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Synthesis and Promising Properties of a New Family of High-Density Energetic Salts of 5-Nitro-3-trinitromethyl-1*H*-1,2,4-triazole and 5,5′-Bis(trinitromethyl)-3,3′-azo-1*H*-1,2,4-triazole

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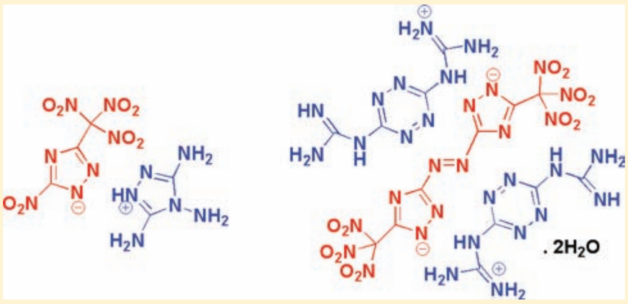
Supporting Information

ABSTRACT: Salts of trinitromethyl-substituted triazoles, 5-nitro-3-trinitromethyl-1*H*-1,2,4-triazole and 5,5′-bis(trinitromethyl)-3,3′-azo-1*H*-1,2,4-triazole (**5**), form a new class of highly dense energetic materials. Single-crystal X-ray structuring supports the formation of the cocrystal of **5** with 3,5-diamino-1,2,4-triazole, which was found to be remarkably less impact-sensitive than the azo precursor. The compounds were fully characterized using IR and multinuclear NMR spectroscopy, elemental analysis, and differential scanning calorimetry. Based on heats of formation calculated with Gaussian 03 and combined with experimentally determined densities, detonation properties of the energetic materials obtained with the EXPLO5 program identify them as potentially explosive compounds. They exhibit high density, moderate to good thermal stability, acceptable oxygen balance, reasonable heat of formation, and excellent detonation properties, which in some cases are superior to those of 1,3,5,-trinitrotriazacyclohexane (RDX).



INTRODUCTION

In the field of high-energy materials, the synthesis and development of new energetic materials continues to focus on new heterocycles with high densities, high heats of formation, and good oxygen balance (index of the deficiency or excess of oxygen in a compound required to convert all carbon into carbon dioxide, and all hydrogen into water).[1] Nitrogen-rich energetic salts are environmentally friendly high-energy-density materials (HEDMs), and they have attracted considerable interest due to the lower vapor pressures, higher heats of formation, and enhanced thermal stabilities compared with their atomically similar nonionic analogues.[2] The general methods for the preparation of energetic salts are by neutralization or metathesis reactions with N-protonated cations such as ammonium, hydrazinium, azolium, azinium, etc., and C-, N-, or O-deprotonated anions such as nitroformate, azolate, or picrate.[3] In the quest for higher detonation performance and lower sensitivity, many energetic salts with nitrogen-rich cations or nitrogen-containing heterocyclic anions have been obtained through combination of carefully selected ions. Their full characterization provides knowledge of structure−property relationships in energetic salts.[4]

After decades of effort in the development of high-energy materials, the key concerns in weapon systems continue to be higher performance and lower sensitivity.[5] The most desirable characteristics for new energetic materials include high positive heat of formation, high density, high detonation velocity and pressure, high thermal stability, and low sensitivity toward external forces such as impact, shock, and friction. High-nitrogen compounds (e.g., azoles) in combination with energetic substituents such as nitro ($-NO_2$), nitrato ($-ONO_2$), nitramine ($-NHNO_2$), and nitroimine ($=NNO_2$) functionalities are of particular interest since these compounds have satisfactory oxygen content.[6] However, the requirements of insensitivity and high energy along with positive oxygen balance are quite often contradictory to each other, making the development of new HEDMs an interesting and challenging problem.[7]

Highly energetic compounds which have polynitro groups are one of the important classes of useful energetic materials. The presence of nitro groups tends to decrease the heat of formation but contributes markedly to the overall energetic performance.[8] Also, the nitro group contributes to enhance the oxygen balance and density, which improves the detonation performance (pressure and velocity).[9] Traditional polynitro compounds produce energy primarily from the combustion of the carbon backbone while consuming the oxygen provided by the nitro groups (Scheme 1).[10] High-energy materials containing large numbers of nitrogen atoms, so-called "high-nitrogen" compounds, have been shown to derive energy from the presence of many energetic N−N and C−N bonds.[11]

Nitrogen-containing heterocycles with more than two nitro groups are expected to be highly powerful but insensitive explosives.[6a] Highly nitrated small-ring heterocycles and

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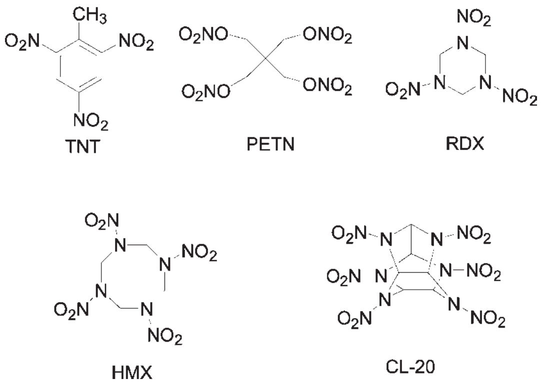
carbocycles are interesting energetic materials based on performance arising from the additional energy release upon opening of the strained ring systems during decomposition.[12] Several explosives are well known, such as triaminotrinitro benzene (TATB), 1,3,5,-trinitrotriazacyclohexane (RDX), 1,3,5,7-tetranitrotetraazacyclooctane (HMX), and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclododecane (CL-20) (Scheme 1). One of the important classes of high-energy materials are polynitro azoles. They have been a recent focus of energetic material research groups because of their high performance and low sensitivity to friction and impact.[13] In addition, nitro azoles are valuable in the pharmaceutical field as nitro-containing synthetic intermediates and drugs.[14]

The need for energetic materials that exhibit a combination of good thermal stability, lower impact sensitivity, and higher heat 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 HEDMs, since salts are intrinsically nonvolatile, are often thermally stable under normal conditions, and are more dense.[15] 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 variation of substituents on those ions obtained from earlier work are important references for screening and designing work.[16]

In a continuing effort to seek more powerful, less sensitive, eco-friendly energetic materials, we are interested in heterocyclic compounds that contain a high percentage of both oxygen and nitrogen, and lower amounts of carbon and hydrogen. Heterocyclic compounds with high nitrogen content are environmentally friendly, have high heats of formation, and are endothermic. The high nitrogen content of these compounds often leads to high crystal density, which is associated with increased performance. In addition, the incorporation of a triazole ring into a compound is a known strategy for increasing thermal stability. Many triazole compounds show high thermal sensitivity coupled with low sensitivity to shock and impact.[17] Recently, the search for a smokeless propellant has encouraged scientists to look for chlorine-free oxidizers as a substitute for ammonium perchlorate because it contributes to acid rain and ozone layer depletion, in addition to having deleterious impacts on the human thyroid and being a persistent contaminant in groundwater.[18] Trinitromethyl groups provide oxygen to the oxidizers, and trinitromethyl-substituted azoles are stable energetic compounds.[19] Recently, we reported the synthesis of trinitromethyl-substituted triazoles, 5-nitro-3-trinitromethyl-1*H*-1,2,4-triazole (**3**) and 5,5′-bis(trinitromethyl)-3,3′-azo-1*H*-1,2,4-triazole (**5**).[19a] The salts of these compounds are likely to exhibit high density and detonation properties and to be insensitive energetic materials. To the best of our knowledge, energetic salts of C-trinitromethyl-substituted azoles which have acidic N−H bonds along with their energetic properties are unknown. In this paper, we report the synthesis of various high-density energetic salts of polynitro-1,2,4-triazoles which contain trinitromethyl groups and display potentially significant physical and energetic properties.

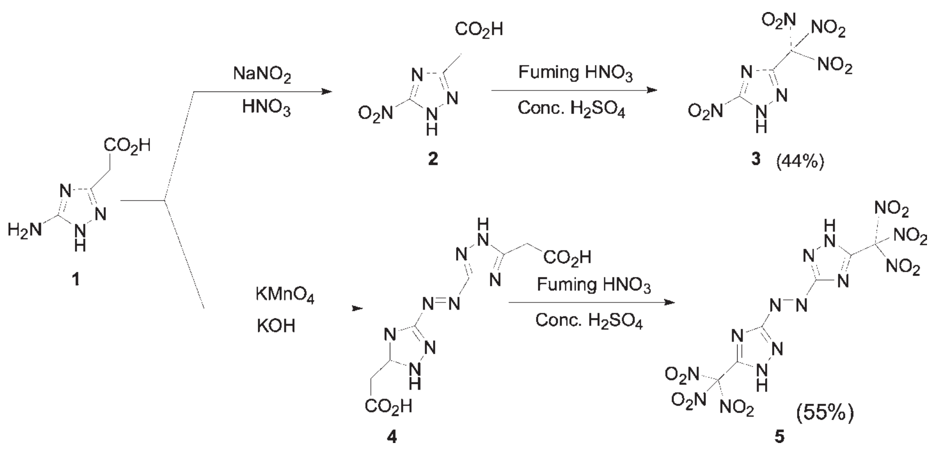
Scheme 1. Traditional Energetic Polynitro Compounds



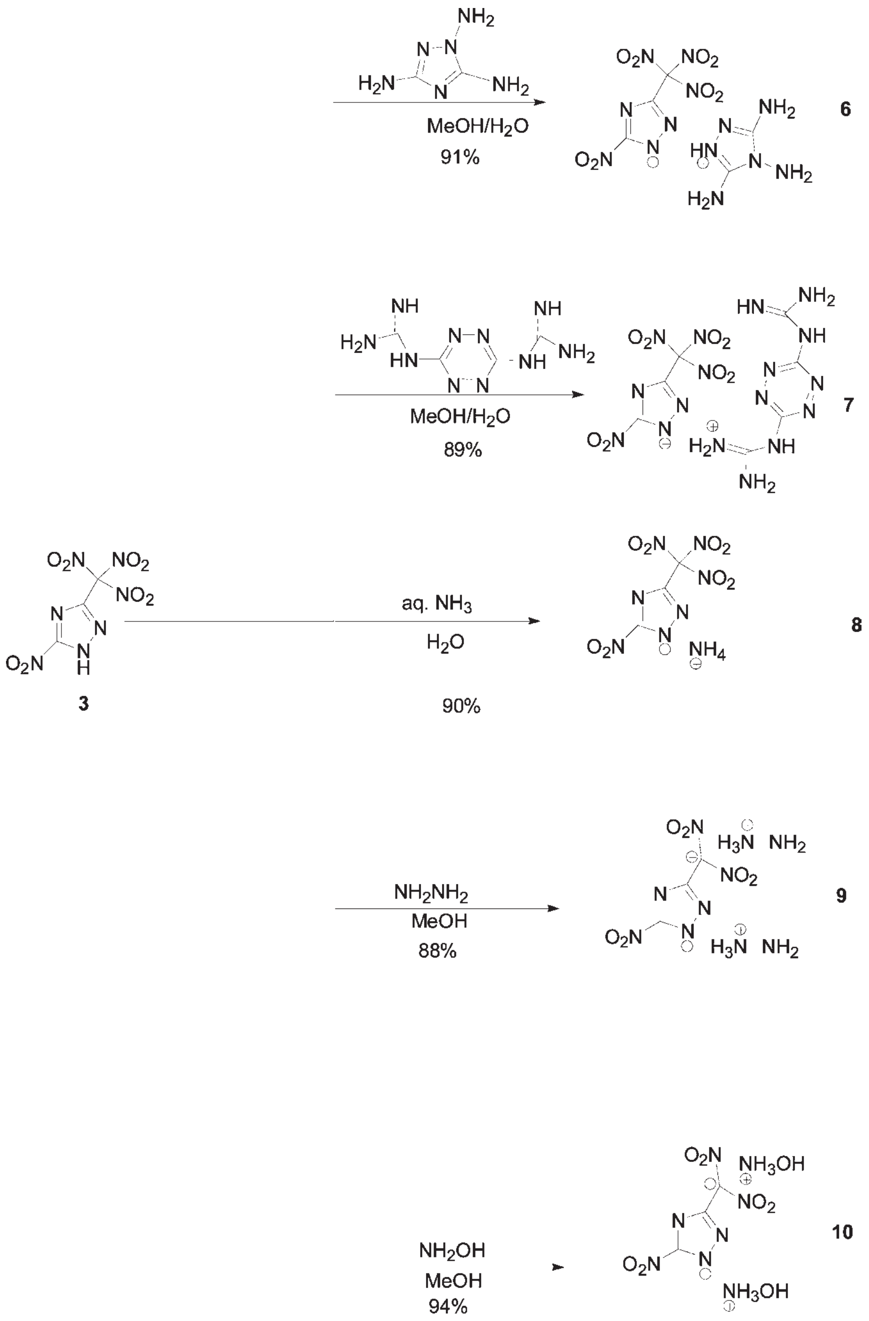
RESULTS AND DISCUSSION

Azoles containing active methylene groups can be converted into corresponding nitromethyls by reacting with mixed acids (fuming nitric acid and concentrated sulfuric acid). Azolylacetic acids give trinitromethyl-substituted compounds in one-pot reactions.[19b] 5-Amino-1,2,4-triazolyl-5-acetic acid (**1**) was prepared by the condensation of aminoguanidine bicarbonate and malonic acid. The amine group of **1** was converted into a nitro group by reacting with sodium nitrite in acidic medium. Nitration using mixed acids produced trinitromethyl triazole **3**. Similarly, the azo-compound **4**, which was prepared by reacting aminotriazole **1** with potassium permanganate, was converted to the corresponding trinitromethyl compound **5** by mixed acid nitration (Scheme 2).[19a,20]

Scheme 2. Synthetic Pathways for Trinitromethyl-Substituted Triazoles 3 and 5



Scheme 3. Synthesis of Energetic Salts of 3

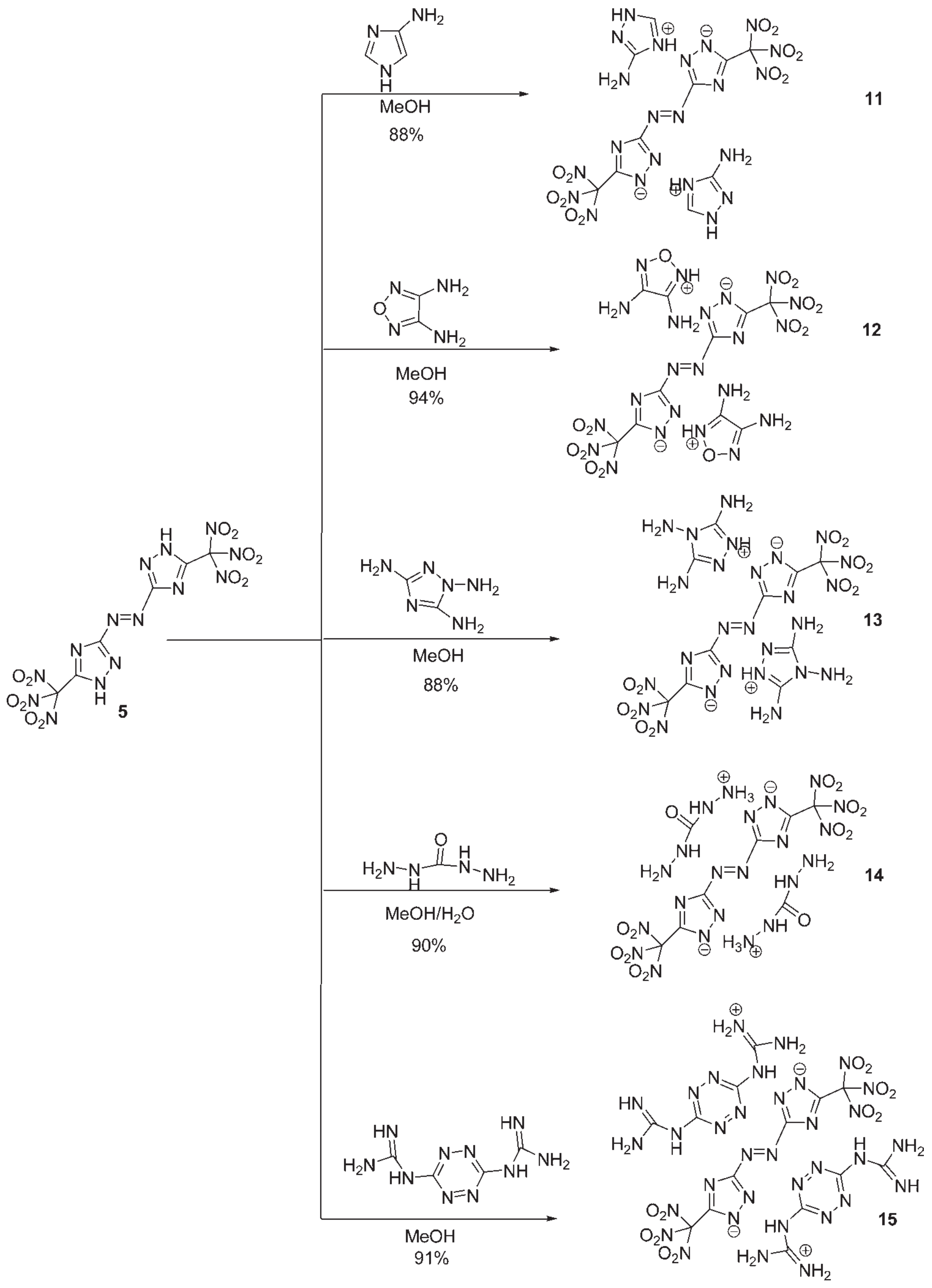


3 has an oxygen content of 48.7% with positive oxygen balance (+9.12) and a positive heat of formation (123.2 kcal mol^{-1}).[19a] Reactions of tetranitro triazole **3** with 3,4,5-triamino triazole, bis(guanidinium) tetrazine, and ammonia resulted in the formation of salts **6**, **7**, and **8** (Scheme 3). Reaction of **3** with excess ammonia also produced the monoammonium salt **8**.[21a] Reaction of **3** with 1 molar equiv of hydrazine or hydroxylamine produced impure mixtures of compounds. Increasing the molar equivalents of hydrazine and hydroxylamine vis-à-vis **3** produced the dihydrazinium (**9**) and dihydroxylammonium (**10**) salts, respectively. Interestingly, one of the nitro substituents of the trinitromethyl group was removed in addition to the N-1 hydrogen of the triazole ring to form dications in the latter two reactions. It may be that hydrazine and hydroxylamine are more nucleophilic than ammonia (Scheme 3).[21b]

Reactions of **5** with 2 mol of 3-aminotriazole, 3,4-oxadiazole, diamino urea, 3,4,5-triamino 1,2,4-triazole, and bis(guanidinium) tetrazine resulted in the formation of dianionic salts **11**−**15** (Scheme 4). All of the salts are nonhygroscopic and stable in air, and were isolated as crystalline materials in good yields. The reaction of hexanitro triazole **5** with hydrazine or hydroxylamine produced a mixture of compounds which were not identified.

The structures of the new salts were determined by ^{1}H and ^{13}C NMR (some salts with ^{15}N NMR) and IR spectroscopy and elemental analysis. In the ^{1}H NMR spectra, the hydrogen signals of the cations were observed and easily assigned since there are

Scheme 4. Synthesis of Energetic Salts of 5



no protons associated with the anions of triazoles 3 and 5. In the IR spectra, several main absorption bands around 1540, 1480, 1420, and 1310 cm^{-1} are attributed to the triazole anions. The intense bands in the range of 1600−1630 cm^{-1} can be assigned to the trinitromethyl groups. In the ^{13}C NMR spectra, resonance bands for the trinitromethyl group appear between 120 and 130 ppm. ^{13}C NMR chemical shifts of the dinitromethyl group of salts **9** and **10** appeared downfield compared to those of the trinitromethyl compounds.[19b] The ^{15}N NMR spectra of the salts of tetranitro triazole (**3**) were measured in DMSO-d_6 solution, and chemical shifts are given with respect to CH_3NO_2 as external standard. In Figure 1, the ^{15}N NMR spectra of **3**, **6**, **8**, and **9** are shown. As in the parent tetranitro triazole **3**, the anionic triazole nitrogen signals are seen upfield relative to the nitro and trinitromethyl groups, with the N2 signal of the triazole ring downfield relative to N3 and N1. The N3 nitrogen resonance falls between N2 and N1 (Figure 1). Based on comparison with the literature, the chemical shifts of the hydroxylamine, hydrazine moieties, and $^{+}NH_3$ groups can be assigned to the resonances at highest field.[5d] The salts of hexanitro triazole **5** are only slightly soluble in organic solvents, including DMSO-d_6, and thus it was not possible to obtain ^{15}N spectra. The salts decomposed when heated in DMSO-d_6.

X-ray Crystallography of Cocrystal of Hexanitro Triazole 5 with 3,5-Diamino Triazole 16. The N-methylated derivative of tetranitro **3** has been studied by X-ray crystallography,[19a] but

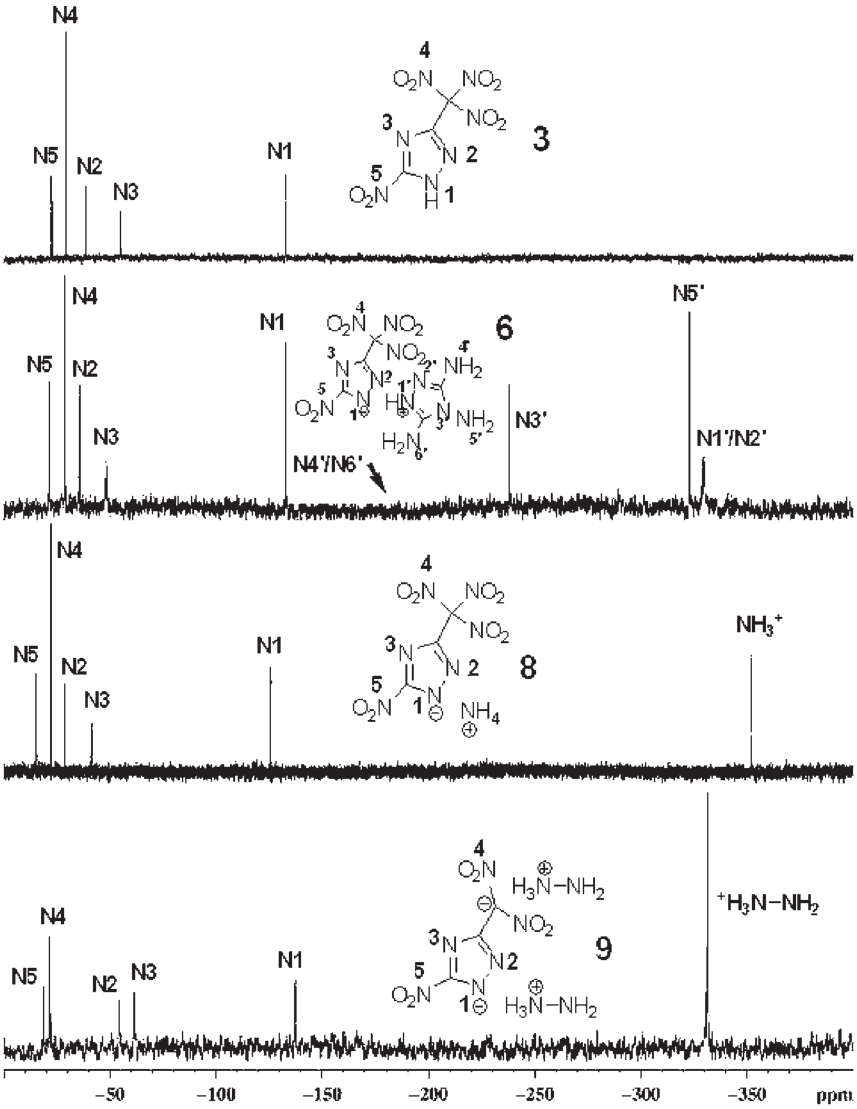


Figure 1. Selected ^{15}N NMR spectra of tetranitro triazole **3** salts.

X-ray structures of hexanitro triazole **5** or its derivatives are unknown.

The preparation of crystals of **5** suitable for X-ray diffraction (XRD) analysis was unsuccessful. Therefore, an attempt was made to prepare cocrystals of **5** with amine-substituted triazoles.

Cocrystallization of different components represents supramolecular synthesis where hydrogen bonds link molecules. Cocrystals are different from solid solutions or mixed crystals and can be considered as molecular complexes. The donor and acceptor functionalities can be brought together more easily than with single-component systems because the partners are more accessible to arrange themselves into an optimal geometry, leading to favorable intermolecular interactions.[22] 3-Amino-1,2,4-triazole, 4-amino-1,2,4-triazole, and 3,5-diamino-1,2,4-triazole were used in attempts to prepare cocrystals with hexanitrotriazole **5**. Through N−H···O interactions, triazole **5** formed cocrystals with 3,5-diamino-1*H*-1,2,4-triazole (**16**) only when equimolar amounts were dissolved in a mixture of 1:1 water:methanol.

Cocrystal **16** has a crystallographic density of 1.67 g cm^{-3} at 100 K, which is somewhat lower than that of the parent hexanitro triazole **5**. A significant decrease in the decomposition temperature of **5** was observed with cocrystal **16**, decomposing at 120 °C. Incorporating insensitive **16** into a cocrystal with hexanitro **5** greatly reduces its impact sensitivity from 1.5 to 9.0 J, potentially improving the viability of **5** in explosive applications.

The cocrystals obtained were suitable for single-crystal XRD determination, crystallizing in a triclinic crystal system (space group $P\bar{1}$) (Figure 2). The N−N bond length of the azo bridge is 1.242(13) Å, which is shorter than N5−N6 bond lengths of the triazole ring [1.342(10) Å]. The triazole ring and three nitro groups are tetragonally attached to C7. The C−N bond length of trinitromethyl is 1.556(15) Å, which is longer than the C−N bond length [1.525(3) Å] of trinitroethyl-containing molecules. Each cation can form a variety of hydrogen bonds. The extensive hydrogen-bonding interactions between the two molecules form a complex 3D network. Further details are provided in the Supporting Information.

Physical Properties. Heat of formation is one of the important characteristics for energetic salts which is directly related to the number of nitrogen−nitrogen bonds in an ionic species.[23] All *ab initio* calculations were carried out using the program package Gaussian 03 (Revision D.01).[24] The geometric optimization of

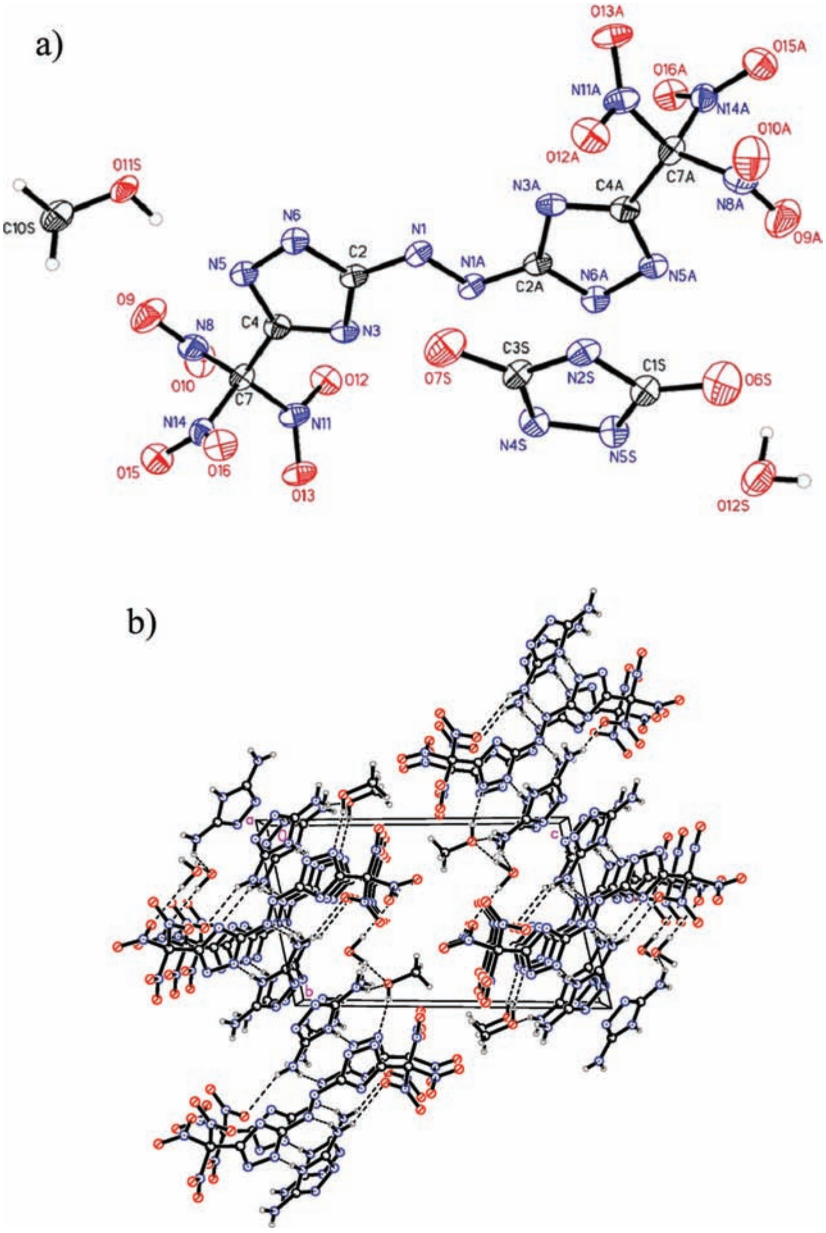


Figure 2. (a) View of the molecular unit of cocrystal **16**. (b) Unit cell view along the *b* axis. Selected bond lengths (Å): N5−N6 1.342(10), C2−N6 1.320(11), C2−N3 1.366(12), N3−C4 1.327(12), N1−C2 1.387(12), C4−C7 1.465(14), C7−N14 1.524(13), N11−O12 1.216(11).

the structures and frequency analyses were accomplished by using B3LYP with the 6-31+G** basis set,[25] and single-point energies were calculated at the MP2/6-311++G** level. Atomization energies were calculated by the G2 method.[26] All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. The remaining task is to determine the heats of formation of the cations and anions, which are computed by using the method of isodesmic reactions or protonation reaction (in case of the anion of **5**) (Scheme 5).

The enthalpy of an isodesmic reaction ($\Delta H_{r298}{}^\circ$) is obtained by combining the MP2/6-311++G** energy difference for the reaction, the scaled zero-point energies (B3LYP/6-31+G**), and other thermal factors (B3LYP/6-31+G**). Thus, the heats of formation of the cations and anions being investigated can be extracted readily (Table 1).

Based on Born−Haber energy cycles (Figure 3), the heats of formation of salts can be simplified by eq 1,

$$\begin{aligned}\Delta H_f{}^\circ(\text{ionic salt, 298 K}) = {} & \Delta H_f{}^\circ(\text{cation, 298 K}) \\ & + \Delta H_f{}^\circ(\text{anion, 298 K}) - \Delta H_L\end{aligned} \qquad (1)$$

The lattice potential energies (U_{POT}) and lattice enthalpies (ΔH_L) were calculated according to the following equations provided by Jenkins, in which ΔH_L is the lattice energy of the salt. The ΔH_L value can be predicted by eq 2,[27]

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

where U_{POT} is the lattice potential energy, n_M and n_X depend on the nature of the ions $M_p{}^+$ and $X_q{}^-$, respectively,

Scheme 5. Isodesmic Reactions or Protonation Reaction of Energetic Ions

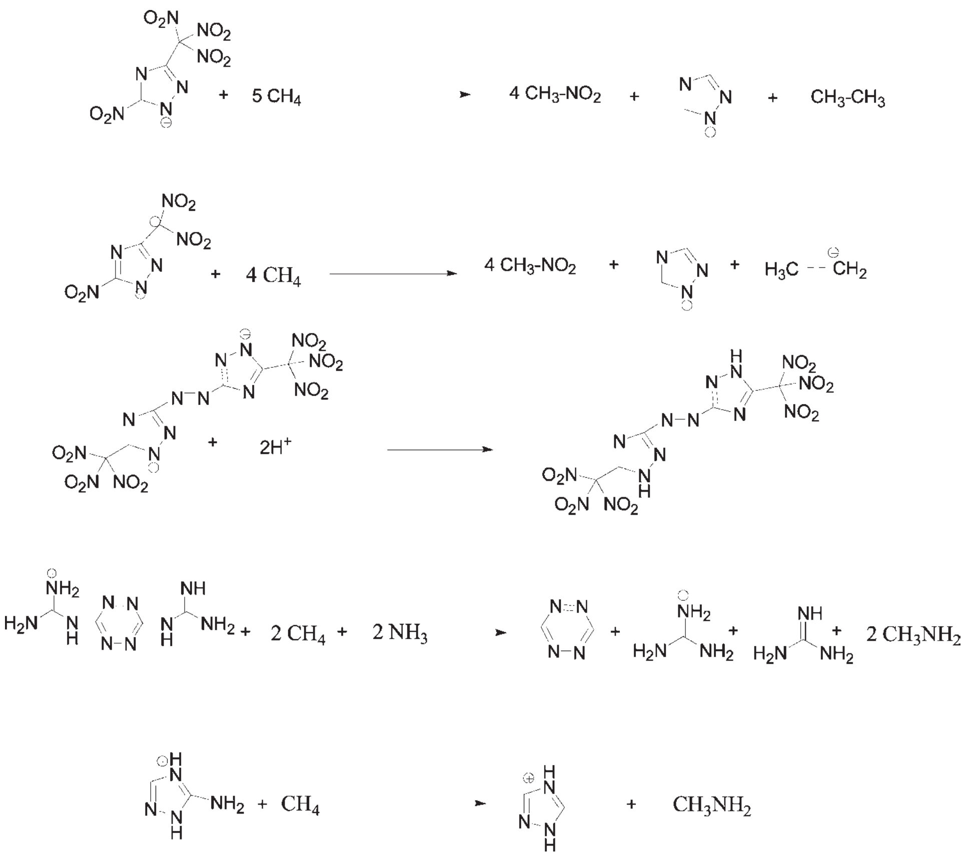


Table 1. Physical Properties of Polynitro Triazole Compounds 6−16

compd	T_{dec},[a] °C	density,[b] g/cm^3	ΔH_f,[c] kJ/mol cation	ΔH_f,[c] kJ/mol anion	lattice energy,[c] kJ/mol	ΔH_f°,[c] kJ/mol (kJ/g)	P,[d] GPa	D,[e] m/s	IS,[f] J	OB,[g] %
3	135	1.94				123.2 (0.46)	35.5	8983	9.0	9.1
5	150	1.83				555.1 (1.20)	36.6	8964	1.5	−8.6
6	145	1.80	877.6	−76.67	442.3	358.6 (0.95)	30.7	8306	9.5	−38.1
7	132	1.81	1124.7	−76.67	421.7	626.4 (1.36)	28.5	8197	10.0	−52.2
8	130	1.78	626.4	−76.67	475.7	74.0 (0.26)	32.4	8475	4.5	−11.4
9	156	1.82	770.0	−693.7	1387.7	−541.4 (−1.91)	30.8	8560	12.0	−56.7
10	172	1.80	669.5	−693.7	1404.7	−759.4 (−2.67)	32.6	8575	10.5	−35.5
11	117	1.70	806.3	310.1	994.4	928.2 (1.47)	26.8	7916	12.5	−45.6
12	140	1.76	935.0	310.1	988.7	1191.3 (1.80)	30.3	8310	13.0	−38.6
13	118	1.70	877.6	310.1	959.6	1105.6 (1.60)	26.6	8053	15.0	−50.9
14	111	1.80	663.0	310.1	1009.4	626.6 (0.97)	32.1	8542	9.0	−39.8
15	113	1.94	1124.7	310.1	929.4	1630.2 (1.90)	36.2	8997	14.5	−97.3
16	120	1.67							9.0	
TNT	295	1.65				−67.0 (0.30)	19.5	6881	15	−74.0
RDX	230	1.82				92.6 (0.42)	35.1	8997	7.4	−21.6

[a] Thermal decomposition temperature (onset) under nitrogen gas (DSC, 5 °C/min). [b] From gas pycnometer (25 °C). [c] Heat of formation (calculated via Gaussian 03). [d] Calculated detonation pressure (Cheetah 5.0). [e] Calculated detonation velocity (Cheetah 5.0). [f] Impact sensitivity (BAM drophammer). [g] OB = oxygen balance (%) for $C_aH_bO_cN_d$: $1600\times(c - 2a - b/2)/M_w$, where M_w is the molecular weight of salt.

and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for the lattice potential energy, U_{POT}, takes the form of eq 3,

$$U_{\mathrm{POT}}\ (\mathrm{kJmol^{-1}}) = \gamma(\rho_m/M_m)^{1/3} + \delta \qquad (3)$$

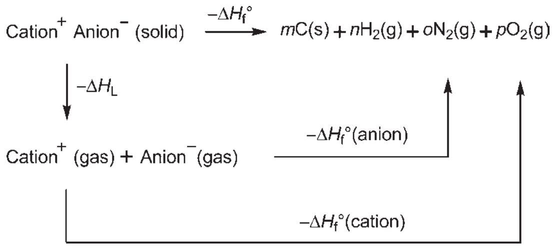


Figure 3. Born−Haber cycle for the formation of polynitro triazole salts.

where ρ_m is the density (g cm^{-3}), M_m is the chemical formula mass of the ionic material (g), and the coefficients γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are assigned literature values.[27]

Table 1 shows that trinitromethyl-subsitituted triazole salts are highly endothermic compounds. The enthalpies of energetic materials are controlled by the molecular structure of the compounds. Consequently, heterocycles with higher nitrogen content (like triazole) show higher heats of formation. All the new compounds (except dinitromethyl salts **9** and **10**) exhibit positive heats of formation ranging between 74.0 and 1630 kJ mol^{-1}. Impact sensitivity measurements were made using standard BAM Fallhammer techniques.[28] Listed in Table 1 are impact sensitivities ranging between 4.5 and 15.0 J. The thermal stabilities of the salts were determined by differential scanning calorimetry (DSC) measurements, and all of the salts decomposed without melting. Decomposition temperatures for salts of **3** range between 130 and 172 °C; dianionic salts **9** and **10** have good thermal stabilities compared to monoanionic compounds **6**, **7**, and **8**. The decomposition temperatures of salts of **5** are lower compared to those of salts of **3** and range from 111 to 140 °C.

As one of the important physical properties of energetic salts, densities of all the salts prepared were measured by using a gas pycnometer (Table 1) and found to fall in the range of 1.70−1.94 g cm^{-3}, which is expected based on the high density of **3**. Bis(guanidinium)tetrazine salt **15** exhibited the highest density at 1.94 g cm^{-3}. These relatively high densities are presumably caused by the high symmetry of the anion and the extensive intra- and intermolecular hydrogen bonds found in these salts.

By using calculated values of the heats of formation and experimental values for densities (gas pycnometer, 25 °C) of the new energetic polynitro triazole salts, the detonation pressures (P) and detonation velocities (D) were calculated using the EXPLO5 program (version 5.05). The detonation pressures of polynitro triazoles range between $P = 26.8$ and $P = 36.2$ GPa (compared with TNT, 19.53 GPa; RDX, 35.2 GPa; and HMX, 39.6 GPa). Detonation velocities lie between $D = 7916$ and $D = 8997$ m s^{-1} (compared with TNT, 6881 m s^{-1}; RDX, 8997 m s^{-1}; and HMX 9320 m s^{-1}). The calculated properties coupled with the rather high thermal and hydrolytic stabilities suggest that these high-nitrogen, oxygen-rich materials may be attractive candidates for energetic applications. The oxygen balance (OB) is the index of the deficiency or excess of oxygen in a compound required to convert all carbon into carbon dioxide, and all hydrogen into water; for a compound with the molecular formula of $C_aH_bN_cO_d$, OB (%) = $1600(d - 2a - b/2)/M_w$ (Table 1). The relatively moderate OB of **8** is −11.4%.

CONCLUSIONS

High-density-energetic salts of trinitromethyl-substituted triazoles, 5-nitro-3-trinitromethyl-1*H*-1,2,4-triazole and 5,5′-bis(trinitromethyl)-3,3′-azo-1*H*-1,2,4-triazole, were synthesized using straightforward methods. Single-crystal X-ray structuring supports the formation of the cocrystal of 5,5′-bis(trinitromethyl)-3,3′-azo-1*H*-1,2,4-triazole with 3,5-diamino-1,2,4-triazole, which was found to be markedly less impact sensitive than the azo precursor. Physical and detonation properties were determined. These trinitromethyl-substituted energetic salts were fully characterized using IR and multinuclear ^{1}H, ^{13}C NMR (some cases ^{15}N NMR) spectroscopy and elemental analysis. These salts exhibit good physical and detonation properties, such as moderate thermal stabilities, high densities, moderate to high heats of formation, and high detonation pressures and velocities. Calculated detonation values for these compounds are comparable to those of explosives such as TNT and RDX. The salts of **5** are impact insensitive (9.0−15.0 J) compared to their molecular precursor (1.5 J). They are less sensitive than or comparable to RDX, which suggests that they could be of interest for future applications as environmentally friendly and high-performing nitrogen- and oxygen-rich materials.

EXPERIMENTAL SECTION

Safety Precautions. *While we have experienced no difficulties in syntheses and characterization of these materials, proper protective measures should be used. Manipulations must be carried out in a hood behind a safety shield. Eye protection and leather gloves must be worn. Caution should be exercised at all times during the synthesis, characterization, and handling of any of these materials, and mechanical actions involving scratching or scraping must be avoided.*

General Methods. ^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded on a 300 MHz (Bruker AVANCE 300) and 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometers operating at 300.13, 75.48, and 50.69 MHz, respectively, by using DMSO-d_6 as solvent and locking solvent unless otherwise stated. The melting and decomposition points were obtained on a differential scanning calorimeter (TA Instruments Co., model Q10) at a scan rate of 5 °C min^{-1}. IR spectra were recorded using KBr pellets for solids on a BIORAD model 3000 FTS spectrometer. Densities of the polynitro triazoles were determined at 25 °C by employing a Micromeritics AccuPyc 1330 gas pycnometer. Elemental analyses were carried out using an Exeter CE-440 elemental analyzer. Details of the XRD analysis of cocrystal **16** are presented. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART PLATINUM 135 CCD detector.

X-ray Crystallography. A thin, small orange plate crystal of dimensions 0.16 × 0.07 × 0.01 mm^3 was mounted on a MiteGen MicroMesh using a small amount of Cargille immersion oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$). An Oxford Cobra low-temperature device was used to keep the crystals at a constant 100(2) K during data collection.

Data collection was performed and the unit cell was initially refined using APEX2 [v2010.3-0].[29] Data reduction was performed using SAINT [v7.60A][30] and XPREP [v2008/2].[31] Corrections were applied for Lorentz, polarization, and absorption effects using SADABS [v2008/1].[32] The structure was solved and refined with the aid of the programs in the SHELXTL-plus [v2008/4] system of programs.[33] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model.

(5-Nitro-1H-1,2,4-triazol-3-yl)acetic acid (***2***). Ten grams of sodium nitrite (145 mmol) was dissolved in 50 mL of water and heated to

40−50 °C. (5-Amino-1*H*-1,2,4-triazol-3-yl)acetic acid (4.26 g, 30 mmol) was dissolved in 25 mL of 20% nitric acid and added to the sodium nitrite solution dropwise. The reaction mixture was stirred at 50 °C for 1 h and cooled to 25 °C. Urea (0.1 g) was added. The reaction mixture was acidified to pH 1 and extracted with ethyl acetate (5 × 100 mL), and the solvent was evaporated (70%).[20b]

*5-Nitro-3-trinitromethyl-1H-1,2,4-triazole (**3**).* To a mixture of 98% sulfuric acid (12 mL) and 100% nitric acid (10 mL) was added **2** (15 mmol) at 0 °C. After being stirred for 15 h at room temperature, the solution was poured into ~30 g of ice and extracted with dichloromethane (3 × 15 mL). The organic layer was dried over $MgSO_4$, and the solvent was evaporated to yield **3** (44%).[19a]

Colorless solid; T_m =113.7 °C, $T_{dec.}$ = 135 °C (onset); IR (KBr) $\tilde{\nu}$ 3443 cm^{-1}; $^{13}C\{^1H\}$ NMR (CD_3CN) δ 157.9, 147.2, 122.2; $^{15}N\{^1H\}$ NMR δ −22.50 (NO_2), −29.33 ($(NO_2)_3$), −38.58 (N2), −54.98 (N3), −132.33 (N1). Elemental analysis for $C_3HN_7O_8$ (MW 263), calcd: C, 13.70; H, 0.38; N, 37.27. Found: C, 14.18; H, 0.30; N, 37.52.

*5,5′-Bis(carboxymethyl)-3,3′-azo-1,2,4-triazole (**4**).* To a suspension of 4.26 g (30 mmol) of (5-amino-1*H*-[1,2,4]triazol-3-yl)acetic acid in 20 mL of water was added a solution of potassium hydroxide (6 g, 107 mmol) in 20 mL of water. Potassium permanganate (4 g, 25 mmol) was added in some portions for 0.5 h. The reaction mixture was stirred at 25 °C for 2 h. The solid was removed by filtration, and the mother liquor was acidified to pH 1. The solid formed was filtered (56%).[20b]

*5,5′-Bis(trinitromethyl)-3,3′-azo-1H-1,2,4-triazole (**5**).* To a mixture of sulfuric acid (98%, 6 mL) and nitric acid (100%, 5.0 mL) was added **4** (1.0 g, 3.57 mmol) at 0 °C. After being stirred for 15 h at room temperature, the reaction mixture was poured into ice water and the precipitate filtered. The mother liquor was extracted with ethyl acetate, and the extract was dried over $MgSO_4$. The solvent was evaporated to give additional product. The combined solids are **5** (55%).[19a]

Yellow solid; $T_{dec.}$ = 150 °C (onset); IR (KBr) $\tilde{\nu}$ 3467, 1630, 1617, 1593, 1442, 1342, 1282, 1194, 1097, 1052, 964, 842, 801, 758 cm^{-1}; $^{13}C\{^1H\}$ NMR δ 165.7, 148.8, 123.8; $^{15}N\{^1H\}$ NMR δ −31.62 ($(NO_2)_3$), −33.0 (N═N), −60.35 (N2), −131.79 (N3), −132.26 (N1). Elemental analysis for $C_6H_3N_{14}O_{12.5}$ (MW 471), calcd: C, 15.29; H, 0.64; N, 41.62. Found: C, 15.56; H, 0.32; N, 41.50.

*3,4,5-Triaminotriazolium 5-nitro-3-trinitromethyl-1,2,4-triazolate (**6**).* 3,4,5-Triaminotriazole (114 mg, 1.0 mmol) was added to a solution of **3** (263 mg, 1.0 mmol) in methanol (5 mL). The reaction was stirred for 2 h at 25 °C. The solvent was evaporated under reduced pressure. The product was washed with diethyl ether and dried under vacuum (343 mg, 91%).

Light brown solid; $T_{dec.}$ = 145 °C (onset); IR (KBr) $\tilde{\nu}$ 3455, 3371, 3302, 1705, 1614, 1597, 1571, 1546, 1483, 1412, 1376, 1330, 1285, 1126, 1030, 801 cm^{-1}; $^{13}C\{^1H\}$ NMR δ 166.1, 150.1, 147.6, 125.2; $^{15}N\{^1H\}$ NMR δ −21.67 (NO_2), −28.97 ($(NO_2)_3$), −35.6 (N2), −48.2 (N3), −131.79 (N1), −185.5 (N4′/N6′), 238.3 (N3′), 322.8 (N5′), 329.6 (N1′/N2′). Elemental analysis for $C_5H_7N_{13}O_8$ (MW 377), calcd: C, 15.92; H, 1.87; N, 48.27. Found: C, 16.43; H, 1.85; N, 47.32.

*3,6-Diguanidino-1,2,4,5-tetrazine-5-nitro-3-trinitromethyl-1,2,4-triazolate Hemihydrate (**7**).* To a solution of **3** (263 mg, 1.0 mmol) in methanol (8 mL) was added 3,6-diguanidine-*s*-tetrazine (196 mg, 1.0 mmol). The reaction was stirred for 3 h at 25 °C. A red solid separated from the reaction mixture and was filtered. The product was washed with diethyl ether and dried under vacuum (410 mg, 89%).

Red solid; $T_{dec.}$ = 132 °C (onset); IR (KBr) $\tilde{\nu}$ 3383, 3330, 3073, 1697, 1629, 1612, 1587, 1541, 1530, 1509, 1451, 1427, 1382, 1345, 1305, 1289, 1130, 1065, 1039, 963, 845, 801 cm^{-1}; $^{13}C\{^1H\}$ NMR δ 165.2, 159.5, 156.2, 147.6, 125.2. Elemental analysis for $C_7H_{10}N_{17}O_{8.5}$ (MW 468), calcd: C, 17.95; H, 2.15; N, 50.85. Found: C, 18.04; H, 1.76; N, 48.91.

*Ammonium 5-Nitro-3-trinitromethyl-1,2,4-triazolate (**8**).* Aqueous ammonia (1.0 mL) was added to a solution of **3** (263 mg, 1.0 mmol) in methanol (5 mL). The mixture was stirred for 2 h at 25 °C. The solvent was evaporated under reduced pressure and the product washed with diethyl ether/hexane. The product was removed by filtration and dried under vacuum (255 mg, 90%).

Yellow solid; $T_{dec.}$ = 130 °C (onset); IR (KBr) $\tilde{\nu}$ 3353, 3151, 3040, 1621, 1599, 1583, 1152, 1460, 1425, 1415, 1383, 1309, 1291, 1145, 1107, 1040, 973, 846, 803 cm^{-1}; $^{13}C\{^1H\}$ NMR δ 166.0, 147.5, 125.2; $^{15}N\{^1H\}$ NMR δ −15.0 (NO_2), −22.3 ($(NO_2)_3$), −28.8 (N2), −41.3 (N3), −125.9 (N1), −351.6 ($^+NH_4$). Elemental analysis for $C_3H_4N_8O_8$ (MW 280), calcd: C, 12.86; H, 1.44; N, 40.00. Found: C, 13.27; H, 1.27; N, 39.31.

*Bishydrazinium 3-Dinitromethyl-5-nitro-1,2,4-triazolate (**9**).* Hydrazine hydrate (160 mg, 5.0 mmol) was added dropwise to a solution of **3** (263 mg, 1.0 mmol) in methanol (5 mL). The mixture was stirred for 2 h at 25 °C. The product that precipitated was filtered and dried (249 mg, 88%).

Orange solid; $T_{dec.}$ = 156 °C (onset); IR (KBr) $\tilde{\nu}$ 3331, 3211, 1630, 1596, 1504, 1460, 1397, 1334, 1288, 1124, 1047, 997, 845, 821, 747 cm^{-1}; $^{13}C\{^1H\}$ NMR δ 164.9, 155.6, 129.0; $^{15}N\{^1H\}$ NMR δ −18.7 (NO_2), −21.6 ($(NO_2)_3$), −54.44 (N2), −61.3 (N3), −137.2 (N1), −331.4 ($^+NH_3$−NH_2). Elemental analysis for $C_3H_{10}N_{10}O_6$ (MW 282), calcd: C, 12.77; H, 3.57; N, 49.64. Found: C, 13.21; H, 3.51; N, 48.95.

*Bis(hydroxyammonium)dinitromethyl-5-nitro-1,2,4-triazolate hydrate (**10**).* To a solution of **3** (263 mg, 1.0 mmol) in methanol (5 mL), was added 50% aqueous hydroxylamine (0.5 mL, 5.0 mmol) dropwise. The reaction was stirred for 3 h at 25 °C. The solvent was evaporated under reduced pressure, and the product was washed with diethyl ether and dried (268 mg, 94%).

Orange solid; $T_{dec.}$ = 172 °C (onset); IR (KBr) $\tilde{\nu}$ 3423, 3335, 3161, 1624, 1557, 1522, 1466, 1398, 1362, 1314, 1267, 1148, 1130, 999, 842, 742, 656 cm^{-1}; $^{13}C\{^1H\}$ NMR δ 164.0, 153.8, 127.2; $^{15}N\{^1H\}$ NMR δ −20.2 (NO_2), −21.9 ($(NO_2)_3$), −70.5 (N2), −81.0 (N3), −136.9 (N1), −289.9 ($^+NH_3$−OH). Elemental analysis for $C_3H_{10}N_8O_9$ (MW 302), calcd: C, 11.92; H, 3.34; N, 37.08. Found: C, 11.29; H, 3.47; N, 38.70.

*Bis(3-amino-1,2,4-triazolium) 5,5′-Bis(trinitromethyl)-3,3′-azo-1,2,4-triazolate (**11**).* 3-Amino-1,2,4-triazole (168 mg, 2.0 mmol) was added to a solution of **5** (462 mg, 1.0 mmol) in methanol. The reaction was stirred for 1.5 h at 25 °C, and the solvent was evaporated under reduced pressure. The product was precipitated by dissolving in acetone, which was removed under slow evaporation, filtered, and dried (551 mg, 88%).

Yellow solid; $T_{dec.}$ = 117 °C (onset); IR (KBr) $\tilde{\nu}$ 3423, 3245, 2983, 1612, 1580, 1554, 1523, 1465, 1401, 1376, 1354, 1257, 1217, 1170, 1103, 1010, 877, 720 cm^{-1}; ^1H NMR δ 8.0 (s); $^{13}C\{^1H\}$ NMR δ 170.8, 153.2, 148.4, 142.0, 125.8. Elemental analysis for $C_{10}H_{10}N_{22}O_{12}$ (MW 630), calcd: C, 19.05; H, 1.60; N, 48.89. Found: C, 19.54; H, 1.58; N, 47.62.

*Bis(3,4-diamino-1,2,5-oxadiazolium) 5,5′-Bis(trinitromethyl)-3,3′-azo-1,2,4-triazolate·2.5H$_2$O (**12**).* Bis-3,4-diaminofurazan (200 mg, 2.0 mmol) was added to a solution of **5** (462 mg, 1.0 mmol) in methanol. The reaction was stirred for 2 h at 25 °C, and the solvent was evaporated under reduced pressure (621 mg, 94%).

Yellow solid; $T_{dec.}$ 140 °C (onset); IR (KBr) $\tilde{\nu}$ 3434, 3324, 1624, 1593, 1475, 1443, 1352, 1283, 1199, 1089, 1059, 968, 843, 801 cm^{-1}; $^{13}C\{^1H\}$ NMR δ 165.7, 149.8, 148.9, 123.8. Elemental analysis for $C_{10}H_{15}N_{22}O_{16.5}$ (MW 707), calcd: C, 16.98; H, 2.14; N, 43.56. Found: C, 16.90; H, 1.78; N, 43.48.

*Bis(3,4,5-triaminotriazolium) 5,5′-Bis(trinitromethyl)-3,3′-azo-1,2,4-triazolate Monohydrate (**13**).* 3,4,5-Triaminotriazole (228 mg, 2.0 mmol) was added to a solution of **5** (462 mg, 1.0 mmol) in methanol (10 mL). The reaction was stirred for 2 h at 25 °C, and the solvent was evaporated under reduced pressure. The product was precipitated from diethyl ether, filtered, and dried (610 mg, 88%).

Yellow solid; $T_{dec.}$ = 118 °C (onset); IR (KBr) $\tilde{\nu}$ 3449, 3385, 3210, 1721, 1672, 1614, 1595, 1529, 1475, 1440, 1381, 1299, 1131, 963, 845, 802, 767, 703 cm^{-1}; ^{13}C{^{1}H} NMR δ 172.7, 150.0, 148.0, 126.9. Elemental analysis for $C_{10}H_{16}N_{26}O_{13}$ (MW 708), calcd: C, 16.95; H, 2.28; N, 51.41. Found: C, 17.10; H, 2.10; N, 50.34.

*Bis(carbonic dihyrazidinium) 5,5′-Bis(trinitromethyl)-3,3′-azo-1,2,4-triazolate Dihydrate (**14**).* To a solution of **3** (462 mg, 1.0 mmol) in methanol (10 mL) was added an aqueous solution (3 mL) of carbohydrazide (180 mg, 2.0 mmol) . The reaction was stirred for 1 h at 25 °C. The solvent was evaporated under reduced pressure and washed with diethyl ether. The product was dried under vacuum (578 mg, 90%).

Yellow solid; $T_{\text{dec.}}$ = 111 °C (onset); IR (KBr) $\tilde{\nu}$ 3349, 3277, 3230, 1690, 1606, 1570, 1545, 1464, 1423, 1348, 1310, 1284, 1220, 1157, 1095, 1029, 980, 844, 802 cm^{-1}; ^{13}C{^{1}H} NMR δ 159.0, 156.5, 148.4, 124.2. Elemental analysis for $C_8H_{18}N_{22}O_{16}$ (MW 678), calcd: C, 14.16; H, 2.67; N, 45.42. Found: C, 14.36; H, 2.66; N, 45.82.

*Bis(3,6-diguanidino-1,2,4,5-tetrazine) 5,5′-Bis(trinitromethyl)-3,3′-azo-1,2,4-triazolate Dihydrate (**15**).* Bis-3,6-diguanidino-1,2,4,5-tetrazine (392 mg, 2.0 mmol) was added to a solution of **5** (462 mg, 1.0 mmol) in methanol (8 mL). The reaction was stirred for 1.5 h at 25 °C, and then the product was removed by filtration, washed with diethyl ether, and dried (779 mg, 91%).

Red solid; $T_{\text{dec.}}$ = 113 °C (onset); IR (KBr) $\tilde{\nu}$ 3510, 3338, 1696, 1614, 1602, 1599, 1541, 1501, 1445, 1385, 1348, 1292, 1133, 1074, 1074, 1035, 959, 872, 884, 801 cm^{-1}; ^{13}C{^{1}H} NMR δ 168.8, 158.7, 153.7, 149.1. Elemental analysis for $C_{14}H_{22}N_{34}O_{14}$ (MW 890), calcd: C, 18.88; H, 2.49; N, 53.48. Found: C, 18.98; H, 2.07; N, 53.11.

*Cocrystal of **5** with **16**.* To a solution of **5** (463 mg, 1.0 mmol) in 6 mL of MeOH, was added a solution of **16** (99 mg, 1.0 mmol) in 6 mL of water. The resulting mixture was covered and allowed to evaporate at room temperature over a period of 3 days. The solution was removed by filtration, and the crystals were dried in air.

Orange solid; $T_{\text{dec.}}$ = 120 °C (onset); IR (KBr) $\tilde{\nu}$ 3397, 3353, 3182, 3134,1697, 1656, 1625, 1596, 1545, 1479, 1413, 1383, 1338, 1308, 1285, 1237, 1132, 1057, 1035, 964, 900, 844, 801, 727, 688, 659, 628 cm^{-1}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray crystallographic file in CIF format for **16**; ^{1}H and ^{13}C NMR and IR spectra and DSC scans of all compounds; ^{15}N NMR of selected compounds; and complete ref 24. This material is available free of charge via the Internet at http://pubs.acs.org.

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(30) *SAINT*, v7.68A; Bruker AXS Inc.: Madison, WI, 2009.

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(32) *SADABS*, v2008/1; Bruker AXS Inc.: Madison, WI, 2008.

(33) *SHELXTL*, v2008/4; Bruker AXS Inc.: Madison, WI, 2008.