3-Amino-6-nitroamino-tetrazine (ANAT)-based energetic salts†

Haixiang Gao,[a] Ruihu Wang,[a] Brendan Twamley,[a] Michael A. Hiskey[b] and Jean'ne M. Shreeve*[a]

The synthesis and properties of several new high-nitrogen materials with 3-amino-6-nitroamino-tetrazine (ANAT) as the anion are reported; all salts were fully characterized by IR and NMR spectroscopy, and elemental analysis.

There has been significant progress in the development of new energetic compounds for use in a variety of applications, e.g., as aerospace propellants,[1] solid fuels in micropropulsion systems,[2] smoke-free pyrotechnic fuels,[3] and fire extinguishers on board military aircraft.[4] The synthesis of energetic salts as an unique class of high energetic materials has received increased interest over the past decade.[5] This is primarily because salt-based energetic materials often possess advantages over non-ionic molecules since these salts tend to exhibit lower vapor pressures and higher densities than their atomically similar non-ionic analogues. Production of these energetic salts involves the combination of unique cations and anions containing energetic functionalities. Most of the cations are based on bulky organic species with high nitrogen-containing heterocycle-based salts predominating, such as triazole, tetrazole, triazine, and tetrazine, etc. Most frequently the anion is inorganic, such as nitrate, perchlorate, and dinitramide.[6] Since some organic anions have considerable nitrogen content and are expected to have appropriate stabilities toward friction, impact, and heat, they are also good candidates for energetic salt design, e.g., 5,5′-azotetrazolate,[7] 3,5-dinitro-1,2,4-triazolate,[8] 4,5-dinitro-imidazolate,[8] 3-nitro-triazolate,[9] 5-nitro-tetrazolate,[9,10] imi-nobis(5-tetrazolate),[11] 5′-bis(tetrazolate),[7c] bisdinitroimidazolate,[12] 3-nitro-1,2,4-triazol-5-one,[13] and picrate.[14]

Recently there has been considerable study of energetic materials based on 1,2,4,5-tetrazine heterocycles.[15] These compounds derive their energy not only from a combination of positive heats of formation and generation of large volumes of N_2 with high order of energy release, but also as a result of high crystal densities. Such properties are important in energetic materials applications.[16] Among them, 3-amino-6-nitroamino-tetrazine (ANAT)[12] has attractive energetic properties. In nitra-mines, a recently introduced class of organic energetic nitrates,[17] the nitroamino group plays an important role because of the presence of an energetic site and an acidic proton[18] making it possible for nitroamino-containing compounds to form their corresponding salts. The nitramino group substantially improves the oxygen balance of the corresponding derivatives and eventually results in a higher exothermicity of the combustion and detonation processes. The most prominent members of this class are

nitraminotetrazole,[19] 4-nitroamino-1,2,4-triazole,[20] and 3,5-bis(nitroamino)-1,2,4-triazole,[21] and their salts are interesting with respect to their use as components in propellants and explosives.[22] The only data given for ANAT are the melting point (164 °C) and impact sensitivity (2.5 J), and no attempt was made to synthesize its salts.[12] We find that it has a high heat of formation (441.0 kJ mol^{-1} calculated for gas phase), and a density ~ 1.82 g cm^{-3}, higher than the density of 3,6-bisnitroguanyl tetrazine (1.76 g cm^{-3}).[16] We have now synthesized novel energetic salts with the 3-amino-6-nitroamino-tetrazinate anion and determined their structural and thermal properties.

The syntheses of the energetic salts 2–7 were easily accomplished by reacting ANAT with one equivalent of guanidine carbonate, aminoguanidine bicarbonate, 3,6-diguanidine tetrazine, aqueous ammonia, or its silver salt with diaminoguanidine chloride, and triaminoguanidine chloride (Scheme 1). All of the salts were recovered as highly crystalline materials in excellent yields and purities. DSC and TGA studies revealed a family of very stable salts which decompose exothermically upon melting. All of the new salts have relatively high melting points for simple heterocyclic salts, which most likely can be attributed to the high basicity of guanidine or ammonia as well as the extent of crystalline phase hydrogen bonding.

Crystals of 3 suitable for X-ray diffraction were obtained by crystallization from water.‡ The crystal structure is shown in Fig. 1. Compound 3 crystallizes in the monoclinic space group $P2_1/c$. As shown in Fig. 1(a), the asymmetric unit consists of the crystallographically independent ANAT anion and guanidine cation, in which the proton transfer from nitramino of ANAT to guanidine is confirmed. In the ANAT anion, the nitramino group is twisted out of the plane of the tetrazine ring with a 43.2° dihedral angle between these planes. The atoms of the nitramino group are approximately coplanar with the mean deviation from the basic
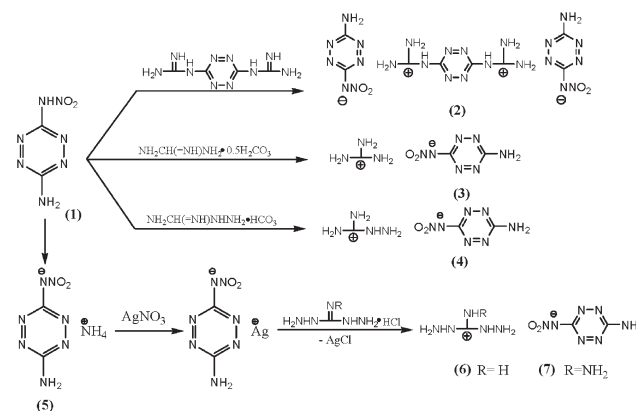
Scheme 1

[a] Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343, USA. E-mail: jshreeve@uidaho.edu; Fax: +1-208-885-9146
[b] Los Alamos National Laboratories, Los Alamos, New Mexico 87545
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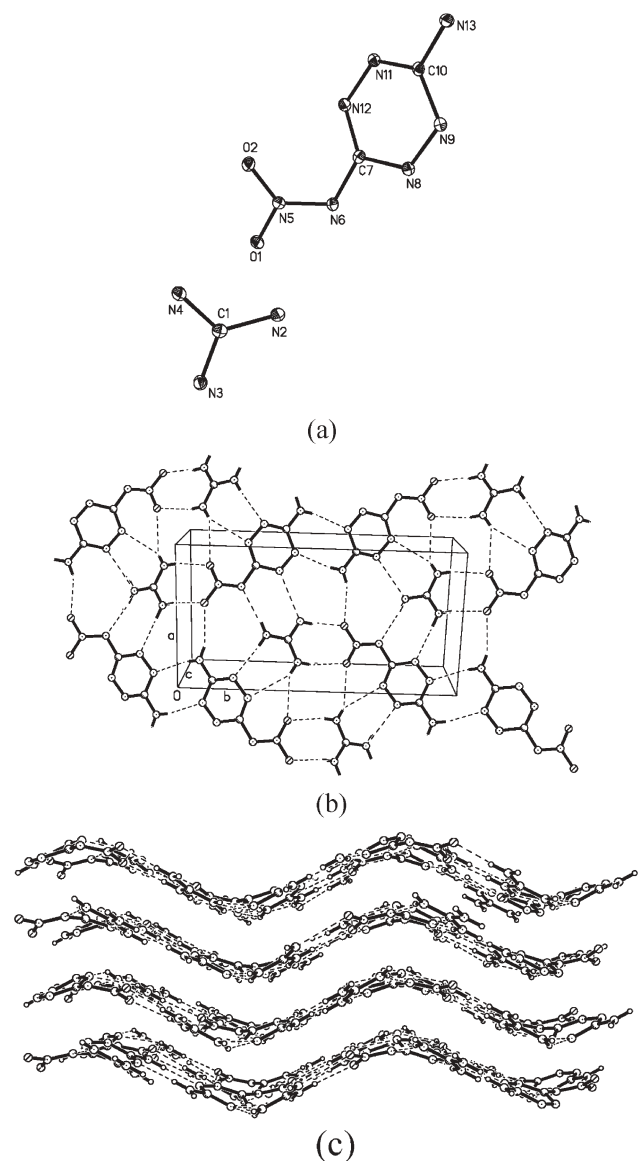
(a)

(b)

(c)

Fig. 1 (a) Thermal ellipsoid plot of the structure of **3** (30% probability). Hydrogen atoms have been omitted for clarity. (b) A ball and stick view of the 2D undulating wave layer formed by hydrogen bonding interactions (dashed lines). (c) Packing diagram of compound **3** viewed parallel to the *b* axis. Dashed lines represent hydrogen bonding.

plane being 0.0035 Å. In the guanidine cation, the mean deviation of C1, N2, N3, N4 from the ring plane is 0.0017 Å: C1 is out of the plane 0.0034 Å. The C–N bond distances and the N–C–N bond angles are in the range 1.318(2)–1.335(2) Å and 119.31(14)–120.61(14)° respectively, which are typical values for the guanidine cation.[23] Since the amino groups in ANAT and guanidine are excellent hydrogen bonding donors, the discrete ANAT and guanidine are linked into a 2D wave-like layer by the extensive hydrogen bonding interactions between ANAT and ANAT [N(13)–H(13A)···O(1)^{i} 3.1103(18); N(13)–H(13B)···N(9)^{ii} 3.0722(19) Å. Symmetry codes: (i) $x - 1$, $-y + $, $z - \frac{1}{2}$; (ii) $-x$, $-y + 1$, $-z + 1$] and between ANAT and guanidine [N(2)–H(2A)···N(6)^{i} 2.9715(18) Å; N(4)–H(4A)···N(8)^{i} 2.9780(19) Å; N(2)–H(2B)···N(11)^{ii} 2.8930(18) Å; N(3)–H(3B)···O(2)^{ii}

3.2063(18) Å; N(3)–H(3B)···N(12)^{ii} 3.3807(19) Å; N(4)–H(4B)···O(1)^{iii} 2.8616(17) Å; N(3)–H(3A)···O(2)^{iii} 3.0128(18) Å. Symmetry codes: (i) x, $-y + $, $z - \frac{1}{2}$; (ii) $x + 1$, y, z; (iii) $-x + 1$, $-y + 2$, $-z + 1$] (Fig. 1(b)).† The packing diagram of the structure is shown in Fig. 1(c). There are no significant interlayer interactions.

The heats of formation for compounds **1–7** were calculated and are summarized in Table 1. The heat of formation of compound **2** was calculated as +1088.8 kJ mol^{-1}. The calculated heats of formation for 3,6-diguanidine tetrazine nitrate (**8**) and 3,6-diguanidine tetrazine perchlorate (**9**) are in good agreement with the experimental values of −255 kJ mol^{-1} and the estimated value of −125 kJ mol^{-1}, respectively.[24] This is impressive, considering that the heat of formation of 3,6-diguanidine tetrazine itself is reported to be 197 kJ mol^{-1}[24]—a clear indication of the degree of energy imparted to the overall molecule by the ANAT anion. Other compounds were also found to have high heats of formation. Salt **3** has the highest thermal stability decomposing at 248.1 °C.

The detonation pressures (*P*) and detonation velocities (*D*) were calculated based on the traditional Chapman–Jouget thermodynamic detonation theory (Table 1).[25,26] For compounds **1–7**, the calculated detonation pressures lie in the range between $P = $ 20.9 GPa [**2**, comparable to tetryl (2,4,6-trinitrophenylmethylnitramine), $P = $ 22.6 GPa][26] and $P = $ 28.9 GPa (**4**, comparable to PETN (pentaerythritol tetranitrate) for which $P = $ 31.0 GPa).[26] Detonation velocities are in the range between $D = $ 7546 m s^{-1} (**2**, comparable to TATB (1,3,5-triamino-2,4,6-trinitrobenzene), $D = $ 7660 m s^{-1})[26] and $D = $ 8898 m s^{-1} (**4**, comparable to RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), $D = $ 8754 m s^{-1}).[26] These properties make these high-nitrogen materials attractive candidates for energetic materials applications.

In order to obtain a better understanding of the ANAT anion, a natural bond orbital (NBO) analysis[27] based on the optimized structure of the isolated anion (B3LYP/6-31G(d,p)) was carried out using Gaussian 03.[28] The NBO analysis showed that the negative charge is delocalized over all nitrogen atoms except for the nitrogen in the nitro group (Fig. 2). The N(6) and N(11) atoms carry the highest negative charge (−0.443e and −0.818e, respectively). For the carbon atoms, positive charges of 0.482e and 0.475e for C(4) and C(3), respectively, were calculated. The tetrazine nitrogen atoms have charges of ∼−0.25e. This charge distribution would imply that stronger hydrogen bonds should be

Table 1 Structure and properties of energetic salts with ANAT anion

No.	T_{d}^{a} (°C)	Density (g cm^{-3})	H_{L}^{b}	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{b\circ}$	P^{c}	D^{d}
1	164.0	1.82	—	441.0^{e}	—	—
2	232.3	1.56	1354.5	1088.8	20.9	7546
3	248.1	1.62	567.6	340.7	23.3	8169
4	205.4	1.71	494.8	443.2	28.9	8898
5	174.0	1.63	526.3	370.0	26.6	8448
6	147.7	1.56	475.4	564.2	23.9	8258
7	163.5	1.59	470.5	671.5	26.1	8582
8^{f}	—	1.72	1555.0	−252.5	25.6	8160
9^{g}	—	1.90	1512.7	−164.8	30.9	8593

^{a} Onset of decomposition. ^{b} kJ mol^{-1}. ^{c} Detonation pressures (GPa). ^{d} Detonation velocities (m s^{-1}). ^{e} Calculated heat of formation in the gas phase. ^{f} 3,6-Diguanidine tetrazine nitrate, Ref. 24. ^{g} 3,6-Diguanidine tetrazine perchlorate, Ref. 24.
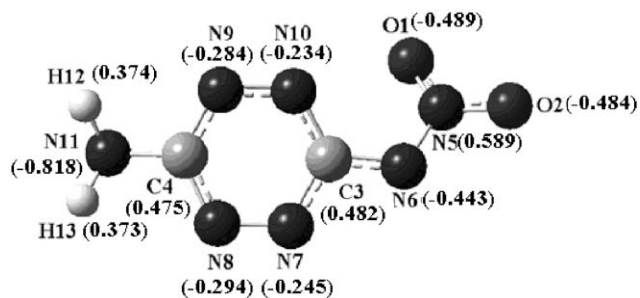
Fig. 2 Charge distribution in the ANAT anion as found with a NBO analysis (B3-LYP/6-311 + G(3df,2p)).

formed with N(6) compared to (N(8) and N(9)) in the tetrazine ring. However, they are essentially identical. This is likely due to steric rather than to electronic effects.

In conclusion, this synthesis of ANAT salts provides a new and easy approach to highly energetic salts. All new salts examined in this work exhibit good physical properties, such as high densities (> 1.55 g cm^{-3}) and good thermal stabilities ($T_d > 147.7\ ^\circ$C). All of these compounds show calculated detonation velocities and detonation pressures comparable to those of explosives such as Tetryl, PETN, TATB and RDX. A combination of theoretical and empirical calculations shows that all the salts have high molar enthalpies of formation. Intermolecular hydrogen bonding plays an important role in crystal packing.

Notes and references

‡ *Crystal data for* **3**: C$_3$H$_8$N$_{10}$O$_2$, M = 216.19. Monoclinic, $P2_1/c$, a = 8.155(2), b = 15.305(4), c = 6.8667(18) Å, β = 99.895(5)°, V = 844.3(4) Å^3, Z = 4, D_c = 1.701 Mg m^{-3}, μ = 0.142 mm^{-1}, T = 89(2) K, R_1 = 0.0318, wR_2 = 0.0782 for $I > 2\sigma(I)$, S = 1.100 for 12622 collected reflections, 1530 independent reflections (R_{int} = 0.0247) and 136 parameters. Data collected on a Bruker SMART APEX using graphite monchromated Mo-Kα radiation (λ = 0.71073 Å). CCDC 610552. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b608214a

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