A Theoretical Study on Decomposition Pathways of N_7^+ and N_7^- Clusters

Qian Shu Li* and Jun Fang Zhao

School of Chemical Engineering and Materials Science, Beijing Institute of Technology, Beijing 100081, China

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A theoretical study on the decomposition pathways of N_7^+ and N_7^- clusters with low spin has been carried out on the basis of ab initio molecular orbital theory and density functional methods. Transition states of dissociation processes were found and characterized on the MP2/6-31(+)G(d) and B3LYP/6-31(+)G(d) potential energy surfaces (PES). Relative energies were further calculated using a basis set extrapolation similar to the G2(MP2) method for the MP2/6-31(+)G(d) optimized geometries. B3LYP/6-311+G(3df, 2p) single-point energy corrections were performed using the B3LYP/6-31(+)G(d) geometries. The present study shows that the elimination of two N_2 in the open-chain anion N_7^- (C_2) is a concerted process, whereas in the open-chain cation N_7^+ (C_{2v}), it is stepwise due to the existence of stable linear N_5^+. The decomposition pathway of the cyclic anion N_7^- (C_s) was also investigated at the above levels. The computed results suggest that the N_7 ions do not seem to be stable enough as a metastable species in a practical sense.

Introduction

In recent years, nitrogen clusters have drawn considerable attention, not only owing to their theoretical interest, but also their potential use as environmentally friendly high-energy-density materials (HEDMs). However, it is still a challenge to synthesize the polynitrogen molecules. Indeed, only three all-nitrogen chemical species in bulk compounds are experimentally known throughout the last three centuries: namely N_2, N_3^-, and N_5^+, of which the last one has been synthesized by Christe and co-workers in 1999.[1] Olah et al.[2] attempted to acquire the dication N_4^{2+} experimentally through the diazotization of the aminodiazonium ion, obtained by the protonation of HN_3 with $NO^+BF_4^-$ in Magic Acid/SO_2ClF solution at −78 °C. Unfortunately, however, they failed in synthesizing the tetranitrogen dication.

Could further varieties of nitrogens exist? In fact, many hypothetical stable structures have been predicted theoretically[3−20] in the past several years. Bartlett et al.[21] made a systematic investigation on the structures, energies, and spectroscopies for the poly-nitrogen species ranging from N_2 to N_{10}, as well as their cations and anions. Quite recently, Gagliardi and Pyykkö[22] reported a theoretical search for MN_n systems and have found that the presence of Sc metal seems to lead to much higher energetic stability with respect to dissociation products. Bartlett et al.[23] also reported an investigation on the pseudo-benzene N_6 ring with oxygen. Gagliardi et al.[24] pointed out that the anion N_5^- might be stable enough to be synthesized and further studied the possibility to form N_{10} from N_5^+ and N_5^- in a recent paper of theirs.

In their exploration of the synthesis of nitrogen clusters, scientists have placed much more hope on the even-numbered nitrogen clusters. Interestingly enough, however, only N_3^- and N_5^+ were successfully synthesized. This suggested to us that it is perhaps more hopeful to synthesize the odd-numbered nitrogen clusters, and N_7 ions might evidently be the next objective to be synthesized. We[25] have recently carried out a theoretical study on the structures and stability of N_7^+ and N_7^- clusters with low spin using ab initio and DFT methods. The study suggested that the open-chain N_7^+ (C_{2v}) and N_7^- (C_2) are the global minima on their respective potential energy surfaces.

As high-energy-density material candidates, the critical questions for nitrogen clusters are their barrier heights to dissociation and the methods of their synthesis. The energy barriers to dissociation must be sufficiently high to provide stability under the conditions in which fuels would normally be stored. It is therefore desirable to have barriers of more than 20 kcal/mol, and preferably more than 30 kcal/mol. Therefore, it is necessary to examine all possible dissociation routes for any new candidates. Only a small number of reports about the potential energy surface (PES) of N_{2n} clusters are recorded, such as N_4,[7−10] N_6,[11−13] and N_8.[16−17] We[26] have studied the possible decomposition pathways of N_9 (C_{2v}) and N_9^+ (C_{2v}) clusters and determined the energy barriers for these reactions with the DFT methods. The goal of this paper is to study the decomposition mechanism of N_7^+ and N_7^- clusters with low spin with ab initio and DFT methods. We attempt to find the possible pathways of decomposition reactions and then determine the energy barriers of these reactions, as well as the kinetic stability of these species.

Calculation Methods

Geometries of the reactants, products, and transition states have been optimized applying two different methods, viz., the second-order perturbation theory (MP2) and the hybrid density functional B3LYP approach, i.e., Becke's three-parameter nonlocal-exchange functional with nonlocal correlation functional of Lee, Yang, and Parr.[27−28] The MP2 method employed is one using the frozen core approximation. For the cation N_7^+, the standard 6-31G(d) basis set is employed which is of double-ζ contraction quality plus six d-like polarization functions, while for the anion N_7^-, the 6-31+G(d) basis set is augmented with diffuse functions. Vibrational frequencies calculated at the same levels have been used for the characterization of stationary points and zero-point energy (ZPE) correction. All the stationary points

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* Corresponding author. Fax: +86-10-6891-2665. E-mail: qsli@mh.bit.edu.cn.

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have been positively identified for minima (number of imaginary frequencies NIMAG = 0) or transition states (NIMAG = 1). Minimum energy pathways connecting the reactants and products were confirmed using the intrinsic reaction coordinate (IRC) method with the Gonzalez-Schlegel second-order algorithm.[29−30]

To obtain more reliable relative energies, a basis set extrapolation similar to what is done in the G2(MP2) method were employed, denoted here as G2*(MP2), in which G2(MP2) is a modification of the Gaussian-2 (G2) approach by Pople and co-workers.[31] The G2*(MP2) energy was computed by the G2(MP2) scheme[31] using MP2/6−31(+)G(d)-optimized geometries as follows:

$$E[\mathrm{G2^*(MP2)}] = E[\mathrm{MP2/6\text{-}311G(d, p)}] + \Delta^{\mathrm{MP2}} + \Delta E^{\mathrm{QCI}} + \mathrm{ZPE} + \Delta \mathrm{E}^{\mathrm{HLC}} + \Delta^{\mathrm{HLC}}$$

$$\Delta^{\mathrm{MP2}} = E[\mathrm{MP2/6\text{-}311{+}G(3df, 2p)}] - E[(\mathrm{MP2/6\text{-}311G(d, p)}]$$

$$\Delta E^{\mathrm{QCI}} = E[\mathrm{QCISD(T)/6\text{-}311G(d, p)}] - E[\mathrm{MP2/6\text{-}311G(d, p)}]$$

$$\Delta E^{\mathrm{HLC}} = -0.00019\eta_{\alpha} - 0.00595\eta_{\beta}$$

where η_α and η_β are the numbers of α and β valence electrons, respectively. Obviously, Δ^{MP2} is an energy correction for the basis set extension from 6-311G(d, p) to 6-311+G(3df, 2p) at the single MP2 level, and ΔE^{QCI} is a correction for the correlation effects from the MP2 to QCISD(T) level with the same 6-311G(d, p) basis set. ΔE^{HLC} is a correction for the remaining correlation energy between spin-paired electrons. The final term, Δ^{HLC}, is known as the higher-level correction for the final G2 energy. Therefore, the quantity of E[G2*(MP2)] is essentially an approximation to an energy calculated directly at QCISD(T)/6-311+G(3df, 2p)//MP2/6-31(+)G(d) level. For comparison, single-point energy corrections at the B3LYP/6-31(+)G(d)-optimized geometries were also obtained with the larger basis set size 6-311+G(3df, 2p). All the energies quoted and discussed in the present paper include the ZPE correction without scaling. Gaussian 98 program[32] was used for all calculations in this study.

Throughout this paper, bond lengths are given in angstroms, bond angles in degrees, total energies in hartrees, relative and zero-point vibrational energies (unless otherwise stated) in kcal/mol.

Results and Discussion

The decomposition of each species considered here will be presented in the following sections. As a convention, each structure is designated by a combination of letters. The letters **C** and **A** stand for cation and anion, respectively. The optimized geometric structures of the species involved in the decomposition pathways are given in Figures 1−3. The lowest vibrational frequencies of the species involved are listed in Table 1 and the relative energies (E_{rel}) and zero-point energies (ZPE) are tabulated in Table 2.

The N_7^+ Cation. Geometries and properties of this cationic system have been examined in detail in our recent paper,[25] in which the C_{2v} symmetric open-chain linear structure **C-1** is the most stable N_7^+ isomer, and thus will warrant no further comments. Here we have found a transition state (**TS1**) for its decomposition into N_5^+ (C_{2v}) + N_2 whose geometrical parameters optimized at the MP2/6-31G(d) and B3LYP/6-31G(d) levels, respectively, are displayed in Figure 1. As shown in Table 1, the imaginary frequencies of **TS1** are calculated as 595*i* and 509*i* at the two levels, respectively. During the deformation process from **C-1** to **TS1**, the bond length of N3−N5 lengthens and the symmetry changes from C_{2v} to C_s, while the other bond lengths and bond angles change slightly. These imply that the bond of N3−N5 would break easily and N_7^+ would dissociate into N_2 and N_5^+. IRC calculations, performed at the same levels, also confirm that **TS1** does connect N_7^+ (C_{2v}) and N_2 + N_5^+. The calculated relative energies including zero-point correction are summarized in Table 2. At the B3LYP/6-311+G(3df, 2p)//B3LYP/6-31G(d) level, the energy difference between **TS1** and N_7^+ (C_{2v}) is 4.8 kcal/mol, whereas G2*(MP2) decreases this value to 3.1 kcal/mol. Such small values suggest that it may be possible to observe this isomer only as a short-lived species, rather than being suitable for preparation and handling in bulk quantities. Nguyen et al.[13] have discussed the decomposition of the cation N_5^+ (C_{2v}) into N_3^+ + N_2 and pointed out that the open-chain N_5^+ is a relatively stable species with a moderately high energy barrier (170−220 kJ/mol). Thus no further discussion on N_5^+ seems to be necessary.

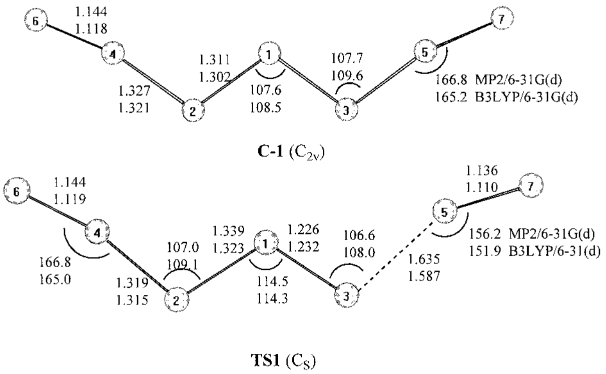

Figure 1. Optimized geometrical parameters of the cation N_7^+ **C-1** and **TS1**.

TABLE 1: The Lowest Vibrational Frequency (cm^{-1}) for the Species Involved in N_7^+ and N_7^- Decomposition Systems

	species	MP2/6-31(+)G(d)	B3LYP/6-31(+)G(d)
N_7^+	**C-1** (C_{2v})	123	130
	TS1 (C_s)	595*i*	509*i*
N_7^-	**A-1** (C_2)	44	75
	TS2 (C_1)	403*i*	138*i*
	A-2 (C_s)	169	210
	TS3 (C_s)	565*i*	
	TS3-a (C_1)		185*i*
	A-3 (C_1)	75	42
	TS3-b (C_1)	567*i*	338*i*
	A-Complex (C_s)	220	129

The N_7^- Anion. $N(N_3)_2^-$ has been previously investigated by Michels et al.[18] in both C_2 and C_s symmetries. Our recent paper[25] has reported the stationary points on the potential energy surface of the N_7^- cluster, and has pointed out that the gauche C_2 form **A-1** is the most stable anion N_7^- isomer using ab initio and DFT methods. As shown in Figure 2, the longest and weakest bond in **A-1** is the central N1−N2 (or N1−N3) bond whose length is comparable to that in N_2H_4 (1.45 Å).[33] Mulliken charge distribution analysis performed at the MP2/6-31+G(d) level indicates that the excess negative charge resides mainly on the central nitrogen atom. The DFT Mulliken charges show a similar pattern. These imply that the decomposition mechanism of **A-1** is the cleavage of a N−N single bond rather than the direct N_2 elimination. We have found a transition state **TS2** (C_1) with only one imaginary frequency (403*i* and 138*i* at the MP2/6-31+G(d) and B3LYP/6-31+G(d) levels, respectively). Energetically **TS2** is only 5.0 kcal/mol higher than **A-1** at the

TABLE 2: Relative Energies (E_{rel}) (kcal/mol) with ZPE Correction and ZPE (in kcal/mol) for the Species Involved in N_7^+ and N_7^- Decomposition Systems

		MP2/6−31(+)G(d)		G2*MP2[b]	B3LYP/6−31(+)G(d)		
	isomers	E_{rel}	ZPE	E_{rel}	E_{rel}	ZPE	B3LYP/6-311+G(3df,2p)[c]
N_7^+	**C-1** (C_{2v})[a]	0.0	17.8	0.0	0.0	18.3	0.0
	TS1 (C_s)	7.8	16.0	3.1	4.5	16.7	4.8
	N_5^+ (C_{2v}) + N_2	−56.2	15.6	−53.0	−40.8	16.2	−44.4
N_7^-	**A-1** (C_2)[a]	0.0	16.6	0.0	0.0	16.4	0.0
	TS2 (C_1)	0.3	15.9	1.2	4.9	16.0	5.0
	A-2 (C_s)	7.2	17.5	10.7	18.0	17.9	23.5
	TS3 (C_s)	19.4	16.4	15.0			
	TS3-a (C_1)				24.1	16.8	29.0
	A-3 (C_1)	4.3	17.6	5.5	12.2	16.5	15.2
	TS3-b (C_1)	13.1	16.4	14.9	23.6	17.6	26.5
	A-Complex (C_s)	−5.9	16.6	8.6	18.2	17.1	20.8
	N_3^- + N_2 + N_2	−161.2	12.5	−140.9	−127.6	13.7	−131.6

[a] The relative energies of the most stable N_7^+ and N_7^- isomers were set to zero, respectively. [b] Single-point energy in G2*(MP2)//MP2/6−31(+)G(d) with ZPE correction in MP2/6-31(+)G(d) level. [c] Single-point energy in B3LYP/6-311+G(3df,2p)//B3LYP/6-31(+)G(d) with ZPE correction in B3LYP/6-31(+)G(d) level.

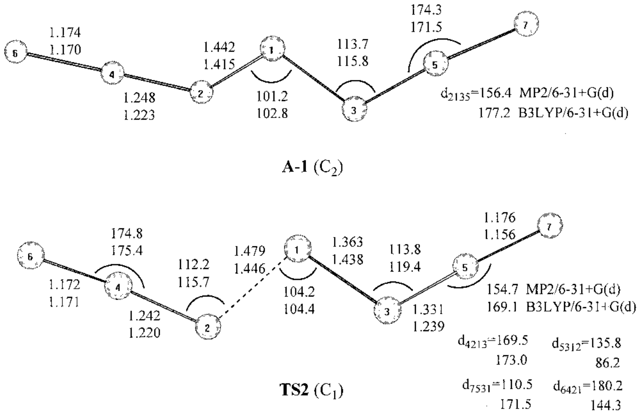

Figure 2. Optimized geometrical parameters of the anion N_7^- **A-1** and **TS2**.

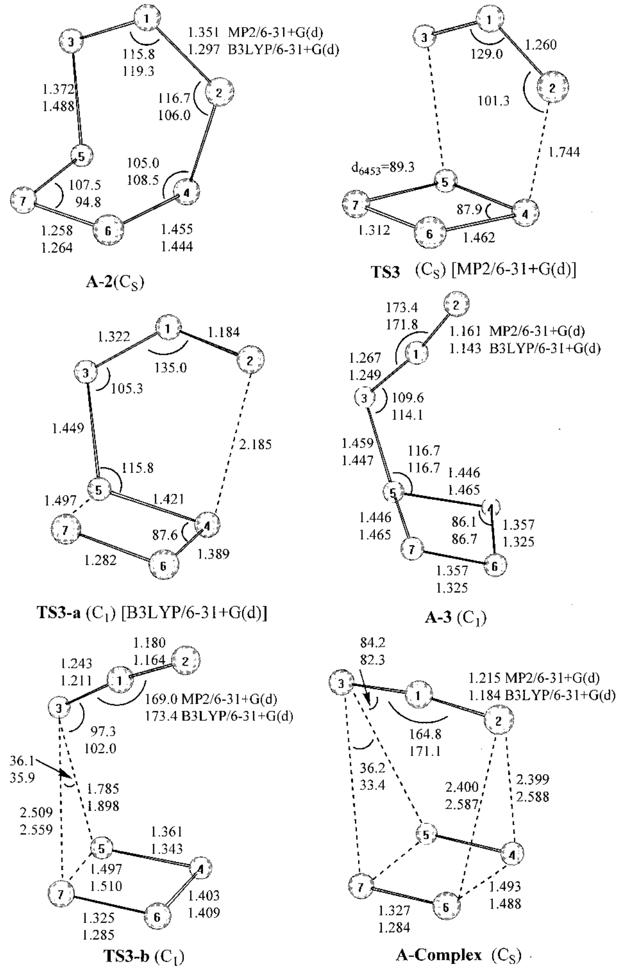

Figure 3. Optimized geometric parameters of the structures involved in the decomposition of the anion N_7^- **A-2**.

B3LYP/6-311+G(3df, 2p)//B3LYP/6-31+G(d) level. The G2*(MP2) calculation decreases the barrier height to 1.2 kcal/mol. Compared with **A-1**, the bond length N1−N2 in **TS2** increases, with a decrease in the bond length of N1−N3 and an increase in the bond N3−N5. Starting from **TS2**, IRC calculations lead directly to dissociation into three parts: N_3^- + N_2 + N_2. Two bonds (N1−N2 and N3−N5) are broken to produce these products. The simultaneous bond breaking is presumably due to the instability of the linear N_4, causing its dissociation into two N_2 molecules. However, from the very low barrier height of **A-1**, it is more than doubtful if this isomer can be observed experimentally.

Our previous study[25] has shown that the cyclic isomer **A-2** (Figure 3) with C_s symmetry and the cage-like isomer **A-complex** (Figure 3) with C_s symmetry are all true minima on the potential energy surface of N_7^-. With the zero-point energy correction, **A-2** is 23.5 and 10.7 kcal/mol less stable than **A-1** at the B3LYP/6−11+G(3df, 2p)//B3LYP/6-31+G(d) and G2*-(MP2) level, respectively. Both levels of theory predict that **A-complex** possesses energies similar to **A-2**. **A-complex** is more stable than **A-2** by 2.7 and 2.1 kcal/mol at the B3LYP/6-311+G(3df, 2p) and G2*(MP2) levels, respectively. Mulliken charge distribution analyses indicate that the excess negative charge resides mainly on N2 and N3. So this structure can be considered as a rather weak ion−molecule complex between the N_4 ring and an azide anion N_3^-.

The decomposition pathway of **A-2** (C_s) has been examined at the MP2/6-31+G(d) and B3LYP/6-31+G(d) levels of theory. From the results presented here, it is noted that the theoretically predicted dissociation process of the cyclic isomer **A-2** is strongly dependent upon the methods employed. As usual, the MP2 method is liable in overestimating the electron correlation effects that can result in some calculated bond lengths being longer than their real values for nitrogen clusters. It seems also that the difference of the decomposition pathways between the MP2 and B3LYP results from overestimating the electron correlation effects. We have located a transition structure **TS3**, as shown in Figure 3, at the MP2/6-31+G(d) level. Compared with the stable isomer **A-2**, **TS3** still possesses C_s symmetry, with the bond distances of N2−N4 and N3−N5 lengthened by about 0.3 Å, whereas the distance of N4−N5 shortened greatly. Energetically **TS3** is only 4.3 kcal/mol higher than **A-2** at the G2*(MP2) level (Table 2). The decomposition process of **A-2**(C_s) → **TS3**(C_s) → $N_3^- + N_2 + N_2$ proceeds through **A-complex** (C_s) as indicated by IRC calculation performed at the MP2 level. However, the pathway that **A-2** deforms into **A-complex** via an isomerization reaction was found at the B3LYP/6-31+G(d) level. Two transition states (**TS3-a** and **TS3-b**) have been located on the B3LYP potential energy surface, as depicted in Figure 3. Indeed, the C_1 symmetric form **A-3** was found to be a stable point for the anion N_7^- with all real vibrational frequencies at the B3LYP/6-31+G(d) and MP2/6-31+G(d) levels of theory. **A-3** is 8.3 kcal/mol and 5.2 kcal/mol more stable than **A-2** at the B3LYP/6-311+(3df, 2p) and G2*(MP2) levels, respectively. IRC calculation verifies that **TS3-a** is connected to **A-2** on the reactant side and to **A-3** on the product side. The energy difference between **TS3-a** and **A-2** is 5.5 kcal/mol at the B3LYP/6-311+(3df, 2p)//B3LYP/6-31+G(d) level of theory. The low barrier suggests that isomerization can happen easily. On the other hand, **TS3-b** was confirmed to connect the two minima, **A-3** and **A-complex**, by IRC calculation at the B3LYP level. **TS3-b** (shown in Figure 3) was also found to be a transition state that connects **A-3** and **A-complex** on the potential energy surface at the MP2/6-31+G(d) level of theory. On the basis of the energy difference between **A-3** and **TS3-b**, the reaction potential barrier heights are predicted to be 11.3 and 9.4 kcal/mol at the B3LYP/6-311+G(3df, 2p) and G2*(MP2) levels, respectively. The modest decomposition barrier heights suggest that it seems possible to detect **A-3** experimentally as a short-lived species. However, in view of such low barrier height at the MP2 and B3LYP levels of theory, it appears to be reasonable to conclude that the cyclic anion N_7^- **A-2** is not stable enough to serve as a good candidate for HEDM. Thus, no further attempts have been made to search the transition states using higher-level methods.

Summary

Mechanisms for the dissociation of N_7^+ and N_7^- clusters have been investigated with the second-order perturbation theory (MP2) and density functional method (DFT). It is suggested that the elimination of two N_2 molecules in the linear N_7^- (C_2) is a concerted process, whereas in the N_7^+ (C_{2v}), it is stepwise due to the existence of the stable linear N_5^+ cation. The G2*(MP2) barrier leading from N_7^+ (C_{2v}) to $N_5^+ + N_2$ is 3.1 kcal/mol. The barrier height for the decomposition reaction of N_7^- (C_2) into $N_3^- + N_2 + N_2$ is predicted to be 1.2 kcal/mol at the above level of theory. For the cyclic anion N_7^- (C_s), the calculated barrier heights at the MP2 and DFT levels are all less than 20 kcal/mol. From the results presented here, it appears that N_7^+ (C_{2v}), N_7^- (C_2), and N_7^- (C_s) are not viable as explosive or propellant candidates because of their kinetic instability. Whether it is possible to form other more stable N_7 ionic compounds will be subjects of study in a forthcoming investigation.

References and Notes

(1) Christe, K. O.; Wilson, W. W.; Sheehy, J. A.; Boatz, J. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2004.

(2) Olah, G. A.; Prakash, G. K. S.; Rasul, G. *J. Am. Chem. Soc.* **2001**, *123*, 3308.

(3) Glukhovtsev, M. N.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1992**, *198*, 547.

(4) Vogler, A.; Wright, R. E.; Kunkley, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 717.

(5) Engelke, R. *J. Chem. Phys.* **1992**, *96*, 10789.

(6) Glukhovtsev, M. N.; Jiao, H.; Schleyer, P. v. R. *Inorg. Chem.* **1996**, *35*, 7124.

(7) Lee, T. J.; Rice, J. E. *J. Chem. Phys.* **1991**, *94*, 1215.

(8) Dunn, K. M.; Morokuma, K. J. *J. Chem. Phys.* **1995**, *102*, 4904.

(9) Lauderdale, W. J.; Stanton, J. F.; Bartlett, R. J. *J. Phys. Chem.* **1992**, *96*, 1173.

(10) Bittererová, M.; Brinck, T.; Östmark, H. *J. Phys. Chem.* A **2000**, *104*, 11999.

(11) Korkin, A.; Balkova, A.; Bartlett, R. J.; Boyd, R. J.; Schleyer, P. v. R. *J. Phys. Chem.* **1996**, *100*, 5702.

(12) Gagliardi, L.; Evangelisti, S.; Barone, V.; Roos, B. O. *Chem. Phys. Lett.* **2000**, *320*, 518.

(13) Nguyen, M. T.; Ha, T.-K. *Chem. Phys. Lett*. **2001**, *335*, 311.

(14) Gagliardi, L.; Evangelisti, S.; Widmark, P. O.; Roos, B. O. *Theor. Chem. Acc.* **1997**, *97*, 136.

(15) Gagliardi, L.; Evangelisti, S.; Roos, B. O.; Widmark, P. O. *J. Mol. Struct. (THEOCHEM)* **1998**, *428*, 1.

(16) Gagliardi, L.; Evangelisti, S.; Bernhardsson, A.; Lindh, R.; Roos, B. O. *Int. J. Quantum Chem.* **2000**, *77*, 311.

(17) Chung, G.; Schmidt, M. W.; Gordon, M. S. *J. Phys. Chem.* A **2000**, *104*, 5647.

(18) Michels, H. H.; Montgomery, J. A., Jr.; Christe, K. O.; Dixon, D. A. *J. Phys. Chem.* **1995**, *99*, 187.

(19) Nguyen, M. T.; Ha, T.-K. *Chem. Ber.* **1996**, *129*, 1154.

(20) Leininger, M. L.; Sherrill, C. D.; Schaefer, H. F. *J. Phys. Chem.* **1995**, *99*, 2324.

(21) Bartlett, R. J. Structure and Stability of Polynitrogen Molecules and Their Spectroscopic Characteristics: http: //www.qtp.ufl.edu/∼bartlett/polynitrogen.doc.gz.

(22) Gagliardi, L.; Pyykkö, P. *J. Am. Chem. Soc.* **2001**, *123*, 9700.

(23) Wilson, K. J.; Perera, S. A.; Bartlett, R. J. *J. Phys. Chem.* A **2001**, *105*, 7693.

(24) Gagliardi, L.; Orlandi, G.; Evangelisti, S.; Roos, B. O. *J. Chem. Phys.* **2001**, *114*, 10733.

(25) Liu, Y-Dong; Zhao, J-Fang; Li, Q-Shu *Theor. Chem. Acc.* **2001**, *107*, 140.

(26) Li, Q-Shu; Wang, L-Jie *J. Phys. Chem.* A **2001**, *105*, 1203.

(27) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(28) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* B **1988**, *37*, 785.

(29) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys*. **1989**, *90*, 2154.

(30) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem*. **1990**, *94*, 5523.

(31) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293.

(32) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(33) Dunning. T. H., Jr. *J. Chem. Phys*. **1989**, *90*, 1007.