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Highly Dense Nitranilates-Containing Nitrogen-Rich Cations

Yangen Huang, Haixiang Gao, Brendan Twamley, and Jean′ne M. Shreeve*[a]

Abstract: High density energetic salts containing nitrogen-rich cations and the nitranilic anion were readily synthesized in high yield by metathesis reactions of sodium nitranilate **2** and an appropriate halide. All of the new compounds were fully characterized by elemental, spectral (IR, ^{1}H, ^{13}C NMR), and thermal (DSC) analyses. The structure of hydrazinium nitranilate (**4**) was also determined by single-crystal X-ray analysis. The high symmetry and oxygen content of the anion give these salts extensive hydrogen bonding capability which further results in the high densities, low water solubilities, and high thermal stabilities ($T_d > 200\,°C$) of these compounds. Theoretical performance calculations were carried out by using Gaussian 03 and Cheetah 5.0. The calculated detonation pressures (P) for these new salts fall between 17.5 GPa (**10**) and 31.7 GPa (**4**), and the detonation velocities (νD) range between 7022 m s^{-1} (**13**) and 8638 m s^{-1} (**4**).

Keywords: energetic materials · nitranilate · nitrogen · nitrogen-rich compounds

Introduction

Energetic materials as controllable storage systems for relatively large amounts of chemical energy are widely applied in military and industrial venues.[1] To meet the continuing need for improved energetic materials, the synthesis of energetic compounds with higher performance or enhanced insensitivity to thermal or shock insults has attracted considerable interest. Based on the special properties of ionic compounds such as lower vapor pressures and higher densities than their atomically similar nonionic analogues, a series of energetic salts as a unique class of high energetic materials has been developed by several groups.[2,3] In these ionic species, nitrogen-containing heterocycle-based salts are predominant. The nitrogen-containing heterocyclic compounds not only can act as cations, for example, 3,4,5-triamino-1,2,4-triazole and 1,5-diaminotetrazole, but also as anions, for example, 2,4,6-trinitroimidazole, 5-nitrotetrazole, and bistetrazole. Some of these salts display attractive explosive properties that make them promising high-energy materials with potential applications. There are several criteria for a new energetic candidate—comparable explosive performance with RDX (1,3,5-trinitro-1,3,5-triazacyclohexane), good thermal stability, low shock and friction sensitivities, hydrolytic stability, low (no) solubility in water, and convenient synthesis at low cost.[3a]

Methods are available now to predict performance and safety characteristics of energetic materials that can guide chemists in designing and screening new high energetic material candidates. Based on these predictive methods, the composition, heat of formation, and density of an energetic material dominate its performance; for example, the detonation pressure (P) is roughly proportional to the square of the density, and the detonation velocity (D) is also proportional to the density.[4] Accurate density estimation of energetic materials can be achieved by several methods.[5] It has long been recognized that a molecule with higher symmetry is likely to have a higher density and the presence of strong intra- or inter-hydrogen bonding also contributes markedly to the density through much more efficient packing in the crystal lattice. Hydrogen bonding also has a special impact on other physical and chemical properties of an explosive. The attractive forces confining the respective species in the crystal lattice are high. Because the solubility of a compound can legitimately be regarded as a partitioning of the compound between a crystal lattice and solvent, explosives with very strong bonding normally have poor solubility in common solvents. For the same reason, they also have very high or no observable melting points and high-impact insen-

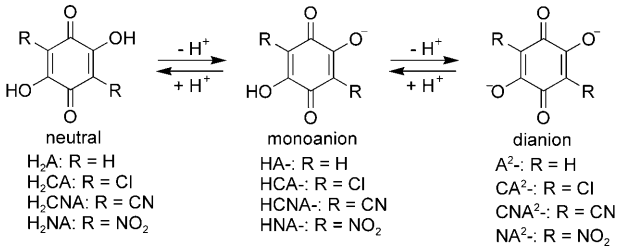
[a] Dr. Y. Huang, H. Gao, Dr. B. Twamley, Prof. Dr. J. M. Shreeve
Department of Chemistry, University of Idaho, Moscow, Idaho, 83844-2343 (USA)
Fax: (+86) 208-885-9146
E-mail: jshreeve@uidaho.edu

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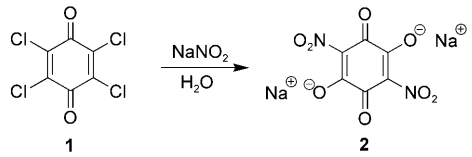
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sitivities as well as low toxicities due to their low solubility in water and low volatilities. Anilic acid and its analogues (Scheme 1) contain a variety of binding sites available to



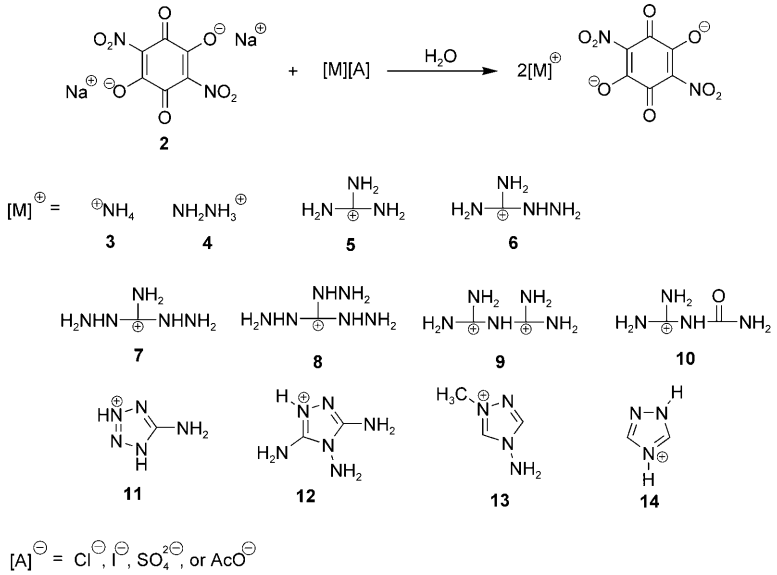
Scheme 1. Anilic acid and its analogues.



Scheme 2. Syntheses of sodium nitranilate **2**.

halide salts in high yields (Scheme 3). Typically, an equivalent or a slight excess of aqueous ammonium chloride was added to a hot aqueous solution of **2**. After stirring for 2 h at 50–60 °C, the reaction mixture was cooled to room temperature and allowed to stand overnight. The product was collected by filtration as a crystalline solid in high purity. No

metal cations in various oxidation states, which causes them to act as versatile multifunctional ligands, and many metal complexes containing such ligands have been reported,[6] for example, hydrogen-bonded electron-transfer complexes have been synthesized.[7] Among anilic acid and its analogues, nitroanilic acid is an attractive candidate for making high energetic density salts when considering its high symmetry, oxygen content, and acidity (pK_{a1} −3.0, pK_{a2} −0.5[8]). Lead nitroanilate has been used as an improvised primary explosive for many years, but only alkali and alkaline earth metal nitranilates had hitherto been reported.[9] Herein, a series of nitranilates with nitrogen-rich cations have been synthesized and fully characterized. The detonation properties of these nitranilates have been calculated, and these suggest that they can be treated as stable energetic materials.



Scheme 3. Synthesis of energetic nitranilates **3**–**14**.

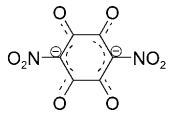
Results and Discussion

The solubilities of potassium and sodium nitranilates at 30 °C are only 0.724 and 0.567 g per 100 g H_2O, respectively,[10] which suggest that nitranilates containing nitrogen-rich cations might be synthesized by metathesis reactions between sodium nitranilate and organic halide salts. Crystalline sodium nitranilate (**2**) can be obtained by treating chloranil (**1**) in hot aqueous sodium nitrite solution (Scheme 2). All nitranilate salts containing nitrogen-rich cations can be easily obtained by the reactions of **2** with the corresponding further recrystallization was required. The driving force for these reactions is the lower solubilities of the products relative to that of sodium nitranilate.

All these new nitranilate salts, namely, ammonium (**3**), hydrazinium (**4**), guanidinium (**5**), aminoguanidinium (**6**), diaminoguanidinium (**7**), triaminoguanidinium (**8**), biguanidinium (**9**), aminocarbonylguanidinium (**10**), 5-aminotetrazolium (**11**), guanizinium (**12**), 1-methyl-4-amino-1,2,4-triazolium (**13**), and 1,2,4-triazolium (**14**) were characterized by IR, and ^1H and ^{13}C NMR spectroscopy, and elemental analyses. The IR spectra exhibit several main absorption bands around 1600, 1450, and 1250 cm^{-1}, which are attributed to the anion. The intense absorption bands in the range 3100–3430 cm^{-1} can be assigned to the N–H bonds of the cations. In the ^1H NMR spectrum, only hydrogen signals of the cation were observed and easily assigned since there is no proton on the anion. In the ^{13}C NMR spectrum, only two

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Scheme 4.

signals for the anion can be detected at about 160 and 135 ppm, in addition to the signals of the cation, which indicates a high delocalization of the negative charge in the ring system as confirmed by the crystal structure (Scheme 4).

Crystals of **4** suitable for single-crystal X-ray analysis were obtained by reacting sodium nitranilate with five equivalents of hydrazinium acetate in dilute aqueous solution. The resultant product, orange parallelepipeds, crystallized in the triclinic $P\bar{1}$ space group with two independent hydrazinium cations per dianionic nitranilate anion. The structure is shown in Figure 1a. The N–N distance in the cation is similar to literature values (1.42–1.45 Å)[11] and the dianionic nitranilate has alternating carbon bond lengths. However, the ring forms an envelope conformation at C5 with a dihedral angle of 14.4° (C6-C5-C4 to ring plane). In other nitranilates,[12] the C6–C1/C5–C4 and C1–C2/C4–C3 bond lengths are comparable. In **4**, though, the C6–C1 and C1–C2 bond lengths differ by about 0.11 Å. This difference may be the result of strong hydrogen bonding assisting charge delocalization.

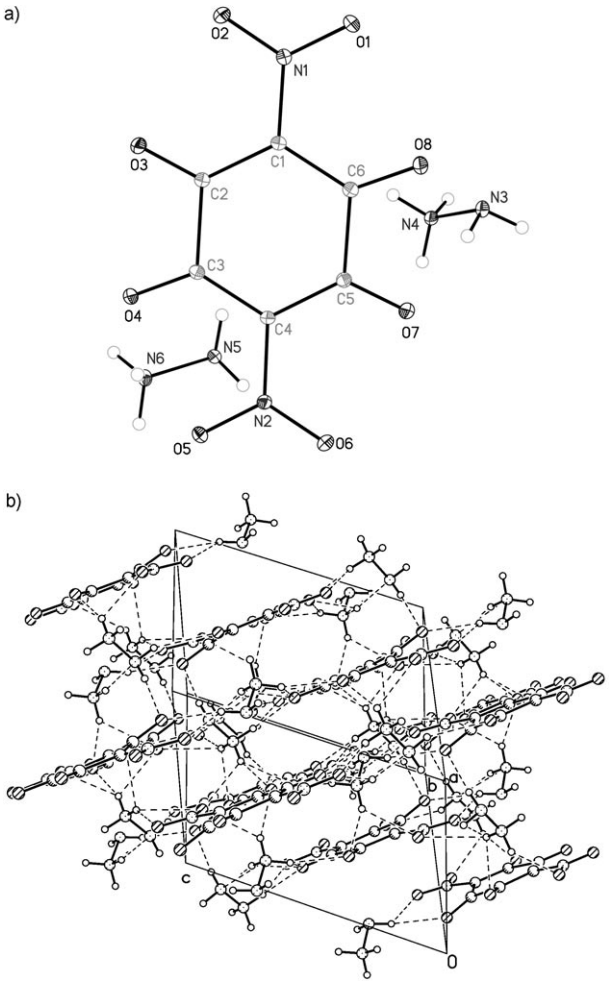


Figure 1. a) Thermal ellipsoid plot (30%) and labeling scheme for hydrazinium nitranilate (**4**). Hydrogen atoms included but are unlabelled for clarity. b) Ball-and-stick packing diagram of **4** viewed down the *c* axis. Dashed lines indicate strong hydrogen bonding.

There is extensive hydrogen bonding. Each amino hydrogen atom forms a bifurcated H-bond (mainly with the nitro groups), but N4 forms a trifurcated H-bond (N4···O5 2.872(1); N4···O4 2.921(1); N4···O1 2.884(1) Å). O3 is involved in three other bifurcated H-bonding interactions (N4···O3 2.762(1); N6···O3 2.782(1) Å). These interactions lock this side of the ring in position and may assist in charge delocalization. The other side has less H-bonding, where O7 is an acceptor for both a strong and a bifurcated hydrogen bond (N3···O7 2.995(1); N5···O6, O7 2.926(1), 2.897(1) Å). O8 is involved in two different parts of bifurcated H-bonding (N3···O8 3.139(1); N4···O8 2.996(1) Å). This hydrogen bonding motif builds up a complex 3D network that forms a honeycomb structure with planes parallel to the (4,4,4) index and with about 3 Å between the planes as shown in Figure 1b (CCDC 703398 (**4**) contains 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).

As one of the most important physical properties of energetic salts, densities for **3**–**14** were measured by using a gas pycnometer (Table 1) and found to fall in the range between 1.62 and 1.91 g cm^{-3}, which places them in a class of relatively dense compounds. Hydrazinium nitranilate (**4**) has the highest density at 1.91 g cm^{-3} (from X-ray data). The high density presumably was caused by the high symmetry of the anion and the extensive presence of intra- and intermolecular hydrogen bonds. The oxygen balances of these salts were also calculated (Table 1) to fall between −48 and −86% (Table 1), which are highly negative and similar to those of TNT (Ω = −74%).

Table 1. Thermal properties of energetic nitranilates.

	ρ[a]	T_m[b]	T_d[c]	Ω[d]	$\Delta_f H_{cation}$[e]	ΔH_L[f]	$\Delta_f H$[e]	P[g]	vD[h]
3	1.85	–	309	−48	626.4	1431.1	−829.7	23.6	7832
4	1.91	–	213	−49	770.0	1391.1	−542.1	31.7	8638
5	1.86	–	333	−64	575.9	1292.7	−832.0	23.5	8001
6	1.70	–	228	−63	667.4	1210.8	−567.0	20.0	7523
7	1.72	–	207	−63	769.0	1181.3	−334.3	23.0	7956
8	1.62	–	205	−62	871.5	1123.6	−71.6	21.5	7742
9	1.83	178	265	−60	1618.2	1955.4	−1028.2	18.5	7327
10	1.74	130	263	−63	350.6	1158.9	−1148.7	17.5	7183
11	1.70	–	216	−48	975.6	1185.1	75.1	22.0	7566
12	1.71	–	302	−66	842.0	1127.7	−134.7	20.4	7529
13	1.67	–	217	−86	895.6	1149.0	−48.8	20.3	7022
14	1.80	–	269	−70	835.0	1250.1	−271.1	20.0	7314

[a] Density [g cm^{-3}]. [b] Melting point [°C]. [c] Decomposition temperature [°C]. [d] Oxygen balance (%), for $C_aH_bO_cN_d$: = 1600(c-2a- b/2)/MW, MW = molecular weight of salt. [e] Heat of formation [kJ mol^{-1}]; $\Delta_f H_{anion} = -690.99$ kJ mol^{-1}. [f] Lattice energy [kJ mol^{-1}]. [g] Detonation pressure [GPa]. [h] Detonation velocity [m s^{-1}].

The thermal stabilities of all nitranilates (**3**–**14**) were determined by using DSC measurements. Except for **9** and **10**, which have clean sharp melting points at 178 and 130 °C, re-

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spectively, all of the compounds (**3**–**8**, **11**–**14**) decomposed without melting. The decomposition temperatures of these salts exceed 200 °C ranging from 205 to 333 °C. The stabilities of these salts are dominated by the structure of their cations. Nitranilates with highly symmetric ammonium, guanidinium, and guanizinium cations have decomposition temperatures above 300 °C. These relatively high stabilities may also arise from the extensive presence of hydrogen bonds.

The heat of formation of the nitranilic dianion was calculated by using the Gaussian 03 (Revision D.01) suite of programs.[13] Then the standard enthalpies of formation (ΔH_f) for all the new salts were calculated by using Born–Haber energy cycles (See Experimental Section). The calculated ΔH_f for nitranilic dianion is $-690.99\ kJ\,mol^{-1}$, which is highly negative due to its low nitrogen content and this also results in very negative ΔH_f for all the salts. With densities and heats of formation of all salts in hand, the detonation performance parameters (pressure and velocity) for each salt was calculated with Cheetah 5.0 (based on traditional Chapman–Jouget thermodynamic detonation theory).[14] The calculated detonation pressures (P) for the new salts fall between 17.5 GPa (**10**) and 31.7 GPa (**4**), and the detonation velocities (vD) are distributed from $7022\ m\,s^{-1}$ (**13**) to $8638\ m\,s^{-1}$ (**4**). Although the enthalpies of formation and oxygen balances for most of the salts are highly negative, the detonation performances are comparable to TNT (P 20.6 GPa, vD $6850\ m\,s^{-1}$) due to their high density values. Hydrazinium nitranilate (**4**, $1.91\ g\,cm^{-3}$ from X-ray data) exhibits the highest performance properties (P 31.7 GPa, vD $8638\ m\,s^{-1}$), which are only slightly lower than RDX (P 34.4 GPa, vD $8750\ m\,s^{-1}$). Impact testing for **4** was carried out with a BAM fall hammer in accordance with the BAM method.[15] No detonations were observed in the drop hammer tests. However, **4** was found to be decomposed when impacted by a 5 kg mass falling through 28 cm equivalent to an impact sensitivity of about 14 J, which is close to that of TNT (15 J) and higher than RDX (7.4 J).[16]

Conclusions

A family of simple energetic compounds based on the nitranilic anion and nitrogen-rich cations has been synthesized from readily available materials in moderate to excellent yields. Each salt was fully characterized by analytical and spectroscopic methods. The structure of **4** was also determined by X-ray diffraction techniques. The extensive presence of intra- and intermolecular hydrogen bonds gives these salts high densities, low water solubilities, and high thermal stabilities. The calculated detonation parameters of all new salts by Cheetah 5.0 reveal that their performances are similar or higher than that of conventional explosives such as TNT.

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 since their nitrogen content is very high.

General methods: ^1H and ^{13}C NMR spectra were recorded on 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 were reported relative to Me_4Si. The melting and decomposition points were recorded on a differential scanning calorimeter (DSC) at a scan rate of $10\ °C\,min^{-1}$ in closed Al containers with a nitrogen flow of $50\ mL\,min^{-1}$. The melting points and the temperatures of decomposition are given as onset temperatures. IR spectra were recorded by using KBr pellets. Densities were measured at room temperature using a Micromeritics Accupyc 1330 gas pycnometer. Elemental analyses were obtained by using a CE-440 elemental analyzer (EAI Exeter Analytical).

X-ray analyses: Crystals of compound **4** were removed from the flask, a suitable crystal was selected, attached to a glass fiber, and data were collected at 90(2) K 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 0.3° per frame for 10 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 by using SMART[17] software and refined by using SAINTPlus[18] on all observed reflections. Data reduction and correction for Lp and decay were performed by using the SAINTPlus software. Absorption corrections were applied by using SADABS.[19] The structure was solved by direct methods and refined by least squares method on F^2 using the SHELXTL program package.[20] The structure was solved in the space group $P\bar{1}$ (no. 2) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located and refined. No decomposition was observed during data collection. De-

Table 2. Crystallographic data and structure refinement parameters.

	4
formula	$C_6H_{10}N_6O_8$
molecular weight	294.20
crystal system, space group	triclinic, $P\bar{1}$
a [Å]	6.8046(3)
b [Å]	8.8110(4)
c [Å]	10.0416(4)
α [°]	67.7367(5)
β [°]	75.4929(5)
γ [°]	67.9690(5)
V [Å^3]	512.34(4)
Z	2
T [K]	90(2)
λ [Å]	0.71073
ρ_{calcd} [$Mg\,m^{-3}$]	1.907
μ [mm^{-1}]	0.177
$F(000)$	304
crystal size [mm^3]	$0.29\times0.23\times0.19$
θ range [°]	2.21 to 27.48
index ranges	$-8\le h\le 8$ $-11\le k\le 11$ $-13\le l\le 13$
no. reflections collected	6714
no. independent reflections	2351 [R(int) = 0.0131]
data/restraints/parameters	2351/0/221
GOF on F^2	1.043
R_1[a] [$I>2\sigma(I)$]	0.0295
wR_2[a] [$I>2\sigma(I)$]	0.0848
$\Delta\rho$ peak/hole ($e\,Å^{-3}$)	0.414 and −0.290

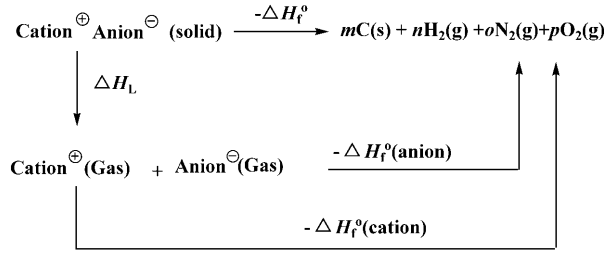
[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

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tails of the data collection and refinement are given in Table 2. Further details are provided in the Supporting Information.

Computational details: Computations were performed with the Gaussian 03 (Revision D.01) suite of programs.[13] The geometric optimization of the structures based on single-crystal structures, where available, and frequency analyses were carried out using the B3LYP functional with 6–31+G** basis set,[21] and single energy points were calculated at the MP_2/6–311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.



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

Based on a Born–Haber energy cycle (Scheme 5), the heat of formation of a salt can be simplified by the formula given in Equation (1):

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

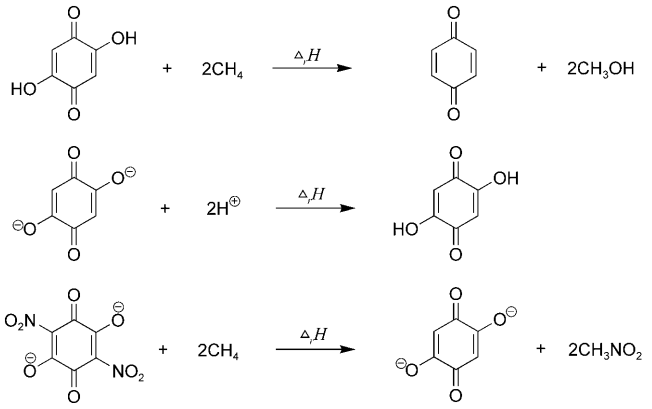
where ΔH_L is the lattice energy of the ionic salts, which could be predicted by using the formula suggested by Jenkins et al.[22] [Eq. (2)]:

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

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

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

where ρ_m [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.[22]



Scheme 6. Isodesmic reactions for calculating the heat of formation of nitranilic anion.

The heats of formation of the cations and anions were computed by using the method of isodesmic reactions. The isodesmic reactions for nitranilic anions are shown in Scheme 6. The enthalpy of reaction ($\Delta_r H^\circ_{298}$) is obtained by combining the MP2/6–311++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 the energetic salts, the detonation pressures (P) and detonation velocities (vD) were calculated based on the traditional Chapman–Jouget thermodynamic detonation theory using Cheetah 5.0.[14a]

Synthesis of sodium nitranilate (2):[8] Chloranil powder (2 g, 8.1 mmol) was added at room temperature to a solution of sodium nitrite (5 g, 72 mmol) in water (200 mL). The reaction mixture was gradually heated to reflux. After stirring for 2 h at reflux, the clear deep orange reaction mixture was concentrated to 100 mL, and then cooled to 5 °C where a yellow-orange crystalline precipitate was formed. It was collected by filtration, washed with cold water (20 mL), dried in vacuum to afford the product (1.2 g, 54 %). No further purification was needed.

Synthesis of ammonium nitranilate (3): An aqueous solution (5 mL) of ammonium chloride (267 mg, 5.0 mmol) was added to a suspension of **2** (274 mg, 1.0 mmol) in water (10 mL). The resulting mixture was heated (ca. 60 °C) until all of the solid dissolved, stirred for 1 h, cooled to 5 °C, and allowed to stand overnight. The precipitate was collected by filtration to afford orange needle crystals (260 mg, 98 %), $\rho = 1.852$ g cm^{-3}, m.p. 309 °C (decomp); IR (KBr): $\tilde{\nu} = 3489, 3197, 1594, 1420, 1248, 1013, 768$ cm^{-1}; ^{1}H NMR: $\delta = 7.28$ (s, 8H) ppm; ^{13}C NMR: $\delta = 169.8, 134.4$ ppm; elemental analysis calcd (%) for $C_6H_8N_4O_8$ (MW = 264.15): C 27.28, H 3.05, N 21.21; found: C 27.21, H 2.96, N 20.28.

Synthesis of hydrazinium nitranilate (4): An aqueous solution (10 mL) of hydrazinium acetate (556 mg, 4.0 mmol) was added to a hot aqueous solution of **2** (274 mg, 1.0 mmol) (15 mL). The resulting reaction mixture was put into a refrigerator (ca. 5 °C) for two days. Orange crystals suitable for X-ray were collected by filtration (270 mg, 92 %), $\rho = 1.891$ g cm^{-3}, m.p. 213 °C (decomp); IR (KBr): $\tilde{\nu} =$ 3470, 3348, 3302, 3192, 3079, 1620, 1569, 1521, 1427, 1252, 1079, 1018, 966, 771 cm^{-1}; ^{1}H NMR: $\delta = 7.18$ (br, 6H), 3.35 (br, 4H) ppm; ^{13}C NMR: $\delta = 171.7, 169.8, 134.6$ ppm; elemental analysis calcd (%) for $C_6H_{10}N_6O_8$ (MW = 294.18): C 24.50, H 3.43, N 28.57; found: C 24.14, H 3.30, N 28.22.

Guanidinium nitranilate (5): An aqueous solution (5 mL) of guanidinium chloride (191 mg, 2.0 mmol) was added to an aqueous suspension of **2** (274 mg, 1.0 mmol) in water (6 mL). The resulting mixture was heated (ca. 60 °C) until all solids were dissolved. It was cooled to room temperature and allowed to stand overnight. The precipitate was filtered, washed with cold water, and dried in vacuum to afford **5** (323 mg, 93 %) as a brown crystalline solid, $\rho = 1.856$ g cm^{-3}, m.p. 333 °C (decomp); IR (KBr): $\tilde{\nu} = 3414, 3204, 1655, 1619, 1567, 1418, 1234, 1015, 768$ cm^{-1}; ^{1}H NMR: $\delta = 7.01$ (s, 12H) ppm; ^{13}C NMR: $\delta = 169.6, 159.3, 134.8$ ppm; elemental analysis (%) calcd for $C_8H_{12}N_8O_8$ (MW = 348.23): C 27.59, H 3.47, N 32.18; found: C 27.23, H 3.43, N 31.93.

Aminoguanidinium nitranilate (6): Compound **6** was synthesized by the same method as for **5** using 1.0 equivalent of aminoguanidinium chloride. Orange crystalline needles, yield 85 %, $\rho = 1.703$ g cm^{-3}, m.p. 228 °C (decomp); IR (KBr): $\tilde{\nu} = 3414, 3339, 3258, 1621, 1574, 1457, 1254, 1018, 763$ cm^{-1}; ^{1}H NMR: $\delta = 8.74$ (s, 2H), 7.22 (s, 4H), 7.05 (s, 4H), 4.68 (s, 4H) ppm; ^{13}C NMR: $\delta = 169.7, 160.2, 134.8$ ppm; elemental analysis (%) calcd for $C_8H_{14}N_{10}O_8$ (MW = 378.26): C 25.40, H 3.73, N 37.03; found: C 25.11, H 3.63, N 37.31.

Diaminoguanidinium nitranilate (7): Compound **7** was synthesized by the same method as for **5** using 1.0 equivalent of diaminoguanidinium chloride. Brown crystalline needles, yield 97 %, $\rho = 1.72$ g cm^{-3}, m.p. 207 °C (decomp); IR (KBr): $\tilde{\nu} = 3408, 3366, 3316, 1637, 1587, 1460, 1264, 1175, 994, 899$ cm^{-1}; ^{1}H NMR: $\delta = 8.65$ (s, 4H), 7.18 (s, 4H), 4.59 (s, 8H) ppm; ^{13}C NMR: $\delta = 169.7, 161.1, 135.0$ ppm; elemental analysis (%) calcd for $C_8H_{16}N_{12}O_8$ (MW = 408.29): C 23.53, H 3.95, N 41.17; found: C 23.06, H 3.90, N 40.71.

Triaminoguanidinium nitranilate (8): Compound **8** was synthesized by the same method as for **5** using 1.0 equivalent of triaminoguanidinium chloride. Yellow crystalline needles, yield 95 %, $\rho = 1.62$ g cm^{-3}, m.p.

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205 °C (decomp); IR (KBr): $\tilde{\nu}$ = 3464, 3330, 3206, 1690, 1605, 1456, 1306, 1132, 994, 762, 643 cm^{-1}; ^1H NMR: δ = 8.57 (s, 6H), 4.49 (s, 12H) ppm; ^{13}C NMR: δ = 169.7, 160.4, 135.2 ppm; elemental analysis (%) calcd for $C_8H_{18}N_{14}O_8$ (MW = 438.32): C 21.92, H 4.14, N 44.74; found: C 21.55, H 4.21, N 44.26.

Biguanidinium nitranilate monohydrate (9): Compound **9** was synthesized by the same method as for **5** using 1.0 equivalent of biguanidinium sulfate. Reddish-orange crystalline needles, yield 86%, ρ = 1.825 $g\,cm^{-3}$, m.p. 178 °C, T_d = 265 °C; IR (KBr): $\tilde{\nu}$ = 3462, 3333, 3157, 2689, 1734, 1664, 1592, 1516, 1458, 1287, 1022, 778 cm^{-1}; ^1H NMR: δ = 8.09 (s, 4H), 4.33 (s, 4H) ppm; ^{13}C NMR: δ = 168.8, 157.2, 134.2 ppm; elemental analysis (%) calcd for $C_8H_{11}N_7O_9$ (MW = 349.21): C 27.51, H 3.17, N 28.08; found: C 27.34, H 3.09, N 27.74.

Aminocarbonylguanidinium nitranilate monohydrate (10): Compound **10** was synthesized by the same method as for **5** using 1.0 equivalent of aminocarbonylguanidinium chloride. Orange solid, yield 82%, ρ = 1.742 $g\,cm^{-3}$, m.p. 130 °C, T_d = 263 °C; IR (KBr): $\tilde{\nu}$ = 3433, 3347, 3197, 1736, 1695, 1587, 1456, 1335, 1251, 1024, 929, 766 cm^{-1}; ^1H NMR: δ = 10.28 (s, 2H), 8.17 (s, 8H), 7.21 (s, 4H) ppm; ^{13}C NMR: δ = 169.6, 156.9, 155.9, 134.4 ppm; elemental analysis (%) calcd for $C_{10}H_{16}N_{10}O_{11}$ (MW = 452.29): C 26.56, H 3.57, N 30.97; found: C 26.80, H 3.27, N 31.86.

5-Aminotetrazolium nitranilate (11): Compound **11** was synthesized by the same method as for **5** using 1.0 equivalent of 5-aminotetrazolium chloride. Brown crystalline needles, yield 96%, ρ = 1.697 $g\,cm^{-3}$, m.p. 216 °C (decomp); IR (KBr): $\tilde{\nu}$ = 3335, 3173, 2986, 2833, 1696, 1626, 1586, 1452, 1312, 1256, 1026, 789 cm^{-1}; ^1H NMR: δ = 7.98 (s, 4H) ppm; ^{13}C NMR: δ = 166.3, 156.8, 132.9 ppm; elemental analysis (%) calcd for $C_8H_8N_{12}O_8$ (MW = 400.22): C 24.01, H 2.01, N 42.00; found: C 23.64, H 1.99, N 41.16.

3,4,5-Triamino-1,2,4-triazolium nitranilate (12): Compound **12** was synthesized by the same method as for **5** using 1.0 equivalent of guanizinium chloride. Orange crystals, yield 96%, ρ = 1.713 $g\,cm^{-3}$, m.p. 302 °C (decomp); IR (KBr): $\tilde{\nu}$ = 3426, 3355, 3290, 3183, 3022, 1699, 1602, 1526, 1457, 1264, 1022, 802, 770 cm^{-1}; ^1H NMR: δ = 7.06 (s, 8H), 5.66 (s, 4H) ppm; ^{13}C NMR: δ = 169.7, 151.3, 134.8 ppm; elemental analysis (%) calcd for $C_{10}H_{14}N_{14}O_8$ (MW = 458.31): C 26.21, H 3.08, N 42.79; found: C 25.97, H 2.96, N 42.24.

1-Methyl-4-amino-1,2,4-triazolium nitranilate (13): Compound **13** was synthesized by the same method as for **5** using 1.0 equivalent of 1-methyl-4-amino-1,2,4-triazolium iodide. Orange crystalline needles, yield 94%, ρ = 1.671 $g\,cm^{-3}$, m.p. 217 °C (decomp); IR (KBr): $\tilde{\nu}$ = 3435, 3275, 3150, 3113, 3047, 1627, 1562, 1434, 1287, 1254, 1174, 997, 764 cm^{-1}; ^1H NMR: δ = 10.19 (s, 2H), 9.16 (s, 2H), 7.05 (s, 4H), 4.04 (s, 6H) ppm; ^{13}C NMR: δ = 169.8, 146.3, 144.4, 134.9, 40.2 ppm; elemental analysis (%) calcd for $C_{12}H_{14}N_{10}O_8$ (MW = 426.30): C 33.81, H 3.31, N 32.86; found: C 33.38, H 3.14, N 32.21.

1,2,4-Triazolium nitranilate (14): Compound **14** was synthesized by the same method as for **5** using 1.0 equivalent of 1,2,4-triazolium chloride. Red crystalline solid, yield 87%, ρ = 1.799 $g\,cm^{-3}$, m.p. 269 °C (decomp); IR (KBr): $\tilde{\nu}$ = 3119, 2949, 2800, 1595, 1526, 1475, 1316, 1035, 947, 881, 632 cm^{-1}; ^1H NMR: δ = 9.87 (s, 4H), 9.07 (s, 4H) ppm; ^{13}C NMR: δ = 167.5, 145.5, 133.5 ppm; elemental analysis (%) calcd for $C_{10}H_8N_8O_8$ (MW = 368.22): C 32.62, H 2.19, N 30.43; found: C 32.66, H 2.06, N 29.81.

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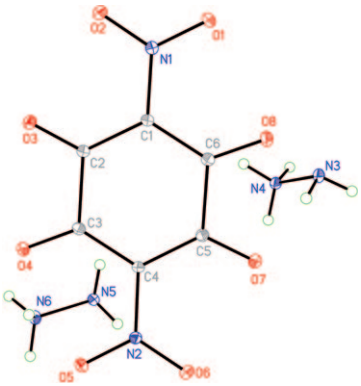
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Highly Dense Nitranilates-Containing Nitrogen-Rich Cations



More explosive than TNT? High density energetic salts containing nitrogen-rich cations and nitranilic anion (see figure) were readily synthesized. The highly symmetric and oxygen-containing anion makes these compounds have high densities, low water solubilities, and high thermal stabilities ($T_d >$ 200 °C). Theoretical performance calculations indicate their potential applications as energetic materials.

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