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2,4,5-Trinitroimidazole-Based Energetic Salts

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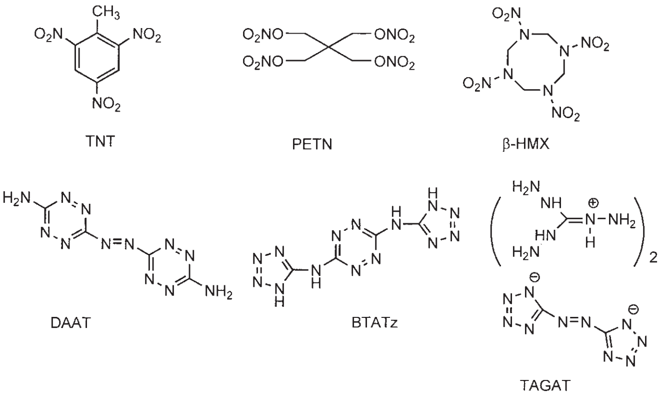
Abstract: 2,4,5-Trinitroimidazolate (TNI) salts with “high-nitrogen” cations tend to be highly hydrogen bonded and have heats of formation ranging up to 616 kJ mol^{-1}. Density, oxygen balance, and thermostability are enhanced by the presence of TNI. Based on theoretical calculations, all of the new salts are potential propellants.

Keywords: ab initio calculations • energetic salts • heat of formation • nitrogen heterocycles • polynitro compounds

Introduction

Polynitro compounds have long been the focal point of useful energetic compounds.[1] The presence of nitro groups tends to decrease heat of formation, but contributes markedly to the overall energetic performance. The energy of traditional polynitro compounds results primarily from the combustion of the carbon backbone, while consuming the oxygen provided by the nitro groups (Scheme 1).[2] Recently, a new class of energetic compounds containing large numbers of nitrogen atoms, so-called “high-nitrogen” compounds, has been shown to derive energy from the innate high positive heats of formation that arise from the presence of a large number of energetic N–N and C–N bonds.[2b,3–7]



Scheme 1. Traditional energetic polynitro and polynitrogen compounds.[2b] TNT: $\rho = 1.65$ g cm^{-3}, $\Delta H_f^0 = -64$ kJ mol^{-1}; PETN: $\rho = 1.78$ g cm^{-3}, $\Delta H_f^0 = -593$ kJ mol^{-1}; β-HMX: $\rho = 1.91$ g cm^{-3}, $\Delta H_f^0 = +75$ kJ mol^{-1}; DAAT: $\rho = 1.78$ g cm^{-3}, $\Delta H_f^0 = +862$ kJ mol^{-1}; BTATz: $\rho = 1.76$ g cm^{-3}, $\Delta H_f^0 = +883$ kJ mol^{-1}; TAGAT: $\rho = 1.60$ g cm^{-3}, $\Delta H_f^0 = +1075$ kJ mol^{-1}.

The need for energetic materials that exhibit a combination of good thermal stability, lower impact sensitivity and higher heats of formation continues to expand. However, these requirements are somewhat mutually exclusive. Materials with higher stability and lower sensitivity often exhibit poorer energetic performance and vice versa. Energetic salts are important systems for the development of high-energy dense materials, since salts are intrinsically nonvolatile, are often thermally stable under normal conditions, and are more dense.[8] Designing energetic materials based on combinations of different ions for a specific purpose provides a powerful methodology. The impact on properties as a function of cations and anions and the variation of substituents on those ions obtained from earlier work are important references for screening and design work.[9]

Highly nitrated small-ring heterocycles and carbocycles are interesting energetic materials based on increasing per-

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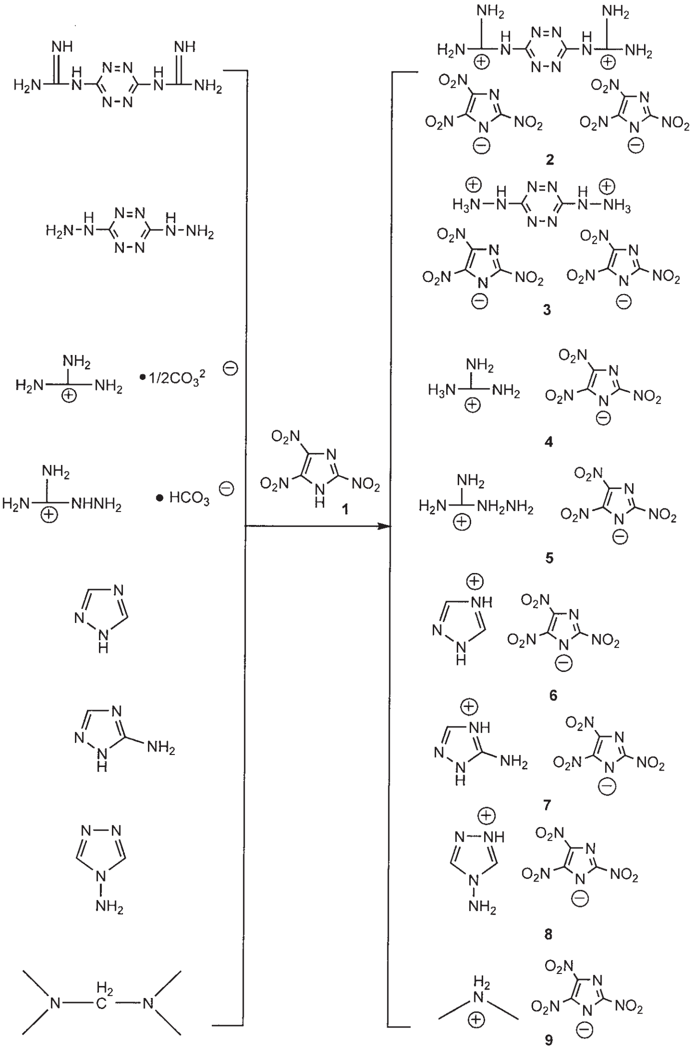
formance arising from the additional energy release upon opening of the strained ring systems during decomposition.[10] Imidazole derivatives with more than two nitro groups are expected to be highly powerful, but insensitive explosives.[11–15] Various nitroimidazole derivatives including 2,4-dinitroimidazole,[11a–d] 4,5-dinitroimidazole,[11e,f] 2,4,5-trinitroimidazole,[11f,g,h] and 4,4′,5,5′-tetranitro-2,2′-biimidazole[11i–k] have been reported previously. Ammonium[11f] and potassium[11g] 2,4,5-trinitroimidazolates are the only salts with this anion that are known.

Since performance is distinctly impacted by introduction of additional energetic groups, further introduction of nitro groups into the imidazole ring should be worthwhile. Theorists suggest that the explosive performance of trinitro-substituted imidazoles should approach that of RDX.[12] Drop-weight impact tests show that 2,4,5-trinitro-imidazole (HTNI; **1**) has a much higher h50 value (68 cm) than cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX, 28 cm), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX, 32 cm), and even higher than 2,4,6-trinitrophenol (picric acid, 64 cm);[13] h50 is defined as the height in centimeters for which the probability of explosion is 50%. There have been a variety of attempts to introduce the third nitro group into an imidazole ring, but these efforts were only marginally successful.[11f,g,14] While ammonium trinitroimidazolate (TNI) is the only energetic salt that contains this anion, its low heat of formation and minimal nitrogen content limit its application. On the other hand, a disadvantage of high-nitrogen compounds is that they frequently have low oxygen balance. In this paper, we take advantage of the acidity of trinitroimidazole (HTNI),[15] its insensitivity and good oxygen content, to react it with a variety of nitrogen-rich bases or their carbonate salts in order to prepare new energetic salts with high heats of formation and also good oxygen balance with the goal of achieving good energetic performance.



Scheme 2. Synthesis of TNI salts.

Results and Discussion

The syntheses of energetic salts **2**–**9** were accomplished by reacting HTNI (**1**) with stoichiometric amounts of guanidine carbonate, aminoguanidine bicarbonate or nitrogen-rich bases (Scheme 2). All of the salts were isolated as highly crystalline materials in excellent yields and purities. DSC and TGA studies show a family of very stable salts that decompose well above their relatively high melting points. This can most likely be attributed to the high thermal stability of the TNI anion[11f] as well as to the marked hydrogen bonding in the salts. Compared with our earlier 4,5-dinitroimidazolate salts **16** and **17** (see Table 2 below) which have cations in common with salts **6** and **8**,[9c] the last two salts have superior oxygen balance, thermal stabilities, and detonation properties (detonation pressure [GPa], detonation velocity [m s^{-1}] and specific impulse), although, not unexpectedly, the heats of formation are somewhat decreased. While several salts containing *N*,*N*,*N*′,*N*′-tetramethylmethylenediamine have been reported,[16] salt **9** was an unexpected product obtained in the reaction of HTNI with the *N*,*N*,*N*′,*N*′-tetramethylmethylenediamine; the single-crystal structure (Figure 2 later) shows that the cation is dimethyl ammonium. The reaction mechanism leading to this transformation is not evident, but clearly the C–N bond in the diamine is subject to cleavage. This phenomenon has only been observed previously in coordination of the ammonium moiety with metal(II) halides and its quaternization in a polar solvent.[17]

Crystals of compounds **2** and **9** suitable for X-ray diffraction were obtained by slow evaporation from an aqueous solution. Compound **2** is the first example of a structural determination of the 3,6-diguanidino-1,2,4,5-tetrazine cation (Table 1; Figure 1). The structure was analyzed at room temperature as the crystals shattered at a variety of lower temperatures. The molecule lies on an inversion center and the rest of the ion-pair is generated by using symmetry (A: $-x+1,-y,-z+1$). As can be seen in Figure 1a, proton transfer from the TNI moiety to 3,6-diguanidino-1,2,4,5-tetrazine

Table 1. Crystallographic data for **2** and **9**.

	2	**9**
formula	$C_{10}H_{10}N_{20}O_{12}$	$C_5H_8N_6O_6$
M_r	602.38	248.17
crystal system	orthorhombic	monoclinic
crystal size [mm^3]	$0.49\times0.29\times0.03$	$0.44\times0.18\times0.14$
space group	*Pbca*	$P2_1/n$
F (000)	1224	256
a [Å]	12.367(2)	8.484(2)
b [Å]	9.518(1)	6.144(2)
c [Å]	19.079(3)	9.439(2)
α [°]	90	90
β [°]	90	100.551(3)
γ [°]	90	90
V [Å^3]	2245.8(5)	483.7(2)
ρ_{calcd} [Mg m^{-3}]	1.782	1.704
Z	4	2
μ [mm^{-1}]	0.161	0.155
Reflns collected/unique	33453/2039	7136/972
R (int)	0.0276	0.0228
data/restraints/parameters	2039/0/190	972/1/157
index ranges	$-14\leq h\leq14$	$-10\leq h\leq10$
	$-11\leq k\leq11$	$-7\leq k\leq7$
	$-22\leq l\leq22$	$-11\leq l\leq11$
R_1/wR_2 $[I>2\sigma(I)]$[a]	0.0402/0.1066	0.0216/0.0554
R_1, wR_2 (all data)[a]	0.0455/0.1107	0.0220/0.0557
GOF on F^2	1.043	1.111
min/max $\Delta\rho$ [e Å^{-3}]	0.385/−0.232	0.181/−0.171

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

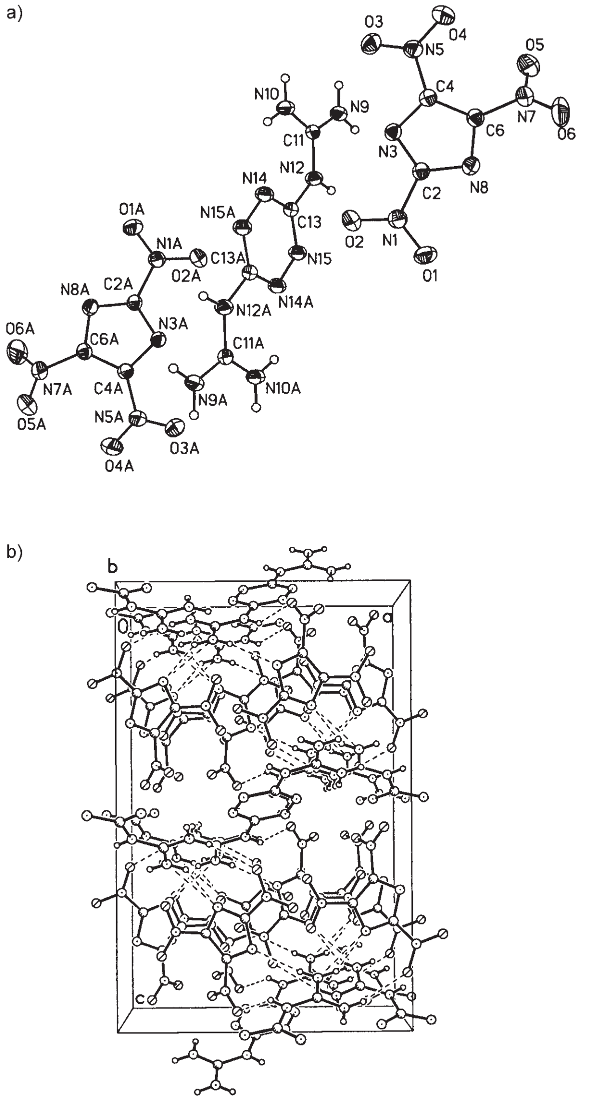


Figure 1. a) Thermal ellipsoid plot (30 %) of **2** showing the symmetry generated cation and additional anion. Hydrogen atoms included but unlabelled for clarity. b) A ball and stick packing diagram of **2** showing the hydrogen bonding (dashed lines).

can be confirmed. In the TNI anion, all the nitro groups are twisted out of the plane of the imidazole ring (6.8, 17.9, and 31.9° from the ring plane). This is similar to the only other structurally characterized TNI compound, 1-methyl-2,4,5-trinitroimidazole, in which the nitro groups vary from 9.7 to 57°.[11h] There is extensive hydrogen bonding between the TNI and tetrazine, templating a wave-like synthon of the tetrazine tecton as viewed parallel to the *ac* plane (see Figure 1b and the Supporting Information).

Compound **9** has a simpler monocation and both ions are symmetry unique. Here the NO_2 groups on the TNI are also tilted, albeit to a lesser degree than in **2**, to the plane of the imidazole (8.3, 9.2 and 21.6°). As in **2**, hydrogen bonding is extensive, mainly between the hydrogen atoms of dimethyl amino NH_2^+ and nitro oxygen atoms (N2···O17, 2.978(2); N2···O10, 3.018(2) Å) as well as to a ring nitrogen atoms (N2···N7, 2.936(2) Å). These interactions form chains parallel to the *a* axis, which are then also hydrogen bound into a sawtooth pattern that extends parallel to the *b* axis (see Figure 2 and the Supporting Information).

Phase-transition temperatures (midpoints of melting points, T_m) for all the salts were determined by differential scanning calorimetry (DSC; Table 2). With a common anion, all the salts have melting points >100 °C with the exception of **5** (m.p. = 80.7 °C), which probably arises from the unsymmetrical structure of the aminoguanidinium cation.

Because its melting point is <100 °C, compound **5** can be classified as an ionic liquid. The decomposition temperatures of the salts were determined by thermogravimetric analysis (TGA). Salt **3** has the highest thermal stability decomposing at 270.2 °C. Relative to the nitrate or perchlorate [3,6-diguanidino-1,2,4,5-tetrazine dinitrate (**10**), and di(perchlorate) (**11**);[7a] 3,6-dihydrazino-1,2,4,5-tetrazine bis(dinitramide) (**12**), dinitrate (**13**), and di(perchlorate) (**14**)[7c]] with common cations, TNI salts show higher thermal stabilities.

The heats of formation for compounds **2**–**9** were calculated (vide infra) and are summarized in Table 2. For comparison with known compounds, we calculated the heats of formation for six salts that share a common cation with salts **2** or **3** (**11**–**14** and ammonium TNI (**15**)[11f]; Table 2). The heat of formation of compound **2** is 266.7 kJ mol^{-1}, which exceeds the values for salts **10** and **11** by 400 kJ mol^{-1}. For **3**, the heat of formation is also higher than that of the nitrate (**12**), perchlorate (**13**), and dinitramide salts (**14**) with the same

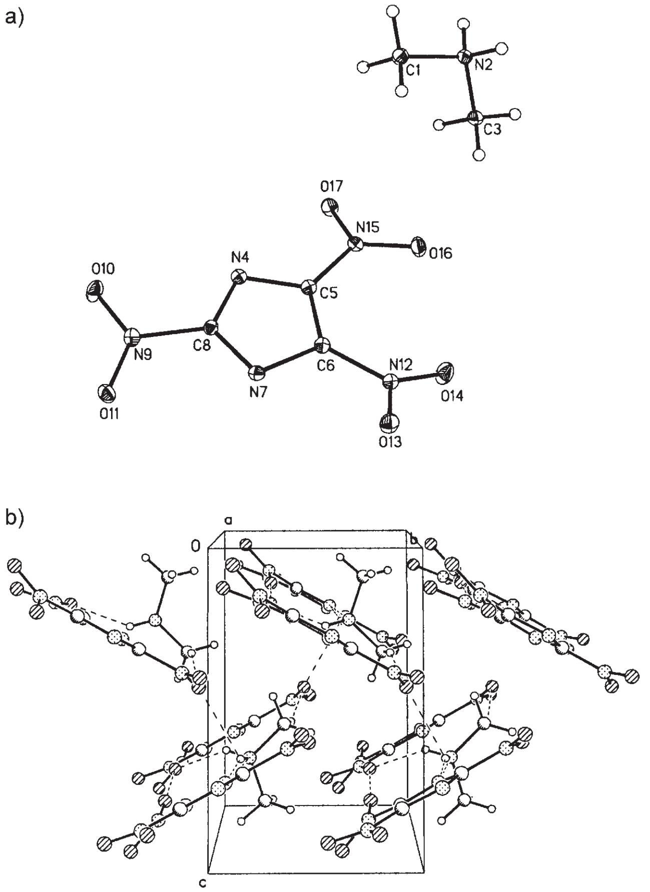


Figure 2. a) Thermal ellipsoid plot (30%) of **9**. Hydrogen atoms included but unlabelled for clarity. b) Ball and stick packing diagram of **9** showing hydrogen bonding (dashed lines).

cation,[7c] and at 615.8 kJ mol^{-1} is the highest value calculated for any compound in this work.

The performance of energetic materials is measured by detonation velocity, vD [m s^{-1}], detonation pressure, P [Gpa], and specific impulse I_{sp} [s].[18] These parameters are directly related to oxygen balance (OB), density, and heat of formation. The detonation pressure and velocity (based on the traditional Chapman–Jouget thermodynamic detonation theory) and I_{sp} were obtained by using CHEETAH 4.0 (Table 2).[19]

For compounds **2**–**9**, the calculated detonation pressures lie in the range between $P = 25.0$ GPa (for compound **4**, comparable to TATB (1,3,5-triamino-2,4,6-trinitrobenzene), 25.9 Gpa)[19b] and $P = 34.1$ GPa (for compound **3**, comparable to RDX, $P = 33.79$ Gpa).[19b] Detonation velocities fall in the range between $D = 7835$ m s^{-1} (for compound **4**, comparable to TATB, $D = 7660$ m s^{-1})[19b] and $D = 8695$ m s^{-1} (for compound **3**, comparable to RDX, $D = 8754$ m s^{-1}).[19b] All the salts have rather high specific-impulse values, with the highest value at ≈254.8 s, which suggests energetic materials applications as propellants.

Theoretical study: To obtain a better understanding of the TNI anion, a natural bond orbital (NBO) population analysis fixed at that of the isolated anion in **2** (determined by X-ray analysis) combined with the optimized structures (HF/6-31+G(d,p) and DFT/6-31+G(d,p)) were used to investigate the bonding and hybridization in this experimentally observed species (single-point at the HF/6–311++G(3df,2p) and DFT/6–311++G(3df,2p)level).[20] The calculation was carried out using Gaussian 03 (Figure 3; Table 3).[21] The NBO analysis showed that the optimized free anion has a symmetric charge distribution (1C = 2C, 4N = 5N, 7O = 8O, 9N = 12N, 10O = 14O, 11O = 13O). The negative charge is delocalized over the oxygen atoms and all the ring nitrogen atoms, but not the nitrogen atoms of the nitro groups. The 4N and 5N atoms carry the largest negative charge in the ring. For the carbon atoms, positive charges were calculated. The analysis results show that the symmetrical charge distribution of anion in the crystal is distorted by the interaction with the cation.

Table 2. Properties of energetic trinitroimidazolates and other salts.

Salt	d[a]	T_m[b]	T_d[c]	OB[d]	ΔH_f[e] cation	ΔH_f[e] anion	Lattice energy[e]	ΔH_f[e]	P[f]	vD[g]	I_{sp}[h]
2	1.76	–	270.2	−35	1903.6	−148.5	1339.9	266.7	26.2	7979	220.2
3	1.86	127.0	198.1	−23	2302.0	−148.5	1389.2	615.8	34.1	8695	254.8
4	1.70	174.2	240.7	−31	566.7	−148.5	478.2	−50.8	25.0	7835	226.6
5	1.75	80.7	253.4	−32	667.4	−148.5	474.9	44.0	28.2	8197	232.4
6	1.76	146.4	220.5	−35	835.0	−148.5	477.9	208.6	26.8	7963	236.4
7	1.86	–	207.8	−36	804.5	−148.5	478.1	179.8	31.0	8416	229.1
8	1.85	182.1	238.9	−36	936.3	−148.5	477.4	310.4	31.5	8450	241.3
9	1.70	–	–	−52	579.5	−148.5	485.3	−54.3	23.8	7691	222.0
10	1.72	–	265.0	−35	1903.6	−300.5	1555.0	−252.5	25.6	8160	196.3
11	1.90	–	226.0	−20	1903.6	−277.8	1512.7	−164.8	30.9	8593	231.5
12	1.82	–	136.0	0	2302	−156.2	1537.9	451.7	36.7	9401	263.5
13	1.80	–	117.0	−12	2302	−300.5	1648.8	52.2	34.5	9221	254.5
14	1.96	–	200.0	0	2302	−277.8	1580.9	165.4	35.3	8939	245.8
15	1.84	248.0	248.0	−15	626.4	−148.5	510.5	−33.0	32.1	8728	254.8
16	1.73	156	165	−60	835.0	−103.2	498.6	233.3	22.8	7603	214.0
17	1.65	137	149	−59	936.3	−103.2	484.4	348.7	22.9	7500	222.9

[a] Density [g cm^{-3}]. [b] Melting point [°C]. [c] Decomposition temperature [°C]. [d] 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 (%) = $1600[(d-2a-b/2)/M_W]$. [e] [kJ mol^{-1}]. [f] Detonation pressure [GPa]. [g] Detonation velocity [m s^{-1}]. [h] I_{sp}—specific impulse [s].

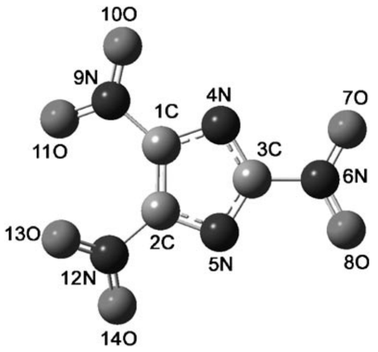


Figure 3. TNI anion (NBO analysis).

Table 3. NBO charge distribution.

Atom	Crystal (HF)[a]	HF[b]	Crystal (DFT)[c]	DFT[d]
1C	0.21	0.22	0.19	0.22
2C	0.23	0.22	0.20	0.22
3C	0.46	0.44	0.41	0.41
4N	−0.49	−0.50	−0.45	−0.45
5N	−0.50	−0.50	−0.46	−0.45
6N	0.61	0.62	0.48	0.47
7O	−0.47	−0.47	−0.40	−0.40
8O	−0.46	−0.47	−0.40	−0.40
9N	0.62	0.64	0.50	0.48
10O	−0.46	−0.45	−0.40	−0.39
11O	−0.46	−0.47	−0.40	−0.40
12N	0.62	0.64	0.50	0.48
13O	−0.45	−0.47	−0.38	−0.40
14O	−0.46	−0.45	−0.39	−0.39

[a] HF/6–311++G(3df,2p) bases on crystal structure. [b] HF/6-31+G(d,p)//HF/6–311++G(3df,2p). [c] B3LYP/6–311++G(3df,2p) bases on crystal structure. [d] B3LYP/6-31+G(d,p)//B3LYP/6–311++G(3df,2p).

The geometric optimization of all the structures and frequency analyses for calculation of heats of formation was carried out by using B3-LYP functional with 6-31+G** basis set,[22] and single-energy points were calculated at the MP_2(full)/6–311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.

Based on Born-Haber energy cycles (Figure 4), the heat of formation of a salt can be simplified and expressed as Equation (1), in which ΔH_L is the lattice energy of the salt. This quantity could be predicted by the formula suggested by Jenkins et al. [Eq. (2)][23] in which nM and n_X depend on the nature of the ions M_p^+ and Xq^-, 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} [kJ mol^{-1}] is given by Equation (3) in which density, ρ_m [g cm^{-3}], M_m [g] (the chemical formula mass of the ionic material), and the coefficients γ [kJ mol^{-1} cm] and δ [kJ mol^{-1}] take their values from the literature.[24]

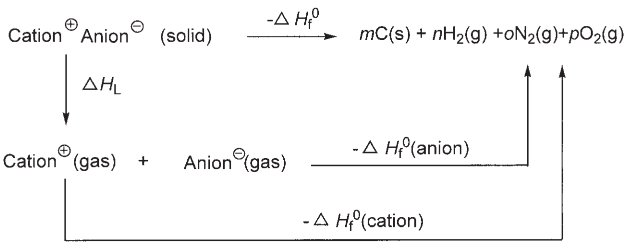


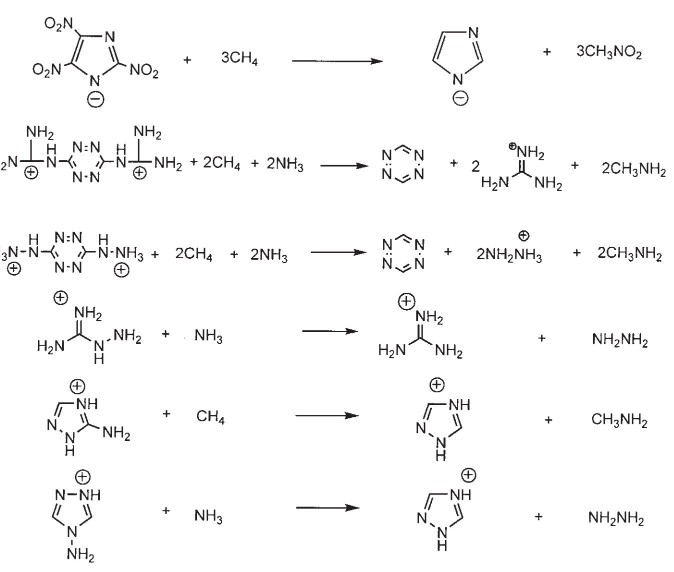
Figure 4. Born–Haber cycle for the formation of TNI-based salts. Salt **2**: $m=10$, $n=5$, $o=10$, $p=6$; Salt **3**: $m=8$, $n=4$, $o=9$, $p=6$; Salt **4**: $m=4$, $n=3$, $o=4$, $p=3$; Salt **5**: $m=4$, $n=3.5$, $o=4.5$, $p=3$; Salt **6**: $m=5$, $n=2$, $o=4$, $p=3$; Salt **7**: $m=5$, $n=2.5$, $o=4.5$, $p=2$; Salt **8**: $m=5$, $n=2.5$, $o=4.5$, $p=3$; Salt **2**: $m=5$, $n=4$, $o=3$, $p=3$.

$$\Delta H_f^0(\text{ionic salt, 298 K}) = \Delta H_f^0(\text{cation, 298 K}) + \Delta H_f^0(\text{anion, 298 K}) - \Delta H_L \quad (1)$$

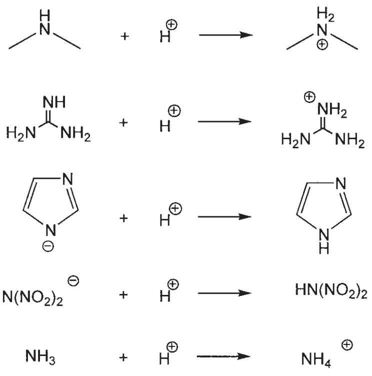
$$\Delta H_L = U_{POT} + [p\{(nM/2)-2\} + q\{(n_X/2)-2\}]RT \quad (2)$$

$$U_{POT}/ = \gamma(\rho_m/M_m)^{1/3} + \delta \quad (3)$$

The remaining task is to determine the heats of formation of the cations and anions; these values were computed by using the method of isodesmic reactions (Scheme 3). The energies of the parent ions in the isodesmic reactions were calculated from protonation reactions (heat of formation of H^+ is 1530 kJ mol^{-1}; Scheme 4).[24,25] The enthalpy of an isodesmic reaction (ΔH^o_{r298}) is obtained by combining the MP2-(full)/6–311++G** energy difference for the reaction, the scaled zero point energies (B3LYP/6-31+G**), and other thermal factors (B3LYP/6-31+G**). The protonation reactions were calculated at G2 level. The heats of formation of formation of the triazole cation, NO_3^-, and ClO_4^- were used directly from the reference values of 835.0,[25] −307.8, and −277.8 kJ mol^{-1}.[26] The heat of formation of the dinitramide anion was calculated based on the experimental value for dinitramide acid and its proton affinity.[27]



Scheme 3. Isodesmic reactions of various nitrogen-containing ions.



Scheme 4. Protonation reactions of the parent species in the isodesmic reactions.

Thus, the heats of formation of the cations and anions being investigated can be extracted readily (see Supporting Information).

With the value of the heats of formation and density of energetic salts, the expected detonation pressures (*P*) and detonation velocities (*D*) were calculated based on the traditional Chapman–Jouget thermodynamic detonation theory by using Cheetah 4.0.[19a]

Conclusion

The formation of TNI salts provides a straightforward approach to highly energetic salts that exhibit acceptable physical properties, such as relatively high densities ($>1.75\,\mathrm{g\,cm^{-3}}$) and thermal stabilities ($Td > 198\,^{\circ}\mathrm{C}$). All of these compounds show calculated detonation velocities and detonation pressures comparable to those of explosives, such as TATB and RDX. Based on a combination of theoretical and empirical calculations, all the salts are shown to have relatively high positive molar enthalpies of formation.

Experimental Section

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

General methods: All the reagents were analytical reagents purchased from commercial sources and used as received. 2,4,5-Trinitroimidazole was prepared by the nitration of imidazole with nitric acid.[14] 3,6-Diguanidino-1,2,4,5-tetrazine[7c] and 3,6-dihydrazino-1,2,4,5-tetrazine[7a] were synthesized by literature methods. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz nuclear magnetic resonance spectrometer operating at 300.13 and 75.48 MHz, respectively. Chemical shifts are reported relative to Me_4Si. The solvent was [D$_6$]DMSO 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 $10\,^{\circ}\mathrm{C\,min^{-1}}$, 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 analysis: Crystals of compound **2** (or **9**) were removed from the flask, a suitable crystal was selected, attached to a glass fiber and data were collected 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 using omega scans of 0.3° per frame for 20 s (5 s for **9**), and a full sphere of data was collected. A total of 2400 frames were collected for each structure with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART[28] software and refined using SAINTPlus[29] on all observed reflections. Data reduction and correction for Lp and decay were performed using SAINTPlus. Absorption corrections were applied using SADABS.[30] The structures were solved by direct methods and refined by the least squares method on F^2 using the SHELXTL program package.[31] The structure of **2** was solved in the space group *Pbca* ($P2_1/n$ for compounbd **9**) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. The absolute structure of **9** could not be determined reliably. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

CCDC-617713 (**2**) and CCDC-617714 (**9**) 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.

3,6-Diguanidino-1,2,4,5-tetrazine di-TNI (2): HTNI (203 mg, 1 mmol) and 3,6-diguanidino-s-tetrazine (98 mg, 0.5 mmol) were added to water (5 mL). After stirring at 80 °C for 1 h and cooling to room temperature, a microcrystalline solid was isolated. Orange plate crystals were obtained upon recrystallization from water (267 mg, 89 %). ^{1}H NMR: $\delta = 8.15$ ppm (s); ^{13}C NMR: $\delta = 159.7$, 155.5, 139.2 ppm; IR (KBr pellet): $\tilde{\nu} = 3439$, 3332, 3282, 3149, 2787, 2637, 2565, 2443, 2297, 1685, 1586, 1541, 1468, 1414, 1321, 1109, 1076, 941, 866, 830, 808, 756, 707, 650, 586, 487 cm^{-1}; elemental analysis calcd (%) for $C_{10}H_{10}N_{20}O_{12}$ (602.31): C 19.94, H 1.67, N 46.51; found: C 19.78, H 1.40, N 46.23.

3,6-Dihydrazino-s-tetrazine di-TNI (3): HTNI (203 mg, 1 mmol) and 3,6-dihydrazino tetrazine (71 mg, 0.5 mmol) were dissolved in water (5 mL). After stirring at 80 °C for 1 h, followed by cooling to 25 °C, the solvent was slowly removed, and brown flat crystals were obtained after recrystallization from water (238 mg, 87 %). ^{1}H NMR: $\delta = 10.7$ ppm (s); ^{13}C NMR: $\delta = 162.5$, 143.7, 139.2 ppm; IR (KBr pellet): $\tilde{\nu} = 3346$, 3294, 3257, 3138, 2964, 2600, 2077, 1869, 1753, 1647, 1472, 1543, 1325, 1306, 1205, 1107, 1058, 1031, 979, 947, 866, 812, 675, 650, 518, 445 cm^{-1}; elemental analysis calcd (%) for $C_8H_8N_{18}O_{12}\cdot 2H_2O$ (584.29): C 16.44, H 2.07, N 43.15; found: C 16.52, H 2.04, N 42.58.

Guanidinium TNI (4): HTNI (203 mg, 1 mmol) and guanidine carbonate (90.1 mg, 1 mmol) were added to water (5 mL). After CO_2 release was complete, the solution was stirred at 25 °C for 3 h, the solvent was slowly removed, and the product isolated as light yellow plate crystals (244 mg, 93 %). ^{1}H NMR: $\delta = 6.89$ ppm (s); ^{13}C NMR [D$_2$](H$_2$O): $\delta = 159.2$, 147.7, 140.7, 139.2 ppm; IR (KBr pellet): $\tilde{\nu} = 3462$, 3382, 3268, 3208, 2602, 2544, 2434, 2361, 1670, 1527, 1457, 1327, 1273, 1140, 1109, 1014, 834, 810, 760,572, 520 cm^{-1}; elemental analysis calcd (%) for $C_4H_6N_8O_6$ (262.14.): C 18.33, H 2.31, N 42.75; found: C 18.40, H 2.32, N 42.38.

Aminoguanidinium TNI (5): After a mixture of HTNI (203 mg, 1 mmol) and aminoguanidinium bicarbonate (136 mg, 1 mmol) in water (10 mL) was stirred at 25 °C for 3 h, the solvent was removed slowly and the product was isolated as yellow plate crystals (255 mg, 92 %). ^{1}H NMR: $\delta =$ 8.53 (s, 1 H), 7.19 (br, 2 H), 6.75 (br, 2 H), 4.67 ppm (s, 2 H); ^{13}C NMR [D$_2$](H$_2$O): $\delta = 160.1$, 147.7, 139.2 ppm; IR (KBr pellet): $\tilde{\nu} = 3479$, 3437, 3370, 3205, 3169, 3072, 3024, 2857, 2733, 2598, 1683, 1663, 1538, 1471, 1325, 1201, 1106, 952, 868, 829, 753, 680, 652, 574 cm^{-1}; elemental analysis calcd (%) for $C_4H_7N_9O_6$ (277.16): C 17.33, H 2.55, N 45.48; found: C 17.34, H 2.35, N 45.44.

Triazolium TNI (6): HTNI (203 mg, 1 mmol) and triazole (69 mg, 1 mmol) were placed in water (5 mL). After stirring at 60 °C for 3 h, followed by cooling to 25 °C, the solvent was removed slowly and a microcrystalline solid was isolated. Light yellow crystals were obtained upon recrystallization from water (256 mg, 94 %). ^{1}H NMR: $\delta = 9.25$ ppm (s, 2 H); ^{13}C NMR [D$_2$](H$_2$O): $\delta = 147.7$, 144.6, 139.2,136.2 ppm; IR (KBr pellet): $\tilde{\nu}=3437$, 3150, 3059, 2363, 1938, 1882, 1757, 1671, 1310, 1253, 1195, 1170, 1107, 1039, 943, 868, 810, 752, 661, 624, 561, 521, 415 cm^{-1}; elemental analysis calcd (%) for $C_5H_4N_8O_6$ (272.14): C 22.07, H 1.48, N 41.18; found: C 21.94, H 1.30, N 41.28.

3-Aminotriazolium TNI (7): HTNI (203 mg, 1 mmol) and 3-aminotriazole (84 mg, 1 mmol) were placed in water (5 mL). The mixture was stirred at 25 °C for 3 h, the solvent was slowly removed, and the product was isolated as light yellow needle crystals (264 mg, 92 %). ^{1}H NMR: $\delta=8.21$ ppm (s); ^{13}C NMR: $\delta=152.8$, 147.7, 141.4, 139.2 ppm; IR (KBr pellet): $\tilde{\nu}=$ 3436, 3315, 3269, 3194, 3171, 2988, 2915, 2774, 2047, 1682, 1541, 1472, 1422, 1356, 1323, 1145, 1109, 1048, 956, 867, 812, 738, 700, 650, 650, 557, 519, 418 cm^{-1}; elemental analysis calcd (%) for $C_5H_5N_9O_6$ (287.15): C 20.91, H 1.76, N 43.90; found: C 21.18, H 1.80, N 43.82.

4-Aminotriazolium TNI (8): HTNI (203 mg, 1 mmol) and 3-aminotriazole (84 mg, 1 mmol) were placed in water (5 mL). The mixture was stirred at room temperature for 3 h, the solvent slowly removed, and the product was isolated as red needle crystals (258 mg, 90 %). ^{1}H NMR: $\delta=9.51$ (s, 2H), 7.83 ppm (brs, 2H); ^{13}C NMR: $\delta=147.7$, 145.3,139.2 ppm; IR (KBr pellet): $\tilde{\nu}=3446$, 3347, 3256, 3136, 2964, 2850, 2735, 2596, 1647, 1544, 1471, 1424, 1205, 1155, 1076, 1032, 979, 885, 812,752, 675, 651, 613 cm^{-1}; elemental analysis calcd (%) for $C_5H_5N_9O_6$ (287.15): C 20.91, H 1.76, N 43.90; found: C 21.23, H 1.59, N 43.97.

Dimethyl ammonium TNI (9): HTNI(406 mg, 2 mmol) and tetramethyldiaminomethane (102 mg, 1 mmol) were placed in water (25 mL), the homogenous solution was stirred for 24 h at 25 °C, the solvent was slowly evaporated, and a yellow crystalline solid was isolated (199 mg, 80 %). ^{1}H NMR: $\delta=7.82$ (br, 2H), 2.70 ppm (s, 6H); ^{13}C NMR: $\delta=214.0$, 188.5, 140.9, 35.5 ppm; IR (KBr pellet): $\tilde{\nu}=3230$, 3035, 2925, 2835, 1598, 1541, 1511, 1458, 1419, 1352, 1324, 1294, 1186, 1103, 1017, 951, 920, 866, 845, 828, 808, 754, 666, 643, 581 cm^{-1}; elemental analysis calcd (%) for $C_5H_8N_6O_6$ (248.15): C 24.20, H 3.25, N 33.87; found: C 24.65, H 3.49, N 33.54.

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