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A theoretical study of ten N_8 isomers

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Abstract

The HF/3s2p1d and MP2/3s2p1d structures, energies and vibrational frequencies were calculated for ten N_8 isomers, corresponding to ten analogous CH structures. Comparative calculations using density functional theory (DFT), with a cc-pVTZ basis set, were also performed. All ten structures were found to be local minima on the energy hypersurface at the Hartree–Fock (HF) level, whereas at the second-order Möller–Plesset (MP2) level nine structures were stable. At the DFT level, eight local minima were found. The total energies were recomputed using 4s3p2d1f basis sets at the HF and MP2 levels of theory. © 1998 Elsevier Science B.V.

Keywords: Ab initio calculations; High energy density material (HEDM); Nitrogen clusters

1. Introduction

N_8 isomers are hypothetical compounds of interest because they are isoelectronic with the corresponding CH compounds, some of which have been experimentally determined to be metastable substances [1,2]. Moreover, their energy content relative to the dissociation products, four N_2 molecules, would be extremely high, making them prime candidates as high energy density materials (HEDMs), with a high ratio between the energy released and the specific weight [3,4].

Recently, there have been a significant number of ab initio calculations performed on pure nitrogen structures, containing four [5,6], six [7–10], eight [11,12] and 20 [13] nitrogen atoms. However, none of these compounds has been synthesized. In these hypothetical molecules, each nitrogen atom can make three single bonds with three neighbouring atoms, giving rise to highly symmetrical structures (tetrahedron, trigonal prism, cube and dodecahedron respectively). In addition, less symmetrical structures have been investigated for N_6 [9,10] and, to some extent, for N_8 [12]. These studies have been summarized in some detail in a recent paper [14] and will not be discussed further. However, two recent contributions must be mentioned: one by Gimarc and Zhao [15] and the other by Glukhovtsev et al. [16]. In these papers, some of the N_8 clusters, the object of the present study, are extensively discussed.

Previously [14], we studied the isomerization reaction of cubic N_8, analogous to pentalene, using multiconfigurational wavefunctions with a second-order estimate of dynamic correlation effects (the

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CASSCF/CASPT2 method). Calculations using second-order Möller–Plesset (MP2) theory and density functional theory (DFT) were also performed. A number of intermediate metastable structures were found, and it was observed that the relative energies obtained with the CASPT2 method and MP2 theory were in reasonable agreement, although MP2 seemed to overestimate somewhat the stability of the structures with many double NN bonds. This is because these systems have more nearly degenerate wavefunctions with a smaller weight of the Hartree–Fock (HF) configuration. The DFT and CASPT2 results were also in reasonably good agreement.

As a further step towards a more complete understanding of the nature of these high energy compounds, we present a study of ten N_8 isomers at different levels of theory in order to verify their stability on the energy hypersurface.

The calculations were performed using the HF and MP2 methods. In parallel, DFT was also applied to verify the results obtained with the other methods. Of the ten structures, five have already been studied at the CASSCF and CASPT2 level [14], but the others have not been investigated previously.

2. Theoretical approach

The HF and MP2 methods were used to describe the electronic structures of the ten N_8 isomers. The geometries were optimized using analytical first derivatives, and harmonic vibrational frequencies were determined via analytical second derivatives. In addition, we also optimized the geometries of the ten structures and determined the vibrational frequencies using the DFT method. The B3LYP approach (as implemented in the GAUSSIAN program) was used to construct the exchange correlation potential.

The HF and MP2 calculations were performed using the CADPAC package of ab initio programs [17], and the DFT calculations were performed with the GAUSSIAN code [18]. The basis set used for the HF and MP2 geometry optimization and frequency determination was the correlation-consistent basis set optimized by Dunning [19], i.e. a basis of (9s5p1d)/[3s2p1d] quality (120 basis functions). This is the smallest basis set which can be used to obtain reasonable estimates of the relative energies. The polarization functions are needed to describe the strained bonds, and also for the major correlation effects. The 3s2p1d basis set was compared with the larger 4s3p2d1f basis set in the preceding work and similar relative energies were found (it should be noted, however, that these basis sets are of atomic natural orbital (ANO) type based on a larger set of primitive functions). The MP2 frequencies of form **6** were obtained with the GAUSSIAN package and a slightly different basis set, i.e. the (9s5p1d)/[3s2p1d] set with only five functions for the d orbitals (112 basis functions), instead of six as in CADPAC. The total HF and MP2 energies were also computed with the (10s5p2d1f)/[4s3p2d1f] basis set (280 basis functions) at the geometries optimized with the (9s5p1d)/[3s2p1d] basis. The DFT calculations were performed with the Dunning cc-pVTZ basis set (240 basis functions [20]).

The geometries of the different structures were optimized with the symmetry constraints reported in Table 1, and Fig. 1 shows the structures of the ten isomers.

3. The calculations

Of the ten structures investigated, the first nine correspond to the nitrogen analogues of C_8H_8 compounds: cubane (**1**), pentacyclooctane (**2**), cuneane (**3**), *cis*-tricycloocta-3,7-diene (**4**), *trans*-tricycloocta-3,7-diene (**5**), bicyclo-octa-2,4,7-triene (**6**), *trans*-cycloocta-1,3,5,7-tetraene (**7**), *cis*-cycloocta-1,3,5,7-tetraene (**8**) and barrelene (**9**). The tenth is the

Table 1
Symmetry classification of the structures

Label	N_8 form of	Symmetry
1	Cubane	O_h
2	Pentacyclooctane	D_{2h}
3	Cuneane	C_{2v}
4	*cis*-Tricycloocta-3,7-diene	C_{2v}
5	*trans*-Tricycloocta-3,7-diene	C_{2h}
6	Bicycloocta-2,4,7-triene	C_s
7	*trans*-Cycloocta-1,3,5,7-tetraene	C_{2h}
8	*cis*-Cycloocta-1,3,5,7-tetraene	D_{2d}
9	Barrelene	D_{3h}
10	Pentalene	D_{2h}

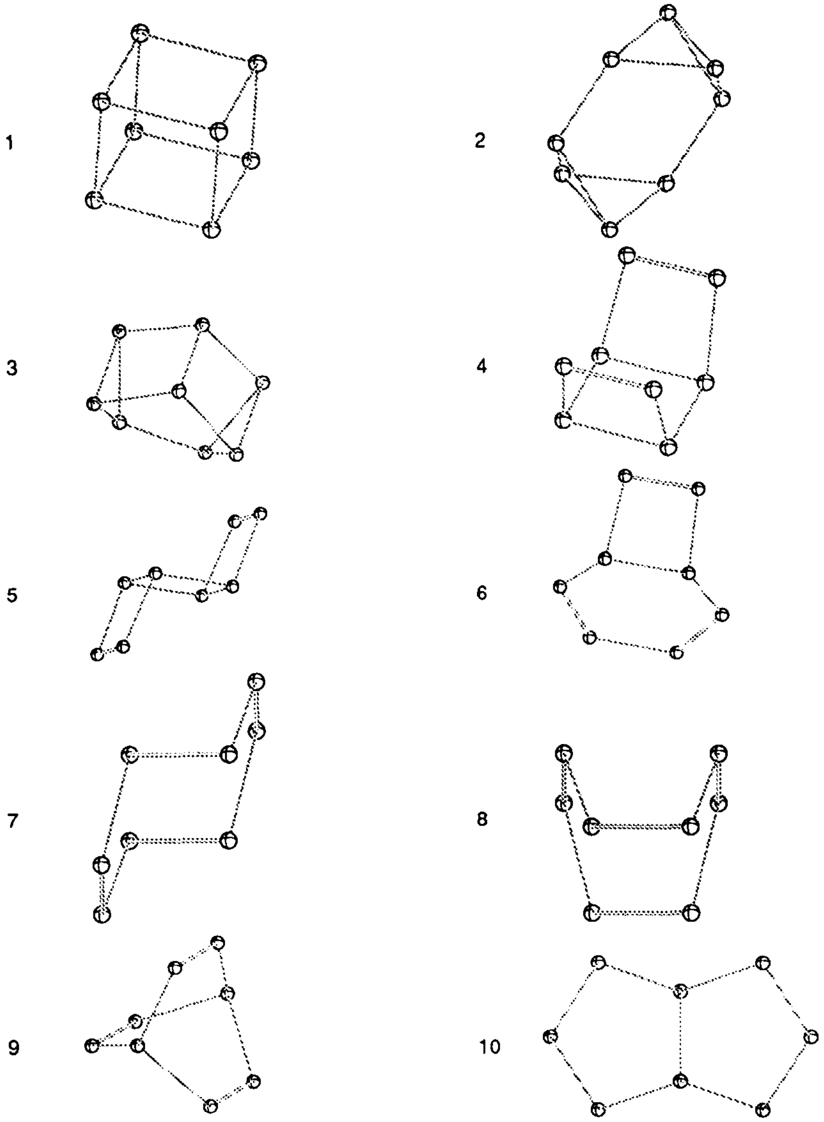

Fig. 1. Molecular structures of the optimized ten isomers of N_8.

nitrogen analogue of the C_8H_6 pentalene molecule (**10**).

At the self-consistent field (SCF) level, all ten structures are local minima on the energy hypersurface. At the MP2 level, all the structures are stable except **9**, for which it is not possible to find a minimum with D_{3h} symmetry. A further destabilization is found at the DFT level of theory, where only eight of the structures are local minima. Structure **7** has one imaginary frequency and **9** two.

4. Results and discussion

In Table 2, we report the bond distances for all the isomers resulting from the different optimizations, i.e. HF and MP2 with the 3s2p1d basis set and DFT with 4s3p2d1f.

Instead of giving all the geometric parameters, we present only the typical distances. They can be classified into four groups: single bonds between three-coordinated atoms (R_{ss}), single bonds between a

Table 2
Structural parameters[a] of the different isomers

Isomer	Structural parameter	HF	MP2	DFT
1	R_{ss}	1.46	1.53	1.52
2	R_{ss}	1.41–1.42	1.45–1.49	1.45–1.48
3	R_{ss}	1.40–1.45	1.43–1.50	1.43–1.49
4	R_{ss}	1.44–1.50	1.49–1.62	1.49–1.57
	R_{sd}	1.41	1.42	1.43
	R_{dd}	1.23	1.31	1.26
5	R_{ss}	1.44–1.47	1.50–1.56	1.49–1.53
	R_{sd}	1.42	1.45	1.45
	R_{dd}	1.22	1.27	1.25
6	R_{ss}	1.41	1.45	1.44
	R_{sd}	1.38–1.40	1.40–1.42	1.39–1.42
	R_{dd}	1.21–1.23	1.25–1.31	1.23–1.27
	$R_{dd'}$	1.46	1.58	1.56
7	R_{dd}	1.21	1.28	1.26
	$R_{dd'}$	1.42	1.49	1.46
8	R_{dd}	1.20	1.27	1.23
	$R_{dd'}$	1.40	1.43	1.43
9	R_{sd}	1.58	–	1.51
	R_{dd}	1.24	–	1.21
10	R_{ss}	1.28	1.37	1.31
	R_{sd}	1.31	1.34	1.33
	R_{dd}	1.29	1.34	1.32

[a] See text for an explanation of the structural parameters.

three-coordinated and a two-coordinated atom (R_{sd}) and, finally, the bonds between two-coordinated atoms, which can have either a double (R_{dd}) or single ($R_{dd'}$) character. In the cubic form **1**, the bond distances (R_{ss} type) are 1.46 Å (HF), 1.53 Å (MP2) and 1.52 Å (DFT). This is a typical R_{ss} bond distance, which varies between 1.40 and 1.50 Å (HF), 1.43 and 1.56 Å (MP2) and 1.43 and 1.57 Å (DFT) for the ten compounds. R_{sd} is also fairly constant, varying between 1.38 and 1.42 Å (HF), 1.40 and 1.45 Å (MP2) and 1.39 and 1.43 Å (DFT). An exception is form **9**, where R_{sd} is considerably longer: 1.58 Å at the HF level and 1.51 Å at the DFT level. The R_{dd} bonds present in **4**, **5**, **6**, **7**, **8** and **9** vary in length between 1.20 and 1.24 Å (HF), 1.25 and 1.31 Å (MP2) and 1.23 and 1.27 Å (DFT). The conjugated single bonds ($R_{dd'}$) in **7** and **8** vary between 1.40 and 1.42 Å (HF), 1.43 and 1.49 Å (MP2) and 1.43 and 1.46 Å (DFT), whereas this bond in **6** is somewhat longer: 1.46 Å (HF), 1.58 Å (MP2) and 1.56 Å (DFT).

The only form that does not fit into this scheme is azapentalene. All N–N bonds in this planar system have a similar length (1.28–1.31 Å (HF), 1.34–1.37 Å (MP2) and 1.31–1.33 Å (DFT)), which shows that the π electrons are completely delocalized [21].

In general, the MP2 bond lengths are larger than the corresponding HF results, and the DFT values are in between the two, slightly closer to MP2. These are the expected trends. Since the NN bonds are rather weak, we might expect MP2 to overestimate the correlation effects and yield bonds which are somewhat too long (the very long $R_{dd'}$ for example). It is therefore probable that the DFT results are the most accurate.

The lowest harmonic vibrational frequencies for each structure at the HF, MP2 and DFT levels of theory are reported in Table 3. All ten structures, except **7** and **9**, are stable points at the three levels of theory. Form **7**, on the other hand, is stable at the HF and MP2 levels, whereas it is a transition state (TS) at the DFT level, since it has one imaginary frequency. Form **9** is stable at the HF level, but at MP2 the optimization does not converge (it was performed in C_{2v} symmetry, i.e. in the largest abelian subgroup of D_{3h}), and the DFT calculations result in two imaginary frequencies. For all the stable points, it should be noted that the HF frequency is higher than the corresponding MP2 value, with the DFT result in between, closer to the MP2 value. This trend is associated with the corresponding trend found for the bond distances.

Therefore correlation has a large effect on the vibrational frequencies, as shown by the 25%–50% decrease in the MP2 values compared with HF, and the 9%–38% decrease in the DFT values compared with HF. It is well known that the SCF method usually overestimates the force constants for bonds. Since the MP2 correction of the correlation is generally too

Table 3
Lowest vibrational frequency for each structure (cm^{-1})

Structure	HF	MP2	DFT	
1	726.266	463.806	529.53	E_u
2	310.553	150.294	192.99	A_u
3	612.569	334.343	425.92	A_2
4	234.327	197.057	214.52	A_2
5	300.731	226.679	254.17	A_u
6	182.535	73.978	160.49	A'
7	274.925	242.554	88.89i	B_u
8	278.458	222.189	241.58	B_1
9	538.395		290.97i	E'
10	299.646	249.361	253.91	B_{3u}

Table 4

Energy differences relative to four N_2 molecules (kcal mol^{-1}) at the HF, MP2 and DFT levels with different basis sets

Structure	HF (3s2p1d)	MP2 (3s2p1d)	HF (4s3p2d1f)	MP2 (4s3p2d1f)	DFT (cc-pVTZ)
1	521.52	470.27	523.49	449.44	440.18
2	482.57	412.17	487.71	397.48	398.31
3	453.18	386.00	457.32	364.28	370.66
4	417.71	362.24	416.82	342.50	340.25
5	402.39	356.66	407.23	338.14	331.00
6	359.27	314.60	364.73	302.61	316.19
7	399.10	338.99	405.58	331.08	316.19
8	335.63	287.85	340.36	278.76	258.95
9	352.48	–	347.14	–	271.53
10	293.47	234.74	294.11	216.85	216.93
4 N_2	0	0	0	0	0

large, the computed force constants at this level of theory are usually too small. This fact, together with the DFT results, indicates that all the structures, except **7** and **9**, should be real minima. At all three levels of theory, the first frequency is quite high for isomers **1** and **3**, which should therefore be narrow minima, but for **2**, **4** and **6** this frequency is low, and they should therefore be shallow minima.

In Table 4, the energy difference with respect to four N_2 molecules is reported for each isomer (see also Fig. 2). This difference was determined at the three levels of theory for which optimization was performed, and also at the HF and MP2 levels with a larger basis set (4s3p2d1f) at the 3s2p1d optimized geometry. The highest energy isomer is **1**, lying about 450 kcal mol^{-1} above four N_2. It is followed by **2** and **3**, which are also strained structures. The most stable isomer is planar **10**, which is the only isomer corresponding to a C_8H_6 form. The stabilization of this form has been attributed to the delocalization of the double bonds [12]. In Table 5, we also report, for each isomer, the energy difference with respect to the most stable structure (**10**).

In Fig. 2, the energy difference with respect to four N_2 molecules is reported for the ten isomeric forms with the different methods. It was noted previously that the energy decreases when the single bonds of the cubane structure are changed into double bonds. Thus **4** and **5** are about 100 kcal mol^{-1} more stable than **1**, with the cis form slightly less stable than the trans. Breaking two more single bonds, we obtain the octatetraene-like structures, where the cis form **8** is 70 kcal mol^{-1} more stable than the cis structure **4**. There is, however, a large energy difference (about 50 kcal mol^{-1}) between the cis form **8** and the corresponding trans form **7**, which cannot be due only to steric effects. It is the trans form which is less stable.

Table 5

Energy differences relative to pentalene (**10**) (kcal mol^{-1}) at the HF, MP2 and DFT levels with different basis sets

Structure	HF (3s2p1d)	MP2 (3s2p1d)	HF (4s3p2d1f)	MP2 (4s3p2d1f)	DFT (cc-pVTZ)
1	228.05	235.53	229.38	232.59	223.25
2	189.10	177.43	193.60	180.63	181.38
3	157.71	151.26	163.21	147.43	153.73
4	124.24	127.50	122.71	125.65	123.32
5	108.92	121.92	113.12	121.29	114.07
6	65.80	79.86	70.62	85.76	66.45
7	105.63	104.25	111.47	114.23	99.26
8	42.16	53.11	46.25	61.91	42.02
9	59.01	–	53.03	–	54.60
10	0	0	0	0	0

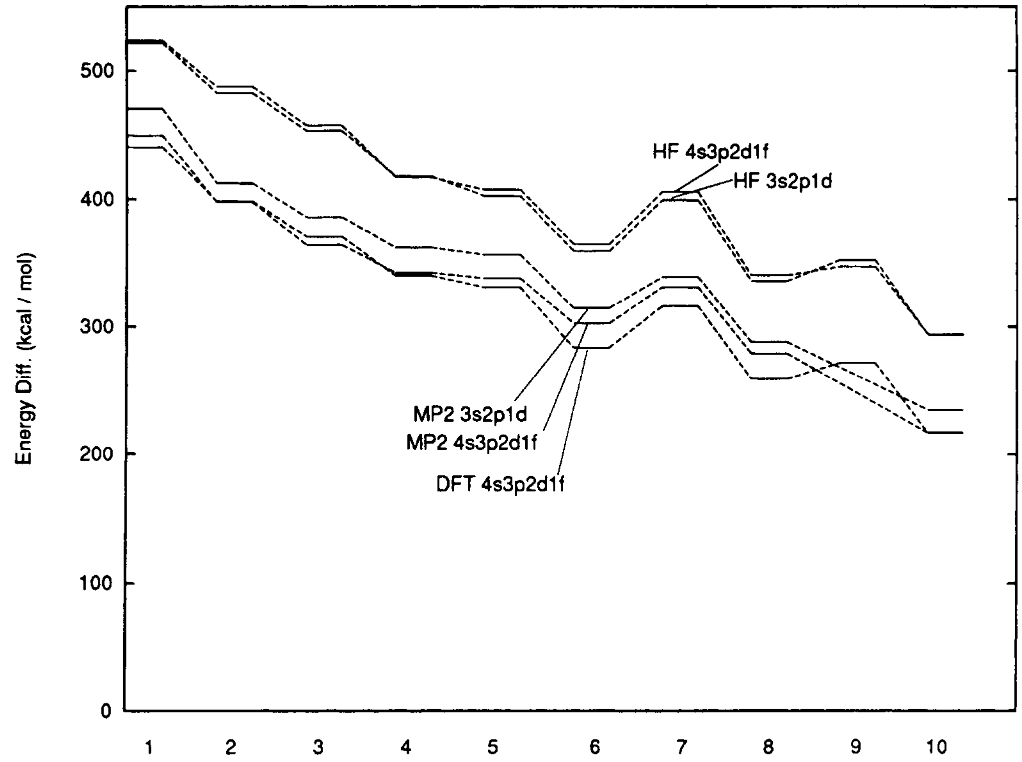

Fig. 2. Energies relative to four N_2 molecules (in kcal mol^{-1}) for the nine isomers of N_8 at the different levels of theory.

At the DFT level of theory, it is not even a minimum on the potential surface. The explanation for the low stability of the trans form is the considerable strain necessary to form four full π bonds. In the cis form, the four nitrogen atoms surrounding a double bond always lie in a plane, and the two atomic π orbitals forming the bond are parallel. Geometry optimization also gives bond angles close to the "ideal" sp^2 value of 120°.

The situation is different for the trans form. Here it is impossible to create a geometry with four fully developed π bonds, because this would require bond angles of 90° (those involving the terminal double bonds). With all angles equal to 120°, the two π atomic orbitals of one of the middle bonds will make an angle of 70° with each other, which reduces the overlap to one-third of the full value. The geometry optimization leads to a structure which is a compromise between strain and π bonding. The bond angles are between 100° and 110°, which gives an angle of 39° between the π atomic orbitals. The reduced bond strength is reflected in the bond distance, which is 1.282 Å for the twisted middle bonds, but 1.265 Å for the four double bonds in the cis form. The "outer" double bonds of the trans form have bond lengths of 1.276 Å, showing that the strained bond angles will also affect these bonds.

A typical N–N single bond energy is about 38 kcal mol^{-1}, that of a double N=N bond is 100 kcal mol^{-1} and that of a triple N≡N bond is 226 kcal mol^{-1} [22]. Azacubane **1**, azacyclooctane **2** and azacuneane **3** have 12 ss bonds (single bonds between three-coordinated nitrogen atoms). With the results in Table 4, this gives an average bond energy of 42 kcal mol^{-1} for the single bond (slightly lower for the more strained cubane system).

To determine the average energies for the bonds sd (E_{sd}), dd (E_{dd}) and dd′ ($E_{dd'}$), we consider the remaining structures, from which it is possible to obtain only relations between the energies and not the absolute values. From structure **8**, we have

$$E_{dd'} \sim 161 \text{ kcal mol}^{-1} - E_{dd} \qquad (1)$$

and from structures **4** and **5**

$$E_{dd}\sim 201\ \text{kcal mol}^{-1} - 2E_{sd} \qquad (2)$$

We also consider the bond length sequence determined from Table 2

$$R_{ss} > R_{dd'} \geq R_{sd} > R_{dd} \qquad (3)$$

If we suppose that E_{dd} is about 100 kcal mol^{-1}, from Eq. (1) we obtain a value for $E_{dd'}$ of about 60 kcal mol^{-1} and from Eq. (2) a value for E_{sd} of about 50 kcal mol^{-1}. If, on the other hand, we consider that the energies are in the same sequence as Eq. 3), but with opposite order, and suppose that $E_{dd'} \approx E_{sd} \approx 50$ kcal mol^{-1}, a value for E_{dd} of about 95 kcal mol^{-1} is obtained. In both cases, the bond energies reproduce the nine relative energies with reasonable accuracy, except for **10**, where the conjugation over both rings gives extra stabilization.

An alternative way of estimating the average values for the bond energies, as suggested by one of the referees, is to consider the structures **1**, **4** and **8**. Since there is virtually no π conjugation energy in **4** and **8**, and assuming that there are only "mean standard" σ or π bond energy increments, the energy difference between **1** and **4**, or between **4** and **8**, can be estimated in terms of these bond increments at about $2(\pi - \sigma)$; these differences are 100 and 80 kcal mol^{-1} respectively. Similarly the energy difference between **1** and **8** is estimated at about $4(\pi - \sigma)$ and corresponds to about 180 kcal mol^{-1}. If the increment of the σ bond is fixed at 38 kcal mol^{-1}, we obtain an increment of $(180/4) + 38 = 83$ kcal mol^{-1} for the π bond, slightly lower than the value obtained previously.

5. Conclusions

The relative energies of a number of isomers of the hypothetical N_8 system have been computed. It is shown that a number of metastable isomers exist with energies between that of the high energy azacubane system and the most stable N_8 compound found so far, azapentalene. It has also been shown that structures with double bonds are more stable than those with only single bonds. A simple bond energy analysis shows that the bond energies are those expected in NN bonds, with single bond energies close to 40 kcal mol^{-1} and double bond energies around 100 kcal mol^{-1}.

All the structures considered in this study lie very high in energy compared with four N_2 molecules and may be suitable candidates to start the dissociation process of N_8. One possible pathway involves the dissociation of structure **6** into an N_6 ring plus one N_2 molecule. It would also be reasonable to start from structure **8**, lower in energy than **6**, with dissociation into a diazide and one N_2 molecule. These dissociation processes will be investigated in a forthcoming publication, together with the dissociation pathways starting from the most stable structure, azapentalene.

The energy of cubic N_8 is extremely high, and this cluster is the most energetic HEDM ever proposed. Indeed, cubic N_8 is even more energetic than two N_4, as already noted by Trinquier et al. [11]. This suggests that the cube has a rather strained structure, which is not in agreement with the conclusions obtained by Engelke [23]. By using isodesmic reactions, this worker found that cubic N_8 has an almost unstrained structure (41.3 and 4.8 kcal mol^{-1} at the SCF and MP2 levels respectively). However, the strain energies computed by Gimarc and Zhao [15] using homodesmotic reactions are much larger: 224.4 and 219.4 kcal mol^{-1} for cubic N_8 and 150.0 and 112.1 kcal mol^{-1} for two tetrahedral N_4. These results indicate that some caution must be used when dealing with the strain energy, a quantity that does not have a unique definition.

Strain energies can also be related to the total energy of different nitrogen clusters, once the energies are normalized to the same number of atoms. Let us consider tetrahedral N_4, cubic N_8 and dodecahedral N_{20}. The angle of a dodecahedron is 108.0°, very close to the value of 109.5° of "ideal" sp^3-hybridized nitrogen. Therefore N_{20} should have a relatively unstrained structure. From Ref. [12], we see that 8/20 the energy of N_{20} is 413/370 kcal mol^{-1} higher than the energy of four N_2. By comparing these values with the corresponding N_8 energies computed with the same basis set (490/450 kcal mol^{-1}), we obtain for N_8 a strain energy of about 77/80 kcal mol^{-1}, intermediate between the results of Refs. [23] and [15]. From Ref. [24], it can be seen that N_4 systems are only 425/343 kcal mol^{-1} higher than four N_2. This confirms that tetrahedral N_4 has a smaller strain energy than cubic N_8. Since the angle of a tetrahedron (60°) is much smaller than the ideal sp^3 angle, this is a rather surprising result.

The bond lengths predicted for the three clusters are in agreement with the energy results. The shortest bonds are found in N_4, with 1.398 and 1.484 bohr at the SCF and MP2 levels respectively, while the longest bonds are in N_8 (1.461 and 1.529 bohr). In N_{20}, we have bonds of intermediate length (1.438 and 1.503 bohr). Therefore longer bond lengths correspond to weaker bonds, as is normally the case for many molecules. These results indicate that the strain of nitrogen clusters seems to show a non-monotonic behaviour as a function of the bond angle distortion, and N_4 is only slightly strained or unstrained. Although the reason for this is unclear, it is tempting to relate it to the very large stabilization of the triple bond in N_2, where formally zero angles between the bonds occur.

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