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Predicted High-Energy Molecules: Helical All-Nitrogen and Helical Nitrogen-Rich Ring Clusters

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Helical all-nitrogen and nitrogen-rich ring clusters, new types of potential high-energy molecules, were investigated in the computational study reported here. Stable helical all-nitrogen clusters N_{26} and N_{46} and nitrogen-rich helical structure $N_{26}H_{16}$ formed by fused six-membered rings were found and characterized as proper energy minima by having real frequencies for all eigenvectors of the Hessian matrix. Furthermore, the stability of [6] N-ring helix was studied by calculating the barrier of dissociation reaction. The potential of these type molecules as high-energy density materials was studied. For a better intuitive understanding of the unusual bonding patterns, the molecular isodensity contour (MIDCO) surfaces for [6] N-ring helix and [6] N-helicene were compared at some characteristic density threshold values of 0.20, 0.32, and 0.35 au. As indicated at these threshold values of the isodensity surfaces, the bonds of all-nitrogen clusters appear stronger than those of nitrogen-rich clusters. Apparently, the nitrogen-rich clusters are of higher energy than the all-nitrogen structures, especially if one takes into account the energy balance of bonds involving hydrogen.

Introduction

There are a few all-nitrogen chemical species known experimentally, for instance, N_2, N_3^-,[1] N_5^+,[2,3] and N_5^-.[4] Other species have been observed only as free gaseous or matrix-isolated ions or radicals, such as $N_3^\bullet$, N_3^+, and N_4^+.[5−10] Since the N−N single-bond energy is much less than one-third of the triple-bond energy or one-half of the double-bond energy, most homonuclear polynitrogen structures are thermodynamically highly unstable, having highly endothermic heats of formation, which explains why so few such structures are known. Many theoretical studies have been carried out in search of new types of further nitrogen clusters. Besides all-nitrogen clusters, other nitrogen-rich compounds have also attracted interest as potential high-energy density materials (HEDMs).[11−15] Bartlett suggested some nitrogen-rich compounds formed by N, O, and H as HEDMs.[16] The clusters CN_x have been studied by Hammerl and Klapötke[17,18] both experimentally and theoretically. Gagliardi and Pyykkö[19,20] designed and calculated the structures of ScN_7 and N_5−metal−N_7 and their dissociation pathways. Some nitrogen-rich sulfides $S(N_3)_m$ and $S(N_4)_m$[21,22] and possible reaction pathways for synthesizing nitrogen-rich ionic compounds HN_8^+, $N_4H_2F^+$, and $N_7H_2^+$[23−25] have also been studied.

Some new types, helical all-nitrogen and helical nitrogen-rich fused-ring clusters, were studied in this work. The novelty of the present study consists in designing a completely new type of all-nitrogen molecules which, hopefully, could initiate the systematic experimental search for these molecules. Helical all-nitrogen fused-ring clusters N_{26} ([6] N-ring helix) and N_{46} ([11] N-ring helix) and nitrogen-rich helical structure $N_{26}H_{16}$ ([6] N-helicene) were found as proper energy minima, with real frequencies for all eigenvectors of the Hessian matrix. The stability of [6] N-ring helix was also studied by calculating the barrier for dissociation. For a better intuitive understanding of the bonding patterns, the molecular isodensity contour (MIDCO) surfaces for [6] N-ring helix and [6] N-helicene were compared at the topologically characteristic density values of 0.20, 0.32, and 0.35 au.

Computational Methodology

The geometric structures of helical nitrogen clusters have been optimized with density functional methods at the B3LYP/6-31G* level.[26−28] For the characterization of energy minima or transition states, harmonic vibrational frequencies were calculated at the same level of theory. Minimum energy path calculations[29] were performed starting at the transition state structures with a coordinate step size of 0.1 $(amu)^{1/2}$ bohr. All calculations were carried out with the Gaussian 03 program package.[30] The shape group method (SGM)[31−36] was used for a quantitative analysis of the shapes of these helical molecules.

A molecular isodensity contour surface (MIDCO) $G(K,a)$ of nuclear configuration K and density threshold a is defined as

$$G(K,a) = \{\mathbf{r}:\rho(K,\mathbf{r}) = a\}$$

that is, as the collection of all points r of the three-dimensional space where the electronic density $\rho(K,\mathbf{r})$ of nuclear configuration K is equal to the threshold value a. The shape groups are the homology groups of truncated objects derived from the continuum of the molecular electron density, based on the local shape properties of MIDCOs. The shape group methodology is well documented in the literature[31−36] and will not be detailed here.

Results and Discussion

The structures of minima [6] N-ring helix and products of dissociation, and of the transition state are represented in Figure 1. The cluster is formed by six fused six-membered rings with

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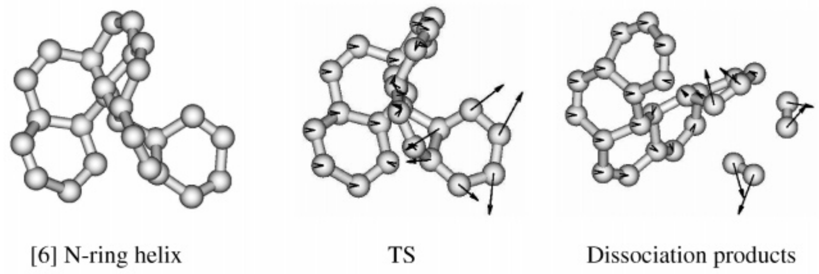

Figure 1. Geometric structures of minima [6] N-ring helix, products of dissociation, and transition state structure.

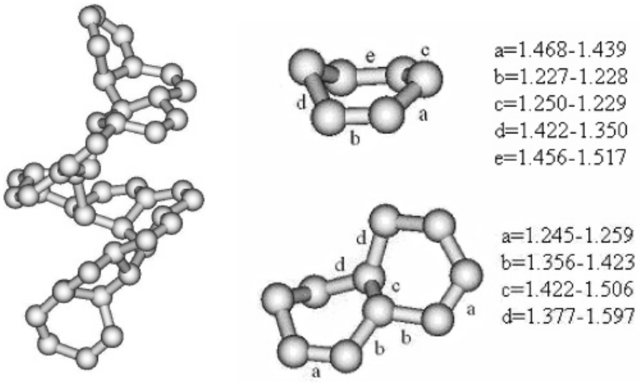

Figure 2. Geometric structure of minimum [11] N-ring helix and parameters of end and intermediate units at the B3LYP/6-31G* level.

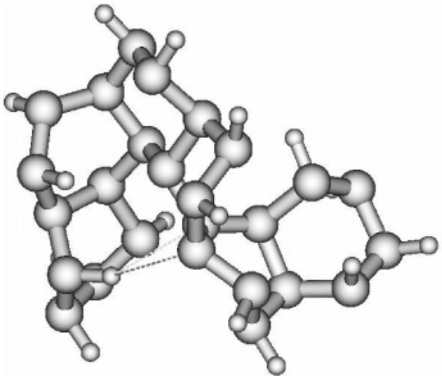

Figure 3. Structure of minimum-energy [6] N-helicene.

a nonplanar overall structure, where the rings in the ends of the helix both have boat conformation. The energy of this structure is 864.6 kcal/mol higher than that of $13N_2$ molecules. The vibrational vector of the imaginary frequency of the transition state indicates that the [6] N-ring helix dissociates, releasing $2N_2$ while giving off 210.6 kcal/mol energy. The low dissociation barrier of 4.85 kJ/mol appears insufficient to keep [6] N-ring helix kinetically stable.

Figure 2 shows the structure of another larger helical nitrogen cluster, [11] N-ring helix, formed by 11 fused-six-membered rings, optimized and found to be an energy minimum at the B3LYP/6-31G* level. The rings in the end units of [11] N-ring helix have boat conformations as well. The geometric parameters of six-membered rings in the ends and intermediate units are also shown in Figure 2.

The bond lengths *b* and *c* in the end units are close to that of a typical N═N double bond; others are close to the length of the N−N single bond. Most bonds in the middle of the helix fall between N═N and N−N, but one bond *d* is longer than a typical N−N bond on some positions of the rings. The energy of [11] N-ring helix is 1538.0 kcal/mol higher than that of 23 N_2 molecules. The energy minima for helical nitrogen clusters suggest a novel family of potential HEDMs. A crucial question, how to stabilize this kind of helix in a practical way, still requires further studies.

The optimized structure of a nitrogen-rich cluster, [6] N-helicene, involving some hydrogen atoms, was found to be an energy minimum (Figure 3). In N-helicene, the overall energy balance is influenced by the N−H bonds and potential hydrogen bonds, of which the latter are more likely to occur in larger systems. Hence, larger helical clusters are more likely to act as HEDMs.

To compare the characteristic ranges of electron densities involved in bond formation between N-ring helices and N-helicenes, their electron densities were calculated. The corresponding isodensity surfaces are presented in Figure 4 with threshold values of 0.20, 0.32, and 0.35 au.

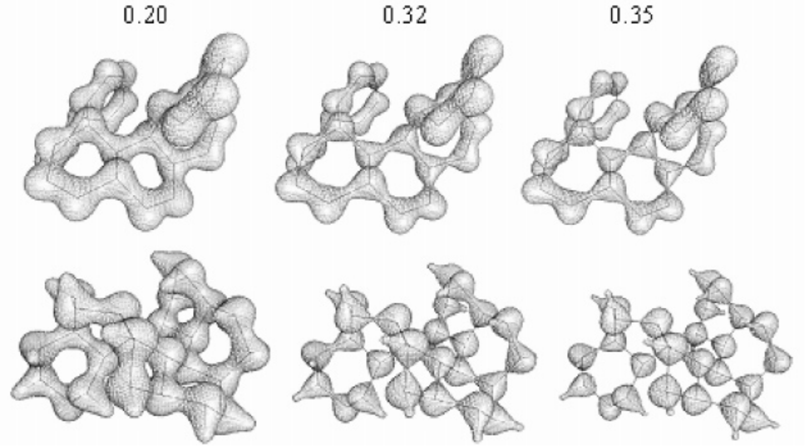

Figure 4. Isodensity surfaces for [6] N-ring helix (first row) and [6] N-helicene (second row). The topologically characteristic density threshold values are 0.20, 0.32, and 0.35 au.

From these isodensity surfaces, one can easily deduce qualitative information concerning the relative strengths of bonds. For the same threshold value of the isodensity surface, the bonds of all-nitrogen clusters appear stronger than those of nitrogen-rich clusters. Although beyond the threshold values these electron density images provide only qualitative information, apparently nitrogen-rich clusters are of higher energy, especially if one takes into account the presence of bonds involving hydrogen.

Summary

These results on helical all-nitrogen and nitrogen-rich fused-ring clusters suggest a new way to design HEDM molecules, and further helical nitrogen clusters are being studied in our laboratory. The design of more stable helical nitrogen clusters and finding stabilizing agents are the main tasks in future works.

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