



A Quire Polycyclic Structure of N_8 - A DFT Treatise

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Abstract

The present study considers a quire polycyclic structure of N_8 and biradicals constructed from it which keep molecular integrity within the limitations of density functional theory at the levels of UB3LYP/6-311++G(2df,2p) and UB3LYP/cc-PVTZ. Certain structural, energetic, quantum chemical and spectral data have been obtained for them and discussed. The both methods of calculations generally produce parallel results.

1. Introduction

One of the most abundant elements in nature is nitrogen. Its highly stable form is N_2 molecule. Whereas, polynitrogen compounds (PNC) having only nitrogen atoms are rare. 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. It has to be noted that no molecular crystal made of these compounds has been prepared yet [1]. Polynitrogen compounds are actually, various allotropic modifications of nitrogen such as N_2 , N_3 , N_4 , etc. Pioneering polynitrogen studies considered the stability and aromaticity of nitrogen rings. N_3^+ , N_4 , and N_6 [2]. The last couple of decades have witnessed numerous computational studies piled up in the literature about some small sized polynitrogen structures, their radicals and ions [3-6]. Actually, polynitrogen structures have high energy content and obviously, produce only N_2 gas [7-10]. Therefore, they are considered as promising candidates of clean (green) high energy

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density materials (HEDM). The decomposition of highly energetic forms of polynitrogen to nitrogen gas should release higher energy than that of most of the propellants or explosives used already. Some forms of nitrogen have been identified as being vibrationally stable and thermodynamically metastable. It is believed that use of polynitrogen compounds will allow solid rocket propellants to compete in terms of energetic efficiency with liquid propellants [7].

Since polynitrogen compounds have been predicted theoretically as potential candidates of clean high energy density materials [11-24] great efforts have been spent in order to synthesize any of them [5-8, 10, 12-14, 21].

In the present study, a polycyclic polynitrogen structure possessing eight nitrogens has been designed and subjected to density functional treatment.

2. Method of Calculation

In the present study, the initial structural optimizations of all the structures leading to energy minima have been achieved by using MM2 method then, followed by semi empirical PM3 self-consistent fields molecular orbital (SCF MO) method [25, 26] at the restricted level [27, 28]. The subsequent optimizations were achieved at Hartree-Fock level using various basis sets hierarchically. Afterwards, the structural optimizations were managed within the framework of density functional theory (DFT) [29, 30] at the levels of and UB3LYP/6-311++G(2df,2p) and UB3LYP/cc-PVTZ [28, 31]. 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 [30, 32]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [33] and Lee, Yang, Parr (LYP) correlation correction functional [34]. In order to minimize the basis set superposition error (BSSE) rather high level of basis sets have been used. Additionally, the vibrational analyses have been 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 which 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 [35].

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. Figure 1 shows the optimized structures of two octet stable N_8 isomers, A and B. The optimized structures obtained at the UB3LYP/cc-PVTZ level are similar to the ones shown in Figure 1.



Figure 1. Two of closed shell polycyclic isomers of N_8 (UB3LYP/6-311++G(2df,2p)).

In the present study, quire polycyclic structure having trigonal rings is called A (Figure 1) and it is considered as the main structure of interest. Starting from structure-A, a latitudinal bond which is common to both of the 3-membered rings is broken (homolytic cleavage) to engender structure-Ah. The homolytic cleavage of one of the longitudinal bonds results in structure-Av. Since the cleavage applied assumingly produces two unpaired electrons (biradical), singlet and triplet multiplicity states may form which are called Ahs, Aht, Avs and Avt. Figures 2 and 3 show those optimized systems at two different level of calculations. Since, Ahs or Avt has similar shapes at both level of calculations and reasonable bond lengths, they are considered as stable biradicals and the others have not been considered anymore. The cubical structure B was considered previously (using different level of calculations) [24]. However, presently some data of it are harvested and presented just to complete the results and discussion.

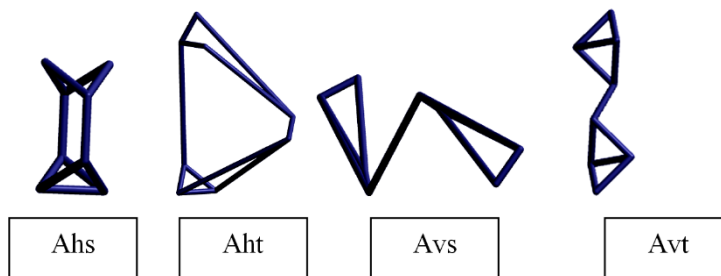


Figure 2. Some biradicals from structure-A (UB3LYP/6-311++G(2df,2p)).

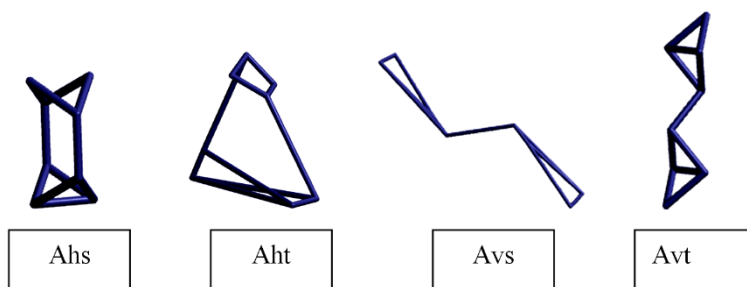


Figure 3. Some biradicals from structure-A (UB3LYP/cc-PVTZ).

Figures 4 and 5 display the IR spectra of the species considered. Notice the high resemblance between A and Ahs, because they have some common ring types.

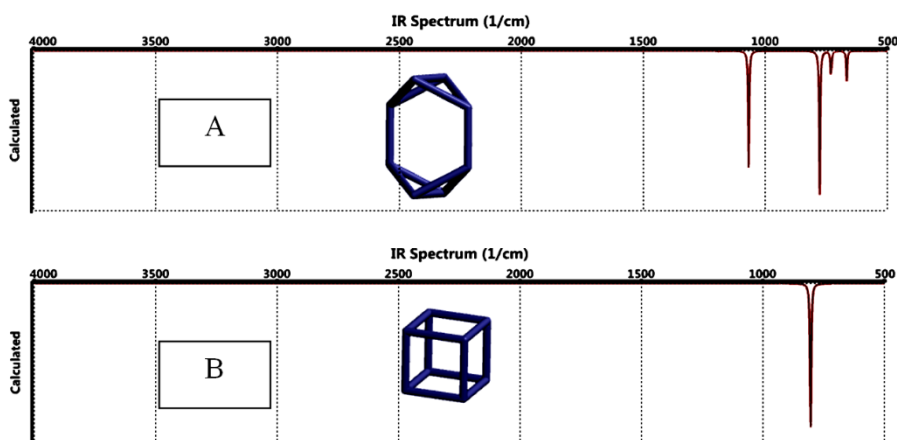


Figure 4. IR spectra of N_8 isomers presently considered (UB3LYP/6-311++G(2df,2p)).

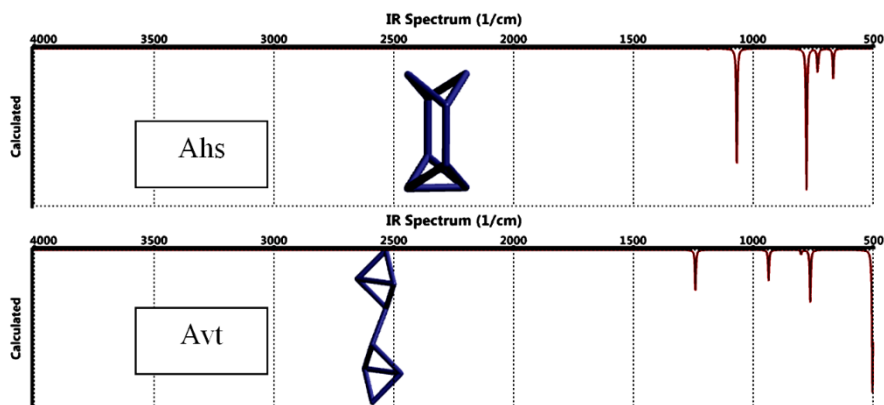


Figure 5. IR spectra of structurally stable N_8 biradicals considered (UB3LYP/6-311++G(2df,2p)).

Table 1 shows the total electronic energy (E), the zero point vibrational energy (ZPE) and the corrected total electronic energy (E_C). The data in the table indicate that within the same level of calculations, the stability order is A=Ahs > Avt > B. Note that structure-A and its biradical derivatives, Ahs and Avt have more-strained 3-membered ring(s) as compared to 4-membered rings contained in B, however they are electronically more stable than B structure. The underlying reason could be the longer longitudinal bonds in A type structures as compared to B.

Table 2 exhibits some calculated properties of the structures considered. Structures A and Ahs are characterized with the same values of the properties of interests. Table 3 shows some thermodynamic properties of the species considered. The data reveal that they are all thermally endothermic and unfavorable structures. According to the data in Table 3, Ahs is slightly more endothermic and less favorable than A. On the other hand, B is comparatively less endothermic and more favorable than A. Structure-Ahs in many respects is very similar to its parent structure A. Figure 6 shows the bond lengths for them.

Table 1. Some energies of the systems considered.

Structure	E	ZPE	E_C
A	-1148994.42	78.86	-1148915.56
A*	-1149021.79	78.46	-1148943.33
Ahs	-1148994.42	78.86	-1148915.56
Ahs*	-1149021.79	78.43	-1148943.36
Avt	-1148919.75	68.39	-1148851.36
Avt*	-1148947.13	68.08	-1148879.05
B	-1148817.52	91.12	-1148726.4
B*	-1148846.77	90.82	-1148755.95

Energies in kJ/mol. UB3LYP/6-311++G(2df,2p), * UB3LYP/cc-PVTZ

Table 2. Some properties of A, B and structurally stable A biradicals.

Structure	Area (Å ²)	Volume (Å ³)	Ovality	Log P	Polarizability
A	94.54	72.26	1.13	1.34	45.93
A*	94.60	72.30	1.13	1.34	45.93
B	89.63	70.25	1.09	1.34	45.87
B*	89.67	70.28	1.09	1.34	45.86
Ahs	94.54	72.26	1.13	1.34	45.93
Ahs*	94.60	72.31	1.13	1.34	45.93
Avt	105.57	76.64	1.21	1.34	-
Avt*	105.59	76.67	1.21	1.34	-

UB3LYP/6-311++G(2df,2p), * UB3LYP/cc-PVTZ

Table 3. Some thermodynamic properties of the species considered.

Structure	H°	G°
A	1965.497	1960.036
A*	1964.843	1959.130
Ahs	1965.505	1960.047
Ahs*	1964.839	1959.107
Avt	1990.878	1966.965
Avt*	1992.893	1968.913
B	1700.311	1714.129
B*	1700.461	1714.116

In kJ/mol. UPM3// UB3LYP/6-311++G(2df,2p), * UPM3// UB3LYP/ cc-PVTZ.

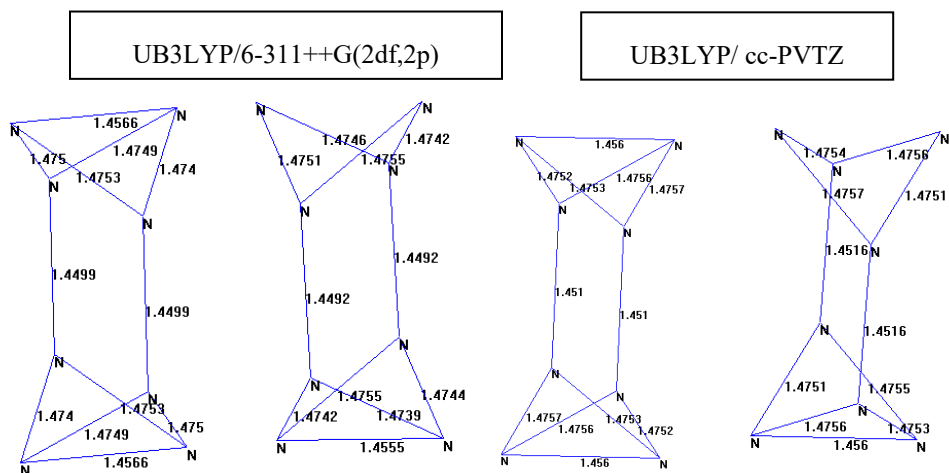


Figure 6. Calculated bond lengths (Å) in A and Ahs systems (UB3LYP/6-311++G(2df,2p)).

Figure 7 stands for the bond densities of structures A and Ahs. As seen in the figure the closed-shell structure A and its supposedly open-shell derivative Ahs have very similar bond density figures.

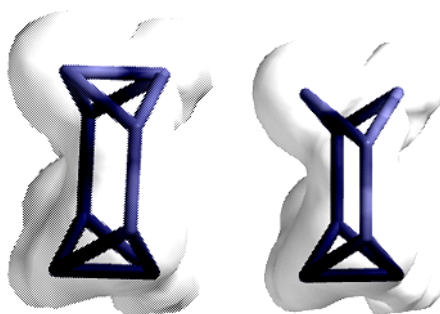


Figure 7. Bond densities of structures A and Ahs (UB3LYP/6-311++G(2df,2p)).

Figure 8 stands for the HOMO and LUMO patterns of structures A and B. Whereas the patterns of open-shell structures are shown in Figure 9. Comparison of the HOMO and LUMO patterns of structures A and Ahs, once again shows the high resemblances between them.

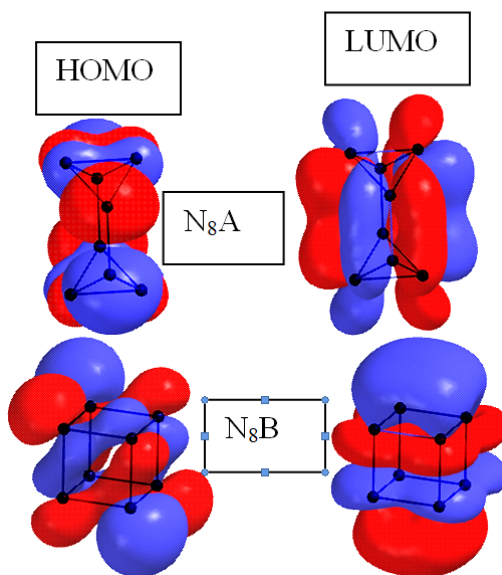


Figure 8. The HOMO and LUMO patterns of structures A and B (UB3LYP/6-311++G(2df,2p)).

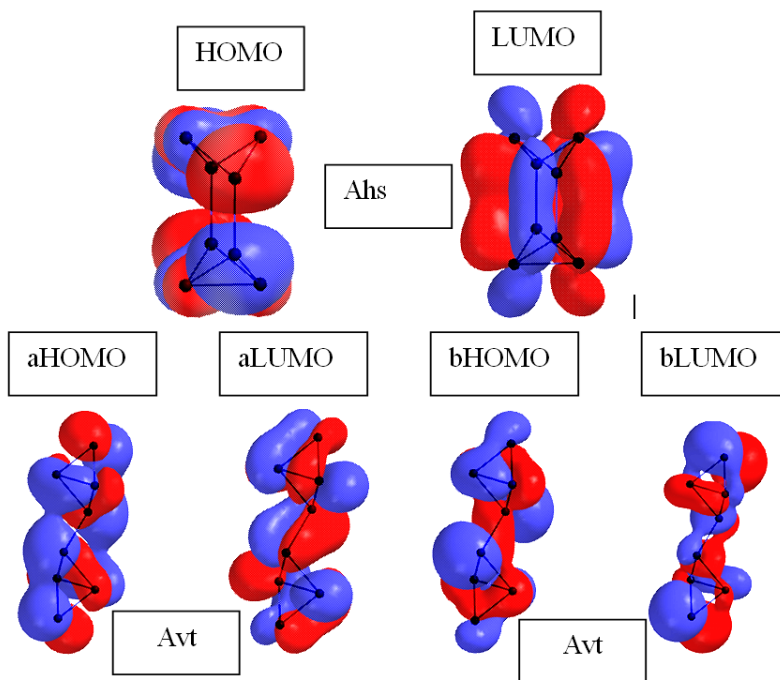


Figure 9. The HOMO and LUMO patterns of structurally stable biradicals of A (UB3LYP/6-311++G(2df,2p)).

In Figure 10 some of the molecular orbital energy levels of N_8 species of present concern are displayed. Note the similarity between A and Ahs cases. Also note that in the case of structure-Avt, α - and β -orbitals arise due to the unrestricted calculations and the triplet state of the system. In the figure, a- and b- stand for α - and β -type orbitals.

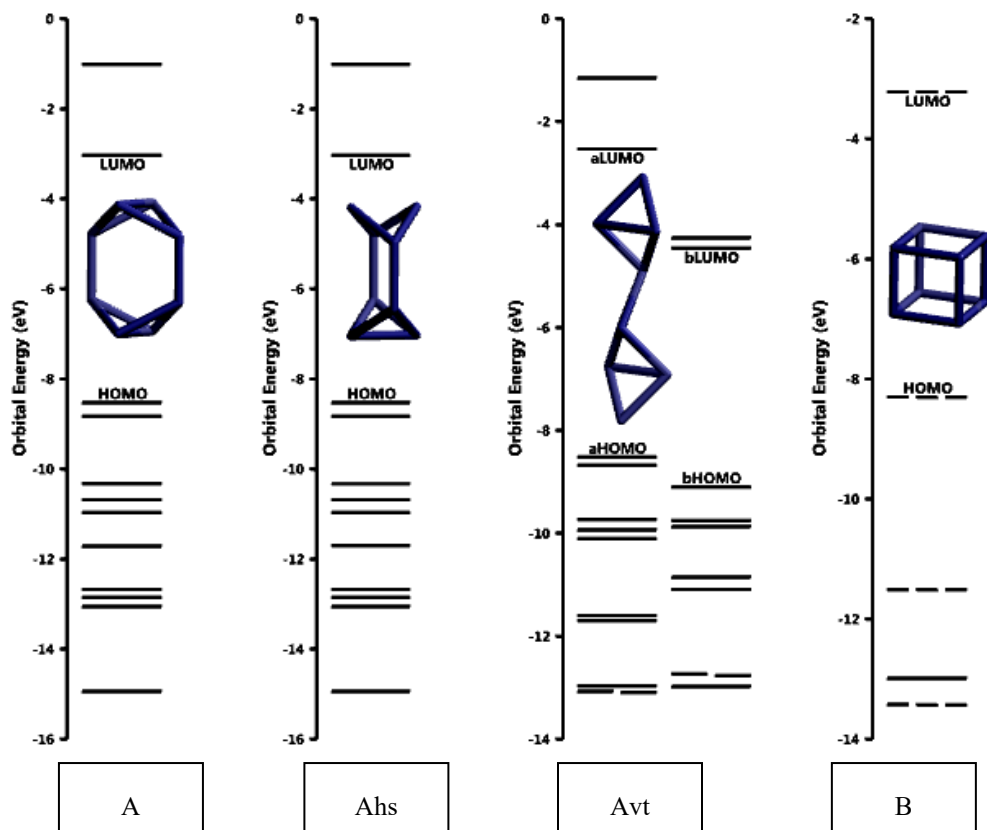


Figure 10. Some of the molecular orbital energy levels of the species considered (UB3LYP/6-311++G(2df,2p)).

Figure 11 shows the calculated UV-VIS spectra of some of the species considered. The appearance of two λ_{\max} values in the case of structure-Avt arises from the triplet nature of it. Whereas the almost the same spectra happen for structures A and Ahs which suggests that still some sort of spin-pairing occurs in the later structure although no bond exists between the nitrogens assumingly having the electrons with opposite spins. The distance between those nitrogens is 1.456 Å (in both methods of calculations) which is equal to the respective bond length in A.

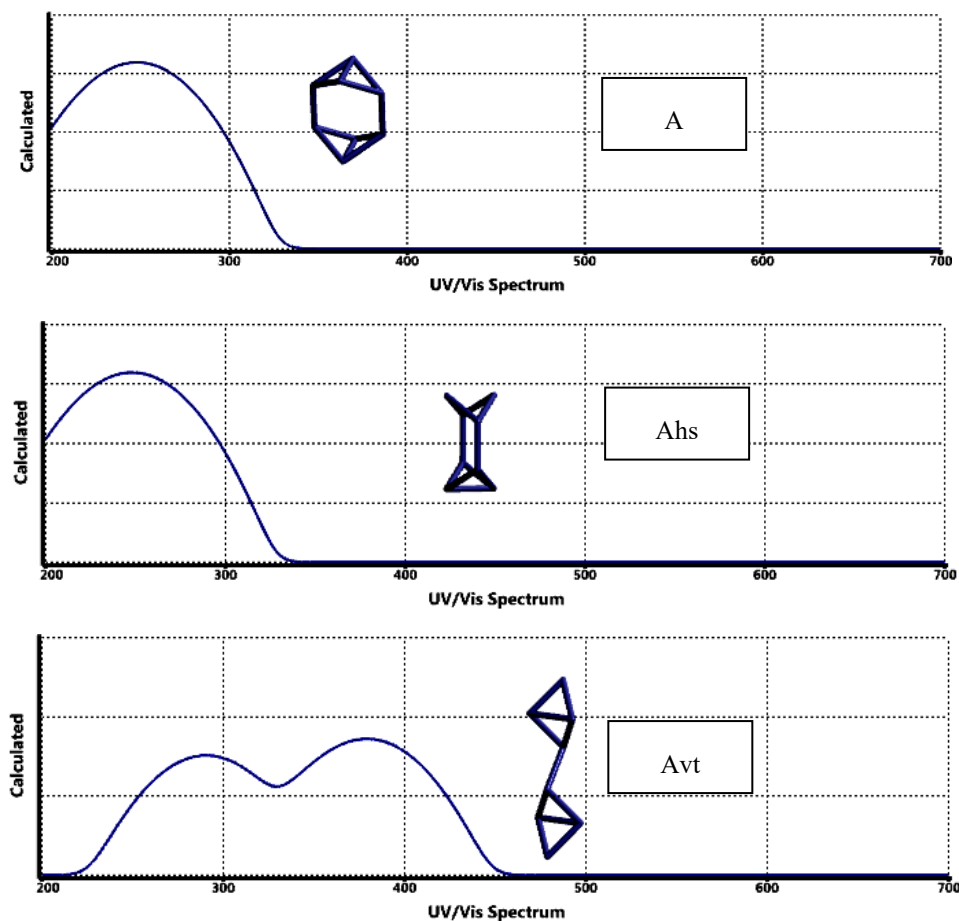


Figure 11. UV-VIS spectra of structures A, Ahs and Avt (UB3LYP/6-311++G(2df,2p)).

Table 10 shows the HOMO, LUMO energies and $\Delta\epsilon$ ($\Delta\epsilon = \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$) values of the systems. The HOMO order is $A < \text{Ahs} < \text{Avt} < B$ (UB3LYP/6-311++G(2df,2p)) whereas $\text{Ahs}^* < A^* < \text{Avt}^* < B^*$ (UB3LYP7cc-PVTZ). As for the LUMO energies, the order is $B < \text{Ahs} < A < \text{Avt}$ and $B^* < A^* < \text{Ahs}^* < \text{Avt}^*$, respectively for UB3LYP/6-311++G(2df,2p) and UB3LYP/cc-PVTZ level of calculations. Accordingly, $\Delta\epsilon$ values fall in to the orders of $\text{Avt} > A > \text{Ahs} > B$ and $\text{Avt}^* > \text{Ahs}^* > A^* > B^*$.

Table 12 shows the homolytic bond dissociation energies for structure-A. The data reveal the cleavage of the longitudinal bond to produce triplet biradical is more energy demanding (somewhat as expected) than the latitudinal one to produce singlet biradical. However, the electrons emerged from bond rupture in Ahs case seem to be still spin-paired due to those nitrogens which are at the bonding distance apart from each other.

Table 10. The HOMO, LUMO energies and $\Delta\varepsilon$ values.

Structure	HOMO	LUMO	$\Delta\varepsilon$
A	-822.34	-292.09	530.25
A*	-812.04	-278.78	533.26
Ahs	-822.27	-292.12	530.15
Ahs*	-812.28	-278.64	533.64
Avt	-821.79	-244.05	577.74
Avt*	-810.86	-228.01	582.85
B	-800.72	-310.61	490.11
B*	-788.21	-291.09	497.12

Energies in kJ/mol. UB3LYP/6-311++G(2df,2p), * UB3LYP/cc-PVTZ

Table 12. Homolytic bond dissociation energies of A leading to structurally stable biradicals considered.

Structure	Energy
Ahs	0.00
Ahs*	-0.03
Avt	64.20
Avt*	64.28

Energies in kJ/mol. UB3LYP/6-311++G(2df,2p), *UB3LYP/ cc-PVTZ.

4. Conclusion

Within the constraints of density functional theory and the basis sets applied, the present study has shown that the yet-non-existed polycyclic polynitrogen structure (A) considered is thermally highly endothermic and disfavored but electronically stable. It is electronically more stable than its cubical isomer (B) which is thermally less endothermic and less disfavored.

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