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# A theoretical study of the nitrogen clusters formed from the ions $N_3^-$ , $N_5^+$ , and $N_5^-$

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The results of a theoretical study on the formation of the nitrogen cluster  $N_{10}$  from the ionic species  $N_5^+$  and  $N_5^-$  are presented. The possibility to form  $N_8$  from  $N_5^+$  and  $N_3^-$  has also been studied but no stable form was found. Structural and vibrational data are given for the different clusters. It is suggested that the anion  $N_5^-$  might be stable enough to be synthesized. The calculations have been carried out using multiconfigurational self-consistent-field wave functions and second-order perturbation theory. © 2001 American Institute of Physics. [DOI: 10.1063/1.1370063]

## I. INTRODUCTION

In recent years, the hypothetical existence of polynitrogen clusters has been the object of several theoretical investigations.<sup>1–13</sup> Besides their theoretical interest, these structures have attracted interest because of their possible use as high energy-density materials (HEDM), i.e., the large ratio between the energy released in a fragmentation reaction and the specific weight. Since 1999 there is exciting new experimental interest in these compounds: Christe *et al.*<sup>14</sup> described the synthesis of  $N_5^+$  as a salt with  $AsF_6^-$ . The cation is the first new all-nitrogen species to be isolated in more than a century, and only the third known besides  $N_2$  and  $N_3^-$ . More recently, Christe *et al.*<sup>15</sup> reported that the  $SbF_6^-$  and  $Sb_2F_{11}^-$  salts of  $N_5^+$  are stable up to 70 °C. With this result at hand one may speculate over the possibility to use the  $N_5^+$  cation to build neutral allotropes of nitrogen such as  $N_8$  or  $N_{10}$ .

In this study we have investigated the formation of the hypothetical compounds  $N_8$  and  $N_{10}$  from the charged clusters  $N_3^-$ ,  $N_5^+$ , and a likewise hypothetical anion  $N_5^-$ . The structures and the molecular properties of the initial ions have been determined together with the corresponding ion pairs. We extensively studied different isomers of  $N_8$  in earlier work, and found that this molecule is probably not stable enough to be a good candidate for a neutral cluster.<sup>9–11</sup> Possible low energy structures for  $N_{10}$  have recently been studied by Manaa.<sup>16</sup> He found a bicyclic structure with two perpendicular five-rings to be most stable and also speculated about the possibility to use them as building blocks for  $N_{60}$ . The stability of the compound towards dissociation was, however, not studied. This issue will be discussed here. Calculations of the vibrational frequencies for the ion pairs show that while  $N_{10}$  is a stable compound,  $N_8$  isomerizes to azido-

pentazole and then dissociates to four  $N_2$  molecules. The  $N_{10}$  ion pair transforms with a small barrier to the stable bicyclic form reported by Manaa. In Figs. 1 and 2 the structure of  $N_8$  and  $N_{10}$  are reported, respectively.

## II. DETAILS OF CALCULATIONS

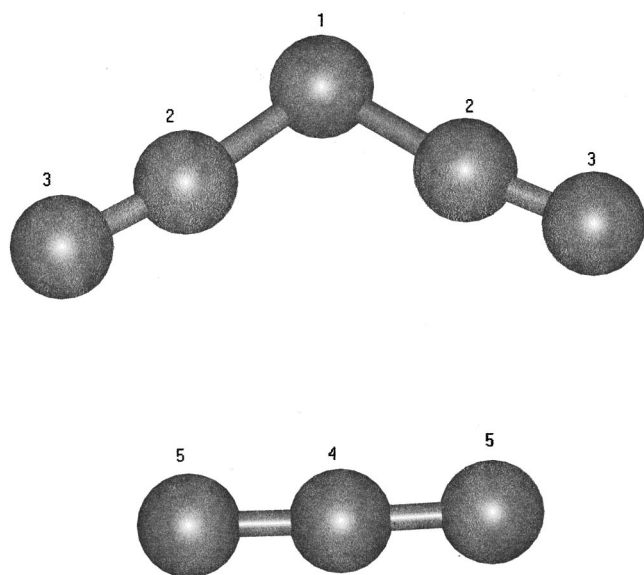
The calculations were performed at the complete active space self-consistent-field (CASSCF) level of theory<sup>17</sup> with dynamic electron correlation added using multiconfigurational second order perturbation theory, CASPT2.<sup>18,19</sup> For some of the systems comparative calculations were performed at the single configurational second order perturbation level, MP2, and with density functional theory, DFT-B3LYP.

The MOLCAS-5 quantum chemistry software<sup>20</sup> was used to perform the CASSCF and CASPT2 calculations, while the Gaussian98<sup>21</sup> package was used for the MP2 and DFT calculations. In the CASSCF/CASPT2 calculations, the atomic natural orbital, ANO-S, 3s2p1d basis,<sup>22</sup> was used for  $N_8$  and  $N_{10}$ . The smaller clusters were optimized also with the ANO-L 4s3p2d basis.<sup>23</sup> A split valence plus polarization 3s2p1d basis, 6-31G\*\*,<sup>24</sup> was used in the MP2 and DFT calculations. For  $N_3^-$  a valence triple-zeta plus polarization 4s3p2d1f basis, 6-311G(2df,2pd),<sup>25</sup> was also used.

A CASSCF geometry optimization was performed on all species, assuming  $C_{2v}$  symmetry for  $N_5^+$ ,  $N_5^-$ ,  $N_8$  and  $N_{10}$ ,  $D_{5h}$  for  $N_5^-$ , and  $D_{2h}$  to represent the linear symmetry of  $N_3^-$  and  $N_3$ . In addition, geometry optimization and frequency calculations were performed at the CASPT2 level of theory for the ions.

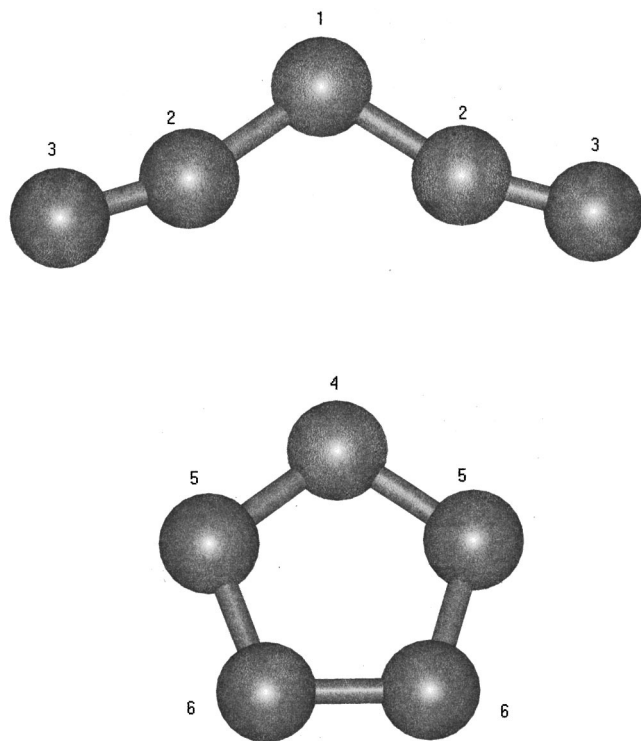
The active space in the CASSCF calculations was chosen based on a number of preliminary tests. An active space formed by the  $\pi$  orbitals was used for  $N_5^-$  and  $N_{10}$  where no in-plane  $\pi$  bonds are formed. The same type of active space was used for the ion pairs  $N_5^+ + N_3^-$  and  $N_5^+ + N_5^-$ . This choice

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FIG. 1. The structure of  $N_5^+ - N_3^-$ ,  $N_8$ .

of active space was checked for the smaller ions by calculations using larger spaces as will be explained below.

CASPT2 geometry optimizations were performed for some of the systems with different active spaces and basis sets. These pointwise optimizations were performed using a triangular grid with the side 0.05 a.u. A triangular grid is constructed as the corners and the edge midpoints of a super-triangle in the degrees of freedom of the given system, with the center of the triangle at a guessed geometry. A second order polynomial fit is used to obtain the stationary point and the set of calculations is repeated until the result is stable. A

FIG. 2. The structure of  $N_5^+ - N_5^-$ ,  $N_{10}$ .TABLE I. Bond lengths (in Å) and vibrational frequencies (in  $\text{cm}^{-1}$ ) for  $N_3^-$  and  $N_3$ .

Basis set (active space)	MP2	CASPT2	CCSD <sup>a</sup>	Expt. <sup>b</sup>
$N_3^-$ bond length				
6-31G**	1.193		1.190	1.188
6-311G(2df,2pd)	1.180			
ANO-S,3s2p1d(3)		1.217		
ANO-L,4s3p2d1f(6)		1.196		
ANO-L,4s3p2d1f(9)		1.194		
$N_3$ bond length				
ANO-S,3s2p1d(3)		1.207	1.183	1.181
ANO-L,4s3p2d1f(6)		1.181		
ANO-L,4s3p2d1f(9)		1.187		
$N_3^-$ vibrational frequencies				
	CASSCF	CASPT2	CCSD <sup>a</sup>	Expt. <sup>c</sup>
$\sigma_g$	1315	1306	1352	1338
$\sigma_u$	2026	2033	2013	1986
$\pi_u$	617	612	637	644

<sup>a</sup>Coupled cluster results, Ref. 26.

<sup>b</sup>The experimental bond distance for  $N_3^-$  (Ref. 29) and for  $N_3$  (Ref. 30).

<sup>c</sup>Gas phase data (Ref. 31).

smaller grid, 0.03, was subsequently used to compute the harmonic force field and the corresponding vibrational frequencies. The largest geometry optimization performed in this way was for the ion pair  $N_5^+ + N_5^-$  in  $C_{2v}$  symmetry with nine degrees of freedom.

### III. RESULTS AND DISCUSSION

#### A. The $N_3^-$ radical and anion

Calculations on this system were performed in order to establish the accuracy of the present approach. Comparison can be made to the accurate coupled cluster (CCSD) calculations of Kaldor<sup>26</sup> and to experiment. Three different active spaces were used: three electrons (or four) in three orbitals, (3(4)/3), all  $\pi$  orbitals, (7(8)/6), and finally all N2p generated orbitals (9(10)/9). The smallest active space is unbalanced, but was chosen because it is the one used for the largest systems.

The results are presented in Table I, which gives computed bond distances and vibrational frequencies. The computed bond distance for both the ion and the radical is 0.02–0.03 Å too long at the lowest level of theory, which improves to less than 0.01 Å when the active space is increased and a larger basis set is used. The too long bond lengths is mainly a basis set effect, as already noticed in previous studies.<sup>27</sup>

The vibrational frequencies have been computed with nine active orbitals and a large ANO-L 4s3p2d1f basis set. The CASPT2 frequencies for  $N_3^-$  are in good agreement with the CCSD and experimental results.

The computed electron affinity for the radical is 2.71 eV at the lowest level of theory, is increased to 2.78 eV when changing to the larger basis set while keeping the small active space (3(4)/3), and finally to 2.64 eV at the highest level of theory. This should be compared to the experimental

TABLE II. Bond lengths ( $R$ ) (in Å), bond angles (in degrees), and vibrational frequencies (in cm<sup>-1</sup>) for N<sub>5</sub><sup>+</sup>. For the atom numbering see Fig. 2. The CASPT2 results are with the ANO-L 4s3p2d basis and MP2 results with the 6-311G\*\* basis.

	MP2	CASPT2 <sup>a</sup>	CCSD(T) <sup>b</sup>	B3LYP <sup>b</sup>	Expt. <sup>c</sup>
$R_{12}$	1.291	1.303(1.306)	1.337	1.299	1.315
$R_{23}$	1.123	1.124(1.222)	1.131	1.106	1.11
$\angle 123$	169.0	167.2(164.3)	166.0	167.2	166.6
$\angle 212$	111.4	112.5(110.8)	108.1	112.5	110.3
$\nu_1(a_1)$		2183(2189)	2229	2336	2270
$\nu_2(a_1)$		874(871)	818	850	872
$\nu_3(a_1)$		739(742)	644	678	680
$\nu_4(a_1)$		184(203)	181	193	209
$\nu_5(a_2)$		433(468)	475	502	
$\nu_6(b_1)$		282(386)	405	424	420
$\nu_7(b_2)$		2149(2147)	2175	2282	2210
$\nu_8(b_2)$		1193(1240)	1032	1167	1088
$\nu_9(b_2)$		435(367)	399	436	

<sup>a</sup>Active space: (6/5). Values within parentheses with (12/10).

<sup>b</sup>CCSD(T) and B3LYP geometries from Ref. 13 and frequencies from Ref. 14.

<sup>c</sup>IR frequencies and "interpolated" geometry from Ref. 14.

value, 2.76 eV.<sup>28</sup> We conclude that this value is not very sensitive to the level of theory used. The CCSD value of Kaldor is 2.50 eV.<sup>26</sup>

## B. The N<sub>5</sub><sup>+</sup> cation and radical

N<sub>5</sub><sup>+</sup> has been previously investigated by Nguyen *et al.*<sup>13</sup> and by Christe *et al.*<sup>14</sup> at the B3LYP and CCSD(T) levels of theory. The present CASPT2 results were obtained with the five  $\pi$  orbitals active. They are presented in Table II. The results for the geometry seem to be in better agreement with the B3LYP and experimentally deduced results than the CCSD(T) approach, which tends to give longer bond lengths. Christe *et al.* have described the two bond lengths in terms of the balance between two valence structures, one with single bonds from the central atom and one where all bonds are double. This is confirmed here. Both B3LYP and CASSCF yields a negatively charged central (N<sub>1</sub>) atom and the positive charge mainly located at N<sub>2</sub>. The vibrational frequencies obtained with the different methods scatter around the experimental values. It is somewhat difficult to make a direct comparison because the experimental values were obtained for the N<sub>5</sub><sup>+</sup>AsF<sub>6</sub><sup>-</sup> crystal.

Additional calculations were performed with the larger active space (12/10), adding the in-plane " $\pi$  orbitals," which is a more balanced set for this quasilinear molecule. As can be seen in Table II, the geometry and vibrational frequencies are only slightly affected (with the exception of some of the bending frequencies, which are considerably improved). The total CASPT2 energy obtained with this larger active space differs only by 4 kcal/mol for the one obtained with the (6/5) active space. The energetics presented below is thus only affected to a small extent.

We have also studied the dissociation of N<sub>5</sub><sup>+</sup> to N<sub>2</sub> and N<sub>3</sub><sup>+</sup> at the B3LYP and CASPT2 levels of theory. There is no barrier to the formation of N<sub>5</sub><sup>+</sup> from N<sub>2</sub> and N<sub>3</sub><sup>+</sup> on the singlet surface. The computed bond strength with respect to the triplet ground state of N<sub>3</sub><sup>+</sup> is 8 kcal/mol on the CASPT2 level of

TABLE III. Bond length ( $R$ ) (in Å), and vibrational frequencies (in cm<sup>-1</sup>) for N<sub>5</sub><sup>-</sup>. The CASPT2 results are with the ANO-L 4s3p2d basis and MP2 results with the 6-31G\*\* basis.

	MP2	CASPT2	B3LYP <sup>a</sup>
$R$	1.327	1.338	1.326
$\nu_1(a'_1)$		1015	1192
$\nu_2(e'_1)$		1173	1250
$\nu_3(e'_2)$		1090	1120
$\nu_4(e'_2)$		971	1026
$\nu_5(e'_2)$		748	773

<sup>a</sup>B3LYP geometry from Ref. 7.

theory (B3LYP gives a 10 kcal/mol larger binding energy). The lowest singlet state lies 36 kcal/mol higher. N<sub>5</sub><sup>+</sup> is thus a very weakly bound ion. N<sub>3</sub><sup>+</sup> on the other hand is 85 kcal/mol more stable than N<sub>2</sub>+N<sup>+</sup>(<sup>3</sup>P).

The N<sub>5</sub> radical was found to have a C<sub>2v</sub> distorted pentagonal structure with the bond lengths 1.41, 1.27, 1.52, 1.27, and 1.41 Å (determined at the CASSCF level of theory with the active space (5/5) and the basis set ANO-L, 4s3p2d). The computed (CASPT2) ionization energy of the radical is 7.07 eV and the electron affinity is as large as 5.36 eV.

## C. The N<sub>5</sub><sup>-</sup> anion

One of the main purposes of the present work has been to study the structure and properties of the N<sub>5</sub><sup>-</sup> anion. Only one previous theoretical study of this ion is known to use us.<sup>7</sup> N<sub>5</sub><sup>-</sup> can be expected to be particularly stable due to the aromatic character of the  $\pi$ -electron system. The calculations show that it is a regular pentagon with the side 1.34 Å (CASPT2; B3LYP and MP2 give 1.33 Å). The vibrational frequencies are all real and large (cf. Table III). The large electron affinity of the corresponding radical is another indication of the stability of the anion.

N<sub>5</sub><sup>-</sup> is 9 kcal/mol more stable than N<sub>3</sub><sup>-</sup>+N<sub>2</sub> (CASPT2; the B3LYP value is 3 kcal/mol). We studied the fragmentation along a planar path of C<sub>2v</sub> symmetry. A planar transition state was found with the CASPT2 approach, located 26 kcal/mol above N<sub>5</sub><sup>-</sup>. The result was checked by computing all frequencies at the transition state using DFT/B3LYP. All are large and real, except the one along the C<sub>2v</sub> reaction coordinate (which is simply the distance between the central atom in N<sub>3</sub><sup>-</sup> and the midpoint of N<sub>2</sub>). This reaction coordinate is symmetry allowed. It is then most likely that it represents the minimum energy path for the reaction. We conclude that N<sub>5</sub><sup>-</sup> is a stable ion with a considerable barrier for fragmentation and a large ionization potential.

## D. The N<sub>8</sub> and N<sub>10</sub> clusters

The ion pair N<sub>3</sub><sup>-</sup>+N<sub>5</sub><sup>+</sup> was optimized at the CASPT2 level assuming a planar system of C<sub>2v</sub> symmetry. A stationary structure was found with the structure shown in Fig. 1. However, computing the analytical Hessian at the CASSCF level of theory, two imaginary frequencies were found. Motion along this reaction coordinate transforms the supermolecular N<sub>8</sub> system into azidopentazole (cf. Fig. 3). In previous studies<sup>11,12</sup> (and references in there) it has been shown

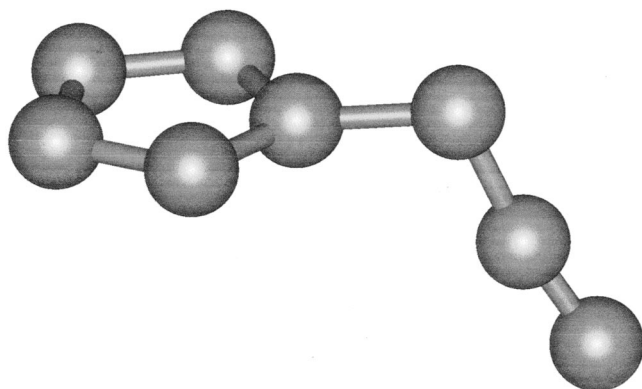


FIG. 3. The structure of azidopentazole.

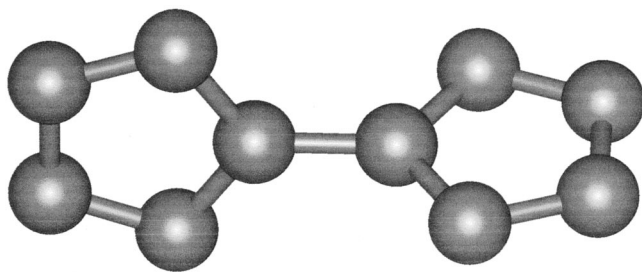
that azidopentazole is the lowest energy  $N_8$  isomer and that it dissociates into four  $N_2$  molecules with a barrier, which is not larger than  $20 \text{ kcal mol}^{-1}$ . We conclude that this new form of  $N_8$  as a salt is not stable.

It has recently been shown<sup>16</sup> that the most stable form of  $N_{10}$  is a bicyclic form with two five rings bound to each other in a perpendicular configuration. (See Fig. 4.)

We have optimized the structure of this compound at the CASSCF and DFT levels of theory. The reaction to form the bicyclic molecule from the free ions proceeds without a barrier. If we, however, allow the two ions to approach each other along the energetically most favorable path, an ion pair can be formed that is bound with  $117 \text{ kcal/mol}$  with respect to the free ions. The structure is shown in Fig. 2. The bond distance between the two central atoms of the two ions,  $R_{14}$ , is  $2.80 \text{ \AA}$ . The intraionic distances are slightly elongated with respect to the free ions, typically between  $0.01$  and  $0.03 \text{ \AA}$ . The ion pair will transform to the bicyclic form (cf. Fig. 4), which is  $24 \text{ kcal/mol}$  more stable. The barrier for this transformation has not been computed.

In Table IV we give the energetics for the transformation of the bicyclic form of  $N_{10}$  to five  $N_2$  molecules via the ionic species. All energies have been computed at the same level of theory. For the strong covalent bonds, for example, the  $N_2$  molecule, this level does not yet give the experimental dissociation energy. We expect, however, most of these errors to cancel because the end products are five  $N_2$  molecules. The small electron affinity of the nitrogen atom,  $EA(N)$ , has not been computed. It cancels in the overall reaction.

Summing up the energies in the different steps yields a computed energy of  $237 \text{ kcal/mol}$  for the total reaction,

FIG. 4. The structure of bicyclic form of  $N_{10}$ .TABLE IV. Energetics (in  $\text{kcal/mol}$ ) for the stepwise fragmentation of  $N_{10}$  to five  $N_2$  molecules via the ionic species (CASPT2 energies).<sup>a</sup>

$N_{10} \rightarrow \text{ion-pair } N_5^+ + N_5^-$	24
$\text{Ion-pair} \rightarrow \text{Free } N_5^+ + N_5^-$	117
$N_5^+ \rightarrow N_3^+ + N_2$	8
$N_5^- \rightarrow N_3^- + N_2$	9
$N_3^+ \rightarrow N_2 + N^+$	85
$N_3^- \rightarrow N_2 + N^-$	55-EA(N)
$N^+ + e \rightarrow N$	-338
$N^- - e \rightarrow N$	EA(N)
$N + N \rightarrow N_2$	-197
$N_{10} \rightarrow 5N_2$	-237

<sup>a</sup>ANO-L 4s3p2d basis set, except for the first reaction where the basis set was ANO-S 3s2p1d. EA(N) is the electron affinity of the nitrogen atom.

$N_{10} \rightarrow 5N_2$ . This value can be compared to Manaa's result:  $286$ ,  $270$ , and  $224 \text{ kcal/mol}$  at the QCISD, MP2, and B3LYP levels of theory, respectively.

#### IV. CONCLUSIONS

The results of a CASSCF/CASPT2 study on the super-systems  $N_8$  and  $N_{10}$ , prepared from the ions  $N_3^-$ ,  $N_5^+$ , and the hypothetical anion  $N_5^-$  have been presented. The structures, energetics, and harmonic frequencies of the initial ions have been computed and compared to earlier results and, when available, to experiment. The ion  $N_5^-$  has been found surprisingly stable. It is  $9 \text{ kcal/mol}$  more stable than  $N_3^- + N_2$  and the barrier to dissociation is close to  $30 \text{ kcal/mol}$ . For the corresponding cation,  $N_5^+$ , we find that the formation from  $N_2$  and  $N_3^+$  proceeds without a barrier, once the crossing to the singlet surface has taken place. The energy difference is  $8 \text{ kcal/mol}$ . Thus, it seems that the anion is as stable as the cation. This, of course, is the situation in the gas phase. The energetics in a medium will be different. Still, it might be worth speculating about the possibility to synthesize also the anion of the  $N_5$  cluster.

From the frequency analysis, the ion pair  $N_5^- + N_5^+$  turns out to be a stable compound, while  $N_8$  is unstable as such and tends to isomerize to azidopentazole and then dissociate to four  $N_2$  molecules. The ion pair form of  $N_{10}$  is, however,  $24 \text{ kcal/mol}$  less stable (in the gas phase) than the bicyclic form described by Manaa.<sup>16</sup>

#### ACKNOWLEDGMENTS

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