On the dissociation of N\textsubscript{6} into 3 N\textsubscript{2} molecules

GAGLIARDI, Laura, et al.

Abstract
The dissociation of the hypothetical system N[6] into three N[2] molecules has been studied using multiconfigurational second order perturbation theory (CASSCF/CASPT2) aided by a preliminary study using the density functional (DFT) approach. A concerted transition state with C\textsubscript{2} symmetry has been found between the most stable linear diazide form of N[6] and three N[2] molecules. The computed barrier is 28.7 kcal/mol (CASPT2) and 17.4 kcal/mol (DFT), respectively.

GAGLIARDI, Laura, et al. On the dissociation of N\textsubscript{6} into 3 N\textsubscript{2} molecules. Chemical Physics Letters, 2000, vol. 320, no. 5-6, p. 518-522

DOI: 10.1016/S0009-2614(00)00281-5

Available at:
http://archive-ouverte.unige.ch/unige:3529

Disclaimer: layout of this document may differ from the published version.
On the dissociation of $N_6$ into 3 $N_2$ molecules

Laura Gagliardi a,*, Stefano Evangelisti b, Vincenzo Barone c, Björn O. Roos d

a Dipartimento di Chimica Fisica e Inorganica, Università di Bologna, viale Risorgimento 4, 40136 Bologna, Italy
b Laboratoire de Physique Quantique, UMR 5626, Université Paul Sabatier, 118, Route de Narbonne, F-31062 Toulouse CEDEX, France
c Dipartimento di Chimica, Università Federico II di Napoli, via Mezzocannone 4, I-80134 Napoli, Italy
d Department of Theoretical Chemistry, Chemical Center, P.O.B. 124, S-221 00 Lund, Sweden

Received 26 January 2000; in final form 27 February 2000

Abstract

The dissociation of the hypothetical system $N_6$ into three $N_2$ molecules has been studied using multiconfigurational second order perturbation theory (CASSCF/CASPT2) aided by a preliminary study using the density functional (DFT) approach. A concerted transition state with $C_2$ symmetry has been found between the most stable linear diazide form of $N_6$ and three $N_2$ molecules. The computed barrier is 28.7 kcal/mol (CASPT2) and 17.4 kcal/mol (DFT), respectively.

1. Introduction

The possible existence of clusters composed of non-metallic light atoms (carbon, nitrogen, oxygen) has been object of several recent theoretical studies [1–11]. The practical interest of these structures is related to their possible use as environmental friendly high energy-density materials (HEDM), i.e. compounds with a high ratio between the energy released in a fragmentation reaction and the specific weight. In our recent work on the hypothetical system $N_8$ [3–5] we have considered several isomers and the reaction paths between them. Recently we have also studied the fragmentation reaction $N_8 \rightarrow N_6 + N_2$ [5]. In the present study we consider the further dissociation of $N_6$ and also the possible structures and the properties of this cluster.

Several isomers of $N_6$ have been considered in recent papers by Engelke and Nguyen [6–10]. In specific in Ref. [9] six isomers were considered, namely the benzene, Dewar benzene, benzvalene, triprismane, bicyclopropenyl and diazide, and the open-chain diazide (hereafter denoted also as ‘linear’ structure) and the cyclic benzene (Fig. 1) were found to be lower in energy than the most compact forms. However, both the cyclic and the linear forms were found to be unstable at the highest level of accuracy that was used, i.e. the Møller–Plesset second order perturbation level of theory (MP2) with a vdzp basis [6,8,7,9]. There is either a hill (the cyclic $D_{6h}$ hexaazabenzene) or a saddle point (the open-chain $C_2$ diazide). In the course of the present study, we have found that the cyclic form is unstable with respect to dissociation into three $N_2$ molecules. This is in agreement with earlier results [10]. Local minima have been found for the cis- and trans-diazide with the trans form most stable.
In this Letter, we present the results of a theoretical study of the two linear isomers and the dissociation of the most stable trans form via a concerted reaction path. Preliminary calculations were performed at self consistent field (SCF) and MP2 level of theory using a correlation-consistent basis sets of Dunning, in the double-zeta (vdzp) and triple-zeta (vtpz) versions [12]. DFT calculations were then performed using the program Gaussian98 [13] at B3LYP level of theory [14] with the vdzp and vtpz basis. Complete active space (CAS) SCF [15] calculations were performed with dynamic electron correlation added using multiconfigurational second order perturbation theory, CASPT2 [16,17], using the MOLCAS-4 program [18]. This approach has in a number of earlier applications shown to give estimates of relative correlation energies with an accuracy of a few kcal/mol (see for example Refs. [17,19]).

The geometry optimizations were in this case made at the CASPT2 level using a point-wise grid. The basis sets used were of the atomic natural orbital type (ANO): ANO-S,3s2p1d (BS1) in the geometry determinations and ANO-L,4s3p2d1f (BS2) for the final calculation of relative energies.

2. Results

In the previous study on N₆ done by Engelke [7], two stationary points were found for the linear form, with symmetry C₂ and C₄, respectively. The nature of these points depends on the type of approximation used. The cyclic form was restricted to have D₆₅₇ symmetry. We have studied the cyclic form at different levels of theory. The largest calculations (CASPT2/BS2) gives a cyclic form with D₂ symmetry. This form is, however, only 0.25 kcal/mol more stable than the planar D₆₅₇ structure, which dissociates (at the same level of theory) without any barrier into three N₂ molecules. It was concluded, in agreement with earlier results, that the cyclic form of N₆ is not stable. We shall therefore concentrate on the properties of the linear forms of N₆.

CASCF/CASPT2 optimizations of the linear structures were performed on a grid, assuming C₂ᵥ and C₂ᵥ symmetry for the trans and cis forms, respectively. A triangular grid with the side 0.05 au was used in the final calculation (a triangular grid is constructed as the corners and the edge midpoints of a super-triangle in the N degrees of freedom with the center of the triangle at a guessed geometry. A second order polynomial is used to obtain the stationary point and the set of calculations is repeated until the result is stable). With symmetry there are five degrees of freedom. However, the outer NNN angle is very close to 180°, so it was assumed to have this value and was determined in a last step with the remaining degrees of freedom fixed at their equilibrium values.

The active space used in the CASSCF calculations was chosen based on a number of preliminary studies. It was found (see below) that an active space with 12 electrons in 12 orbital orbitals gives a balanced description of the different structures, and can also describe the dissociation process.

Linear N₆ is the most stable form of the molecule, as has been shown in a number of earlier studies [20,8,7,21]. Glukhovtsev and Schleyer [21] made a thorough analysis of the electronic structure and found that it is best described as: N₁―N₂ ―N₃ ―N₄ ―N₅ ―N₆ (I) since very little charge was found on the end atoms. The results were based on an SCF wave function. The present CASSCF results should be more accurate and indicate that the electronic structure is actually a mixture of (I) and the valence structure (II): N₁ ―N₂ ―N₃ ―N₁ ―N₂ ―N₃ (II). The Mulliken charges on the three atoms are: q(N₁) = -0.13, q(N₂) = +0.26, and q(N₃) = -0.13, which shows
that the negative charge is more delocalized than the first valence structure alone would suggest. The CASSCF wave function shows considerable multi-configurational character. The weight of the leading (SCF) configuration is 83.8% with basis set BS2 at equilibrium geometry.

The resulting bond distance would be $N_1N_3$ single, $N_1N_2$ between single and double, and $N_2N_3$ between double and triple as is born out by the bond distances presented in Table 1. Further, one expects the $N_1N_2N_3$ angle to be close to $180^\circ$, which is also what is obtained. Earlier discussions concerning hyper-valent structures in this $N_6$ conformer (see for example [7]) is based on a misunderstanding of the electronic structure as was also pointed out by Glukhovtsev et al. [21].

Engelke [7] found two stationary points very close in energy, with symmetry $C_1$ and $C_2$, respectively. The $C_2$ structure is the lowest one, but its energy is only 0.05 kcal/mol below the energy of the other isomer. Moreover, both structures are almost planar. Since for an exactly planar geometry both forms merge into the $C_{2v}$ form, the two isomers are practically coincident and are most probably only an artefact of the calculation.

A virtually planar system was found also in the present work and the studies at the CASPT2 level were made under this assumption. At this level both the trans and cis forms were studied. The results are presented in Table 1. The different levels of approximation give rather similar geometries. We note that the $N_1N_2N_3$ angle is slightly enlarged in the cis form due to the increased repulsion between the end atoms. This form was found to be 6.2 kcal/mol less stable than the trans form. The energy difference between the linear trans form and cyclic $N_6$ was found to be 25.7 kcal/mol. These energies were obtained with the large ANO basis set. Nguyen [8] obtained an energy difference of 35.3 kcal/mol in his best MP2 study.

The dissociation of linear $N_6$ into three nitrogen molecules was studied at the DFT and CASSCF/CASPT2 levels of theory. The linear structure was optimized at DFT level and the calculation of the harmonic vibrational frequencies confirmed that the linear structure is a local minimum, with all the harmonic vibrational frequencies real. The search for

<table>
<thead>
<tr>
<th>Basis set</th>
<th>Method</th>
<th>$R_{11}$</th>
<th>$R_{12}$</th>
<th>$R_{23}$</th>
<th>$\theta_{112}$</th>
<th>$\theta_{123}$</th>
<th>$\theta_{2112}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>vdzp</td>
<td>SCF</td>
<td>1.431</td>
<td>1.236</td>
<td>1.100</td>
<td>107.4</td>
<td>174.8</td>
<td>180.0</td>
</tr>
<tr>
<td>vdzp</td>
<td>MP2 (1)</td>
<td>1.463</td>
<td>1.261</td>
<td>1.154</td>
<td>107.3</td>
<td>171.5</td>
<td>180.0</td>
</tr>
<tr>
<td>3s2p1d</td>
<td>CASPT2($C_{2v}$)</td>
<td>1.479</td>
<td>1.266</td>
<td>1.163</td>
<td>105.3</td>
<td>171.3</td>
<td>180.0</td>
</tr>
<tr>
<td>3s2p1d</td>
<td>CASPT2($C_1$)</td>
<td>1.483</td>
<td>1.278</td>
<td>1.172</td>
<td>118.1</td>
<td>173.1</td>
<td>180.0</td>
</tr>
<tr>
<td>vdzp</td>
<td>DFT</td>
<td>1.447</td>
<td>1.247</td>
<td>1.141</td>
<td>109.4</td>
<td>171.4</td>
<td>180.0</td>
</tr>
<tr>
<td>vtzp</td>
<td>DFT</td>
<td>1.445</td>
<td>1.239</td>
<td>1.119</td>
<td>109.4</td>
<td>172.1</td>
<td>180.0</td>
</tr>
</tbody>
</table>

transition state for dissociation

<table>
<thead>
<tr>
<th>Basis set</th>
<th>Method</th>
<th>$R_{11}$</th>
<th>$R_{12}$</th>
<th>$R_{23}$</th>
<th>$\theta_{112}$</th>
<th>$\theta_{123}$</th>
<th>$\theta_{2112}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>vdzp</td>
<td>DFT</td>
<td>1.302</td>
<td>1.427</td>
<td>1.131</td>
<td>115.9</td>
<td>149.4</td>
<td>110.4</td>
</tr>
<tr>
<td>3s2p1d</td>
<td>CASPT2($C_2$)</td>
<td>1.301</td>
<td>1.455</td>
<td>1.141</td>
<td>113.7</td>
<td>151.0</td>
<td>101.3</td>
</tr>
</tbody>
</table>

a CASPT2 calculations were performed both for the trans and the cis structure.
b CASPT2 results with assumed $C_2$ symmetry.
a transition state led to a structure with $C_2$ symmetry at DFT level, with the angle 110° between the two $N_1N_2N_3$ planes. The calculation of the harmonic frequencies confirmed that the structure found was a transition state, with one imaginary frequency equal to $1024i$ cm$^{-1}$. A barrier for dissociation of 17.4 kcal/mol was obtained at DFT level. The inclusion of the zero point energy in the barrier calculation, lowers the barrier by 3 kcal/mol. The calculations were repeated at the CASSCF/CASPT2 level assuming $C_2$ symmetry. The BS1 basis set was used for the optimization of the geometry. Final energy calculations were performed with BS2. The search for the transition state was performed at the CASPT2 level of theory using a grid in seven dimensions.

The resulting geometries are presented in Table 1. We notice that the results obtained at the DFT and CASPT2 levels are similar. The multiconfigurational nature of the CASSCF wave function has not changed much and the weight of the leading configuration is now 85%, which shows that the reaction is symmetry allowed. A picture of the electron density at the equilibrium and the transition state is given, respectively, in Figs. 2 and 3. It can be seen that while the minimum geometry can be viewed as two coupled $N_1$ units, the TS clearly shows the three $N_2$ molecules, now only weakly linked. While the DFT and CASPT2 transition state geometries are similar, this is not the case for the energy barrier. The DFT value is 17.4, while the CASPT2 result is 27.4 kcal/mol with BS1 and 28.7 kcal/mol with BS2. The latter value is believed to be accurate to within a few kcal/mol. We consider the zero point energy correction of 3 kcal/mol obtained at DFT level a reasonable estimation of the CASPT2 zero point energy correction. Thus we conclude from the present study that $N_2$ forms a stable molecule in a linear arrangement with a barrier to dissociation of 25–30 kcal/mol. The reaction mechanism is an allowed concerted dissociation directly into three $N_2$ molecules.

**Acknowledgements**

This work was partially supported by Ministero dell’Università e della Ricerca Scientifica, (MURST), the French `Centre National de la Recherche Scientifique' (CNRS), and the Swedish Natural Science Research council (NFR).

**References**


