High-Nitrogen Compounds

Polyazido High-Nitrogen Compounds: Hydrazo- and Azo-1,3,5-triazine[**]

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The performance of a high explosive is measured by its detonation velocity (v_D (km sec^{-1})) and detonation pressure (P_{CJ} (kbar)). These parameters are determined by the oxygen balance (OB_{CO}),[1a] density (ρ), and heat of formation (ΔH_f),[1b] the higher the oxygen balance, density, and heat of formation, the better the performance. The energy of traditional polynitro compounds (Scheme 1) is primarily derived from the combustion of the carbon backbone using the oxygen carried by the nitro group.[2]

For modern polynitro compounds (Scheme 2), the performance is enhanced not only by an excellent oxygen balance but also by a ring/cage strain which improves both the heat of formation and density.[4]

Recently, a new class of energetic compounds containing a large fraction of nitrogen has been investigated.[5–8] These "high-nitrogen" compounds form a unique class of energetic materials[5a,9] whose energy is derived from their very high positive heat of formation rather than from the combustion of the carbon backbone or the ring/cage strain (Scheme 3). The high heat of formation is directly attributable to the large number of inherently energetic N−N and C−N bonds.

High-nitrogen compounds containing polyazides possess even higher heats of formation because their energy content rapidly increases with the number of energetic azido groups in the molecule. However, they are notorious for their extreme sensitivity[10a] to spark, friction, and impact (H_{50})[10b] as well as poor thermal stability,[10a,11,12] so their applications are very limited. Examples include 3,6-diazido-1,2,4,5-tetrazine[13] and cyanuric azide (2,4,6-triazido-1,3,5-triazine;[14] Scheme 4).

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 compounds (4,4′-di(chloro)-6,6′-di(isopropylamino)azo-1,3,5-triazine, 4,4′,6,6′-tetra(dimethylamino)azo-1,3,5-triazine, and 4,4′,6,6′-tetra(chloro)azo-1,3,5-triazine) in 1976, few physical properties and no crystal structures were available.[15]

We report herein the synthesis and properties of novel 4,4′,6,6′-tetra(azido)hydrazo-1,3,5-triazine (**3**) and 4,4′,6,6′-tetra(azido)azo-1,3,5-triazine (**4**), see Scheme 5. The hydrazo and azo linkages not only desensitize but also dramatically increase the melting point of the polyazido products. Remarkably, the heats of formation of these polyazido compounds (Scheme 5) are much higher than those of polynitro and high-nitrogen compounds (Scheme 1–3).

Rapid reaction occurs between 4,4′,6,6′-tetra(chloro)hydrazo-1,3,5-triazine (**1**)[15] and an excess of hydrazine monohydrate ($H_2NNH_2{\cdot}H_2O$) in CH_3CN to give 4,4′,6,6′-tetra(hydrazino)hydrazo-1,3,5-triazine (**2**) which underwent diazotization to yield **3** (Scheme 5). A suspension of **3** in 1:2 (*v*/*v*) H_2O:$CHCl_3$ solution was oxidized by chlorine gas at room temperature to **4**.

All products, **2**–**4**, were isolated and fully characterized by elemental analysis, differential scanning calorimetry (DSC), heat of formation, and IR and $^1H/^{13}C$ NMR spectroscopies.[16] Compounds **3** and **4** were also characterized by X-ray crystallography, Figure 1–3.[17] Compound **3** has only one polymorph ($\rho = 1.649$ g cm^{-3}) in which two 1,3,5-triazine rings are not co-planar but have a central torsion angle of 105° (Figure 1). Compound **4** crystallized in α and β polymorphs, $\rho = 1.724$ g cm^{-3} and $\rho = 1.674$ g cm^{-3} (Figure 2). The β poly-

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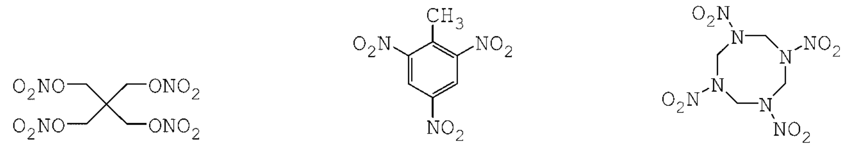
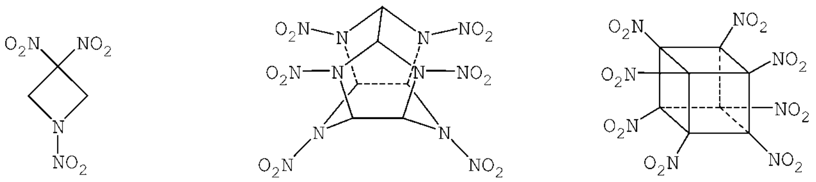


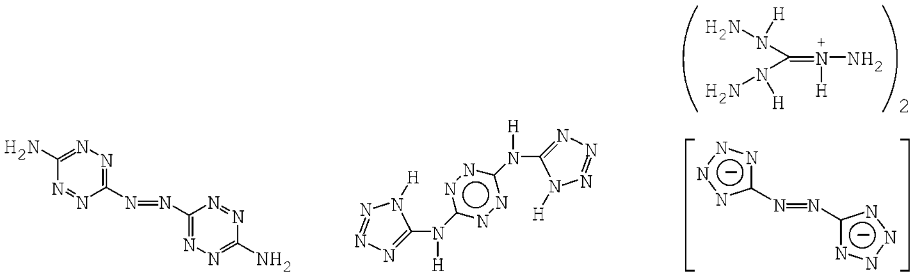
PETN	**TNT**	**β-HMX**
$C_5H_8N_4O_{12}$	$C_7H_5N_3O_6$	$C_4H_8N_8O_8$
OB_{CO} = +15.18 %	OB_{CO} = −17.17 %	OB_{CO} = 0.00 %
ρ = 1.78 g cm^{-3}	ρ = 1.65 g cm^{-3}	ρ = 1.91 g cm^{-3}
ΔH_f = −593 kJ mol^{-1}	ΔH_f = −64 kJ mol^{-1}	ΔH_f = +75 kJ mol^{-1}
N(ΔH_f) = −20.45 kJ atom^{-1}	N(ΔH_f) = −3.05 kJ atom^{-1}	N(ΔH_f) = +2.68 kJ atom^{-1}

Scheme 1. Traditional energetic polynitro compounds.[3a]



TNAZ	**ε-CL-20**	**ONC**
$C_3H_4N_4O_6$	$C_6H_6N_{12}O_{12}$	$C_8N_8O_{16}$
OB_{CO} = +8.33 %	OB_{CO} = +10.95 %	OB_{CO} = +27.58 %
ρ = 1.86 g cm^{-3}	ρ = 2.04 g cm^{-3}	ρ = 1.979 g cm^{-3}
ΔH_f = +21 kJ mol^{-1}	ΔH_f = +377 kJ mol^{-1}	ΔH_f = +594 kJ mol^{-1} (calc)
N(ΔH_f) = +1.24 kJ atom^{-1}	N(ΔH_f) = +10.47 kJ atom^{-1}	N(ΔH_f) = +18.56 kJ atom^{-1}

Scheme 2. Modern energetic polynitro compounds.[3b]



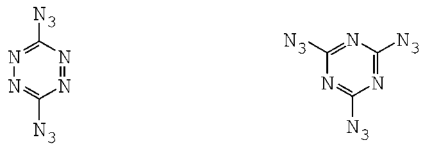
DAAT	**BTATz**	**TAG-AT**
$C_4H_4N_{12}$	$C_4H_4N_{14}$	$C_4H_{18}N_{22}$
OB_{CO} = −43.60 %	OB_{CO} = −38.68 %	OB_{CO} = −55.56 %
ρ = 1.78 g cm^{-3}	ρ = 1.76 g cm^{-3}	ρ = 1.60 g cm^{-3}
ΔH_f = +862 kJ mol^{-1}	ΔH_f = +883 kJ mol^{-1}	ΔH_f = +1075 kJ mol^{-1}
N(ΔH_f) = +43.10 kJ atom^{-1}	N(ΔH_f) = +40.14 kJ atom^{-1}	N(ΔH_f) = +24.43 kJ atom^{-1}

Scheme 3. High-nitrogen compounds.[3c]

morph has two conformers whose azido substituents orient in different directions (Figure 3).

Reminiscent of 3,6-di(azido)1,2,4,5-tetrazine and cyanuric azide, none of the azido substituents of **3** and **4** tautomerize to form fused tetrazolo rings even though they were heated in polar solvents.

The hydrazo linkage in **3** and azo linkage in **4** result in a non-observable melting point up to their fast decomposition at 200 and 202 °C (DSC), respectively. Consequently, the azo and hydrazo linkages have significantly decreased volatility and increased melting point relative to cyanuric azide.



3,6-Di(azido)-1,2,4,5-tetrazine
C_2N_{10}
m.p. = Not Observable
DSC Exo. = 130 °C
H_{50} < 1 cm
Friction < 0.5 kg
Spark < 0.36 J
ΔH_f = N/A[18b]
N(ΔH_f) = N/A[18b]

2,4,6-Tri(azido)-1,3,5-triazine
C_3N_{12} (cyanuric azide)
m.p. = 94 °C
DSC Exo. = 187 °C
H_{50} = 6.2 cm
Friction < 0.5 kg
Spark < 0.36 J
ΔH_f = +1053 kJ mol^{-1} [18a]
N(ΔH_f) = +70.20 kJ atom^{-1} [18a]

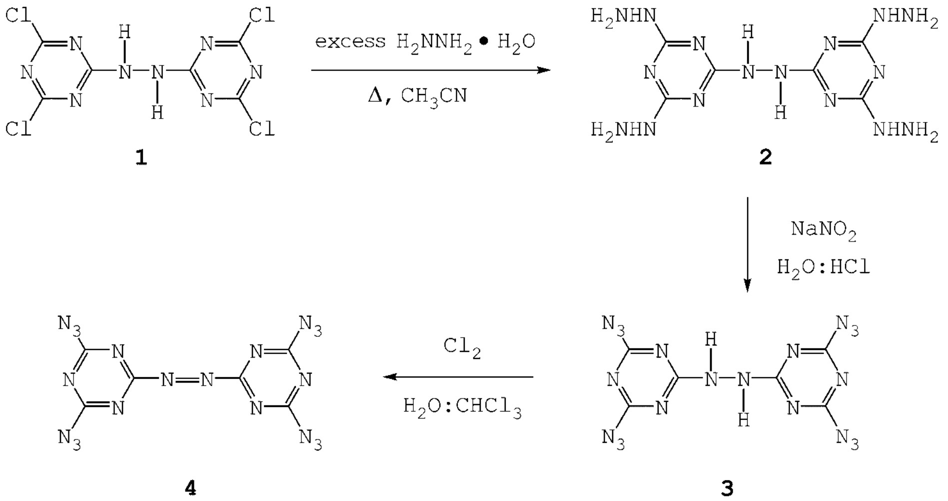
Scheme 4. Energetic materials containing azido groups. DSC Exo. = differential scanning calorimetry exotherm

Remarkably, the experimentally measured heat of formation for **4** (Scheme 5) is the highest reported for energetic materials.[18] As shown by the ΔH_f data in ref. [16] and Scheme 5, the replacement of four hydrazino by four azido substituents in the hydrazo-1,3,5-triazine compound (**2**→**3**) increases the energy by 1347 kJ mol^{-1}, and 418 kJ mol^{-1} is gained in the transformation from **3** into **4** (Scheme 6).

For comparison, the explosive properties and sensitivity of reference PETN, (Figure 1), cyanuric azide, **3**, and **4** are given in Table 1.[10]

Cyanuric azide is extremely sensitive to friction and spark, and its impact is a half less than that of PETN. Compound **3** is spark sensitive, but its impact and friction are three and six times less sensitive than those of cyanuric azide, respectively (Table 1). The impact and spark sensitivity of **4** are comparable to cyanuric azide, but its friction sensitivity is at least five times less than that of cyanuric azide (Table 1).

The compounds in this study are novel and important in demonstrating that the hydrazo and azo linkages can be



4
C_6N_{20}
m.p. = Not Observable
DSC Exo. = 200 °C
OB_{CO} = −27.26 %
ρ = 1.72 g cm^{-3}
ΔH_f = +2171 kJ mol^{-1}
N(ΔH_f) = +83.50 kJ atom^{-1}

3
$C_6H_2N_{20}$
m.p. = Not Observable
DSC Exo. = 202 °C
OB_{CO} = −31.62 %
ρ = 1.65 g cm^{-3}
ΔH_f = +1753 kJ mol^{-1}
N(ΔH_f) = +62.61 kJ atom^{-1}

Scheme 5. Preparation and properties of **3** and **4**.

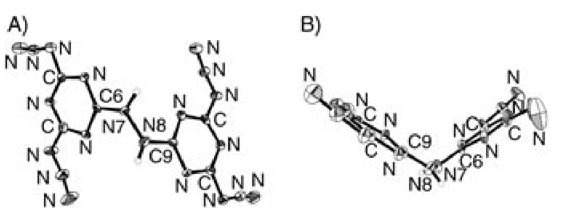


Figure 1. A) ORTEP diagram (thermal ellipsoids set at 25 % probability) for **3**, B) end-on view: the central torsion angle C6-N7-N8-C9 is 105°, and the two halves of the molecule are fairly planar.

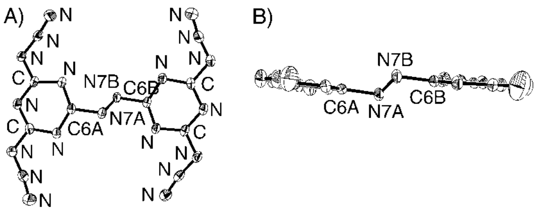


Figure 2. The α-polymorph of **4**: A) ORTEP diagram (thermal ellipsoids set at 25 % probability) of **4**, B) an edge-on view of the molecule, showing the "step" in the azo chain that connects the two separate, essentially planar halves of the molecule.

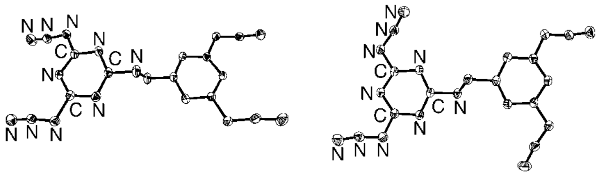


Figure 3. ORTEP diagrams (thermal ellipsoids set at 25 % probability) and labeling scheme of the β polymorph crystallized in two conformers for **4**. Both molecules sit on a center of symmetry, and neither molecule is completely planar.

$$\text{A)}\quad \mathbf{2} \xrightarrow{\Delta(\Delta H_f)\ =\ 1347\ \text{kJ mol}^{-1}} \mathbf{3}$$

$$\text{B)}\quad \mathbf{3} \xrightarrow{\Delta(\Delta H_f)\ =\ 418\ \text{kJ mol}^{-1}} \mathbf{4}$$

Scheme 6. A) $\Delta E_{\text{substitution}}$ from the hydrazino to azido substituent and B) $\Delta E_{\text{transformation}}$ from the hydrazo to azo linkage.

Table 1: Explosive properties and sensitivity.

Compound	DSC fast decomp [°C]	Impact H_{50} (Type 12) [cm]	Friction (BAM)[Kg]	Spark [J]
PETN	178	14.5	5.4	>0.36
cyanuric azide	187	6.2	<0.5	<0.36
3	202	18.3	2.9	<0.36
4	200	6.2	2.4	<0.36

utilized to desensitize and to decrease volatility of polyazido compounds. The compound 4,4′,6′6,-tetra(azido)azo-1,3,5-triazine (**4**) has the highest measured heat of formation.

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[1] a) OB_{CO} is an index of the deficiency or excess of oxygen in a compound required to convert all C into CO and all H into H_2O. For a compound with the molecular formula of $C_aH_bN_cO_d$, $OB_{CO}(\%) = 1600[(d-a-\tfrac{1}{2}b)\,FW^{-1}]$; b) A normalized heat of formation ($N(\Delta H_f)$ in kJ atom^{-1}) is calculated from the heat of formation divided by the number of atoms in a compound.

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[3] a) PETN = pentaerythritol tetranitrate; TNT = 2,4,6-trinitrotoluene; β-HMX = octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; b) TNAZ = 1,3,3-trinitroazetidine; ε-CL-20 = 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaaza-tetracyclo[5.5.0.05,9.03,11]dodecane; ONC = octanitrocubane; c) DAAT = diaminoazotetrazine or 3,3′-azobis(6-amino-1,2,4,5-tetrazine); BTATz = 3,6-bis(1*H*-1,2,3,4-tetrazol-5-ylamino)-1,2,4,5-tetrazine; TAGAT = triaminoguanidinium-5,5′-azobis(1*H*-tetrazolate).

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[10] a) For an explanation of methods for characterizing explosive sensitivity, see R. T. Paine, W. Koestle, T. T. Borek, E. Duesler, M. A. Hiskey, *Inorg. Chem.* **1999**, *38*, 3738 – 3743; b) Definition of H_{50}: the height in centimeters at which the probability of an explosion is 50 %—determined by a drop-weight machine or drop-hammer to evaluate impact sensitivity. In the test, a 2.5-kg weight is dropped from a set height onto a 40-mg sample of an explosive placed on 150-grit garnet sandpaper. A series of drops is made from different heights and an explosion or non-explosion is recorded; the test results are summarized as H_{50}.

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[16] Characterization: **2**: Elemental analysis (%) 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, ΔH_f: 406(± 5) kJ mol^{-1}, IR (cm^{-1}): $\tilde{\nu}$(N-H) 3312 (s), 3269 (s); $\tilde{\nu}$(triazine) 1571 (vs), 1523 (vs), 1073 (vs), 941 (vs), 801 (vs), ^{13}C NMR (75 MHz, [D$_6$]DMSO/DCl/D$_2$O, 25 °C): δ = 164.9, 165.4, 167.7 ppm. **3**: Elemental analysis (%) 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, ΔH_f: 1753($\pm$3) kJ mol^{-1}, IR (cm^{-1}): $\tilde{\nu}$(N_3) 2172 (vs), 2129 (vs), $\tilde{\nu}$(N-H) 3221 (s), 3091 (s); $\tilde{\nu}$(triazine) 1541 (vs), 1352 (vs), 1252 (vs), 972 (vs), 806 (vs), ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 10.59 ppm, ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 168.3, 169.6, 170.2 ppm. **4**: Elemental analysis (%) calcd for C_6N_{20}: C 20.46, H 0.00, N 79.54; found: C 20.82, H 0.07, N 79.18, ΔH_f: 2171($\pm$10) kJ mol^{-1}, IR (cm^{-1}): $\tilde{\nu}$(N_3) 2208 (vs), 2155 (vs), 2132 (vs); $\tilde{\nu}$(triazine) 1549 (vs), 1521 (vs), 1435 (vs), 1161 (vs), 1011 (vs), 823 (vs), ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 173.7, 176.4 ppm.

[17] CCDC-235587 (**3**) and CCDC-235586 and CCDC-235588 (α and β polymorphs of **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[18] a) Cyanuric azide: $\Delta H_f = +1053$ kJ mol^{-1} ($N(\Delta H_f) =$ 70.20 kJ atom^{-1}) obtained from E. G. Gillan, *Chem. Mater.* **2000**, *12*, 3906–3912; b) Although the heat of formation for 3,6-di(azido)-1,2,4,5-tetrazine is the only one that is predicted to be higher than that for **4**, the material is too sensitive to work with. A detonation occurred even when 70%:30% (wt/wt) benzoic acid:3,6-di(azido)-1,2,4,5-tetrazine was gently mixed in water.