Energetic polyazole polynitrobenzenes and their coordination complexes†

Zhuo Zeng,[a] Yong Guo,[b] Brendan Twamley[b] and Jean'ne M. Shreeve*[b]

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New energetic polyazole polynitrobenzenes exhibit high heats of formation and thermal stabilities, and react as useful ligands with silver dinitramide to give an energetic coordination complex.

Polynitroarylenes play important roles as intermediates in the syntheses of pharmaceuticals, agrochemicals, polymers, and energetic materials.[1a–c] Substituted trinitrobenzenes comprise an important class of explosives for commercial and military use, *e.g.*, for 2,4,6-trinitrotoluene (TNT) [detonation velocity (v_D) = 6881 m s^{-1}; density (*d*) = 1.65 g cm^{-3}], 2,4,6-trinitrophenol (picric acid) (v_D = 7350 m s^{-1}, *d* = 1.71 g cm^{-3}), and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) (v_D = 8108 m s^{-1}, *d* = 1.94 g cm^{-3}).[1d]

The development of new energetic materials continues to focus on the synthesis of new heterocycles with high densities, high heats of formation, and good oxygen balance.[2] Mono-, di-, or tri-azole-substituted 1,3,5-trinitrobenzene moieties are good models which enable investigation of the structure–property relationship in energetic materials.

Reactions of polyhalo-substituted 1,3,5-trinitrobenzene with strong nucleophiles in dimethylformamide (DMF) at room or elevated temperature are difficult to control and often result in unwanted replacement of one or more of the nitro groups, and/or incomplete substitution of halogen which complicates isolation and purification.[3] Elevated temperature increases the hazard level in procedures for manufacturing energetic materials.

Fortunately, fluorosubstituted 1,3,5-trinitrobenzene is relatively sensitive to nucleophilic substitution.[4] 1-Trimethylsilylimidazole and 1-trimethylsilyltriazole are important as nucleophilic reagents for transfer of imidazole, and triazole groups since they exhibit better solubility in organic solvents and superior regioselective nucleophilicity than their respective sodium salts. The formation of trimethylsilyl fluoride (TMSF; bp 16 °C) which is a readily volatile product provides the driving force for reactions of fluorosubstituted 1,3,5-trinitrobenzene with 1-trimethylsilylazoles. This results in smooth and rapid nucleophilic substitution reactions at 25 °C.

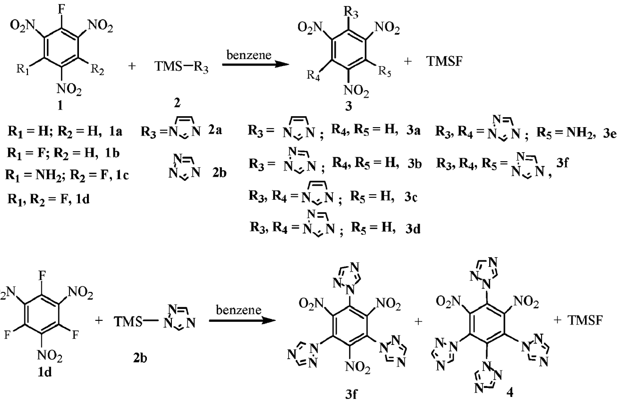
In this work, we utilize the mild nucleophiles **2a** and **2b** for regioselective nucleophilic substitution reactions by taking advantage of the formation of TMSF with fluorosubstituted 1,3,5-trinitrobenzenes (**1**), to form mono-, di-, tri-, and tetra-azole-substituted 1,3,5-trinitrobenzenes at 25 °C in one-pot reactions as shown in Scheme 1. This is a new and practical route to polyazole-substituted 1,3,5-trinitrobenzenes.

Additionally, development of new metal-coordinated complexes with these polyazole-substituted 1,3,5-trinitrobenzenes results in high performance energetic materials. 2,4,6-Tri-1*H*-triazol-1-yl-1,3,5-trinitrobenzene, **3f**, or 2,3,4,6-tetra-1*H*-triazol-1-yl-1,3-dinitrobenzene, **4**, compounds with high heats of formation, were coordinated with oxygen-rich silver dinitramide, to give an unexpected product 2,4,6-tri-1*H*-triazol-1-yl-3,5-dinitrophenol silver monohydrate, as well as the desired 2,3,4,6-tetra-1*H*-triazol-1-yl-1,3-dinitrobenzene silver dinitramide coordination complex (*vide infra*).

2-1*H*-Imidazol-1-yl-1,3,5-trinitrobenzene (**3a**) and 2-1*H*-triazol-1-yl-1,3,5-trinitrobenzene (**3b**) have been reported.[5] Polynitrobenzene impurities, the by-products from these syntheses, are difficult to remove from the DMF–H_2O mixture. However, when **2a** or **2b** was reacted with 2-fluoro-1,3,5-trinitrobenzene, **1**, at 25 °C in benzene, **3a** or **3b** resulted immediately which could be purified in high yield.

The reactions of 2,4-difluoro-substituted 1,3,5-trinitrobenzene, **1b** (1 mmol), with **2a** (2 mmol) and **2b** (2 mmol) were investigated and found to give the disubstituted products 2,4-di-1*H*-imidazol-1-yl-1,3,5-trinitrobenzene, **3c**, in moderate yield, and 2,4-di-1*H*-triazol-1-yl-1,3,5-trinitrobenzene, **3d**, in high yield. 1-Amino-3,5-di-1*H*-1,2,4-triazolyltrinitrobenzene, **3e**, was also prepared in high yield by interacting 1-amino-3,5-difluoro-trinitrobenzene (**1c**) with **2b**. A thermal ellipsoid plot of **3e**‡ is given in Fig. 1.

An efficient synthetic method for triazole-(imidazole-) substituted 1,3,5-trinitrobenzene, 2,4,6-tri-1*H*-imidazol-1-yl-1,3,5-trinitrobenzene, and 2,4,6-tri-1*H*-triazol-1-yl-1,3,5-trinitrobenzene, **3f**, has not been reported.



Scheme 1 Synthesis of polyimidazolyl or triazolyl 1,3,5-trinitrobenzenes.

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[a] *College of Chemistry & Environment, South China Normal University, Guangzhou, Guangdong 510006, P. R. China*
[b] *Department of Chemistry, University of Idaho, Moscow, ID 83844-2343, USA. E-mail: jshreeve@uidaho.edu; Fax: +1 12088859146; Tel: +1 12088856215*

† Electronic supplementary information (ESI) available: Experimental details, differential scanning calorimeter (DSC) figures for **3a–3f**, **4**, **6**, **7**. CCDC 732611–732614. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b915090k

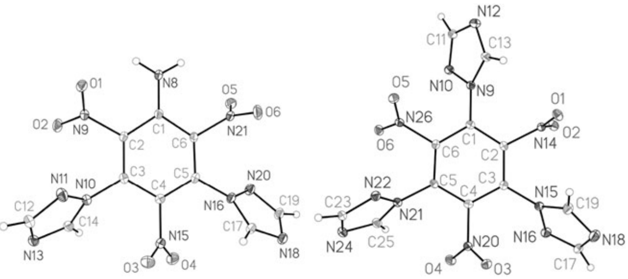
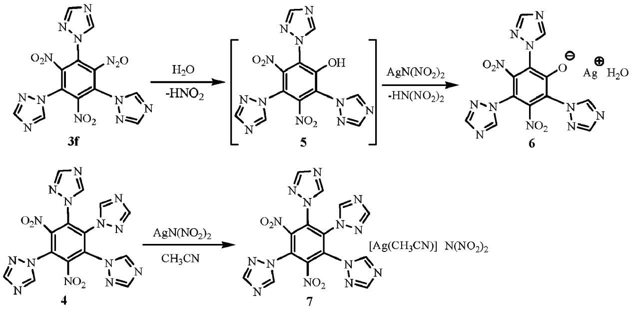


Fig. 1 Structure of one of the unique molecules in the asymmetric unit of **3e** (left) and **3f** (right) (displacement ellipsoids shown at 30% probability). Hydrogen atoms represented by spheres of arbitrary radius.

When 3 mmol 1-trimethylsilylimidazole (**2a**) was reacted with 1 mmol of 2,4,6-trifluoro-1,3,5-trinitrobenzene (**1d**) in an attempt to prepare 2,4,6-tri-1*H*-imidazol-1-yl-1,3,5-trinitrobenzene, a mixture was obtained. The product could not be isolated using column chromatography. However, synthesis of the triazole analogue, **3f**, occurred in 80% yield, by slowly dropping **2b** into **1d** dissolved in benzene (mole ratio 3 : 1) over 12 h at 25 °C. Importantly, if **2b** was added too rapidly or **1d** was present in the benzene solution at a concentration >0.1 mmol mL^{-1}, an inseparable mixture was generated. 2,4,6-Tri-1*H*-triazol-1-yl-1,3,5-trinitrobenzene, **3f**, was structured by single crystal X-ray diffraction§ (Fig. 1).

Polynitroarylenes easily undergo nucleophilic attack resulting in the displacement of one or more of the nitro groups.[6] Combining **2b** and **1d**, in a mole ratio of 4.5 : 1 under the same reaction conditions, gave, after separation of the reaction mixture, **3f** (30% yield) and 2,3,4,6-tetra-1*H*-triazol-1-yl-1,3-dinitrobenzene (**4**) (50% yield). In the latter case, in addition to replacement of the fluorine atoms, one nitro group was also displaced by triazole to give the tetratriazole-substituted 1,3-dinitrobenzene (**4**) suggesting that nitro groups positioned *meta* to one another are rather susceptible to nucleophilic attack even under mild reaction conditions.

Metal coordination complexes offer significant energetic performance improvement because of the presence of both oxidizing and reducing groups in the same complex molecules.[7] Combination of the oxygen-rich silver dinitramide[8] with **3f** (ΔH_f = 737.1 kJ mol^{-1}) or **4** (ΔH_f = 920.2 kJ mol^{-1}) results in attractive new metal coordination complexes which could lead to the development of new energetic materials (Scheme 2).



Scheme 2 Synthesis of a silver dinitramide polytriazole polynitrobenzene coordination complex.

Compound **3f** was reacted with silver dinitramide in an acetonitrile–methanol mixture at 25 °C for two weeks to give red crystals of the unexpected 2,4,6-tri-1*H*-triazol-1-yl-3,5-dinitrophenol silver monohydrate, [Ag(TTDP)(H_2O)] (**6**).

Highly nitrated derivatives of benzene readily react with water to form phenols, *e.g.*, 1,2,3,5-tetranitrobenzene is readily converted to picric acid by reaction with hot water, and some hindered nitro groups of hexanitrobenzene are also displaced smoothly even at 25 °C.[9] A possible mechanism is that **3f** in which three nitro groups are hindered by two adjacent triazole rings initially reacted with water to give the intermediate **5**. The latter subsequently reacted with silver dinitramide to give the silver coordination complex, [Ag(TTDP)(H_2O)] (**6**), and dinitramide acid. The immediate conversion of the latter into N_2O and HNO_3 would tend to drive the reaction forward.[10]

The yellow solid, 2,3,4,6-tetra-1*H*-triazol-1-yl-1,3-dinitrobenzene silver dinitramide coordination complex, [Ag(TTDB)(CH_3CN)][$N(NO_2)_2$] (**7**) was obtained after one week from **4** and $AgN(NO_2)_2$ in acetonitrile–methanol. That 2,3,4,6-tetra-1*H*-triazol-1-yl-1,3-dinitrobenzene (**4**) is more stable chemically than 2,4,6-tri-1*H*-triazol-1-yl-1,3,5-trinitrobenzene (**3f**) based on the results of the reaction with silver dinitramide suggests that **4** could be useful as a suitable ligand to form energetic metal coordination complexes.

The reaction with $AgN(NO_2)_2$ to create dinitramide salts of **3f** and **4** led to the synthesis and isolation of the unexpected product, **6**¶ (Fig. 2), and the sought 2,3,4,6-tetra-1*H*-triazol-1-yl-1,3-dinitrobenzene silver dinitramide coordination complex, [Ag(TTDB)(CH_3CN)][$N(NO_2)_2$] (**7**)‖ (Fig. 2). In **6**, a complex honeycomb structure is formed with each Ag four coordinate (Ag1–N = 2.285(3)–2.414(3)). The phenolic O– is stabilized by intramolecular H-bonding (C11–H11···O1 = 2.699(4) Å), and possibly by the solvent H_2O molecules. The higher nitrogen-containing dinitramide complex **7** is shown in Fig. 2. The silver atom is five-coordinate, and in a distorted trigonal bipyramid geometry. The triazoles N10, N15 and N20 form the equatorial plane and the dinitramide, and disordered solvent MeCN molecules are the apical components of the coordination geometry (Ag–N = 2.339(2), 2.231(2), 2.324(2), 2.668(2) and 2.599(8) Å, respectively).

Physical characteristics and some key properties of these energetic materials are given in Table 1.

To assess the potential of the newly prepared polyazole-substituted trinitrobenzene compounds, their energetic

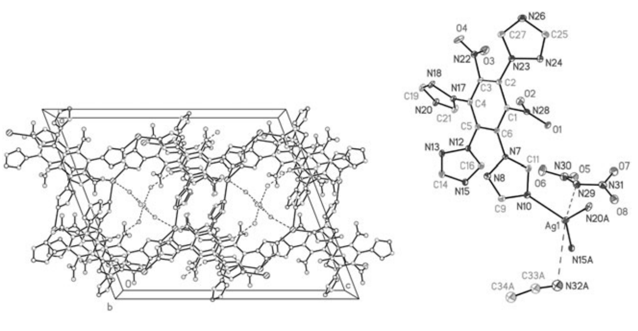


Fig. 2 Packing diagram of **6** (left) showing the honeycomb voids along the *b*-axis. Dashed lines indicate close contacts. Structure of **7** (right) (displacement ellipsoids shown at 30% probability). Only the major disordered component is shown.

Table 1 Thermal and physical properties of polyazole polynitrobenzene

Comp	d^a	$T_d{}^b$	$\Delta H_f{}^c$	P^d	$v_D{}^e$	$I_{sp}{}^f$	IS^g
3a	1.67	216.0	167.6	19.7	7164	210.0	40
3b	1.70	256.0	361.8	19.5	7255	216.8	40
3c	1.68	156.0	223.5	21.5	7380	204.1	35
3d	1.71	261.0	476.4	22.1	7549	215.4	35
3e	1.72	298.3	463.8	22.4	7178	212.3	35
3f	1.75	228.0	737.1	22.4	7197	214.8	35
4	1.56	249.5	920.2	15.3	6778	201.4	45
6	1.96	293.0	—	—	—	—	30
7	1.83	164.0	—	—	—	—	20
TNT	1.65	295.0	−67	19.5	6881	213.0	15
TATB	1.94	330.0	−139.8	31.1	8114	—	50

^{a} Density (g cm^{-3}). ^{b} Decomposition temperature (°C). ^{c} Heat of formation (kJ mol^{-1}). ^{d} Detonation pressure (GPa). ^{e} Detonation velocity (m s^{-1}). ^{f} I_{sp}—specific impulse (s). ^{g} Impact sensitivity (BAM fallhammer) (J).

characteristics are compared with 2,4,6-trinitrotoluene (TNT) and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). As shown in Table 1, the density increases with the increasing number of azolate substituents in the polyazole trinitrobenzenes. The [Ag(TTDB)(CH_3CN)][N(NO_2)$_2$] (**7**) silver dinitramide coordination complex with a density of 1.83 g cm^{-3} is higher than the ligand TTDB at 1.56 g cm^{-3}.

These polyazole trinitrobenzene compounds exhibit good thermal stabilities, ranging from 156 to 298 °C. The 1-amino-3,5-di-1*H*-1,2,4-triazolyltrinitrobenzene (**3e**), which decomposes at 298 °C, has the highest thermal stability due to strong intramolecular hydrogen bonding. The heats of formation for **3a**, **3b**, **3c**, **3d**, **3e**, **3f**, and **4** were calculated using the Gaussian 03 suite of programs[11] (see ESI†), and are summarized in Table 1. The heat of formation increases with the number of azolate substituents for 1,3,5-trinitrobenzene. 2,3,4,6-Tetra-1*H*-triazol-1-yl-1,3-dinitrobenzene (**4**) (ΔH_f = 920.2 kJ mol^{-1}) has the highest heat of formation. These values are also considerably more positive than that of TATB (−139.8 kJ mol^{-1}). Calculation of detonation properties and specific impulse values was obtained using Cheetah 5.0.[12] In general, an increase in the number of azole substituents in trinitrobenzene (higher density) results in higher detonation pressures and velocities. With the exception of **4**, all have higher detonation pressures and velocities than TNT. Their impact sensitivities (BAM fallhammer) range from 20 to 45 J and are relatively insensitive. The new polyazole polynitrobenzenes exhibit good thermal stabilities, and high heats of formation that make them new energetic materials.

In conclusion, the energetic polyazole-substituted polynitrobenzenes were obtained in good yield by the regioselective nucleophilic substitution of fluorosubstituted 1,3,5-trinitrobenzene with trimethylsilylazoles at 25 °C in one-pot reactions. Polyazole polynitrobenzenes with high heats of formation used as energetic ligands reacted with silver dinitramide, to give an unexpected hydrolysis product, and a five-coordinate silver dinitramide complex.

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Notes and references

‡ Crystal data for **3e**: $C_{12}H_9N_{11}O_6$, M = 403.30, monoclinic, a = 9.6692(4), b = 9.4624(4), c = 19.0356(8) Å, β = 97.696(1)°, U = 1725.95(13) Å^3, T = 90(2) K, space group = $P2(1)/c$ (no. 14), Z = 4, 25 293 reflections measured, 3967 unique (R_{int} = 0.0386) which were used in all calculations. The final w$R(F^2)$ was 0.0975 (all data).

§ Crystal data for **3f**: $C_{12}H_6N_{12}O_6$, M = 414.29, monoclinic, a = 12.2582(17), b = 10.7107(15), c = 24.007(3) Å, β = 92.253(2)°, U = 3149.5(7) Å^3, T = 90(2) K, space group = $P2(1)/c$ (no. 14), Z = 8, 72 957 reflections measured, 7224 unique (R_{int} = 0.0423) which were used in all calculations. Rotational twin—179.9° rotation about the reciprocal axis 1.000, 0.000, −0.001, refined twinning ratio = 0.3122(9). The final w$R(F^2)$ was 0.0909 (all data).

¶ Crystal data for **6**: $C_{12}H_{12}AgN_{11}O_8$, M = 546.20, monoclinic, a = 20.041(3), b = 8.2412(8), c = 24.046(3) Å, β = 111.131(9)°, U = 3704.4(8) Å^3, T = 90(2) K, space group = $C2/c$ (no. 15), Z = 8, 27 473 reflections measured, 3333 unique (R_{int} = 0.0342) which were used in all calculations. The final w$R(F^2)$ was 0.0886 (all data).

‖ Crystal data for **7**: $C_{16}H_{11}AgN_{18}O_8$, M = 691.30, triclinic, a = 8.8611(4), b = 11.1986(5), c = 13.3871(6) Å, α = 78.4787(6)°, β = 74.2808(6)°, γ = 84.8365(7)°, U = 1252.07(10) Å^3, T = 90(2) K, space group = $P\bar{1}$ (no. 2), Z = 2, 18 562 reflections measured, 5758 unique (R_{int} = 0.0354) which were used in all calculations. The final w$R(F^2)$ was 0.0802 (all data).

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