Azidopentazole is Probably the Lowest-Energy N_8 Species – A Theoretical Study

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Ab initio molecular orbital calculations at the quadratic configuration interaction [QCISD(T)/6-31G(d)] and coupled-cluster theory [CCSD(T)/DZP] levels based on MP2/6-31G(d) optimized geometries show that azidopentazole is likely to be the global minimum of the N_8 isomers lying 13 and 18 kcal/mol below the acyclic diazidyldiimide and the cyclic pentalene analogue, respectively. Azidopentazole is characterized by a significant energy barrier to ring closure and is expected to be stable with respect to cycloreversion and thus constitutes the most realistic N_8 target for a synthetic preparation.

There has been considerable interest in the polynitrogen compounds (N_n with $n > 4$), in part owing to their intriguing molecular structures. Due to their low thermodynamic stabilities, chemical information on these species came, up to now, exclusively from theoretical calculations. Recently, polynitrogen compounds also attracted attention as potential candidates for efficient, safe, and environment-friendly high-energy density materials (HEDM)[1]. Owing to their high energy content, a large amount of energy could indeed be released upon their complete combustion.

Each of the N_n systems exhibits a large number of isomers, and the identity of the lowest-energy isomer has been the subject of some discussions in the past few years. As far as the simplest systems are concerned (n = 4, 5, and 6), the main results obtained from recent theoretical studies can be summarized as follows:

(i) The lowest-energy N_4 molecule has a planar acyclic form (C_{2h}) and a triplet ground state which lies ca. 20 kcal/mol below the singlet cyclic tetrahedrane (T_d) and tetrazete (D_{2h}) isomers[2].

(ii) While no study of the N_5 radicals is presently available, the potential energy surface of the N_5^- anion was examined in detail[3,4]. Accordingly, the cyclic pentazole anion lies ca. 30 kcal/mol above the N_3^- + N_2 fragments but is separated from the latter by an energy barrier to cycloreversion of ca. 20 kcal/mol. Comparison of the interacting behavior of the five-membered rings in the $(N_5)M(CO)_3$ and $(C_6H_5)M(CO)_3$ complexes with M = Cr, Mn^+ and Fe^{2+} also suggested that the pentazole complexes should be relatively stable[4].

(iii) The N_6 system has been the subject of several investigations[5–8]. While hexaazabenzene (D_{6h}) does not correspond at all to an equilibrium structure, the twisted acyclic form (C_2) of two azidyl groups, having a singlet ground state, turned out to be the lowest lying isomer. The most stable cyclic isomer lies ca. 25 kcal/mol above the diazide. Recently, the N_6^- radical anion was generated and detected by time-resolved infrared nanosecond laser-flash photolysis techniques[9]. The N_6^- anion is thus characterized by a visible absorption centered at 700 nm and an IR band at 1842 cm^{-1}. MO calculations further revealed that this anion radical resembles a complex between two azidyl units with rather long intermolecular distance. This result provides a strong support for the higher stability of the neutral diazide. Apparently, there is, in both N_4 and N_6 systems, a clear preference for acyclic isomers.

Regarding the N_8 system, the first SCF calculations on its cubane form **1** were reported in 1981[10], obviously by applying a simple structural analogy with the isoelectronic hydrocarbon C_8H_8. The two following papers by Engelke and Stine (ES) in 1990[11] and Lauderdale, Stanton and Bartlett (LSB) in 1992[12] again considered only the cubic form but using higher levels of theory. More recently, Leininger, Sherrill and Schaefer (LSS) reported in 1995[13] calculations on the boat **2** and pentalene **3** forms and showed that **2** and **3** are far more stable than **1**. Of these isomers, **3** is the more stable one lying ca. 198 and 35 kcal/mol below **1** and **2**, respectively [values from CCSD(T)/DZP calculations without ZPE corrections[13]]. The bicyclic pentalene form **3** is indeed interesting with respect to the aromaticity in polynitrogen compounds. Nevertheless, the fact that only cyclic structures have been considered is so far surprising, given the higher stability of acyclic N_4 and N_6 species mentioned above. Owing to its low energy content, the azidyl group ($-N=N=N$) is expected to play the role of a basic structural unit in polynitrogen systems. Therefore the purpose of the present note is to point out that N_8 structures featuring azidyl group(s) have a lower energy content than the cyclic ones reported in previous papers.

In principle, two azidyl groups may be formed within a N_8 framework by attaching them to a N_2 unit which can have either a diimide or an aminonitrene form, the latter being known to be less than the former. Thus, a completely acyclic N_8 species is simply a diazidyldiimide (**4**) (or azidopentazene) which also exists in other *Z* or *cis* conformations. It is also known that, within the five-nitrogen atom framework, the open pentazene ($N=N-N=N=N$) is much less stable than its cyclic pentazole counterpart[14]. The pentazene → pentazole conversion is acutally a 1,5-electrocyclization whose mechanism is similar to that of the azidoimine → tetrazole and vinylazide → triazole isomerisations[15,16]. In this class of compounds, a five-membered ring has a certain aromatic character and is consistently more favorable than its corresponding azide. Hence, azidopentazole **5** is another half-open half-cyclic N_8 isomer which is formally connected with **3** by a ring closure and

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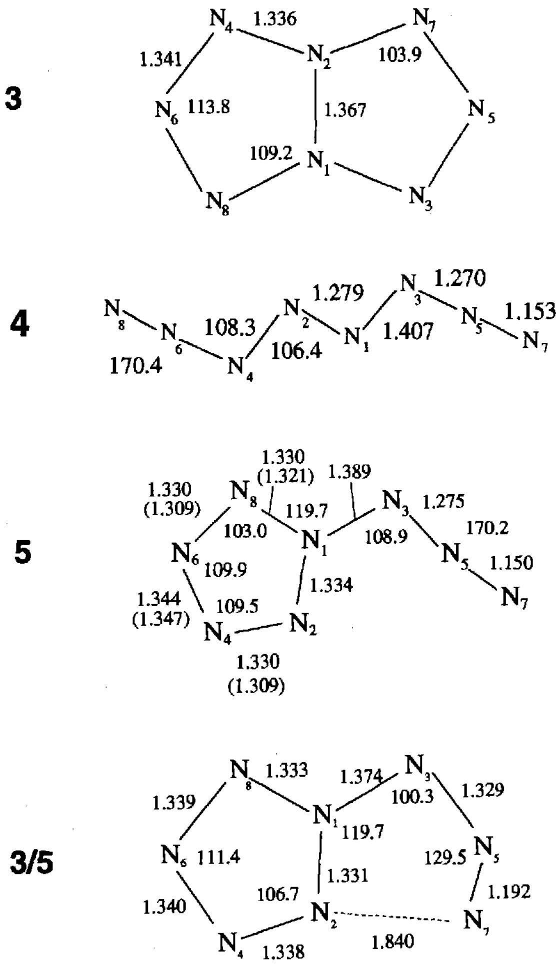
with **4** by a ring opening followed by a rotation. Preliminary calculations indicated that the aminonitrene form does not exist as discret local minimum.

Ab initio molecular orbital calculations were performed to determine the relative stabilities of **3**, **4**, and **5** as well as the transition structure connecting **3** and **5** (designated by **3/5**). Their geometrical parameters were optimized by using both HF and MP2 calculations in conjunction with the 6-31G(d) basis set[17]. Characterization by vibrational analyses was only carried out at the HF level. Figure 1 displays MP2/6-31G(d) parameters of the four structures considered. **4** and **5** are not planar at the HF level with a small distortion of the azidyl group. The MP2/6-31G(d) geometry of **3** is similar to the MP2/DZP one reported by LSS[13] where higher-level calculations are also available. The geometry of the pentazole ring in **5** is not significantly different from that of hydrogenpentazole[18]. With respect to **5**, the main nuclear motion in the TS **3/5** for ring closure corresponds to an azidyl bending leading to the formation of the novel bond (Figure 1).

Figure 1. MP2/6-31G(d,p) geometries of four N_8 structures considered; **3** has D_{2h} symmetry and the other structures have C_s symmetry. Bond lengths are given in Å and bond angles in degrees. Given in parentheses in **5** are the crystal structure values of a phenylpentazole derivative taken from ref.[20]



The calculated total and relative energies of N_8 structures are listed in Table 1. Single-point electronic energies were computed by making use of MP2/6-31G(d)-optimized geometries at both levels of quadratic configuration interaction, QCISD(T) with the 6-31G(d) basis set, and coupled-cluster theory CCSD(T) with the DZP basis set. Relative energies between N_8 structures derived from these calculations are rather similar. Thus, *azidopentazole* (**5**) *is consistently more stable than two other isomers.* Of the latter, **4** turned out to be slightly lower in energy than **3**. Our best estimate places **5** ca. 13 and 18 kcal/mol below the diimide **4** and all-nitrogen pentalene **3**, respectively. The TS **3/5** lies ca. 11 kcal/mol above **3** and 28 kcal/mol above **5** (Table 1). Thus, the pentalene form **3** is not particularly stable with respect to ring opening.

The higher stability of **5** can be accounted for by the existence of a five-membered ring within its skeleton. As a matter of fact, pentazoles are known compounds; the first synthesis of phenylpentazole derivatives by Huisgen and Ugi dates back to the fifties[19], and their crystal structures were also determined[20]. Recently, kinetics and mechanism of degradation of arylpentazoles has been reported[21]. For the purpose of comparison, some experimentally determined bond lengths of the pentazole ring are also given in Figure 1. Using the same level of theory mentioned above, we calculated the cyclic hydrogenpentazole (HN_5) to be 29 kcal/mol more stable than its open pentazene isomer. In this regard, the azidyl substituent actually destabilizes the pentazole ring **5** relative to the acyclic isomer **4**. Formation of a second ring in **3** seems to force both bridge-head atoms to adopt a certain pentavalent character, and this might disfavor the bicyclic form. It has also been demonstrated on the one hand that the aromaticity in nitrogen rings is quite low relative to isoelectronic hydrocarbons and, on the other hand, that the flow of unshared electron pairs into the σ(N−N) bonds results in a destabilization of the conjugated nitrogen ring systems[22]. The azidopentazole form **5** appears to be a compromise taking the advantages of both cyclic and open frameworks. The pentazole ring is also stable with respect to 1,3-dipolar cycloreversion giving an azide and molecular nitrogen[14,18]; therefore, this group is expected to constitute another basic unit of polynitrogen systems. In view of the fact that **5** contains both low-energy N_3 and N_5 units, it is likely to be the lowest-energy N_8 isomer.

Now a question of interest is: how might **5** be prepared? A seemingly reasonable route, but not necessarily easy, is to use the classical procedure for preparing pentazole from diazonium salts and azide anions[19]. The difficult part of this route is presumably the subsequent replacement of X^- by N_3^- at the pentazole ring:

$$X{-}N{=}N^+ + N_3^- \rightarrow X{-}N_5$$

$$X{-}N_5 + N_3^- \rightarrow N_3{-}N_5 + X^-$$

It is also worth noting that when the N_5 unit is used for larger polynitrogen species, bis-pentazole is expected to be a low-energy N_{10} species[18], bis(pentazolyl)diimide a low-energy N_{12} species etc. ... Similarly, pentazolylnitrene **6** is another possible N_6 isomer which was not considered in previous papers. **6** is of interest as it is formally connected with **5** by a N_2 elimination of the azide function: $5 \rightarrow 6 + N_2$. Preliminary calculations indicate that **6** is a low-energy N_6 isomer having a triplet ground state and lying ca. 24 kcal/mol above the diazide.

In summary, the half-open half-cyclic azidopentazole is likely to be the global minimum of the N_8 system lying ca. 13 and 18 kcal/mol below the acyclic diazidodiimide and the cyclic pentalene analogue, respectively, and azidopentazole is expected to be stable with respect to ring closure.

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Table 1. Calculated total (Hartress), zero-point and relative energies (kcal/mol) of the N_8 structures considered

Structure[a]	MP2(F)[b] 6-31G(d)	QCISD 6-31G(d)	QCISD(T) 6-31G(d)	CCSD(T) DZP	ZPE[c]
Total Energies					
4 (N_2)[d]	−437.04628	−437.02520	−437.07496	−437.11460	14.2
N_6 + N_2[e]	−436.75355	−436.71565	−436.77814	−436.80915	18.7
3	−436.67258	−436.61985	−436.69027	−436.71708	24.8
4	−436.66419	−436.62495	−436.69135	−436.71889	21.3
5	−436.69488	−436.64924	−436.71580	−436.74301	23.4
3/5 TS	−436.63860	−436.59899	−436.66994	−436.69750	23.2
Relative Energies[f]					
4 (N_2)	0.0	0.0	0.0	0.0	
N_6 + N_2	188.2	198.7	190.8	196.2	
3	245.1	265.0	252.0	260.0	
4	246.9	258.3	247.8	255.4	
5	229.7	245.1	234.6	242.4	
3/5 TS	264.8	276.4	263.2	270.7	

[a] Based on MP2/6-31G(d,p) geometries; core orbitals are frozen unless noted otherwise. – [b] Using full sets of MOs. – [c] Zero-point vibrational energies from HF/6-31G(d) calculations and scaled by 0.9. – [d] Four separated N_2 molecules. – [e] N_6 has the diazide structure. – [f] At the indicated level plus ZPE corrections.

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