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STRUCTURES AND ENERGY CONTENT OF THE POSSIBLE HIGH-ENERGY MATERIAL N_5H_3 AND THEIR NITRO DERIVATIVES

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Abstract

Substances with high nitrogen content are common targets for new high-energy materials. Here we present calculations on the minimum-energy structures of the polycyclic N_5H_3 molecule, including vibrational spectra, enthalpies of formation, and proton affinities. Because many high-energy materials contain nitro groups, we also sequentially replaced the H atoms in the parent molecule with NO_2 groups and determined enthalpies of formation and subsequent enthalpies of decomposition.

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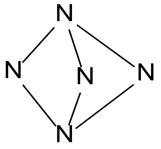
Introduction

The search for new high-energy (HE) materials is ongoing.[1] There are several criteria for good HE materials, including fast decomposition, formation of gaseous products, and relative instability with respect to decomposition or combustion products.[2] Another tactic has been to consider systems that have a high nitrogen (N) content, as the expected product of the decomposition, N_2, is very stable. There have been several high-profile presentations of newly-synthesized compounds with high nitrogen content, including azidotetrazolate (CN_7^-) salts,[3] azobis(tetrazole) (C_2N_{10}),[4] the pentanitrogen cation (N_5^+) salts,[5] and dinitraminotetrazole ($CH_2N_8O_4$).[6] We note that these are compounds that have actually been isolated, and we do not include reports of polynitrogen cluster ions as detected at very low temperatures by, for example, mass spectrometry.[7]

Even with the isolation of these compounds, there are still some simple nitrogen-containing molecules that have not been experimentally characterized or even, apparently, studied. For example, we reported on the structures and energetics of tetrazane, N_4H_6,[8] tetrazetidine, c-N_4H_4,[9] and triazene, N_3H_3.[10] Borrowing from the structure of the smallest propellane, [1.1.1]propellane, or C_5H_6,[11,12] we propose the following backbone for a new molecule that heretofore has not been reported:



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One difference from [1.1.1]propellane is the absence of an axial N-N bond. Another difference is that nitrogen is trivalent, so only one hydrogen atom would be bonded to the equatorial nitrogen atoms, while the axial nitrogen atoms are already trivalent in **1**. However, because the N atoms are still nominally sp^3-hybridized, the hydrogen atoms and lone electron pairs on the equatorial nitrogen atoms can point in different directions three-dimensionally, leading to the possibility of stereoisomerism for a molecule whose formula is simply N_5H_3.

Here, we present a computational study of N_5H_3, based on the structure shown above, which has the IUPAC name bicyclo[1.1.1] pentaazane.[13] Minimum-energy geometries, vibrational frequencies, and the energetics of several reactions were determined, ultimately using the G4 compound computational method. Finally, because many high-energy materials contain nitro ($-NO_2$) groups, we also determined the enthalpies of formation and decomposition of the nitro, dinitro, and trinitro derivatives of the parent molecule. For these molecules, we focused on the energy properties rather than performing a more detailed analysis as we did for the parent molecules.

Computational Details

A total of eight different stereoisomers for N_5H_3 were set up using the GaussView graphical interface,[14] which was also used for visualizing the results. The stereoisomers differed by the directions the hydrogen atoms pointed in the initial geometries. Those stereoisomers were subjected to geometry optimization and frequency calculations using Gaussian09[15] on a desktop personal computer. Here, we performed Hartree-Fock calculations using the Pople-style 6-31+G basis set.[16] No constraints were placed on the geometry optimization. The lack of imaginary vibrational frequencies confirmed that the molecules were at a minimum-energy structure.

Upon analysis of the results, we found that all eight initial stereoisomers converged into one of only two minimum-energy stereoisomers. These two stereoisomers were then subjected to geometry optimization and energy determination using the compound G4 method[17] which as a stated mean absolute deviation of 0.83 kcal/mol (3.47 kJ/mol) for the benchmark set of molecules. For these calculations, we used the same version of Gaussian[18] on the systems of the Ohio Supercomputer Center in Columbus, Ohio. For these higher-level calculations, for increased computational efficiency, symmetry was imposed on the structures in that all equivalent bond lengths and angles were defined with the same values. From the data calculated, we determined the enthalpies of formation of the two stereoisomers of N_5H_3, the value of which has the opposite sign as the enthalpy of decomposition. Given the unusual nature of this molecule, we also calculated the first and second proton affinities by determining the structures and energies of $N_5H_4^+$ and $N_5H_5^{2+}$, where the axial nitrogen atoms and equatori-

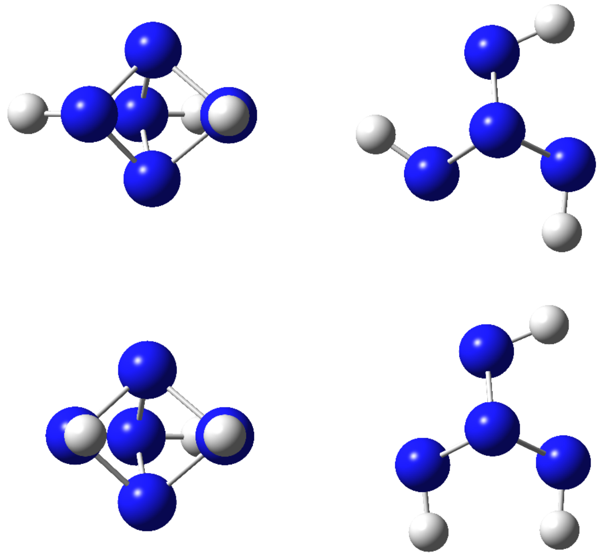

Figure 1. The two minimum structures of bicyclo[1.1.1]pentaazane, viewed equatorially (left) and axially (right) (a) The C3 stereoisomer. (b) The CS isomer.

al nitrogen atoms were protonated sequentially. Axial/equatorial protonations were not considered to minimize the number of possible permutations.

Results and Discussion

Optimized Structures

Figure 1 shows equatorial and axial views of the two minimum-energy geometries that N_5H_3 adopts. In this section, we will refer to the three equatorial nitrogen atoms as N_{eq}, while the two axial nitrogen atoms will be labeled as N_{ax}. The top structure, Figure 1(a), has the N-H bonds all pointing in the same (nominally clockwise) direction and has C_{3h} symmetry, so we will refer to this as the C3 structure. The bottom structure, Figure 1(b), has one N-H bond pointing in the opposite direction as the other two bonds and has C_s symmetry, so we will refer to this as the CS isomer (not Cs, for obvious reasons). The molecules have been oriented in a similar fashion so that differences between the structures are more visible. It is clear that the C3 structure has three-fold symmetry (and indeed, is reminiscent of a classical triskelion); however, in the CS structure the three-fold symmetry of the equatorial nitrogen atoms is absent. An examination of the molecular orbitals and electron density maps confirms that there is insignificant bonding between the equatorial nitrogen atoms.

Table 1 lists the structural parameters of the two stereoisomers. Because the C3 structure has higher symmetry, it has fewer independent bonding parameters than the CS structure. The bonding parameters give a hint of how relatively stable these molecules might be, in particular the bond angles: N_{eq}-N_{ax}-N_{eq} bond angles of less than 90°, and N_{eq}-N_{eq}-H bond angles of greater than 135°, are significantly outside the range of normal bond angles for an sp^3-hybridized nitrogen atom and suggest significant angle strain energy in the molecules.

The structural parameters for both stereoisomers are similar, but as expected the CS isomer shows some variation depending on the

Table 1. Structural and Other Parameters of the Two Stereoisomers of Bicyclo[1.1.1]pentaazane. Distances in Å, angles in degrees.

Structural Parameter	C3 Value	CS Values
r(N_{eq}-N_{ax})	1.513	1.515
r(N-H)	1.030	1.029(05), 1.029(29)
a(N_{eq}-N_{ax}-N_{eq})	85.18	81.54, 85.27, 88.74
a(N_{ax}-N_{eq}-N_{ax})	77.21	77.08(508), 77.08(510)
a(N_{eq}-N_{eq}-H)	140.4	142.31, 142.52, 145.91
r(N_{eq}-H····N_{eq})	2.142	2.154, 2.272
Relative energy	0	0.01113 h (29.2 kJ/mol)
Dipole moment, D	0	2.55

Table 2. Vibrational frequencies (in cm^{-1}, unscaled), infrared absorption intensities (in km/mol), and approximate descriptions of the normal modes of bicyclo[1.1.1]pentaazane.

C3 stereoisomer*

Frequency	Intensity	Approx Desc
683.1†	23.0	sym in-plane N-H wag
754.9†	0	asym N_{eq}-N_{eq}-N_{eq} str
762.2	0.6	N_{ax}-N_{eq} str
791.1†	0.4	asym N_{eq} bend
975.5	0	N_{eq} breathe[a]
1174.9	0	N_{ax}-N_{ax} str + sym N-H wag
1248.3	0	sym in-plane N-H wag
1262.4	95.7	sym out-of-plane N-H wag
1311.1†	0	asym out-of-plane N-H wag
1311.6†	77.2	asym in-plane N-H wag
3344.2	0	sym N-H str
3351.6†	1.4	asym N-H str

*Doubly degenerate frequencies are labeled with a † on the frequency value.

CS stereoisomer

Frequency	Intensity	Approx Desc
701.8	17.2	asym in-plane N-H wag
716.7	5.9	H-N-N-H bend
740.4	4.4	asym out-of-plane N-H rock
745.8	22.1	N_{eq}-N_{eq} str + N-H wag
746.0	1.9	asym N_{eq}-N_{ax}-N_{eq} str
762.3	<0.1	N_{ax}-N_{eq} str
792.7	0.6	asym N_{eq}-N_{eq}-N_{eq} str
972.4	0.3	N_{eq} "ring" breathe[a]
1174.8	1.3	N_{ax}-N_{ax} str + sym N-H wag
1199.4	80.3	asym in-plane N-H wag
1203.1	7.0	asym out-of-plane N-H wag
1286.9	21.5	asym out-of-plane N-H wag
1325.5	79.8	asym in-plane N-H wag
1334.1	48.2	sym out-of-plane N-H wag
1356.1	2.3	asym in-plane N-H wag
3335.8	3.2	N-H str
3355.1	3.9	asym N-H str
3374.3	1.3	N-H str

[a] Although this mode has the three equatorial N atoms moving in and out symmetrically, the atoms are not bonded to each other and so do not constitute a true ring in the structure of the molecule.

relative orientations of the N-H bonds. To six decimal points, the N-N bond distances are the same (hence the listing of only one value). The N-H bond distances are very close, varying only in with the fourth decimal place (as indicated by the numbers in the parentheses). Interestingly, the shorter N-H bond belongs to the hydrogen atom that can interact with the lone electron pair of the adjacent N atom, which one might think would influence that bond length due to intramolecular hydrogen bonding. The axial-equatorial-axial N-N-N bond angles are also very similar, varying only with the third decimal place (in parentheses). The largest deviations in this structure relate to the placement of the N and H atoms in the equatorial plane of the molecule, as shown by the equatorial-axial-equatorial N-N-N bond angles and the N-N-H bond angles (as measured using equatorial atoms only). The smallest N-N-N bond angle is between the two equatorial N atoms whose N-H bonds are pointing away from each other, while the largest N-N-N bond angle is between the equatorial N atoms whose N-H bonds are pointing toward each other. Similarly, the N-N-H bond angle (measured with respect to two adjacent equatorial nitrogen atoms) is smallest, paradoxically based on its bond length for the N-H bond that might be participating in intramolecular hydrogen bonding, while the two larger N-N-H bond angles are for the two hydrogen atoms that are in proximity to each other, perhaps slightly repelling each other.

Table 1 also lists the nonbonding N_{eq}-H···N_{eq} bond distances in each isomer. In the C3 isomer, this distance is 2.142 Å (for the two N-H bond pointing toward the adjacent N atom) and 2.272 Å (for the two N-H bonds pointing towards each other). The fact that the latter two N-H bonds are longer than the other N-H bonds (including in the C3 isomer) is due to the distortion of the N_5 backbone of the CS isomer, which reduces any interatomic repulsions that might constrain the bonds. The fact that the former N-H bond is shorter than the other two, despite the proximity of an electronegative N atom, opposes the argument of an intramolecular hydrogen bond. By definition, a hydrogen bond is expected to lengthen an X-H bond,[19] and this is not the case here.

Finally. Table 1 lists the relative energies of the two isomers, indicating that the CS isomer is 0.01113 h (29.2 kJ/mol) higher than the C3 isomer. While it can be argued (see above) that intramolecular hydrogen bonding is not a contributing factor, it is probable that the proximity of two hydrogen atoms in the CS conformer raises the total energy over that of the C# conformer.

Vibrational Frequencies

Vibrational frequency determinations indicate that both of these structures are minimum-energy geometries, by virtue of all-positive frequencies. The two stereoisomers will have significantly different infrared and Raman spectra, however, because of the different symmetries of the structures. The C3 isomer has C_{3h} symmetry, with the two axial N atoms defining the C_3 rotational symmetry axis. The vibrations of the C3 isomer transform as

$$\Gamma = 4A' \oplus 2A'' \oplus 4E' \oplus 2E'' \qquad \text{in } C_{3h} \qquad [1]$$

with the A" and E' modes being infrared-active, yielding 6 nonzero infrared absorptions. On the other hand, the vibrations of the CS isomer transform as

$$\Gamma = 12A' \oplus 6A'' \qquad \text{in } C_s \qquad [2]$$

with all of the modes being infrared-active, giving 18 nonzero infrared absorptions. Table 2 lists the (unscaled) calculated vibrational frequencies and infrared intensities for the two isomers, along with a rough description of the modes. Some similar frequencies have similar descriptions, as expected, but the different N-H molecular environments yield a richer frequency pattern involving those atoms in the CS isomer than the C3 isomer.

Table 3. Energy changes for various standard reactions of N_5H_3. All values in kJ/mol unless otherwise specified.

Reaction	C3 Isomer	CS Isomer
ΔH_f	916.8	1020.7
ΔH_{dec} kJ/g	12.2	13.6
ΔH_{comb}	-1345.5	-1449.4
PA1, N_{ax}	756.7	
PA2, N_{ax}	193.3	
PA1, N_{eq}	769.8	
PA2, N_{eq}	222.7	

Table 3 lists the energy changes for various processes involving these molecules. A fundamental thermodynamic property of any substance is the enthalpy of formation, which was calculated using the G4 enthalpies of all species in this reaction and employing a "products-minus-reactants" approach:

$$5N(g) + 3H(g) \rightarrow N_5H_3(g) \qquad [3]$$

This energy change was then corrected for the enthalpies of formation for the N and H atoms, taken from the NIST Chemistry Webbook website.[20] The resulting overall chemical reaction was

$$5/2\ N_2(g) + 3/2\ H_2(g) \rightarrow N_5H_3(g) \qquad [4]$$

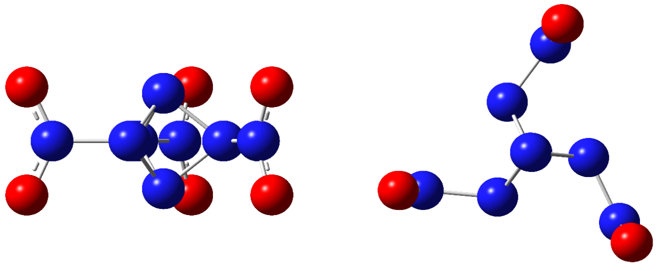

Figure 2. Side and top views of trinitrobicyclo[1.1.1]pentaazane.

which is the formation reaction for N_5H_3.

The enthalpy of formation of the C3 isomer is calculated to be +916.8 kJ/mol, a very large positive number and consistent with the fact that the molecule has significant angle strain. The enthalpy of formation of the CS isomer is slightly higher, at 1020.7 kJ/mol. This is attributed to the additional steric strain of having two of the N-H bonds in proximity of each other, causing a slight amount of repulsion and contributing even more to the angle strain of the nitrogen backbone. These numbers imply that there may be a significant hurdle for synthesis of these substances, but this is only one factor; kinetic factors will also influence their isolability.

The formation reactions are also the reverse decomposition reactions for these two molecules, so the enthalpies of decomposition are simply the negatives of the ΔH_f values. One metric for HE materials is the specific enthalpy of decomposition, which is the energy change per unit mass. Table 3 lists specific enthalpies of decomposition of 12.2 and 13.6 kJ/g for the two isomers, a significant value. Because N_5H_3 has no oxygen atoms, if it were combusted instead of decomposed, an external source of oxygen would have to be supplied. The presumed reaction is

$$N_3H_5 + 5/2\ O_2 \dashrightarrow 3/2\ N_2 + 5/2\ H_2O(l) \qquad [5]$$

The resulting enthalpies of combustion are also listed in Table 3. These numbers may appear large, but at a specific combustion enthalpy of about 17.9 kJ/g, they are small compared to values for even simple hydrocarbons, which for CH_4 is about 50 kJ/g.[20] One reason for the similarities in enthalpies of decomposition and combustion is because of the high nitrogen content, as only the hydrogen atom content contributes any difference between the two processes (forming H_2O instead of H_2).

As a basic measure of the chemical reactivity of these molecules, we also calculated the first and second proton affinities (PA) of the C3 stereoisomer using the gas-phase reactions

$$N_3H_5 + H^+ \dashrightarrow N_5H_4^+ \qquad [6]$$

$$N_5H_4^+ + H^+ \dashrightarrow N_5H_5^{2+} \qquad [7]$$

For the first PA, there are different N-atom environments to probe, an equatorial N site and an axial N site. For the second PA, however, there are several different possibilities for a second protonation site. To simplify our calculations, we only calculated a second PA for protonation at the same type of site as the original protonation; hence, the PA2 values are either for protonation at two axial N atoms or two equatorial N atoms. Table 3 gives PA1 values of 756.7 and 769.8 kJ/mol for the axial and equatorial N atoms, respectively, showing that protonation at an equatorial nitrogen atom is slightly preferred energetically. As a comparison, the proton affinities of NH_3 and CH_3OH are 853.6 kJ/mol and 754.3 kJ/mol, respectively[20], so these calculated values are not out of expectation for a molecule that has a lone electron pair on a relatively electronegative atom. As expected, the second proton affinity, PA2, is significantly lower, as in this case the reaction is the attachment of a cation to a cation. When both added protons are in the axial position, PA2 has a value of 193.3 kJ/mol, which as expected is a substantial drop from PA1. For comparison, the lowest (first) proton affinity is for the He atom, whose PA is 177.8 kJ/mol.[20] When both protons are in the equatorial position, PA2 has a value of 222.7 kJ/mol, indicating again that the preferred site of protonation is at the equatorial nitrogen atom. Although we would have thought that steric effects between the hydrogen atoms might make a second protonation at this site less energetically favorable, a study of the geometry shows that the protonations actually decrease the bond angles around the nitrogen atom, likely decreasing the strain energy slightly. Also, the intramolecular hydrogen-hydrogen distance actually increases for the doubly-protonated molecule. In the CS stereoisomer, the proximal H--H distance is 1.973 Å, whereas when doubly protonated at adjacent equatorial nitrogen atoms, the proximal H--H distance is 2.183 Å.

Nitrobicyclo[1.1.1]pentaazanes

Starting with the C3 isomer, the hydrogen atoms in N_5H_3 were sequentially replaced with NO_2 groups to generate the nitro, dinitro, and trinitro derivatives of bicyclo[1.1.1]pentaazane. Given the symmetry of the parent molecule, there exists only one of each derivative, making the pattern of NO_2 substitutions unambiguous; hence, we will simply refer to them as the nitro, dinitro, and trinitro derivatives.

Rather than showing all three derivatives, Figure 2 shows a top and side view of just the trinitro derivative, which shows the general structure that is representative of all three derivatives. The nitro groups all adopt a position parallel to the principal rotational axis as a way of avoiding steric interference; the same orientation is seen in the nitro and dinitro derivatives. Table 4 lists some of the structural parameters of the trinitro derivative and some comparisons to the parent molecule. While the structural parameters are similar, the overall geometry of the N_5 central cluster shows that it has distorted a bit, with the distance between the axial nitrogen atoms increasing a bit while the distance between equatorial nitrogen atoms decreases a bit. The largest deviation between the two structures is the angle that the third nitrogen bond makes to the equatorial N-N bond. In N_5H_3, the N_{eq}-N_{eq}-H bond angle is 140.8°, while the N_{eq}-N_{eq}-NO_2 bond angle is 150.2°, significantly larger but likely due to the larger van der Waals radii of the N and O atoms in the nitro group.[21]

Table 4. Structural parameters of trinitrobicyclo[1.1.1]pentaazane, with some comparisons to the C3 parent molecule. Distances in Å, angles in degrees.

Structural Parameter	Trinitro Value	C3 Value
r(N-N)	1.515	1.513
r(N-NO_2)	1.510	---
a(N_{eq}-N_{ax}-N_{eq})	83.54	85.18
a(N_{ax}-N_{eq}-N_{ax})	79.45	77.21
a(N_{eq}-N_{eq}-X)	150.2	140.4
r(N_{ax}---N_{ax})	1.937	1.888
r(N_{eq}---N_{eq})	2.019	2.047

Table 5 lists selected thermodynamic properties of all three nitro derivatives. The enthalpies of formation were determined in the same way as for the parent molecules, using atomization reactions and correcting the calculated enthalpy change for the enthalpy of formation of the atoms.Adding a single nitro group increases the enthalpy of formation by about 95 kJ/mol from the parent molecule although subsequent substitution of additional NO_2 groups increases the ΔH_f by a lesser amount. Because the oxygen balance of all three nitro derivatives is positive, there is no combustion reaction different from the decomposition reaction, which is thus equal to the negative of the enthalpy of formation. As such, Table 5 only lists the specific enthalpy of decomposition, in units of kJ/g and assumed to be energy given off. As has been the case with other systems we have studied, while the specific enthalpies of decomposition are reasonable, they decrease with increasing NO_2 content, demonstrating once again that the energy given off per unit mass does not keep up with the increase in mass due to added.

Table 5. Energy changes for various standard reactions of the nitro derivatives of bicyclo[1.1.1]pentaazane.

Reaction	Nitro	Dinitro	Trinitro
ΔH_f, kJ/mol	1011.6	1042.1	1084.7
ΔH_{dec} kJ/g	8.57	6.39	5.21

nitro groups

Finally, in Table 6 we present a comparison of the specific enthalpies of decomposition of the molecules presented here with other well-known HEDMs from the literature.[2] The parent compound N_3H_5 has a very high specific enthalpy of decomposition, but as mentioned above this value decreases quickly as nitro groups are added to the backbone. Despite that, the nitro derivatives all have values for ΔH_{dec} that are commensurate with current HEDMs. Other properties need to be determined or predicted, but from a strict thermodynamic perspective, N_3H_5 and its nitro derivatives are definitely in the class of high energy-density materials.

Table 6. Comparisons of specific enthalpies of decomposition of N_3H_5, $N_3H_{5-x}(NO_2)_x$ (x = 1, 2, 3), and other HE materials. (Sources: This work, Reference 2.)

Substance	ΔH_{dec} kJ/g
N_3H_5, C3 isomer	12.2
N_3H_5, CS isomer	13.6
$N_3H_4NO_2$	8.57
$N_3H_3(NO_2)_2$	6.39
$N_3H_2(NO_2)_3$	5.21
nitroglycerine	6.19
PETN	5.79
TNT	4.25
RDX	5.04
HMX	5.01
tetryl	4.34

Conclusions

We have determined the minimum-energy structures of the N_5H_3 molecule modeled on the [1.1.1]propellane structure. Our results show two possible stereoisomers depending on the orientations of the N-H bonds, all of which lie in the equatorial plane of the molecule. High-level energy calculations show that these molecules have high, positive enthalpies of formation, and at the same time have large specific enthalpies of formation. Calculations of the proton affinities of the more stable isomer indicate that the PA values are in the expected range for an electronegative N atom. We have also determined the energy content of three nitro-substituted N_5 molecules. As has been noted in previous studies, the specific energy of decomposition, expressed in energy per unit mass, decreases as the nitro content of the parent molecule increases. However, the predicted specific enthalpies of decomposition are commensurate with current HEDMs.

Acknowledgements

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