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Acyclic N_{10} Fails as a High Energy Density Material

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A molecule is a good candidate for a high energy density material (HEDM) if it reacts to release large amounts of energy but resists dissociation and/or isomerization well enough to serve as a stable fuel. Recent theoretical studies have suggested that acyclic N_8 is not a good candidate for HEDM but acyclic N_9 is. To determine a possible trend among acyclic all-nitrogen molecules, theoretical calculations are carried out on an acyclic isomer of N_{10}. The potential energy surface has been calculated for the dissociation reaction $N_{10} \rightarrow N_8 + N_2$, and barriers to that reaction have been calculated using Hartree−Fock theory, perturbation theory, and coupled-cluster theory (CCSD and CCSD(T)). The Dunning correlation-consistent basis sets are employed, and basis set effects on the N_{10} dissociation barrier are discussed. The CCSD(T) results indicate a barrier of approximately 17−18 kcal/mol, which is too low for an HEDM. The acyclic N_{10} would dissociate easily, resulting in an N_8 molecule that would also dissociate easily. Acyclic N_{10} fails as a candidate for high energy density material.

Introduction

Molecules containing only nitrogen atoms have come under recent scrutiny as candidates for high energy density materials (HEDM). The idea is a simple one: any all-nitrogen molecule N_x could dissociate to very stable N_2 molecules, a process that would be expected to be very highly exothermic. Such a reaction, with N_x molecules as a starting material, would release more than $50x$ kcal/mol of energy.[1,2] The difficulty lies in finding all-nitrogen molecules that are metastable enough to serve as stable fuels. It has been suggested that a molecule should have barriers to decomposition and isomerization of at least 30 kcal/mol in order to be considered a viable candidate for HEDM.[3]

Tetrahedral N_4 and cubic N_8 have been examined[4−7] through theoretical calculations and have been found to have reaction barriers that are too low for these molecules to be considered as HEDM. Other N_8 isomers with rings and linear chains have been studied[3] and have also been found to decompose and/or isomerize below the 30 kcal/mol threshold. Also, a study[1] has been carried out on N_8 isomers that are likely reaction products of an addition reaction between the well-known azide ion N_3^- and the recently synthesized N_5^+ cation.[8] None of those reaction products was found to hold any promise as viable HEDM, again due to low reaction barriers. However, a recent study[9] of neutral and cationic N_9 linear chains indicated that neutral, acyclic N_9 may be a promising candidate for HEDM.

In the current study, acyclic N_{10} is examined through the use of theoretical calculations to determine the barrier to the dissociation reaction $N_{10} \rightarrow N_8 + N_2$. In light of the previous results that acyclic N_8 fails as HEDM but N_9 may be a candidate, it becomes necessary to determine if a trend exists among the acyclic N_x molecules. Do the large acyclic N_x have promise as HEDM? Is N_9 a sort of threshold molecule that opens the door to viable N_x HEDM? These questions are addressed by the current study. The $N_{10} \rightarrow N_8 + N_2$ is chosen specifically as a focus of study because it is the dissociation process likely to have the lowest barrier, owing to the special stability of the N_2 molecule. Therefore, this reaction is the most stringent test of the metastability of acyclic N_{10}.

Computational Methods

Geometries have been optimized at the Hartree−Fock (HF) level of theory and also with second-order perturbation theory (MP2).[10] Energy points have been calculated using fourth-order perturbation theory (MP4(SDQ))[10] and coupled-cluster theory (CCSD and CCSD(T)).[11,12] All geometries are optimized as closed-shell singlets, and all energy points are carried out in the closed-shell singlet electronic state. The basis sets are the correlation-consistent basis sets[13] of Dunning, specifically the polarized valence double-ζ (CC-PVDZ) and triple-ζ sets (CC-PVTZ) as well as the double-ζ set with diffuse functions (AUG-CC-PVDZ). All calculations in this study have been performed using the Gaussian 98 quantum chemistry package.[14]

Results and Discussion

CC-PVDZ Barrier Heights. The structure of the N_{10} acyclic molecule is shown in Figure 1 and has been confirmed as a minimum at the HF/CC-PVDZ level of theory. The structure has C_{2h} point group symmetry. The structure of the N_{10} molecule has been optimized at the HF/CC-PVDZ and MP2/CC-PVDZ levels of theory, and the geometric parameters for both optimizations are shown in Figure 1. The $N_{10} \rightarrow N_8 + N_2$ dissociation transition state has also been optimized with HF/CC-PVDZ and MP2/CC-PVDZ, and the structure of the transition state is shown in Figure 2, along with the geometric parameters from both optimizations. Single-point energies with MP4, CCSD, and CCSD(T) have been carried out for both the HF geometries and the MP2 geometries.The results with the CC-PVDZ basis set are tabulated in Table 1. The MP4//HF, CCSD//HF, and CCSD(T)//HF barriers are 16.3, 15.3, and 15.9 kcal/mol, respectively, with the HF barrier significantly lower at 10.4 kcal/mol. With the MP2 geometries, the MP4, CCSD, and CCSD(T) barriers are somewhat higher: 18.5, 17.4, and 17.6 kcal/mol, respectively. The MP2 barrier itself is substantially higher at 24.9 kcal/mol. The CC-PVDZ calculations with the MP4, CCSD, and CCSD(T) methods strongly agree on a barrier of less than 20 kcal/mol with either HF or MP2 geometries, which would indicate that the acyclic N_{10} does not meet the metastability criterion for a HEDM.

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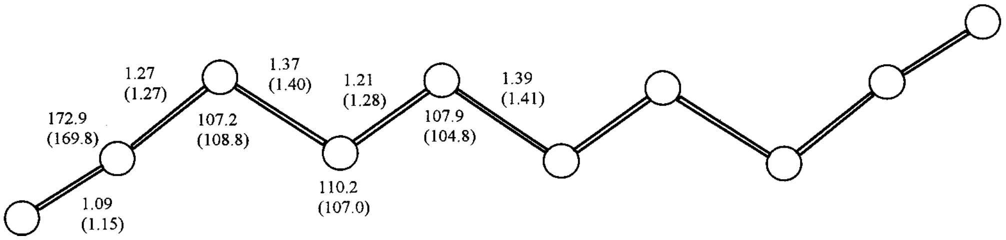

Figure 1. Optimized geometry for acyclic N_{10} (C_{2h} point group symmetry). HF/CC-PVDZ geometric values are indicated, with MP2/CC-PVDZ values in parentheses.

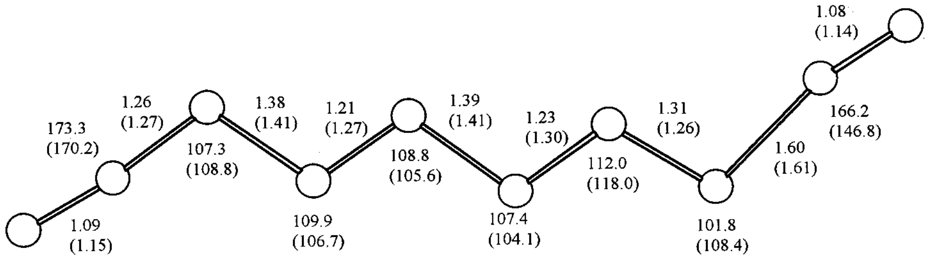

Figure 2. Optimized geometry for the $N_{10} \rightarrow N_8 + N_2$ dissociation transition state (C_s point group symmetry). HF/CC-PVDZ geometric values are indicated, with MP2/CC-PVDZ values in parentheses.

TABLE 1: Reaction Barriers and Transition State Bond Lengths for $N_{10} \rightarrow N_8 + N_2$ (Energies in kcal/mol) with the CC-PVDZ Basis Set

method	barrier (kcal/mol)	TS bond length (Å)	method	barrier (kcal/mol)
HF	10.4	1.599	CCSD(T)//HF	15.9
MP2	24.9	1.613	MP4//MP2	18.5
MP4//HF	16.3		CCSD//MP2	17.4
CCSD//HF	15.3		CCSD(T)//MP2	17.6

TABLE 2: Reaction Barriers and Transition State Bond Lengths for $N_{10} \rightarrow N_8 + N_2$ (Energies in kcal/mol) with the CC-PVTZ Basis Set

method	barrier (kcal/mol)	TS bond length (Å)	method	barrier (kcal/mol)
HF	11.2	1.611	MP4//HF	17.4
MP2	26.2	1.614	MP4//MP2	19.2

TABLE 3: Reaction Barriers and Transition State Bond Lengths for $N_{10} \rightarrow N_8 + N_2$ (Energies in kcal/mol) with the AUG-CC-PVDZ Basis Set

method	barrier (kcal/mol)	TS bond length (Å)	method	barrier (kcal/mol)
HF	10.9	1.616	MP4//HF	15.9
MP2	24.8	1.631	MP4//MP2	17.9

Basis Set Effects. HF and MP2 geometry optimizations have been carried out with the Dunning triple-ζ set (CC-PVTZ). Geometries for the minimum and transition state have been optimized at the HF/CC-PVTZ and MP2/CC-PVTZ levels of theory. Energy points are only calculated with the MP4 method, since the DZ results indicate that MP4 agrees well with CCSD and CCSD(T). The CC-PVTZ results are tabulated in Table 2. Across the board, the barrier is about 1 kcal/mol higher with the TZ basis set than with the DZ set. The CC-PVTZ barrier energies may therefore be considered well-converged with respect to the basis set. If the Dunning quadruple-ζ set (CC-PVQZ) were used for similar calculations, it is likely that the energy changes between QZ and TZ would be much smaller than the tabulated changes between TZ and DZ. MP4/CC-PVTZ with HF and MP2 geometries indicates that the barrier is 17.4 and 19.2 kcal/mol, respectively, still too low for a HEDM.

The effect of additional diffuse basis functions on the barrier height is examined through the use of the Dunning augmented double-ζ basis set (AUG-CC-PVDZ). As with the other basis sets, HF and MP2 geometry optimizations are carried out with the AUG-CC-PVDZ set. The AUG-CC-PVDZ results are tabulated in Table 3. Relative to the CC-PVDZ results, the diffuse functions have the effect of slightly (less than 0.02 Å) lengthening the transition state bond length at the HF and MP2 levels of theory, but the MP4/AUG-CC-PVDZ barrier heights are not substantially different from the corresponding CC-PVDZ barriers.

Conclusion

The calculated energetic barriers for the $N_{10} \rightarrow N_8 + N_2$ are less than 20 kcal/mol with both MP4 and CCSD and CCSD(T), and basis set effects are relatively small. The N_{10} linear chain is therefore not a viable candidate for a HEDM, a result that follows the previous conclusion that acyclic N_8 is not an HEDM. Linear chains larger than N_{10} are also not likely to have high barriers because those molecules can also dissociate an N_2 molecule from the end of the chain, probably with a low dissociation barrier. Why, then, does N_9 stand as a candidate for HEDM, as previously suggested? It should be noted that the N_9 study[9] cites the barrier for N_9 dissociation as the $N_9 \rightarrow N_6 + N_3$ barrier, with the chain losing N_3 rather than N_2. The barrier for N_2 loss from N_9 is likely lower than the barrier for N_3 loss. If, in fact, acyclic N_9 loses N_2 with a high barrier, then there may be an odd−even alternation in the N_2 loss barriers of N_x linear chains. From the N_{10} results and the previous N_8 results, it may be supposed than any even-numbered chain could easily lose an N_2 molecule from the end of the chain, although further calculations would be required to verify this.

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