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A theoretical study of the N_8 cubane to N_8 pentalene isomerization reaction

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Abstract. The isomerization reaction of cubic N_8 to the planar bicyclic structure analogous to pentalene has been investigated using multiconfigurational self-consistent field and second-order perturbation theory (CASPT2). Comparative calculations using density functional theory have also been performed. Five local minima on the energy surface have been found, and the transition states between each two consecutive minima have been determined. The results show that all steps in the isomerization process, except one, can proceed via a set of transition states with moderately high energy barriers (10–20 kcal/mol).

Key words: CASPT2 – N_8 Isomers – Transition states – Perturbation theory – High energy density material – Multiconfigurational SCF theory

1 Introduction

There is a great deal of interest in the development of efficient and safe propellants, with the quality of a high ratio between energy release and mass. Several theoretical studies have been carried out in recent years to identify some of these so-called high energy density materials (HEDM) [1].

Nitrogen compounds are interesting candidates as potentially metastable substances, since the strength of the N_2 triple bond makes this molecule an appealing end point of strongly exothermic reactions. The hypothetical compounds N_4 [2], N_6 [3–6], N_8 [7] and N_{20} [8] have all recently been examined theoretically in order to investigate whether such an assumption is at all realistic. In the most symmetrical structures (a tetrahedron, a prisma, a cube, and a dodecahedron respectively), each nitrogen makes single bonds with three neighbour atoms.

Cubic N_8 is isoelectronic with cubane, $(CH)_8$, which is a metastable species. Whereas $(CH)_8$ has been known experimentally for many years [9], N_8 has never been synthesized. Nevertheless, the high thermal stability of cubane suggests that cubic N_8 could also be a metastable compound and it is thus an interesting hypothetical system for which theoretical studies could aid in describing the thermodynamic properties. Since a nitrogen single bond is much weaker than the analogous bond between two CH groups, the replacement of the CH by nitrogen atoms should produce a structure with higher energy content than cubane. The problem is, of course, that the same weak bonds lead to lower barriers for decomposition.

A number of different theoretical studies have already been performed on isomers of N_8. Trinquier et al. [10] were the first to perform ab initio calculations on the system. They did pseudopotential self-consistent-field (SCF) calculations on tetrahedral X_4 and on cubic X_8 molecules (with $X = N$, P, As). Double-zeta basis sets without *d* functions were used in the calculations on the N_8 molecules. The cubic equilibrium geometry was supposed to be a minimum; rather surprisingly their results appeared to show that the X_8 systems were almost degenerate in energy with $2X_4$ (calculated with the same basis) with N_8 only a little higher in energy than $2N_4$.

More recently, Engelke and Stine [7] reported a restricted Hartree-Fock self-consistent field (RHF-SCF) study of cubic N_8 using STO-3G, 4-31G, and 4-31G* basis sets. Vibrational frequency calculations at the same three levels of theory were also performed, and the effects of correlation were examined using Möller-Plesset (MP) perturbation theory. According to these results, cubic N_8 would be a highly energetic material, metastable to dissociation into four N_2 molecules with the liberation of a significant amount of energy (530 ± 50 kcal/mol), if it could be synthesized. A $[2+2]$ forbidden reaction path was suggested and a rough estimate of the barrier for dissociation was given, 40 kcal/mol.

Engelke [11] also calculated some properties of the 22 possible mixed cubanoids $(CH)_{8-n}N_n$ (with $n = 0$–8), using the semi-empirical models Austin Model 1 (AM1) and Parameter Method 3 (PM3). After the optimization of the geometries of the C/N cubanoids within the two models, the vibrational frequencies were calculated to demonstrate that the stationary-point geometries are

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locally stable points. From the AM1 and PM3 calculations the enthalpies for the optimized structures were also estimated, in order to see whether these compounds could be used as high energetic material. The results predicted that all the 22 cubanoids are metastable with respect to rearrangement into smaller species. Ten of the 22 possible structures were also studied using ab initio methods, HF and MP2 with 6-31G* basis sets [12].

Lauderdale et al. [13] studied cubic N_8, by means of ab initio SCF, coupled-cluster (CC) and many-body perturbation theory (MBPT). They determined geometries and harmonic frequencies at the SCF and MBPT(2) level. Their SCF results agree qualitatively with those of Engelke and Stine [7]. From symmetry arguments they deduced that N_8 should have a significant barrier to decomposition. By correlating the orbitals of N_8 with those of $4N_2$ through D_{2h} symmetry, they obtained an orbital crossing between occupied and unoccupied orbitals, which demonstrated that N_8 corresponds asymptotically to an excited state of $4N_2$ molecules on the D_{2h} energy surface. The decomposition of N_8 to $4N_2$ is thus symmetry forbidden along this reaction coordinate. Similarly, the decomposition via a D_{2d} pathway is forbidden, and it was therefore expected that N_8, if it could be formed, would be relatively stable.

Finally we mention a recent contribution to the study of these compounds by Leininger et al. [14], who studied three isomers of N_8, the octaazacubane structure, the D_{2d} structure analogous to cyclooctatetraene and a planar bicyclic form analogous to pentalene. The geometries were optimized with SCF, Möller Plesset perturbation theory at the second order (MP2), single and double excitation configuration interaction (CISD) and coupled-cluster (CCSD) methods. The harmonic vibrational frequencies and infrared intensities were obtained at the SCF and MP2 levels of theory. Their highest-quality results placed the pentalene-like structure approximately 225 kcal/mol above $4N_2$, 198 kcal/mol below the octaazacubane structure, and 35 kcal/mol below the cyclooctatetraene-like one.

The tetrahedral and dodecahedral systems N_4 and N_{20}, and several isomeric forms of N_6, have been also investigated as potential HDEM candidates. Lee and Rice [2] carried out an investigation on N_4, going from SCF to CC with perturbative inclusion of the effect of triple excitations, CCSD(T). They predicted that the energy difference between T_d N_4 and two N_2 molecules is about 186 kcal/mol, with a barrier of 61 kcal/mol. This appears to confirm that N_4 is a good candidate for a HDEM. Dumm and Morokuma [15] explored the dissociation of tetrahedral N_4 to $2N_2$ at several levels of ab initio molecular orbital theory. The transition state for dissociation was located at the complete active space (CAS) SCF level of theory and the energy barrier was estimated to be 63 kcal/mol.

Engelke [3, 5, 6] has investigated six isomeric forms of N_6 at the SCF and MP2 level analogous to the carbon structures benzene, Dewar benzene, benzvalene, trisprismane, bicyclopropenyl and diazide. At the MP2 level of theory, Dewar benzene, benzvalene, and trisprismane were found to be stable points on the energy hypersurface, while bicyclopropenyl and diazide were found to be transition states and benzene a stationary point with more than one negative eigenvalue of the Hessian.

The dodecahedral molecule N_{20} was studied by Bliznyuk et al. [8]. Since there is less strain in this structure, it ought to be more stable than cubic N_8. By using both SCF and MP2 theory they predicted N_{20} to be a relative minimum on its potential energy hypersurface, lying above separated nitrogen molecules by about 50 kcal/mol per nitrogen atom.

In a previous paper [16] we have investigated the possible dissociation reaction of cubic N_8 towards 4 N_2 molecules in D_{4h} symmetry, at the CASSCF level. The energy release for this reaction was predicted to be around 526 kcal/mol, with an energy barrier to dissociation of 159 kcal/mol.

The few reactions for the dissociation of N_8 into four N_2 molecules, so far studied, have all been highly symmetrical and strongly forbidden. It is unlikely that the dissociation of N_8 will follow these paths. The path is more likely to be a stepwise dissociation process from N_8 first to $N_6 + N_2$, then to $N_4 + 2N_2$, etc. As a first step towards a more complete understanding of the dissociation channels of N_8, we present below results from a study of the isomerization reaction from the high energy azacubane structure to the more stable azapentalene structure. We show that this reaction can proceed via a series of intermediate metastable structures with moderately low barriers (10–20 kcal/mol). We do not claim to have found the true minimum energy reaction path, since some symmetry elements have been maintained. The barriers should therefore be considered as upper limits.

The calculations have been performed using multiconfigurational wave functions (the CASSCF method) [17] with dynamic correlation effects estimated by second-order perturbation theory (CASPT2) [18–20]. In parallel, density functional theory (DFT) has also been applied and we show that this approach cannot describe the energy barriers for the symmetry forbidden reactions.

2 Theoretical approach

Multiconfigurational wave functions (CASSCF) are used to describe the electronic structure of the different isomers of N_8 and the transition states between them. The reaction path studied passes over a number of symmetry forbidden transition states where near-degeneracy occurs between different electronic configurations. In such situations, a multiconfigurational approach is the only way to describe the electronic structure accurately. The CASSCF wave function is in a subsequent step used as a reference function for a second-order estimate of the remaining (dynamic) correlation energy, using the CASPT2 approach. In a number of applications this approach has proved to give estimates of relative correlation energies with an accuracy of a few kcal/mol (see, for example, Refs. [20, 21]).

In addition, we have also computed relative energies using the DFT approach. It is clear, however, that this approach will not be able to give accurate values for the energy barriers for symmetry forbidden reactions, since the electronic structure changes rapidly in the transition state region. The empirical B3LYP approach (as implemented in the GAUSSIAN program) was used to construct the exchange-correlation potential. For the closed shell systems, total energies at the optimized geometries were also computed at the MP2, MRCI (multireference CI), and CCSD (coupled cluster) levels of theory. The geometries of the minima and transition states were optimized at the CASSCF level using analytical first derivatives. Harmonic vibrational frequencies were determined via finite differences of the analytic CASSCF first derivatives. In addition, vibrational frequencies of all the local minima on the energy hypersurface were determined using DFT. The CASSCF, CASPT2, MP2, and MRCI calculations were performed using the MOLCAS package of ab initio programs [22], the DFT calculations with the GAUSSIAN code [23], and the CCSD calculations with the TITAN code [24].

ANO-S type basis sets have been used in the CASSCF and CASPT2 calculations [25]. All structures were studied with a $3s2p1d$ basis (112 basis functions). For those with higher symmetry (see below) the calculations were repeated with three increasing-quality basis sets, respectively contracted to $2s1p$ (40 basis functions), $3s2p1d$ (112 basis functions), and $4s3p2d1f$ (240 basis functions; the ANO-L basis set was used in this case [26]). The Dunning $cc-pVTZ$ (240 basis functions [27]) were used for the DFT calculations. The geometries for the different structures were optimized with the symmetry constraints reported in Table 1. Figure 1 shows the structures for the five metastable energy minima and the intervening transition states.

3 The calculations

The choice of the active orbitals is the crucial step in a CASSCF calculation. Preliminary calculations were therefore performed using a large active space but with the wave function restricted to single and double substitutions from a closed shell reference state. The restricted active space (RAS) SCF option of the MOLCAS code was used for this purpose. Calculations were first performed for the cubic structure **1**. The geometry was then distorted along a vibrational mode of T_{2u} symmetry, which transforms **1** into **4** with a C_{2v} symmetry constraint. Along this path, a slope discontinuity on the energy hypersurface occurred, due to a molecular orbital crossing between occupied and unoccupied orbitals. In order to be able to describe the full reaction path the CASSCF approach was then introduced and the active space was chosen by inspection of the RASSCF occupation numbers. Eight orbitals with

Table 1. Symmetry classification of the structures

Label	Structure	Symmetry
1	Octaazacubane	O_h
2	Tricyclooctaaza-3,7-diene	C_{2v}
3	Bicyclooctaaza-2,4,7-triene	C_s
4	Octazacyclooctatetraene	D_{2d}
5	Azapentalene	D_{2h}
Transition states		
TS_{12}	between 1 and 2	C_{2v}
TS_{24}	between 2 and 4	C_{2v}
TS_{23}	between 2 and 3	C_s
TS_{34}	between 3 and 4	C_s
TS_{45}	between 4 and 5	C_2

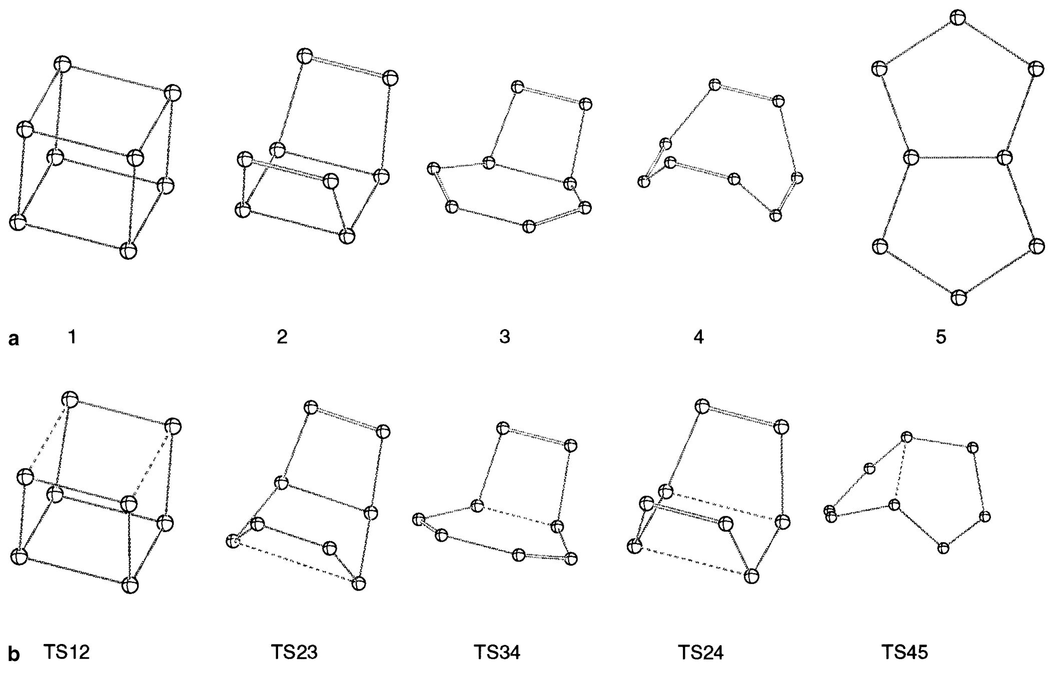

Fig. 1a,b. Structures of the five isomers of N_8 (**a**) and the five transition states (**b**) occupation numbers significantly different from 0 or 2 were selected for the active space with eight active electrons. The active space was selected according to the same principle for the reaction paths of C_s and C_2 symmetry. Inspection of these orbitals shows that they describe the breaking of the four bonds that take place in the transformation from **1** to **4**. In **1** they are four bonding and four antibonding orbitals, in **2**, two of the pairs have been transformed to π-orbitals, etc., such that in **4** all active orbitals have π character. A slightly extended active space was used for the transformation from **4** to **5** (see below).

A local minimum (**2**) was found along the path from **1** to **4** corresponding to a structure with two broken bonds on one of the faces of **1**, while the final structure **4** has four broken bonds, two on one face, and two on the opposite face. A transition state (TS) between **1** and **2**, (TS_{12}) was located as well as the TS between **2** and **4** (TS_{24}). For each of these structures we determined the vibrational frequencies and optimized the geometry, at the CASSCF level. CASPT2 energies were computed at the CASSCF optimized geometries. The geometries and the vibrational frequencies were also determined at the DFT level. The CASSCF and CASPT2 calculations were finally repeated with the three basis sets of increasing quality.

One other local minimum was found on the reaction path from **2** to **4** corresponding to one more broken NN bond. This new minimum (**3**) has C_s symmetry. The TS between **2** and **3**, TS_{23}, as well as between **3** and **4**, TS_{34}, were found and optimized and energies and frequencies were computed according to the procedure outlined above. The final step is to transform the cyclooctatetraene structure to the more stable pentalene structure, **5**. This is done by distorting **4** along a coordinate (of C_2 symmetry), which leads to contact between the central nitrogen atoms. A transition state, TS_{45}, was located along this reaction path. This reaction involves more active electrons and the (8/8) active space was extended to 12 electrons in ten orbitals, (12/10), in order to incorporate also the π lone pair orbitals in azapentalene. This extension of the active space had, however, only a small effect on computed CASPT2 energies.

4 Results and discussion

All the reactions studied are symmetry forbidden. In order to illustrate this we show in Fig. 2 how the occupation numbers vary along the direct reaction path from the cubane structure **1**, via the boat structure **2** to cyclooctatetraene, **4**. This figure shows the typical change of occupation occurring in a symmetry forbidden reaction. In the first reaction, two σ-bonds of structure **1** are transformed to the π-bonds of **2**. Since the π-bonds are weaker than the σ-bonds, the corresponding bonding-antibonding pair of orbitals will have occupation numbers more different from two and zero, respectively. In the second step two more pairs of σ-orbitals will transform into π-orbitals such that in **4** all active orbitals are of π-type.

Table 2 gives bond distances for all isomers and transition states computed with the CASSCF method and the $3s2p1d$ basis set. Instead of giving all the geometry parameters in the table we present only the typical distances. They are divided into three classes: the single bonds between three-coordinated atoms (R_{ss}),

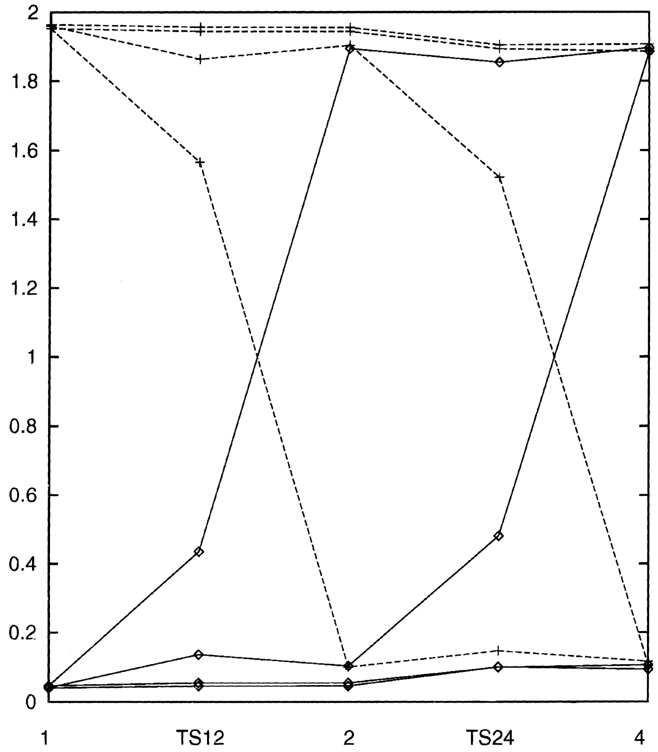

Fig. 2. Variations of the occupation numbers for the eight active orbitals along the reaction path leading from **1** to **4** along the reaction path through **2** and through the transition states TS_{12} and TS_{24}

Table 2. Ranges of NN bond distances (Å) for the different structures and transition states (R_{ss} = distances between three-coordinated atoms, R_{sd} between three- and two-coordinated atoms, and R_{dd} between two-coordinated atoms); $3s2p1d$ CASSCF results (DFT results in parentheses)

Structure	R_{ss}	R_{sd}	R_{dd}
1	1.50	–	–
	(1.52)	–	–
2	1.48, 1.52	1.41	1.25
	(1.49)	(1.43)	(1.26)
3	1.47	1.41–1.44	1.21–1.22,1.41
	(1.44)	(1.39–1.42)	(1.23–1.27), (1.56)
4	–	–	1.23, 1.44
	–	–	(1.23, 1.43)
5	1.31	1.33	1.32
	(1.33)	(1.33)	(1.32)
Transition states			
TS_{12}	1.53	1.46	1.43
TS_{24}	–	1.42–1.43	1.23
TS_{23}	1.50	1.41–1.44	1.21–1.22, 1.41
TS_{34}	–	–	1.23, 1.44
TS_{45}	(1.76)	1.32, 1.43	1.21, 1.38

the single bonds between three-coordinated and two-coordinated atoms (R_{sd}), and finally the bond lengths between two-coordinated atoms (R_{dd}), which can have either single or double bond character. The bond distance in the cube is 1.50 Å. This is also the typical R_{ss} bond distance, which varies between 1.47 and 1.52 Å. The R_{sd} distance is also rather constant, varying between 1.41 and 1.44 Å. The R_{dd} distances are of two types, double bonds as in **2** and **4**, which vary in length between 1.21 and 1.25 Å, and conjugated single bonds of lengths between 1.41 and 1.44 Å. The only molecule that does not fit into this picture is azapentalene. In this planar system, all the NN bonds have similar lengths (1.31–1.33 Å), which shows that the π-system is completely delocalized [28]. The bond distances obtained for structures **1, 4,** and **5** are very similar to those obtained by Leininger et al. in their recent CCSD study [14]. The geometries of the stable clusters have also been optimized using the DFT approach. The results are given in the same table. They are very similar to the CASSCF results, with one exception being the single bond R_{dd} distance in the six-ring of structure **3**. Here DFT predicts a very long bond length (1.56 Å), while the CASSCF result is 1.41 Å. We have no explanation for this striking difference. The transition states could, of course, not be optimized using DFT theory.

Table 3. Lowest vibrational frequency (cm^{-1}) for each of the stable structures and the imaginary frequencies of the intervening transition states

Method	CASSCF	DFT	
Basis set	ANO $3s2p1d$	$cc-pVTZ$	
Structure			
1	931	529	E_g
2	368	214	A_2
3	226	160	A''
4	382	241	B_1
5	245	253	B_{3u}
Transition states			
TS_{12}	1157i		
TS_{24}	1423i		
TS_{23}	524i		
TS_{34}	303i		
TS_{45}	1001i		

In Table 3 the lowest harmonic vibrational frequencies for each structure, at the CASSCF and DFT levels of theory, are reported. Also the imaginary frequencies at the transition states are given. There is little resemblance between the CASSCF and DFT results (except for the pentalene structure). The DFT frequencies are considerably lower. There is no obvious explanation for the difference. As we shall see later, the CASSCF barriers are in general lower than the barriers obtained at the DFT level and one would consequently also expect the frequencies to be lower.

We present in Table 4 the relative energies of the different structures and also the energy barriers. The same information is also given in Fig. 3. The CASPT2 value for the energy difference between the cubic and the pentalene structures is 216 kcal/mol, 18 kcal/mol larger than the CCSD(T) value reported by Leininger et al. Also the other relative energies, for which a direct comparison can be made, are larger. This is most likely a basis set effect, as can be seen in Table 5, where some of the structures have been computed with basis sets of increasing quality. When the basis set is extended from $3s2p1d$ to $4s3p2d1f$ we see an increase in all relative energies. The most likely explanation for the difference between the CASPT2 and CCSD(T) is therefore the small basis set used by Leininger et al. (a $4s2p1d$ basis from a $9s5p1d$ primitive set was used). A CCSD calculation performed with the $3s2p1d$ ANO basis gives an energy difference between **4** and **1** of 166.7 kcal/mol compared with 161.2 kcal/mol obtained by Leininger et al. (cf. Table 6). Note that the difference lies more in the choice of the primitive basis and the contraction technique than in the size of the final contracted basis set.

Comparing the CASPT2 and DFT results, we see the opposite trend. The DFT energy difference between **5** and **1** is 17 kcal/mol larger than the CASPT2 energy. Again we have no explanation for the rather large difference between the two sets of results. The CASPT2 method has now been used in a large number of studies of relative energies. Based on this experience we believe the present results to be accurate to at least ±5 kcal/mol.

Table 4. Energy differences between the different structures of N_8 and the corresponding energy barriers (in kcal/mol)

	CASSCF (ANO $3s2p1d$)	CASPT2 (ANO $3s2p1d$)	DFT ($cc-pVTZ$)	CCSD(T) (from Ref. [14])
Energy differences				
2–1	−116.0	−90.0	−105.7	
3–2	−32.9	−49.8	−61.3	
4–2	−93.5	−79.7	−82.9	
4–3	−60.6	−29.9	−21.6	
4–1	−209.5	−169.8	−188.7	−162.9
5–4	−3.1	−46.6	−44.5	−35.1
5–1	−212.6	−216.4	−233.1	−198.0
Energy barriers				
TS_{12}-**1**	9.3	22.4	31.7	
TS_{24}-**2**	18.3	18.2	43.3	
TS_{23}-**2**	16.6	11.4	28.2	
TS_{34}-**3**	7.9	11.1	20.3	
TS_{45}-**4**	100.6	37.3	49.7	

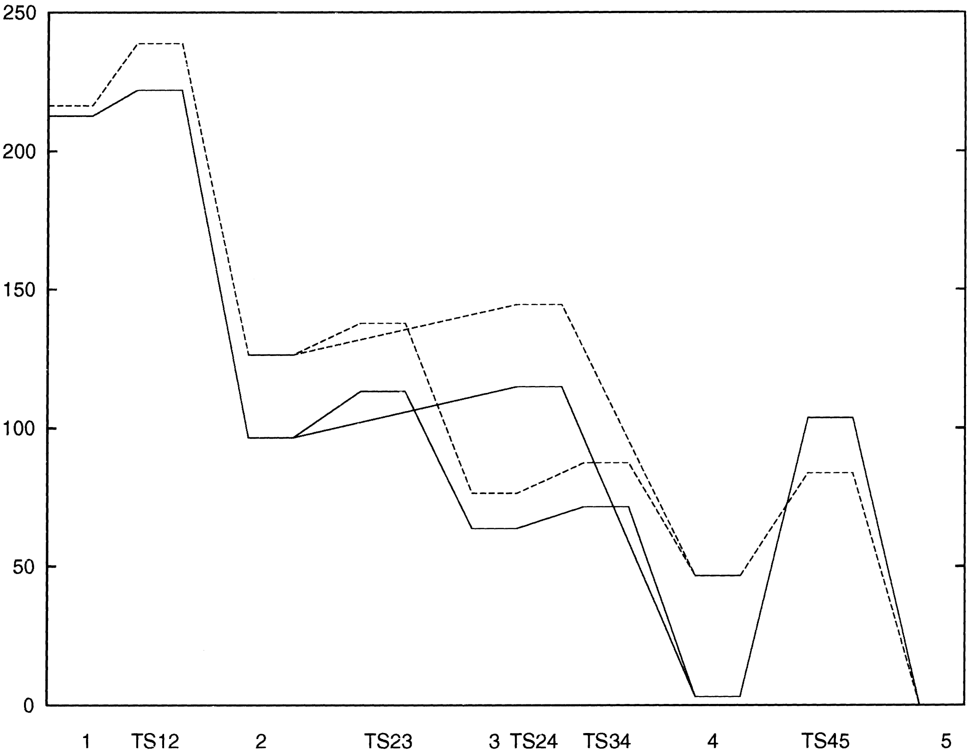

Fig. 3. Local minima and transition states along the reaction path from **1** to **5**. *Solid lines* indicate CASSCF results, *dashed lines* the CASPT2 results. Relative energies in kcal/mol

Table 5. Relative energies for the reaction path from **1** to **4** as a function of the ANO basis set (in kcal/mol)

	TS$_{12}$-1	**2–1**	**TS$_{24}$-2**	**4–1**
CASSCF				
$2s1p$	24.0	−31.4	−4.5	−106.0
$3s2p1d$	9.3	−116.0	18.3	−209.5
$4s3p2d1f$	10.2	−116.1	19.1	−208.7
CASPT2				
$2s1p$	27.0	−26.1	−5.3	−101.6
$3s2p1d$	22.4	−90.0	18.4	−169.8
$4s3p2d1f$	22.3	−93.6	20.4	−172.5

Table 6. The energy difference between **1** and **4** computed with different methods and ANO-type basis sets (in kcal/mol)

Method	MP2	CCSD	ACPF[a]	CASPT2
$2s1p$	108.9	94.6	95.7	101.6
$3s2p1d$	175.2	166.7	168.5	169.8
$4s3p2d1f$	176.2	–	–	172.5

[a] The averaged coupled pair functional approach as implemented in the MRCI program of MOLCAS was used

In Table 6 we compare different correlation treatments for the energy difference between **1** and **4**. With the basis set $3s2p1d$ we obtain very similar relative energies with the CCSD, ACPF, and CASPT2 methods, while MP2 slightly overestimates the energy difference. There is a simple explanation for this inability of the MP2 approach to give an accurate estimate of the relative energy. Inspection of the corresponding CASSCF wave functions shows that the weight of the HF configuration in **1** is 91%, while in **4** it is only 80%. Thus the electronic structure for **4** is more degenerate and consequently the MP2 approach will overestimate the energy difference. Also the other structures are more degenerate than **1**. The HF weights in the CASSCF wave function are: 85%, 93%, and 86% for **2**, **3**, and **5**, respectively. Only MP2 and CASPT2 calculations could be performed with the larger basis set. Again the MP2 energy is slightly larger, but the basis set effect is the same as with CASPT2.

The most important result of the present study is the finding that the azacubane structure of N_8 can be transformed into the azapentalene structure via a set of intermediate metastable structures. The first transformation, from **1** to **2**, breaks two of the single bonds in cubane to form two double bonds in **2**. The barrier for this reaction is 22 kcal/mol. Keeping the C_{2v} symmetry, **2** can be transformed directly into **4** by breaking two more single bonds and forming two new double bonds instead. The barrier is now 18 kcal/mol. Thus, it seems that the energy barrier for transforming one single bond into a double bond is about 10 kcal/mol. And indeed, the reaction path from **2** to **4**, which proceeds via the intermediate structure **3**, has two barriers, each with a value of 11 kcal/mol. The transformation from **4** to **5** is, however, different. Here a new single bond is formed and the remaining π-bonds are changed into two allylic systems strongly interacting via the bridging nitrogen lone pairs. The energy barrier for this transformation is higher (37 kcal/mol at the CASPT2 level of theory). In this case the change in the electronic structure is more extensive and involves, apart from the transformation of the double bonds in **4** to one single bond and a strongly conjugated π-system, also the transformation of two nitrogen lone pairs into doubly occupied π-orbitals, which interact strongly with the π-system. Twelve electrons are involved in ten active orbitals. This active space was therefore used in one calculation at the transition state geometry determined with the smaller active space. It turned out, however, that the total CASPT2 energy changed very little (2.6 kcal/mol) when the active space was extended from (8/8) to (12/10), and we conclude that the lone pair electrons can also be treated as inactive in azapentalene.

The high barrier in the last reaction indicates that a dissociation reaction that starts from the cubic structure is not likely to proceed via pentalene. According to the results discussed above one would expect azacyclooctatetraene to dissociate to $N_6 + N_2$ with a considerably lower barrier by breaking two single bonds. This possibility will be considered in a forthcoming publication together with dissociation paths starting from the most stable N_8 structure, azapentalene.

5 Conclusions

In this contribution we have presented results from a CASSCF/CASPT2 study of the transformation of N_8 from the highly energetic azacubane structure to the more stable azapentalene isomer. It has been shown that the transformation can proceed via a series of intermediate metastable structures, where the single bonds of azacubane are transformed stepwise into π-orbitals of the more open structures, and finally to the "quasi-aromatic" pentalene structure. Dissociation of one single bond and the simultaneous formation of a double bond seems to proceed via a transition state with a barrier of about 10 kcal/mol. It is likely that similar barrier heights will occur when N_2 moieties are dissociated from the cluster leading eventually to the 4 N_2 product. If this is the case, it is unlikely that N_8 will exist for a long time as a stable product at room temperature.

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