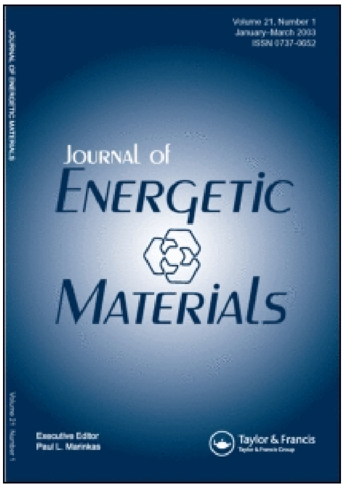

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4,4',6,6'-Tetra-Substituted Hydrazo- and Azo-1,3,5-Triazines

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4,4′,6,6′-Tetra-Substituted Hydrazo- and Azo-1,3,5-Triazines

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The syntheses of 4,4′,6,6′-tetra(amino)- (1), tetra(hydroxylamino)- (2), tetra(hydrazino)- (3), and tetra(azido) hydrazo-1,3,5-triazines (4) are described. Compound (4) was oxidized to 4,4′,6,6′-tetra(azido)azo-1,3,5-triazine (5). The thermal and sensitivity properties of (4) and (5) are reported in addition to all physical properties of new compounds.

Keywords: triazines, synthesis, properties, azo, hydrazo

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Introduction

At Los Alamos National Laboratory, the synthesis of high-nitrogen compounds has been the focus of our efforts for the past decade and a half. High-nitrogen compounds form a unique class of energetic materials, deriving most of their energy from their very high positive heats of formation rather than from oxidation of the carbon backbone, as with traditional energetic materials. We have previously reported the preparation and properties of high-nitrogen energetic materials based on the 1,2,4,5-tetrazine [1–3], 1,2,4-triazole [4, 5], 1,2,3,4-tetrazole [6, 7], and 1,2,5-oxadiazole (furazan) [8] ring systems.

There is no literature precedence for high-nitrogen energetic materials containing hydrazo- and azo-1,3,5-triazine backbones. Although Loew and Weis reported the preparations of three inert hydrazo-compounds [4,4′-dichloro-6,6′-di(isopropylamino) hydrazo-1,3,5-triazine; 4,4′,6,6′-tetra(dimethylamino)hydrazo-1,3,5-triazine; and 4,4′,6,6′-terachlorohydrazo-1,3,5-triazine], few physical properties and no crystal structures were available [9]. We report here the synthesis and properties of a series of energetic 4,4′,6,6′-tetra(substituted)hydrazo- and 4,4′,6,6′-tetra(substituted)azo-1,3,5-triazines.

Experimental

Notations and Abbreviations

The following compounds appear in this study:

4,4′,6,6′-tetra(amino)hydrazo-1,3,5-triazine (1)
4,4′,6,6′-tetra(hydroxylamino)hydrazo-1,3,5-triazine (2)
4,4′,6,6′-tetra(hydrazino)hydrazo-1,3,5-triazine (3)
4,4′,6,6′-tetra(azido)hydrazo-1,3,5-triazine (4)
4,4′,6,6′-tetra(azido)azo-1,3,5-triazine (5)
2,4,6-tri(azido)-1,3,5-triazine (6)
4,4′,6,6′-tetra(chloro)hydrazo-1,3,5-triazine (7)

Materials

House water was purified with a Barnstead E-Pure deionization system. High-purity tetrahydrofuran, acetonitrile, and chloroform were used as received from Aldrich. Hydroxylamine (50 weight % solution in water) and anhydrous hydrazine were purchased from Aldrich and used without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. Other chemicals employed in the preparations were reagent grade and used without further purification.

Instrumentations and Measurements

FT-IR spectra were recorded on a Nexus 670 FT-IR spectrophotometer at 4 cm^{-1} resolution interfaced with an IBM compatible PC. IR measurements were made in Nujol mulls. $^{1}\mathrm{H}/^{13}\mathrm{C}$ NMR spectra were obtained on a JEOL Eclipse 300 Fourier Transform Spectrometer, and chemical shifts are reported relative to internal tetramethylsilane. Melting points were determined by Differential Scanning Calorimetry (DSC) at 5°C/min using a TA Instruments DSC 2920 Modulated instrument. Elemental analyses were performed by Atlantic Microlabs (Norcross, GA) and Los Alamos National Laboratory. Heats of formation were the averages of three independent measurements using a Parr Adiabatic Calorimeter model 1720.

Syntheses and Characterizations

Caution: Compounds (4) and (5) are sensitive to friction, impact, and electrostatic discharge. Extreme care and appropriate precautions should be taken at all times, that is, always handle with thick gloves behind a safety shield and limit the amount to less than 500 mg.

4,4′,6,6′-Tetra(chloro)hydrazo-1,3,5-triazine (7). This compound was made according to the reference literature with comparable yield [9]. The crude product is stirred in with acetonitrile for 2 hr and filtered to remove an insoluble by-product. The acetonitrile was removed by rotary evaporation at room temperature, and the dried product was stored in the freezer to avoid its further decomposition. $^{1}\mathrm{H}$ NMR (DMSO-d_6) δ 10.59 (s, 2H); $^{13}\mathrm{C}$ NMR (DMSO-d_6) δ 168.31, 169.58, 170.28.

4,4′,6,6′-Tetra(amino)hydrazo-1,3,5-triazine (1). A 500 ml capacity pressure reactor equipped with a magnetic stirrer was charged with 5 g (15.2 mmol) of (7) and 200 ml acetonitrile. Ammonia, 3.12 g (183.2 mmol), was introduced to the reactor over 20 min with stirring at ambient temperature. The reaction mixture was heated on a steam bath for 3 hr and cooled to room temperature to form a white precipitated product that was filtered and thoroughly washed with water, yield 3.2 g (84%). The product is stable to 300°C as determined by DSC. ^{13}C NMR (methanesulfonic acid with a DMSO-d_6 coaxial insert) δ 152.60, 153.54, 155.52. Anal. Calcd. for $C_6H_{10}N_{12}$: C, 28.80; H, 4.03; N, 67.17. Found: C, 28.48; H, 4.20; N, 62.27. Infrared (cm^{-1}): ν(N$-$H) 3421 (s), 3403 (s), 3271 (s), and 3132 (s); ν(triazine) 1644 (vs), 1536 (vs), 1080 (vs), 1024 (vs), 809 (vs), and 589 (s).

4,4′,6,6′-Tetra(hydroxylamino)hydrazo-1,3,5-triazine (2). To 200 ml of acetonitrile was added 5 g (15.2 mmol) of (7) and 12.1 g (183.2 mmol) of 50% hydroxylamine in water with vigorous stirring. The mixture was refluxed for 3 hr with stirring. The precipitate was filtered, washed thoroughly with water, and air dried to yield 4.2 g (88%) of white product whose fast decomposition occurs at 178°C as determined by DSC. ^{1}H NMR (DMSO-d_6) δ 9.1 (bs, 10H); ^{13}C NMR (DMSO-d_6) δ 167.14, 168.88, 168.97. Anal. Calcd. for $C_6H_{10}N_{12}O_4$: C, 22.93; H, 3.21; N, 53.49. Found: C, 23.32; H, 3.61; N, 50.54. Infrared (cm^{-1}): ν(O$-$H) 3267 (vb); ν(N$-$H) 3190 (s); ν(triazine) 1725 (vs), 1571 (vs), 1161 (vs), 1009 (vs), 979 (vs), 797 (s), and 567 (s).

4,4′,6,6′-Tetra(hydrazino)hydrazo-1,3,5-triazine (3). To 200 ml of acetonitrile solution containing 3.28 g (10.0 mmol) of (7) at 0°C, 1.93 g (60.2 mmol) of hydrazine in 10 mL acetonitrile was added dropwise with vigorous overhead stirring. The mixture was then refluxed for 2 hr, cooled to room temperature, and filtered. The damp filter cake was washed thoroughly with water and air dried to yield 3.02 g (97%) of white product whose fast decomposition occurs at 293°C as determined by DSC. ^{13}C NMR (DMSO-d_6/DCl/D_2O) δ 164.89, 165.36, 167.66. Anal.

Calcd. for $C_6H_{14}N_{16}$: C, 23.23; H, 4.55; N, 72.23. Found: C, 23.47; H, 4.65; N, 70.36. Infrared (cm^{-1}): ν(N−H) 3312 (s) and 3269 (s); ν(triazine) 1571 (vs), 1523 (vs), 1073 (vs), 941 (vs), and 801 (vs). $\Delta H_f = +406 \pm 5$ kJ/mol.

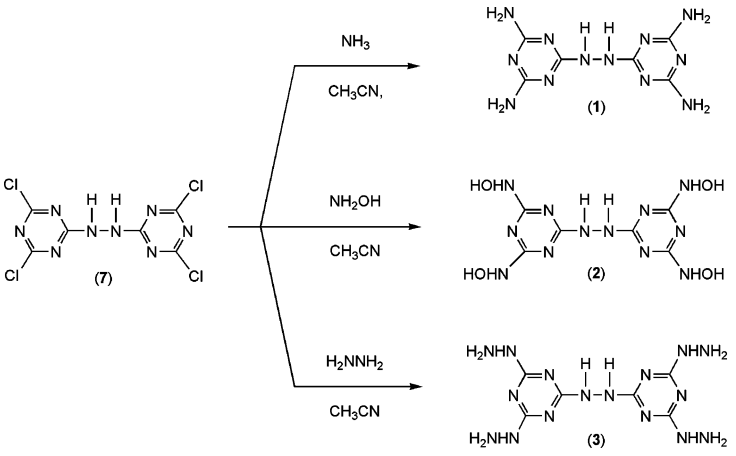
4,4′,6,6′-Tetra(azido)hydrazo-1,3,5-triazine (4). To a jacketed beaker containing 40 ml of 3.5 M HCl was added 0.5 g (1.61 mmol) of (3) and the suspension stirred until complete dissolution occurred. The temperature was then adjusted to −5°C with a constant temperature bath, while 1.33 g $NaNO_2$ (19.27 mmol) dissolved in 10 ml of water was added dropwise with vigorous stirring while maintaining the temperature below 3°C. Foaming was controlled by the addition of a few drops of diethyl ether. The pale yellow crude product was recrystallized from acetonitrile, yield 0.5 g (87%). The product does not melt but starts to decompose at 202°C as determined by DSC. ^{1}H NMR (DMSO-d_6) δ 10.6 (s, 2H); ^{13}C NMR (DMSO-d_6) δ168.3, 169.6, 170.2. Elemental analysis: Anal. Calcd. for $C_6H_2N_{20}$: C, 20.34; H, 0.57; N, 79.09. Found: C, 20.04; H, 0.75; N, 79.44. $\Delta H_f = +1753 \pm 3$ kJ/mol. Infrared (cm^{-1}): $\nu(N_3)$ 2172 (vs) and 2129 (vs); ν(N−H) 3221 (s) and 3091 (s); ν(triazine) 1541 (vs), 1352 (vs), 1252 (vs), 972 (vs), and 806 (vs).

4,4′,6,6′-Tetra(azido)azo-1,3,5-triazine (5). A solution of sodium hydrogen carbonate (0.475 g, 5.65 mmol) in 15 ml of water was added to 30 ml of chloroform in which 1.0 g of (4) (2.82 mmol) was suspended. A slow stream of chlorine gas was bubbled through the chloroform layer with gentle stirring until a dark reddish orange homogeneous chloroform layer was formed. The organic layer was separated and dried with magnesium sulfate. The volume of the solution was reduced to 15 mL and then passed down a silica gel columm using chloroform as the eluent. The product crystallized on standing at room temperature for a few days to give 0.354 g (75%). The product becomes viscous at 150°C as visually determined and decomposes at 200°C as determined by DSC. ^{13}C NMR (acetone-d_6) δ 173.7, 176.4. Anal. Calcd. for C_6N_{20}: C, 20.46; H, 0.00; N, 79.54. Found: C, 20.82; H, 0.07; N, 79.18.

$\Delta H_f = +2171 \pm 10\,\mathrm{kJ/mol}$. Infrared ($\mathrm{cm}^{-1}$): $\nu(N_3)$ 2208 (vs), 2155 (vs), and 2132 (vs); ν(triazine) 1549 (vs), 1521 (vs), 1435 (vs), 1161 (vs), 1011 (vs), and 823 (vs).

Results and Discussions

As described in the Syntheses section, (7) undergoes nucleophilic substitution reactions with ammonia, hydroxylamine, and hydrazine to give the 4,4′,6,6′-tetra(substituted)hydrazo–1, 3,5-triazine to



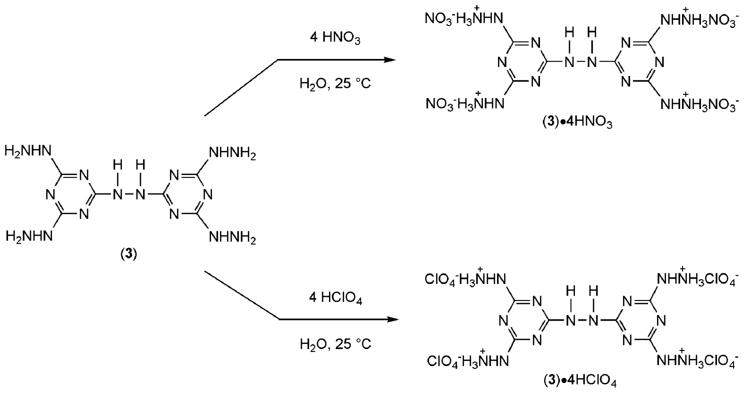
(1a)

(1b)

(1c)

When ammonia and hydroxylamine were used as the nucleophiles, the reactions were started at room temperature and heated to reflux for 3 hr. In the case of hydrazine as the nucleophile, the reaction solution was kept at 0°C during the addition of hydrazine to compensate for the temperature increase due to the highly exothermic reaction followed by 2 hr of refluxing.

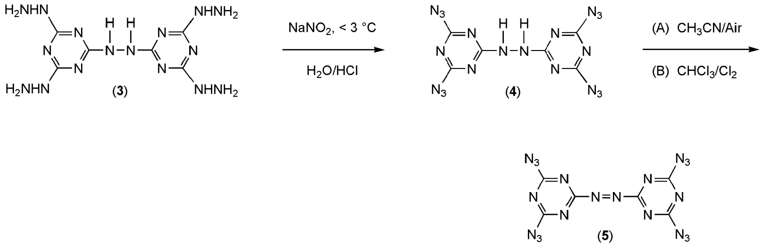
The products (1) and (2) were extremely insoluble, which made it difficult to oxidize them cleanly to the corresponding azo-compounds. The tetra(nitrate) salt of (3), (3)•4HNO_3, was nondetonable at 0.5 inch. The tetra(perchlorate) salt of (3), (3)•4$HClO_4$, was very hygroscopic; hence, work on it was abandoned to



(2a)

(2b)

Compound (4) was synthesized through diazotization of (3) in 3.5 M HCl at <3°C. A small amount of an insoluble byproduct was separated using acetonitrile at room temperature under nitrogen atmosphere. Compound (5) is the oxidation product of (4), and the oxidation can be carried out either in acetonitrile and air or in chloroform with chlorine gas as oxidant. Over a period of 10 hr in the presence of air, an acetonitrile solution of (4) slowly underwent air oxidation to (5). In a mixture of 1:2 (v/v) H_2O:$CHCl_3$ at room temperature, compound (4) was oxidized by chlorine gas to (5). In both cases, the product was purified by column chromatography using silica gel with chloroform as the eluent to



(3)

The purified compounds (4) and (5) were isolated and fully characterized by elemental analysis, differential scanning calorimetry, heat of formation, infrared and $^1H/^{13}C$ NMR spectroscopies, and X-ray crystallography.

Compound (4) has only one polymorph ($\rho = 1.649\,\mathrm{g\,cm^{-3}}$) in which the two 1,3,5-triazine rings are not coplanar but have a central torsion angle of 105° (Figure 1). Compound (5) crystallized in α and β polymorphs, $\rho_\alpha = 1.724\,\mathrm{g\,cm^{-3}}$ (Figure 2) and $\rho_\beta = 1.674\,\mathrm{g\,cm^{-3}}$ (Figure 3). The β-polymorph has two conformers whose azido substituents orient in different directions. Reminiscent of 2,4,6-tri(azido)-1,3,5-triazine [10–12] (6), the azido substituents of (4) and (5) do not tautomerize to form fused tetrazolo rings even though they were heated in polar solvents.

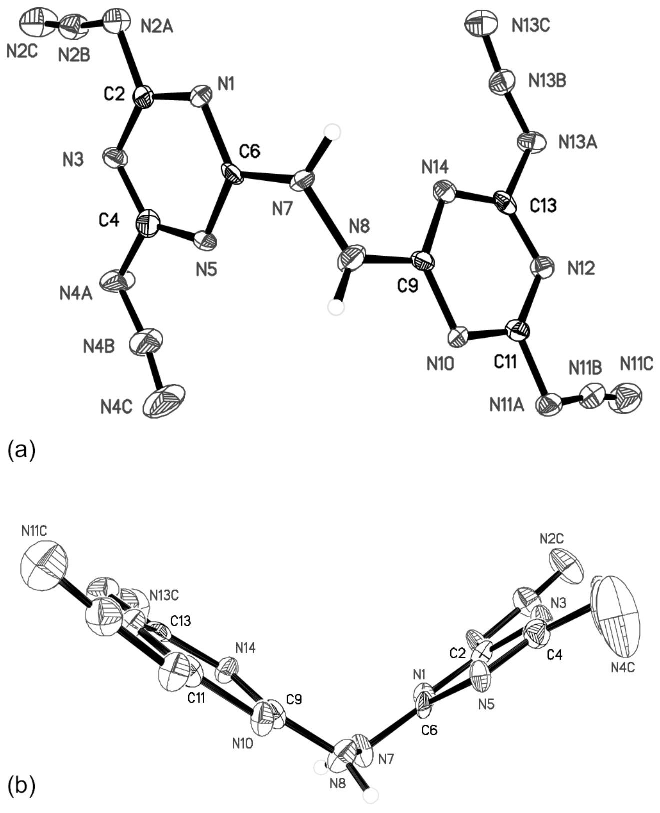


Figure 1. (a) ORTEP diagram (25% ellipsoids) and labeling scheme for 4,4′,6,6′-tetra(azido)hydrazo-1,3,5-triazine (4). (b) End-on view: the central torsion angle C6-N7-N8-C9 is 105°, and the two halves of the molecule are fairly planar.

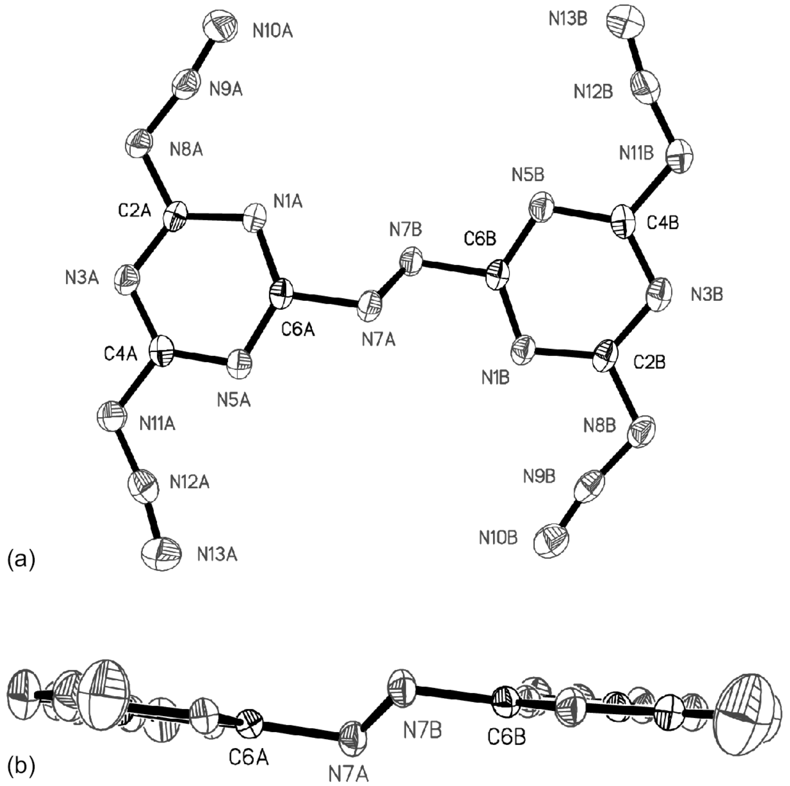


Figure 2. (a) α-polymorph of (5): ORTEP diagram (25% ellipsoids) and labeling scheme for 4,4′,6,6′-tetra(azido) azo-1,3,5-triazine. (b) Edge-on view of the molecule, showing the "step" in the azo-chain that connects the two separate, essentially planar halves of the molecule.

The primary explosive (6) is easily prepared from 2,4,6-tri(chloro)-1,3,5-triazine and sodium azide [11, 12]. Although it is more than twice as powerful as mercury fulminate [13], its applications are very limited because it is notorious for its extreme sensitivity to spark, friction, and impact and for its high volatility. We reasoned that linking two 1,3,5-triazine rings together through a hydrazo- or an azo-linkage to form the corresponding compounds (4) and (5) would not only

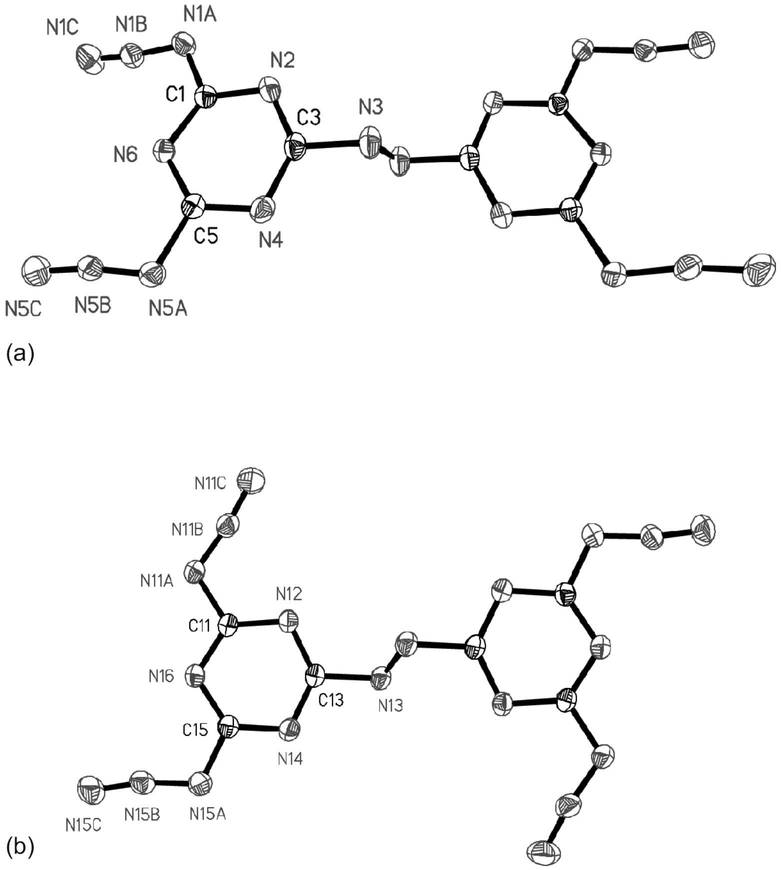


Figure 3. ORTEP diagrams (25% ellipsoids) and labeling scheme of the β-polymorph of (5) in the two conformers for 4,4′,6,6′-tetra(azido)azo-1,3,5-triazine. Both molecules sit on centers of symmetry, and neither molecule is completely planar.

partially desensitize the material, but could also dramatically increase the melting point and thereby lower volatility.

As shown in Figure 4 below, the hydrazo linkage in (4) and azo linkage in (5) result in a nonobservable melting point up to their fast decomposition at 202 and 200°C, respectively. Consequently, the azo- and hydrazo-linkages have significantly decreased volatility and increased melting point.

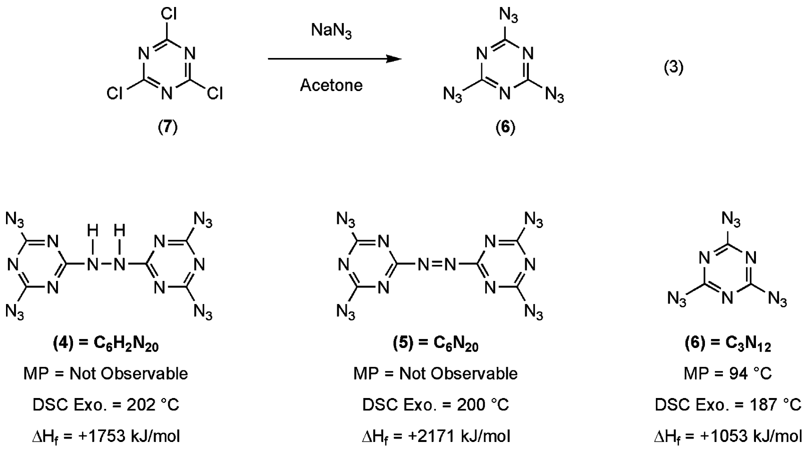
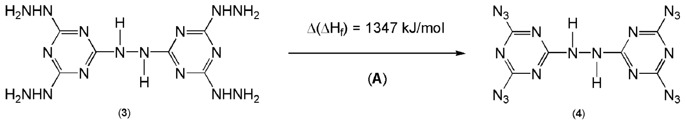
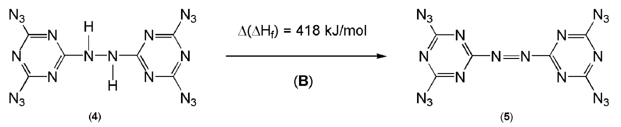


Figure 4. Preparation of (6) and comparison of thermal properties and heat of formation of (6) to (4) and (5).

It is also notable that the experimentally measured normalized heat of formation for (5) is the highest ever reported for energetic materials including polynitro, high-nitrogen, and polyazido compounds [10]. As shown in the Experimental section and equations (4a–b), the replacement of four hydrazino by four azido substituents in the hydrazo-1,3,5-triazine compound increases 1347 kJ/mol in energy, whereas the energy of 418 kJ/mol is gained in the transformation from (4) to (5).



(4a)



(4b)

Table 1
Sensitivity properties

Compound	DSC fast decomp. (°C)	Impact H_{50} (type 12) (cm)	Friction (BAM) (Kg)	Spark (J)
PETN	178	14.5	5.4	>0.36
Tetra(azido)hydrazo-1,3,5-triazine (4)	202	18.3	2.9	<0.36
Tetra(azido)azo-1,3,5-triazine (5)	200	6.2	2.4	<0.36
2,4,6-tri(azido)-1,3,5-triazine (6)	187	6.2	<0.5	<0.36

For comparison, the sensitivity properties of PETN (pentaerythritol tetranitrate) and 2,4,6-tri(azido)-1,3,5-triazine (6) as references and (4) and (5) are given in Table 1.

Compared to PETN, (4), (5), and (6) are all spark sensitive. Compared to (6), (4) and (5) are six and five times less sensitive to friction, respectively. Compound (4) is three times less sensitive to impact than (5) and (6).

Conclusions

These sensitivity data of (4) and (5) compared to (6) illustrate that the hydrazo- and azo-linkages can be utilized to desensitize and to decrease volatility of polyazido compounds. Compound (5) possesses the highest measured normalized heat of formation for an energetic compound. The nucleophilic substitution reactions of (7) give a series of new high-nitrogen compounds containing triazine as the parent backbone, and this novel approach is currently being extended to other high-nitrogen systems.

Acknowledgments

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