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# Theoretical Study of the Triplet $N_4$ Potential Energy Surface

**Martina Bittererová**[†] **and Tore Brinck***

*Physical Chemistry, Royal Institute of Technology, SE- 100 44 Stockholm, Sweden*

**Henric Östmark**

*Division of Energetic Materials, National Defence Research Establishment, SE−172 90 Stockholm, Sweden*

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The $N_4$ molecule in its triplet state has been studied using the DFT-B3LYP, CASSCF, and CCSD(T) computational methods. The previously reported $C_s$ ($^3A''$) minimum was not found to be stable using these methods. A $D_{2d}$ ($^3A_1$) minimum was found to be the lowest energy triplet with a closed structure. This minimum is 20.2 kcal/mol higher in energy than $T_d$ ($^1A_1$) $N_4$ at the CCSD(T)/cc-pVTZ//CCSD(T)/DZP level of theory. The barrier to dissociation has been estimated to ca. 7.5 kcal/mol from CAS(8,8)+MR-ACPF and CAS-(8,8)+MR-AQCC calculations. CASSCF(12,12) calculations indicate that the open-chain $N_4$ of $C_{2h}$ ($^3B_u$) symmetry is not stable. The open-chain $C_s$($^3A''$) structure has been found to be a true minimum at all investigated levels of theory. It is 13.4 kcal/mol lower in energy than $T_d$ ($^1A_1$) $N_4$ at the CCSD(T)/cc-pVTZ//CCSD(T)/DZP level.

## 1. Introduction

Isomers of $N_4$, e.g., tetraazatetrahedrane, are of great interest because of their potential use as high energy density materials. Despite numerous theoretical studies predicting that the $N_4$ molecule has a local energy minimum with $T_d$ symmetry (**1**),[1−10] experimental studies aimed at its synthesis have so far been unsuccessful. The energy of the tetrahedral $N_4$ relative to $2N_2$ has been estimated to be 183 kcal/mol from CCSD(T) calculations with a relatively large atomic natural orbital (ANO) basis set.[2] Several theoretical studies have shown that the barrier for dissociation to two ground-state $N_2$ molecules is close to 60 kcal/mol.[2,6,7] While theory clearly indicates tetrahedral $N_4$ to be stable, its high energy content makes it hard to synthesize from ground state molecules. The most commonly suggested route is $\tilde{A}^3\Sigma_u^+$ $N_2$ + $\tilde{A}^3\Sigma_u^+$ $N_2$ → $N_4(T_d)$, but this demands the collision of two exited states, which is experimentally very difficult to achieve. A more appealing route would be the collision of ground-state $N_2$ with an excited-state $N_2$. The most interesting candidates for this type of process are excited states of triplet character, since these generally have longer lifetimes than the singlet excited states. However, the collision between the singlet ground state and an excited triplet state is likely to result in a product of triplet character. Consequently, the existence of a stable triplet state of $N_4$ would facilitate greater possibilities for its synthesis in that many more synthetic routes could be explored.

Lee and Rice investigated the lowest energy triplet form of $N_4$ in the tetrahedral region of the potential energy surface.[2] They found that the lowest triplet in this region is of $C_s$ symmetry (**2**) at the SCF and UMP2 computational levels. On the basis of single point calculations at higher levels of theory, it was estimated that **2** is 13 kcal/mol higher in energy than **1**.

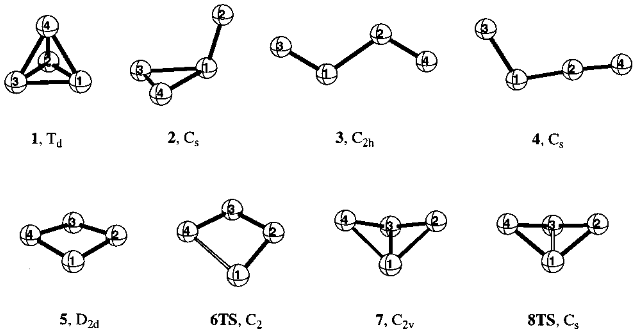

**Figure 1.** Optimized geometries of the stationary points discussed in this article. For structures **3-8TS** the numbering of the atoms is the same as in Tables 4−9.

Yarkony investigated the spin-forbidden decay of **1** via the minimum energy crossing between the $^1A'$ and $^3A''$ surfaces:[4]

$$N_4(^1A_1) \rightarrow N_4(^3A'') \rightarrow N_2(\tilde{X}^1\Sigma_g^+) + N_2(\tilde{A}^3\Sigma_u^+)$$

Energy and geometries of the $^3A''$ minimum **2** were obtained from CI−SD wave functions. The structural parameters and relative energies of the $^1A_1$ and $^3A''$ minima are similar to those found by Lee and Rice.[2] The barrier for the spin-forbidden decay channel was estimated to 28 kcal/mol,[4] which is approximately half the value of the reported barrier for the spin-allowed decay channel.[2,6,7]

The lowest energy $N_4$ computed by ab initio techniques is the planar $C_{2h}$ ($^3B_u$) open-chain structure (**3**).[5,8,9] Korkin et al. have discussed its stability with respect to the singlet state calculated at the optimized triplet state geometry.[7] The singlet state was found to be 41.5 kcal/mol lower in energy than the triplet state. This defines **3** as an exciplex, and as such, it is expected to have a very short lifetime. However, Korkin et al. found a $C_s$ ($^3A''$) open-chain $N_4$ minimum (**4**) that is 8.5 kcal/mol higher in energy than **3**.[7] At this minimum, the singlet state

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* To whom correspondence should be addressed.

[†] Permanent address: Slovak University of Technology, Department of Physical Chemistry, SK- 812 37 Bratislava, Slovak Republic.

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lies 15.7 kcal/mol above the triplet one, and it was suggested that it might be observed experimentally under certain conditions.[7]

In this work, we have investigated stationary points on the triplet potential energy surface using the DFT-B3LYP, CASSCF, and CCSD(T) methods. The energies of these stationary points are compared to the energy of tetrahedral $N_4$.

## 2. Methods and Procedure

Structures of stationary points on the potential energy surface were first located by density functional theory (DFT) calculations using Becke's three-parameter nonlocal exchange potential[12,13] with the nonlocal correlation of Lee, Yang, and Parr[14] denoted as B3LYP in text. The standard double-$\zeta$ plus polarization DZP basis set was used in the initial calculations. The primitive nitrogen set of Huzinaga[15] was contracted according to Dunning's scheme (9s5p1d)/[4s2p1d].[16] To assess the effects of basis set on the geometries and relative energies of the stationary points, we have also performed calculations using the correlation consistent valence triple-$\zeta$ basis set (cc-pVTZ) (10s5p2d1f)/[4s3p2d1f].[17,18] Harmonic vibrational frequencies were calculated from analytical derivatives, using the same basis set expansions. This allowed us to state conclusively whether the stationary points found were local minima or saddle points on the potential energy surface. To confirm that the obtained transition states connect the right reactants and products, IRC calculations[19,20] were carried out at the B3LYP/DZP level. All DFT-B3LYP calculations reported here were performed with the GAUSSIAN 98 series of programs.[21]

To assess the reliability of the B3LYP energies and structures, the RCCSD(T)[22] method was used subject to frozen core electrons. Accurate calculations of transition states for dissociation processes require the use of an electron correlation method that includes the effects from nondynamical electron correlation. Therefore, we have also used the CASSCF approach.[23,24] A correct characterization of the $^1A_1$ tetrahedral state requires that all six N−N bonds are treated equivalently. The active space in the CASSCF calculations was selected to fulfill this requirement, and included all molecular orbitals arising from the valence atomic nitrogen *p*-orbitals. As a result, 12 electrons were distributed over 12 active orbitals [CAS(12,12)]. The 8 inner orbitals were inactive and held doubly occupied in the CASSCF wave function. To estimate the importance of dynamical correlation, multireference CI−SD calculations, including the higher order excitations estimated by means of the multireference analogue of the Davidson correction [MRCI−SD(Q)],[25] were carried out on the top of the CAS(12,12) wave function. Since using all configurations from the CAS(12,12) wave function as references in the MRCI would be too computationally expensive, a selection of the references was used, i.e., an occupation was included in the reference space only if the absolute value of its coefficient in the CASSCF wave function exceeded a threshold of 0.05. However, for computing stationary points of low symmetry ($C_s$ or $C_2$) we found even this method to be too computationally demanding, and multireference CI calculations on the energy difference between the stationary points **5** and **6TS** were therefore performed on top of CAS(8,8) wave functions. In this case, the selection of configurations was done in a slightly different manner, i.e., an occupation was included in the reference space if the absolute value of its coefficient in the CASSCF wave function exceeded a threshold of 0.05 for at least one of the stationary points. Thus, the same reference space was used in both calculations. In addition to the MRCI−SD(Q) approach, the energy difference between **5** and **6TS** was also calculated using the multireference average coupled pair functional (MR-ACPF)[26] and average quadratic coupled cluster (MR-AQCC)[27] methods, which can be considered as modifications to the MRCI−SD method. They include corrections for higher order excitations and are approximately size extensive.[28] Basis set effects on the calculated energies, structures and vibrational frequencies have been analyzed by comparing results from calculations with the DZP and cc-pVTZ basis sets. The MOLPRO98 program package was used for all CCSD(T), CASSCF and MRCI calculations.[29]

## 3. Results and Discussion

Prior to locating the $N_4$ stationary points, we carried out calculations of the $N_2$ molecule in the ground and excited states with the DZP and cc-pVTZ basis sets. Spectroscopic quantities such as equilibrium bond distances and harmonic frequencies are used as criteria for assessing the suitability of a given computational approach. An obvious choice of active space for CASSCF calculation would comprise the $3\sigma_g$, $1\pi_u$, $1\pi_g$, and $3\sigma_u$ orbitals, denoted CAS(6,6), giving a CASSCF wave function with 32 configurations ($D_{2h}$ symmetry). The importance of the $2\sigma_u$ orbital has been discussed earlier.[30] Including this orbital to the active space gives 80 reference configurations [CAS(8,7)]. The $2\sigma_u$ orbital is crucial for the $\tilde{B}\ ^3\Pi_g$ state, but it is of much less importance for describing the lower lying states. In the subsequent MRCI−SD(Q) calculations of the $N_2$ molecule, and in the CASSCF $N_4$ calculations, this orbital is always kept doubly occupied. The results of the calculations on the nitrogen molecule are listed in Table 1 and compared to the relevant experimental data.[11,31] It can be seen that the DFT-B3LYP method predicts the equilibrium distances reasonably well, but that the harmonic frequencies are 5−10% higher than their experimental values. All ab initio approaches [CASSCF, CCSD(T), and MRCI−SD(Q)] overestimate the equilibrium distances in the case of the DZP basis set. The use of the cc-pVTZ basis set eliminates most of these errors. Energies calculated at the equilibrium distance of the $N_2$ ground and excited states are used in the investigation of the $N_4$ dissociation limit of the singlet and triplet potential energy surfaces. The lowest triplet dissociation limit corresponds to the $N_2(\tilde{X}^1\Sigma_g^+)$ and $N_2(\tilde{A}^3\Sigma_u^+)$ molecules. This dissociation limit is separated from the dissociation limit corresponding to two $N_2$ molecules in their ground electronic states by close to 141 kcal/mol at the B3LYP/DZP, CASSCF/DZP, and CCSD(T)/DZP computational levels. This is in reasonable agreement with the experimental value of 143.5 kcal/mol (Table 1).[11] When the cc-pVTZ basis set is used, all methods, but the MRCI−SD(Q) method, overestimate the difference between triplet and singlet dissociation limits by 4 to 6 kcal/mol.

The tetrahedral structure **1** has been the focus of several theoretical studies.[1−10] In this work, B3LYP and CAS(12,12) structural parameters and harmonic frequencies are given and compared to the relevant results reported previously (Table 2).[2] The CAS(12,12) and CCSD(T) structural parameters and vibrational frequencies are in very good agreement. The B3LYP method predicts the geometry and the frequencies surprisingly well, although the results are somewhat closer to those obtained at the CCSD level than the CCSD(T) level. The energy for the dissociation of **1** to two ground-state $N_2$ molecules has also been examined. Currently, the most accurate evaluation of this energy difference is 181.6 kcal/mol (183 kcal/mol when corrected for the zero point energy) as determined with the CCSD(T) method using a ANO basis set contracted to[4*s*3*p*2*d*1*f*].[2] It has been estimated that this value is accurate to within ± 2 kcal/mol.[2]

**TABLE 1: $N_2$ Spectroscopic Constants**

| basis set | | DZP | | | cc-pVTZ | | |
|---|---|---|---|---|---|---|---|
| state | method | $R_e$ (Å) | $\omega_e$ (cm$^{-1}$) | $T_e$ (kcal/mol) | $R_e$ (Å) | $\omega_e$ (cm$^{-1}$) | $T_e$ (kcal/mol) |
| $\tilde{X}\,^1\Sigma_g^+$ | B3LYP | 1.113 | 2397 | | 1.091 | 2450 | |
| | CAS(6,6) | 1.121 | 2321 | | 1.104 | 2352 | |
| | CAS(8,7) | 1.122 | 2318 | | 1.104 | 2348 | |
| | CCSD(T) | 1.127 | 2290 | | 1.104 | 2351 | |
| | MRCI-SD(Q)[a] | 1.129 | 2269 | | 1.105 | 2321 | |
| | Exp.[11] | 1.097 | 2358 | 0.0 | | | |
| $\tilde{A}\,^3\Sigma_u^+$ | B3LYP | 1.292 | 1557 | 140.8 | 1.273 | 1567 | 149.3 |
| | CAS(6,6) | 1.318 | 1391 | 140.8 | 1.304 | 1397 | 147.4 |
| | CAS(8,7) | 1.317 | 1400 | 141.4 | 1.303 | 1405 | 147.9 |
| | CCSD(T) | 1.316 | 1414 | 140.7 | 1.293 | 1451 | 150.6 |
| | MRCI-SD(Q) | 1.321 | 1390 | 131.0 | 1.296 | 1424 | 140.3 |
| | Exp.[11] | 1.287 | 1460 | 143.5 | | | |
| $\tilde{W}\,^3\Delta_u$ | B3LYP | 1.295 | 1545 | 162.7 | 1.276 | 1555 | 171.0 |
| | CAS(6,6) | 1.306 | 1466 | 177.0 | 1.291 | 1469 | 183.4 |
| | CAS(8,7) | 1.306 | 1470 | 177.1 | 1.292 | 1473 | 183.4 |
| | CCSD(T) | 1.307 | 1485 | 169.9 | 1.285 | 1506 | 176.8 |
| | MRCI-SD(Q) | 1.291 | 1560 | 163.1 | 1.289 | 1486 | 169.2 |
| | Exp.[31] | 1.280 | 1507 | 171.0 | | | |
| $\tilde{B}\,^3\Pi_g$ | B3LYP | 1.220 | 1809 | 155.7 | 1.202 | 1819 | 164.2 |
| | CAS(6,6) | 1.248 | 1792 | 207.0 | 1.235 | 1567 | 213.8 |
| | CAS(8,7) | 1.235 | 1700 | 184.0 | 1.223 | 1698 | 190.5 |
| | CCSD(T) | 1.240 | 1706 | 162.6 | 1.219 | 1727 | 176.8 |
| | MRCI-SD(Q) | 1.243 | 1692 | 158.6 | 1.222 | 1719 | 166.4 |
| | Exp.[11] | 1.213 | 1734 | 170.5 | | | |

[a] A CAS(6,6) reference function was used in the MRCI-SD(Q) calculations.

**TABLE 2: Total energy ($E_h$), Equilibrium Structure (Å), Harmonic Frequencies (cm$^{-1}$), Zero Point Energy and Relative Energy (kcal/mol) for 1, $T_d$ ($^1A_1$)[a]**

| | present work | | | | | Lee and Rice[a] | |
|---|---|---|---|---|---|---|---|
| method/ basis set | B3LYP/ DZP | B3LYP/ cc-pVTZ | CAS(12,12)/ DZP | CAS(12,12)/ cc-pVTZ | CCSD(T)/ DZP | CCSD/ ANO[b] | CCSD(T)/ ANO[b] |
| energy | −218.81178 | −218.84678 | −217.85566 | −217.88622 | −218.27279 | −218.43241 | −218.48407 |
| $R_e$ | 1.458 | 1.448 | 1.470 | 1.466 | 1.472 | 1.442 | 1.461 |
| $\omega_1$ (e) | 760 | 755 | 726 | 721 | 722 | 774 | 727 |
| $\omega_2$ ($t_2$) | 983 | 971 | 934 | 924 | 938 | 1004 | 939 |
| $\omega_3$ ($a_1$) | 1384 | 1357 | 1299 | 1275 | 1317 | 1387 | 1297 |
| ZPE | 8.4 | 8.3 | 7.9 | 7.8 | 8.0 | 8.5 | 8.0 |
| $\Delta E_{\text{diss}}$[c] | 160.8 | 182.0 | 209.8 | 221.3 | 174.0<br>**181.3**[d]<br>*173.6*[e] | 189.7 | 181.6 |

[a] Values are taken from Reference 2. [b] Atomic natural orbital basis set contracted to [4*s*3*p*2*d*1*f*]. [c] Relative energy with respect to two $N_2$. ($\Delta E_{\text{diss}} = E_1 - 2E_{N2}$). [d] Relative energy obtained at the CCSD(T)/cc-pVTZ//CCSD(T)/DZP level. [e] Relative energy obtained at the CAS(12,12)+MRCI-SD(Q)/DZP//CCSD(T)/DZP level. The dissociation energy has been computed using the supermolecule approach with the $N_2$ units separated by 20 a.u.

**TABLE 3: Total Energy ($E_h$), Equilibrium Structure (Å and deg), Harmonic Frequencies (cm$^{-1}$), Zero Point Energy, and Relative Energy (kcal/mol) for 5, $D_{2d}$ ($^3A_1$)**

| method/ basis set | B3LYP/ DZP | B3LYP/ cc-pVTZ | CAS(12,12)/ DZP | CAS(12,12)/ cc-pVTZ | CCSD(T)/ DZP |
|---|---|---|---|---|---|
| energy | −218.79814 | −218.83285 | −217.82529 | −217.85382 | −218.24683 |
| $R_{12}$ | 1.380 | 1.370 | 1.396 | 1.391 | 1.394 |
| $\alpha_{123}$ | 88.4 | 88.5 | 89.2 | 89.2 | 88.4 |
| $\phi_{1234}$ | 18.9 | 18.4 | 13.5 | 12.8 | 18.8 |
| $\omega_1$ ($b_1$) | 442 | 272 | 1044 | 1030 | |
| $\omega_2$ ($a_1$) | 708 | 716 | 454 | 439 | |
| $\omega_3$ (e) | 815 | 775 | 742 | 707 | |
| $\omega_4$ ($b_2$) | 1038 | 1049 | 1086 | 1092 | |
| $\omega_5$ ($a_1$) | 1281 | 1270 | 1197 | 1186 | |
| ZPE | 7.3 | 6.9 | 7.5 | 7.4 | |
| $\Delta E_{\text{Td}}$[a] | 8.6 | 8.7 | 19.0 | 20.3 | 16.3<br>**20.2**[b]<br>*15.9*[c] |

[a] Relative energy with respect to **1**, $T_dN_4$. ($\Delta E_{\text{Td}} = E_5 - E_1$). [b] Relative energy obtained at the CCSD(T)/cc-pVTZ// CCSD(T)/DZP level. [c] Relative energy obtained at the CAS(12,12)+MRCI-SD(Q)/DZP//CCSD(T)/DZP level.

Our CCSD(T)/cc-pVTZ//CCSD(T)/DZP value (181.3 kcal/mol) is in good agreement with the CCSD(T)/ANO result. The B3LYP/DZP value for the dissociation energy is around 21 kcal/mol lower than the CCSD(T)/ANO value.[2] However, the use of the larger cc-pVTZ basis set leads to an almost perfect agreement with the best CCSD(T) result;[2] the two values differ by only 0.3 kcal/mol. The CAS(12,12)/DZP dissociation energy is high as 209.8 kcal/mol. The dissociation energy increases further by 11.5 kcal/mol when the cc-pVTZ basis is used. The high dissociation energies obtained using CAS(12,12) can be

**TABLE 4: Total Energy ($E_h$), Equilibrium Structure (Å and deg), Harmonic Frequencies (cm$^{-1}$), Zero Point Energy, and Relative Energy (kcal/mol) for 6TS, $C_2$ ($^3$B); the Transition State towards Dissociation from 5**

| method/ basis set | B3LYP/ DZP | B3LYP/ cc-pVTZ | CAS(12,12)/ DZP | CAS(12,12)/ cc-pVTZ |
|---|---|---|---|---|
| energy | −218.79148 | −218.83107 | −217.80970 | −217.83952 |
| $R_{12}$ | 1.265 | 1.248 | 1.312 | 1.299 |
| $R_{23}$ | 1.480 | 1.505 | 1.462 | 1.485 |
| $\alpha_{123}$ | 93.0 | 91.7 | 92.1 | 90.9 |
| $\phi_{1234}$ | 22.8 | 20.4 | 26.6 | 25.6 |
| $\omega_1$ (a) | 798i | 739i | 1035i | 1026i |
| $\omega_2$ (a) | 436 | 295 | 406 | 278 |
| $\omega_3$ (a) | 587 | 578 | 698 | 703 |
| $\omega_4$ (b) | 783 | 788 | 937 | 939 |
| $\omega_5$ (b) | 1214 | 1179 | 997 | 958 |
| $\omega_6$ (a) | 1456 | 1475 | 1241 | 1240 |
| ZPE | 6.4 | 6.2 | 6.1 | 5.9 |
| $\Delta E_{\mathrm{Td}}$[a] | 12.7 | 9.9 | 28.8 | 29.3 |

[a] Relative energy with respect to **1**, $T_dN_4$. ($\Delta E_{\mathrm{Td}} = E_{\mathbf{6TS}} - E_{\mathbf{1}}$).

**TABLE 5: Barrier to Dissociation of 5 at Various Levels of Theory in kcal/mol**

| basis set | DZP[a] | cc-pVTZ[b] |
|---|---|---|
| B3LYP | 4.1[c] | 1.1[d] |
| CCSD | 7.1 | 6.1 |
| CCSD(T) | 4.9 | 3.4 |
| CAS(4,4) | 28.3 | 26.7 |
| CAS(8,8) | 15.8 | 16.6 |
| +MRCI-SD | 10.4 | |
| +MRCI-SD(Q) | 5.2 | |
| +MR-ACPF | 8.4 | |
| +MR-AQCC | 8.9 | |
| CAS(12,12) | 9.8 | 9.0 |

[a] CAS(12,12)/DZP optimized geometries unless otherwise noted. [b] CAS(12,12)/cc-pVTZ optimized geometries unless otherwise noted. [c] B3LYP/DZP optimized geometry. [d] B3LYP/cc-pVTZ optimized geometry.

attributed to the lack of dynamical electron correlation in this approach. When a MRCI−SD(Q) treatment is added to the CAS(12,12)/DZP wave function, the dissociation energy is decreased to 173.6 kcal/mol, which is in almost perfect agreement with the CCSD(T) value (174.0 kcal/mol) obtained with the same basis set. Since the basis set effects for MRCI−SD(Q) and CCSD(T) can be expected to be of similar magnitude, this confirms that 182 kcal/mol is a good estimate of the dissociation energy. It should be noted that it is especially in cases such as this when structures with very different bonding patterns are compared that the lack of dynamic electron correlation in the CASSCF method is likely to result in inaccurate energy differences. The results from the study of Lee and Rice confirm that a proper treatment of electron correlation is essential in order to describe the energetics for the dissociation of **1**.[2] For example, they show that the inclusion of noniterative triples to the CCSD wave function, i.e., going from CCSD to CCSD(T) leads to a decrease in the dissociation energy by nearly 9 kcal/mol. On the other hand, they found only a marginal effect upon adding a second set of *f*-functions to the basis set.

The bound triplet state of $C_s$ symmetry $^3A''$ (**2**), which Lee and Rice[2] found to be a true minimum at the SCF and UMP2 levels of theory, arises from excitation from the bonding orbital 4a″ to the antibonding 11a′. Its reference configuration is as follows

$$1a'^2 1a''^2 2a'^2 3a'^2 4a'^2 5a'^2 6a'^2 2a''^2 7a'^2 8a'^2 9a'^2 3a''^2 10a'^2 11a' 4a''$$

Our calculations performed at the B3LYP, CCSD(T), and CAS(12,12) levels show that this structure is not a true minimum on the potential energy surface and in each case the structure dissociated during the optimization.

We have found other stationary points on the triplet potential energy surface. At first we considered a $D_{2h}$ planar structure similar to the singlet $D_{2h}$ structure of $N_4$. However, the triplet structure was found to have one imaginary frequency, and we expected an out-of-plane minimum with lower energy. During the optimization the system reached a nonplanar cyclic local minimum $^3A_1$ of $D_{2d}$ symmetry (**5**) (Table 3) with two unpaired electrons in the 4e orbital,

$$1a_1^2 1e^4 1b_2^2 2a_1^2 2e^4 1b_1^2 2b_2^2 3a_1^2 3b_2^2 3e^4 4e4e$$

This structure has previously been reported to be a true minimum at the MP2/6-31G(d) level.[5] Our frequency calculations confirm that the structure is a minimum also at the B3LYP and CAS(12,12) levels of theory. As for the $T_d$ structure, the B3LYP method predicts a shorter N−N distance than CAS(12,12) and CCSD(T). In Table 3, we have also listed the energy difference between the triplet $D_{2d}$ **5** and the singlet $T_d$ minima **1** calculated at different levels of theory. There is a very good agreement between the results from the CAS(12,12)+MRCI−SD(Q)/DZP//CCSD(T)/DZP and CCSD(T)/DZP calculations;

**TABLE 6: Total Energy ($E_h$), Equilibrium Structure (Å and deg), Harmonic Frequencies (cm$^{-1}$), Zero Point Energy and Relative Energy (kcal/mol) for 7, $C_{2v}$ ($^3B_1$)**

| method/ basis set | B3LYP/ DZP | B3LYP/ cc-pVTZ | CAS(12,12)/ DZP | CAS(12,12)/ cc-pVTZ | CCSD(T)/ DZP |
|---|---|---|---|---|---|
| energy | −218.75030 | −218.78368 | −217.77605 | −217.80439 | −218.20172 |
| $R_{12}$ | 1.438 | 1.430 | 1.456 | 1.452 | 1.451 |
| $R_{13}$ | 1.543 | 1.537 | 1.545 | 1.543 | 1.557 |
| $\alpha_{234}$ | 90.5 | 90.5 | 90.2 | 90.2 | 90.2 |
| $\phi_{2314}$ | 114.5 | 114.7 | 113.4 | 113.5 | 114.1 |
| $\omega_1$ (a$_2$) | 259 | 10 i | 329 | 265 | |
| $\omega_2$ (a$_1$) | 694 | 700 | 649 | 654 | |
| $\omega_3$ (b$_2$) | 770 | 745 | 758 | 740 | |
| $\omega_4$ (a$_1$) | 831 | 839 | 807 | 811 | |
| $\omega_5$ (b$_1$) | 981 | 952 | 884 | 864 | |
| $\omega_6$ (a$_1$) | 1261 | 1238 | 1178 | 1164 | |
| ZPE | 6.8 | 6.4 | 6.6 | 6.4 | |
| $\Delta E_{\mathrm{Td}}$[a] | 38.6 | 39.6 | 50.0 | 51.3 | 44.6<br>**48.3**[b]<br>*42.0*[c] |

[a] Relative energy with respect to **1**, $T_dN_4$. ($\Delta E_{\mathrm{Td}} = E_{\mathbf{7}} - E_{\mathbf{1}}$). [b] Relative energy obtained at the CCSD(T)/cc-pVTZ//CCSD(T)/DZP level. [c] Relative energy obtained at the CAS(12,12)+MRCI-SD(Q)/DZP//CCSD(T)/DZP level.

**TABLE 7: Total Energy ($E_h$), Equilibrium Structure (Å and deg), Harmonic Frequencies ($cm^{-1}$), Zero Point Energy, and Relative Energy (kcal/mol) for 8TS, $C_s$ ($^3A''$); the Transition State between 5 and 6**

| method/ basis set | B3LYP/ DZP | B3LYP/ cc-pVTZ | CAS(12,12)/ DZP | CAS(12,12)/ cc-pVTZ | CCSD(T)/ DZP |
|---|---|---|---|---|---|
| energy | −218.74112 | −218.77504 | −217.76399 | −217.79260 | −218.18754 |
| $R_{12}$ | 1.377 | 1.366 | 1.389 | 1.382 | 1.377 |
| $R_{13}$ | 1.704 | 1.693 | 1.736 | 1.731 | 1.748 |
| $R_{23}$ | 1.483 | 1.479 | 1.502 | 1.501 | 1.499 |
| $\alpha_{234}$ | 85.8 | 85.8 | 85.3 | 85.1 | 84.5 |
| $\phi_{2314}$ | 123.3 | 123.4 | 123.8 | 124.0 | 125.0 |
| $\omega_1$ (a′) | 1173i | 1185i | 1346i | 1296i | |
| $\omega_2$ (a″) | 297 | 93 | 380 | 312 | |
| $\omega_3$ (a′) | 824 | 833 | 820 | 820 | |
| $\omega_4$ (a′) | 893 | 877 | 866 | 859 | |
| $\omega_5$ (a″) | 985 | 957 | 916 | 893 | |
| $\omega_6$ (a′) | 1247 | 1232 | 1174 | 1164 | |
| ZPE | 6.1 | 5.7 | 5.9 | 5.8 | |
| $\Delta E_{Td}$[a] | 44.3 | 45.0 | 57.5 | 58.7 | 53.5<br>**57.3**[b] |

[a] Relative energy with respect to **1**, $T_dN_4$. ($\Delta E_{Td} = E_{\mathbf{8TS}} - E_1$). [b] Relative energy obtained at the CCSD(T)/cc-pVTZ// CCSD(T)/DZP level.

**TABLE 8: Total Energy ($E_h$), Equilibrium Structure (Å and deg), Harmonic Frequencies ($cm^{-1}$), Zero Point Energy, and Relative Energy (kcal/mol) for 3, $C_{2h}$ ($^3B_u$)**

| method/ basis set | B3LYP/ DZP | B3LYP/ cc-pVTZ | CCSD(T)/ DZP |
|---|---|---|---|
| energy | −218.85699 | −218.90579 | −218.30838 |
| $R_{12}$ | 1.503 | 1.518 | 1.523 |
| $R_{13}$ | 1.195 | 1.172 | 1.211 |
| $\alpha_{213}$ | 114.4 | 114.9 | 112.6 |
| $\omega_1$ ($a_u$) | 70 | 76 | |
| $\omega_2$ ($b_u$) | 274 | 275 | |
| $\omega_3$ ($a_g$) | 520 | 499 | |
| $\omega_4$ ($a_g$) | 704 | 670 | |
| $\omega_5$ ($b_u$) | 1758 | 1764 | |
| $\omega_6$ ($a_g$) | 1791 | 1820 | |
| ZPE | 7.3 | 7.3 | |
| $\Delta E_{Td}$[a] | −28.4 | −37.0 | −22.3<br>**−20.9**[b]<br>*−21.6*[c] |

[a] Relative energy with respect to **1**, $T_dN_4$. ($\Delta E_{Td} = E_3 - E_1$). [b] Relative energy obtained at the CCSD(T)/cc-pVTZ//CCSD(T)/DZP level. [c] Relative energy obtained at the CAS(12,12)+MRCI-SD(Q)/ DZP//CCSD(T)/DZP level.

both levels predict the triplet to be around 16 kcal/mol higher in energy than the singlet. Single point CCSD(T) calculations using the larger cc-pVTZ basis set indicate that the energy difference is close to 20 kcal/mol. The B3LYP/cc-pVTZ energy difference is significantly lower, only 8.7 kcal/mol.

Although the geometrical parameters of **5** show small variations at the different computational levels, the harmonic frequencies differ considerably, e.g., the first $a_1$ and $b_1$ normal modes of **5** are 708 and 442 $cm^{-1}$ at B3LYP/DZP level, and 454 and 1044 $cm^{-1}$ at the CAS(12,12)/DZP level. Our studies indicate that following the $b_2$ mode leads to the dissociation of **5** via a $C_2$ transition state (**6TS**) (Table 4). This frequency differs less than 50 $cm^{-1}$ between the two levels. We were not able to find this transition state at the CCSD(T)/DZP level. The small dissociation barrier of only 4.1 kcal/mol at the B3LYP/DZP level indicates that this configuration of the $N_4$ molecule is not particularly stable. The barrier is further reduced upon the use of the larger cc-pVTZ basis set. However, it is questionable if the B3LYP method can give a proper description of the electronic structure and energy of the transition state, since the CAS(12,12) calculations show that the transition state is considerably multi-configurational in nature. In addition, earlier studies have shown that the B3LYP method has a general tendency to underestimate transition state barriers.[32,33] The CAS(12,12) calculations indicate a considerably larger barrier, 9.8 kcal/mol with the DZP basis set and 9.0 kcal/mol with the cc-pVTZ basis set. The zero point energy correction reduces the barrier height less than 1 kcal/mol at the B3LYP/DZP level and only 0.5 kcal/mol at the CAS(12,12)/DZP level. A series of single point calculations at the CAS(12,12) optimized geometries of **5** and **6TS** were performed in order to get a better estimate of the barrier (Table 5). The coupled cluster calculations give a lower barrier than that obtained from the CAS(12,12) calculations. The barrier is 6.1 and 3.4 kcal/mol at the CCSD/cc-pVTZ and the CCSD(T)/cc-pVTZ levels, respectively.

**TABLE 9: Total Energy ($E_h$), Equilibrium Structure (Å and deg), Harmonic Frequencies ($cm^{-1}$), Zero Point Energy and Relative Energy (kcal/mol) for 4, $C_s$ ($^3A''$)**

| method/ basis set | B3LYP/ DZP | B3LYP/ cc-pVTZ | CAS(12,12)/ DZP | CAS(12,12)/ cc-pVTZ | CCSD(T)/ DZP |
|---|---|---|---|---|---|
| energy | −218.85511 | −218.90374 | −217.85310 | −217.89119 | −218.29430 |
| $R_{12}$ | 1.277 | 1.258 | 1.297 | 1.283 | 1.289 |
| $R_{13}$ | 1.282 | 1.258 | 1.364 | 1.350 | 1.337 |
| $R_{24}$ | 1.159 | 1.140 | 1.133 | 1.117 | 1.160 |
| $\alpha_{213}$ | 125.0 | 127.8 | 111.2 | 112.0 | 116.2 |
| $\alpha_{124}$ | 168.1 | 167.4 | 176.2 | 175.0 | 172.0 |
| $\omega_1$ (a′) | 181 | 177 | 204 | 219 | |
| $\omega_2$ (a”) | 276 | 297 | 404 | 433 | |
| $\omega_3$ (a′) | 602 | 613 | 614 | 638 | |
| $\omega_4$ (a′) | 980 | 976 | 936 | 936 | |
| $\omega_5$ (a′) | 1196 | 1220 | 1051 | 1028 | |
| $\omega_6$ (a′) | 2096 | 2114 | 2225 | 2165 | |
| ZPE | 7.6 | 7.7 | 7.8 | 7.7 | |
| $\Delta E_{Td}$[a] | −27.2 | −35.7 | 1.6 | 3.1 | −13.5<br>**−13.4**[b] |

[a] Relative energy with respect to **1**, $T_dN_4$. ($\Delta E_{Td} = E_4 - E_1$). [b] Relative energy obtained at the CCSD(T)/cc-pVTZ//CCSD(T)/DZP level.

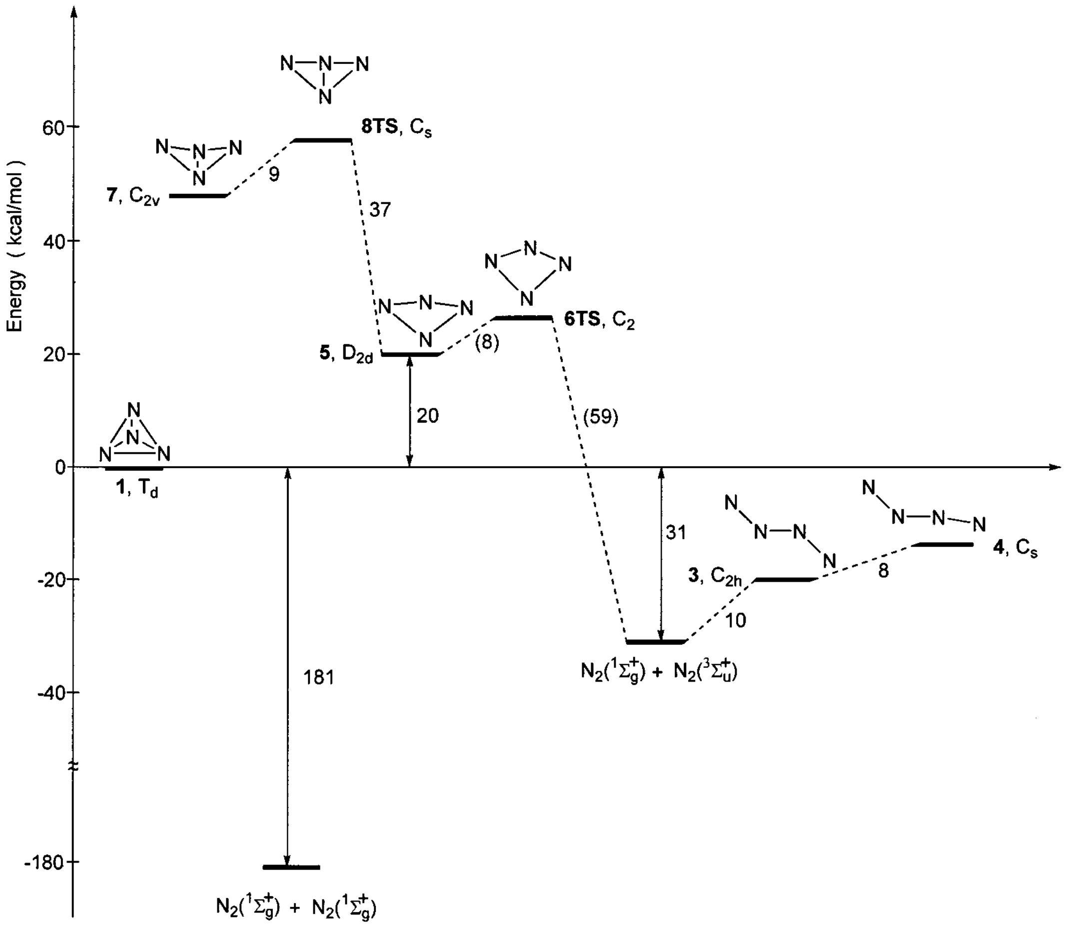

**Figure 2.** A summary of the energetics at the CCSD(T)/cc-pVTZ//CCSD(T)/DZP level of theory. Energies (kcal/mol) are relative to the $N_4$ ($T_d$). Values in parentheses are based on our best estimate of the energy difference between **6TS** and **5.**

However, these results should be considered with caution, since the $T_1$ diagnostic value is rather large for both stationary points, 0.039 and 0.028 for **6TS** and **5**, respectively, at the CCSD/cc-pVTZ level. According to Lee and Taylor,[34] the single reference approach cannot be expected to produce highly reliable results when the $T_1$ diagnostic value is larger than 0.02. In contrast, MRCI calculations based on CAS(8,8) wave functions should be capable of describing both the dynamical and nondynamical correlation effects and therefore provide reliable relative energies. At the MRCI−SD/DZP level, the barrier is 10.4 kcal/mol. This value is reduced to 5.2 kcal/mol after correction for higher order excitations using the Davidson correction. The MR-ACPF and MR-AQCC methods, which are expected to account for higher order effects more accurately than the Davidson correction, give barriers of 8.4 and 8.9 kcal/mol, respectively. A comparison with the CCSD and CAS(12,12) results indicates that these values are likely to be reduced by around 1 kcal/mol if the bigger cc-pVTZ basis set were to be used. In summary, our results indicate that the barrier is between 3 and 9 kcal, where the CCSD(T)/cc-pVTZ result sets the lower limit and the CAS(12,12)/cc-pVTZ result the upper limit. Our best estimate of the barrier is 7.5 kcal/mol, which is based on the MR-ACPF and MR-AQCC calculations and an extrapolation of the basis set effects. This should render **5** sufficiently stable to be characterized experimentally under certain conditions.

A second minimum of $C_{2v}$ symmetry (**7**) was found on the triplet potential energy surface by rotating one of the nitrogen atoms on **1** away from $T_d$ symmetry. The reference configuration of the $C_{2v}$ ($^3B_1$) local minimum **7** is

$$1a_1^2 1b_2^2 1b_1^2 2a_1^2 3a_1^2 2b_1^2 2b_2^2 4a_1^2 5a_1^2 1a_2^2 6a_1^2 3b_1^2 3b_2^2 4b_1 7a_1$$

Structural parameters, frequencies and total energies are given in Table 6. All investigated levels of theory predict **7** to be around 30 kcal/mol higher in energy than **5**. In the lower symmetry group $C_s$, both our minima have the 10a′ and 5a″ orbitals singly occupied, in contrast to the reported reference configuration for **2** which has the 11a′ and 4a″ orbitals singly occupied.[4] This is a result of the different ordering of the orbitals of symmetries a′ and a″.

We located a $^3A''$ transition state of $C_s$ symmetry (**8TS**) that connects the **5** and **7** minima (Table 7). This transition state was confirmed to connect the two minima by IRC calculations that followed the Hessian eigenvector with negative eigenvalue. The transition state barrier going from **7** to **5** is between 5 and 9 kcal/mol depending upon the computational level. However, the barrier toward dissociation from **7** (the transition state is of $C_2$ symmetry) is close to 1 kcal/mol at all investigated levels of theory. Thus, **7** is not likely to be stable, and if **7** is formed in any process, it will dissociate rather than transform into **5**. It should also be noted that **7** has one small imaginary frequency at the B3LYP/cc-pVTZ level.

The minimum structure and harmonic frequencies of the $C_{2h}$ open-chain triplet minimum **3** has been calculated at the B3LYP/DZP and B3LYP/cc-pVTZ levels of theory (Table 8). The CCSD(T)/DZP optimized geometry is similar to the B3LYP geometries, with one long central bond (1.52 Å), and two shorter terminal bonds (1.21 Å). The spin allowed dissociation of this minimum to $\tilde{X}^1\Sigma_g^+$ $N_2$ and $\tilde{A}^3\Sigma_u^+$ $N_2$ is 4.3 kcal/mol endothermic at the B3LYP/cc-pVTZ level and 9.8 kcal/mol exothermic at the CCSD(T)/cc-pVTZ//CCSD(T)/DZP level. The later result is, similar to the QCISD(T)/6-311+G(d)//MP2/6-31G(d) value of 12 kcal/mol.[7] We were not able to find a stable $C_{2h}$ minimum at the CAS(12,12) level. The geometry optimizations did in all cases lead to dissociation. The value of the largest CI coefficient gradually decreased during the optimization and when the central NN bond reached 1.7 Å, the wave function was of multireference character with two dominant configurations. Our attempts to find a minimum of lower symmetry ($C_s$ or $C_1$) were also unsuccessful and resulted in dissociated structures.

Korkin et al.[7] located another open-chain $N_4$ triplet minimum (**4**, $C_s$) on the $^3A''$ potential energy surface with a short central NN bond. They found this minimum to be about 15 kcal/mol lower in energy than the $T_d$ structure **1** at the QCISD(T)/6-311+G(d)//MP2/6-31G(d) level. Our B3LYP/cc-pVTZ and CCSD(T)/cc-pVTZ/ /CCSD(T)/DZP calculations show that this minimum is lower than **1** by about 36 and 13 kcal/mol, respectively. At the CAS(12,12)/cc-pVTZ level, **4** is 3.1 kcal/mol higher in energy than **1**. However, as for the dissociation energy of **1**, we expect that this value is too high due to the insufficient treatment of dynamic electron correlation in the CAS(12,12) method. It should be noted that the natural orbital analysis at the CAS(12,12) level shows that one of unpaired electrons occupies a nonbonded orbital localized to atom 3, and the other a 1−3 bonding orbital. The strong localization of the unpaired electrons indicates that the molecule will react easily with other molecules. Thus, **4** is expected to have a very short lifetime under normal conditions.

## 4. Conclusions

Stationary points on the triplet $N_4$ potential energy surface have been characterized using the DFT-B3LYP, CAS(12,12), CCSD(T) computational methods. A summary of the energetics relative to tetrahedral $N_4$ is shown in Figure 2. Our studies show that the previously located $C_s$ ($^3A''$) minimum (**2**) in the tetrahedral region of potential energy surface, which was optimized at the MP2 and CISD levels of theory, is not a true minimum at higher levels of theory. Instead, we have found the $D_{2d}$ ($^3A_1$) minimum **5** to be the lowest triplet with a closed structure. This minimum is 20.2 kcal/mol higher in energy than $T_d$ $N_4$ (**1**) at the CCSD(T)/cc-pVTZ//CCSD(T)/DZP level of theory. The barrier to dissociation has been estimated to ca. 7.5 kcal/mol from CAS(8,8)+MR-ACPF and CAS(8,8)+MR-AQCC calculations. A second minimum of $C_{2v}$ ($^3B_1$) symmetry (**6**) has also been identified. It is around 30 kcal/mol higher in energy than **5** and has a very small barrier to dissociation.

The open-chain $C_{2h}$ structure **3**, which has been considered the lowest energy triplet $N_4$, is not stable at the CAS(12,12) level of theory. Since this structure also have been shown to be an exciplex at the QCISD(T)/6-311+G(d)//MP2/6-31G(d) level of theory,[7] it seems highly unlikely that it should be stable enough to facilitate experimental characterization. The open-chain $C_s$ minimum **4** of Korkin et al.[7] was found to be a minimum at all investigated levels of theory. According to the CCSD(T)/cc-pVTZ//CCSD(T)/DZP calculations, it is 13.4 kcal/mol lower in energy than **1**. The strong radical character of **4** is likely to make the molecule very reactive.

Our calculations show that the triplet potential energy surface is very sensitive to electron correlation effects. However, the very good agreement in the relative energies of minima between CAS(12,12)+MRCI−SD(Q) and CCSD(T) with the DZP basis set suggests that the CCSD(T)/cc-pVTZ//CCSD(T)/DZP relative energies for minimum structures should be highly reliable. The calculation of activation barriers, on the other hand, clearly requires the use of MRCI approaches. On the basis of the results obtained in this study, we conclude that **5** is the most likely candidate to be observed experimentally.

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