

## Synthesis of Polyazapolycyclic Caged Polynitramines

Arnold T. Nielsen,\* Andrew P. Chafin,\* Stephen L. Christian, Donald W. Moore,  
Melvin P. Nadler, Robin A. Nissan, and David J. Vanderah†

Chemistry and Materials Branch, Research and Technology Group  
Naval Air Warfare Center Weapons Division, China Lake, CA 93555-6100

Richard D. Gilardi, Clifford F. George, and Judith L. Flippen-Anderson

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, DC 20375-5000

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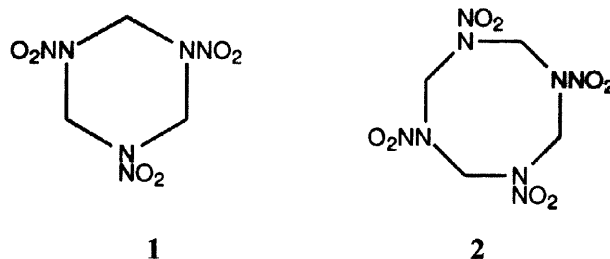
**Abstract.** Syntheses of new polyazapolycyclic caged polynitramines are described. Sequentially reacting 4,10-dibenzyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane (**5a**) with  $\text{NOBF}_4$  and  $\text{NO}_2\text{BF}_4$  in sulfolane solvent produces 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo-[5.5.0.0<sup>5,9</sup>.0<sup>3,11</sup>]dodecane, **6**). Syntheses of two new polyazapolycyclic caged trinitramines, 3,5,12-trinitro-3,5,12-triazawurtzitane (**7a**) and 2,4,10-trinitro-2,4,10-triaadamantane (**12a**), as well as their labile parent secondary amines, are discussed. A new caged polynitrosamine, 3,5,12-trinitroso-3,5,12-triazawurtzitane (**7d**), has been obtained by ring-cleavage nitrosation of the new hexamine-wurtzitane compound 3,5,7,9-tetraazahexacyclo-[9.3.1.1<sup>3,7</sup>.0<sup>2,9</sup>.0<sup>4,13</sup>.0<sup>5,10</sup>]-hexadecane (**10**). © 1998 Elsevier Science Ltd. All rights reserved.

### INTRODUCTION

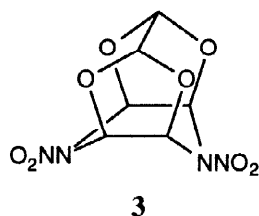
Polyazamonocyclic polynitramines 1,3,5-trinitro-1,3,5-hexahydrotriazine (RDX, **1**,  $d = 1.81 \text{ g/cm}^3$ )<sup>1</sup> and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX, **2**,  $\beta$ -form  $d = 1.90 \text{ g/cm}^3$ )<sup>2,3</sup> are stable, high-density, highly energetic materials. The detonation pressure of an energetic compound is proportional to its density squared;<sup>4</sup> high density compounds are also of value in volume-limited propellant applications.<sup>5</sup> The monocyclics **1** and **2** have a desirable low 1:1 ratio of carbon to nitramino, with the general formula  $(\text{CH}_2\text{NNO}_2)_n$ , which contributes to their high energy. Polycyclic caged molecules have significantly higher densities than their related monocyclics. For example, the observed densities at ambient temperatures of cubane ( $1.29 \text{ g/cm}^3$ )<sup>6</sup> and dodecahedrane ( $1.45 \text{ g/cm}^3$ )<sup>7</sup> are nearly twice those of cyclobutane ( $0.70 \text{ g/cm}^3 @ 0^\circ\text{C}$ ) and cyclopentane ( $0.74 \text{ g/cm}^3 @ 20^\circ\text{C}$ ). When many nitramino groups are placed within a polycyclic caged structure with a resulting general formula such as  $(\text{CHNNO}_2)_n$ , a high density, high-energy compound should result. Densities of several high-energy polyazapolycyclic caged polynitramines have been calculated; values of 2.0–2.2  $\text{g/cm}^3$  have been reported for compounds  $\text{C}_x\text{H}_y(\text{NNO}_2)_n$  having equal, or nearly equal values of  $x$ ,  $y$  and  $n$ .<sup>8–11</sup>

In this report the synthesis of the first example of a high density, high-energy polyazapolycyclic caged polynitramine is described—2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0<sup>5,9</sup>.0<sup>3,11</sup>]-dodecane, **6**, Scheme 1).<sup>12</sup> The procedure

† Present address: Biotechnology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.



involves reductive acetylation of the rather stable caged polyamine 2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazaisowurtzitane (**4**), which leads to 4,10-dibenzyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane (**5a**). Reaction of **5a**, sequentially, with  $\text{NOBF}_4$  and  $\text{NO}_2\text{BF}_4$  in sulfolane solvent produces **6** directly in 90% overall yield. The structure **6** incorporates an equal number of carbons and nitramino groups  $(\text{CHNNO}_2)_n$  ( $n = 6$ ); structures and densities of its four stable polymorphs have been established by X-ray crystallography.<sup>12-14</sup> A high density, less energetic diazaisowurtzitane dinitramine has been reported—4,10-dinitro-4,10-diaza-2,6,8,12-tetraoxaisowurtzitane (**3**,  $d = 1.99 \text{ g/cm}^3$ ); it was synthesized in high yield by nitration of a mixture of 1,4-diformyl-2,3,5,6-tetrahydropiperazine and glyoxal trimer with mixed nitric and sulfuric acids.<sup>15,16</sup>



Other new synthetic routes to polyazapolycyclic caged polynitramines have been examined. Syntheses of two new polyazapolycyclic caged trinitramines, 3,5,12-trinitro-3,5,12-triazawurtzitane (**7a**) and 2,4,10-trinitro-2,4,10-triazaadamantane (**12a**), as well as their very labile parent secondary amines, are discussed. 2,4,10-Trinitro-2,4,10-triazaadamantane (**12a**) is obtained by the cyclization reaction of *cis,cis*-1,3,5-tris(*N*-nitro-*N*-tri-*n*-butylstannyl)aminocyclo-hexane (**11i**) with  $\text{CHClF}_2$ . 1,3-Dinitrohexahydropyrimidine has been prepared by a new nitramine synthesis involving reaction of 1,3-bis(trimethylstannyl)hexahydropyrimidine with  $\text{NO}_2\text{BF}_4$ . This new process has also been applied in studies of reactions of 2,4,10-tris(trimethylstannyl)-2,4,10-triazaadamantane (**12e**) with  $\text{NO}_2\text{BF}_4$ . A new caged polynitrosamine, 3,5,12-trinitroso-3,5,12-triazawurtzitane (**7d**), has been obtained by ring-cleavage nitrosation of the new hexamine-wurtzitane compound 3,5,7,9-tetraazahexa-cyclo[9.3.1.1<sup>3,7</sup>.0<sup>2,9</sup>.0<sup>4,13</sup>.0<sup>5,10</sup>]hexadecane (**10**).

## RESULTS AND DISCUSSION

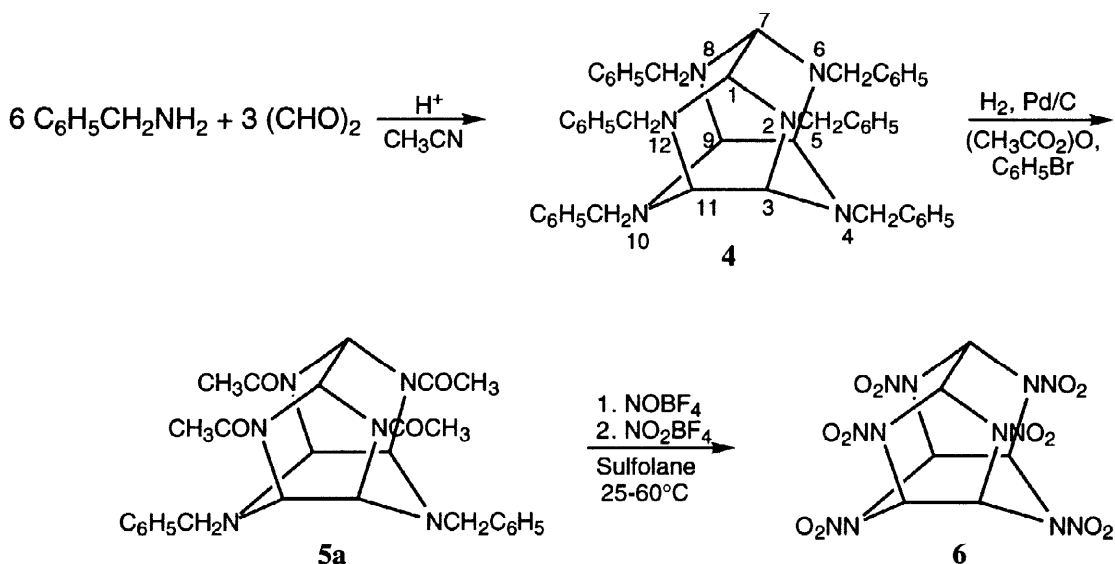
### 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane

The polyazapolycyclic caged polynitramine, 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW, CL-20, **6**) is obtained readily in three procedural steps with isolation of two intermediates (**4** and **5a**, Scheme 1).<sup>12</sup> The caged polyazapolycyclic intermediate 2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazaisowurtzitane **4** is prepared by condensation of stoichiometric quantities of benzylamine and glyoxal in aqueous acetonitrile solvent at 25°C in the presence of formic acid catalyst.<sup>17</sup> The quite pure crystalline product (80% yield; 72% yield recrystallized) separates from the reaction mixture and may be employed with or without recrystallization in the next step. In a recent report, employing similar reaction conditions, a second condensation product, a decabenzyl bi(2,4,6,8-tetraazabicyclo[3.3.0]octane),  $\text{C}_{80}\text{H}_{80}\text{N}_{10}$ , was isolated in ca.

1% yield, with 65% yield of recrystallized **4**.<sup>18</sup> In another recent publication which also reexamines the condensation of benzylamine with glyoxal, mineral acids were found to be favorable catalysts (65% yield of recrystallized **4** with HNO<sub>3</sub> catalyst).<sup>19</sup>

The second isolated intermediate, 4,10-dibenzyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane (**5a**) is prepared in 60–65% yield by reductive acetylation of **4** in acetic anhydride solvent with an acid catalyst (H<sub>2</sub>, Pd/C, 1–50 psi, 10–30°C, 2–24 h).<sup>12</sup> Mineral acid catalysts such as H<sub>2</sub>SO<sub>4</sub>, HCl or HBr (not HI) are preferred and may be added directly to the reaction mixture prior to hydrogenation. However, best results are obtained with HBr, especially when generated by dehydrohalogenation of selected organic bromo compounds (such as benzyl bromide or bromobenzene); slower generation of HBr and acetyl bromide are thus

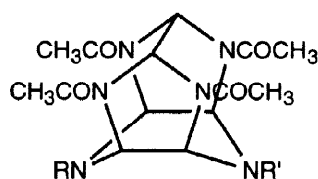
Scheme 1



allowed. The concentration of HBr is important; maximum yields of **5a** are obtained at a 1:8 molar ratio of the HBr source to **4**. Palladium hydroxide on carbon (Pearlman's catalyst) was found to be the preferred catalyst. The isolated crude **5a** is quite pure and may be employed for the next step without further purification. Recently, an interesting detailed study of the reductive acetylation of **4** with excess acetic anhydride (H<sub>2</sub>, palladium catalyst) under a wide variety of reaction conditions has been reported (51–58% yield of **5a**; acetic acid catalyst).<sup>20</sup> Hydrogenation of pure **5a** in acetic anhydride solvent containing 10–20 volume % acetic acid was found to produce 4,10-diethyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane (**5b**, R = R' = C<sub>2</sub>H<sub>5</sub>) in quantitative yield.<sup>20</sup> The intermediate 4-ethyl-10-benzyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane (**5c**, R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, R' = C<sub>2</sub>H<sub>5</sub>), was detected at shorter reaction times, but there was no evidence of formation of hexaacetylhexaazaisowurtzitane (**5d**, R = R' = COCH<sub>3</sub>).<sup>20</sup> In recent reports reductive acetylation of **4** in ethylbenzene solvent (H<sub>2</sub>, Pd/C), employing *N*-acetoxy succinimide and acetic anhydride, produced **5a** in 75% yield;<sup>21</sup> with palladium acetate and acetic acid, hydrogenation of **5a** produced 2,6,8,12-tetraacetylhexaazaisowurtzitane (**5e**, R = R' = H) in 73% yield.<sup>21a</sup> Acetylation of **5e** yields **5d**.<sup>21a</sup> Hydrogenation of **5a** in formic acid solvent (Pd catalyst) yields 4,10-diformyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane (**5f**, R = R' = CHO).<sup>22a</sup> Compound **5a** is only very slightly soluble in acetic anhydride and precipitates from the reaction mixture during hydrogenation; however, it is soluble, and stable, in acetic acid. Favored acid-catalyzed ring cleavage reactions occurring at cage-internal C–N bonds adjacent to the 4,10-dibenzyl-substituted positions in **4**, compared to those adjacent to the 2,6,8,12-substituted positions, are probably related to the acid-catalyzed reversal of the final steps in the formation of **4**. These final

steps in the proposed reaction mechanism leading to **4** involve formation of the 4,10-dibenzyl-4,10-diaza-substituted positions of the hexaazaisowurtzitane ring.<sup>17-19</sup>

The synthesis of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW, **6**) proceeds directly from the tetraacetyl precursor **5a**.<sup>12</sup> In a simple one-pot procedure **5a** is nitrosated and nitrated stepwise to yield HNIW (Scheme 1). The reaction is conducted in sulfolane solvent employing a suspension of **5a** in sulfolane containing a small amount of water. Nitrosation with NOBF<sub>4</sub> (3 mole-equivalents) (25–60°C, 4h) is followed by reaction with NO<sub>2</sub>BF<sub>4</sub> (12 mole-equivalents) (25–60°C, 4h); NOBF<sub>4</sub> separates from the reaction mixture and may be recovered by filtration. Quenching the filtrate with water leads to precipitation of crude **6**, which is purified by dissolving in ethyl acetate and filtering the solution through a silica gel column; addition of chloroform to the eluate precipitates very pure HNIW (**6**, 90% yield).



- 5a**, R = R' = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
**5b**, R = R' = C<sub>2</sub>H<sub>5</sub>  
**5c**, R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, R' = C<sub>2</sub>H<sub>5</sub>  
**5d**, R = R' = COCH<sub>3</sub>  
**5e**, R = R' = H  
**5f**, R = R' = CHO  
**5g**, R = R' = NO  
**5h**, R = R' = NO<sub>2</sub>

The synthesis of HNIW (**6**) from **5a** involves several intermediates, two of which are described in the present report. Removal of the benzyl groups in **5a** is achieved by nitrosative debenylation which oxidizes the benzyl groups forming benzaldehyde, and nitrosates the ring nitrogens to yield 4,10-dinitroso-2,4,6,8,10,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane (**5g**, R = R' = NO). In sulfolane solvent reaction with NOBF<sub>4</sub> produces **5g** in 55% yield; under comparable conditions in acetonitrile solvent the yield of **5g** is 10%. Reaction of **5a** with excess N<sub>2</sub>O<sub>4</sub><sup>23</sup> at 25°C produces **5g** in 92% yield. Without isolation of **5g**, after nitrosation of **5a** with NOBF<sub>4</sub> in acetonitrile solvent, its nitrolysis may be achieved by reaction with NO<sub>2</sub>BF<sub>4</sub> (45°C) leading to 4,10-dinitro-2,4,6,8,10,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane (**5h**, R = R' = NO<sub>2</sub>) in 59% overall yield from **5a**. The structures of **5a**, **5g** and **5h** have been established by X-ray crystallography.<sup>13</sup> In sulfolane solvent, nitration of **5h** with NO<sub>2</sub>BF<sub>4</sub> also produces HNIW (**6**) in 90% yield. Recently, some syntheses of HNIW have been reported (some without much detail),<sup>14,20-22,24</sup> including nitration of **5a**<sup>20,21</sup>, **5g**<sup>21</sup> and **5h**.<sup>21</sup> Nitrosation of **5e** (acetic acid, NaNO<sub>2</sub>) produced **5g** (95% yield), which on reaction with 100% HNO<sub>3</sub> gave **5h** in 95% yield.<sup>21a</sup> Treatment of **5h** with HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> at ambient temperature led to HNIW in 30% yield.<sup>21a</sup> Isolation of another intermediate, a monoacetylpentanitro-hexaazaisowurtzitane, has been reported.<sup>14c,e</sup> Hexakis-(trimethylsilylethylcarbonyl)-hexaazaisowurtzitane (**4**, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub> = (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>OC=O), prepared from **4** by reaction with (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>OCOCl, has been converted to HNIW.<sup>21c</sup>

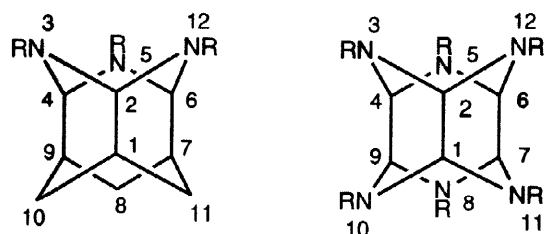
Several recent publications describe some chemical and physical properties of hexanitrohexaazaisowurtzitane (HNIW, **6**). The kinetics and mechanism of HNIW thermal decomposition have been subjects of various studies;<sup>24-30</sup> these include mass spectroscopy<sup>24,25</sup> and photochemically generated NO<sub>2</sub> studies employing EPR, including samples with <sup>15</sup>N-labeled nitro groups.<sup>26,29</sup> Hexanitrohexaazaisowurtzitane is thermally more stable neat than are RDX (**1**) and HMX (**2**).<sup>14a</sup> At atmospheric pressure heating HNIW produces a complex solid residue having an average molecular formula of C<sub>2</sub>H<sub>2</sub>N<sub>2</sub>O; the residue reveals C=O,

C=N and NH bands in its infrared spectrum.<sup>27</sup> Decomposition of neat HNIW evolves large amounts of N<sub>2</sub> and CO<sub>2</sub>.<sup>28</sup> A new technique of high-pressure thermal-shock decomposition of HNIW, with low-temperature matrix isolation which produces many isolated intermediate products, can assist in interpretation of the deflagration mechanism.<sup>30c</sup> The mechanism of HNIW thermal decomposition has also been studied in acetone solvent; results are compared with the behavior of other nitramines, including RDX and HMX; the observed thermal stability order in solution is: HMX > RDX > HNIW.<sup>28</sup>

Hexanitrohexaazaisowurtzitane exists in four stable polymorphic forms ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\epsilon$ ) under ambient conditions, the structures and densities of which have been established by X-ray crystallography (Table 1).<sup>13</sup> A labile  $\zeta$  form, existing only at high pressure, has been identified and described in phase diagram studies.<sup>30</sup> In the present work a disulfolane adduct of HNIW is decomposed by heating with water (95°C) to yield the crude hydrated  $\alpha$ -form. Recrystallization of HNIW from 70% HNO<sub>3</sub> leads to crystalline  $\alpha$ -hemihydrate (80–85% recovery). Crystals of the  $\alpha$ -polymorph contain centrosymmetric cavities; their frequency is such that if each contains one water, the crystal is a hemihydrate,  $d = 2.001 \text{ g/cm}^3$ ; if 50% of the cavities are filled a 0.25 hydrate is produced with density =  $1.981 \text{ g/cm}^3$ , as cited in Table 1; the anhydrous  $\alpha$ -form  $d = 1.961 \text{ g/cm}^3$ . The anhydrous  $\beta$ -form is obtained by recrystallization from benzene,  $d = 1.985 \text{ g/cm}^3$ . On heating the  $\beta$ -form between thin glass discs (examined under a microscope) a change to a third stable crystalline form ( $\gamma$ ) is observed to occur at ca. 185°C; the density of the  $\gamma$  form at 20°C =  $1.916 \text{ g/cm}^3$ . Heating the  $\gamma$ -form above 185°C leads to a second change in crystalline form (described initially in the present work as  $\delta$ ), which occurs at 230°C, just below the decomposition temperature (250–260°C); subsequently obtained FTIR data reveal that this stable " $\delta$ " material is most likely a different crystalline form of the  $\gamma$  polymorph, not the crystalline form of a different polymorph. The  $\epsilon$ -form has the highest density ( $d = 2.044 \text{ g/cm}^3$ ); densities increase in the order:  $\gamma < \alpha < \beta < \epsilon$ . The FTIR, <sup>1</sup>H and <sup>13</sup>C NMR, CIMS and UV spectra of all four stable polymorphs have been published,<sup>24,26b,30-32</sup> as well as the FTIR spectrum of the labile  $\zeta$  form.<sup>30</sup> The thermal stability order is  $\epsilon > \gamma > \alpha\text{-hydrate} > \beta$  based on DSC, DTA and TGA analyses,<sup>31</sup> or  $\alpha\text{-hydrate} > \epsilon > \alpha\text{-anhydrous} > \beta > \gamma$  based on phase diagram temperature and pressure studies.<sup>30a,b</sup> The solubility of HNIW in various solvents has been determined.<sup>31d</sup> Hexanitrohexaazaisowurtzitane forms complexes with certain solvents;<sup>14d</sup> a disulfolane complex is described in the present work (see experimental). Density, heat of formation, specific impulse, sensitivity and other properties of HNIW have been measured and calculated.<sup>8-14,33-35</sup>

### 3,5,12-Trinitro-3,5,12-triazawurtzitane

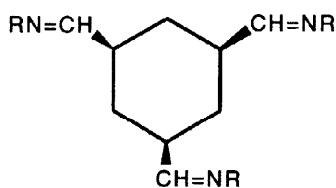
Following is a discussion of our studies of synthetic routes to 3,5,12-trinitro-3,5,12-triazawurtzitane (**7a**). 3,5,12-Tribenzyl-3,5,12-triazawurtzitane (**7b**), a precursor to **7a**, is prepared by condensation of benzylamine with *cis,cis*-1,3,5-triformylcyclohexane.<sup>36</sup> The benzyl-substituted **7b** is much more stable than other such amine-derived N-substituted wurtzitanes. Tri- and hexa-substituted 1,3,5-triazacyclohexanes, including very stable 1,3,5-tribenzyl-1,3,5-triazacyclohexane,<sup>37</sup> have been prepared by condensation of formaldehyde or other aldehydes with ammonia or amines.<sup>36-38</sup> It was thought at the initiation of the present work that if condensation of benzylamine with glyoxal could lead to 1,3,5-tribenzyl-2,4,6-triformyl-1,3,5-triazacyclohexane, as an intermediate it might react with additional benzylamine to produce 3,5,8,10,11,12-hexabenzyl-3,5,8,10,11,12-hexaazawurtzitane **8b**, a potential precursor to the high energy hexanitrohexaazawurtzitane **8a**. Instead, the condensation of benzylamine with glyoxal led to hexabenzylhexaazaisowurtzitane **4**.<sup>17</sup> The physical properties of **8a** (including density, heat of formation, detonation velocity and detonation pressure) have been calculated and found to be similar to those of HNIW (**6**).<sup>8-11</sup>



7a, R = NO<sub>2</sub>  
 7b, R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
 7c, R = H  
 7d, R = NO  
 7e, R = COCH<sub>3</sub>

8a, R = NO<sub>2</sub>  
 8b, R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>

3,5,12-Trinitro-3,5,12-triazawurtzitane (**7a**) is a polyazapolycyclic caged trinitramine of interest in our studies. 3,5,12-Tribenzyl-3,5,12-triazawurtzitane (**7b**) is much less stable in protic and aprotic solvents (especially in acidic media) than is hexabenzylhexaazaisowurtzitane (**4**).<sup>17,36</sup> In solution in various solvents it exists in equilibrium with its triimine precursor **9a** at ambient temperature, thus making it more difficult to convert into desired 3,5,12-substituted triazawurtzitane products.



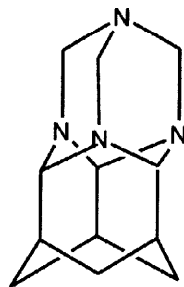
9a, R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
 9b, R = H

The reaction of *cis,cis*-1,3,5-triformylcyclohexane with concentrated NH<sub>4</sub>OH in aqueous NaOH (pH 13.5) produces 3,5,12-triazawurtzitane **7c**.<sup>36</sup> Owing to its instability in neutral or acidic media, involving equilibration to readily polymerizable triimine **9b**, pure triamine **7c** could not be isolated by extraction from reaction product mixtures. Reaction of extracts possibly containing **7c**, when treated with nitrous acid, failed to yield 3,5,12-trinitroso-3,5,12-triazawurtzitane, **7d**.

Reaction of caged triamine **7c**, 5 minutes after its preparation in concentrated NH<sub>4</sub>OH/aqueous NaOH *in situ* at 0–5°C, with an aqueous solution of formaldehyde (20 mole-equivalents) allowed trapping of **7c** as the caged hexamine-wurtzitane structure 3,5,7,9-tetraazaahexacyclo-[9.3.1.1<sup>3,7</sup>.0<sup>2,9</sup>.0<sup>4,13</sup>.0<sup>5,10</sup>]hexadecane (**10**).<sup>39</sup> Hexamine, also formed in the reaction, was removed from the reaction mixture by sublimation and chromatography. A crude amorphous sample of **10** was isolated (19% yield) having <sup>1</sup>H NMR and mass spectra in agreement with its assigned structure.

Nitrosation of **10** with nitrous acid (NaNO<sub>2</sub> and excess acetic acid in water at 0°C) produced a stable amorphous product, mp 135–140°C, believed to be a crude sample of 3,5,12-trinitroso-3,5,12-triazawurtzitane **7d** (ca. 4% yield) containing traces of 1,3,5-trinitroso-1,3,5-triazacyclohexane [R-salt (**1**, NO<sub>2</sub> = NO), mp 105°C] derived from traces of hexamine. The <sup>1</sup>H NMR spectrum of **7d** ((CD<sub>3</sub>)<sub>2</sub>SO) reveals the CH<sub>2</sub> and CH signals of the protons at C-1 and C-7 through C-11, in addition to four doublets at δ 5.22, 5.86, 5.90 and 6.55 (J = 10 Hz) of relative intensities 1:1:1:1 expected for the C-2,4,6 protons of **7d**. Traces of R-salt are present in the crude product as seen by the presence of weak signals of its characteristic <sup>1</sup>H NMR spectrum of four singlets of equal intensities.<sup>38c</sup> In agreement with the structure assignment of **7d**, its mass spectrum reveals an M+1 peak at 253 and peaks at 208 (M - N<sub>2</sub>O) and 164 (M - 2 N<sub>2</sub>O). In the infrared spectrum of crude **7d** (KBr)

nitrosamine bands appear at 1430 and 1340  $\text{cm}^{-1}$ . Attempts at direct nitrosation of tribenzyl derivative **7b** with nitrous acid or, separately,  $\text{NOBF}_4$  in pyridine failed to produce **7d**.



**10**

A route to 3,5,12-trinitro-3,5,12-triazawurtzitane **7a**, which also leads to trinitroso **7d**, was examined. Reaction of the tribenzyl derivative **7b** with 2-nitropropyl hydroperoxide, in pyridine solvent,<sup>40</sup> gave an amorphous product which revealed the absence of benzyl groups; its mass spectrum has strong parent mass signals at 300, 284, 268 and 252 corresponding to trinitro **7a**, 3,5-dinitro-12-nitroso-3,5,12-triazawurtzitane, 5,12-dinitroso-3-nitro-3,5,12-triazawurtzitane and trinitroso **7d**, respectively, as well as characteristic **7d** cleavage peaks of masses 208 and 164. The amorphous product, as well as a partially crystalline product from a parallel run (mp 135–145°C), decomposed when subjected to attempted purification by silica gel column chromatography.

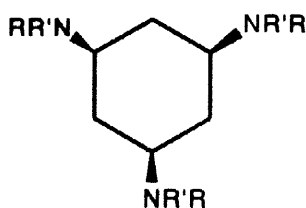
Attempted direct nitration of hexacyclic **10** with 100% nitric acid failed to produce 3,5,12-trinitro-3,5,12-triazawurtzitane **7a**. Attempts to prepare **7a** by reaction of *cis,cis*-1,3,5-triformylcyclohexane with nitramide were unsuccessful. 3,5,12-Triacetyl-3,5,12-triazawurtzitane (**7e**, previously reported<sup>36</sup>) has been prepared from **7c**<sup>36</sup> and **10**, but could not be prepared by reductive acetylation of the tribenzyl derivative **7b**. Similarly, in another study, attempted reductive acetylation of 2,4,6,8-tetrabenzyl-2,4,6,8-tetraazabicyclo[3.3.0]octane failed to yield the corresponding tetraacetyl derivative; ring opening occurred.<sup>41</sup>

#### 2,4,10-Trinitro-2,4,10-triazaadamantane

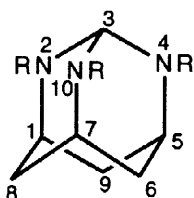
Following is a discussion of our studies of synthetic routes to 2,4,10-trinitro-2,4,10-triazaadamantane (**12a**). 2,4,10-Tribenzyl-2,4,10-triazaadamantane (**12b**), a known compound,<sup>42</sup> has been prepared in 51% yield by an improved procedure involving cyclization of *cis,cis*-1,3,5-tribenzylaminocyclohexane **11b** in refluxing dimethylformamide dimethyl acetal; its structure has been confirmed by X-ray crystallography.<sup>13</sup>

Unsubstituted triamine 2,4,10-triazaadamantane **12c** has been isolated and found to be a very reactive, hygroscopic, unstable substance resembling 1,3,5-hexahydrotriazines lacking substitution on nitrogen.<sup>38</sup> It has been prepared by catalytic hydrogenation of 2,4,10-tribenzyl-2,4,10-triazaadamantane **12b** ( $\text{H}_2$ , Pd/C,  $\text{C}_2\text{H}_5\text{OH}$ ) in 88% yield.<sup>43</sup> The anhydrous crystalline product, mp 115°C, is extremely hygroscopic. In air (45% humidity) it becomes liquid within a few minutes; after about 90 minutes a crystalline hydrate, mp 120°C, forms. After standing in air for an additional 4 hours an opaque solid is formed, mp 190–200°C (decomposition with gas evolution); the  $^1\text{H}$  NMR spectrum of this material ( $\delta = 8.3$  in  $\text{D}_2\text{O}$ ) is different from that of freshly prepared **12c** (apical CH at C-3 signal,  $\delta = 7.6$  in  $\text{D}_2\text{O}$ ). This result suggests reaction of **12c**, a strongly basic amine, with  $\text{CO}_2$  of the air to form a bicarbonate salt of ring-opened amidine **13**. Acidification of a freshly prepared solution of **12c** in  $\text{D}_2\text{O}$  with  $\text{D}_2\text{SO}_4$  causes immediate disappearance of the  $\delta 7.6$  peak and its conversion to the  $\delta 8.3$  signal (unchanged intensity); on making the solution basic again ( $\text{K}_2\text{CO}_3$ , pH 9) the  $\delta 8.3$  signal remains unchanged. Bicarbonate, acetate and fluoroborate salts of **13** have been prepared separately by reaction of **12c**, suspended in hexane, with  $\text{CO}_2$ , acetic acid or  $\text{BF}_3$ ; these salts all reveal the  $\delta 8.3$  signal in  $\text{D}_2\text{O}$ . (Both formamidinium acetate and 1,4,5,6-tetrahydropyrimidine hydrochloride show a vinyl CH signal at

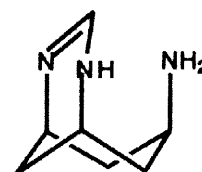
$\delta$  8.0 in D<sub>2</sub>O.) The formation of a **13** cation from **12c** also occurs in D<sub>2</sub>O in air in the presence of triethylamine, indicating **12c** to be a strong base.



- 11a**, R = NO<sub>2</sub>, R' = H  
**11b**, R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, R' = H  
**11c**, R = R' = H  
**11d**, R = SO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, R' = H  
**11e**, R = CO<sub>2</sub>CH<sub>3</sub>, R' = H  
**11f**, R = NO<sub>2</sub>, R' = CO<sub>2</sub>CH<sub>3</sub>  
**11g**, R = NO<sub>2</sub>, R' = Sn(CH<sub>3</sub>)<sub>3</sub>  
**11h**, R = NO<sub>2</sub>, R' = Sn(*n*-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>  
**11i**, R = NO<sub>2</sub>, R' = Sn(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>



- 12a**, R = NO<sub>2</sub>  
**12b**, R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
**12c**, R = H  
**12d**, R = SO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
**12e**, R = Sn(CH<sub>3</sub>)<sub>3</sub>  
**12f**, R = NO

**13**

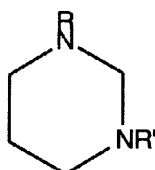
Attempts to directly nitrosate or nitrate 2,4,10-triazaadamantane **12c** with NOBF<sub>4</sub> or NO<sub>2</sub>BF<sub>4</sub> in acetonitrile solvent containing triethylamine were unsuccessful; ring opening reactions leading to products derived from **13** occurred. We have found this procedure (NO<sub>2</sub>BF<sub>4</sub>, acetonitrile) to produce a mixture of 1,3-dinitro- and 1-nitro-3-nitrosohexahydropyrimidine from hexahydropyrimidine. This procedure has also been successfully applied to nitration of 2,4,6-trimethyl-1,3,5-hexahydrotriazine to form 2,4,6-trimethyl-1,3,5-trinitro-1,3,5-hexahydrotriazine.<sup>44</sup> Reaction of **12c** with NO<sub>2</sub> in aqueous NaOH<sup>45,46</sup> produced an oily, water-insoluble product believed to contain traces of 2,4,10-trinitro-2,4,10-triazaadamantane **12a** and nitroso-substituted derivatives of **12c**, based on NMR evidence; no pure trinitro **12a** nor trinitroso **12f** could be isolated (<sup>1</sup>H NMR revealed absence of a  $\delta$  8.3 signal, indicating no ring opening). On the other hand, reaction of **12c** with NO under similar reaction conditions led primarily to ring-opened products.

Reaction of 2,4,10-triazaadamantane (**12c**) with benzenesulfonyl chloride in aqueous NaOH gave 2,4,10-tris(benzenesulfonyl)-2,4,10-triazaadamantane (**12d**, mp 288–290°C). This product has been reported to form by heating *cis,cis*-1,3,5-tris(benzenesulfonamido)cyclohexane (**11d**, obtained from *cis,cis*-1,3,5-triaminocyclohexane **11c**), with triethylorthoformate at 270°C; however, the reported melting point, 165–166°C,<sup>47</sup> is significantly lower than the value we have observed. We have obtained three identical samples of **12d** by three different methods: (1) directly from the triamine **12c** by reaction in aqueous NaOH with benzenesulfonyl chloride, (2) from **11d** by the published procedure,<sup>47</sup> and (3) by a similar procedure which produced **12d** in 26% yield. All three procedures were found to form **12d** having the higher mp 288–290°C; the assigned structure **12d** has been established by X-ray crystallography data obtained using our samples.<sup>13</sup> Attempts to prepare 2,4,10-trinitro-2,4,10-triazaadamantane **12a** by nitration of **12d** with NO<sub>2</sub>BF<sub>4</sub> in acetonitrile were unsuccessful; only nitrophenyl-type products were isolated.

2,4,10-Trinitro-2,4,10-triazaadamantane (**12a**) has been prepared from *cis,cis*-1,3,5-tris(nitramino)cyclohexane (**11a**), which was obtained in three steps from *cis,cis*-1,3,5-tris(carbomethoxyamino)cyclohexane (**11e**). Nitration of **11e** (HNO<sub>3</sub>, HOAc) to produce *cis,cis*-1,3,5-tris(carbomethoxynitramino)cyclohexane (**11f**), followed sequentially by treatment with NH<sub>4</sub>OH and HCl, produced **11a** in 65% overall yield from **11e**. Reaction of trinitramine **11a** with bis-(tri-*n*-butyltin) oxide<sup>48</sup> in refluxing benzene produced *cis,cis*-1,3,5-tris(*N*-nitro-*N*-tri-*n*-butylstannyl)aminocyclohexane (**11i**). Also prepared were the tri-*n*-propylstannylamino- and



trimethylstannylamino-derivatives **11h** and **11g**, respectively. Reactions of **11g**, **11h** and **11i** with various haloforms,  $\text{HCX}_3$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) and  $\text{CHClF}_2$ <sup>49</sup> were examined in benzene solvent heated in a sealed container at 150°C for 15 hours; reactions of these compounds with triethylorthoformate at 270°C were also studied. Only the tri-*n*-butyl tin compound **11i** was found to be sufficiently soluble in solvents employed to produce a significant formation of **12a**; less soluble reactants **11g** and **11h** were usually recovered mostly unchanged and gave lower yields of **12a**. With **11i** it was also recovered in most reactions with the haloforms, except with  $\text{CHClF}_2$ <sup>49</sup> which gave a small amount of partially crystalline 2,4,10-trinitro-2,4,10-triazaadamantane **12a**, mp 155-160°C, revealing a parent mass spectrum peak at 274. The <sup>1</sup>H NMR spectrum ( $\text{CDCl}_3$ ) of **12a** shows a singlet at  $\delta$  6.03, assigned to the apical C-3 hydrogen, and signals at  $\delta$  4.5 (CH) and  $\delta$  1-3 ( $\text{CH}_2$ ). Singlets observed in <sup>1</sup>H NMR spectra of RDX (**1**) and HMX (**2**) appear at  $\delta$  6.09 and 6.04, respectively [ $(\text{CD}_3)_2\text{SO}$  solvent].<sup>50</sup>



- 14a**,  $\text{R} = \text{R}' = \text{NO}_2$   
**14b**,  $\text{R} = \text{R}' = \text{H}$   
**14c**,  $\text{R} = \text{R}' = \text{Sn}(\text{CH}_3)_3$   
**14d**,  $\text{R} = \text{NO}_2, \text{R}' = \text{NO}$   
**14e**,  $\text{R} = \text{R}' = \text{NO}$

A new nitramine synthesis has been developed as another route to 2,4,10-trinitro-2,4,10-triazaadamantane **12a**. Reaction of 2,4,10-triazaadamantane **12c** with dimethylaminotrimethyl tin<sup>51</sup> yields 2,4,10-tris(trimethylstannyl)-2,4,10-triazaadamantane **12e**. Reaction of **12e** with excess  $\text{NO}_2\text{BF}_4$  in acetonitrile solvent (25-50°C) produced an oil from which a small amount of a crude crystalline product, mp 65-85°C was isolated; its <sup>1</sup>H NMR ( $(\text{CD}_3)_2\text{SO}$ ) signals at  $\delta$  7.5 (singlet) and at 4.8-5.0 and 0.5-2.5, as well as its melting point and mass spectrum peaks at 213 and 155, indicate a product different from **12a** and trinitroso **12f**. A possible structure is 2-nitro-4-nitroso-2,4,10-triazaadamantane (mol wt 213), obtained owing to incomplete reaction of **12e**. The apical C-3 proton signal at  $\delta$  7.5 is in agreement with hydrogen and/or nitroso substitution at adjacent nitrogens<sup>52-54</sup> (the apical C-3 <sup>1</sup>H NMR signal of triamine **12c** is at  $\delta$  7.6 in  $\text{D}_2\text{O}$ ). The <sup>1</sup>H NMR spectra of N-nitrosamines reveal a lower field chemical shift for certain conformers than their N-nitro-substituted analogues.<sup>52-54</sup> For example, 1,3,5-trinitroso-1,3,5-triazacyclohexane (R-salt) reveals an anti conformation CH signal at  $\delta$  7.03, with other CH signals at 6.40, 6.38 and 5.77 in  $(\text{CD}_3)_2\text{CO}$ .<sup>38c</sup> Present results suggest that **12a** may form only as a minor product from **12e** (under the reaction conditions described, in acetonitrile solvent) but not as a major product, as implied in an earlier review report based on preliminary evidence.<sup>9</sup>

The new nitramine synthesis has been applied successfully to the preparation of known 1,3-dinitrohexahydropyrimidine **14a**. Reaction of hexahydropyrimidine (**14b**) with dimethylaminotrimethyltin produces 1,3-bis(trimethylstannyl)hexahydropyrimidine **14c** in quantitative yield. Reaction of **14c** with  $\text{NO}_2\text{BF}_4$  in acetonitrile solvent at 50°C, under reaction conditions very similar to those applied to synthesis of **12a** from **12e**, produced 1,3-dinitrohexahydropyrimidine **14a** in 31% yield. Reaction of **14c** with  $\text{NO}_2\text{BF}_4$  was examined under a variety of reaction conditions, including reaction in sulfolane solvent. At lower temperatures (0-25°C, acetonitrile solvent), a mixture of products is produced, including **14a**, 1-nitro-3-nitrosohexahydropyrimidine (**14d**) and 1,3-dinitrosohexahydropyrimidine (**14e**). The observed physical properties of our samples of **14a**, **14d**, and **14e** are in agreement with the reported data for these known compounds.<sup>50,53-57</sup>

## CONCLUSIONS

Three synthetic approaches to polyazapolycyclic caged polynitramines, and polynitrosamines, have been examined in the present work. Synthesis may proceed from a preformed polyazapolycyclic caged structure which precisely incorporates the desired final heterocyclic ring, as in the preparation of HNIW (**6**) from hexabenzylhexaazaisowurtzitane (**4**, Scheme 1), and the trinitrotriazawurtzitane **7a** (and trinitroso **7d**) from tribenzyltriazawurtzitane **7b**. A precursor polyaza caged structure may be different from the desired product, but include the final structure within the cage, as in conversion of the tetraazaahexacyclic **10** into trinitroso **7d**. This process is employed in the conversion of hexamine into RDX (**1**) and HMX (**2**). A third process involves cyclization of a precursor polynitramine to produce the desired final cage, as in the conversion of the trisnitraminocyclohexane **11i** into the trinitrotriazadamantane **12a**. The conversions of  $\alpha,\omega$ -dinitraminoalkanes into cyclic dinitramines by reaction with formaldehyde are known examples.<sup>57,58</sup>

The thermal and chemical stabilities of many cyclic polynitramines are usually significantly greater than those of most of their amine precursors, especially secondary amines. Thus, synthetic routes to energetic polynitramines from structurally related unstable amines may fail in the initial steps of synthesis. Although certain polynitramines may actually not be thermally and/or chemically very stable, one must not prematurely attribute synthesis failure to a presumed instability of the target polynitramine, nor its intermediate precursors. The amine precursor stability, of course, can vary greatly. The polyazapolycyclic caged polynitramine HNIW (**6**) is a thermally stable, high-energy compound, as are RDX (**1**) and HMX (**2**). However, the tertiary amine precursor to HNIW, hexabenzylhexaazaisowurtzitane (**4**), is much more sensitive to decomposition in strongly acidic media than is HNIW.<sup>17,19,41</sup> Some polyazapolycyclic polynitramines and their parent amines may both be quite stable, as are 1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin and the parent secondary amine, 1,4,5,8-tetraazadecalin.<sup>54,59-61</sup> The less energetic caged trinitramines **7a** and **12a** appear to be thermally stable, although more reactive than HNIW, but their parent secondary amines **7c** and **12c** are remarkably chemically reactive, unstable materials. The secondary polyamines 2,4,6,8,10,12-hexaazaisowurtzitane (**6**, NO<sub>2</sub> = H) and 1,3,5,7-tetraazacyclooctane (**2**, NO<sub>2</sub> = H, parent of HMX<sup>62</sup>) are believed to be very unstable; they are unknown as isolated compounds. 1,3,5-Triazacyclohexane (**1**, NO<sub>2</sub> = H, parent of RDX) is a relatively unstable material which has not been isolated in an absolutely pure state; on storage at ambient temperature it transforms into hexamine.<sup>38c</sup> Development of suitable synthetic methods which ultimately replace all of the amine hydrogens of selected hypothetical polyazapolycyclic caged secondary polyamines (especially those having a low, near 1:1 carbon to amino ratio) with nitro groups should produce some new thermally stable, high-energy polyazapolycyclic caged polynitramines. Advanced theoretical calculations should greatly assist in predictions of physical and chemical properties of target compounds.<sup>63</sup> A relevant example is a recent report which examines calculations of bond-dissociation energies of RDX conformations.<sup>64</sup>

## EXPERIMENTAL

**General Methods.** Melting points were determined microscopically on a Kofler hot stage and are uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on an IBM NR-80, a Varian EM360 or XL-100, or a Nicolet NT200 spectrometer with a pulsed Fourier transform system; spectra were recorded at ambient temperature (near 30°C) unless otherwise stated and are referenced to tetramethylsilane. Infrared spectra (IR) were determined on a Nicolet 605X or Perkin-Elmer 137 or 1330 instrument, and mass spectra on a Hewlett Packard Model 5985 GC/MS system. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. MgSO<sub>4</sub> was used as a drying agent for extracted solutions, unless otherwise stated.

**CAUTION.** Polynitramines are powerful explosives and should be handled with care. Employ all standard energetic materials safety procedures in experimental operations involving such substances.

**4,10-Dibenzyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane (5a).** A mixture of recrystallized 2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazaisowurtzitane (**4**<sup>17</sup>, mp 155–157°C, 150 g, 0.212 mol), acetic anhydride (500 mL, 5.3 mol), Pearlman's palladium hydroxide on charcoal catalyst (37.5 g containing 20% palladium on a dry weight basis) and bromobenzene (4.2 g, 26.5 mmol) was shaken in a 2.5-liter glass bottle in a Parr apparatus (50 psi, 10–30°C, 18 h). After cooling to 25°C the catalyst, mixed with product, was removed by filtration and extracted with two or three 2-liter portions of boiling chloroform. Concentration of the extract yielded crude **5a**, which was triturated with acetonitrile and filtered to yield purified **5a**. The acetic anhydride filtrate was concentrated under reduced pressure at 30–70°C to remove volatiles; the residue was triturated with acetonitrile to yield an additional amount of **5a**; total yield 69.0 g (63%), mp 315–325°C; yields in parallel runs were 60–65%. Recrystallization from acetonitrile gave small prisms, mp 322–323°C; lit<sup>20</sup> mp 319–321.5°C; <sup>1</sup>H NMR (CD<sub>3</sub>)<sub>2</sub>SO δ 7.38, 7.31 (m, 10H, C<sub>6</sub>H<sub>5</sub>), 6.50 (broad s, 2H, CH), 5.43 (broad s, 4H, CH), 4.07 (s, 4H, CH<sub>2</sub>), 2.03 (broad m, 12H, CH<sub>3</sub>); mass spectra (CI, CH<sub>4</sub>), m/z 545 (M + 29, 18%), 518 (MH<sub>2</sub><sup>+</sup>, 32%), 517 (MH<sup>+</sup>, 100%), 476 (5), 455 (11), 363 (10), 111 (21). Anal. Calcd. for C<sub>28</sub>H<sub>32</sub>N<sub>6</sub>O<sub>4</sub>: C, 65.10; H, 6.24; N, 16.27. Found: C, 65.18; H, 6.50; N, 16.03. The structure of **5a** has been established by X-ray crystallography.<sup>13</sup>

**2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW, 6).** To a mixture of pure 4,10-dibenzyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane **5a** (15.49 g, 0.03 mol), water (1.08 g, 0.06 mol) and sulfolane (300 mL) NOBF<sub>4</sub> (14.02 g, 0.12 mol) was added during 30 minutes (< 25°C). The mixture, with a Drierite tube attached, was stirred mechanically (1 h at 25°C, then at 55–60°C, 1 h). The clear yellow-orange solution was then cooled to 25°C; NO<sub>2</sub>BF<sub>4</sub> (47.8 g, 0.36 mole) was added rapidly (< 25°C). The mixture was stirred at 25°C for 2 h and at 55–60°C for 2 h to produce a precipitate of NOBF<sub>4</sub>, suspended in a yellow solution. The NOBF<sub>4</sub> may be removed by filtration, or the mixture may be cooled to below 10°C and water (4.5 L) slowly added (< 25°C); during addition of water the mixture changed color to green, then yellow, and brown fumes evolved. The temperature was maintained at 25°C with continuous stirring for 3–18 h, during which time a white precipitate was produced. (In an alternate work-up procedure the precipitated NOBF<sub>4</sub> was recovered by filtration prior to quenching the sulfolane solution filtrate with water. Even more NOBF<sub>4</sub> may be recovered by passing NO<sub>2</sub> into the sulfolane solution prior to water treatment.) The mixture was filtered and the precipitated solid washed several times with water to yield 12.8 g of hydrated (< 1% H<sub>2</sub>O) amorphous crude **6**; <sup>1</sup>H NMR data indicate greater than 99% purity of a dried sample of this crude material (95–96% yield). The crude product was dissolved in ethyl acetate (40 mL) and filtered through a short silica gel column and washed with ethyl acetate to yield a clear, pale yellow solution. The solution was poured into chloroform (500 mL) to precipitate 11.9 g (90.5% yield) of the β-form of crystalline **6**; d = 1.98 g/cm<sup>3</sup> by X-ray crystallography.<sup>13</sup> Recrystallization from benzene also produced the β-form of **6** as needle-shaped prisms; mp 260°C, with decomposition without appearance of a liquid phase; d = 1.98 g/cm<sup>3</sup>;<sup>13</sup> crystalline form changes occur while heating between glass discs, observed under a microscope, at 185°C and 230°C, ascribed to γ- and δ-forms of **6**, respectively (see discussion); <sup>1</sup>H NMR, (CD<sub>3</sub>)<sub>2</sub>CO δ 8.33 (s, 4H, CH), 8.18 (s, 2H, CH); <sup>13</sup>C NMR, (CD<sub>3</sub>)<sub>2</sub>CO δ 75.29 (2C), 72.13 (4C); mass spectrum (CI, CH<sub>4</sub>) m/z 467 (M + 29, 24%), 439 (M + 1, 30%), 347 (26), 301 (28), 255 (14), 209 (18). Anal. Calcd. for C<sub>6</sub>H<sub>6</sub>N<sub>12</sub>O<sub>12</sub>: C, 16.45; H, 1.38; N, 38.36. Found: C, 16.49; H, 1.35; N, 38.18. The structures of the polymorphs of **6** have been established by X-ray crystallography (see discussion).<sup>13</sup> 4,10-Dinitro-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane (**5h**; see preparation described below) as reactant in the above procedure instead of **5a** (omitting the NOBF<sub>4</sub> treatment) also produces HNIW (**6**) in 90% yield).

Occasionally the crude HNIW (**6**) was isolated (after water quenching) as a disulfolane adduct (very pale yellow crystals, mp 92–100°C). Anal. Calcd for C<sub>6</sub>H<sub>6</sub>N<sub>12</sub>O<sub>12</sub>·2C<sub>4</sub>H<sub>8</sub>SO<sub>2</sub>: C, 24.78; H, 3.27; N, 24.77; S, 9.45. Found: C, 24.88; H, 3.26; N, 24.51; S, 9.35. The disulfolane adduct was decomposed by heating and

stirring with water (15 mL/g) at 95°C for 10 minutes, then cooling to 0°C. After standing for 1–6 h, the mixture was filtered and the product washed with cold water to yield amorphous, crude hydrated **6** (< 1% H<sub>2</sub>O). Recrystallization from 70% HNO<sub>3</sub> produced chunky, rhombic crystals of a hemihydrate of the  $\alpha$ -polymorph of **6** (80–85% recovery), mp 260°C (decomposition); its structure has been established by X-ray crystallography (see discussion).<sup>13</sup> Anal. Calcd. for C<sub>6</sub>H<sub>6</sub>N<sub>12</sub>O<sub>12</sub>·0.5 H<sub>2</sub>O: C, 16.12; H, 1.58; N, 37.58. Found: C, 16.10; H, 1.46; N, 37.31.

*4,10-Dinitroso-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane (5g). Procedure A.* Nitrosonium tetrafluoroborate (2.92 g, 0.025 mol) was added to a suspension of 4,10-dibenzyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane (**5a**, 5.16 g, 0.01 mol) in sulfolane (100 mL) and water (0.36 g, 0.02 mol). The mixture was stirred at 25°C for 2.6 h to produce a pale yellow solution, which was heated at 55°C for 1 h. After cooling to 25°C, the solution was diluted with water (1.5 L). The clear pale-yellow solution was extracted with methylene chloride (5 x 150 mL). The combined extracts were dried and concentrated under reduced pressure to remove some volatiles and leave a yellow oil (109.3 g) having a benzaldehyde odor. The oil was chromatographed on silica gel by elution, first with benzene to remove sulfolane and benzaldehyde and other products, and then with ethyl acetate to yield a solution of crude **5g** which was triturated with water to yield a solid which was removed by filtration and washed with water to yield 2.18 g (55%) of crystalline **5g**, mp 290–295°C, dec.; <sup>1</sup>H NMR (CD<sub>3</sub>)<sub>2</sub>SO  $\delta$  7.70, 7.30 (apparent ABq, J = 16 Hz, 4H, CH), 6.83 (broad s, 2H, CH), 1.85, 2.08 (singlets, 12H total, CH<sub>3</sub>); mass spectrum (CI, CH<sub>4</sub>) m/z 395 (MH<sup>+</sup>, 41), 366 (23), 365 (13), 335 (19), 208 (33), 207 (100), 165 (16). Anal. Calcd. for C<sub>14</sub>H<sub>18</sub>N<sub>8</sub>O<sub>6</sub>: mol wt 394.35, C, 42.64; H, 4.60; N, 28.41. Found: C, 42.56; H, 4.72; N, 28.00. The structure of **5g** has been established by X-ray crystallography.<sup>13</sup>

*Procedure B.* In a parallel run employing Procedure A, but with dry acetonitrile as solvent, a 10% yield of **5g** was obtained, mp 280–288°C, having identical <sup>1</sup>H NMR and mass spectra to the sample prepared by procedure A. Concentration of the filtrate remaining from the isolation of **5g** produced an oil having a strong benzaldehyde odor; benzaldehyde and 4-nitrobenzaldehyde were identified as products in the oil by conversion into their 2,4-dinitrophenylhydrazones, which were isolated and found to be identical with authentic samples.

*Procedure C.*<sup>23</sup> 4,10-Dibenzyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-tetraazaisowurtzitane (**5a**, 10.0 g, 0.0194 mol) was dissolved by slow addition to a mixture of N<sub>2</sub>O<sub>4</sub> (50 mL, 0.787 mol) and water (1.0 mL, 0.055 mol) with rapid stirring, keeping the solution cooled to 5°C in an ice/water bath. After allowing to slowly warm to 25°C, followed by storage at 25°C for 16 h, a stream of nitrogen was passed into the solution (maintained at 35°C) to remove excess N<sub>2</sub>O<sub>4</sub>. Ethanol (75 mL) was added to the viscous, green residue and the mixture heated at 75°C (water bath). After cooling to 0°C, the pale yellow product which precipitated was removed by filtration and washed with cold ethanol to yield 7.02 g (92%) of crystalline **5g**, mp 286–288°C; <sup>1</sup>H NMR and mass spectra were identical with the sample prepared by procedure A. The filtrate remaining after removal of **5g** was assayed by thin layer chromatography; benzaldehyde and benzoic acid were identified as major products.

*4,10-Dinitro-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane (5h).* A mixture of 4,10-dibenzyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane (**5a**, 412 mg, 0.80 mmol), dry acetonitrile (20 mL) and NOBF<sub>4</sub> (0.98 g, 8 mmol) was stirred at 0–10°C for 2 h and then at 25°C for 2 h. After cooling the mixture to 0°C, NO<sub>2</sub>BF<sub>4</sub> (1.06 g, 8 mmol) was added and the mixture stirred at 0°C for 10 min, 25°C for 20 min, 45°C for 2 h, and finally at 25°C for 16 h. The mixture was diluted with water (60 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (6 x 40 mL). The combined extracts were washed once with water (50 mL), dried, and concentrated to yield

0.66 g of a yellow solid, crystallization of which from acetonitrile (3 mL) gave 200 mg (59%) of colorless chunky, rhombic crystalline **5h**, mp 313–315°C (decomposition with change in crystalline form between 240–290°C);  $^1\text{H NMR}$  ( $(\text{CD}_3)_2\text{SO}$ )  $\delta$  7.38 (s, 4H, CH), 6.78 (s, 2H, CH), 2.1 (s, 12H,  $\text{CH}_3$ );  $^{13}\text{C NMR}$  ( $(\text{CD}_3)_2\text{SO}$ )  $\delta$  167.35 (C=O), 78.64 (C at C-3,5,9,11), 67.38 (C at C-1,7), 20.98 ( $\text{CH}_3$ ); mass spec (CI,  $\text{CH}_4$ )  $m/z$  427 ( $\text{MH}^+$ , 100), 385 (18), 382 (33), 335 (14), 293 (36), 208 (24), 207 (49), 165 (17); Anal. Calcd. for  $\text{C}_{14}\text{H}_{18}\text{N}_8\text{O}_8$ : mol wt 426.35, C 39.44; H, 4.26; N, 26.28. Found: C, 39.03; H, 4.36; N, 26.37. The structure of **5h** has been established by X-ray crystallography.<sup>13</sup>

*Reaction of cis,cis-1,3,5-Triformylcyclohexane with Ammonium Hydroxide and Formaldehyde.* *Cis,cis-1,3,5-Triformylcyclohexane*<sup>36</sup> (1.18g, 7.0 mmol) dissolved in methanol (5 mL) was added dropwise with stirring during a 5 minute period to concentrated  $\text{NH}_4\text{OH}$  (70 mL, 1.05 mol) (6°C). Formalin (11.2 mL of 37% aqueous solution; 140 mmol of formaldehyde) was added dropwise, with stirring, to the slightly turbid solution during a 4 minute period (6–8°C); stirring was continued for 15 h at 25°C. The reaction mixture, containing a small amount of white precipitate was heated at 70°C in a vented flask for 5 h causing the precipitate to dissolve. The solution was concentrated to dryness under reduced pressure to yield a white solid which was sublimed at 0.05 mm (160°C). The sublimate (3.2 g) was identified as hexamine by comparison of its IR and  $^1\text{H NMR}$  spectra with those of an authentic sample. The remaining white residue (1.62 g) was chromatographed on silica gel (elution with  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ ) to remove traces of hexamine and produce an amorphous sample of 3,5,7,9-tetraazahexacyclo-[9.3.1.1<sup>3,7</sup>.0<sup>2,9</sup>.0<sup>4,13</sup>.0<sup>5,10</sup>]hexadecane (**10**), 0.29 g, 19% yield, mp 120°C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  4.8 (s, 6H,  $\text{CH}_2\text{N}$ ), 4.7 (observed doublet, 3H, CHN), 1.0–2.6 (m, 9H, CH,  $\text{CH}_2$ ); mass spectrum (CI,  $\text{CH}_4$ )  $m/z$  M 218; Calcd. mol wt of **10**,  $\text{C}_{12}\text{H}_{18}\text{N}_4$  = 218.30; attempts to further purify this sample by sublimation (0.01 mm, 200–240°C) caused extensive decomposition.

Acetic acid (3.3 g, 35 mmol) was added during a 10-minute period to a mixture of crude **10** (0.67 g, ca. 3.0 mmol), containing traces of hexamine, and a solution of  $\text{NaNO}_2$  (1.05 g, 15.2 mmol) in water (50 mL); 0°C reaction temperature. The slightly turbid solution (pH 4.3) was stored at 0°C for 16 h. A precipitate which formed was removed by filtration and washed with water to yield 35 mg of an amorphous light tan solid, mp 135–140°C, a crude sample (ca. 4% yield) of 3,5,12-trinitroso-3,5,12-triazawurtzitane (**7d**);  $^1\text{H NMR}$  ( $(\text{CD}_3)_2\text{SO}$ )  $\delta$  6.55, 5.90, 5.86, 5.22 (doublets,  $J$  = 10 Hz, intensities 1:1:1:1, 3H, NCHN), 1.7–2.3 (m, 9H, CH/ $\text{CH}_2$ ) in addition to weak signals at 6.9, 6.3 and 5.7 in a ratio of 1:2:1 indicating traces of 1,3,5-trinitroso-1,3,5-hexahydrotriazine (R-salt). Mass spectra and infrared data are discussed in the text.

*Reaction of 3,5,12-Tribenzyl-3,5,12-triazawurtzitane (7b) with 2-Nitropropyl Hydroperoxide.*<sup>40</sup> Cuprous chloride (68 mg, 0.345 mmol) and 2-nitropropane (0.19 g, 2.1 mmol) are added to 3,5,12-tribenzyl-3,5,12-triazawurtzitane (**7b**,<sup>36</sup> 100 mg, 0.23 mmol) dissolved in pyridine (8 mL). The mixture was shaken with oxygen (1 atm) in a 250 mL glass container for 36 h (25°C). The resulting dark green solution was poured onto a mixture of ice (100 g) and concentrated hydrochloric acid (20 mL). The turbid mixture was extracted with  $\text{CH}_2\text{Cl}_2$  and the dried extract concentrated to dryness to yield 20 mg of an orange gum;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) revealed absence of benzyl  $\text{CH}_2$  and  $\text{C}_6\text{H}_5$  signals; mass spectrum (CI,  $\text{CH}_4$ )  $m/z$  300 (0.9), 284 (1.1), 268 (0.9), 253 (1.5), 252 (1.5), 209 (3.0), 208 (1.7), 164 (2.5), 163 (13), 135 (49), 91 (80), 79 (100); Calcd. mol wts for 3,5,12-trinitro-3,5,12-triazawurtzitane, **7a**,  $\text{C}_9\text{H}_{12}\text{N}_6\text{O}_6$  = 300.2; 3-nitro-5,12-dinitroso-3,5,12-triazawurtzitane,  $\text{C}_9\text{H}_{12}\text{N}_6\text{O}_5$  = 284.2; 3,5-dinitro-12-nitroso-3,5,12-triazawurtzitane,  $\text{C}_9\text{H}_{12}\text{N}_6\text{O}_4$  = 268.2; 3,5,12-trinitroso-3,5,12-triazawurtzitane, **7d**,  $\text{C}_9\text{H}_{12}\text{N}_6\text{O}_3$  = 252.2. Attempts to purify the material by column chromatography on silica gel (ether elution) led to decomposition products, although thin layer chromatography analysis revealed two principal spots (silica gel and ether elution). In a parallel run, the reaction mixture was stirred under oxygen contained in a gas burette (1 atm, 25°C) until oxygen uptake ceased (about 3 mole-

equivalents in 108 h). The principal isolated product was an amorphous solid mixed with some crystals (flat prisms, mp 135–145°C); column chromatography on silica gel caused decomposition of the material.

**2,4,10-Tribenzyl-2,4,10-triazaadamantane (12b).** A mixture of *cis,cis*-tris(benzylamino)cyclohexane (**11b**<sup>42</sup>, 13.92 g, 34.8 mmol) and dimethyl formamide dimethyl acetal (20.83 g, 174 mmol) was heated under reflux (24 h; oil bath temperature 209°C), followed by 24 h at 220°C. Concentration of the reaction mixture under reduced pressure to remove volatiles gave 14.6 g of oil; crystallization from hexane/2-propanol gave 5.55 g of 2,4,10-tribenzyl-2,4,10-triazaadamantane **12b**, mp 83–85°C (lit<sup>42</sup> mp 79–80°C). A second crop separated from the concentrated filtrate (1.75 g, mp 78–83°C; total yield 7.30 g, 51.2%); the filtrate was concentrated to remove all volatiles to yield 6.75 g of oil, principally unreacted **11b** by <sup>1</sup>H NMR assay. The structure of **12b** has been confirmed by X-ray crystallography;<sup>13</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.3–7.6 (m, 15H, C<sub>6</sub>H<sub>5</sub>), 3.83 (s, 6H, benzyl CH<sub>2</sub>), 3.62 (s, 1H, CH), 3.10 (s, 3H, CH), 1.42, 2.57 (apparent q, J = 12 Hz, 6H, ring CH<sub>2</sub>).

**2,4,10-Triazaadamantane (12c).** 2,4,10-Tribenzyl-2,4,10-triazaadamantane (**12b**) (0.50 g, 1.22 mmol), 10% Pd/C catalyst (0.5 g) and triethylamine (0.20 g) were mixed with absolute ethanol (100 mL); pH ca. 10.5. The mixture was shaken with hydrogen in a Parr apparatus (50 psi, 50°C, 7 h) and promptly cooled to 35°C; the catalyst was removed by filtration and washed with absolute ethanol. The filtrate was promptly concentrated in vacuum (25°C, 0.05 mm, 24 h) to yield 0.15 g (88%) of **12c** as a white, crystalline solid, mp 102–115°C; <sup>1</sup>H NMR (D<sub>2</sub>O) δ 7.6 (s, 1H, CH), 3.5–4.0 (m, 3H, CH), 1.8–2.3 (m, 6H, CH<sub>2</sub>). Anal. Calcd. for C<sub>7</sub>H<sub>13</sub>N<sub>3</sub>: C, 60.40; H, 9.40; N, 30.19. Found: C, 60.50; H, 9.40; N, 30.27. Under certain conditions the reaction fails; the pH of the reaction mixture during hydrogenation is critical. Unreacted **12b** is recovered when NaOH or excessive amounts of triethylamine are added to produce solutions which are too alkaline (pH 11–12). In other experiments, if insufficient triethylamine is present and the pH of the reaction mixture is less than 10, a water-insoluble product, apparently polymer, is obtained. It was found necessary to store **12c** in a desiccator over NaOH pellets to prevent decomposition; the compound is extremely hygroscopic and decomposes in air at ambient temperature (see discussion in text).

**2,4,10-Tris(benzenesulfonyl)-2,4,10-triazaadamantane (12d).** *Procedure A.* 2,4,10-Triazaadamantane (**12c**, 0.34 g, 2.45 mmol) dissolved in aqueous NaOH (20 mL, 2.5% NaOH) was shaken with benzenesulfonyl chloride (1.55 g, 8.78 mmol) at 25°C. Additional NaOH solution was added at intervals to maintain an alkaline solution. After shaking for 1.5 h, the mixture was heated under reflux for 0.5 h. After cooling to 25°C additional NaOH solution was added to make the solution basic. The insoluble product was removed by filtration and washed with water to yield 0.17 g (12.4%) of crude **12d**, mp 220–275°C; recrystallization from acetonitrile gave pure **12d**, prisms, mp 288–290°C; lit<sup>47</sup> mp 165–166°C; <sup>1</sup>H NMR (CD<sub>3</sub>)<sub>2</sub>SO δ 7.5–8.0 (m, 15H, C<sub>6</sub>H<sub>5</sub>), 7.37 (s, 1H, apical CH), 3.94 (s, 3H, CH), 1.24, 1.55 (apparent q, J = 12 Hz, 6H, CH<sub>2</sub>); Anal. Calcd for C<sub>25</sub>H<sub>25</sub>N<sub>3</sub>O<sub>6</sub>S<sub>3</sub>: C, 53.65; H, 4.50; N, 7.51; S, 17.19. Found: C, 53.80; H, 4.67; N, 7.55; S, 17.39. The structure of **12d**, prepared as described above, has been established by X-ray crystallography.<sup>13</sup>

*Procedure B.* *cis,cis*-1,3,5-Tris(benzenesulfonamido)cyclohexane (**11d**,<sup>42</sup> mp 250–252°C, 0.61 g, 1.1 mmol) was heated at 270–275°C with triethyl orthoformate (10 mL, 58.3 mmol) in a glass-lined pressure vessel for 18 h. Cooling to 25°C, followed by filtration and washing with ether and ethanol gave 0.22 g (26%) of **12d**, mp 280–290°C. The compound is insoluble in aqueous NaOH. Recrystallization from acetonitrile gave prisms, mp 287–290°C, having an <sup>1</sup>H NMR spectrum identical to the sample prepared by Procedure A.

*cis,cis*-1,3,5-Tris(carbomethoxyamino)cyclohexane (**11e**). *cis,cis*-1,3,5-Triaminocyclohexane trihydrochloride,<sup>47</sup> 3.2 g, 13.3 mmol) was dissolved in a solution of NaOH (4.0 g) in water (15 mL). Methyl

chloroformate (5.2 g, 55 mmol) was added dropwise, with stirring during 10 min ( $< 10^{\circ}\text{C}$ ). After stirring for 3 h ( $20^{\circ}\text{C}$ ), additional methyl chloroformate (1.0 g, 10.6 mmol) and 10% aqueous NaOH (5 mL) were added. Stirring was continued for 3 h ( $25\text{--}30^{\circ}\text{C}$ ). The precipitated product was removed by filtration and washed with water to yield 4.10 g (100%) of **11e**, mp  $244\text{--}246^{\circ}\text{C}$ ; recrystallization from 2:1 2-propanol/ethanol gave prisms, mp  $238\text{--}242^{\circ}\text{C}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  4.55 (d,  $J = 8$  Hz, 3H, NH), 3.67 (s, 9H,  $\text{CH}_3$ ), 3.3–3.9 (m, 3H, CHN), 2.30 (apparent d,  $J = 12$  Hz, 3H, equatorial CH of  $\text{CH}_2$ ), 1.02 (apparent q,  $J = 12$  Hz, 3H, axial CH of  $\text{CH}_2$ ). Anal. Calcd. for  $\text{C}_{12}\text{H}_{21}\text{N}_3\text{O}_6$ : C, 47.52; H, 6.98; N, 13.86. Found: 47.62; H, 7.04; N, 13.94.

*cis,cis-1,3,5-Tris(nitramino)cyclohexane (11a)*. Nitric acid (90%, 1.9 mL) was added dropwise to *cis,cis-1,3,5-tris(carbomethoxyamino)cyclohexane (11e)*, 2.0 g, 6.6 mmol in acetic anhydride (7 mL) during 10 min ( $< 5^{\circ}\text{C}$ ). Stirring was continued at  $10\text{--}20^{\circ}\text{C}$  for 1.5 h and at  $20^{\circ}\text{C}$  for 20 minutes, after which time the solution was poured over ice (50 g) and the mixture extracted three times with  $\text{CH}_2\text{Cl}_2$ . The combined extracts were washed once with water, dried, and concentrated to yield 3.42 g of oil. Concentrated  $\text{NH}_4\text{OH}$  (30 mL) was added to the product and the mixture stirred at  $25^{\circ}\text{C}$  for 30 minutes to yield a clear, pale yellow solution. After concentration under reduced pressure, concentrated HCl was added to adjust pH to 1 ( $< 10^{\circ}\text{C}$ ). The clear solution stored at  $0^{\circ}\text{C}$  overnight deposited a crystalline product which was washed with water to yield 0.93 g of **11a**; a second crop was recovered (total yield of crude **11a**, 1.19 g, 65% overall yield from **11e**, mp  $180\text{--}222^{\circ}\text{C}$ ). Recrystallization from ethanol gave purified **11a** monohydrate as rhombic crystals, mp  $220\text{--}222^{\circ}\text{C}$ , with vigorous decomposition and efflorescence at  $100^{\circ}\text{C}$ ; Anal. Calcd. for  $\text{C}_6\text{H}_{12}\text{N}_6\text{O}_6\cdot\text{H}_2\text{O}$ : C, 25.44; H, 5.00; N, 29.78. Found: C, 25.63; H, 5.01; N, 29.54. An anhydrous sample was prepared by drying the monohydrate at  $110^{\circ}\text{C}$  (0.1 mm);  $^1\text{H NMR}$  ( $\text{CD}_3)_2\text{SO}$   $\delta$  11.9 (s, 3H, NH), 3.8–4.4 (m, 3H, CHN), 2.16 (apparent t,  $J = 12$  Hz, 3H, CH of  $\text{CH}_2$ ), 1.18 (apparent q,  $J = 12$  Hz, 3H, CH of  $\text{CH}_2$ ). Anal. Calcd. for  $\text{C}_6\text{H}_{12}\text{N}_6\text{O}_6$ : C, 27.27; H, 4.58; N, 31.81. Found: C, 27.35; H, 4.53; N, 31.70.

*cis,cis-1,3,5-Tris(N-nitro-N-tri-n-butylstannyl)aminocyclohexane (11i)*. A solution of *cis,cis-1,3,5-tris(nitramino)cyclohexane monohydrate (11a-H<sub>2</sub>O)*, 0.56 g, 2 mmol and bis(tri-*n*-butyltin) oxide<sup>48</sup> (1.8 g, 3.0 mmol) in benzene (40 mL) was heated under reflux (6 h) with a Dean-Stark tube attached. The solution was cooled to  $25^{\circ}\text{C}$  overnight, and the product removed by filtration and washed with benzene to yield 1.90 g (91%) of **11i**, as a white, amorphous solid, mp  $190\text{--}195^{\circ}\text{C}$ ; IR (KBr)  $1550, 1330\text{ cm}^{-1}$  ( $\text{NO}_2$ ); NH, OH signals absent. Recrystallization from benzene gave chunky prisms, mp  $205\text{--}206^{\circ}\text{C}$ . Anal. Calcd. for  $\text{C}_{42}\text{H}_{90}\text{N}_6\text{O}_6\text{Sn}_3$ : C, 44.59; H, 8.02; N, 7.43; Sn, 31.48. Found: C, 44.67; H, 7.96; N, 7.26; Sn, 31.79.

In a similar experiment **11a-H<sub>2</sub>O** (0.56 g, 2 mmol) and bis(tri-*n*-propyltin) oxide (1.54 g, 3.0 mmol) were heated in benzene (100 mL) for 15 h under reflux to yield 1.91 g (95%) of *cis,cis-1,3,5-tris(N-nitro-N-tri-n-propylstannyl)aminocyclohexane 11h*, mp  $216\text{--}219^{\circ}\text{C}$ ; crystals form near the mp;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  4.0 (m, CH), 0.5–2.5 (m,  $\text{CH}_2, \text{CH}_3$ ). Anal. Calcd. for  $\text{C}_{33}\text{H}_{72}\text{N}_6\text{O}_6\text{Sn}_3$ : C, 39.44; H, 7.22; N, 8.36; Sn, 35.43. Found: C, 39.44; H, 6.92; N, 8.53; Sn, 35.16. In another experiment, **11a** was heated with trimethyltin hydroxide in refluxing benzene to yield *cis,cis-1,3,5-tris(N-nitro-N-trimethylstannyl)aminocyclohexane (11g)*, mp  $190\text{--}200^{\circ}\text{C}$ . Samples of **11g**, **11h** and **11i** were heated in various solvents, separately, with haloforms ( $\text{CHX}_3$ , X = F, Cl, Br, I, and  $\text{CHClF}_2$ ) generally leading to recovered tin reactants, except with  $\text{CHClF}_2$ ;<sup>49</sup> see discussion.

*Reaction of cis,cis-1,3,5-Tris(N-nitro-N-tri-n-butylstannyl)aminocyclohexane (11i) with CHClF<sub>2</sub>*.<sup>49</sup> A mixture of  $\text{CHClF}_2$  (0.86 g, 10 mmol), dry benzene (25 mL) and **11i** (0.25 g, 0.22 mmol) was heated in a rocking stainless steel bomb ( $150^{\circ}\text{C}$ , 15 h). The resulting clear, yellow solution was concentrated to remove solvent and volatiles to leave 0.19 g of oil. Column chromatography of this residue on silica gel (2 x 20 cm packed column, ether elution) gave an oily, partly crystalline solid believed to contain principally 2,4,10-trinitro-

2,4,10-triazaadamantane, **12a**, mp 155–165°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.03 (s, 1H, CH), 4.5 (m, 3H, CH), 1–3 (m, 6H,  $\text{CH}_2$ ); mass spec (CI,  $\text{CH}_4$ )  $m/z$   $M^+$  274 (6.2), 93 (100); calculated for **12a**,  $\text{C}_7\text{H}_{10}\text{N}_6\text{O}_6$ , mol wt 274.2. In a parallel run the crude product was not chromatographed, but was fractionally triturated with acetone to yield a partly crystalline acetone-soluble fraction having an  $^1\text{H}$  NMR spectrum identical to the sample obtained by chromatography.

*2,4,10-Tris(trimethylstannyl)-2,4,10-triazaadamantane (12e)*. A mixture of pure, anhydrous, freshly prepared 2,4,10-triazaadamantane (**12c**, 0.33 g, 2.37 mmol) and diethylaminotrimethyl tin (2.87 g, 12.16 mmol) was stirred at 25°C for 16 h with  $\text{CaCl}_2$ /Drierite tube attached, to produce a clear solution. Heating at 50°C for 3 h gave 2.62 g of a clear, viscous oil; volatiles were removed at 25°C (0.1 mm) with stirring for 1.5 h to yield 0.99 g (67%) of **12e** as a colorless, very hygroscopic grease which failed to crystallize;  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  7.02 (s, 1H, apical CH), 3.58 (m, 3H, CH), 1.5–2.5 (m, 6H,  $\text{CH}_2$ ), 0.4 (s, 27H,  $\text{CH}_3$ ). Anal. Calcd. for  $\text{C}_{16}\text{H}_{37}\text{N}_3\text{Sn}_3$ : C, 30.61; H, 5.94; N, 6.70. Found: C, 30.55; H, 5.80; N, 6.82.

*Reaction of 2,4,10-Tris(trimethylstannyl)-2,4,10-triazaadamantane (12e) with  $\text{NO}_2\text{BF}_4$* . Pure  $\text{NO}_2\text{BF}_4$  (0.99g, 7.45 mmol) was added to pure, freshly prepared **12e** (0.91 g, 1.45 mmol) suspended in anhydrous acetonitrile (10 mL) during 15 min ( $< 0^\circ\text{C}$ ). The resulting clear yellow solution was stored at 20°C (14 h) to produce a white crystalline precipitate of tin compound, removed by filtration (0.205 g, mp 340°C, dec). The filtrate (at 0°C) was treated with additional  $\text{NO}_2\text{BF}_4$  (0.77 g, 5.8 mmol) and the clear solution stored at 20°C (13 h) and heated at 50°C for 3.5 h. After cooling to 25°C, dilution with ice water (50 mL) and extraction with  $\text{CH}_2\text{Cl}_2$  (5 x 20 mL), the dried extracts were concentrated to dryness to yield an oil (100 mg); the oil was dissolved in ethanol (2 mL) and diluted with water until turbid. After storage at 0°C for 3 days a crystalline deposit was produced (16 mg, mp 65–85°C), believed to contain principally 2-nitro-4-nitroso-2,4,10-triazaadamantane ( $\text{C}_7\text{H}_{11}\text{N}_5\text{O}_3$ , mol. wt. 213.20);  $^1\text{H}$  NMR ( $(\text{CD}_3)_2\text{SO}$ )  $\delta$  7.5 (s, 1H, CH), 4.8–5.0 (m, 3H, CH), 0.5–2.5 (m, 6H,  $\text{CH}_2$ ); mass spectrum (CI,  $\text{CH}_4$ )  $m/z$  213 (0.4), 155 (1.3), 149 (4.8), 130 (10.0), 44 (52), 43 (100).

*1,3-Bis(trimethylstannyl)hexahydropyrimidine (14c)*. A mixture of hexahydropyrimidine (**14b**, 0.86 g, 1 mmol) and dimethylaminotrimethyl tin (4.2 g, 2.1 mmol), after standing at 25°C for 4 h (Drierite tube attached), was heated under reduced pressure to remove volatiles (95°C, 2 minutes) leaving 4.1 g (100%) of **14c** as a colorless liquid;  $^1\text{H}$  NMR (neat sample)  $\delta$  4.0–4.5 (m, 2H,  $\text{CH}_2$  at C-2), 3.0–3.5 (m, 4H,  $\text{CH}_2$  at C-4 and C-6), 1.5–2.0 (m, 2H,  $\text{CH}_2$  at C-5), 0.5 (s, 18H,  $\text{CH}_3$ ); adjacent signals appear owing to  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  coupling;  $J = 28$  Hz; signals of reactants are absent. Anal. Calcd. for  $\text{C}_{10}\text{H}_{26}\text{N}_2\text{Sn}_2$ : C, 29.17; H, 6.37; N, 6.80; Sn, 57.66. Found: C, 29.01; H, 6.58; N, 6.83; Sn, 57.42.

*1,3-Dinitrohexahydropyrimidine (14a)*. A solution of 1,3-bis(trimethylstannyl)hexahydropyrimidine (**14c**, 0.19 g, 0.46 mmol) in dry acetonitrile (1.0 mL) was added during 1 minute to a stirred suspension of purified  $\text{NO}_2\text{BF}_4$  (0.21 g, 1.58 mmol) in dry acetonitrile (2.5 mL) (Drierite tube attached), 0°C, 5 min; 50°C, 1 h). The mixture was cooled to 25°C, treated with additional purified  $\text{NO}_2\text{BF}_4$  (0.14 g, 1.05 mmol) and heated at 50°C (3 h); brown fumes evolved during the heating and a clear yellow solution was formed. After cooling to 25°C, water (20 mL) was added and the clear solution extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 25 mL). Concentration of the dried extracts under reduced pressure (25°C) gave 25 mg (31%) of crude **14a**, with  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) identical to that reported for an authentic sample.<sup>50,53,55,56</sup>

Numerous parallel experiments were performed in which reaction parameters were varied, including solvent (acetonitrile, sulfolane, hexane,  $\text{CH}_2\text{Cl}_2$ , nitromethane and  $(\text{CH}_3)_2\text{SO}$ ), reaction temperature (0–50°C), time (3–18 h) and molar ratio of reactants ( $\text{NO}_2\text{BF}_4$ : **14c** = 2:1 to 5.7:1). Only dried solvents were employed. A lower reaction temperature of 25°C, shorter reaction times, and a lower ratio of  $\text{NO}_2\text{BF}_4$  to **14c**, lead to



mixtures of products, including **14a**, 1-nitro-3-nitrosohexahydropyrimidine (**14d**) and 1,3-dinitrosohexahydropyrimidine (**14e**), all known compounds; properties observed, including <sup>1</sup>H NMR spectra, agree with previously reported data.<sup>53,55</sup>

**Table 1.** Crystal Data, X-ray Refinement Parameters and Aza-Cage Structural Parameters.

Compound	<b>5a</b>	<b>5g</b>	<b>5h</b>	<b>6α*</b>	<b>6β</b>	<b>6γ</b>	<b>6ε</b>	<b>12b</b>	<b>12d</b>
Space Group <sup>1,2</sup>	P2 <sub>1</sub> /c	P2 <sub>1</sub> /n	P2 <sub>1</sub> /n	Pbca	Pb2 <sub>1</sub> a	P2 <sub>1</sub> /n	P2 <sub>1</sub> /n	P2 <sub>1</sub> /c	Pna2 <sub>1</sub>
a, Å	7.690(1)	10.862(2)	11.241(2)	9.485(2)	9.676(2)	13.231(3)	8.852(2)	9.542(3)	25.693(5)
b, Å	17.769(3)	14.851(2)	14.221(3)	13.225(4)	13.006(4)	8.170(2)	12.556(3)	10.999(4)	13.299(3)
c, Å	19.662(4)	11.058(2)	11.491(2)	23.673(3)	11.649(4)	14.876(3)	13.386(3)	21.843(6)	7.389(2)
β, deg.	94.43(1)	99.74(1)	102.26(3)			109.17(2)	106.82(2)	95.24(2)	
formula wt.	516.60	394.36	426.36	442.23	438.23	438.23	438.23	409.56	559.66
ρ(calc), g/cc	1.281	1.490	1.578	1.981	1.985	1.916	2.044	1.192	1.472
No. data collected	3200	2383	2126	2254	1062	2618	3760	3632	1874
No. indep. data	2808	2245	1877	1939	1023	2424	2514	3032	1808
No. Obs (I > 2σI)	1903	2081	1278	1385	987	2260	2075	2558	1563
Parameters <sup>3</sup>	348	272	277	295	290	290	290	372	334
R-factors <sup>4</sup> R	0.047	0.036	0.049	0.063	0.022	0.043	0.036	0.053	0.056
obs data R <sub>w</sub>	0.100	0.092	0.109	0.158	0.057	0.114	0.092	0.053	0.142
R-factors R	0.084	0.039	0.078	0.087	0.023	0.045	0.046	0.065	0.066
all data R <sub>w</sub>	0.120	0.100	0.122	0.181	0.058	0.116	0.101	0.053	0.153
<b>Cage Structural Parameters</b>									
Ave. <C - C>, Å	1.571(5)	1.570(3)	1.572(5)	1.571(7)	1.573(4)	1.575(3)	1.580(3)	1.530(4)	1.530(11)
Ave. <C - N>, Å	1.457(4)	1.455(3)	1.455(5)	1.454(7)	1.454(4)	1.456(3)	1.455(3)	1.469(3)	1.471(9)
Bend <sup>5</sup> at N2 (deg.)	5.0	13.7	3.1	43.2	35.4	40.0	39.7	45.2	18.2
at N4 (deg.)	42.8	6.2	24.8	22.9	22.9	15.0	1.4	48.9	22.2
at N6 (deg.)	14.7	12.7	19.6	31.6	32.4	27.5	30.3	-	-
at N8 (deg.)	2.8	0.4	1.3	37.7	37.1	49.5	32.7	-	-
at N10 (deg.)	42.3	6.4	37.2	27.1	15.1	36.7	23.7	45.3	21.0
at N12 (deg.)	9.2	9.1	4.7	23.7	34.2	36.2	40.0	-	-

Notes: \*The data cited in this table for 6α have been obtained for a sample in which ca. 50% of the centrosymmetric cavities are filled with water (i.e., a ca. 0.25 hydrate, since the cavity frequency is 50%).

1. Crystal systems are monoclinic except for 6α, 6β and 12d which are orthorhombic.
2. Mol 6β is reported in Pb2<sub>1</sub>a to emphasize its similarity to 6α; the normal setting for sp. grp. 29 is Pca2<sub>1</sub>.
3. All refinements used full-matrix algorithms, on F<sup>2</sup> differences, except 12b, which used |F| differences.
4. R-factors:  $R = \sum |F_o| - |F_c| / \sum |F_o|$  and  $R_w = [\sum (w\Delta^2) / \sum (w(F_o^2)^2)]^{1/2}$ , where  $\Delta = (F_o^2 - F_c^2)$ . For 12b (refined with older software),  $R_w = \sum w|F_o| - |F_c| / \sum w|F_o|$ .
5. The "Bend angle" at an aza-cage atom is the amount that the aza-substituent bond is bent out of the C-N-C plane formed by the aza atom and its two bonded neighbors in the cage; its normal range is from 0.0° for an sp<sup>2</sup> hybrid to 54.8° for a pyramidal sp<sup>3</sup> hybrid.
6. All crystal data were obtained at 20°C.

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