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Trinitromethyl-Substituted 5-Nitro- or 3-Azo-1,2,4-triazoles: Synthesis, Characterization, and Energetic Properties

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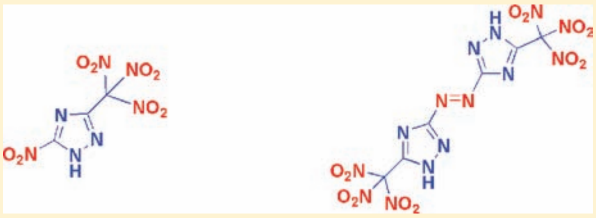
Supporting Information



ABSTRACT: Various new polynitro-1,2,4-triazoles containing a trinitromethyl group were synthesized by straightforward routes. These high nitrogen and oxygen-rich compounds were fully characterized using IR and multinuclear NMR spectroscopy, elemental analysis, natural bonding orbital (NBO) analysis, and differential scanning calorimetry (DSC) and, in the case of **12**, with single crystal X-ray structuring. The heats of formation for all compounds were calculated with Gaussian 03 (revision D.01) and then combined with experimentally determined densities to determine detonation pressures (P) and velocities (D) of the energetic materials (Cheetah 5.0). They exhibit high density, good thermal stability, acceptable oxygen balance, positive heat of formation, and excellent detonation properties, which, in some cases, are superior to those of TNT, RDX, and HMX.

INTRODUCTION

After decades of effort in the preparation of energetic compounds, higher performance and lower sensitivity continue to be keen concerns in weapon systems.[1] Desirable characteristics for new energetic materials include positive heat of formation, high density, high detonation velocity and pressure, high thermal stability, and low sensitivity toward external forces such as impact and friction. Of particular interest are high-nitrogen compounds (e.g., azoles) in combination with energetic substituents such as nitro ($-NO_2$), nitrato ($-ONO_2$), and nitramine ($-NHNO_2$) functionalities, because these compounds have satisfactory oxygen content.[2] 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 high energy density materials an interesting and challenging problem.[3]

Several explosives 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) are well-known.[1a] Recently, 1,1-diamino-2,2-dinitroethene (FOX-7) emerged as a potential candidate for use as an insensitive high explosive attracting substantial interest because its density and detonation performance is superior to that of and its sensitivity is much less than that of RDX.[4] Polynitro azoles have been a recent focus because of their high performance and low sensitivity to friction and impact.[5−7] Azoles with more than two nitro groups are highly powerful, and, as a result, a large variety of nitroazoles have been prepared.[8] In reaction of the latter with bases such as ammonia, hydrazine, and guanidine, stable energetic salts are obtained, which may hold promise for future applications.[9] In addition, nitro azoles are valuable in the pharmaceutical field as nitro-containing synthetic intermediates and drugs.[10]

Ammonium perchlorate (AP) is the main oxidizer used in solid rocket fuels. Oxidizers provide the oxygen needed for oxidation of the fuel to provide the necessary thrust. The search for a smokeless propellant has encouraged scientists to look for chlorine-free oxidizers as a substitute for AP 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. Although it has some drawbacks, including a low melting point, high impact sensitivity, and negative heat of formation, ammonium dinitramide (ADN) is an alternative oxidizer to AP.[11] Current research issues in the field of high energetic materials include increasing oxygen content, which may give rise to a suitable replacement for AP.

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. 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.[12] In this Article, we report the synthesis of various polynitro-1,2,4-triazoles, which contain trinitromethyl groups and which display potentially significant physical and energetic properties.

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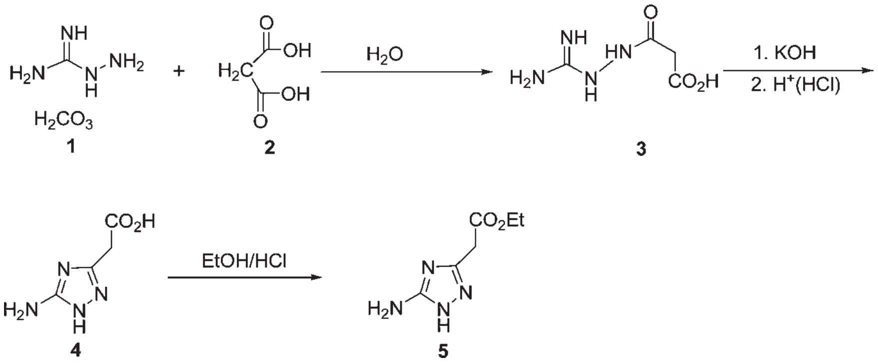
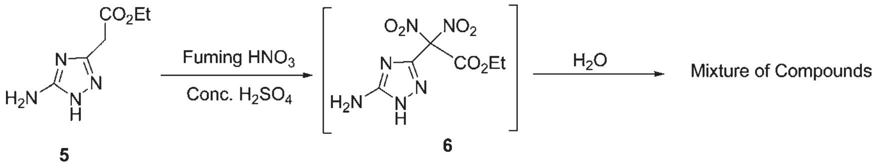
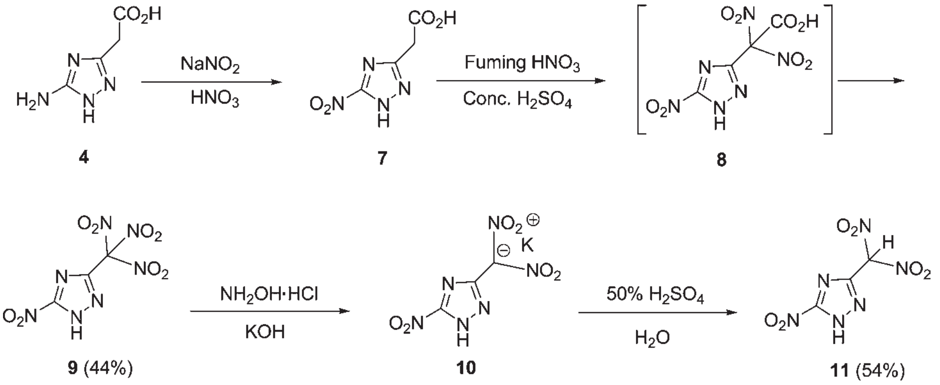
Scheme 1. Synthetic Pathway for Intermediates 4 and 5



Scheme 2. Nitration of Triazole 5



Scheme 3. Synthesis of Trinitromethyl (9) and Dinitromethyl (11) 1,2,4-Triazoles



RESULTS AND DISCUSSION

Azolyl acetic acids can be converted into corresponding trinitromethyl azoles by nitration with mixed acids, HNO_3 and H_2SO_4.[13] Compounds such as aminotriazolylacetic acids, for example, **4** and **5**, give the corresponding polynitro compounds by nitration with mixed acids. Aminotriazolylacetic acid (**4**) was synthesized by intramolecular condensation of the malonyl derivative of aminoguanidine bicarbonate in alkaline medium (Scheme 1).[14]

Nitration of amino triazole **4** was attempted by using different nitrating methods such as 70% HNO_3, 100% HNO_3, or mixed acids (HNO_3/H_2SO_4), but the product was not isolable from the reaction mixture. When the ethyl ester of aminotriazole (**5**) was treated similarly with nitric acid, the attempted nitration reaction was not successful. With mixed acids, nitration of the ethyl ester produced a mixture of unknown compounds, which were difficult to separate (Scheme 2). Compound **6** is a likely intermediate, but it was neither observed nor isolated.

It was thought that a nitro group could prove useful in lieu of the 5-amino group. Therefore, amino triazole **4** was converted into corresponding nitro compound **7** by reacting with sodium nitrite and HNO_3 (Scheme 3).[14b] In the reaction of **7** with mixed acids, 5-nitro-3-trinitromethyl-1*H*-1,2,4-triazole (**9**) was obtained as a single product at ambient temperature.

During this process, the proposed intermediate trinitro carboxylic acid (**8**) was not isolated. The reaction was complete in 12 h. Because no precipitate formed when the reaction mixture was added to ice, the aqueous solution was extracted with dichloromethane, resulting, after solvent removal, in a colorless crystalline product (**9**) in 45% yield (Scheme 3).

Conversion of a trinitromethyl group to the corresponding dinitromethylide salt and subsequently to the dinitromethylene compound has been reported.[13,15] Using that methodology, potassium salt **10** was obtained when **9** was treated with an alkaline solution of hydroxylamine. Acidification with 50% sulfuric acid gave 3-dinitromethyl-5-nitro-1*H*-[1,2,4]triazole (**11**) as a yellow solid (Scheme 3).

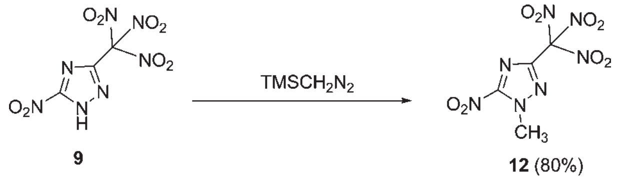
N-Methyl azoles are often less sensitive to impact and friction as compared to the corresponding *N*-H azoles. The methyl derivative was difficult to prepare by reacting with methyl iodide or dimethylsulfate in the presence of bases, for example, triethyl amine, potassium *tert*-butoxide, potassium hydroxide, or sodium hydride. In all of these cases, low yields of the impure methylated product (**12**) were obtained. When tetranitro **9** was reacted with commercially available trimethylsilyl diazomethane,[14] 1-methyl-5-trinitro-3-trinitromethyl-1*H*-[1,2,4]triazole (**12**) was obtained in 80% yield (Scheme 4).

Next, similar successful attempts were made to synthesize **14** and **15**. The amino triazolylacetic acid **4** was converted into the azo compound, **13**, by treating with alkaline potassium permanganate.[14b] Compound **13** was reacted with mixed acids at room temperature to form 5,5′-bis(trinitromethyl)-3,3′-azo-1,2,4-triazole (**14**). When an attempt was made to convert the trinitromethyl groups of hexanitro **14** to the corresponding dinitromethylene groups by treating with alkaline hydroxylamine followed by acidification, a low yield mixture of compounds was formed. The reaction also failed with potassium iodide in methanol. Methylation of hexanitro **14** was carried out using various reagents; however, reaction was successful with trimethylsilyl diazomethane to produce 1,1′-dimethyl-5,5′-bis(trinitromethyl)-3,3′-azo-1,2,4-triazole (**15**) (Scheme 5).

The structures of the new polynitro triazoles are supported by IR, ^{1}H, ^{15}N, and ^{13}C NMR spectroscopic data as well as elemental analysis. In the IR spectra, strong absorption bands at ~1630−1610 cm^{-1} are attributed to the trinitromethyl group. In the ^{13}C NMR spectra, resonance bands for the trinitromethyl group appear between 120 and 130 ppm. The ^{15}N NMR spectra of the nitrotriazoles were measured in DMSO[d_6] solution, and chemical shifts are given with respect to CH_3NO_2 as external standard. In Figure 1, selected ^{15}N NMR spectra of **9**, **12**, and **14** are shown. The triazole nitrogen signals are seen upfield relative to nitro and azo 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). The resonance peaks for N3 and N1 are nearly overlapping in **14**. That area of the spectrum has been expanded in the inset. The N4 signals of **9** and **14** appear downfield as compared to the N5 signals. The N5 signal of **12** appears slightly downfield from N4. The ^{15}N NMR spectra for **11** and **15** may be found in the Supporting Information.

Crystals of **12** suitable for single crystal X-ray diffraction were obtained by dissolving the compound in a minimum amount of methanol, held at 0 °C, followed by filtration of crystals. It crystallizes in an orthorhombic crystal system (space group *Pna*2$_1$). The N1−N2 bond length is 1.3484(15) Å, which is normal in triazoles. N1−C5, N4−C5, N4−C3, and N2−C3 bond lengths are 1.3485(15), 1.3112(16), 1.3518(15), and 1.3298(16) Å, respectively. The bond lengths of C5−N17 and C6−N1 are

Scheme 4. Methylation of Tetranitro 9



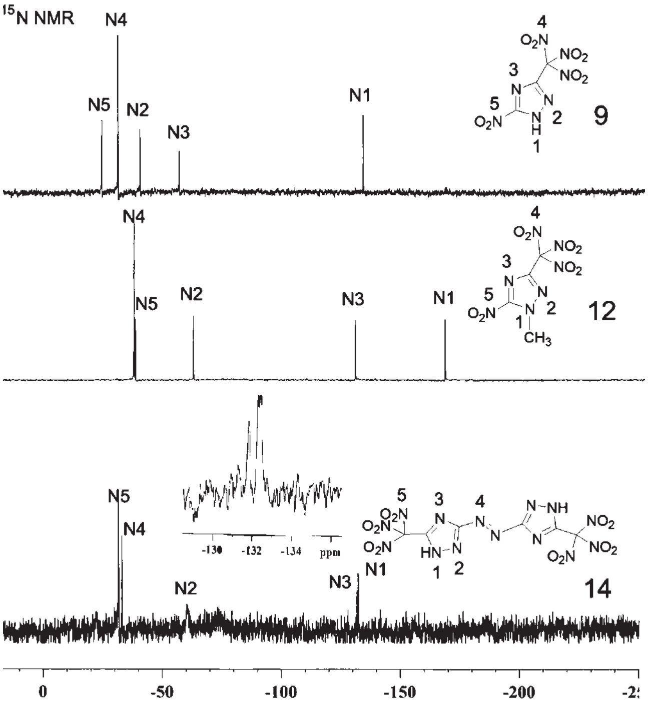
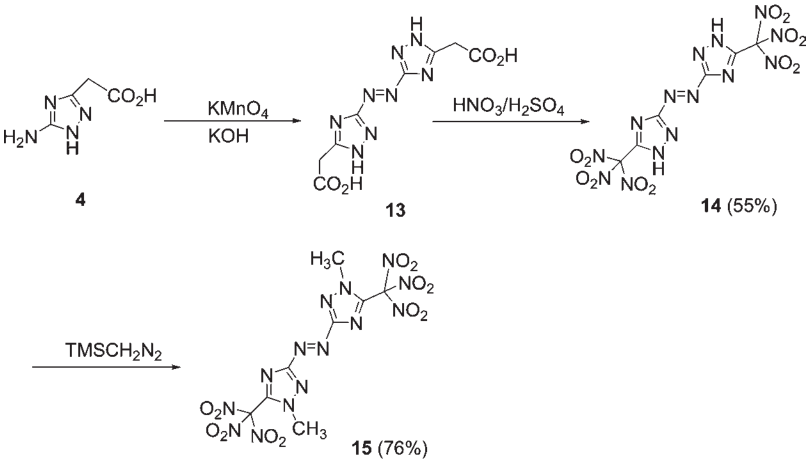


Figure 1. Selected ^{15}N NMR spectra of polynitro-1,2,4-triazoles.

Scheme 5. Synthesis of Triazoles 14 and 15



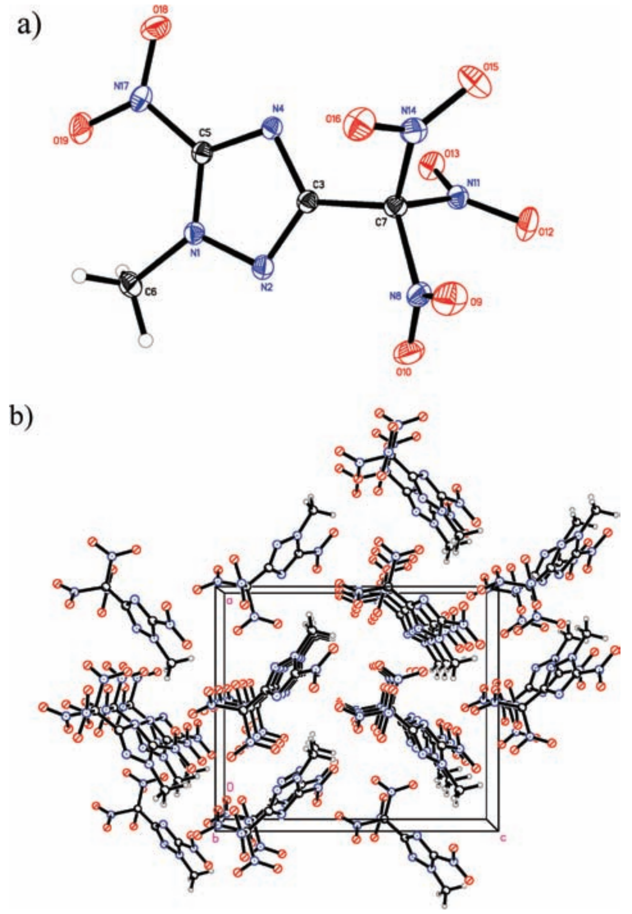


Figure 2. (a) A view of the molecular unit of **12**. (b) Unit cell view along the *b* axis. Selected bond lengths [Å]: N1−N2 1.3484(15), N1−C5 1.3485(15), N1−C6 1.4684(16), N2−C3 1.3298(16), N4−C5 1.3112(16), C5−N17 1.4555(16), C7−N14 1.5337(15), C7−N11 1.5373(17), N8−O9 1.2122(14), N8−O10 1.2138(15).

1.4555(16) and 1.4684(16) Å, which is in the expected range. Yet C7−N8, C7−N11, and C7−N14 are 1.5316(15), 1.5373(15), and 1.5316(17) Å, respectively, which are longer than normal C−N single bonds (Figure 2). The N17−O18 and N17−O19 bond lengths are 1.2172(15) and 1.2216 Å. The N−O bond lengths of the nitro functionality of the trinitromethyl group are N8−O9 1.2122(14), N8−O10 1.2138(15), N11−O13 1.2073(14), N11−O12 1.2195(14), N14−O15 1.2100(15), N14−O16 1.2173(15), N17−O18 1.2172, and N17−O19 1.2216(15) Å, respectively. The triazole ring and three nitro groups are tetragonally attached to C7. The C−N bond length [1.533(15) Å] of the trinitromethyl group of **12** is slightly longer than the C−N bond length [1.525(3) Å] of trinitroethyl-containing molecules.[4] This is in agreement with the greater stability of the latter compounds.

■ PHYSICAL PROPERTIES

As shown in Table 1, the polynitro triazoles exhibit excellent energetic properties. The enthalpies of energetic materials depend on the molecular structures of the compounds. Consequently, heterocycles with high nitrogen content exhibit higher heats of formation. All ab initio calculations were carried out using the program package Gaussian 03 (revision D.01).[16] The geometric optimization of the structures and frequency analyses were accomplished by using the B3LYP with the 6-31+G** basis set,[17] and single-point energies were calculated at the MP2/6-311++G** level. Atomization energies were calculated by the G2 method.[18] 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 polynitro triazoles, which are computed by using the method of isodesmic reactions (Scheme 6). Thus, the heat of formation of the species being investigated can be easily extracted. All of the polynitro triazoles exhibit positive heats of formation and are comparable to or greater than those of TNT, RDX, and HMX. Compound **9** is far superior to ADN in all respects, including detonation velocity and pressure, enthalpy of formation, impact sensitivity, and density, with the exception of oxygen balance, although **9** is positive at 9% as compared to 25.8% for ADN.[19] The densities of these compounds are in the range of 1.78−1.94 g/cm^3, which equals or exceeds that of common explosives. Tetranitro triazole (**9**) has the highest density at 1.94 g/cm^3. The calculated densities are in good agreement with the experimentally determined values (Table 1).[20]

Impact sensitivity measurements were made using standard BAM Fallhammer techniques.[21] For all of the compounds, the impact sensitivities range from those of the relatively less sensitive **9**, **11**, **12**, and **15** between 5.5 and 13 J to the very sensitive compound **14** (1.5 J). *N*-Methyl derivatives (**12** and **15**) are less sensitive than the corresponding *N*-H compounds **9** and **14**. Thermal stabilities of the energetic compounds were determined with differential scanning calorimetry (DSC) at a scan rate of 5 °C min^{-1}. Compound **9** melted at 113 °C and decomposed at 135 °C, whereas its methyl derivative (**12**) melted at 77 °C and decomposed at 153 °C. Azo compounds **14** and **15** decomposed at 150 and 165 °C, respectively, without melting. Surprisingly, the trinitro compound **11** decomposed at 86 °C, which is thermally less stable than the tetranitro compound **9**.

By using the calculated values of the heats of formation and the experimental values for the densities (gas pycnometer, 25 °C) of the new energetic polynitro triazoles, the detonation pressures (P) and detonation velocities (D) were calculated on the basis of traditional Chapman−Jouget thermodynamic detonation theory using Cheetah 5.0 (Table 1).[19] The detonation pressures of polynitro triazoles lie in the range between P = 33.83 and P = 38.41 GPa (as compared to TNT 19.53 GPa, RDX 35.2 GPa, and HMX 39.6 GPa). Detonation velocities lie between D = 8742 and D = 9229 m s^{-1} (as compared to TNT 6881 m s^{-1}, RDX 8997 m s^{-1}, and HMX 9320 m s^{-1}). The specific impulse values (CHEETAH 5.0) of these polynitrotriazoles, which range between 233 and 264 s, suggest propellant possibilities. 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.

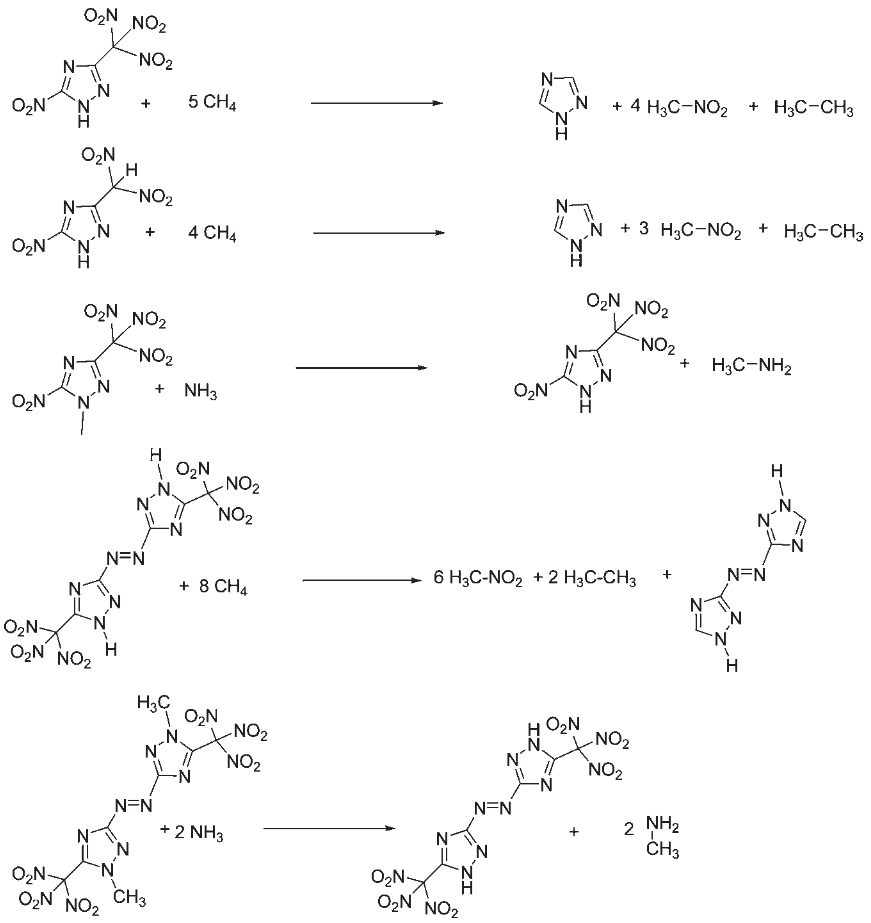
Oxygen balance (OB) is the index of the deficiency or excess of oxygen in a compound required to convert all carbon into carbon dioxide, and all hydrogen into water; for a compound with the molecular formula of $C_aH_bN_cO_d$, OB (%) = $(d - 2a - b/2)$/MW (Table 1). Positive oxygen balance has significance in explosives, which can be used as oxidizers. Compound **9** has a positive oxygen balance of 9.1%; the oxygen balances of **11**, **12**, and **14** are −7.3%, −3.6%, and −8.6%, respectively, which are superior to RDX (−22%) and HMX (−22%). The oxygen percentages of **9**, **11**, and **12** are 48.65%, 44.02%, and 46.19%, respectively, which are superior to TNT (42.26%), RDX (43.22%), and HMX (43.22%) and nearly competitive with AP.

Table 1. Physical Properties of Polynitro Triazoles

compd	T_m,[a] °C	T_{dec},[b] °C	density,[c] g cm^{-3}	OB,[d] %	O,[e] %	ΔH_f°,[f] kJ/mol (kJ/g)	IS,[g] J	P,[h] GPa	D,[i] m/s	I_{sp},[j] s
9	113	135	1.94 (1.92)[k]	+9.12	48.7	123.2 (0.46)	9.0	35.51	8983	233
11		87	1.91 (1.85)	−7.33	44.0	84.1(0.38)	9.5	38.41	9229	243
12	77	153	1.88 (1.88)	−3.46	46.2	95.6 (0.34)	13.0	36.88	9006	264
14		150	1.83 (1.87)	−8.6	41.5	555.1 (1.20)	1.5	36.65	8964	264
15		165	1.78 (1.77)	−22.8	39.2	505.8 (1.03)	5.5	33.83	8742	262
TNT	81	295	1.65	−74	42.3	−67.0 (0.30)	15	19.53	6881	
RDX	dec	230	1.82	−21.6	43.2	92.6 (0.42)	7.4	35.17	8997	
HMX	dec	287	1.91	−21.6	43.2	104.8 (0.35)	7.4	39.63	9320	

[a] Melting point. [b] Thermal decomposition temperature (onset) under nitrogen gas (DSC, 5 °C/min^{-1}). [c] Gas pycnometer (25 °C). [d] OB = oxygen balance (%) for $C_aH_bO_cN_d$: $1600 \times (c - 2a - b/2)/M_w$, M_w = molecular weight of compound. [e] Oxygen content. [f] Heat of formation (Gaussian 03, revision D.01). [g] Impact sensitivity (BAM drophammer). [h] Detonation pressure (Cheetah 5.0). [i] Detonation velocity (Cheetah 5.0). [j] Specific impulse (Cheetah 5.0). [k] Calculated density, ref 20.

Scheme 6. Isodesmic Reactions of Polynitro Triazoles



To obtain a better understanding of the stabilities of the polynitrotriazoles, a natural bonding orbital (NBO) population analysis fixed at the optimized structure (DFT/3-21G) was used to investigate the bonding and hybridization in these molecules (single-point energy calculated at the DFT/3-21G level). The natural bond orbital (NBO) analysis was carried out with the 3.1 version that is included in Gaussian 09 program[16] at the mp2-(full)/6-311++g(d,p) level. The geometry optimizations of the structures and frequency analysis were carried out with the B3LYP functional with the 3-21G basis set. The optimized structures were characterized as true local energy minima on the potential energy surface without imaginary frequencies.

Natural bond orbital analysis provides an efficient method for investigating charge distribution in molecular systems. The charge distribution data calculated by the NBO method for optimized geometries of **9** and **12** and for **14** and **15** are tabulated in Tables S3 and S4 and Tables S5 and S6, respectively (Supporting Information). NBO analysis shows that the C−NO_2

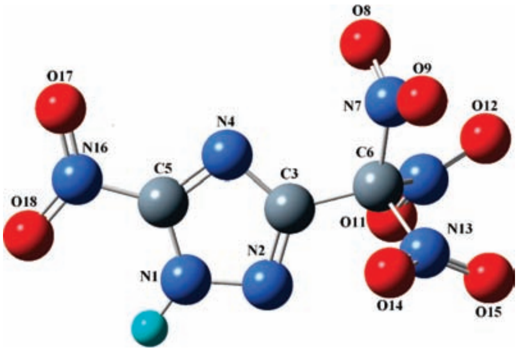


Figure 3. NBO analysis of **9** (charge densities: Table S3 of the Supporting Information).

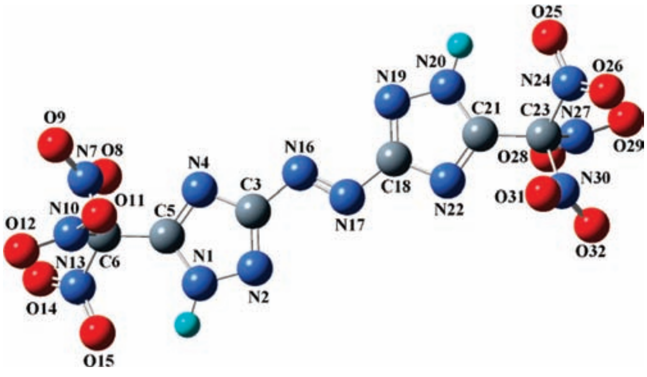


Figure 4. NBO analysis of **14** (charge densities: Table S4 of the Supporting Information).

carbon is more positively charged than C$-$C(NO_2)$_3$. The C5 carbon of the triazole ring is more positively charged than the C3 carbon in **9** and **12**, while the reverse is the case for **14** and **15**. All of the ring nitrogen atoms have negative charge densities, and the nitrogen atoms of the nitro groups have essentially the same positive charge density. Oxygen atoms of the NO_2 group bonded to C5 exhibit a more negative charge density as compared to the oxygen atoms of the trinitromethyl group (**9** and **12**). Optimized **9** and **12** have an unsymmetric charge distribution in the entire molecule. The electron-withdrawing effect of the NO_2 group considerably reduces the electronic charge of the connected atoms, and the negative charge is mainly delocalized over the carbon atoms in the triazole ring and the methyl group (in case of **12**) on the ring due to the conjugative and resonance effects of the ring. N1 of **9** and **14** show a higher negative charge density than the analogous nitrogen of **12** and **15** arising from the presence of the methyl group (Figures 3 and 4). The azo nitrogens of both **14** and **15** have nearly equal charge densities.

Nitro compounds are very strong electron acceptors, and this ability can be represented by the net charges of the nitro group. A higher negative charge on the nitro group implies lower electron attraction and therefore more stability of the nitro compound.[22] Recently, a nitro group charge method (NGCM) was established and applied to predict the properties of nitro compounds or explosives, including molecular stability and impact sensitivity.[23] The molecular stability of the compounds was evaluated and compared to the nitro group charges (Q_{Nitro}). Q_{Nitro} is the algebraic sum of charges of all three atoms of a nitro group (eq 1). The average value for Q_{Nitro} can be calculated by eq 2. The more negative nitro charges (Q_{Nitro}) correspond to the more stable nitro compounds,[23] because there is more than one nitro group in our synthesized molecules. In this Article, the Q_{Nitro} values for compounds **9**, **12**, **14**, and **15** are listed in Table S7 (Supporting Information). From Table S7, we can find that average Q_{Nitro} decreases when the methyl group was introduced into the molecule for compounds **9** (-0.175 as compared to -0.179 of **12**) and **14** (-0.164 as compared to -0.166 of **15**). The more negative average Q_{Nitro} value indicates that compounds **12** and **15** are more stable than compounds **9** and **14**, respectively, which are similar to the results for impact sensitivity tests or thermal decomposition results (Table 1).

$$Q_{\mathrm{Nitro}} = Q_{\mathrm{N}} + Q_{\mathrm{O1}} + Q_{\mathrm{O2}} \tag{1}$$

$$\overline{Q}_{\mathrm{Nitro}} = \frac{1}{n}\sum_{i=1}^{n} Q_{\mathrm{Nitro},\,i} \tag{2}$$

The structure of **12** is compared to the X-ray diffraction data. Most of the optimized bond lengths by B3LYP are similar to the experimental values. The triazole ring appears to have a slightly distorted structure, with N2$-$C3(1.3325) and C3$-$N4(1.3500) bond lengths next to the point of substitution not being equal to the bonds N4$-$C5(1.3135) and N1$-$C5(1.3617), respectively. This is also evident from the increase and decrease of bond angles exactly at the point of substitution as shown in Table S2 (Supporting Information). As is seen from Table S2, theoretical calculations generally give good values for C$-$N and C$-$C bond lengths of **9** when compared to experimental data. Although theoretical results deviate slightly from the experimental values, this may arise because theoretical calculations were carried out on the gas-phase molecule, whereas the experimental results were obtained in the solid state. The calculated geometric parameters also represent a good approximation, and they can be used as a foundation to calculate the other parameters for the compound.

■ CONCLUSIONS

The syntheses of high energy density polynitro triazoles, 5-nitro-3-trinitromethyl-1*H*-[1,2,4]triazole) (**9**), 3-dinitromethyl-5-nitro-*1H*-[1,2,4]triazole (**11**), 1-methyl-5-nitro-3-trinitromethyl-*1H*-[1,2,4]triazole (**12**), 5,5′-bis(trinitromethyl)-3,3′-azo-1,2,4-triazole (**14**), and 1,1′-dimethyl-5,5′-bis(trinitromethyl)-3,3′-azo-1,2,4-triazole (**15**), were carried out, and their physical and detonation properties were determined. These compounds exhibit good physical and detonation properties, such as moderate thermal stabilities, high densities, 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, RDX, and HMX. Tetranitro triazole **9** has a positive oxygen balance, 48.6% oxygen content, and a decomposition temperature of 135 °C, which suggests its use as a new stable oxidizer. In all aspects, except for oxygen balance, it is far superior to ADN. The other triazoles have good oxygen balance that is superior to RDX and HMX. The *N*-methylated compounds are less sensitive than the corresponding *N*-H triazoles. Triazoles **9**, **11**, and **12** are less sensitive than RDX and HMX, which suggests that these compounds might be of interest for future applications as environmentally friendly and high-performing nitrogen or oxygen-rich materials and may serve as a series of promising alternatives to RDX and HMX.

EXPERIMENTAL SECTION

Safety Precautions. While we have experienced no difficulties in the 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 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 X-ray diffraction analysis of compound **12** 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 colorless plate of dimensions 0.26 × 0.24 × 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 MoK_α radiation (λ = 0.71073). An Oxford Cobra low temperature device was used to maintain 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].[24] Data reduction was performed using SAINT [v7.60A][25] and XPREP [v2008/2].[26] Corrections were applied for Lorentz, polarization, and absorption effects using SADABS [v2008/1].[27] The structure was solved and refined with the aid of the programs in the SHELXTL-plus [v2008/4] system of programs.[28] 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-3-trinitromethyl-1*H*-[1,2,4]triazole (9). To a mixture of 98% sulfuric acid (12 mL) and 100% nitric acid (10 mL) was added (5-nitro-1*H*-[1,2,4]triazol-3yl)-acetic acid (**7**) (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 **9** (44%).

Colorless solid: T_{m} 113.7 °C, T_{dec} 135 °C (onset). IR (KBr): $\tilde{\nu}$ 3443, 3134, 1632, 1610, 1572, 1519, 1481, 1371, 1280, 1174, 1080, 1041, 962, 839, 800, 634 cm^{-1}. ^{13}C{^{1}H} NMR (CD_3CN): δ 157.9, 147.2, 122.2. ^{15}N{^{1}H} NMR: δ −22.50 (NO_2), −29.33 ($(NO_2)_3$), −38.58 (N2), −54.98 (N3), −132.33 (N1). Anal. Calcd for $C_3HN_7O_8$, 263: C, 13.70; H, 0.38; N, 37.27. Found: C, 14.18; H, 0.30; N, 37.52.

3-Dinitromethyl-5-nitro-*1H*-[1,2,4]triazole Hemihydrate (11). To a solution of potassium hydroxide (385 mg, 1.55 mmol) in ethanol (3 mL) was added a solution of hydroxylamine hydrochloride (239 mg, 3.42 mmol) in water (0.5 mL). After being stirred for 15 min, the potassium chloride precipitate was removed by filtration, and the mother liquor cooled to 0−5 °C was added dropwise to a solution of tetranitro triazole (**9**) (410 mg, 1.55 mmol) in ethanol (2 mL). The mixture was stirred for 3 h, and the precipitate was separated. The suspension of potassium salt (**8**) in water (2 mL) at 0−5 °C was acidified with 50% sulfuric acid (0.5 mL). The precipitate was removed by filtration. The filtrate was extracted with ethyl acetate (3 × 10 mL), dried over $MgSO_4$, and the solvent was evaporated. The products were combined to yield **11** (54%) and dried in a vacuum desiccator over P_4O_{10}.

Yellow solid; T_{dec} 87 °C (onset). IR (KBr): $\tilde{\nu}$ 3433, 3314, 1602, 1562, 1544, 1462, 1392, 1318, 1239, 1181, 1058, 840, 777, 682 cm^{-1}. ^{13}C{^{1}H} NMR: δ 163.7, 151, 124.9. Anal. Calcd for $C_3H_3N_6O_{6.5}$, 227: C, 15.87; H, 1.33; N, 37.01. Found: C, 16.28; H, 0.95; N, 36.25.

1-Methyl-5-nitro-3-trinitromethyl-1*H*-[1,2,4]triazole (12). To a solution of **9** (100 mg, 0.38 mmol) in diethyl ether was added a 2 M solution of trimethylsilyl diazomethane (0.3 mL) dropwise at 0 °C. The reaction mixture was stirred for 30 min, the solvent was evaporated, and the product was purified by column chromatography (eluted with 40% CH_2Cl_2/hexane from silica gel) to give **12** (80%).

White solid; T_{m} 77 °C, T_{dec} 153 °C (onset). IR (KBr): $\tilde{\nu}$ 3454, 1619, 1598, 1569,1504, 1443, 1400, 1337, 1290, 1281, 1171, 1110, 957, 844, 798 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.38. ^{13}C{^{1}H} NMR: δ 153.9, 144.4, 121.8, 42.1. ^{15}N{^{1}H} NMR: δ −35.02 (NO_2), −35.58 ($(NO_2)_3$), −59.99 (N2), −128.03 (N3), −165.68 (N1). Anal Calcd for $C_4H_3N_7O_8$, 277: C, 17.34; H, 1.09; N, 35.38. Found: C, 17.88; H, 0.99; N, 35.58.

5,5′-bis(Trinitromethyl)-3,3′-azo-1,2,4-triazole Hemihydrate (14). To a mixture of sulfuric acid (98%, 6 mL) and nitric acid (100%, 5 mL) was added [5-(5-carboxymethyl-1*H*-[1,2,4]triazole)-2*H*-[1,2,4]-triazol-3-yl]-acetic acid (1 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 was 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 **14** (55%).

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{^{1}H} NMR: δ 165.7, 148.8, 123.8. ^{15}N{^{1}H} NMR: δ −31.62 ($(NO_2)_3$), −33.0 (*N*═N), −60.35 (N2), −131.79 (N3), −132.26 (N1). Anal. Calcd for $C_6H_3N_{14}O_{12.5}$, 471: C, 15.29; H, 0.64; N, 41.62. Found: C, 15.56; H, 0.32; N, 41.50.

1,1′-Dimethyl-5,5′-bis(trinitromethyl)-3,3′-azo-1,2,4-triazole (15). To a solution of **14** (100 mg, 0.21 mmol) in diethyl ether was added a 2 M solution of trimethylsilyl diazomethane (0.5 mL) dropwise at 0 °C. The reaction mixture was stirred for 30 min, filtered, and the precipitate was washed with diethyl ether (5 mL) to give **15** (76%).

Yellow solid; T_{dec} 150 °C (onset). IR (KBr): $\tilde{\nu}$ 3441, 1625, 1593, 1474, 1443, 1346, 1290, 1220, 1108, 962, 844, 801, 754 cm^{-1}. ^{1}H NMR: δ 4.39. ^{13}C{^{1}H} NMR: δ 159.7, 147.7, 122.8. Anal. Calcd for $C_8H_6N_{14}O_{12}$, 490: C, 19.60; H, 1.23; N, 40.00. Found: C, 19.69; H, 1.13; N, 38.00.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** X-ray crystallographic files in CIF format for **12**, ^{1}H, ^{13}C NMR and IR spectra of all compounds, DSC scans of all compounds, and NBO charge densities. This material is available free of charge via the Internet at http://pubs.acs.org.

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