Dissociation Barriers for Odd-Numbered Acyclic Nitrogen Molecules N_9 and N_{11}

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Molecules containing only nitrogen atoms have been extensively studied as possible candidates for high energy density materials (HEDMs). An all-nitrogen molecule N_x can dissociate to N_2 with the release of a large quantity of energy. To be a viable HEDM, a molecule must resist dissociation well enough to serve as a stable fuel. Recent studies of acyclic N_8 and N_{10} molecules suggest that these even-numbered molecules lose N_2 too easily to be HEDMs. However, another study of acyclic N_9 suggests that N_9 may be stable enough. In the current study, the dissociation pathways of acyclic N_9 and N_{11} are examined extensively by theoretical calculations to determine the stability of these acyclic odd-numbered N_x molecules. Dissociation barriers for N_9 and N_{11} are calculated using Hartree−Fock (HF) theory, perturbation theory (MP2 and MP4), and coupled-cluster (CCSD and CCSD(T)) theory. The correlation-consistent basis sets of Dunning are employed. The results indicate that N_9 and N_{11} can dissociate as easily as N_8 and N_{10}, thereby contradicting the previous conclusion regarding N_9.

Introduction

Molecules that consist solely of nitrogen atoms have recently been examined as candidates for high energy density materials (HEDMs), on the basis of the straightforward idea that an all-nitrogen molecule N_x can dissociate into N_2 molecules. Such a reaction would be highly exothermic, releasing in excess of $50x$ kcal/mol of energy.[1,2] The difficulty in identifying viable HEDM candidates lies in finding molecules that resist dissociation and isomerization well enough to serve as stable fuels. It has been suggested that a viable HEDM should have dissociation and isomerization reaction barriers of at least 30 kcal/mol.[3]

Several recent studies have suggested that linear, cyclic, and small cage N_x molecules generally do not meet this criterion for stability. Tetrahedral N_4 and cubic N_8 have been shown[4−7] not to meet the stability criterion, most likely due to the highly strained bond angles and torsional strain in the molecules. N_8 isomers with rings and linear chains have been studied[3] and 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 azide ion N_3^- and the recently synthesized N_5^+ cation.[8] None of those reaction products were found to hold any promise as viable HEDMs, again due to low reaction barriers. The N_5^+ cation has itself been the subject of a detailed theoretical investigation[9] into its properties, and another theoretical study[10] predicted that the N_5^- anion may be stable and eventually synthesized in the laboratory. A wide variety of N_{11} isomers have been investigated[11] to determine the structural properties and relative stability of the N_{11} molecules. The buckminsterfullerene analogue N_{60} has also been studied,[12] along with the N_{10} units into which N_{60} might decompose.

A recent study[13] of neutral and cationic N_9 linear chains indicated that neutral, acyclic N_9 may be a candidate for HEDM, but that study did not contain results of all dissociation pathways. A study of acyclic N_{10} has shown[14] that molecule to lose N_2 too easily to be an HEDM. This apparent contradiction motivates further investigation of the dissociation pathways for acyclic N_x molecules. In the current study, dissociation barriers are calculated for odd-numbered acyclic molecules N_9 and N_{11}. For N_9, the reactions to be studied are $N_9 \rightarrow N_7 + N_2$, $N_9 \rightarrow N_6 + N_3$, and $N_9 \rightarrow N_5 + N_4$. For N_{11}, there are four reactions, corresponding to the loss of N_2, N_3, N_4, and N_5, respectively. For each molecule, if any one reaction has a barrier below the 30 kcal/mol threshold, then the molecule can dissociate along that path, and the molecule is not stable enough to be an HEDM. The goal of this study is to determine if the dissociation barriers for odd-numbered N_x are substantially different from the dissociation barriers of their even-numbered counterparts.

Computational Methods

Geometries have been optimized with Hartree−Fock (HF) theory and second-order perturbation theory[15] (MP2). Energy points have been calculated using fourth-order perturbation theory[15] (MP4(SDQ)) and coupled-cluster theory[16,17] (CCSD and CCSD(T)). N_9 and N_{11} molecular structures are calculated in the doublet electronic state, and the dissociation transition-state structures are also optimized in the doublet state. The basis sets are the correlation-consistent basis sets[18] of Dunning, specifically the polarized valence double-ζ (CC-PVDZ) and triple-ζ (CC-PVTZ) sets, 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.[19]

Results and Discussion

The structure of the N_9 molecule (C_{2v} symmetry point group) is shown in Figure 1, along with geometric values from the HF/CC-PVDZ and MP2/CC-PVDZ geometry optimizations. Dissociation transition-state structures (all in the C_s symmetry point group) corresponding to loss of N_2, N_3, and N_4 are shown in Figures 2−4, respectively. The N_{11} molecule (C_{2v} symmetry point group) is shown in Figure 5, and the transition states (all in the C_s symmetry point group) for losses of N_2, N_3, N_4, and N_5 are shown in Figures 6−9, respectively.

The N_9 dissociation barriers for calculations with the CC-PVDZ basis sets are shown in Table 1. At all levels of theory,

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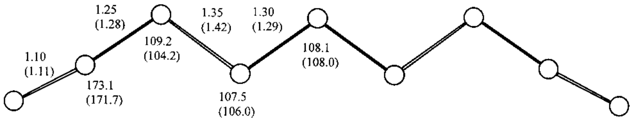

Figure 1. N_9 molecule (C_{2v} symmetry point group). Bond lengths in angstroms and bond angles in degrees are shown as HF/CC-PVDZ-optimized values, with MP2/CC-PVDZ values in parentheses.

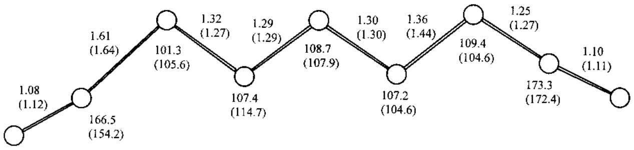

Figure 2. $N_9 \rightarrow N_7 + N_2$ transition state (C_s symmetry point group). Bond lengths in angstroms and bond angles in degrees are shown as HF/CC-PVDZ-optimized values, with MP2/CC-PVDZ values in parentheses.

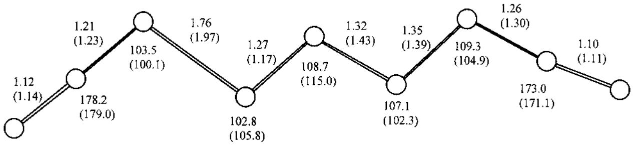

Figure 3. $N_9 \rightarrow N_6 + N_3$ transition state (C_s symmetry point group). Bond lengths in angstroms and bond angles in degrees are shown as HF/CC-PVDZ-optimized values, with MP2/CC-PVDZ values in parentheses.

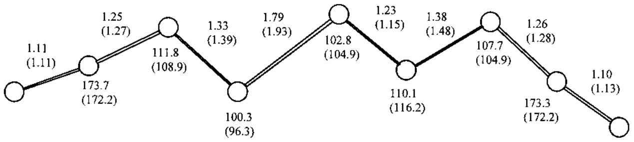

Figure 4. $N_9 \rightarrow N_5 + N_4$ transition state (C_s symmetry point group). Bond lengths in angstroms and bond angles in degrees are shown as HF/CC-PVDZ-optimized values, with MP2/CC-PVDZ values in parentheses.

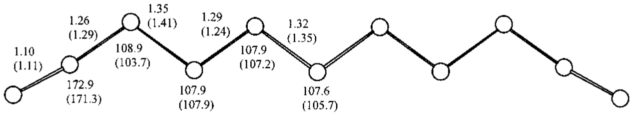

Figure 5. N_{11} molecule (C_{2v} symmetry point group). Bond lengths in angstroms and bond angles in degrees are shown as HF/CC-PVDZ-optimized values, with MP2/CC-PVDZ values in parentheses.

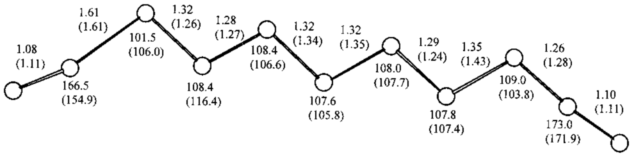

Figure 6. $N_{11} \rightarrow N_9 + N_2$ transition state (C_s symmetry point group). Bond lengths in angstroms and bond angles in degrees are shown as HF/CC-PVDZ-optimized values, with MP2/CC-PVDZ values in parentheses.

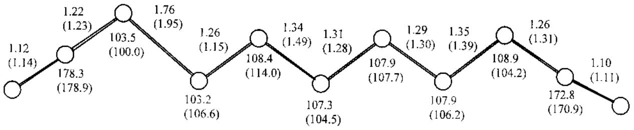

Figure 7. $N_{11} \rightarrow N_8 + N_3$ transition state (C_s symmetry point group). Bond lengths in angstroms and bond angles in degrees are shown as HF/CC-PVDZ-optimized values, with MP2/CC-PVDZ values in parentheses.

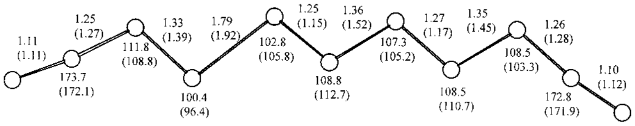

Figure 8. $N_{11} \rightarrow N_7 + N_4$ transition state (C_s symmetry point group). Bond lengths in angstroms and bond angles in degrees are shown as HF/CC-PVDZ-optimized values, with MP2/CC-PVDZ values in parentheses.

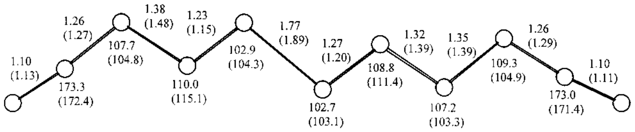

Figure 9. $N_{11} \rightarrow N_6 + N_5$ transition state (C_s symmetry point group). Bond lengths in angstroms and bond angles in degrees are shown as HF/CC-PVDZ-optimized values, with MP2/CC-PVDZ values in parentheses.

TABLE 1: N_9 Dissociation Barriers for Calculations with the CC-PVDZ Basis Set (kcal/mol)

	$N_9 \rightarrow N_7 + N_2$	$N_9 \rightarrow N_6 + N_3$	$N_9 \rightarrow N_5 + N_4$
HF	12.7	21.5	29.7
MP2	20.2	47.5	43.0
MP4//HF	16.9	30.5	37.4
CCSD//HF	17.0	20.8	26.6
CCSD(T)//HF	17.7	18.0	24.0
MP4//MP2	16.5	37.9	40.1
CCSD//MP2	16.6	31.6	37.6
CCSD(T)//MP2	16.6	30.7	36.0

TABLE 2: N_9 Dissociation Barriers for Calculations with the CC-PVTZ and AUG-CC-PVDZ Basis Sets (kcal/mol)

		$N_9 \rightarrow$ $N_7 + N_2$	$N_9 \rightarrow$ $N_6 + N_3$	$N_9 \rightarrow$ $N_5 + N_4$
HF	CC-PVTZ	13.2	22.6	31.2
MP2	CC-PVTZ	22.3	51.8	46.9
MP4//HF	CC-PVTZ	18.4	33.6	40.3
MP4//MP2	CC-PVTZ	18.7	41.1	43.5
HF	AUG-CC-PVDZ	13.2	22.5	31.3
MP2	AUG-CC-PVDZ	20.7	50.7	45.2
MP4//HF	AUG-CC-PVDZ	16.7	32.0	39.2
MP4//MP2	AUG-CC-PVDZ	16.7	39.9	42.1

the N_2 loss pathway has the lowest barrier. At both the HF- and MP2-optimized geometries, MP4, CCSD, and CCSD(T) predict reaction barriers of less than 20 kcal/mol. These barriers are certainly too low for a viable HEDM, and these barriers are approximately the same as similar barriers calculated for acyclic isomers of N_8 and N_{10}. Also, at the MP2 geometries, the N_3 loss process $N_9 \rightarrow N_6 + N_3$ has barriers of 37.9, 31.6, and 30.7 kcal/mol with MP4, CCSD, and CCSD(T), respectively. These barriers are in good agreement with the $N_9 \rightarrow N_6 + N_3$ density functional theory results[13] from the previous N_9 study. For each reaction, HF theory predicts the lowest barrier and MP2 predicts the highest barrier, with the MP4, CCSD, and CCSD(T) results falling between those of HF and MP2.

Basis set effects are tested by calculations with the CC-PVTZ basis set, and the influence of diffuse functions is tested by calculations with the AUG-CC-PVDZ basis set. Results from both basis sets are shown in Table 2. Relative to the CC-PVDZ calculations, the CC-PVTZ calculations tend to raise the dissociation barriers by 1−2 kcal/mol for $N_9 \rightarrow N_7 + N_2$ and by 1−3 kcal/mol for the other reactions. The basis set effects are small enough that the CC-PVTZ results should be considered converged with respect to the basis set. The influence of the diffuse functions in AUG-CC-PVDZ is less than 1 kcal/mol relative to the corresponding CC−PVDZ results.

TABLE 3: N_{11} Dissociation Barriers for Calculations with the CC-PVDZ Basis Sets (kcal/mol)

	$N_{11} \rightarrow N_9 + N_2$	$N_{11} \rightarrow N_8 + N_3$	$N_{11} \rightarrow N_7 + N_4$	$N_{11} \rightarrow N_6 + N_5$
HF	11.6	21.8	31.9	25.0
MP2	16.9	46.5	44.8	35.6
MP4//HF	14.4	30.5	43.5	30.1
CCSD//HF	14.7	20.4	29.6	19.4
CCSD(T)//HF	15.4	17.5	26.4	17.1
MP4//MP2	14.0	36.7	43.2	32.5
CCSD//MP2	14.3	29.8	41.3	28.5
CCSD(T)//MP2	14.1	28.5	39.8	26.5

TABLE 4: Magnitude of Imaginary Frequencies from Frequency Calculations on the Dissociation Transition States (cm^{-1})

	HF/CC-PVDZ	MP2/CC-PVDZ
$N_9 \rightarrow N_7 + N_2$	511.0, 211.6	749.0, 46.3
$N_9 \rightarrow N_6 + N_3$	732.1	454.4
$N_9 \rightarrow N_5 + N_4$	605.6	468.3
$N_{11} \rightarrow N_9 + N_2$	516.1, 75.3	783.0
$N_{11} \rightarrow N_8 + N_3$	740.0	488.4, 93.1
$N_{11} \rightarrow N_7 + N_4$	599.4	479.2, 113.3, 7.5
$N_{11} \rightarrow N_6 + N_5$	640.0	543.6, 15.4

Dissociation barriers for N_{11} from calculations with the CC-PVDZ basis set are tabulated in Table 3. The results generally follow the pattern displayed by N_9 and N_{10} (ref 14). With the MP4 and coupled-cluster methods, N_{11} loses N_2 with a barrier of about 14−15 kcal/mol. This is slightly lower than the 16−17 kcal/mol barrier for N_9 and the 16−18 kcal/mol barrier for N_{10} with the same methods and basis set. Also, as with N_9, the barriers for the loss of larger nitrogen fragments are higher than for the loss of N_2, and some of those barriers are below 30 kcal/mol. Since basis set effects are small for N_9 and N_{10}, it is unlikely that larger basis sets would substantially change the N_{11} dissociation barriers.

All of the transition states in this study have been characterized by explicit frequency calculations at the HF/CC-PVDZ and MP2/CC-PVDZ levels of theory. The imaginary frequencies for the transition states are tabulated in Table 4. In each case, the transition state has a dominant imaginary frequency corresponding to the in-plane (A' in C_s symmetry) dissociation of the expected fragment of the molecule. Several cases, however, have an additional imaginary frequency corresponding to nonplanar distortions of the molecule (A'' in C_s symmetry). These second imaginary frequencies are small in magnitude and likely false results resulting from errors in the frequency calculations. Even if such nonplanar distortions are genuine, they are unlikely to substantially alter the dissociation barriers in this study.[20] Furthermore, any energy changes resulting from such nonplanar distortions would lower the energy of the transition states and lower the corresponding transition barriers, thereby strengthening the argument that N_9 and N_{11} dissociate too easily to be viable high energy density materials.

Conclusion

Acyclic isomers of N_9 and N_{11} dissociate with barriers well below the suggested[3] 30 kcal/mol threshold for high energy density materials. These odd-numbered nitrogen molecules dissociate with approximately the same ease as their even-numbered counterparts.[3,14] The accumulation of theoretical data on N_8, N_9, N_{10}, and N_{11} seems sufficient to draw the conclusion that *all* acyclic nitrogen molecules will lose N_2 (and possibly other fragments) too easily for any such molecule to be a viable HEDM. A viable all-nitrogen HEDM will have to take some form other than acyclic molecules, perhaps nitrogen cages or other three-dimensional forms.

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(20) Another example of an intramolecular distortion is the C−C rotation of ethane. The eclipsed conformation is a transition state between staggered conformers. At the HF/CC-PVDZ and MP2/CC-PVDZ levels of theory, eclipsed ethane has imaginary frequencies of magnitude 329.7 and 324.9 cm^{-1}, respectively. Following the reaction coordinate down to the staggered minimum results in energy lowering of 3.3 and 3.2 kcal/mol with HF/CC-PVDZ and MP2/CC-PVDZ, respectively. All of the nonplanar distortion imaginary frequencies in this study are of a magnitude far lower than these ethane results.