J. Am. Chem. Soc. 1993, 115, 7465–7471

Thermochemistry, Energy Comparisons, and Conformational Analysis of Hydrazine, Triazane, and Triaminoammonia

H. Bernhard Schlegel and Anne Skancke[*,†]

Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Received December 9, 1992

Abstract: The series NH_3, H_2NNH_2, $HN(NH_2)_2$ (triazane), and $N(NH_2)_3$ (triaminoammonia) has been studied by computational methods (HF/6-31G* and MP2/6-31G* optimizations for all species, G2 (see paragraph on computations) energies for the most stable form of each molecule). Thermodynamic functions have been computed. Structural aspects have been discussed in terms of stabilizing and destabilizing factors. The importance of hydrogen bonding and hyperconjugation has been discussed on the basis of potential surface differences and vibrational spectra. Relative stabilities have been discussed from isodesmic reaction schemes, from which also the following estimates of N–N bond energy are obtained: hydrazine, 64 kcal/mol; triazane, 66 kcal/mol; triaminoammonia, 59 kcal/mol. The kinetic stabilities of triazane and triaminoammonia have been considered from various modes of decomposition.

Introduction

The nitrogen atom is present in a large number of functional groups throughout the organic and inorganic worlds. Its $2s^22p^3$ ground state configuration is consistent with a bonding scheme having an (approximately) sp^3-hybridized, three-coordinated, covalently bonded nitrogen atom (e.g. NH_3 and NCl_3). But there are many other bonding schemes including polar covalent bonds (e.g. alkali salts of NH_2^- and NH^{2-}), ionic bonds (such as group II salts of N^{3-}, e.g. Ba_3N_2), multiple bonding (like in FN═NF, the cyanide group, and a large number of alicyclic systems), coordinate sigma bonds (like in NH_4^+ and $[Cu(NH_3)_4]^{2+}$), and even coordinate pi bonding (like in the planar trisilylamine, $N(SiH_3)_3$). The planarity of this system can be explained in terms of two factors: an sp^2-hybridized nitrogen with p–d π bonding, and electrostatic repulsions rising from the high polarity of the N–Si bonds.[1]

Despite the versatility and abundance of nitrogen chemistry, there are comparatively few compounds containing the singly bonded >N–N< fragment. Such systems are destabilized by lone pair–lone pair repulsions. The parent compound, hydrazine (H_2NNH_2), is kinetically stable, albeit thermodynamically unstable,[2] and is well characterized. Other systems within this family have been prepared only recently. Triazane (N_3H_5) and cyclic triaziridine (N_3H_3) have been synthesized in the form of silver complexes, but neither of them have been isolated as free molecules.[3] The latter system and two open-chain isomers have been the subject of a thorough *ab initio* study and have been predicted to be sufficiently stable to be candidates for isolation.[4] Derivatives of the cyclic form have also been reported,[5] and photoelectron spectra are available for a number of these derivatives.[6] A 1,2,4-triazane ring has been isolated.[7] Recent experimental findings furthermore indicate the existence of tetrazetidine (an N_4 ring system) in the form of a benzenophane derivative, and *ab initio* calculations suggest that the parent ring system may be kinetically stable.[8]

The purpose of the present paper is to discuss the stability and conformational preferences of derivatives of ammonia with one, two, or three hydrogens replaced by $-NH_2$ groups. The main emphasis will be on the hitherto unknown systems triazane ($HN(NH_2)_2$) and triaminoammonia ($N(NH_2)_3$) ("TAA"). Vibrational spectra and barriers to rotation and inversion have been calculated with special attention to the role of hydrogen bonding and hyperconjugation. Heats of formation have been computed at the G2 level of theory and have been used to discuss the thermodynamic stability of N_3H_5 and N_4H_6. Kinetic stability has been discussed by considering various modes of decomposition. The dication of TAA, $N(NH_2)_3^{2+}$, has also been studied. *A priori* one would expect the dication to be stable because of the absence of a central nitrogen lone pair while the existence of the neutral species may be more questionable. We note in this connection the existence of the cation $(H_2NNR_2NH_2)^+$, which apparently is more stable[9] than the parent neutral N_3H_5.

This work is an extension of previous studies of systems with the general formula $M(MH_2)_3$ and its ions, M being a first-row element. Previous calculations on this series of molecules include trimethylmethane ("TMM")[10] and its dianion[11,12] and dication,[13] and triborylborane ("TBB") and its dianion.[14] These systems have been studied from different viewpoints: the carbon system is part of a study of Y-aromaticity, and the boron analogue is an example of "neoclassical" boron hydrides. The present work is directed toward finding a possible new candidate for a branched –N–N– (Y-shaped) system, but a "horizontal" comparison of the previously studied systems within this series is also within the scope of this article. In this connection it should be pointed out that TAA^{2+} is isoelectronic with TMM^{2-} and with the guanidinium ion, which is noted for its remarkable stability.[15]

[†] On leave from the Department of Chemistry (IMR), University of Tromsø, N-9037 Tromsø, Norway.

(1) Livant, P.; McKee, M. L.; Worley, S. D. *Inorg. Chem.* **1983**, *22*, 895.

(2) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. The NBS Tables of Chemical Thermodynamics Properties. *J. Phys. Chem. Ref. Data* **1982**, *11*, Supplement 2.

(3) Kim, Y.; Gilje, J. W.; Seff, K. *J. Am. Chem. Soc.* **1977**, *99*, 7057.

(4) Magers, D. H.; Salter, E. A.; Bartlett, R. J.; Salter, C.; Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1988**, *110*, 3435.

(5) Leuenberger, C.; Hoesch, L.; Dreiding, A. *J. Chem. Soc., Chem. Commun.* **1980**, *24*, 1197.

(6) Gleiter, R.; Sigwart, C.; Irngartinger, H.; Gries, S.; Marterer, W.; Klingler, O.; Prinzbach, H. *Tetrahedron Lett.* **1988**, *29*, 185.

(7) Katritzky, A. R.; Pate, R. C.; Read, D. M. *Tetrahedron Lett.* **1977**, *43*, 3803.

(8) Ritter, G.; Häfelinger, G.; Lüddecke, E.; Rau, H. *J. Am. Chem. Soc.* **1989**, *111*, 4627.

(9) Linke, K. H.; Turley, R. *Z. Anorg. Allg. Chem.* **1970**, *377*, 139.

(10) (a) Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; p 1. (b) Yarkoni, D. R.; Schaefer, H. F. *J. Am. Chem. Soc.* **1974**, *96*, 3754. (c) Dixon, D. A.; Dunning, T. H., Jr.; Eades, R. A.; Kleier, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 2878.

(11) Agranat, I.; Skancke, A. *J. Am. Chem. Soc.* **1985**, *107*, 867.

(12) Agranat, I.; Radhakrishnan, T. P.; Herndon, W. C.; Skancke, A. *Chem. Phys. Lett.* **1991**, *181*, 117.

(13) Agranat, I.; Skancke, A. *Nouv. J. Chim.* **1988**, *12*, 87.

(14) Skancke, A.; Liebman, J. *THEOCHEM* **1992**, *259*, 411.

(15) Gund, P. *J. Chem. Educ.* **1972**, *49*, 100.

0002-7863/93/1515-7465$04.00/0

Table I. Total Energies (au) and Zero-Point Energies (kcal/mol) for NH_3, N_2H_4, N_3H_5, and N_4H_6[a]

system	symm	*E*(HF/6-31G*//HF/6-31G*)	*n*	ZPE	*E*(MP2/6-31G*//MP2/6-31G*)	*n*	*E*(G2)
H		−0.5000			−0.5000		−0.500 00
H_2	$D_{\infty h}$	−1.1268		6.64	−1.1441	0	−1.166 36
N		−54.3854			−54.4595		−54.517 98
N_2	$D_{\infty h}$	−108.9440		3.94	−109.2553	0	−109.392 61
NH_2 ($2B_1$)	C_{2v}	−55.5577	0	12.9	−55.6909	0	−55.789 02
NH_3	C_{3v}	−56.1844	0	23.2	−56.3542	0	−56.458 65
N_2H_4 *anti* form	C_{2h}	−111.1649	0	36.2	−111.4956	0	
	C_s	−111.1562	1	35.1			
gauche form	C_2	−111.1694	0	36.4	−111.4979	0	−111.680 45
N_3H_5 A	C_1	−166.1663	0	48.5	−166.6575	0	−166.929 07
B	C_s	−166.1671	0	48.6	−166.6474		−166.929 77
C	C_s	−166.1576	0	48.1	−166.6473	0	
Ts1	C_1	−166.1588	1	48.2	−166.6534		
Ts2 (NNN planar)	C_s	−166.1543	1	47.7	−166.6433		
Ts3	C_{2v}	−166.1468	1	47.4	−166.6348		
$N(NH_2)_3$	C_3	−221.1678	0	59.8	−221.8246	0	−222.165 88
	C_{3v}	−221.1368	1	59.3			
	C_{3h}	−221.1504	1	59.5			
all planar	D_{3h}	−220.7679	2	46.2			
	C_{2v}	−220.8301	4	46.8			
	D_{3h}	−220.4428	1	58.7			
	C_1	−221.0617	1	56.2	−221.7409		
$N(NH_2)_3^{++}$ (NNN planar)	D_3	−220.4437	0	59.3			

[a] *n* is the number of imaginary frequencies.

Table II. Enthalpies of Formation at 0 K ($\Delta H_f°$) (Including Zero-Point Energies) (kcal/mol) and Entropies (*S*) (cal/(mol K)) for NH_3, N_2H_4, N_3H_5, and N_4H_6 and Their Constituent Molecules

		$\Delta H_f°$				$S°$	
molecule[a]	symm	HF/ 6-31G*	MP2/ 6-31G*	G2	expt[b]	HF/ 6-31G*	expt[b]
H_2[b,c,d]	$D_{\infty h}$	0	0	0	0	31.1	31.2
N_2[b,c,d]	$D_{\infty h}$	0	0	0	0	45.7	45.8
NH_2[c]	C_{2v}	−49.5	−35.5	46.2	44.9	46.4	46.7
		107.8	70.7	45.8			
NH_3[c]	C_{3v}	−2.7	2.9	−8.1	−9.4	45.9	46.0
		80.0	19.9	−8.9			
N_2H_4[c]	C_2	36.9	44.2	28.4	26.2	54.7	57.1
		181.8	68.6	27.5			
N_3H_5[c]	C_1	67.8	73.1	47.5		62.5	
		275.6	107.4	46.6			
N_4H_6[c]	C_3	95.7	99.9	74.3		66.8	
		367.5	141.3	73.9			

[a] For each molecule, the first row is $\Delta H_f°$ computed from the formation reaction, eq 1, and the second row is $\Delta H_f°$ computed from the atomization reaction, eq 2. [b] Experimental data are from ref 2. [c] G2 energy data for these systems were taken from ref 19. [d] The experimental $\Delta H_f°$ for H is 51.67 kcal/mol, and for N, 112.64 kcal/mol.

Summary of Computational Procedures

The Gaussian 90[16] and Gaussian 92[17] computer programs have been used throughout this work. For the conformational analysis, optimized geometries and analytic vibrational frequencies were computed at the HF/6-31G* level. Relative energies of the various conformers were calculated by second-order Møller–Plesset perturbation theory (MP2/6-31G*, frozen core). Total energies are listed in Table I. Heats of formation were calculated at the G2 level of theory.[18] The G1[19] and G2 methods are capable of predicting energy differences with an average absolute error of 2 kcal/mol or better. The G1 method assumes that corrections for diffuse functions, polarization functions, and higher order correlation corrections are approximately independent and involves the following steps:

(1) Zero-point energy is calculated from analytical vibrational frequencies computed at the HF/6-31G* level and scaled by 0.893.

(2) Equilibrium geometries are calculated at the MP2/6-31G* level (including core electron correlation).

(3) The total energy is calculated at the MP4/6-31G** level. This value is modified by corrections for diffuse functions (from an MP4/6-311+G** computation), higher polarizations on nonhydrogens (MP4/6-311G(2df,p)), correlation beyond fourth-order perturbation theory (QCISD(T)/6-311G**), and higher level contributions.

The G2 procedure requires an additional MP2/6-311+G(3df,2p) calculation to take into account the nonadditivity of some of the basis set effects. The reader is referred to the original articles for a complete description of the G1 and G2 procedures.

Results and Discussion

Rotational Potential Surfaces. Hydrazine. The total energies for various conformers of hydrazine are given in Table I; the optimized geometries at HF/6-31G* and MP2/6-31G* levels are shown in Figure 1 as Newman-type projections along the N–N bond. The C_{2h} symmetry form with the nitrogen lone pairs *anti* and the C_2 form with the lone pairs *gauche* are minima as confirmed by vibrational frequency calculations at both HF/6-31G* and MP2/6-31G* levels. Our results agree with those of Riggs and Radom[20] and Schmitz and Euler.[21] The *gauche* conformer is 1.4 kcal/mol more stable, and its geometry is in good agreement with the electron diffraction structure reported by Kuchitsu and co-workers.[22] The calculated N–N bond length of 1.4395 Å compares well with the experimental value of 1.449(0.002) Å. The NNH(inner) and NNH(outer) angles are significantly different in the experimental structure, 112 ± 2° and 106 ± 2°, in accord with the calculated values for the lowest energy conformer. The C_s structure given in Figure 1 is a

---

[16] Gaussian 90, Revision I: M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1990.

[17] Gaussian 92, Revision C: M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1992.

[18] Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. *J. Chem. Phys.* **1991**, *94*, 7221.

[19] Curtiss, L. A.; Jones, C.; Trucks, G. W.; Raghavachari, K.; Pople, J. *J. Chem. Phys.* **1990**, *93*, 2537.

[20] Riggs, N. V.; Radom, L. *Aust. J. Chem.* **1986**, *39*, 1917. See also references therein concerning experimental frequencies for hydrazine.

[21] Schmitz, B. K.; Euler. *J. Mol. Struct.* (*Theochem*) **1992**, *257*, 227.

[22] Kohata, K.; Fukuyama, T.; Kuchitsu, K. *J. Phys. Chem.* **1982**, *86*, 602.

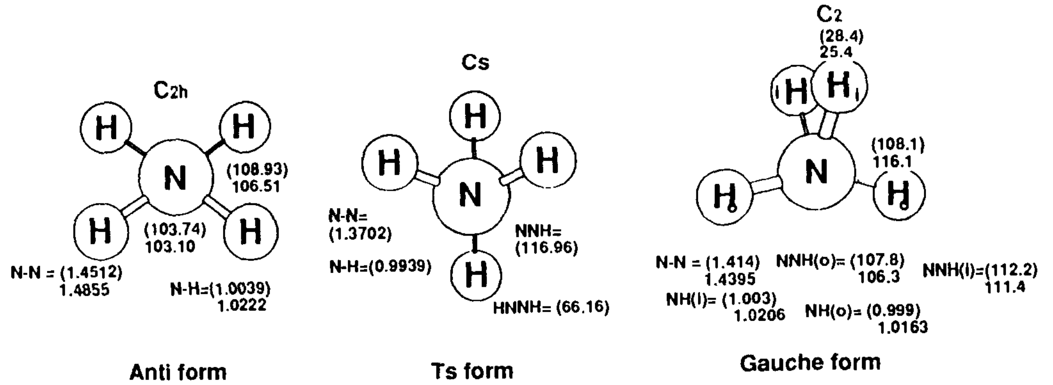


Figure 1. Structures and symmetries for various forms of N_2H_4. Numbers in parentheses are from HF/6-31G* optimizations. Numbers without parentheses are from MP2/6-31G* optimizations. The C_s form is a transition state; the other forms refer to minima. The *gauche* form of C_2 symmetry is the most stable. See Table I for energies.

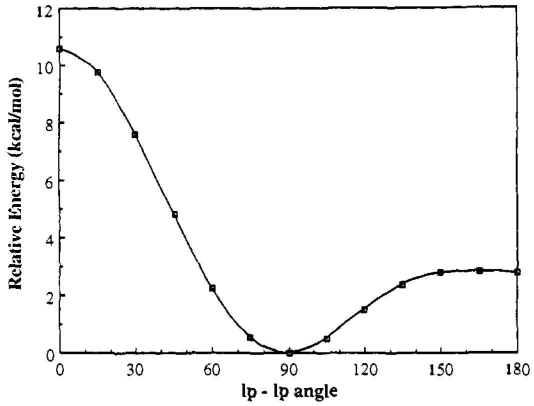


Figure 2. Energy variation in N_2H_4 as a function of the dihedral angle lp–N–N–lp (from single-point HF/6-31G* calculations). Angle zero represents parallel lone pairs.

transition state for inversion of the $-NH_2$ group and is found to be 8 kcal/mol above the *gauche* ground state. Figure 2 gives the potential for rotation about the N–N bond. The large barrier at 0° can be attributed to the lone pair–lone pair interaction. There is a minimum at 90° when the lone pairs are *gauche* and a rather flat region between 150 and 210° when the lone pairs are *anti*. These features also dominate the conformational potential energy surface for triazane and TAA.

Triazane. Although triazane was synthesized about 15 years ago in the form of silver complex, $Ag_2(N_3H_5)_3^{2+}$, the literature on the neutral form is still rather sparse. The N–N bond length of the silver complex was found to be 1.60 Å by X-ray crystallography.[3] The present calculations give three stable conformers, all of which have N–N bond lengths of ca. 1.43 Å at the MP2/6-31G* level. A similar shortening was found[4] when *ab initio* calculations on cyclic N_3H_3 were compared with those of the corresponding silver complex.[4] Thus the central silver ion has the effect of lengthening the N–N bond. Figure 3 gives the geometries of the minima and transition states; the corresponding energies are given in Table I. Structure A is a minimum with C_1 symmetry and can be viewed as being derived from the C_3 form of TAA (see below) by substituting one of the NH_2 groups by hydrogen. The two other minima, B and C, are both of C_s symmetry. All three minima have only *gauche* interactions between adjacent lone pairs. Structures A and B are very close in energy at the HF/6-31G* and MP2/6-31G* levels (see Table I). Hence, G2 calculations were performed on both. As can be seen from Table I, A and B are within 0.5 kcal/mol at the G2 level, with B being slightly more stable.

The relationship between the minima and transition states can be seen in the potential surface shown in Figure 4. The energy is plotted as a function of the two dihedral angles between the central nitrogen lone pair and the terminal $-NH_2$ lone pairs. The plane of symmetry along one of the diagonals corresponds to interchange of the two identical terminal $-NH_2$ groups. The pronounced maximum at (0, 0) at the corners of the energy surface plot corresponds to an eclipsing interaction between lone pairs for both N–N bonds. The energy minima, A, A′ (the mirror image of A), B, and C occur near (±90°, ±90°), where all of the lone pair interactions are *gauche*. The low-energy transition states between the minima, ca. (±90°, ±180°) and (±180°, ±90°), correspond to an *anti* interaction between one set of lone pairs and a *gauche* interaction between the other set. The higher energy ridges separating the minima have one eclipsing interaction between lone pairs. Thus, the most prominent features of the triazane rotational potential energy surface can be understood in terms of the interactions that are present in the hydrazine rotational potential.

The two additional structures shown in Figure 3 are transition states for nitrogen inversion. The C_s structure has a symmetry plane through the N1N2N3H4 atoms and may be thought of as a transition state for inversion of the central nitrogen in A. The C_{2v} structure is the transition state for inversion of the central nitrogen in B. Trends in the inversion barriers are discussed below.

Triaminoammonia (TAA). No mention of this species has been found in the literature. Several possible high symmetry structures (D_{3h}, C_{2v}, C_3, C_{3v}, and C_{3h}) were chosen as targets for calculations. The D_{3h} and C_{2v} forms are high in energy and have several imaginary frequencies; hence, they were not pursued further. The optimized geometries of the C_3, C_{3v}, and C_{3h} structures are shown in Figure 5. The C_3 form is a minimum and has no imaginary frequencies. This conformer is taken as the ground state of TAA and is used in the thermochemical calculations discussed below.

The C_{3h} structure is a transition state and has a planar nitrogen framework. The imaginary frequency, 482*i* cm^{-1}, is a″ symmetry and corresponds to the inversion of the central nitrogen. The energy difference between the C_3 and C_{3h} forms is 10.9 kcal/mol at the HF/6-31G* level. The C_{3v} structure shown in Figure 5 is also a transition state. The a″ imaginary frequency, 340*i* cm^{-1}, corresponds to the synchronous rotation of the three amino groups. Figure 5 shows that the C_{3v} transition state with *anti* lone pairs has slightly longer N–N bonds than the C_3 ground state, but the C_{3h} inversion transition state has shorter N–N bonds. A corresponding change in the N–N bond length is seen in hydrazine (Figure 1). The *anti* conformation has a longer N–N bond, and the C_s inversion transition state has a shorter N–N bond. Triazane (Figure 3) shows analogous changes.

Inversion Barriers. Experimentally the barriers for ammonia and hydrazine have been determined to be 5.8[23] and 7.48[24] kcal/

---

[23] Swalen, J. D.; Ibers, J. A. *J. Chem. Phys.* **1962**, *36*, 1914.

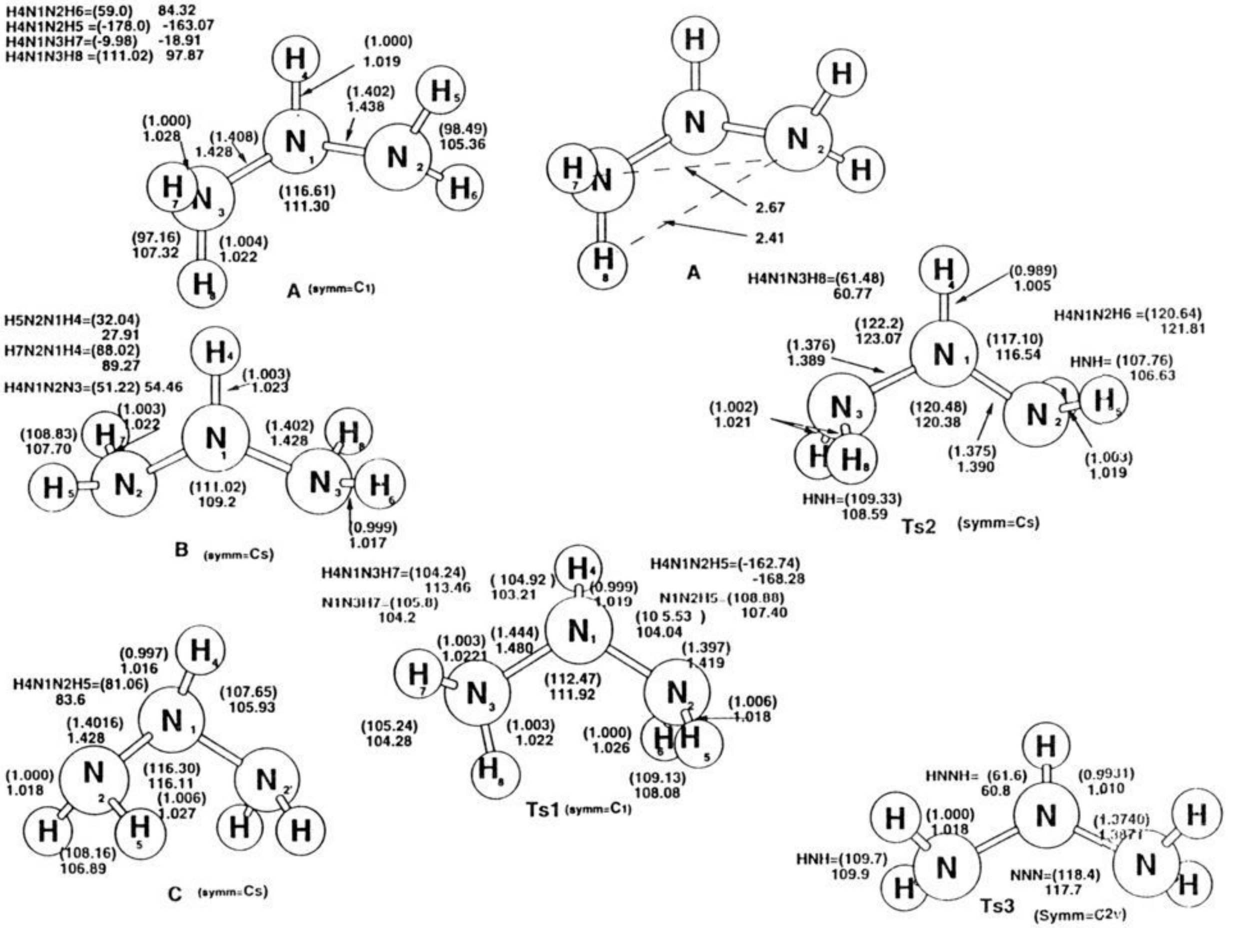


Figure 3. Structures and symmetries for various forms of N_3H_5. Notations are as described for Figure 1. The A, B, and C forms are energy minima, and Ts1 is a transition state for rotation of amino groups, while Ts3 and Ts4 are transition states for inversion of the central nitrogen of forms A and B, respectively.

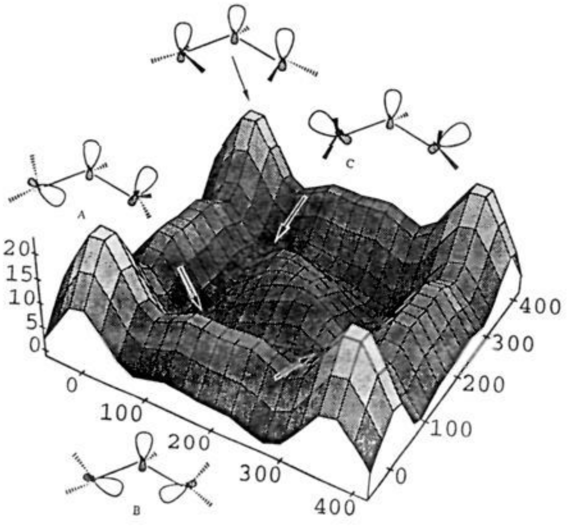


Figure 4. A potential surface of N_3H_5 using dihedral angles −60 to +420° The minima B and C (see Figure 3) are on the symmetry plane, A and its mirror image A′ on each side of the plane. The plot is obtained by use of the program *Mathematica*.

mol, respectively. No experimental values are available for N_3H_5 and N_4H_6. The calculated inversion barriers are listed in Table III. There is a small increase upon successive amination of the central atom. This can be compared to the series of methyl- and fluorine-substituted ammonia, which have been studied experimentally as well as computationally.[25] The inversion barrier is nearly constant in the series NH_3, NH_2CH_3, and $NH(CH_3)_2$ (ca. 5 kcal/mol), while $N(CH_3)_3$ has an inversion barrier of 7.5 kcal/mol. By contrast, the inversion barriers for the haloamines increase sharply with increasing substitution. The inversion barriers for NH_2F, NHF_2, and NF_3 are calculated to be 20.3, 41.7, and 67.3 kcal/mol, respectively (9s,5p + polarization[25]). Lehn[25] attributed the high inversion barrier for NH_2F to an increase in the N–F bond strength upon change in hybridization. Wolfe et al.[26] suggest the main source of destabilization is the four-electron/two-orbital interaction between the lone pairs on nitrogen and fluorine. The terminal nitrogens in the C_{3h} form of TAA and the C_1 form of triazane have lone pairs twisted away from the central N lone pair. Thus, the effect of four-electron/two-orbital repulsion should be considerably smaller for the amino-substituted species than for their fluorinated counterparts and more akin to the methyl-substituted amines, in agreement with the present study.

Stabilizing Interactions. Two possible sources of stabilization of these systems are hydrogen bonding and hyperconjugation. Compared to hydrazine, conformer A of triazane is stabilized by 1,3 hydrogen bonding between the hydrogens on one of the

---

[24] Hamada, Y.; Hirakawa, A. Y.; Tamagake, K.; Tsuboi, M. *J. Mol. Spectrosc.* **1970**, *35*, 420.

[25] (a) Eades, R. A.; Weil, D. A.; Dixon, D. A.; Douglass, C. H., Jr. *J. Phys. Chem.* **1981**, *85*, 976 and references cited therein. (b) Bach, R. D.; Raban, M. Theoretical Studies on Stereochemistry of Trivalent Nitrogen. In *Cyclic Organonitrogen Stereodynamics*; Lambert, J. B., Takeuchi, Y., Eds.; VCH Publishers: New York, 1992; Chapter 4. (c) Lehn, J. M. *Top. Curr. Chem.* **1970**, *15*, 311.

[26] Wolfe, S.; Mitchell, D. J.; Schlegel, H. B. *Can. J. Chem.* **1982**, *60*, 1291.

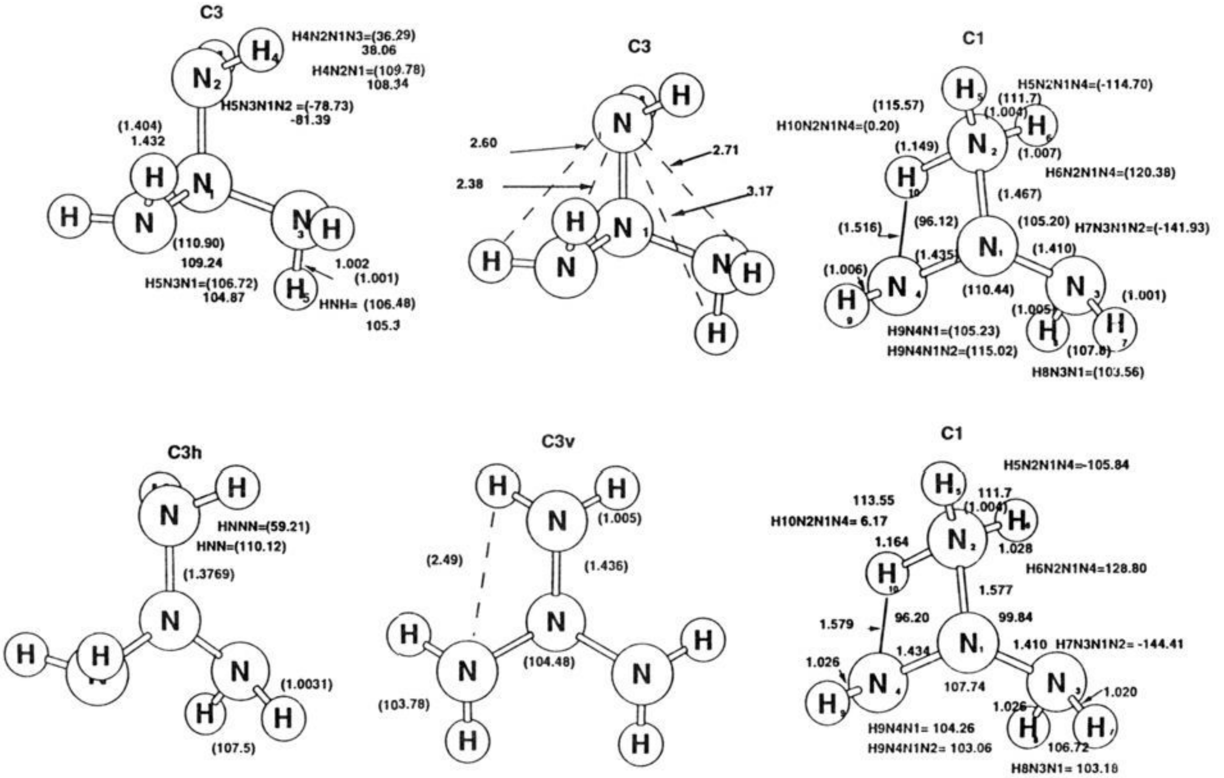


Figure 5. The C_3 energy minimum of TAA, a C_{3h} transition state for its inversion, a C_{3v} transition state for rotation of all amino groups, and a C_1 transition state for a 1,3 hydrogen shift. Notation is as in Figure 1. The dotted lines on the central drawings indicate nonbonded N–H distances. See discussion of hydrogen bonding.

Table III. Inversion Barriers for NH_3, N_2H_4, N_3H_5, and N_4H_6

system	inversion barrier (kcal/mol)	comment
NH_3	6.51	HF/6-31G*
	6.61	MP2/6-31G*
	5.8	experimental value (ref 22)
N_2H_4	6.17	HF/6-31G* (ref 20)
	6.26	MP2/6-31G** (ref 20)
	7.48	experimental value (ref 20)
N_3H_5	7.52, 12.74	HF/6-31G* (present work)[a]
	8.90, 7.91	MP2/6-31G* (present work)[a]
N_4H_6	10.9	HF/6-31G* (present work)

[a] Barriers for A → Ts2 and B → Ts3, respectively.

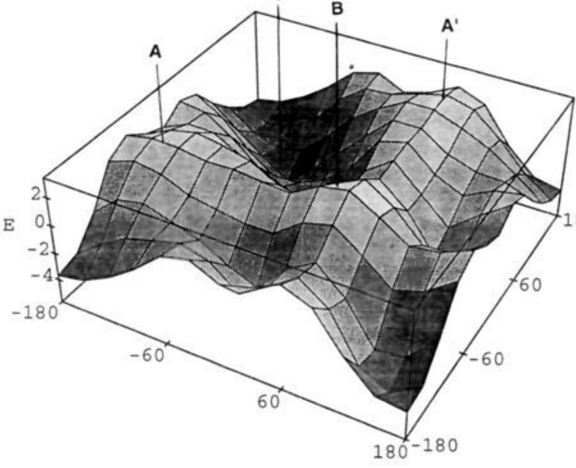


Figure 6. A difference potential plot (hydrazine–triazane). Positive energy values mean stabilization (in kcal/mol) of triazane over hydrazine.

terminal amino groups and the lone pair on the other. This is a bifurcated hydrogen bond with N–H distances of 2.41 and 2.67 Å. Conformations B and C of triazane are not stabilized by hydrogen bonds because of unfavorable alignment of the lone pairs relative to the N–H bonds. Triaminoammonia is ideally set up to take advantage of hydrogen bonding. A network of three bifurcated hydrogen bonds stabilizes the C_3 conformation. The N–H distances, 2.38 and 2.60 Å, are very similar to those of conformer A of triazane. The other nonbonded N–H distances are not hydrogen bonded because of improper orientation of the lone pairs relative to the N–H bonds.

Hyperconjugation between the nitrogen lone pair and adjacent σ^* orbitals can also stabilize certain conformations. In hydrazine, hyperconjugation between the lone pairs and the inner N–H bonds stabilizes the *gauche* conformation and lengthens the inner N–H bonds. In triazane, the lone pairs can interact with either N–N or N–H bonds. In A, the N1–N2 bond *anti* to the lone pair on N3 is 0.010 Å longer. However, hyperconjugation with N–H bonds appears to be favored over that with N–N bonds. Conformer B has two hyperconjugative interactions with the central N–H but none with the N–N bonds; its energy is the same as that of A even though it has no hydrogen bonds to stabilize it.

To probe the conformational dependence of the stabilizing interactions, the rotational potential energy surface of triazane was compared to that of hydrazine. Figure 6 is a difference plot constructed by subtracting the triazane surface (Figure 4) from the sum of two hydrazine potentials given in Figure 2. Positive values indicate stabilizing interactions. As discussed above, conformer A and its mirror image, A′, are stabilized by hydrogen bonding. Conformer B is stabilized by hyperconjugation. Other conformations, including C, are not stabilized or are somewhat destabilized.

Vibrational Spectra. The vibrational spectra for the lowest energy conformations of hydrazine, triazane (A with C_1 symmetry and B with C_s symmetry), and TAA (C_3 symmetry) have been calculated at the MP2/6-31G* level and are listed in Table IV. Because of basis set effects and neglect of anharmonicity, the

Table IV. Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for the Most Stable Forms of Hydrazine (C_2 Symmetry), Triazine (Isomer A with C_1 Symmetry and isomer B with C_s Symmetry), and TAA (C_3 Symmetry) at the MP2/6-31G*//MP2/6-31G* Level

hydrazine			triazine		triazine B			TAA A		
mode	frequency[a]	int	frequency	int	mode	frequency	int	mode	frequency	int
a	427 (377)	61	217	83	a''	152	18	a	195	99
a	894 (780)	64	362	17	a'	268	74	e	296	15
b	1082 (937)	124	510	34	a'	551	20	a	508	2
a	1169 (1098)	21	828	19	a'	841	38	e	509	37
b	1343 (1283)	10	935	138	a''	858	30	a	844	11
a	1381 (1324)	4	1076	101	a'	1047	154	e	979	116
b	1737 (1587)	9	1142	35	a''	1140	76	a	1132	3
a	1750 (1628)	24	1261	39	a'	1232	2	e	1257	62
b	3486 (3297)	21	1302	14	a''	1324	1	e	1333	21
a	3492 (3726)	4	1394	7	a'	1388	6	a	1443	12
a	3615 (3325)	2	1546	2	a''	1534	4	e	1720	22
b	3619 (3390)	7	1722	14	a''	1715	10	a	1731	40
			1756	19	a'	1743	13	a	3364	32
			3444	7	a'	3431	22	e	3382	4
			3473	7	a'	3473	8	a	3573	2
			3522	2	a''	3574	7	e	3574	4
			3592	1	a'	3612	0			
			3607	2	a'	3613	2			

[a] Numbers in parentheses are experimental frequencies taken from ref 20.

calculated frequencies can be expected to be 5–10% higher than the experimental values, as is seen for the case of hydrazine where the experimental spectrum is included. The low-frequency part of the spectra (less than 500 cm^{-1}) may be identified as rotation of the $-NH_2$ groups, while the bands in the region 835–980 cm^{-1} are associated with distortions in the nitrogen framework of the molecules. In the TAA spectrum, the a frequency of 1132 cm^{-1} is a $-NH_2$ wagging mode, while the rest of this region is rather complex to interpret. The bands in the 3430–3620-cm^{-1} range are N–H stretching modes. In the triazane (B) spectrum, the a' frequency at 3431 cm^{-1} is associated with the hydrogen on the central nitrogen. The higher frequency N–H stretches arise from N–H bonds *gauche* to lone pairs, while the lower frequency N–H stretches come from N–H bonds *anti* to lone pairs. The latter is related to the Bohlmann band effect seen in alkylamines[27] and can be attributed to hyperconjugative interactions between a σ^* orbital and an *anti* lone pair. The five highest frequencies of form A of triazane are the N–H stretching frequencies. The 3522-cm^{-1} frequency can be assigned to the central N–H bond and is shifted 90 cm^{-1} from the more strongly hyperconjugated B form. Hydrogen bonding can also perturb vibrational frequencies, but unfortunately, it is not easy to assess the importance of hydrogen bonding from these spectra because of the interference from hyperconjugative effects, and in general, the shifts in the N–H stretching frequencies due to hydrogen bonding are expected to be less than 100 cm^{-1}.[28] Form A of triazane has two terminal N–H bonds that are hydrogen bonded and two that are not hydrogen bonded. The 3473- and 3607-cm^{-1} frequencies may be assigned to N2–H bonds, whereas the 3444- and 3592-cm^{-1} bands correspond to the hydrogen-bonded N3–H bonds.

Thermochemistry and Energetics. The heats of formation for the N_nH_{n+2} series can be computed from atomization energies or directly as the heat of reaction for the formation from N_2 and H_2.

$$\frac{n}{2}N_2 + \frac{n+2}{2}H_2 \rightarrow N_nH_{n+2} \qquad (1)$$

$$N_nH_{n+2} \rightarrow nN + (n+2)H \qquad (2)$$

The results are shown in Table II. Not unexpectedly, the HF/6-31G* and MP2/6-31G* levels are quite inadequate for these nonisodesmic reactions. The G2 level is sufficiently accurate to give consistent results for $\Delta H_f°$ computed from the atomization and formation reactions. These results are in good agreement with the experimental $\Delta H_f°$ values for ammonia and hydrazine. The G2 values should also be within ±2 kcal/mol of the, as yet undetermined, experimental $\Delta H_f°$ values of triazane and TAA.

The thermodynamic stability of triazane and TAA can be judged from the following isodesmic bond separation reactions:

$$N_3H_5 + NH_3 \rightarrow 2N_2H_4 \qquad \Delta H = 17.4 \text{ kcal/mol}$$

$$N_4H_6 + NH_3 \rightarrow N_3H_5 + N_2H_4 \qquad \Delta H = 9.6 \text{ kcal/mol}$$

$$N_4H_6 + 2NH_3 \rightarrow 3N_2H_4 \qquad \Delta H = 27.0 \text{ kcal/mol}$$

The interaction of two N–N bonds (or equivalently, the two terminal $-NH_2$ groups) in triazane is stabilizing by 17.4 kcal/mol. Adding a third N–N bond to form TAA is stabilizing by an additional 10 kcal/mol. Thus triazane and TAA are thermodynamically stable relative to hydrazine. This is the result of the hydrogen bonding and hyperconjugation discussed above.

Kinetic stability is somewhat harder to assess. Possible channels for unimolecular decomposition include N–H and N–N bond cleavage, H_2 elimination, and NH_3 elimination:

$$\begin{aligned} N_nH_{n+2} &\rightarrow N_nH_{n+1} + H \\ &\rightarrow N_{n-1}H_n + NH_2 \\ &\rightarrow N_nH_n + H_2 \\ &\rightarrow N_{n-1}H_{n-1} + NH_3 \end{aligned}$$

The N–H bond strength in NH_3 is 92 kcal/mol; similar values can be expected for hydrazine, triazine, and TAA. The average N–N bond strengths in N_nH_{n+2} at the G2 level of theory are as follows:

$$N_2H_4 \rightarrow 2NH_2 \qquad \Delta H = 64.3 \text{ kcal/mol}$$

$${}^1/_2N_3H_5 \rightarrow NH_2 + {}^1/_2NH \qquad \Delta H = 65.8 \text{ kcal/mol}$$

$${}^1/_3N_4H_6 \rightarrow NH_2 + {}^1/_3N \qquad \Delta H = 58.7 \text{ kcal/mol}$$

Thus, neither N–H nor N–N bond dissociation offers a low-energy pathway for unimolecular decomposition.

---

[27] (a) Bohlmann, F. *Angew. Chem.* **1957**, *69*, 641. (b) Bohlmann, F. *Chem. Ber.* **1958**, *91*, 2157. (c) Wolfe, S.; Schlegel, H. B.; Whangbo, M.-H. *Can. J. Chem.* **1974**, *52*, 3787.

[28] See, for example: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980.

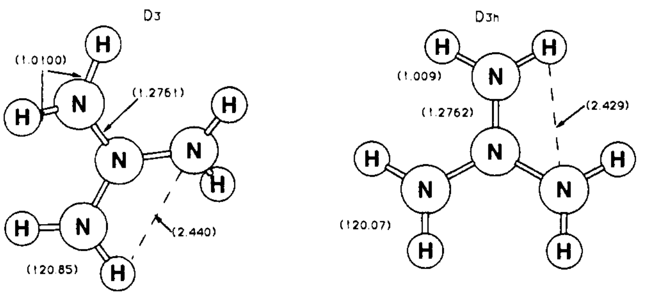
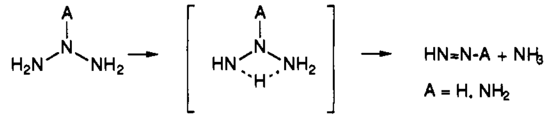


Figure 7. Structure of $N(NH_2)_3^{++}$ from HF/6-31G** optimizations. The D_3 form has an out-of-plane dihedral NNNN angle of 17.6° and is the ground state; D_{3h} is a transition state for inversion.

The 1,1 elimination of H_2 from any of the terminal $-NH_2$ groups leads to a high-energy nitrene. A 1,3 H_2 elimination would also yield a high-energy isomer. A 1,2 elimination of triazane gives a thermodynamically stable imine, but it is known from other systems that 1,2 H_2 eliminations have high barriers. This is confirmed by the fact that hydrazine is kinetically stable with respect to decomposition into HN=NH and H_2. Likewise, 1,2 elimination of NH_3 to form a nitrene can be ruled out in triazane and TAA because $N_2H_4 \rightarrow NH + NH_3$ is not observed. Thus H_2 elimination and 1,2 elimination are probably not viable low-energy routes for unimolecular decomposition.

One potential pathway for decomposition that is available for triazane and TAA but not for hydrazine is 1,3 elimination of NH_3:



At the MP2/6-31G* level, this process has a barrier of 52.5 kcal/mol for TAA. This may be compared to other 1,3 hydrogen shifts in closed-shell molecules (e.g. 87.6 kcal/mol barrier for $CH_2CHOH \rightarrow CH_3CHO$[29]). Thus, there appears to be no low-energy channels for the unimolecular decomposition of triazane and TAA that are not also available for hydrazine. Triazane and TAA are therefore predicted to be similar to hydrazine in terms of kinetic stability toward unimolecular decomposition.

The TAA Dication. The neutral form of TAA adopts a C_3 symmetry conformation to minimize the lone pair repulsions and maximize the stabilizing interactions. Another means of greatly enhancing the stability of TAA is the removal of two electrons to form the dication. Calculations show the system adopts a planar nitrogen framework and has D_3 symmetry. The D_{3h} structure represents a transition state for synchronous rotation of the amino groups and has an imaginary frequency of 268i cm^{-1} (a_1'' symmetry). The geometries of the D_3 and D_{3h} forms are very similar and differ in energy by only 0.6 kcal/mol. The N–N bond in the dication is considerably shorter than in the neutral complex and is comparable to an N–N double bond. See Figure 7.

Table V. Conformational Preference for Some $X(XH_2)_3$ Systems from Theoretical Calculations

X	charge	geometry	symm	ref
B	0	triply twisted	D_{3h}	14
	2–	planar	D_{3h}	14
C	2+	planar	D_{3h}	13
	0	planar (triplet)	D_{3h}	10
	2–	planar carbon framework	C_s	35
N	2+	planar nitrogen framework	D_3	this work
	0	pyramidal nitrogen framework	C_3	this work

Table V shows the conformational preferences for a number of systems of the general formula $X(XH_2)_3$ as predicted by theoretical calculations. These serve as model systems for testing theories such as Y-delocalization and Y-aromaticity. The trimethylmethane diradical has been identified as a reaction intermediate;[30] a derivative of the corresponding dication (tris(tropylidene)methane dication) has been reported,[31] and lithium-stabilized salts of the dianion have been prepared[32] (the nature of the counterion may effect the geometry[33]). Other systems in this series have not been identified experimentally. Even though the Y-aromaticity effect for trimethylmethane dianion is negligible[34] or nonexisting, it is worth noting that TAA^{2+} belongs to the class of $(4n + 2)$ π-electron cross-conjugated systems with four p_π orbitals predicted to be thermodynamically preferable to any linear isomer.[35] The question of Y-aromaticity of TAA^{2+} will be discussed in a later work.

Summary

The unknown systems triazane and triaminoammonia (TAA) have been found to be stabilized by hyperconjugation and hydrogen bonding. Structural details and calculated vibrational spectra confirm this. They are both thermodynamically stable relative to hydrazine. Consideration of various possible pathways for decomposing leads to the conclusion that both systems are promising candidates for synthesis.

Acknowledgment. A.S. thanks the Norwegian Research Council for Science and Humanities for granting computer time at the SINTEF Supercomputer Center and for the possibility of visiting Wayne State University. This work was in part carried out during a stay there, and A.S. extends thanks for the facilities placed at her disposal during her stay.

---

(29) Poirier, R. A.; Majlessi, D.; Zielinski, T. J. *J. Comput. Chem.* **1986**, *7*, 464.

(30) Dowd, P. *J. Am. Chem. Soc.* **1966**, *88*, 2587.

(31) Mizumoto, K.; Kawai, H.; Okada, K.; Oda, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 916.

(32) Klein, J.; Medlik, A. *J. Chem. Soc., Chem. Commun.* **1973**, 275.

(33) Wilhelm, D.; Dietrich, H.; Clark, T.; Mahdi, W.; Kos, A. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 7299.

(34) Gobbi, A.; MacDougall, P. J.; Frenking, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1001. See also ref 12.

(35) Inagaki, S.; Hirabayashi, Y. *Chem. Lett.* **1982**, 709.