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Energetic Nitrate, Perchlorate, Azide and Azolate Salts of Hexamethylenetetramine

Hong Xue,[a] Haixiang Gao,[a] Brendan Twamley,[a] and Jean'ne M. Shreeve*[a]

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Hexamethylenetetrammonium salts, composed of energetic anions 3,5-dinitropyrazolate, 4,5-dinitroimidazolate, 3,5-dinitro-1,2,4-triazolate, 5-nitrotetrazolate, perchlorate, nitrate and azide, were synthesized and characterized. The structure of *N*-methyl-hexamethylenetetrammonium 3,5-dinitro-1,2,4-triazolate (**6**) was confirmed by X-ray analysis. The standard enthalpies of formation for the new salts were calculated by using the computationally feasible DFT(B3LYP) and MP2 methods in conjunction with an empirical approach based on the densities of the salts. The calculated values range from $\Delta H_f° = -30.6$ (**7**) to +468.8 kJ·mol^{-1} (**10**) where the experimental densities > 1.35 g cm^{-3}.

Introduction

In recent years, the synthesis of energetic heterocyclic compounds has attracted considerable interest,[1–7] especially the syntheses of new members of heterocyclic-based energetic, low-melting salts.[8,9] Energetic materials that are salt-based often possess advantages over non-ionic molecules because these salts tend to exhibit lower vapor pressure and higher densities than their atomically similar non-ionic analogues. The cation is generally a bulky organic species with low symmetry. Nitrogen-containing heterocyclic-based salts predominate. The anion most frequently is inorganic, such as nitrate,[8,9,10g] perchlorate,[8,9,10e] dinitramide,[8,9c,10] azide[10g] and tetraazidoborate anion.[11] However, reports are already available that describe analogous salts with organic anions, such as α-cyano-4-hydroxycinnamate, anthraquinone-2-sulfonate,[12] salicylate and lactate,[13] imidazolate and triazolate and tetrazolate.[9e,14,15] Some metal salts composed of organic anions, such as lithium 4,5-dicyano-1,2,3-triazolate, were reported as electrolytes.[16] Alkali metal salts of 5,5′-azotetrazolate[17] and transition-metal salts of 5-nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one[18] were also synthesized as energetic compounds.

Hexamethylenetetramine is an interesting raw material which is useful in the production of antibacterial agents, adhesives, coatings, dye fixatives, anticorrosive agents as well as powerful explosives, e.g., 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and pentaerythrol tetranitrate (PETN).[19] The mechanisms of nitration of hexamethylenetetramine were also studied in detail.[20] The preparation of certain salts of hexamethylenetetramine has long been known, including both inorganic salts, such as chloride, sulfate, phosphate, and organic salts, such as formate, methanesulfonate, *p*-toluenesulfonate and many others.[21] The literature data of energetic hexamethylenetetramine dinitrate (HEXADI) and related compounds were given recently.[22] The syntheses and crystal structures of various energetic urotropinium salts with azide, nitrate, dinitramide and azotetrazolate counterions are also reported,[23] but no energetic characterization was cited. Our main interest in this work is to investigate the syntheses and thermal properties of hexamethylenetetrammonium salts containing both energetic inorganic and organic anions, such as nitrate, perchlorate, and azide, and 3,5-dinitropyrazolate, 4,5-dinitroimidazolate, 3,5-dinitro-1,2,4-triazolate, and 5-nitrotetrazolate, respectively. The calculated heats of formation of these compounds based on DFT(B3LYP) and MP2 methods in conjunction with an empirical approach based on densities of salts are also presented.[10h]

Results and Discussion

Hexamethylenetetrammonium salts with nitrate, azide, dinitramide and azotetrazolate counterions have been prepared either from hexamethylenetetramine and nitric acid or the metathesis reaction from the corresponding iodide (or sulfate) with AgN_3, $[AgNCCH_3][N(NO_2)_2]$, or barium azotetrazolate.[23] It was found that 4,5-dinitroimidazole and 5-nitrotetrazole, which are strong NH acids (pK_a = –0.8 for 5-nitrotetrazole)[24] with electron-withdrawing nitro substituents on the ring, can be readily quaternized with azoles to form energetic azolium-azolate salts.[9e] Here we synthesized several new hexamethylenetetrammonium salts

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[a] Department of Chemistry, University of Idaho,
Moscow, Idaho 83843-2343, USA
E-mail: jshreeve@uidaho.edu

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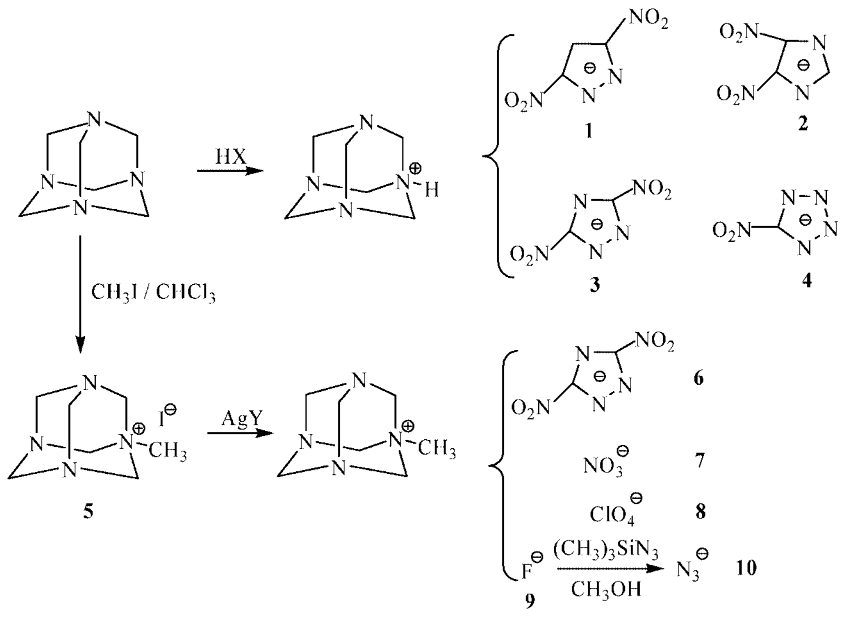


X = 3,5-dinitropyrazolate, 4,5-dinitroimidazolate, 3,5-dinitro-1,2,4-triazolate, 5-nitrotetrazolate
Y = 3,5-dinitro-1,2,4-triazolate, NO_3, ClO_4, F

Scheme 1. Syntheses of energetic hexamethylenetetrammonium salts.

based on energetic azolate anions (3,5-dinitropyrazolate, 4,5-dinitroimidazolate, 3,5-dinitro-1,2,4-triazolate and 5-nitrotetrazolate) and inorganic anions (nitrate, perchlorate and azide). Typical examples for preparation of such salts are given in Scheme 1. It was found that 3,5-dinitropyrazole, 4,5-dinitroimidazole, 3,5-dinitro-1,2,4-triazole and 5-nitrotetrazole can readily quaternize hexamethylenetetramine in methanol. The salts were formed in nearly quantitative yields and in high purity (**1**–**4**). However, although excess 4,5-dinitroimidazole (or 5-nitrotetrazole) was heated with hexamethylenetetramine, it was not possible to react more than one mol of either azole. This is in contrast with the diammonium salt which resulted when excess nitric acid was employed.[22]

N-(Methyl)hexamethylenetetrammonium iodide (**5**) was prepared in quantitative yield from hexamethylenetetramine and CH_3I with chloroform as solvent based on a modified literature method.[23] Initially, the synthesis of *N*-(methyl)-hexamethylenetetrammonium 3,5-dinitro-1,2,4-triazolate was attempted by metathesis reactions of the corresponding iodide salt with sodium 3,5-dinitro-1,2,4-triazolate.[25] However, the reaction did not work well. Although silver 3,5-dinitro-1,2,4-triazolate[26] was water-insoluble, it had good solubility in acetonitrile. Therefore, metathesis of the quaternary iodide **5** with silver 3,5-dinitro-1,2,4-triazolate with CH_3CN as solvent led to the formation of the new quaternary salt **6** in nearly quantitative yield and in high purity. The quaternary salts **7**–**9** were also obtained in high yield using a similar method as **6**, from compound **5** and $AgNO_3$, $AgClO_4$ and AgF with water as solvent. *N*-(Methyl)hexamethylenetetrammonium azide (**10**) was obtained from compound **9** and $Si(CH_3)_3N_3$ in methanol as solvent in high purity and in quantitative yield.[27]

The structure of compound **6** was determined by single-crystal X-ray diffraction, and the asymmetric unit is shown in Figure 1. This consists of two independent ion pairs.

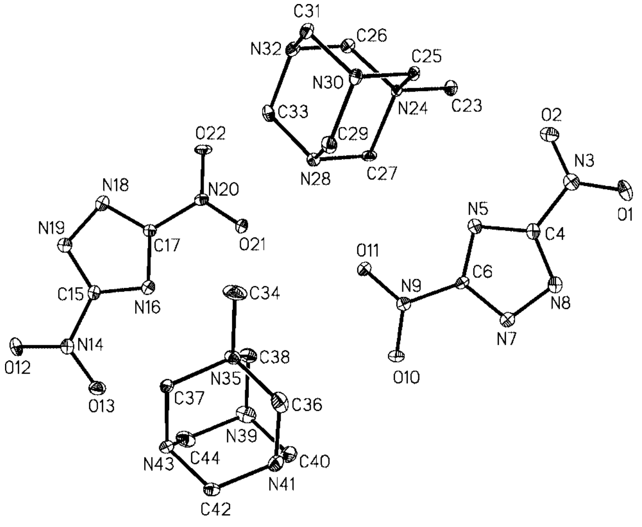


Figure 1. Thermal ellipsoid plot (30%) of the asymmetric unit of compound **6**. Hydrogen atoms omitted for clarity.

The most distinctive feature of this structure is the angle of the NO_2 groups to the triazolate anion which vary widely (O1–N3–O2, 2.7°; O10–N9–O11, 7.8°; O12–N14–O13, 7.5°; O21–N20–O22, 14°). These dinitrotriazolate anions pack in offset stacks parallel to the *b* axis, with an inter anion spacing of 3.11 Å (see supporting information). A summary of the crystal data for compound **6** is given in Table 1.

Table 1. Crystallographic data for compound **6**.

Compound	**6**
Formula	$C_9H_{15}N_9O_4$
Formula weight	313.30
Crystal system	monoclinic
Space group	$P21/n$
a [Å]	20.499(6)
b [Å]	6.2209(18)
c [Å]	20.890(6)
β [°]	102.924(6)
V [Å^3]	2596.4(13)
Z	8
T [K]	87(2)
λ [Å]	0.71073
$\rho_{calcd.}$ [Mg m^3]	1.603
μ [mm^{-1}]	0.129
$F(000)$	1312
Crystal size [mm]	$0.30 \times 0.07 \times 0.04$
θ range [°]	1.00 to 25.25
Index ranges	$-24 \leq h \leq 24$, $-7 \leq k \leq 7$, $-25 \leq l \leq 25$
No. reflections collected	37831
No. indepentent reflections	4691 [R(int) = 0.0624]
Data/restraints/parameters	4691/0/400
GOF	1.083
R_1 [$I > 2\sigma(I)$][a]	0.0549
wR_2 [$I > 2\sigma(I)$][a]	0.1276
Largest diff. peak, hole [e·Å^{-3}]	0.419, –0.250

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

Comparison of the melting points of compounds **1**–**4**, and **6**, **7**, **8**, **10** (Table 2), clearly illustrates the influence of different anions, e.g., the melting point for compound **4** (m.p. 166 °C), which has 5-nitrotetrazolate as anion, is considerably lower than that of 3,5-dinitropyrazolate, 4,5-dinitroimidazolate and 3,5-dinitro-1,2,4-triazolate as anions in **1** (m.p. 180 °C), **2** (m.p. 183 °C) and **3** (m.p. 177 °C), respectively. The melting point for compound **6** (m.p. 170 °C), which has 3,5-dinitro-1,2,4-triazolate as anion, is lower or higher than that of nitrate, perchlorate or azide as anions, which melts at 194 °C, 200 °C, and 165 °C, respectively. It is also can be seen that compounds **3** and **6** have the same anion (3,5-dinitro-1,2,4-triazolate), for **6**, which has a *N*-methyl group on the cation ring, its melting point and decomposition temperature (**6**, T_d = 202 °C) are lower and higher than that of compound **3** (T_d = 182 °C), respectively.

Table 2. Phase transition, decomposition temperatures, densities, oxygen coefficient (α), nitrogen content (N), and thermochemical results for synthesized salts.

Compd.	T_m[a] [°C]	T_d[b] [°C]	d[c] [g cm^{-3}]	N [%]	α[d] [%]	$-\Delta H_L$[e] [kJ·mol^{-1}]	$\Delta_f H_m°$[f] [kJ·mol^{-1}]
1	180	184	1.56	37.6	16	452.7	–
2	183	183	1.41	37.6	16	441.3	–
3	177	182	1.72	42.1	18	463.7	268.7
4	166	169	1.48	49.4	10	464.7	435.3
6	170	202	1.45	40.2	16	438.9	250.7
7	194	196	1.42	32.2	14	479.2	–30.6
8	200	205	1.47	22.0	–	464.2	14.5
10	165	176	1.35	49.7	0	484.9	468.8
11[g]	160	–	1.57	–	–	–	–388.3

[a] Melting point (T_m). [b] Thermal degradation (T_d). [c] Measured density using gas pycnometer at 25 °C. [d] For $C_aH_bO_cN_d$: $\alpha = 100\ c/(2a + b/2)$. [e] Lattice energy. [f] Calculated molar enthalpy of formation. [g] Hexamethylenetetrammonium dinitrate, ref.[22].

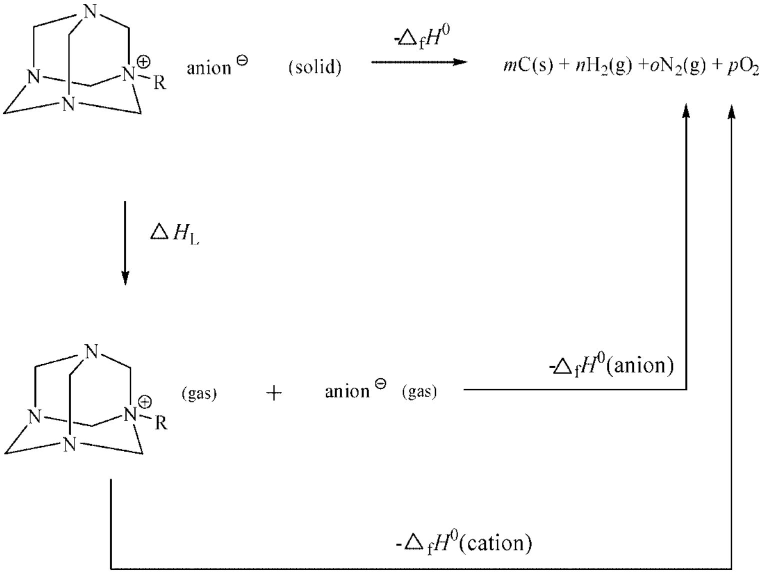
Density, oxygen coefficient, and enthalpy of formation are important characteristics of energetic compounds, and are governed by their molecular structures. Increasing the number of nitrogen atoms in a heterocycle results in a considerable gain in the heat of formation.[5] Density, oxygen coefficients, nitrogen content and the calculated heats of formation for the energetic salts are listed in Table 2. Densities for all of the compounds exceed 1.35 g cm^{-3}, and compound **3** has the highest density (1.72 g cm^{-3}). The oxygen coefficient (α), which is defined as $\alpha = c/(2a + b/2)$ for the molecular formula $C_aH_bO_cN_d$, is calculated by a literature method.[28a] Incorporation of a nitro group can substantially improve the oxygen balance of the corresponding compounds, and eventually results in higher exothermicities of the combustion and detonation processes. The oxygen coefficient values of C,H,O,N-containing energetic compounds belong to the classes of fuels ($\alpha < 0.4$), explosives ($0.4 \leq \alpha \leq 1.0$), and oxidants ($\alpha > 1.0$).[28b] The oxygen coefficients for the new salts are between 0.10–0.18 (Table 2), which fall at < 0.4 among the majority of the known energetic compounds.[28b] The calculated nitrogen contents for the new salts are between 22–50% (Table 2).

The standard molar enthalpy of formation ($\Delta_f H_m°$) for the salts **3**, **4**, **6**–**8**, **10** were calculated by the following Born–Haber energy cycles (Scheme 2). Calculations were made with the Gaussian03 (Revision D.01) suite of programs.[29] The geometric optimization of the structures and frequency calculations were performed at (DFT)[30,31]/B3LYP[32] level of theory using the 6-31+G** basis set. Single-point energies were calculated at the MP2/6-311++G** level.[33,34] According to the previous studies, the computed harmonic vibrational frequencies were scaled uniformly by a factor of 0.96 to take into account the systematic overestimation of these frequencies in the B3LYP/6-31+G** calculations.[35] Based on this data, the heats of formation of the anions and cations were calculated and combined with the lattice energy of the salts to give the heats of formation of the salts. Because the most efficient computational procedure for finding accurate heats of formation is based on isodesmic (bond type conserving) reactions,[36] in the present case, the reactions used to calculate the heat of formation of both cations and anions are given in Scheme 3.

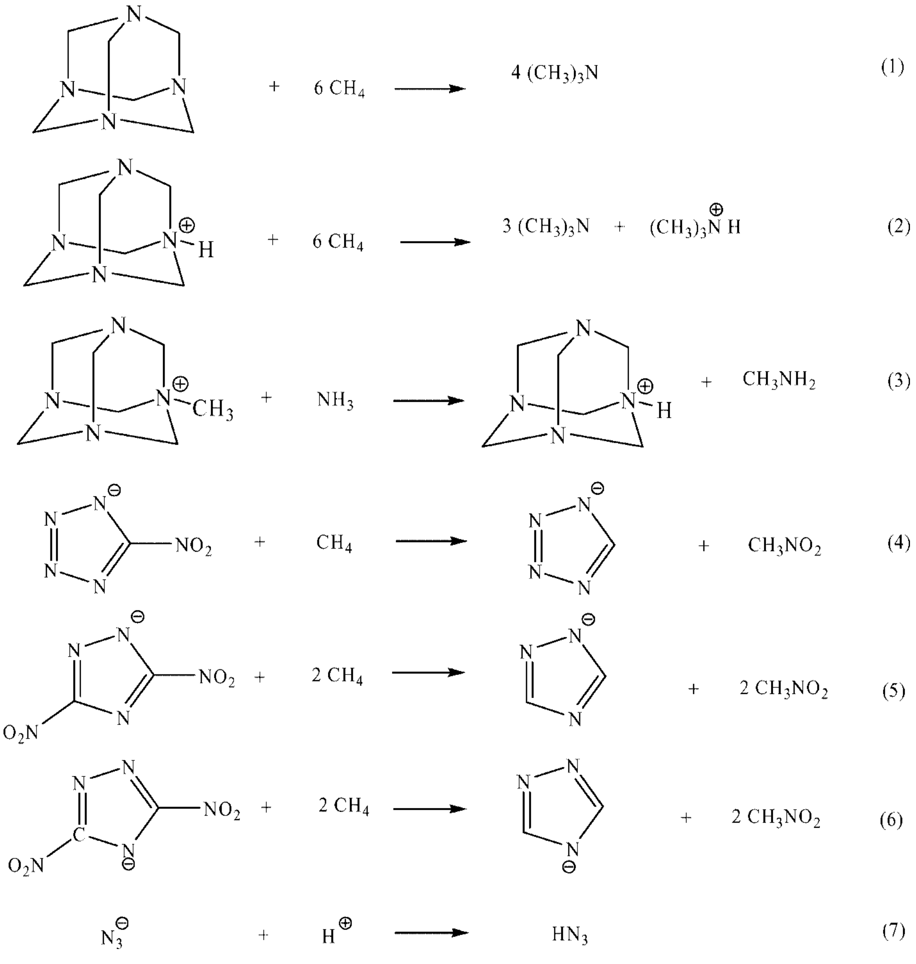
The heat of formation of 3,5-dinitrotriazole was calculated by averaging its actual resonance hybrids shown in Equations (5) and (6) in Scheme 3. The lattice potential energy ΔH_L for M_pX_q was calculated using the relationship provided by Jenkins (equation **A**),[37] where n_M and n_X depend on the nature of the ions M_p^+ and Xq^-, respectively, and is equal to

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

with n = 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions.



Scheme 2. General Born–Haber cycle for the formation of hexamethylenetetrammonium salts. For **3:** R = H, anion = 3,5-dinitrotriazolate, $m = 8$, $n = 6.5$, $o = 4.5$, $p = 2$, $q = 0$; **4:** R = H, anion = 5-nitrotetrazolate, $m = 7$, $n = 6.5$, $o = 4.5$, $p = 1$, $q = 0$; **6:** R = CH_3, anion = 3,5-dinitrotriazolate, $m = 9$, $n = 7.5$, $o = 4.5$, $p = 2$, $q = 0$; **7:** R = CH_3, anion = NO_3^-, $m = 7$, $n = 7.5$, $o = 2.5$, $p = 1.5$, $q = 0$; **8:** R = CH_3, anion = ClO_4^-, $m = 7$, $n = 7.5$, $o = 2$, $p = 2$, $q = 0.5$; **10:** R = CH_3, anion = N_3^-, $m = 7$, $n = 7.5$, $o = 3.5$, $p = 0$, $q = 0$.



Scheme 3. Isodesmic reactions for calculating the heats of formation of both cations and anions.

The equation for lattice potential energy U_{POT} (equation **B**) has the form

$$U_{POT}\ [\mathrm{kJ{\cdot}mol^{-1}}] = \gamma\ (\rho_m/M_m)^{1/3} + \delta \qquad (\mathbf{B})$$

where ρ_m [g cm^{-3}] is the density, M_m is the chemical formula mass of the ionic material [g or Mg]; the coefficients γ [kJ·mol^{-1} cm] and δ [kJ·mol^{-1}] are equal to 8375.6 and –178.8, respectively. Comparison of the data for compounds **3** and **4** reveals that $\Delta_f H_m°$ for **4** (+435.3 kJ·mol^{-1}), which has 5-nitrotetrazolate as the anion, is considerably higher than that for the 3,5-dinitro-1,2,4-triazolate anion and **3** (+268.7 kJ·mol^{-1}). From the $\Delta_f H_m°$ values for **6**, **7**, **8**, **10** it can be seen that for the same cation, the heat of formation of the compound with azide as anion, is considerably higher than those of corresponding compounds with 3,5-dinitro-1,2,4-triazolate, perchlorate or nitrate as anions, which varies as **10** (azide) > **6** (3,5-dinitro-1,2,4-triazolate) > **8** (perchlorate) > **7** (nitrate) (+468.8, +250.7, +14.5, –30.6 kJ·mol^{-1}), respectively.

In conclusion, we have synthesized new hexamethylenetetrammonium salts composed of the energetic anions 3,5-dinitropyrazolate, 4,5-dinitroimidazolate, 3,5-dinitro-1,2,4-triazolate, 5-nitrotetrazolate, perchlorate, nitrate and azide. Most of the new salts exhibit valuable physical properties, including relatively high densities (>1.35 g cm^{-3}) and high positive heats of formation.

Experimental Section

Caution: Although we have not experienced any problems in handling these compounds, based on the high positive heats of formation, all materials should be handled with extreme care.

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. Chemical shifts were reported relative to Me_4Si. The melting and decomposition points were recorded with a differential scanning calorimeter and a thermogravimetric analyzer at a scan rate of 10 °C min^{-1}, respectively. IR spectra were recorded using KBr pellets for solids. Densities of solid salts were measured at room temperature using a Micromeritics Accupyc 1330 gas pycnometer. Elemental analyses were measured with a CE-440 elemental analyzer.

3,5-Dinitropyrazole,[42] 4,5-dinitroimidazole,[43] 3,5-dinitro-1,2,4-triazolate[25] 5-nitrotetrazole[44] and silver 3,5-dinitro-1,2,4-triazolate[26] were synthesized according to literature procedures.

X-ray Crystallographic Studies: Crystals of compound **6** were removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber and placed in the low-temperature nitrogen stream.[38] Data for **6** were collected at 87(2) K with 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 ω scans of 0.3° per frame for 60 s, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.83 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART[39] software and refined using SAINTPlus[40] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[41a] The structure was solved by direct methods and refined by least-squares method on F^2 using the SHELXTL program package.[41b] The structure was solved in the space group $P21/n$ (#14) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. No decomposition was observed during data collection.

CCDC-294742 (for **6**) contains the complete set of 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.

Supporting Information (see footnote on the first page of this article): Ball and stick packing diagrams of **6** and a table with hydrogen bonds for **6**.

Hexamethylenetetrammonium 3,5-Dinitropyrazolate (1): A dry, nitrogen-filled Schlenk glass tube was charged with hexamethylenetetramine (0.140 g, 1.0 mmol), dry methanol (5 mL), and 3,5-dinitropyrazole (0.158 g, 1.0 mmol). The mixture was stirred 10 h at room temperature. The solvent was removed under vacuum overnight to leave a white solid **1**: 97% yield (0.29 g), m.p. 180 °C. IR (KBr): ṽ = 3151, 2949, 2899, 2253, 1540, 1487, 1438, 1346, 1315, 1262, 1224, 1161, 1066, 1016, 982, 871, 823, 748, 686, 662 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 4.82 (s, 12 H), 7.29 (s, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 157.24, 99.16, 72.17 ppm. $C_9H_{14}N_8O_4{\cdot}0.5H_2O$ (307.11): calcd. C 35.18, H 4.88, N 36.48; found C 35.52, H 4.52, N 36.89.

Hexamethylenetetrammonium 4,5-Dinitroimidazolate (2): A dry, nitrogen-filled Schlenk glass tube was charged with hexamethylenetetramine (0.140 g, 1.0 mmol), dry methanol (5 mL), and 4,5-dinitroimidazole (0.158 g, 1.0 mmol). The mixture was stirred for 10 h at room temperature. The solvent was taken off under vacuum overnight to give a yellow solid **2**: 97% yield (0.29 g), m.p. 183 °C. IR (KBr): ṽ = 3106, 2937, 2777, 2555, 2485, 1760, 1535, 1506, 1462, 1351, 1311, 1261, 1219, 1184, 1098, 1063, 985, 817, 751, 659 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 4.83 (s, 12 H), 6.96 (s, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 141.69, 140.77, 72.70 ppm. $C_9H_{14}N_8O_4$ (298.11): calcd. C 36.24, H 4.73, N 37.57; found C 35.88, H 4.56, N 37.11.

Hexamethylenetetrammonium 3,5-Dinitro-1,2,4-triazolate (3): Compound **3** was prepared by a similar procedure as above, from hexamethylenetetramine (0.140 g, 1.0 mmol) and 3,5-dinitro-1,2,4-triazole (0.159 g, 1.0 mmol) to form a white solid in 98% yield, m.p. 177 °C. IR (KBr): ṽ = 3092, 2967, 2679, 2390, 1549, 1489, 1384, 1350, 1285, 1265, 1206, 1101, 1010, 977, 840, 815, 748, 650 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 4.84 (s, 12 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 163.75, 72.07 ppm. $C_8H_{13}N_9O_4$ (299.11): calcd. C 32.11, H 4.38, N 42.13; found C 31.79, H 4.17, N 41.88.

Hexamethylenetetrammonium 5-Nitrotetrazolate (4): Compound **4** was prepared by a similar procedure as above, from hexamethylenetetramine (0.140 g, 1.0 mmol) and 5-nitrotetrazole (0.115 g, 1.0 mmol) to form a white solid in 98% yield, m.p. 166 °C. IR (KBr): ṽ = 2953, 2813, 2771, 2548, 2410, 2133, 1541, 1466, 1413, 1364, 1314, 1267, 1216, 1143, 1011, 818, 745, 654 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 4.84 (s, 12 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 170.27, 72.57 ppm. $C_7H_{13}N_9O_2{\cdot}H_2O$ (273.12): calcd. C 30.77, H 5.49, N 46.15; found C 30.99, H 4.66, N 46.68.

***N*-Methylhexamethylenetetrammonium Iodide (5):** Compound **5** was prepared by a minor modification of the previous synthesis,[23] from hexamethylenetetramine and CH_3I at room temperature, using chloroform as solvent to give a white solid **5** in quantitative yield: m.p. 202 °C. IR (KBr): ṽ = 2955, 1736, 1462, 1431, 1382, 1312, 1253, 1150, 1043, 1018, 993, 958, 816, 712, 648 cm^{-1}. ^{1}H NMR

([D$_6$]DMSO): δ = 2.49 (s, 3 H), 4.41–4.62 (q, ^2J = 12.0 Hz, 6 H), 5.09 (s, 6 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 80.81, 71.22, 43.70 ppm.

General Procedure for the Preparation of Salts from 5

***N*-Methylhexamethylenetetrammonium 3,5-Dinitro-1,2,4-triazolate (6):** To a magnetically stirred solution of **5** (0.282 g, 1.0 mmol) in CH_3CN (5 mL) was added silver 3,5-dinitro-1,2,4-triazolate (0.266 g, 1.0 mmol). After 2 h at room temperature, silver iodide was removed by filtration. The filtrate was dried in vacuo to give a yellow solid (0.30 g, 96% yield), m.p. 170 °C. IR (KBr): $\tilde{\nu}$ = 2960, 2713, 2434, 2139, 1535, 1483, 1463, 1375, 1335, 1244, 1150, 1097, 1039, 1015, 990, 956, 823, 648 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 2.47 (s, 3 H), 4.40–4.64 (q, ^2J = 12.0 Hz, 6 H), 5.04 (s, 6 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 164.43, 80.93, 71.27, 43.76 ppm. $C_9H_{15}N_9O_4$ (313.12): calcd. C 34.51, H 4.83, N 40.24; found C 34.53, H 4.58, N 40.14.

***N*-Methylhexamethylenetetrammonium Nitrate (7):** Compound **7** was prepared by a similar procedure as compound **6**, from **5** (0.282 g, 1.0 mmol) and silver nitrate (0.170 g, 1.0 mmol) using H_2O as solvent to form a white solid in 98% yield, m.p. 194 °C. IR (KBr): $\tilde{\nu}$ = 2959, 2712, 2152, 2059, 1742, 1634, 1470, 1376, 1246, 1145,1043, 993, 957, 817, 785, 713, 650 cm^{-1}. ^{1}H NMR ([D$_6$]-DMSO): δ = 2.47 (s, 3 H), 4.40–4.64 (q, ^2J = 12.0 Hz, 6 H), 5.05 (s, 6 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 80.88, 71.24, 43.70 ppm. $C_7H_{15}N_5O_3$ (217.12): calcd. C 38.70, H 6.96, N 32.24; found C 38.22, H 6.85, N 32.10.

***N*-Methylhexamethylenetetrammonium Perchlorate (8):** Compound **8** was prepared by a similar procedure as compound **6**, from **5** (0.282 g, 1.0 mmol) and silver perchlorate (0.208 g, 1.0 mmol) using H_2O as solvent to give a white solid in 98% yield, m.p. 200 °C. IR (KBr): $\tilde{\nu}$ = 3012, 2972, 2453, 2178, 1634, 1469, 1381, 1267, 1247, 1147, 1086, 992, 952, 821, 785, 650, 619 cm^{-1}. ^{1}H NMR (D_2O): δ = 2.65 (s, 3 H), 4.55–4.75 (q, ^2J = 12.0 Hz, 6 H), 5.09 (s, 6 H) ppm. ^{13}C NMR (D_2O): δ = 81.00, 70.95, 44.11 ppm. $C_7H_{15}N_4ClO_4$ (254.08): calcd. C 33.01, H 5.94, N 22.00; found C 33.10, H 5.98, N 21.88.

***N*-Methylhexamethylenetetrammonium Fluoride (9):** Compound **9** was prepared by a similar procedure as compound **6**, from **5** (0.282 g, 1.0 mmol) and silver fluoride (0.127 g, 1.0 mmol) using H_2O as solvent to form a white solid in 98% yield, m.p. 68 °C. IR (KBr): $\tilde{\nu}$ = 3397, 2958, 1666, 1457, 1389, 1246, 1148, 1011, 959, 933, 816, 648 cm^{-1}. ^{1}H NMR (D_2O): δ = 2.65 (s, 3 H), 4.55–4.75 (q, ^2J = 12.0 Hz, 6 H), 5.08 (s, 6 H) ppm. ^{13}C NMR (D_2O): δ = 80.98, 70.93, 44.08 ppm. ^{19}F NMR (D_2O): δ = –122.35 (s, 1F) ppm. $C_7H_{15}N_4F{\cdot}0.8H_2O$ (188.53): calcd. C 44.58, H 8.82, N 29.72; found C 44.60, H 8.88, N 30.03.

***N*-Methylhexamethylenetetrammonium Azide (10):** Compound **10** was prepared by a modified literature method,[23,27] from **9** (0.174 g, 1.0 mmol) and $(CH_3)_3SiN_3$ (0.173 g, 1.5 mmol) using dry methanol as solvent, stirred at room temperature for 5 h to leave a white solid in quantitative yield, m.p. 165 °C. IR (KBr): $\tilde{\nu}$ = 3443, 3282, 2956, 2890, 2446, 2293, 2030, 1627, 1460, 1386, 1315, 1248, 1147, 1043, 993, 956, 817, 713, 648 cm^{-1}. ^{1}H NMR (D_2O): δ = 2.66 (s, 3 H), 4.56–4.76 (q, ^2J = 12.0 Hz, 6 H), 5.10 (s, 6 H) ppm. ^{13}C NMR (D_2O): δ = 81.00, 70.95, 44.09 ppm.

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