but few thermochemical properties were reported for these salts.[11]

Recently, that work was extended to prepare the 4-aminotriazolium, 5-aminotetrazolium, triazolium, and 3-azidotriazolium 5-nitroiminotetrazolate salts with full characterization being carried out.[1d] These salts have densities of ca. 1.7 g/cm^3, thermal decomposition temperatures from 130 (azidotriazolium) to 184 °C, positive heats of formation, and detonation properties approaching those of triaminotrinitrobenzene. In these instances, the nitroimino group was bonded to carbon. However, if that group were attached to a ring heteroatom to create a rather long chain of catenated heteroatoms, such a structure could result in unique properties for energetic compounds. 4-Nitroamino-1,2,4-triazole (**2**) is a good example of such a compound. The thermal decomposition process of **2** has been investigated[11d,12] but the properties and reactivity of this compound were poorly studied, most of the work having been focused on its alkylation reactions, and its metal salts.[13]

In this paper, we report the syntheses and characterization of salts obtained from reaction of silver 4-nitroamino-1,2,4-triazolate and high nitrogen-containing organic halides. Additionally, for the first time, 1-nitroamino-1,2,3-triazole (**5**) was synthesized and its salts formed with high nitrogen-containing organic cations were synthesized and fully characterized.

Results and Discussion

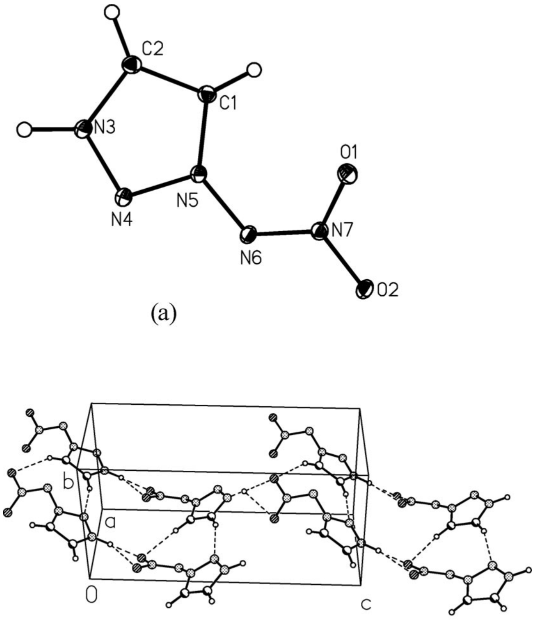
Several methods are available for the nitration of *N*-aminoazoles: 1) nitric acid in Ac_2O;[14] 2) alkyl nitrate in alcohol;[15] 3) nitronium salt (NO_2BF_4) in acetonitrile;[13c,13e,13f] and 4) nitric acid in sulfuric acid.[16] Using 70% nitric acid as the nitrating reagent, 4-amino-1,2,4-triazole was readily nitrated to form 4-nitroamino-1,2,4-triazole (**2**) in good yield (65%) (Scheme 2).[17]



Scheme 2. Syntheses of nitroaminotriazoles and their silver salts. Reagents and conditions, a: 95% H_2SO_4, 70% HNO_3, 0 °C, 30 min, room temp. 2 h; b: 1) NaOH, H_2O, r. t., 2) $AgNO_3$.

4-Nitroamino-1,2,4-triazole (**2**) was treated with an equivalent amount of aqueous sodium hydroxide and with an equivalent of silver nitrate. The silver salt **3** was precipitated which was then collected by filtration, dried under vacuum and obtained as a white powder in quantitative yield with no further purification required for metathesis reactions. 1-Nitroamino-1,2,3-triazole (**5**) can also be prepared by using the same nitration conditions as for 1-amino-1,2,3-triazole in satisfactory yield. Nitric acid (70%) was added dropwise to a solution of 1-amino-1,2,3-triazole in concentrated sulfuric acid at 0–5 °C. After stirring for 2 h at room temperature, the reaction mixture was poured onto ice/water. While **2** precipitated immediately from cold aqueous solution, in contrast, **5** is water soluble requiring extraction with ethyl acetate. The silver salt **6** was synthesized in quantitative yield by the same method as for **3**.

The zwitterionic structure of **2** had been confirmed earlier by X-ray diffraction.[18] Crystals of 1-nitroamino-1,2,3-triazole (**5**) were obtained by crystallization from a ethyl acetate and diethyl ether solution. The solid-state structure of **5** was determined by X-ray crystallography and was found to be a zwitterion as shown in Figure 1.



(a)

(b)

Figure 1. a) Thermal ellipsoid plot (30%) and labeling scheme for 1-nitroamino-1,2,3-triazole (**5**). Hydrogen atoms included but are unlabelled for clarity. b) Packing diagram of **5** viewed down the *a* axis. Dashed lines indicate hydrogen bonding.

The asymmetric unit contains an independent molecule of **5** and hydrogen atoms were located and refined on C1, C2 and N3 of the triazole ring. Bond lengths lie within the ring range from 1.3181(12)–1.3661(15) Å. Unlike the similar structure 4-nitroamino-1,2,4-triazole (**2**) where bond localization is evident,[18] the bonding in the triazole ring in **5** suggests delocalization of the positive charge. The dihedral angle between the nitroamino group and triazole ring planes is ca. 44.2° and the amino-triazole N–N bond length is relatively long, 1.4011(12) Å, indicating little interaction between the π systems. This is similar to the geometry seen in **2** with an angle of 50.9° and an N–N distance of ca.

1.407 Å. The extended structure of **5** consists of undulating intermolecular H-bonded sheets parallel to the *ac* plane as shown in Figure 1, b, with asymmetric bifurcated H-bonds between the nitro group [N3···O2, 2.6679(12); N3···O1, 3.1362(11) Å], C–H···O [C1···O2, 3.2764(13) Å] and weak C–H···N [C2···N4, 3.4177(13) Å] interactions.

4-Nitroamino-1,2,4-triazole (**2**) can only be reacted with the strong base, hydrazine, to form the hydrazinium salt **7** and can not be reacted directly with other neutral nitrogen-rich bases, e.g., guanidine carbonate or aminoguanidine hydrogen carbonate to form the corresponding salt. 1-Nitroamino-1,2,3-triazole (**5**) does react easily with hydrazine but satisfactory elemental analysis was not obtained. However, **5** was reacted directly with stoichiometric amounts of guanidine carbonate, aminoguanidine hydrogen carbonate or neutral nitrogen-rich bases to afford the corresponding organic energetic salts, **8**–**11** (Scheme 3). For example, 2 mmol of **5** reacted with 1 mmol of 3,6-diguanidino-1,2,4,5-tetrazine in water at 80 °C for 2 h gave **10** which precipitated directly from the reaction mixture as red needle crystals in quantitative yield suitable for X-ray single-crystal analysis. The higher reactivity of **5** compared with **2** may arise from: 1) the higher basicity of the 1,2,4-triazole ring (pK_a 10.0)[19] relative to that of the 1,2,3-triazole ring (pK_a 8.2)[20] causing the proton bonded to the 1,2,4-triazole ring to be less acidic; and 2) the lower aqueous solubility of **2** compared to **5** causes the reactions to proceed with greater difficulty.

Suitable crystals of **10** for single-crystal X-ray analysis were obtained from a water solution. The structure of **10**, shown in Figure 2, shows the symmetry generated tetrazine ditriazolium salt where the tetrazine lies on an inversion center (symmetry transformation 0.5 – *x*, 1.5 – *y*, –*z*). Hydrogen atoms were located and refined.

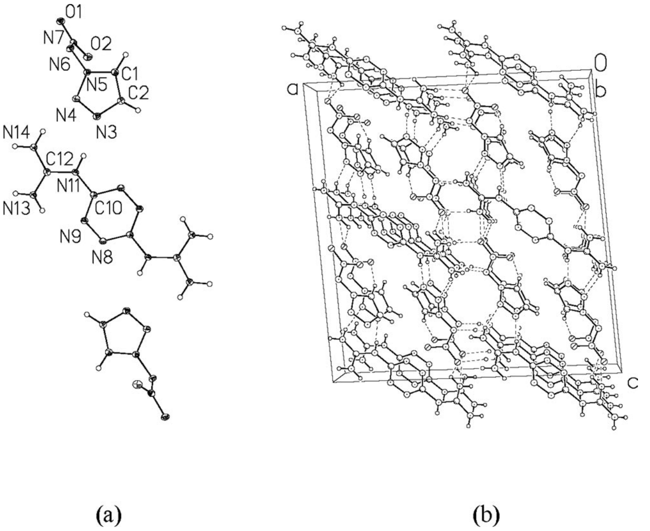
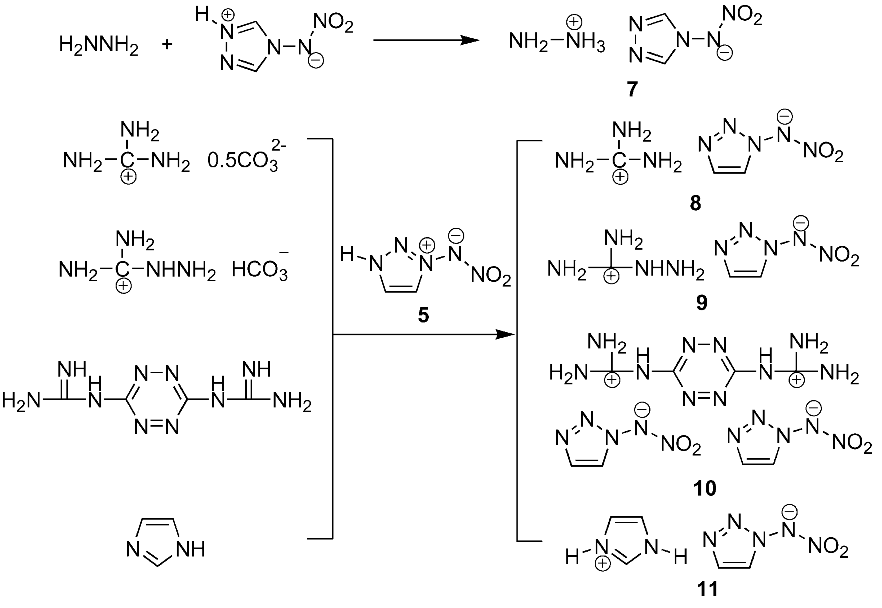


Figure 2. a) Thermal ellipsoid plot (30%) and labeling Scheme for **10**. Hydrogen atoms included but are unlabelled for clarity. b) Ball and stick packing diagram of **10** viewed down the *c* axis. Dashed lines indicate strong hydrogen bonding.

The diguanidine-tetrazinium cation is approximately planar with a dihedral angle of ca. 1.8° between the guanidine moieties and the tetrazine thus indicating a strong delocalization of the charge over the entire diguanidine tetrazinium moiety. The only other examples of this cation in the literature have larger angles between the substituent moieties and the tetrazine ring planes (e.g. 3,6-diguanidino-1,2,4,5-tetrazinium nitroformate,[21] ca. 8.5°, and 3,6-diguanidino-1,2,4,5-tetrazinium trinitroimidazole,[1h] ca. 7.6°). Bond lengths in these cations are very similar. The transition from neutral **5** to anion affects the molecular geometry

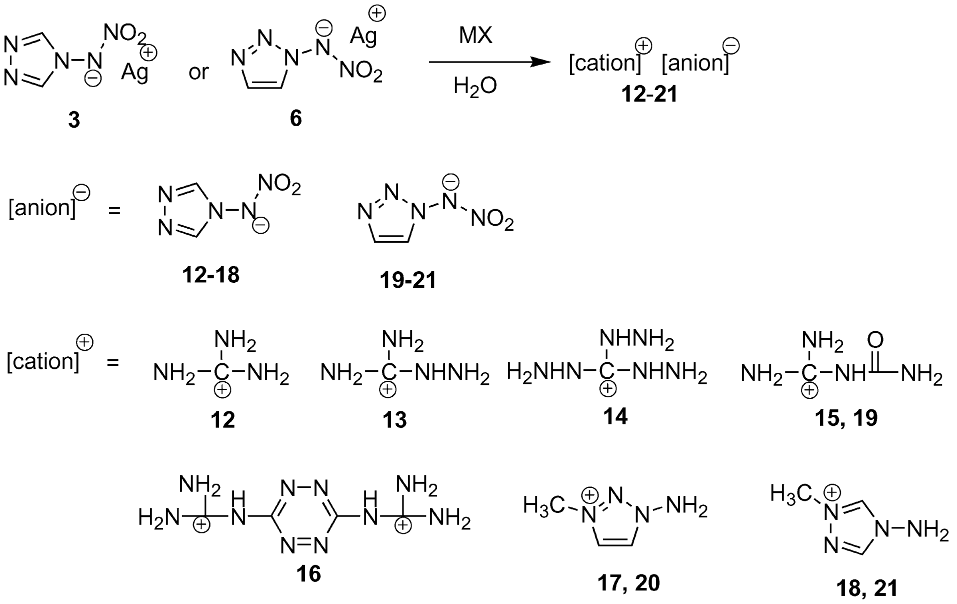


Scheme 3. Syntheses of nitroamino salts by acid-base reactions.

with the dihedral angle between the triazine ring and the nitroamino moiety opening to ca. 88.5° and with contractions of the bond lengths in the triazine ring itself. The extended structure also forms a strongly hydrogen-bonded complex 3D network with one of the major synthons being the NH_2–NO_2 interaction [N13···O1, 2.9537(18) Å, Figure 2, b].

Organic salts, **12**–**21**, can be synthesized by metathesis reactions of the silver salts **3** and **6** with the corresponding organic halide salts (Scheme 4). The aqueous solubilities of **3** and **6** are very low but they are more soluble than the silver halide causing these reactions to proceed smoothly. For example, to a suspension of **3** (1 mmol) in water (10 mL) was added a solution of guanidinium chloride (1 mmol) in water (2 mL). After stirring at room temperature in the absence of light for 6 h, the mixture was filtered, and the filtrate was concentrated. Compound **12** was obtained in 89% yield by recrystallization from methanol and diethyl ether.

Densities and thermochemical data for **2**, and **5**, and the salts **7**–**21** are summarized in Table 1. DSC and TGA were used to determine the relative thermal stabilities of the compounds and are measured under comparable conditions. While 1-nitroamino-1,2,3-triazole (**5**) undergoes explosive decomposition at 105 °C, 4-nitroamino-1,2,4-triazole (**2**) is more stable with a sharp melting point at 172 °C and a



Scheme 4. Syntheses of nitroamino salts by metathesis reactions.

Table 1. Thermal properties of energetic salts on the basis of nitroaminotriazoles.

Salt	d[a]	T_m[b]	T_d[c]	ΔH_f[d] cation	ΔH_f[d] anion	Lattice energy[d]	ΔH_f kJ/mol	kJ/g	P[e]	vD[f]
2	1.82	172	180	–	–	–	340.1	2.64	33.4	8793
5	1.80	–	105	–	–	–	367.0	2.84	33.0	8743
7	1.66	135	194	770.0	141.5	539.9	371.6	2.31	29.7	8868
8	1.51	189	230	566.7	195.5	505.4	256.8	1.36	20.4	7587
9	1.50	71	187	667.4	195.5	494.5	368.4	1.81	20.9	7783
10	1.62	–	226	1903.6	195.5	1406.2	888.3	1.96	21.2	7765
11	1.51	86	147	711.5	195.5	499.3	407.7	2.07	18.6	7403
12	1.48	184	240	566.7	141.5	502.8	205.4	1.09	19.7	7700
13	1.50	138	220	667.4	141.5	500.0	308.9	1.52	22.0	8011
14	1.55	167	200	871.5	141.5	481.3	531.7	2.28	24.4	8366
15	1.60	–	205	350.6	141.5	486.3	5.8	0.02	18.8	7501
16	1.58	–	211	1903.6	141.5	1396.6	790.0	1.74	20.2	7506
17	1.47	–33	206	963.2	141.5	477.9	626.8	2.76	20.0	7663
18	1.54	138	213	895.6	141.5	483.7	553.4	2.44	21.4	7487
19	1.54	142	162	350.6	195.5	481.5	64.6	0.28	19.3	7282
20	1.43	–45	195	963.2	195.5	474.6	684.2	3.01	19.2	7532
21	1.63	92	192	895.6	195.5	490.9	600.2	2.64	22.7	7957

[a] Density [$g\,cm^{-3}$]. [b] Melting point [°C]. [c] Decomposition temperature [°C]. [d] [$kJ\,mol^{-1}$]. [e] Detonation pressure [GPa]. [f] Detonation velocity [$m\,s^{-1}$].

decomposition temperature of 180 °C. Salts in which **5** has been converted to its anion exhibit remarkably improved thermal stabilities. For example, the salts **8** and **10** are thermally stable to 230 °C. On the basis of the decomposition temperatures of the salts **7**–**21**, the thermal stabilities of the salts with either the 1-nitroamino-1,2,3-triazole or the 4-nitroamino-1,2,4-triazole anion are similar; for example, with a common guanidinium cation, **8** and **12** decomposed at 230 and 240 °C, respectively, which supports the general observation that salt formation improves the thermal stability for energetic compounds. In general, 1-nitroamino-1,2,3-triazole salts melt at lower temperatures than their 4-nitroamino-1,2,4-triazole analogs. The 1-amino-3-methyl-1,2,3-triazolium salts **17** and **20** are liquids at room temperature and thus fall into the ionic liquid class.

On the basis of our calculations, the heats of formation of all the salts have positive values. The heats of formation of 1-nitroamino-1,2,3-triazolate salts have larger positive values than the analogous 4-nitroamino-1,2,4-triazolate salts with common cations (salts **12** and **8**, **13** and **9**, **17** and **20**, **15** and **19**, **18** and **21**, **16** and **10**). This apparently arises because the 1,2,3-triazole molecule has a larger positive heat of formation than 1,2,4 triazole. Our earlier calculations showed that nitrogen–nitrogen bonds usually contribute more to a positive heat of formation than does a nitrogen–carbon bond.[22] For the purpose of comparison, we calculated the gas-phase heats of formation of 1,2,3-triazole, 1,2,4-triazole, pyrazole and imidazole. The results show that 1,2,3-triazole has a higher positive heat of formation (267.6 kJ/mol) than 1,2,4-triazole (194.0 kJ/mol). Not unexpectedly the same relationship is found for pyrazole whose calculated heat of formation is more positive (183.7 kJ/mol) than that of imidazole (136.2 kJ/mol), which is in good agreement with the experimental value for pyrazole (179.4 kJ/mol) and imidazole (132.9 kJ/mol).[23]

The density is one of the most important physical properties of energetic salts. Values for **7**–**21** were measured using a gas pycnometer (Table 2) and found to fall in the range between 1.43 to 1.66 g/cm^3 which are considerably lower than the densities of the parent compounds, **2** (1.82 gcm^{-3}) and **5** (1.80 gcm^{-3}). The performance of a high explosive is measured by its detonation velocity, *vD* [m/s], and detonation pressure, *P* (Gpa).[24] These parameters are directly related to the oxygen balance (OB), density, and heat of formation. The detonation pressure and velocity (on the basis of traditional Chapman–Jouget thermodynamic detonation theory) were obtained by using Cheetah 4.0 (Table 2).[25] Neutral compounds **2** (P = 33.4 GPa, vD = 8793 ms^{-1}) and **5** (P = 33.0 GPa, vD = 8743 ms^{-1}) displayed detonation properties comparable with RDX (P = 33.8 GPa, vD = 8750 ms^{-1}). The calculated detonation pressures (P) for the new salts fall between 18.58 GPa (**11**) to 24.38 GPa (**14**), and the detonation velocities (vD) are distributed from 7282 ms^{-1} (**19**) to 8366 ms^{-1} (**14**). Although the denotation data are lower than the corresponding values for RDX, most of them are superior to TNT (P 20.6 GPa, vD 6850 ms^{-1}) and may well be of interest as potential energetic materials.

Table 2. Crystallographic data and structure refinement parameters.

	5	**10**
Formula	$C_2H_3N_5O_2$	$C_8H_{14}N_{20}O_4$
Molecular weight	129.09	454.39
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$
a [Å]	5.6122(3)	18.4760(7)
b [Å]	6.4941(3)	4.9003(2)
c [Å]	13.1089(6)	19.5452(7)
α [°]	90	90
β [°]	92.1370(10)	93.334(1)
γ [°]	90	90
V [Å^3]	477.44(4)	1766.59(12)
Z	4	4
T [K]	90(2)	90(2)
λ [Å]	0.71073	0.71073
$\rho_{\text{calcd.}}$ [Mg/m^3]	1.796	1.708
μ [mm^{-1}]	0.157	0.141
F(000)	264	936
Crystal size [mm]	0.60 × 0.27 × 0.15	0.30 × 0.07 × 0.03
θ range [°]	3.11 to 27.48	2.09 to 27.50
Index ranges	$-7 \le h \le 7$, $-8 \le k \le 8$, $-17 \le l \le 17$	$-24 \le h \le 24$, $-6 \le k \le 6$, $-25 \le l \le 25$
Reflections collected	6830	12773
Independent reflections	1099 [R(int) = 0.0161]	2039 [R(int) = 0.0340]
Data/restraints/parameters	1099/0/94	2039/0/173
GOF on F_2	1.068	1.022
R_1[a] [$I > 2\sigma(I)$]	0.0293	0.0370
wR_2[b] [$I > 2\sigma(I)$]	0.0783	0.0922
$\Delta\rho$ peak/hole [eÅ^{-3}]	0.295 and –0.247	0.248 and –0.218

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

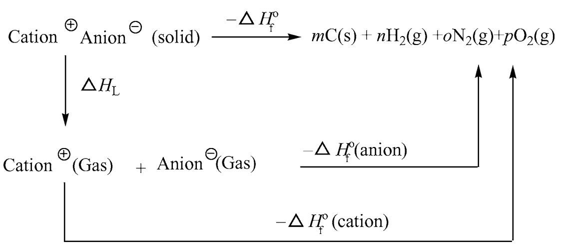
Compounds **17** and **20**, respective salts of the 3-methyl-1-amino-1,2,3-triazolium cation, are true ionic liquids with T_m = –33 and –45 °C; additionally they exhibit relatively high thermal decomposition temperatures at ca. 200 °C, positive heats of formation of ca. 3 kJ/g, detonation pressures at ca. 20 GPa, detonation velocities at ca. 7600 ms^{-1}, and densities at ca. 1.45 gcm^{-3}. These values, are in all cases, superior to TNT except for density (1.65 gcm^{-3}) and thermal stability, and they do have the advantage of being room temperature liquids.

Conclusions

1-Nitroamino-1,2,3-triazole (**5**), which contains five catenated nitrogen atoms, was synthesized and its zwitterionic structure was established using single-crystal X-ray analysis. The neutral compounds **2** and **5** displayed good detonation properties. A variety of new energetic salts based on both the 1-nitroamino-1,2,3-triazolate and 4-nitroamino-1,2,4-triazolate anions were synthesized and characterized. Relative to the parent compounds, **2** and **5**, the thermal stabilities of these salts were improved remarkably. Comparison of the salts of 1-nitroamino-1,2,3-triazolate and 4-nitroamino-1,2,4-triazolate having cations in common shows that while the 1,2,4-triazolates in general have higher decomposition temperatures, the 1,2,3-analogs invariably have higher positive heats of formation. The densities of the pairs of salts do not vary more than 0.1 g cm^{-3}; however, these small differences are reflected clearly in the detonation pressures. On the basis of a combination of theoretical and empirical calculations, all the salts are shown to have relatively high positive molar enthalpies of formation and moderate detonation properties. This work also concurs with previous observations that salts of energetic compounds normally exhibit higher thermal stabilities than the parent neutral compounds.

Computational Details

Computations were performed with the Gaussian 03 (revision D.01) suite of programs.[26] The geometric optimization of the structures based on single crystal structures, where available, and frequency analyses are carried out using B3-LYP functional with 6-31+G** basis set,[27] and single energy points were calculated at the MP$_2$(full)/6-311++G** level. Atomization energies were calculated by the G2 method.[28] All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.



Scheme 5. Born–Haber cycle for the formation of energetic salts.

On the basis of a Born–Haber energy cycle (Scheme 5), the heat of formation of a salt can be simplified by the formula:

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

where ΔH_L is the lattice energy of the ionic salts which could be predicted by the formula suggested by Jenkins et al.[29] as:

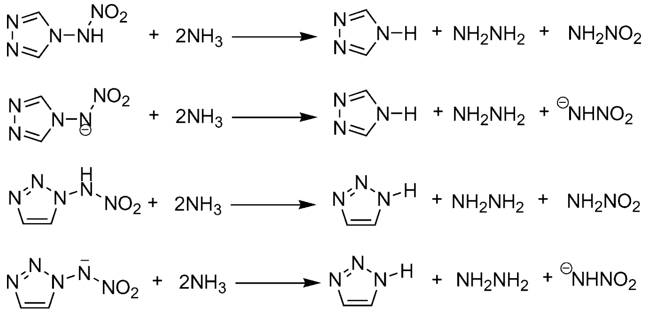
$$\Delta H_L = U_{POT} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \qquad \textbf{(A)}$$

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} (Equation **B**) has the form

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

where ρ_m/g cm^{-3} is the density, M_m is the chemical formula mass of the ionic material, and values for g and the coefficients γ/kJ mol^{-1} cm and δ/kJ mol^{-1} are taken from the literature.[29]

The heats of formation of the cations and anions are computed using the method of isodesmic reactions. The isodesmic reactions for **2**, and **5** and their anions are shown in Scheme 6. The enthalpy of 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, and other thermal factors. Thus, the heats of formation of the species being investigated can be readily extracted. With the value of the heats of formation and density of energetic salts, the expected detonation pressures (P) and detonation velocities (vD) were calculated on the basis of the traditional Chapman–Jouget thermodynamic detonation theory using Cheetah 4.0.[25a]



Scheme 6. Isodesmic reactions for **2** and **5** and their corresponding anions.

Experimental Section

Caution*:** Although none of the compounds described herein has exploded or detonated in the course of this research, these materials should be handled with extreme care using the best safety practices because their shock and impact sensitivities have not been extensively determined. ***1-Nitroamino-1,2,3- triazole (5) is extremely shock-sensitive, decomposing violently when the melting point was measured, and it has an impact sensitivity < 1 J. It should be handled in less than 10 mg amounts with eye protection, face shield, leather gloves. If the best safety practices are not observed, severe injury could result.

General Methods: ^{1}H and ^{13}C NMR spectra were recorded with a 300-MHz nuclear magnetic resonance spectrometer operating at 300.13, and 75.48 MHz, respectively, using [D$_6$]DMSO as solvent unless otherwise indicated. Chemical shifts are reported relative to Me$_4$Si. The melting and decomposition points were recorded with a differential scanning calorimeter (DSC) and a thermogravimetric analyzer (TGA) at a scan rate of 10 °C/min, respectively. IR spectra were recorded using KBr pellets for solids. Densities were measured at room temperature using a Micromeritics Accupyc 1330 gas pycnometer. Elemental analyses were obtained using a CE-440 elemental analyzer (EAI Exeter Analytical).

1-Amino-1,2,3-triazole,[30] 4-nitroamino-1,2,4-triazole[17] and its silver salt[13b] were synthesized on the basis of published procedures.

X-ray Analyses: Crystals of compound **5** (**10**) were removed from the flask, a suitable crystal selected, attached to a glass fiber, and data were collected at 90(2) K using a Bruker/Siemens SMART APEX instrument (Mo-K_α radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans 0.3° per frame for 5 (20) s, and a full sphere of data was collected. A total of 2400 frames was collected with a final resolution of 0.77 Å. Cell parameters were retrieved using SMART[31] software for **5** (**10**), and refined using SAINTPlus[32] on all observed reflections. Data reduction and correction for Lp and decay were performed using SAINTPlus software. Absorption corrections were applied using SADABS.[33] The structures were solved by direct methods and refined by least-squares method on F^2 using the SHELXTL program package.[34] Structures were solved in the space groups $P2_1/n$ (#14) and $C2/c$ (#15) for Compounds **5** and **10**, respectively, by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were freely refined (Table 2). No decomposition was observed during data collection.

CCDC-664575 (for **5**) and -664576 (for **10**) 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.

Preparation of 1-Nitroamino-1,2,3-triazole (5): 1-Amino-1,2,3-triazole (**4**) (1.68 g, 20 mmol) was dissolved in 95% sulfuric acid (8 mL). The resulting solution was cooled to 0 °C in an ice bath, and 70% concentrated nitric acid (8 mL) was added dropwise over a period of 15 min while maintaining the temperature below 2 °C. The mixture was stirred at 0 °C for 30 min and then warmed up slowly to room temperature. After stirring for additional 2 h at room temperature, the reaction mixture was poured onto ice water (80 mL), and extracted with ethyl acetate (30 mL × 4). The combined organic phase was washed with brine (20 mL × 2), dried with anhydrous Na_2SO_4, filtered, concentrated under reduced pressure, dried in vacuo to afford the analytically pure product (1.9 g, 74%) as colorless crystals, m.p. 105 °C (dec. explosively). IR (KBr): $\tilde{\nu}$ = 3159, 3033, 1944, 1774, 1566, 1414, 1320, 1088, 932, 848, 760, 490 cm^{-1}. ^1H NMR: δ = 9.06 (br. s, 1 H), 8.29 (d, J = 1.1 Hz, 1 H), 8.08 (d, J = 1.1 Hz, 1 H) ppm. ^{13}C NMR: δ = 132.4, 127.3 ppm. Because of its explosive nature, elemental analyses could not be accomplished. It was possible to store **5** at room temperature for several months without incident. ***However, this compound is extremely shock-sensitive and should be handled with all possible care.***

Preparation of Hydrazinium 4-Nitroamino-1,2,4-triazolate (7): 4-Nitroamino-1,2,4-triazole (**2**, 0.129 g, 1.0 mmol) was added to a solution of hydrazine (51% in water, 0.98 g, 10 mmol) in methanol (5 mL) at room temperature. The white solid dissolved slowly. The reaction mixture was stirred at room temperature for 4 h. The solvent was evacuated with high vacuum overnight and then the residue was recrystallized from methanol/ethyl ether to afford the title compound (0.14 g, 87%) as white solid, m.p. 135 °C. IR (KBr): $\tilde{\nu}$ = 3284, 3181, 3117, 1626, 1506, 1391, 1308, 1115, 1018, 851, 620 cm^{-1}. ^1H NMR: δ = 8.21 (s, 2 H), 6.89 (br. s, 2 H), 3.20 (br. s, 3 H) ppm. ^{13}C NMR: δ = 142.8 ppm. $C_2H_7N_7O_2$ (161.07): calcd. C 14.91, H 4.38, N 60.85; found C 14.91, H 4.39, N 60.28.

Preparation of Guanidinium 1-Nitroamino-1,2,3-triazolate (8): Solid 1-nitroamino-1,2,3-triazole (**5**) (0.129 g, 1.0 mmol) was added to a solution of guanidinium carbonate (0.09 g, 1.0 mmol) in methanol (10 mL) at room temperature with stirring. After stirring for 8 h at room temperature, the solvent was removed in vacuo and then the residue was recrystallized from methanol/ethyl ether to afford the title compound (0.185 g, 84%) as white solid, m.p. 189 °C. IR (KBr): $\tilde{\nu}$ = 3410, 3246, 3167, 1655, 1404, 1283, 1070, 876, 794 cm^{-1}. ^1H NMR: δ = 7.68 (s, 1 H), 7.54 (s, 1 H), 6.89 (s, 6 H) ppm. ^{13}C NMR: δ = 159.4, 132.5, 124.2 ppm. $C_3H_8N_8O_2$ (188.15): calcd. C 19.15, H 4.29, N 59.56; found C 19.21, H 4.15, N 58.19.

Preparation of Aminoguanidinium 1-Nitroamino-1,2,3-triazolate (9): Compound **9** was prepared following the procedure for **8**, from aminoguanidinium hydrogen carbonate (0.136 g, 1.0 mmol) and 1-nitroamino-1,2,3-triazole, **5**, (0.129 g, 1.0 mmol) to obtain colorless crystals (0.192 g, 95%), m.p. 71 °C. IR (KBr): $\tilde{\nu}$ = 3450, 3196, 2758, 1673, 1605, 1387, 1312, 1228, 955, 876, 595 cm^{-1}. ^1H NMR: δ = 8.56 (br. s, 1 H), 7.81 (s, 1 H), 7.63 (s, 1 H), 7.18 (br. s, 2 H), 6.73 (br. s, 2 H), 4.69 (s, 2 H) ppm. ^{13}C NMR: δ = 160.1, 133.0, 124.7 ppm. $C_3H_9N_9O_2$ (203.09): calcd. C 17.74, H 4.47, N 62.05; found C 18.17, H 4.45, N 62.16.

Preparation of 3,6-Diguanidino-1,2,4,5-tetrazinium 1-Nitroamino-1,2,3-triazolate (10): A solution of 1-nitroamino-1,2,3-triazole (**5**, 0.206 g, 1.6 mmol) in water (10 mL) was added to a suspension of 3,6-diguanidino-1,2,4,5-tetrazine (0.202 g, 0.8 mmol) in water (10 mL). The resulting mixture was heated to 80 °C and stirred for 2 h. After cooling to room temperature, **10** was precipitated directly from the reaction mixture as red needle crystals (suitable for X-ray single crystal analysis) (0.382 g, 94%), m.p. 226 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3351, 3091, 1699, 1613, 1566, 1408, 1273, 1038, 941, 801, 637 cm^{-1}. ^1H NMR: δ = 8.15 (br. s, 10 H), 7.79 (s, 2 H), 7.62 (s, 2 H) ppm. ^{13}C NMR: δ = 159.8, 155.6, 132.9, 124.7 ppm. $C_8H_{14}N_{20}O_4$ (454.33): calcd. C 21.15, H 3.11, N 61.66; found C 21.50, H 2.99, N 60.79.

Preparation of Imidazolium 1-Nitroamino-1,2,3-triazolate (11): The title compound **11** was prepared following the procedure for **8**, from imidazole (0.068 g, 1.0 mmol) and **5** (0.129 g, 1.0 mmol) to give colorless crystals (0.168 g, 85%). M.p. 86 °C. IR (KBr): $\tilde{\nu}$ = 3155, 2984, 2861, 2762, 2637, 1939, 1593, 1388, 1288, 1228, 1122, 1039, 829, 627 cm^{-1}. ^1H NMR: δ = 9.05 (s, 1 H), 7.67 (s, 1 H), 7.58 (s, 2 H), 7.54 (s, 1 H), 5.38 (br. s, 2 H) ppm. ^{13}C NMR: δ = 135.6, 132.5, 124.2, 120.5 ppm. $C_5H_7N_7O_2$ (197.15): calcd. C 30.46, H 3.58, N 49.73; found C 30.19, H 3.51, N 49.79.

General Procedure for the Preparation of 4-Nitroamino-1,2,4-triazolates 12–18 and 1-Nitroamino-1,2,3-triazolates 19–21: a solution of the corresponding halide salt (1 mmol) in water (5 mL) was slowly added to a suspension of the silver salt **3** (1 mmol) or **6** (1 mmol) in water (8 mL). The resulting reaction mixture was stirred in the absence of light for 6 h and filtered. The filtrate was concentrated under reduced pressure. The residue was recrystallized from methanol/ethyl ether to afford the corresponding product in excellent yield.

Guanidinium 4-Nitroamino-1,2,4-triazolate (12): White solid (0.167 g, 89%), m.p. 184 °C. IR (KBr): $\tilde{\nu}$ = 3465, 3108, 2814, 1700, 1663, 1506, 1401, 1316, 1070, 970, 864, 620 cm^{-1}. ^1H NMR: δ = 8.32 (s, 2 H), 6.92 (s, 6 H) ppm. ^{13}C NMR: δ = 159.2, 143.1 ppm. $C_3H_8N_8O_2$ (188.15): calcd. C 19.15, H 4.29, N 59.56; found C 19.07, H 4.18, N 59.62.

Aminoguanidinium 4-Nitroamino-1,2,4-triazolate (13): Colorless crystals (0.179 g, 88%), m.p. 138 °C. IR (KBr): $\tilde{\nu}$ = 3411, 3176, 3010, 2770, 1682, 1606, 1508, 1387, 1335, 1292, 1178, 941, 843, 621 cm^{-1}. ^1H NMR: δ = 8.59 (s, 1 H), 8.33 (s, 2 H), 7.23 (br. s, 2 H), 6.82 (br. s, 2 H), 4.69 (s, 2 H) ppm. ^{13}C NMR: δ = 160.1, 143.1 ppm. $C_3H_9N_9O_2$ (203.09): calcd. C 17.74, H 4.47, N 62.05; found C 17.99, H 4.54, N 62.67.

Triaminoguanidinium 4-Nitroamino-1,2,4-triazolate (14): White solid (0.193 g, 83%), m.p. 167 °C. IR (KBr): $\tilde{\nu}$ = 3319, 3213, 1686, 1616, 1503, 1400, 1325, 1178, 949, 840, 610 cm^{-1}. ^1H NMR: δ = 8.58 (br. s, 3 H), 8.30 (s, 2 H), 4.49 (br. s, 6 H) ppm. ^{13}C NMR: δ = 160.4, 143.1 ppm. $C_3H_{11}N_{11}O_2$ (233.11): calcd. C 15.45, H 4.75, N 66.07; found C 15.35, H 4.93, N 65.61.

***N*-Guanylurea 4-Nitroamino-1,2,4-triazolate (15):** Colorless crystal (0.194 g, 84%), m.p. 205 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3344, 3300, 3201, 1749, 1695, 1611, 1398, 1315, 1178, 1068, 620 cm^{-1}. ^1H NMR: δ = 8.22 (s, 2 H), 8.12 (br. s, 2 H), 7.07 (br. s, 1 H), 3.15 (br. s, 4 H) ppm. ^{13}C NMR: δ = 155.9, 155.7, 142.6 ppm. $C_4H_9N_9O_3$ (231.08): calcd. C 20.78, H 3.92, N 54.53; found C 20.69, H 3.90, N 54.17.

3,6-Diguanidino-1,2,4,5-tetrazinium 4-Nitroamino-1,2,4-triazolate (16): Orange solid (0.186 g, 82%), m.p. 211 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3380, 3195, 2801, 1699, 1606, 1428, 1300, 1176, 1070, 620 cm^{-1}. ^{1}H NMR: δ = 8.58 (s, 4 H), 7.94 (br. s, 8 H), 5.33 (br. s, 2 H) ppm. ^{13}C NMR: δ = 160.2, 156.5, 143.2 ppm. $C_8H_{14}N_{20}O_4$ (454.15): calcd. C 21.15, H 3.11, N 61.66; found C 20.84, H 3.23, N 59.58.

1-Amino-3-methyl-1,2,3-triazolium 4-Nitroamino-1,2,4-triazolate Monohydrate (17): Colorless liquid (0.223 g,91%), T_g = –33 °C. IR (KBr): $\tilde{\nu}$ = 3430, 3149, 3070, 1630, 1506, 1391, 1310, 1186, 1078, 814, 629 cm^{-1}. ^{1}H NMR: δ = 8.74 (s, 1 H), 8.54 (s, 1 H), 8.30 (s, 2 H), 8.17 (s, 2 H), 4.26 (s, 3 H) ppm. ^{13}C NMR: δ = 142.6, 132.7, 127.9 ppm. $C_5H_{11}N_9O_3$ (245.20): calcd. C 24.49, H 4.52, N 51.41; found C 24.54, H 4.26, N 51.63.

4-Amino-1-methyl-1,2,4-triazolium 4-Nitroamino-1,2,4-triazolate (18): White solid (0.202 g, 89%), m.p. 138 °C. IR (KBr): $\tilde{\nu}$ = 3318, 3095, 1624, 1506, 1390, 1294, 1071, 982, 617 cm^{-1}. ^{1}H NMR ([D$_6$]-DMSO): δ = 10.09 (s, 1 H), 9.08 (s, 1 H), 8.16 (s, 2 H), 6.98 (s, 2 H), 4.06 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 146.2, 144.2, 143.1 ppm. $C_5H_9N_9O_2$ (227.18): calcd. C 26.43, H 3.99, N 55.49; found C 26.38, H 3.93, N 55.37.

***N*-Guanylurea 1-Nitroamino-1,2,3-triazolate (19):** White solid (0.187 g, 81%), m.p. 142 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3366, 3160, 2779, 1746, 1700, 1604, 1453, 1386, 1342, 1067, 982, 611 cm^{-1}. ^{1}H NMR: δ = 7.72 (s, 1 H), 7.56 (s, 1 H), 7.60 (br. s, 7 H) ppm. ^{13}C NMR: δ = 158.0, 132.7, 131.7, 124.3 ppm. $C_4H_9N_9O_3$ (231.17): calcd. C 20.78, H 3.92, N 54.53; found C 20.43, H 3.83, N 52.89.

1-Amino-3-methyl-1,2,3-triazolium 1-Nitroamino-1,2,3-triazolate (20): Colorless liquid, yield (0.168 g, 85%), T_g = –47 °C. IR (KBr): $\tilde{\nu}$ = 3456, 3262, 3129, 1631, 1537, 1385, 1304, 1228, 990, 872, 798, 633 cm^{-1}. ^{1}H NMR: δ = 8.75 (s, 1 H), 8.56 (s, 1 H), 7.64 (s, 1 H), 7.52 (s, 1 H), 5.65 (br. s, 2 H), 4.25 (s, 3 H) ppm. ^{13}C NMR: δ = 132.9, 132.7, 127.8, 124.6 ppm. $C_5H_9N_9O_2$ (227.18): calcd. C 26.43, H 3.99, N 55.49; found C 26.35, H 4.27, N 56.75.

4-Amino-1-methyl-1,2,4-triazolium 1-Nitroamino-1,2,3-triazolate (21): Colorless crystals (0.190 g, 96%), m.p. 92 °C. IR (KBr): $\tilde{\nu}$ = 3324, 3213, 3142, 3100, 1626, 1395, 1285, 1165, 980, 874, 615 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 10.12 (s, 1 H), 9.05 (s, 1 H), 7.64 (s, 1 H), 7.52 (s, 1 H), 7.01 (s, 2 H), 4.07 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = 146.1, 144.2, 132.4, 124.1 ppm. $C_5H_9N_9O_2$ (227.18): calcd. C 26.43, H 3.99, N 55.49; found C 26.81, H 3.92, N 54.76.

Supporting Information (see also the footnote on the first page of this article): Ab initio computational data.

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