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Stability of High-Energy $N_{14}H_4^{2+}$ Ion and the Effects of Carbon and Halogen Substitution

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Previous studies of oxygen addition into an N_{12} cage framework revealed the possibility of stable high-energy density materials (HEDM) resulting from such additions. In the current study, nitrogen addition into N_{12} is studied as a means of generating stable HEDM. Nitrogen addition into N_{12} is shown to yield an $N_{14}H_4^{2+}$ ion, which is examined by theoretical calculations to determine its stability with respect to dissociation. Other variations on this ion are generated by substituting carbon for nitrogen and/or halogens for hydrogen. The cage structures will be compared with respect to stability, and factors that enhance stability will be discussed.

Introduction

Nitrogen molecules have been the subjects of many recent studies because of their potential as high-energy density materials (HEDM). An all-nitrogen molecule N_x can undergo the reaction $N_x \rightarrow (x/2)N_2$, a reaction that can be exothermic by 50 kcal/mol or more per nitrogen atom.[1,2] To be a practical energy source, however, a molecule N_x would have to resist dissociation well enough to be a stable fuel. Theoretical studies[3−7] have shown that numerous N_x molecules are not sufficiently stable to be practical HEDM, including cyclic and acyclic isomers with 8−12 atoms. Cage isomers of N_8 and N_{12} have also been shown[7−10] by theoretical calculations to be unstable. Experimental progress in the synthesis of nitrogen molecules has been very encouraging, with the N_5^+ and N_5^- ions having been produced[11,12] in the laboratory. More recently, a network polymer of nitrogen has been produced[13] under very-high-pressure conditions. Experimental successes have sparked theoretical studies[1,14,15] on other potential all-nitrogen molecules. More recent developments include the experimental synthesis of high-energy molecules consisting predominantly of nitrogen, including azides[16,17] of various heteroatom-containing compounds and polyazido isomers[18] of compounds such as 1,3,5-triazine. Future developments in experiment and theory will further broaden the horizons of high-energy nitrogen research.

The stability properties of N_x molecules have also been extensively studied in a computational survey[19] of various structural forms with up to 20 atoms. Cyclic, acyclic, and cage isomers have been examined to determine the bonding properties and energetics over a wide range of molecules. A more recent computational study[20] of cage isomers of N_{12} examined the specific structural features that lead to the most stable molecules among the three-coordinate nitrogen cages. Those results showed that molecules with the most pentagons in the nitrogen network tend to be the most stable, with a secondary stabilizing effect due to triangles in the cage structure. A recent study[21] of larger nitrogen molecules N_{24}, N_{30}, and N_{36} showed significant deviations from the pentagon-favoring trend. Each of these molecule sizes has fullerene-like cages consisting solely of pentagons and hexagons, but a large stability advantage was found for molecules with fewer pentagons, more triangles, and an overall structure more cylindrical than spheroidal. Studies[22,23] of intermediate-sized molecules N_{14}, N_{16}, and N_{18} also showed that the cage isomer with the most pentagons was not the most stable cage, even when compared to isomer(s) containing triangles (which have 60° angles that should have significant angle strain). For each of these molecule sizes, spheroidally shaped molecules proved to be less stable than elongated, cylindrical ones.

However, although it is possible to identify in relative terms which nitrogen cages are the most stable, it has been shown[7] in the case of N_{12} that even the most stable N_{12} cage is unstable with respect to dissociation. The number of studies demonstrating the instability of various all-nitrogen molecules has resulted in considerable attention toward compounds that are predominantly nitrogen but contain heteroatoms that stabilize the structure. In addition to the experimental studies[16−18] cited above, theoretical studies have been carried out that show, for example, that nitrogen cages can be stabilized by oxygen insertion[24−26] or phosphorus substitution.[27]

In the current study, an isomer of N_{12} will be subjected to insertion of additional nitrogen atoms, resulting in an $N_{14}H_4^{2+}$ ion. The additional nitrogen atoms are intended to relieve ring strain and stabilize the parent N_{12}. The hydrogen atoms simply satisfy the valences of the additional nitrogen atoms. The overall structure is still very nitrogen-rich. The stability of the ion will be evaluated by theoretical calculations of various dissociation processes. Variations of the $N_{14}H_4^{2+}$ structure will also be examined, including carbon substitutions for nitrogen atoms and halogen substitution for the hydrogen atoms. The effects of these substitutions on stability will be calculated and discussed, with the goal of identifying stable molecules and identifying stabilizing structural features that may lead to the experimental synthesis of stable high-energy molecules.

Computational Methods

Geometries are optimized with the Hartree−Fock (HF) method, and single energy points are calculated with fourth-order perturbation theory[28] (MP4(SDQ)). The basis set is the correlation-consistent polarized valence double-ζ (cc-pVDZ) set

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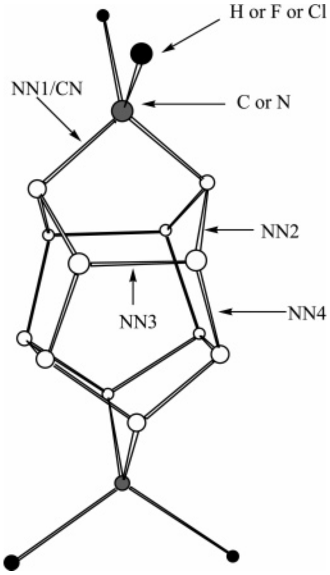

Figure 1. Structural diagram for $N_{14}H_4^{2+}$ and substituted molecules in this study. Atoms shown in white are nitrogen in all molecules. Gray represents the site for carbon/nitrogen substitution. Black represents the site for hydrogen/halogen substitution. Symmetry-independent framework bonds are labeled.

of Dunning.[29] This choice of theory method and basis set is valid for the molecules in this study for several reasons: (1) MP4 theory has been previously shown to agree well with CCSD(T) in a similar bond-breaking study,[30] (2) MP4 theory, when used for single points, has been previously shown[26] to be insensitive to the choice of geometry, and (3) basis set effects were shown[30] to be small in a similar bond-breaking study. (In fact, for several intermediates in this study, density functional theory (DFT) optimizations were attempted. Failure of DFT for molecules of this type is also consistent with previous work.[26]) Geometries of intact molecules are optimized in the singlet state, and dissociation intermediates are optimized in the triplet state, which is the ground state for all dissociations in this study. The intact molecules and all of their dissociation intermediates have been verified as local minima by HF/cc-pVDZ vibrational frequencies. All calculations have been carried out with the Gaussian03 quantum chemistry software[31] and its Windows-based counterpart Gaussian03W.

Results and Discussion

The structure of $N_{14}H_4^{2+}$ is shown in Figure 1. This structural framework is applicable to all molecules in this study. The other molecules in this study result from substitutions on the $N_{14}H_4^{2+}$ molecule. Carbon substitution for the four-coordinate nitrogens leads to a molecule of $N_{12}C_2H_4$. Both $N_{14}H_4^{2+}$ and $N_{12}C_2H_4$ are subjected to substitutions of halogens for the hydrogens, resulting in molecules $N_{14}F_4^{2+}$, $N_{14}Cl_4^{2+}$, $N_{12}C_2F_4$, and $N_{12}C_2Cl_4$. Therefore, this study includes six molecules in all. All of the molecules have D_{2d} point group symmetry, and each cage structure has four symmetry-independent framework bonds, which are labeled in Figure 1. Energies are calculated for one-bond-breaking processes on each of the framework bonds. Bond dissociation energies are computed as energy differences between the reactant molecule with all bonds intact and the respective dissociation intermediates with one bond broken. The bond with the lowest bond-breaking energy is considered the weakest link in the framework and the likeliest site where the detonation of the high-energy molecule would begin.

TABLE 1: Bond-Breaking Energies for $N_{14}H_4^{2+}$, $N_{14}F_4^{2+}$, and $N_{14}Cl_4^{2+a}$

method	bond	$N_{14}H_4^{2+}$	$N_{14}F_4^{2+}$	$N_{14}Cl_4^{2+}$
HF	NN1	+3.7	+0.1	−5.1
	NN2	+9.2	+4.1	+9.6
	NN3	+3.0	−1.3	+5.4
	NN4	+42.7	+38.5	+42.3
MP4/HF	NN1	+30.6	+28.5	+23.6
	NN2	+36.1	+30.8	+36.2
	NN3	+34.1	+30.3	+34.5
	NN4	+65.4	+62.4	+64.0

[a] All calculations carried out with cc-pVDZ basis set (energies in kcal/mol).

TABLE 2: Bond-Breaking Energies for $N_{12}C_2H_4$, $N_{12}C_2F_4$, and $N_{12}C_2Cl_4{}^a$

method	bond	$N_{12}C_2H_4$	$N_{12}C_2F_4$	$N_{14}C_2Cl_4$
HF	CN	+57.0	+56.0	+42.7
	NN2	+21.9	+19.7	+18.7
	NN3	+8.3	+5.9	+8.4
	NN4	+53.8	+52.7	+53.0
MP4/HF	CN	+81.5	+81.0	+69.9
	NN2	+48.7	+46.2	+45.5
	NN3	+37.1	+35.1	+36.7
	NN4	+77.9	+77.8	+76.7

[a] All calculations carried out with cc-pVDZ Basis Set (energies in kcal/mol).

Bond-breaking energies for the $N_{14}X_4^{2+}$ (X = H, F, Cl) ions are shown in Table 1. All framework bonds are nitrogen−nitrogen bonds and are labeled NN1, NN2, NN3, and NN4, as shown in Figure 1. Hartree-Fock theory predicts that the NN3 bond is weakest for $N_{14}H_4^{2+}$ and $N_{14}F_4^{2+}$, but that NN1 is the weakest bond for $N_{14}Cl_4^{2+}$. With the more accurate MP4/HF level of theory, the NN1 bond is the weakest for $N_{14}H_4^{2+}$, $N_{14}F_4^{2+}$, and $N_{14}Cl_4^{2+}$. Further, it appears that the presence of the halogens weakens the NN1 bond, because the NN1 dissociation energies progress as $N_{14}H_4^{2+} > N_{14}F_4^{2+} > N_{14}Cl_4^{2+}$. In $N_{14}H_4^{2+}$, the NN1 dissociation energy is about 30 kcal/mol, so it is possible that this ion is stable enough to be a high-energy density material. Because this bond is weaker for the halogens, the halogenated ions may dissociate too easily to be practical energetic materials.

The weakness in the NN1 bond can be resolved, with a loss of some nitrogen content, by substituting a carbon atom on each end of the molecule. Including halogen substitutions, it is possible to devise molecules with the formulas $N_{12}C_2H_4$, $N_{12}C_2F_4$, and $N_{12}C_2Cl_4$, which are based on the same framework shown in Figure 1 (Table 2). Due to the strength of the C−N bond, the weakest bond in these molecules is now the NN3 bond. At the MP4/HF level of theory, this bond has over 35 kcal/mol resistance to dissociation for all of the carbon-containing molecules in this study. Further, the NN3 bond strength is relatively insensitive to the halogen substitution, which may be due to the distance from the NN3 bond to the hydrogen/halogen sites. Each of these molecules should have stability sufficient for a high-energy density material.

Energy Release Properties. The carbon substitution renders the molecules stable enough to be HEDM, but how much energy is released by decomposition of the molecules? Table 3 shows the energies of decomposition reactions of $N_{12}C_2H_4$, $N_{12}C_2F_4$, and $N_{12}C_2Cl_4$. Energies are calculated at the MP4/HF level of theory with the cc-pVDZ basis set. The decomposition reactions shown are unimolecular, making no assumptions about atmosphere or the availability of additional reactants. Therefore, the energies are entirely the result of decomposition. The energies

TABLE 3: Energy Release Properties of the Nitrogen−Carbon Molecules $N_{12}C_2H_4$, $N_{12}C_2F_4$, and $N_{12}C_2Cl_4$[a,b]

molecule	reaction	kcal/mol	kcal/g
$N_{12}C_2H_4$	$N_{12}C_2H_4 \rightarrow 6\ N_2 + C_2H_4$	−440.5	−2.2
$N_{12}C_2F_4$	$N_{12}C_2F_4 \rightarrow 6\ N_2 + C_2F_4$	−433.2	−1.6
$N_{12}C_2Cl_4$	$N_{12}C_2Cl_4 \rightarrow 6\ N_2 + C_2Cl_4$	−465.4	−1.4

[a] Energies are calculated at the MP4/HF level of theory with cc-pVDZ basis set. [b] Energies are calculated for unimolecular dissociations, with no assumptions about the atmosphere in which the energy release takes place.

per mole are roughly the same for the three molecules, meaning that the three molecules are equally energetic. The energies per unit mass decrease with halogen substitution because of the decreasing nitrogen content of the molecules.

Conclusion

The stability of predominantly nitrogen cages is influenced by a number of factors, including structure and composition. An effective high-energy density material is one that has favorable energetic properties and sufficient stability to be of practical use. Nitrogen content provides the energy release, but nitrogen content may have to be exchanged for substituents that stabilize the structure. For the molecules in this study, carbon substitution for nitrogen brings about greater stability, with some loss of nitrogen content. Halogen substitution causes instability in $N_{14}H_4^{2+}$, and although halogens do not destabilize the carbonated molecules, they cause a decrease in per mass energy release with no increase in stability. The results of this study indicate which structural features are stabilizing and which are destabilizing, which may influence the experimental synthesis of high-energy molecules in the future. Tailoring high-energy nitrogen materials for practical use involves the inclusion of heteroatoms to maximize stability while maintaining high energy release properties.

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