J. Am. Chem. Soc. **2001,** *123,* 3308−3310

N_6^{2+} and N_4^{2+} Dications and Their N_{12} and N_{10} Azido Derivatives: DFT/GIAO-MP2 Theoretical Studies[1]

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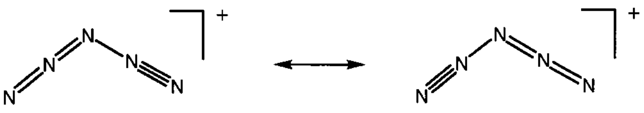
Received June 22, 2000. Revised Manuscript Received February 1, 2001

Abstract: The structures and energies of N_6^{2+} and N_4^{2+} were calculated by using the density functional theory method at the B3LYP/cc-aug-pVTZ level. The C_{2h} symmetric form **1** and $D_{\infty h}$ form **5** were found to be the stable minima for N_6^{2+} and N_4^{2+}, respectively. Dissociation of **1** into **5** and N_2 was computed to be endothermic by 25.1 kcal/mol. ^{15}N NMR chemical shifts and vibrational frequencies of **1** and **5** were also calculated. Interactions of **1** and **5** with azide ions were also probed representing N_{12} and N_{10}.

Introduction

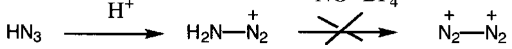
Christe et al. recently reported[2] the preparation of the remarkable N_5^+ cation. The highly energetic cation was characterized as the $N_5^+AsF_6^-$, $N_5^+SbF_6^-$, and $N_5^+Sb_2F_{11}^-$ salts by ^{15}N NMR, IR, and Raman spectroscopy. N_5^+ is considered, besides N_2 and N_3^-, only the third known compound containing a stable homoleptic polynitrogen moiety. Ab initio and density functional theory (DFT) calculations show the preferred C_{2v} symmetrical structure for the N_5^+ cation.[2] Recently Christe et al. also obtained the structure of N_5^+ by single-crystal X-ray diffraction studies.[3]



N_5^+

In 1991 Pyykkö and Runeberg calculated a series of ABCBA-type compounds including N_5^+ at the MP2/6-31G* level.[4] In 1992 one of us (GR) also proposed and calculated the N_5^+ cation by the ab initio method and suggested its possible synthesis from FN_2^+ and N_3^-.[5] However, this was not further pursued or published. Christe's pioneering work thus rightly deserves full credit.

Previously we have reported[6] the ab initio calculation of the suggested bisdiazonium dication N_4^{2+} which showed that the linear tetranitrogen dication is a minimum on the potential energy surface (PES). We have also attempted to generate the dication experimentally[6] by the diazotization of the aminodiazonium ion, obtained by protonation of HN_3 with $NO^+BF_4^-$ in Magic Acid/SO_2ClF solution at −78 °C. However, no diazotization of the aminodiazonium ion was observed.



Recently Bartlett calculated[7] the structures and energies of neutral, monocationic, as well as monoanionic forms of polynitrogen species ranging from N_2 to N_{10} using DFT and ab initio methods. All of them were found to be stable minima on their potential energy surfaces. Neither N_6^{2+} nor N_4^{2+} was, however, considered in this comprehensive study. Previously, Glukhovtsev et al. have calculated the structure and stability of neutral polynitrogen molecules (N_4, N_6, N_8, N_{10}, and N_{12}) by ab initio and DFT methods.[8]

We report now the investigation of the dications N_6^{2+} and N_4^{2+} by the DFT theoretical method. We also report their DFT calculated vibrational frequencies and ab initio GIAO-MP2 calculated ^{15}N NMR chemical shifts. We also calculated reaction energies of these intriguing tetra- and hexanitrogen dications with the azide (N_3^-) anion, resulting in N_{12} and N_{10}, respectively.

Results and Discussion

Calculations were carried out with the Gaussian 98 program system.[9] The geometry optimizations were performed by the density functional theory (DFT)[10] method employing the B3LYP functional[11] and using the correlation consistent aug-cc-pVTZ basis set (i.e. B3LYP/aug-cc-pVTZ level). Vibrational frequencies at the B3LYP/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level

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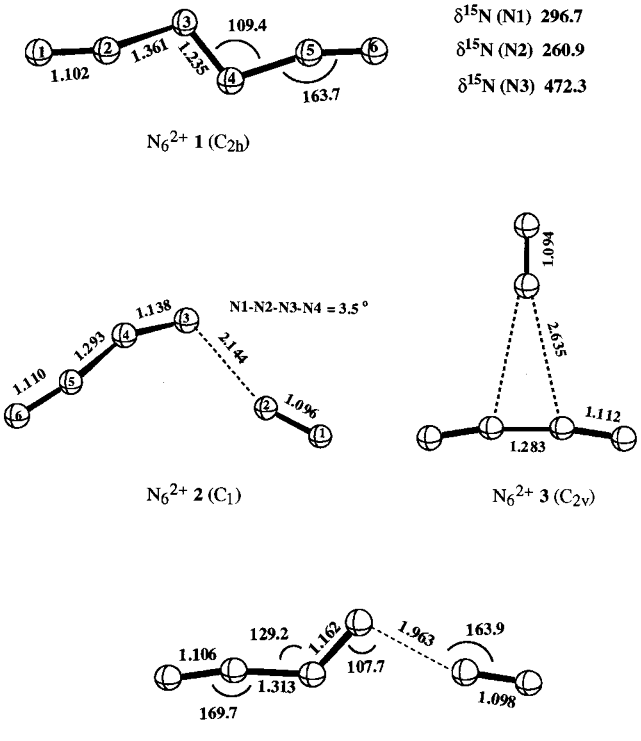

N_6^{2+} **1** (C_{2h})

N_6^{2+} **2** (C_1)

N_6^{2+} **3** (C_{2v})

N_6^{2+} **4** (C_s) TS

Figure 1. B3LYP/aug-cc-pVTZ optimized structures of **1**−**4** and GIAO-MP2/tzp calculated ^{15}N NMR chemical shifts of **1**.

N_4^{2+} **5** ($D_{\infty h}$)

Figure 2. B3LYP/aug-cc-pVTZ optimized structure and GIAO-MP2/tzp calculated ^{15}N NMR chemical shifts of **5**.

Table 1. Relative Energies (kcal/mol)[a]

no.	rel energy (kcal/mol)
1	0.0
2	4.7
3	10.2
4	8.7
5 + N_2	25.1
9N_{12}	0.0
10N_{12}	20.7

[a] Relative energies at the B3LYP/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ + ZPE level.

Table 2. B3LYP/aug-cc-pVTZ Calculated Frequencies[a] and IR Intensities

no.	freq in cm^{-1} (IR intensities in km/mol)
1	140 (0), 157 (0), 294 (0), 309 (0), 497 (0), 537 (25), 559 (0), 750 (14), 883 (0), 1520 (0), 2338 (335), 2351 (0)
5	235 (1), 457 (0), 915 (0), 2277 (330), 2400 (0),

[a] Not scaled.

(for N7 to N12 at the B3LYP/6-31G*//B3LYP/6-31G* level) were used to characterize stationary points as minima (number of imaginary frequencies (NIMAG) = 0) or transition states (NIMAG = 1) and to evaluate zero-point vibrational energies (ZPE) which were scaled by a factor of 0.96. Final energies were calculated at the B3LYP/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ + ZPE level. Heat of formation (ΔH_f) values were computed with the Gaussian-2 (G2) theory.[12] ^{15}N NMR chemical shifts were calculated by the GIAO method.[13] GIAO-MP2[14] calculations using a tzp basis set[14,15] have been performed with the ACES II program.[16] The ^{15}N NMR chemical shifts were referenced to NH_3 (calculated absolute shift, i.e., $\sigma(N) = 284.0$).

At the B3LYP/aug-cc-pVTZ level the C_{2h} symmetric form **1** is found to be a stable minimum for the N_6^{2+} dication as indicated by frequency calculations at the same level (i.e. number of imaginary frequency NIMAG = 0). The corresponding cis isomer (C_{2v} symmetry) was also calculated at the same B3LYP/cc-aug-pVTZ level. However, it was not found to be a true minimum as it contains one imaginary frequency. Energetically the cis isomer is also 10.2 kcal/mol less stable than the trans isomer **1**. The terminal N1−N2 bond distance in **1** is 1.102 Å. This is significantly shorter than the N2−N3 bond (1.361 Å) and also shorter than the central N3−N4 bond (1.235 Å). From the bond lengths it appears that there is little resonance interaction between the terminal triple bonds and central double bond. Resonance interactions involving the lone pairs of the central nitrogen atoms (N3 and N4) in fact create unfavorable strain and charge−charge repulsions.

Structures **2** and **3** were also found to be minima on the potential energy surface (PES) of N_6^{2+}. Each of the structures can be considered as a complex between N_4^{2+} and N_2. However, the structures **2** and **3** are less stable than **1** by 4.7 and 10.2 kcal/mol, respectively (Table 1).

We have located the transition structure, **4** (Figure 1), for the N_2 elimination process in **1** which lies 8.7 kcal/mol higher in energy (Table 1). This elimination process proceeds through complex **2** as indicated by IRC (intrinsic reaction coordinate) calculations.[9] Thus, **1** has a moderate kinetic barrier for N_2 loss and the process is endothermic by 25.1 kcal/mol. Dissociation of **1** into $2N_2^+$ and N_2, however, was computed to be exothermic by 17.9 kcal/mol. The possible dissociation of **1** into N_4^+ and N_2^+ could not be computed as the N_4^+ cation was found not to be a minimum. The heat of formation (ΔH_f) of **1** was calculated by using G2 theory. Expectedly, the dication has a very high heat of formation of 742 kcal/mol.

We have also calculated the ^{15}N NMR chemical shifts of **1** by the correlated GIAO-MP2 method[14] using B3LYP/aug-cc-pVTZ geometry as depicted in Figure 2. Calculated δ^{15}N of N1, N2, and N3 of **1** are 296.7, 260.9, and 472.3, respectively. The δ^{15}N of N3 (azo nitrogen) of 472.3 can be compared with the experimental δ^{15}N of *trans*-azobenzene of 508.0. However, we have to remember that these calculated ^{15}N NMR chemical shifts, even at the correlated GIAO-MP2 level, refer to the idealized gas phase and differ significantly from experimental values. The experimental ^{15}N NMR chemical shifts are very dependent on the nature of solvents and temperature. Calculated vibrational frequencies of **1** are given in Table 2.

The linear $D_{\infty h}$ structure **5** was found to be a minimum on the PES of N_4^{2+} (Figure 2) at the B3LYP/aug-cc-pVTZ level. No other minima were found. N_4^{2+} is isoelectronic with oxalyl dication $OCCO^{2+}$.[17] Similar linear structure of N_4^{2+} was also

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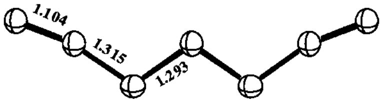
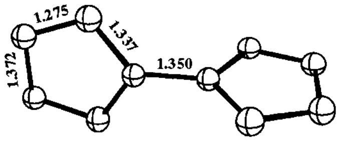
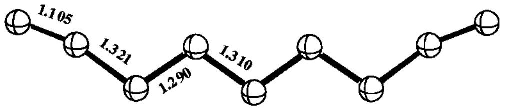


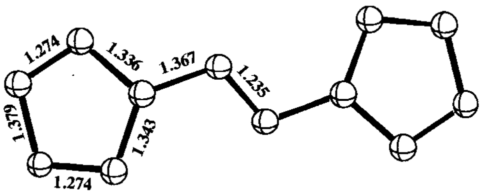
N_7^+ **6** (C_{2v})



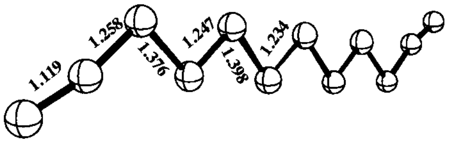
N_{10} **7** (D_{2d})



N_9^+ **8** (C_{2v})



N_{12} **9** (C_{2h})



N_{12} **10** (C_{2v})

Figure 3. B3LYP/aug-cc-pVTZ optimized structures of **6**−**10**.

found to be a minimum for $OCCO^{2+}$ at the MP2/6-31G* level.[17] It is interesting to note that the dimer of carbon monoxide, ethylenedione (O═C−C═O), is kinetically and thermodynamically unstable with respect to dissociation into 2 equiv of CO.[18] The terminal N1−N2 and central N2−N3 bond distances of **5** are 1.111 and 1.285 Å, respectively, representing bisdiazonium character. The heat of formation (ΔH_f) of **5**, calculated by G2 theory, was found to be 763 kcal/mol. The calculated δ^{15}N of N1 and N2 of **5** are 296.1 and 186.3, respectively. The value of 296.1 for terminal nitrogen is very close to the δ^{15}N value of the terminal nitrogen of **1** (296.7). Calculated vibrational frequencies of **5** are also given in Table 2.

Interactions of **1** and **5** with azide (N_3^-) ions yielding N_9^+, N_{12}, N_7^+, and N_{10}, respectively, were also calculated (Figure 3). Reactions of **5** with 1 and 2 equiv of N_3^- to give N_7^+ **6** and N_{10} **7**, respectively, were calculated to be highly exothermic by 422.8 and 585.4 kcal/mol. Similarly, reactions of **1** with 1 and 3 equiv of N_3^- to give N_9^+ **8** and N_{12} (**9** and **10**), respectively, were calculated. These interactions were computed to be also highly exothermic by 338.4 and 503.7 kcal/mol, respectively. The calculated global minimum structure of N_{12} was found to be of C_{2h} symmetry, **9** (Figure 3). The C_{2v} symmetric structure **10** is also a minimum on the potential energy surface. However, **10** is 20.7 kcal/mol less stable than **9** (Table 1). The heat of formation (ΔH_f) of **9** was computed to be 315.9 kcal/mol (B3LYP/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ + ZPE level). Calculated structures of **6**−**10** agree well with those reported.[7,8]

Conclusions

The present DFT study at the B3LYP/aug-cc-pVTZ level shows that the N_6^{2+} dication **1** is a minimum on its potential energy surface. Structure **1** with C_{2h} symmetry was characterized as a bisdiazo azo compound. Similar studies also show that the N_4^{2+} dication **5** with $D_{\infty h}$ symmetry is also a minimum. Interactions of **1** and **5** with azide (N_3^-) ions were computed to be highly exothermic yielding N_{12} and N_{10}, respectively. ^{15}N NMR chemical shifts and vibrational frequencies of **1** and **5** were also calculated.

Acknowledgment. This work supported by the National Science Foundation and the Office of Naval Research. Dr. Karl O. Christe is thanked for his valuable comments.

Supporting Information Available: Cartesian coordinates and total energies (hartrees) of the optimized geometries (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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