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Contemplation on some cyclic N_8 isomers-A DFT treatment

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ABSTRACT

Various cyclic N_8 isomers are considered at the levels of B3LYP/6–311++G(d,p) and B3LYP/cPVTZ. Some energies and molecular orbital properties are obtained. The structures are found to be stable in the singlet state but mostly unstable in the triplet. The heats of formation values calculated by means of T1 recipe reveals that they are highly endothermic. NICS(0) values have been calculated and aromaticity/antiaromaticity of the rings are discussed. Additionally, theoretical IR,UV-VIS spectra and the calculated impulse values have been obtained.

1. Introduction

One of the most abundant elements in nature is nitrogen. It forms the highly stable N_2 molecule in its elemental state. However, in contrast to this form of it, polynitrogen compounds (PNC), comprising only nitrogen atoms are rare, and no molecular crystal made of these compounds has been prepared yet [1].

Various allotropic modifications of nitrogen, namely, compounds consisting only of nitrogen atoms (of the form N_2, N_3, N_4, etc.), are classified as polynitrogen compounds. They are considered as promising candidates of clean(green) high energy density materials (HEDM) because they produce N_2 gas only and have high energy content [2–5].

In order to seek novel high energy density compounds (HEDCs) having no air pollution, attempts of scientists have been focused on the concept of polynitrogen compounds, which attract significant interest for propulsion or explosive applications. Through the years, potential candidates of polynitrogen compounds have been predicted by the theoreticians since the early 1990s and lots of systematic and great efforts have been undertaken in order to synthesize any of them [6–16].

It is believed that use of polynitrogen compounds will allow solid rocket propellants to compete in terms of energetic efficiency with liquid propellants [2,17]. According to theoretical calculations and (still scarce) experimental data, the polynitrogen compounds are characterized by high enthalpy of formation (2–5 kcal/g) and sufficiently high density in the condensed phase (2–4 g/cm^3) [17]. It has been theoretically estimated that the use of polynitrogen compounds can provide a specific impulse of 350–500 s with material density in a range of 2.0–3.9 g/cm^3 [2].

In general polynitrogen molecules are expected to release large amounts of energy when they decompose into the very stable N_2 molecules. Due to that fact, these structures are potentially promising molecules as high-energy-density materials (HEDM) [18–20]. In recent years, pure polynitrogen molecules have been particularly attractive, among the different energetic nitrogen compounds (such as nitrates, ammonia, nitramines, azides, polyazides and so on), not only because of both the expected high energy density but also N_2 is the sole product of their decomposition, which is inert, non-toxic and not a greenhouse gas [1].

So far, the quest for HEDMs based on nitrogen atoms has produced several theoretical articles. Only one solid-state material containing a N_5^+ cation and a gas phase $N_5{}^-$ anion were reported experimentally in addition to the well-known N_3^- anion and N_3 radical. Other species, such as N_4, were only observed as short-lived transients. Several topical reviews have portrayed the difficulty in preparing all nitrogen compounds [21–24]. Christe and coworkers recently reported two breakthroughs in the field: the synthesis of the N_5^+ cation in a salt [7] and of the cyclo-N_5^- anion in the gas phase [25]. According to theoretical calculations, the cation is V-shaped whereas the anion is cyclic [23].

Hirshberg et al., made use of PW-DFT with the PBE-D [26,27] functional to investigate the relative thermodynamic stability, the

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enthalpies of the N_8 solid and cg-N form (cubic gauche) at pressures up to 50 GPa [1]. Their work reveals the possibility of existence of such a molecular solids, consisting of N_8 molecules although it is metastable even at ambient pressure. Their calculations predict a conceptually interesting new material on condition that, if it could be prepared, as HEDM it may find some applications.

In the present study, various cyclic N_8 structures have been considered within the constraints of density functional theory.

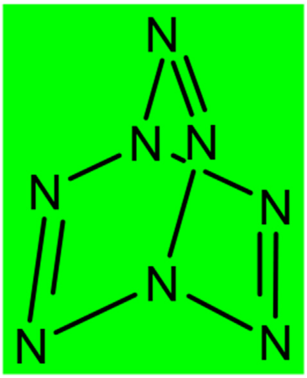
2. Method of calculation

Geometry optimizations of all the structures leading to energy minima were initially achieved by using MM2 method followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [28,29] at the restricted level [30,31]. Subsequent optimizations were achieved at Hartree-Fock level using various basis sets. Then, geometry optimizations were managed within the framework of density functional theory (DFT, B3LYP) [32,33] finally at the level of 6−311++G(d,p) (restricted closed-shell) [30]. Additionally, UB3LYP/6−311++G(d,p) and B3LYP/CC-PVTZ level of calculations were performed for energies. The exchange term of B3LYP consists of hybrid Hartree−Fock and local spin density (LSD) exchange functions with Becke's gradient correlation to LSD exchange [33,34]. Note that the correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [35] and Lee, Yang, Parr (LYP) correlation correction functional [36]. The vibrational analyses were also done. The total electronic energies are corrected for the zero point vibrational energy (ZPE). The normal mode analysis for each structure yielded no imaginary frequencies for the $3N-6$ vibrational degrees of freedom, where N is the number of atoms in the system. This indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. All these calculations were done by using the Spartan 06 package program [37]. The NICS(0) values were calculated (B3LYP/6−311++G(d,p)) by the use of Gaussian 03 package program [38].

3. Results and discussion

Cyclic only-nitrogen structures are interesting not only because of their extra ring-strain energy as compared to their acyclic counterparts but also due to some other properties. Note that in the present treatment yet-non-existing structures considered are called isomers rather than allotropes.

Fig. 1 shows the optimized structures of N_8 isomers (singlet states) obtained at the level of B3LYP/6−311++G(d,p) calculations. In the present treatise six (see Fig. 1) N_8 isomers are considered. Bicyclic N_8 structure shown below was found to be unstable in the singlet and triplet states. Therefore, it has not been considered furthermore.



3.1. Some properties and energies

Table 1 shows some properties of the isomers. Except **1** and **3** all the others have zero dipole moment. Note that **2** is the *trans* form (of 4-membered rings) of **3** and it does not have any dipole moment but **1** (has a 4-membered ring) and **3** have. So the 4-membered ring(s) contributes into the total asymmetry to develop dipole moment via individual bond dipoles. In the *trans* structure-**2**, the direction of dipole moment indicates that two of the 4-membered rings are non-identical in terms of electron population.

The structures included in Table 1 all have either low or zero dipole moments. Fig. 1 also displays the direction of the dipole moments.

Tables 2–4 show the total electronic energies, zero point vibrational energies (ZPE) and the corrected total electronic energies. The B3LYP/6−311++G(d,p) and B3LYP/cc-PVTZ level of calculations yield the stability order of **4** > **6**>**5** > **1**>**2** > **3** where the values of 4 and 6 are the same. The UB3LYP/6−311++G(d,p) level of calculations exhibit the stability order of **4** > **6**>**5** > **1** = **2** > **3**. In the case of B3LYP/ccPVTZ level of calculations, the stability order mimics the order of B3LYP/6−311++G(d,p) level of calculations. Note that in every case the energies of **4** and **6** are very close to each other. The reason for it will be given in the sections below.

The stability orders indicate that it is adversely affected by the number(s) of 4 m-membered rings. Although, structure-**4** is a 4 m-membered ring (m = 2) it is the most stable one among the group. Note that it does not have any dipole moment. Structures-**5** and **6** do not have any 4-memebered rings. The direction of dipole moment in **1** indicates that the 4-membered ring is somewhat deprived of electrons in the favor of the 6-membered ring. At first sight, a question arises whether some aromatic character having 6π-electrons (see the following NICS section) associates with the hexagonal ring system and the 4-membered ring having a localized (N=N) double bond which is distant from the fusion site of the rings exists.

Fig. 2 shows the optimized triplet state of N_8 isomers considered. As seen in the figure some bonds are highly elongated indicating some fragmentation. Table 5 displays the various energies of the structures in the triplet state. Note that for the decomposed structures, the energies in the table stand for the composite (fragmented) systems. Although system 1 has the lowest energy, actually it is the decomposed one. Structure 1 and 5 seem to be splitted into N_2 fragments. Structures-**2** and -**3** have partially broken skeletons (see Fig. 2). Whereas structures 4 and 6 keep their integrity having reasonable bond lengths. They show high mutual similarity in the singlet and triplet state geometry and energy.

The triplet state stability order is **1** > **5**>**6** > **4**>**2** > **3**. Otherwise mentioned below the structures considered are all in their singlet states.

3.2. Heats of formation

The heats of formation (ΔH_f^0) values for the N_8 species (singlet state) considered are obtained by using T1 method [39,40]. The T1 method is a little bit less accurate than the expensive G3(MP2) method. For the comparison purpose, T1 and G3(MP2) results obtained for structure 1 and presently they have been found to be 303.94 kcal/mol and 304.67 kcal/mol, respectively (−0.09% deviation). Table 6 shows the heats of formation values for the N_8 species (singlet state). The order of endothermicity is **3** > **2**>**1** > **5**>**4** > **6**. So structures-4 and 6 are distinguished as electronically the most stable and least endothermic ones in the group.

Structure-**3** which possesses the *cis* configuration of 4-

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