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Some strong dimers of borazine – A DFT treatment

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Abstract

Borazine is an interesting compound, and considered weakly aromatic. In the present study, weak and strong dimers of borazine are defined and some strong dimers of borazine are considered within the restrictions of density functional theory at the level of B3LYP/cc-PVTZ. All the structures considered are electronically stable, thermodynamically exothermic and have favorable Gibbs' free energy of formation values at the standard states. Various quantum chemical properties of them, including the HOMO and LUMO energies, UV-VIS spectra, etc., have been obtained and discussed. Also the NICS (0) data have been obtained for the simplest strong dimer and some discussion is provided.

1. Introduction

Recent advances in the fundamental understanding of boron chemistry and breakthroughs in the synthesis of its compounds have revealed that boron playing an increasingly important role in applications such as small-molecule activation for fuel synthesis, organic light-emitting diodes (OLEDs), hydrogen production and storage, and electrolyte materials [1].

Impressive recent advances in the synthesis of novel boron-containing molecules and the diverse materials derived there from, combined with a significantly improved understanding of the properties of these boron-based molecules and materials, have been published [1].

Nitrogen enriched boron-based heterocyclic high energy density materials (HEDMs) have received a considerable interest because of their remarkable explosive properties [2].

Borazine have been the focus of great interest in science through the decades. It has attracted the attention of various scientists of different formations. The peculiar character and bonding capability of boron enabled the chemists to synthesize various interesting compounds. Anitoff was one of the first who studied the routes to the synthesis of nitrated boron-nitrogen compounds without any successes [3]. In recent decades, various article on boron compounds or borazine piled up in the literature [4-12].

Presently, weak and strong dimers of borazine are defined and some strong dimers of it have been treated in the realm of density functional theory to investigate the various quantum chemical properties.

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 followed by semi-empirical PM3 self-consistent fields molecular orbital

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(SCF MO) method [13,14] at the restricted level [15,16]. Subsequent optimizations were achieved at Hartree-Fock level using various basis sets. Then, the structural optimizations were managed within the framework of density functional theory (DFT) [17,18] at the level of B3LYP/cc-PVTZ [19,20]. 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 [18,21]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [22] and Lee, Yang, Parr (LYP) correlation correction functional [23]. Also, the vibrational analyses have been done and 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 [24]. Whereas the nucleus-independent chemical shift, NICS(0), calculations have been performed by using Gaussian 03 program [25].

3. Results and Discussion

The dimers considered in the present study are derived from certain cyclophanes [26,27]. By means of centric boron and nitrogen perturbations alternatingly or certain intermolecular perturbations [28,29]. Using two borazine skeletons accordingly, the nitrogen atoms occupy positions 1,3 and 5 whereas borons at 2,4 and 6, so that only B-N bonds (bridges) form between the two borazine rings (or decks). The dimer possessing a single B-N bond between the borazine rings is called weak dimer and as the number of bridges increases it is called a strong dimer. Note that very many strong dimers having different topologies are possible.

Figure 1 shows two canonical structures of borazine.

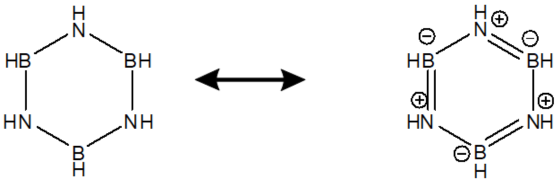


Figure 1. Two canonical structures of borazine.

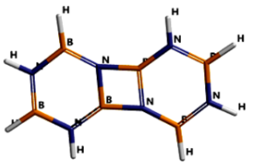
Table 1 shows some structural information necessary for the dimers of consideration. The codes originate from positional numbers starting with any nitrogen atom, in upper deck. The dimers, except dimer-1 are nonplanar structures (see Figure 2). As the number of bridges increases borazine dimers turn into cyclophane like structures having upper and lower borazine decks.

Figure 2 shows the optimized structures of some strong dimers of borazine. It also shows the codes (in arabic numbers) of each associated structure number (Roman number), its bruto formula and numbers of certain types of rings present. They all have the same boron and nitrogen content (B_6N_6), only hydrogen numbers decrease progressively by two, as each B-N bridge between the decks forms. Whenever the bridges originate from adjacent atoms, 4-membered ring(s) emerge between two hexagonal decks (borazine moieties). The B_2N_2 rings are 4-membered and some of them contain a boron-nitrogen double bond (B=N, such as dimers I, IV) but some possess only a single B-N bond (such as V). If there exist more than one B_2N_2 rings then some of them contain single and some double boron-nitrogen bonds. During the structure optimization, not only the bond lengths and angles are affected but also the π-topology arranged to increase the overall stability so that the number of longitudinal bonds between the hexagonal decks namely in B_2N_2 ring(s) is/are varied.

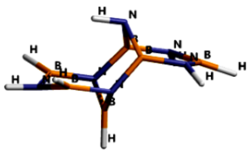
Table 1. Some structural information about the dimers considered.

Structure No	Code	Bruto formula	Number of bridges	Number of rings	Number of B_2N_2 rings
I	12	$B_6N_6H_8$	2	3	1
II	13	$B_6N_6H_8$	2	3	0
III	14	$B_6N_6H_8$	2	3	0
IV	123	$B_6N_6H_6$	3	4	2
V	124	$B_6N_6H_6$	3	4	0
VI	135	$B_6N_6H_6$	3	4	0
VII	1234	$B_6N_6H_4$	4	5	3
VIII	1235	$B_6N_6H_4$	4	5	2
IX	1245	$B_6N_6H_4$	4	5	2
X	12345	$B_6N_6H_2$	5	6	4
XI	123456	B_6N_6	6	7	6

$B_6N_6H_8$



12, I



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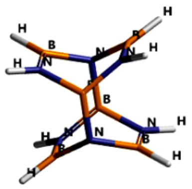
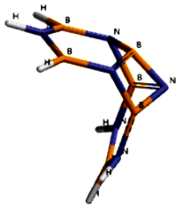
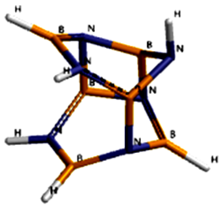


14, III

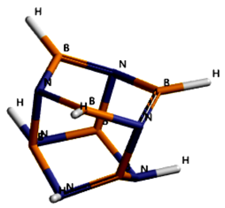
$B_6N_6H_6$



123, IV

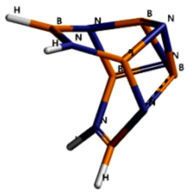


124, V

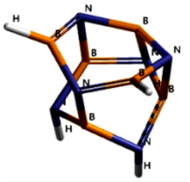


135, VI

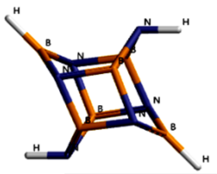
$B_6N_6H_4$



1234, VII



1235, VIII



1245, IX

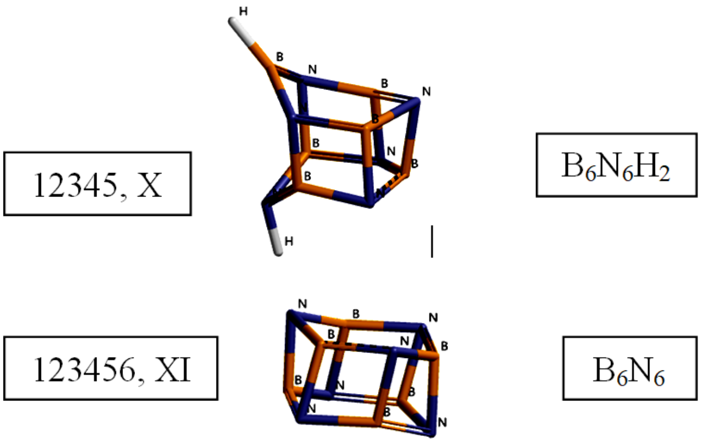


Figure 2. Optimized structures of some strong dimers of borazine.

Structures I-III are the strong dimers of $B_6N_6H_8$ type. Others strong dimers are $B_6N_6H_6$, $B_6N_6H_4$ etc., namely the number of hydrogens progressively decrease as the number of bridges increases. Note that I-III have only two bridges between the hexagonal decks.

Table 3 lists some of the standard thermo chemical formation data of the dimers considered. The data reveal that the standard heat of formation (H^o) values of all the dimers are exothermic and they are favored according to their G^o values. The dimers can be grouped according to the number of bridges they possess, thus I-III, IV-VI, VII-IX, X and XI. The general trend among the groups is that both H^o and G^o values become less negative as the bridge number increases. However, within each group there is no regularity.

Table 3. Some thermo chemical properties of the dimers considered.

Structure No	H^o	S^o (J/mol°)	G^o
I	-1268085.465	385.88	-1268200.518
II	-1267641.851	380.55	-1267755.313
III	-1267710.771	386.93	-1267826.134
IV	-1264608.446	368.17	-1264718.221
V	-1264453.028	366.31	-1264562.245
VI	-1264205.848	362.01	-1264313.784
VII	-1261264.801	353.16	-1261370.096
VIII	-1261105.934	349.84	-1261210.241
IX	-1261143.878	350.21	-1261248.296
X	-1257925.640	334.44	-1258025.355
XI	-1254650.624	320.80	-1254746.272

Energies in kJ/mol.

Table 4 shows some energies of the dimers considered where E, ZPE and E_C stand for the total electronic energy, zero point vibrational energy and the corrected total electronic energy, respectively. According to the data, they are all electronically stable structures. The stability decreases as the number of bridges increases but keeping the number be the same (within each group) no regularity exists.

Table 4. Some energies of the dimers considered.

Structure No	E	ZPE	E_C
I	-1268482.82	382.94	-1268099.88
II	-1268030.35	373.97	-1267656.38
III	-1268096.41	369.64	-1267726.77
IV	-1264943.19	322.44	-1264620.75
V	-1264783.90	318.45	-1264465.45
VI	-1264531.62	313.78	-1264217.84
VII	-1261539.66	264.59	-1261275.07
VIII	-1261377.84	262.10	-1261115.74
IX	-1261415.89	262.16	-1261153.73
X	-1258142.63	209.61	-1257933.02
XI	-1254810.60	154.68	-1254655.92

Energies in kJ/mol.

Table 5 lists some calculated properties of the dimers considered. The polarizability is defined according to a multivariable formula [24] which is the functions of van der Waals volume and hardness, respectively. The later one is dictated by energies of the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals [24]. Consequently, the polarizability order among the groups (mentioned before) is such that it decreases as the number of bridges increase. The same trend is also effective on the other properties and the area, volume and ovality values progressively decrease from one group to other depending on the increase of the number of bridges.

The polar surface area (PSA) is defined as the amount of molecular surface area arising from polar atoms (N,O) together with their attached hydrogen atoms. Thus, the PSA values differ from each other even though the same kind of atoms might be considered due to the fact that they might be influenced by electronic factors differently at different positions.

Table 5. Some properties of the dimers considered.

No	Molecular Wt.(amu)	Area (Å^2)	Volume (Å^3)	PSA (Å^2)	Ovality	Polarizability	Cv (J/mol^o)
I	156.972	191.25	172.71	42.706	1.28	53.88	134.56
II	156.972	173.97	165.09	49.583	1.20	53.57	138.62
III	156.972	172.05	163.91	49.481	1.19	53.17	142.74
IV	154.956	171.22	159.88	44.453	1.20	52.88	127.65
V	154.956	160.78	154.78	46.808	1.15	52.79	129.64
VI	154.956	152.60	150.46	46.019	1.12	52.49	130.70
VII	152.940	154.58	148.40	41.851	1.14	52.04	119.47
VIII	152.940	149.28	145.29	44.166	1.12	52.13	118.96
IX	152.940	149.12	145.35	43.549	1.12	52.15	118.97
X	150.924	141.35	137.95	39.773	1.09	51.35	108.22
XI	148.908	132.60	130.23	35.895	1.07	50.61	97.95

All belongs to C1 point group.

Dimer-1 (I) is an interesting system having a 4-membered as well as two 6-membered rings fused with each other. According to the classical treatment a 4π-system having cyclic conjugation is an antiaromatic whereas 6π-cyclic conjugation results an aromatic system thus decreasing and increasing the stability of the overall structure, respectively at different extents. Other strong dimers also have more than one 4-membered rings but they are not coplanar with the 6-membered rings. As seen in Figures 2 and 3 there exist some essential single and double bonds [28,29].

Figure 3 shows the atom and ring labels of dimer-1. Considering the bonds of 4-membered ring in dimer-1, they might be single or double to have different extended π-topologies or as shown in the figure one might be single and the other double. Then, each of ring-A and ring-B might be 6π or 4π-cyclic conjugated systems. On the other hand, the whole system can gain the most extended form having 10π-cyclic conjugated system spread over rings-A to C, being B_2-N_5 bond to be essentially olefinic, but 10π-system is predicted to be an aromatic one by the Hückel rule (Note that 12π-system is antiaromatic). The local aromaticities of the rings by employing NICS calculations might give some idea.

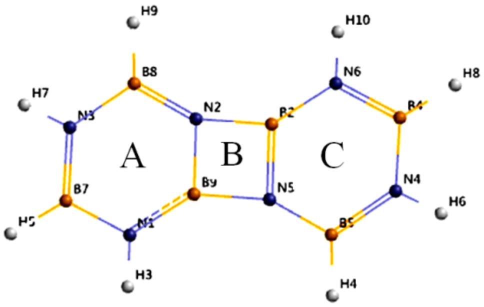


Figure 3. Atom and ring labels of dimer-1.

Table 6 lists the nucleus-independent chemical shift (NICS) values of the rings of dimer-1 (the simplest strong dimer). Note that NICS is the computed value of the negative magnetic shielding at some selected point in space, generally at center of a ring or cage [30-42].

Table 6. The NICS(0) values of the rings of dimer-1.

A	B	C
-0.0642	+0.7366	-0.0663

Since the present NICS data are close to zero the conclusions based on it are not clear. However, the data may indicate that rings A and C are weakly aromatic (or nonaromatic) whereas ring B (which is a 4-membered ring) is weakly antiaromatic (or nonaromatic). However, other possibilities should come into mind such as 8π-system covering rings A and B or in the most extended form having 12π-cyclic conjugated system, but it should be an antiaromatic system too.

Considering borazine itself, the evidence has been gathered by means of the magnetic and energetic criteria which indicated that borazine has an aromatic character, but less than benzene in the singlet state. The magnetic response shows that despite being approximately 30% of benzene, borazine has a "hidden" ring current where the contribution is only from the π_3 orbital, the results show that this orbital contributes in the same way as the π_3 orbital of benzene.

The results confirm that borazine should be considered as a weakly aromatic system with a hidden ring current and that the combination of Hückel's and Baird's rules can be used in a complementary way for an appropriate assignment of aromaticity [43].

Figure 4 displays the bond densities of the dimers considered. The bond density contains fewer electrons in total and demarks atomic connectivity. In dimer-I, the bond density spreads over ring-A and ring-B, (8π-electrons) thus both of them cannot exhibit what they should exhibit based on the number of π-electrons involved. Ring-A no longer possesses 6π-electrons only and ring-B is a 4π-electron system to exhibit a strong antiaromatic character. So the NICS values presented in Table 5 feebly correlate with the general trend of NICS treatment lacking of any strong evidence for the local aromaticities of the rings. Even ring-B might be simply olefinic, then one of its B-N bonds should be essentially single bond in terms of the classical treatment.

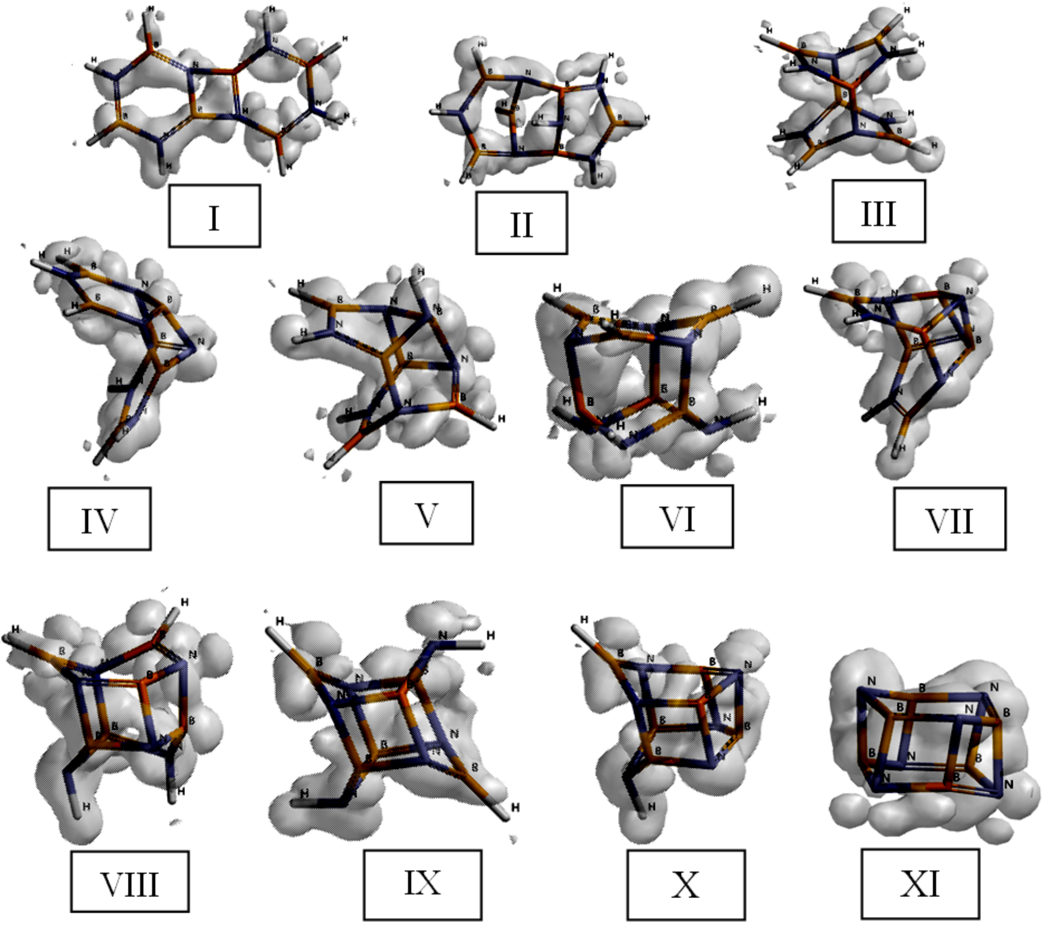


Figure 4. Bond densities of the dimers considered.

Figure 5 shows the calculated bond lengths (Å) in dimers I and XI as two extreme representative dimers where structures I (planar) and XI (solid) are strong and very strong dimers, respectively.

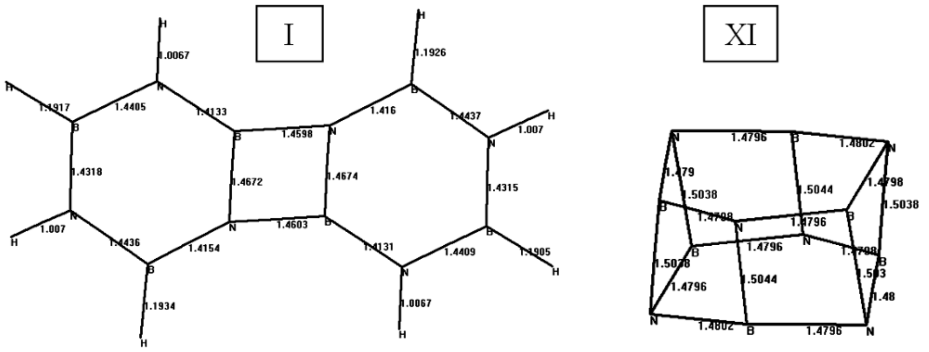


Figure 5. The calculated bond lengths (Å) in dimers I and XI.

Figure 6 shows the electrostatic potential (ESP) maps of the dimers considered. Electrostatic potential map paints the value of electrostatic potential onto an electron density surface. The maps based on the ESP charges which are obtained by the program based on a numerical method that generates charges that reproduce the electrostatic potential field from the entire wavefunction [24]. Namely, atomic charges chosen to best match the electrostatic potential at points surrounding a molecule, subject to overall charge balance [44]. It is evident from the figure that as the decks become quasi-parallel or parallel the molecule surrounded by more positive potential field implying that inter-deck interactions progressively more influential.

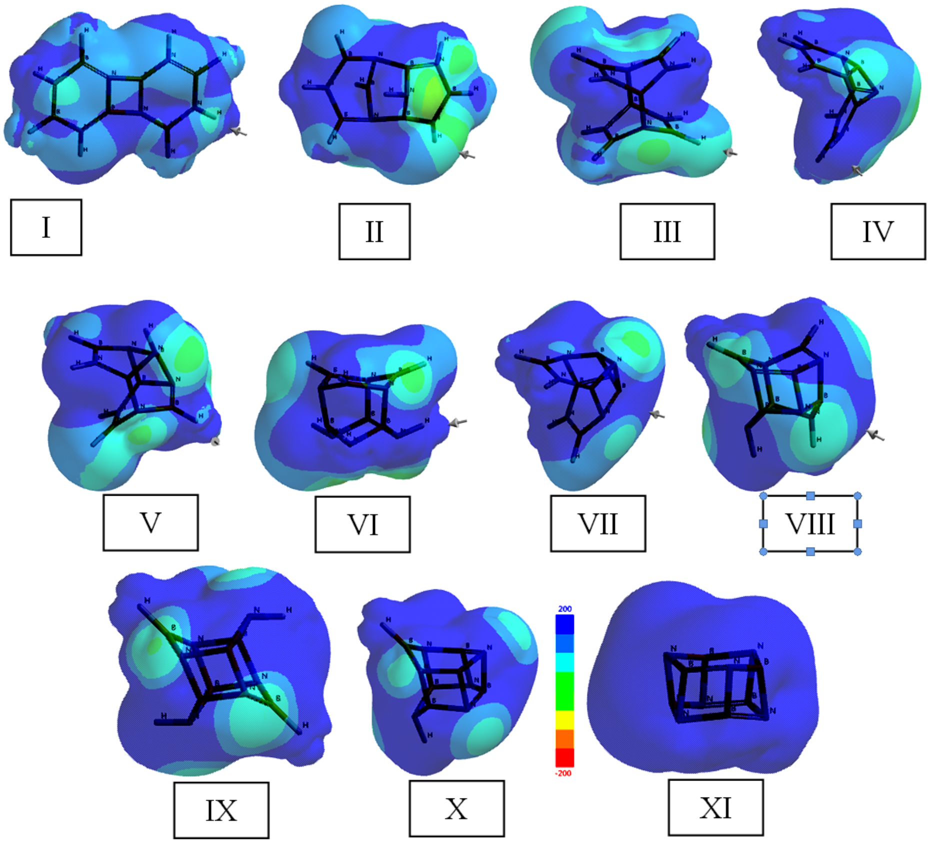
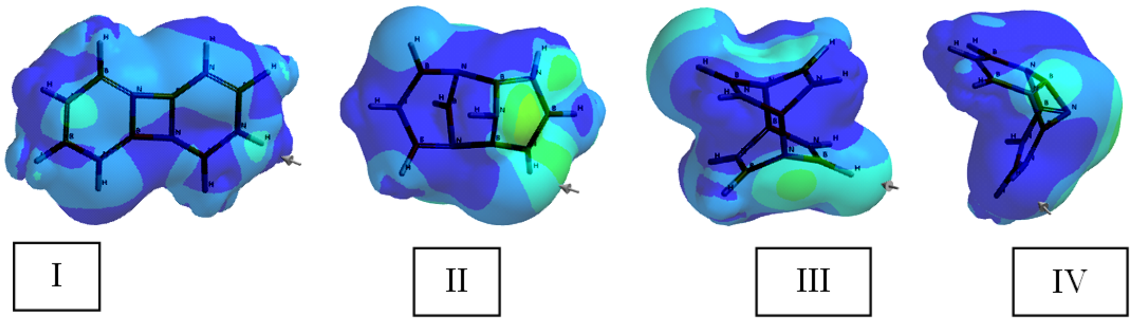


Figure 6. The ESP maps of the dimers considered.

Figure 7 shows the local ionization potential maps of the molecules considered where conventionally red/reddish regions (if any exists) on the density surface indicate areas from which electron removal is relatively easy, meaning that they are subject to electrophilic attack. Note that a local ionization potential map is a graph of the value of the local ionization potential on an isodensity surface corresponding to a van der Waals surface.



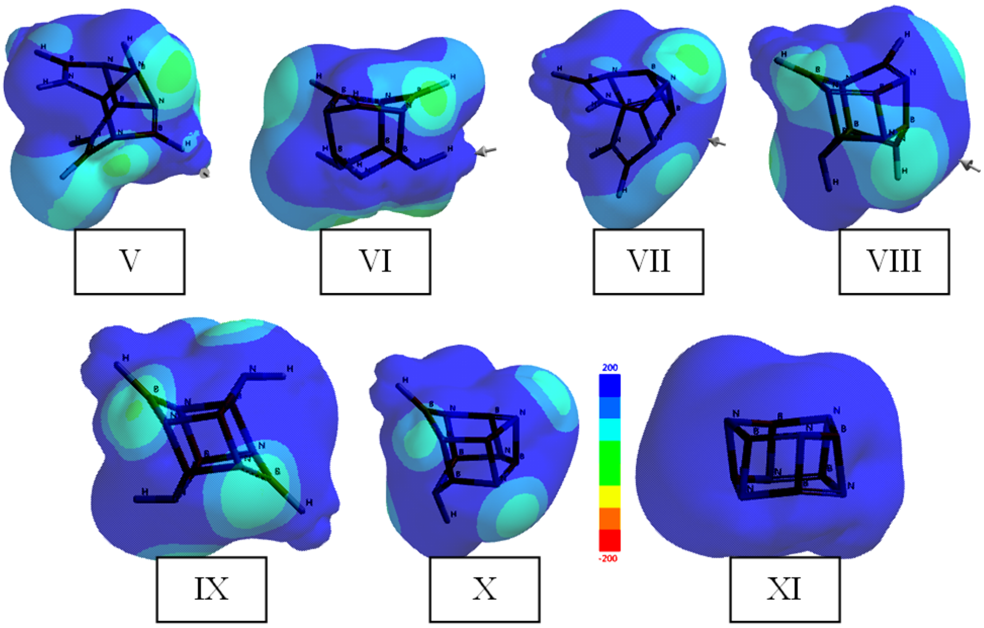


Figure 7. The local ionization maps of the dimers considered.

Figure 8 shows the LUMO maps of the species considered. Note that a LUMO map displays the absolute value of the LUMO on the electron density surface. It indicates the most likely regions for the electrons to be added and would be expected to correlate with the likelihood of nucleophilic attack. The blue color (if any exists) stands for the maximum value of the LUMO and the red colored region, associates with the minimum value.

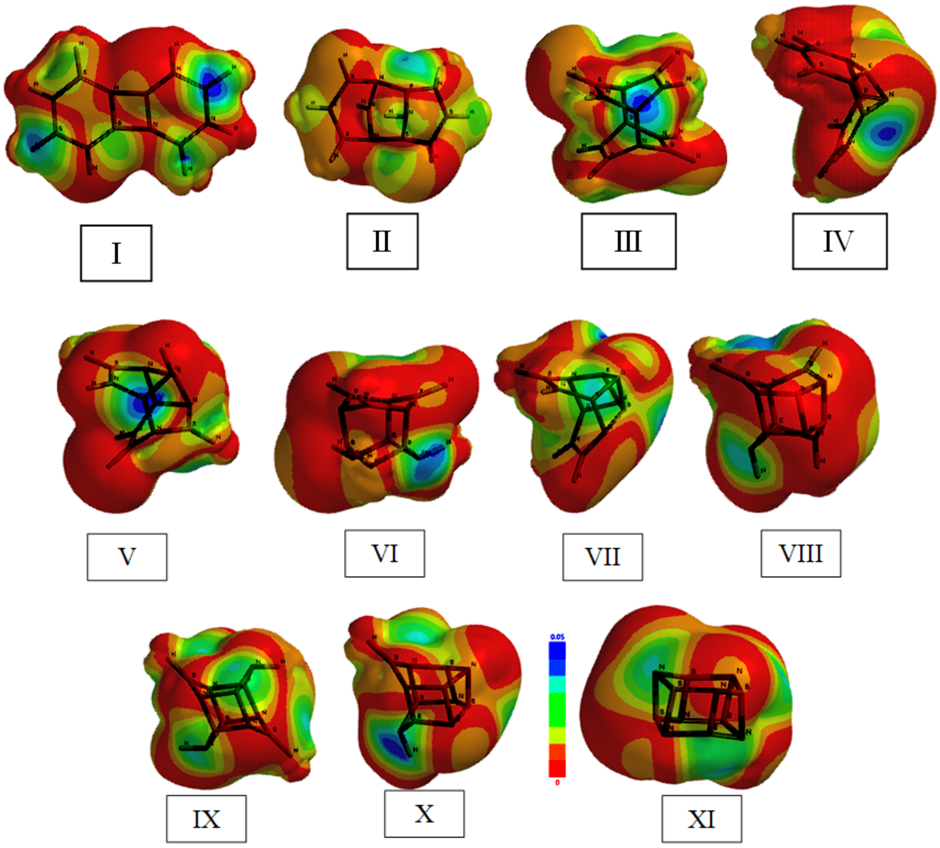


Figure 8. The LUMO maps of the dimers considered.

Table 7 lists the HOMO, LUMO energies and the interfrontier molecular orbital energy gap values, Δε, ($\Delta\varepsilon = \varepsilon_{LUMO} - \varepsilon_{HOMO}$) of the dimers considered. Inspection of the data reveals that in group of I-III which has only two bridges between the decks, the HOMO energies become less negative from I to II, than more negative for III compared to I and II.

Table 7. The HOMO, LUMO energies and Δε values of the dimers considered.

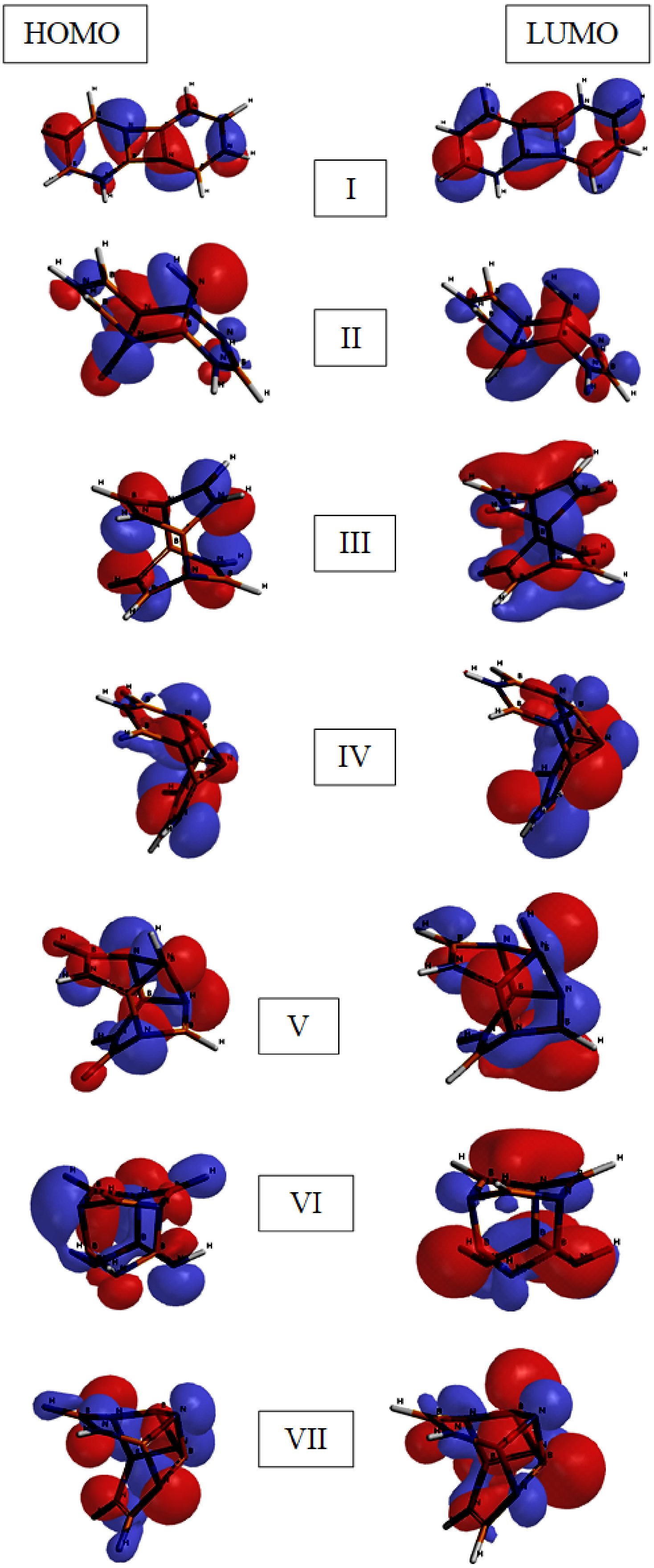
Structure No	HOMO	LUMO	Δε
I	-655.68	-40.57	615.11
II	-650.51	-163.50	487.01
III	-665.70	-52.69	613.01
IV	-693.64	-95.31	598.33
V	-647.16	-181.34	465.82
VI	-706.80	-263.81	442.99
VII	-701.35	-141.05	560.30
VIII	-691.76	-270.72	421.04
IX	-676.80	-264.77	412.03
X	-729.19	-232.35	496.84
XI	-792.26	-250.20	542.06

Energies in kJ/mol.

Whereas the LUMO energies of them decrease from I to II but then increases but still being less than the value of I. Various conformational factors which dictate mainly π- and π-σ interactions, some acting through space, are to be concerned for the variations.

In the group of dimers from IV to VI, which have three bridges, the HOMO energies first becomes less negative (increases in energy) then becomes more negative than the respective value of first member (IV) of the group. The LUMO energies follows the algebraic order of VI<V<IV. Since for those dimers the upper and lower hexagonal rings are quasi-parallel or parallel to each other, through space π-π interactions beside other above mention ones should be more and more influential. As the number of bridges increases, above interactions affect the HOMO and LUMO energy levels in more intricate manner. Overall, any electron donating effect raises the HOMO and LUMO energy levels and electron attracting effect opposite to that. Consequently, the interfrontier energy gap values (Δε) values are formed as the resultant effect of very many quantum chemical descriptors.

Figure 9 displays the HOMO and LUMO patterns of the dimers considered. As seen in the figure, dimer-I exhibits a π-symmetry having nodes between the nitrogens and boron atoms.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LUMO
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VI
VII

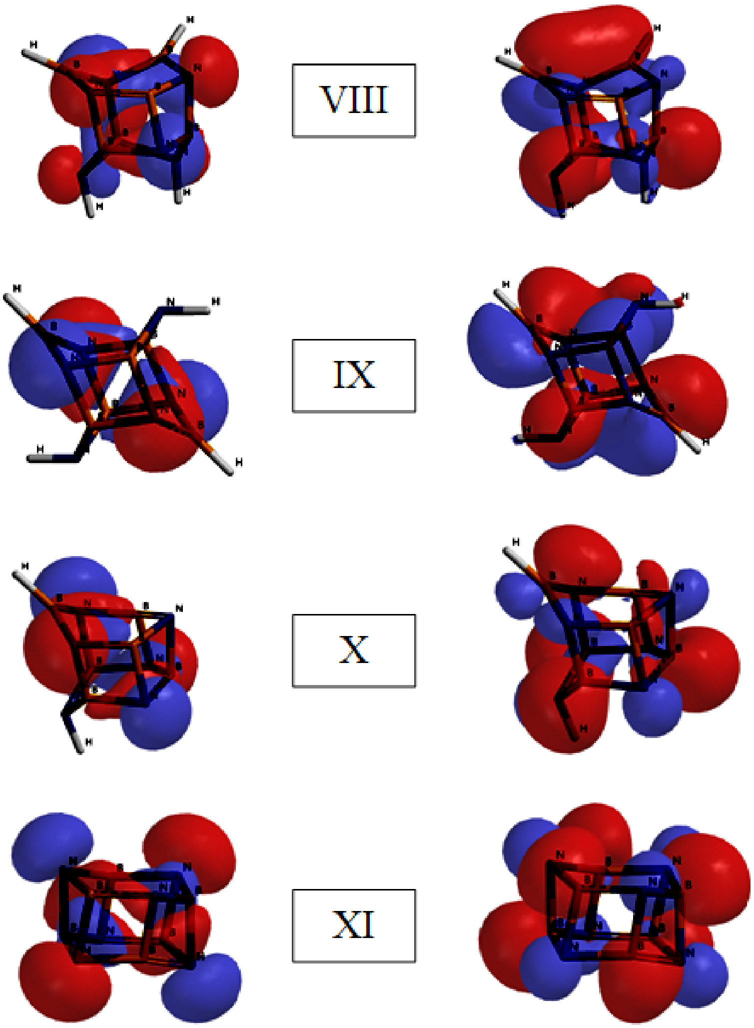
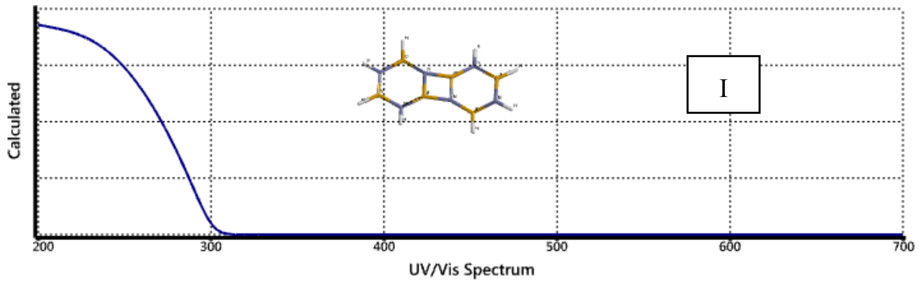
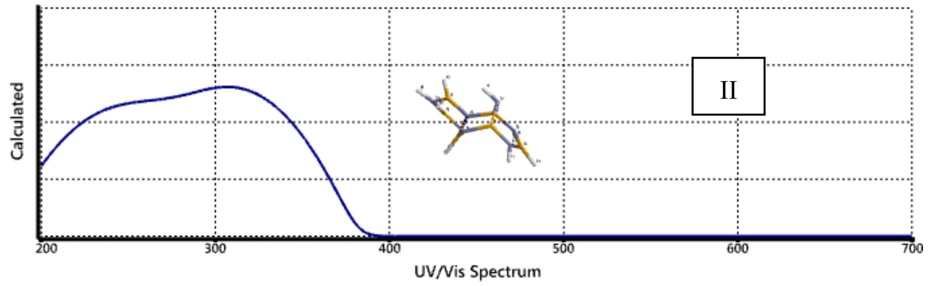


Figure 9. The HOMO and LUMO patterns of the dimers considered.

As the systems become more complicated the HOMO and LUMO spread over in more complicated way even between the atoms of upper and lower decks.

Figure 10 displays the calculated UV-VIS spectra (time dependent density functional) of the dimers. As seen in the figure, all the spectrums with the exceptions of VIII and IX are confined to UV region, mostly below 300 nm whereas in the case of II, V and VI below 400 nm. All the spectra with the exceptions of II, V, VI, VIII, IX and X have only a single peak whereas those exceptional ones have either a shoulder or two peaks. The bathochromic [45] effect observed in the cases of exceptional ones indicate that some sort of extended conjugation occurs [44-47].




II
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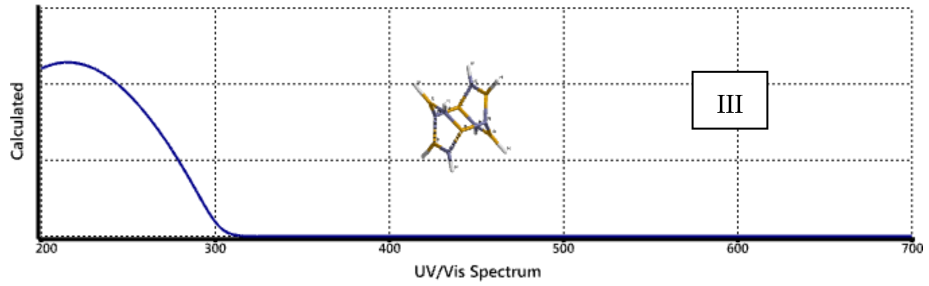
III
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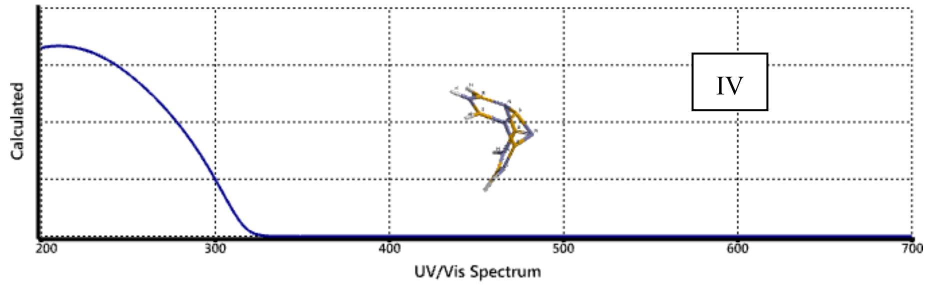
IV
Calculated
200
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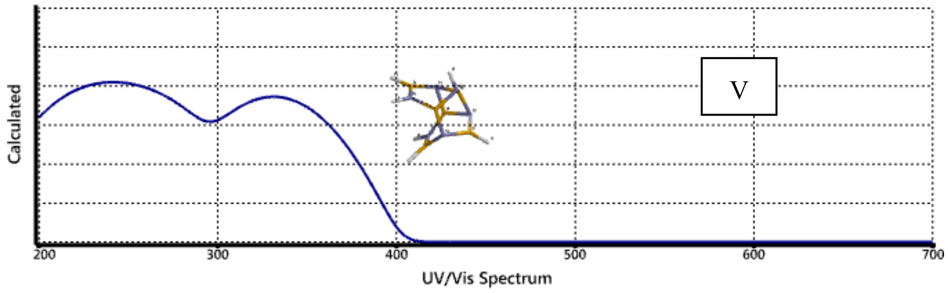
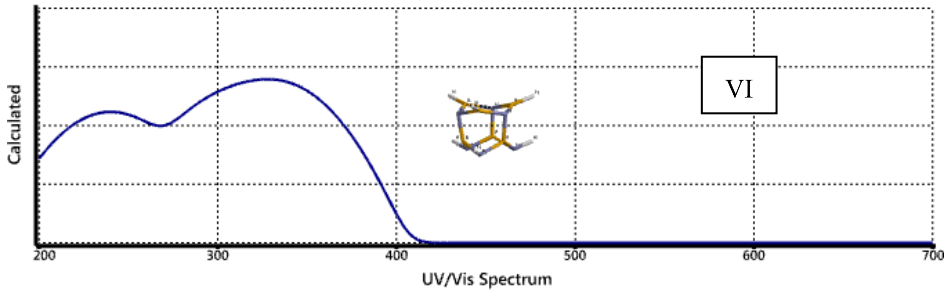
700
UV/Vis Spectrum


V
Calculated
200
300
400
500
600
700
UV/Vis Spectrum


VI
Calculated
200
300
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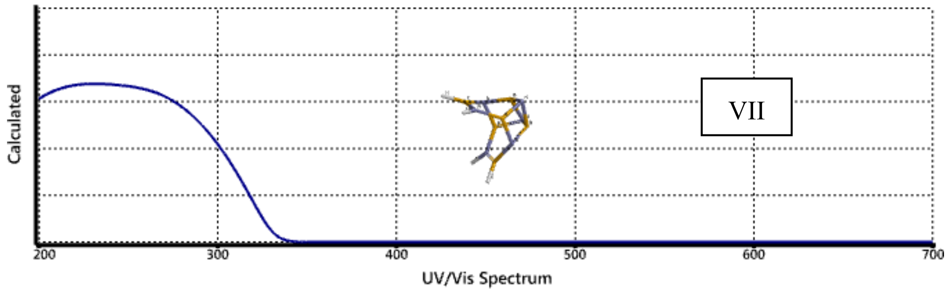
600
700
UV/Vis Spectrum


VII
Calculated
200
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600
700
UV/Vis Spectrum

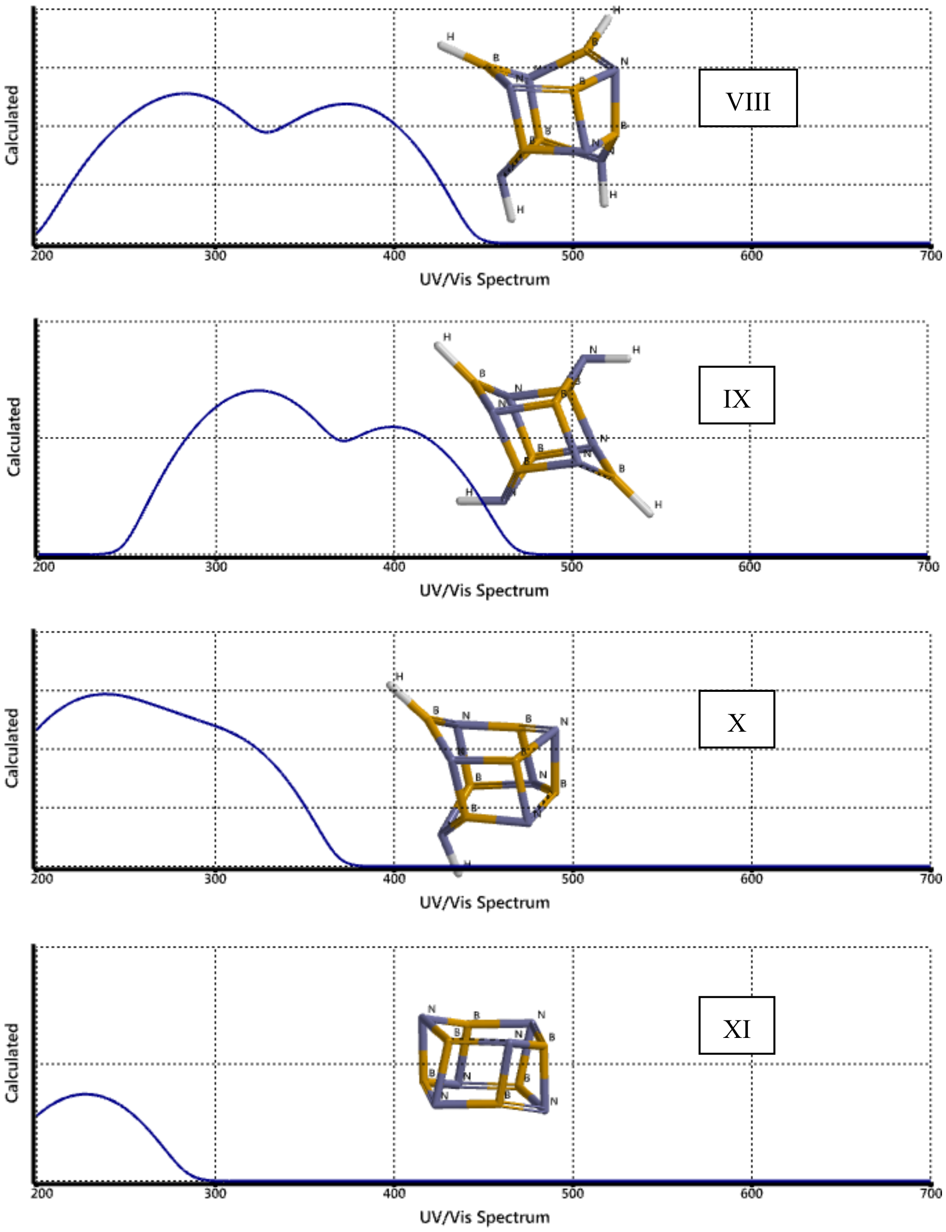

Figure 10. The calculated UV-VIS spectra of the dimers considered.

4. Conclusion

The present computational study, within the restrictions of DFT study at the level of B3LYP/cc-PVTZ considers some strong dimers of borazine. The present results indicate that in the vacuum conditions, all the dimers are characterized with exothermic heat of formation and favorable Gibbs free energy of formation values and they are electronically stable. The general trend among the groups (the number of bridges within each group is the same) is that both H^o and G^o values become less negative as the number of bridges increases. However, within each group there is no regularity. The stabilities decrease as the number of bridges increases from group to group. The calculated UV-VIS spectra reveals that all the spectrums with the exceptions of just two dimers are confined to UV region, mostly below 300 nm., whereas in dimers of II, V and VI below 400 nm.

The present treatise helps understanding of the role of certain topological and quantum chemical factors on certain geometrical and physicochemical properties of the borazine dimers to exploit them for certain application in future studies.

References

[1] Huang, Z., Wang, S., Dewhurst, R. D., Ignat'ev, N. V., Finze, M., & Braunschweig, H. (2019). Boron: Its role in energy-related processes and applications. *Angewandte Chemie International Edition*, *59*(23), 8800-8816. https://doi.org/10.1002/anie.201911108

[2] Zlotin, S. G., Dalinger, I. L., Makhova, N. N., & Tartakovsky, V. A. (2020). Nitro compounds as the core structures of promising energetic materials and versatile reagents for organic synthesis. *Russian Chemical Reviews*, *89*(1), 1-54. https://doi.org/10.1070/RCR4908

[3] Anitoff, O. (1977). Study of routes to the synthesis of nitrated boron-nitrogen compounds (thesis). Sorbonne University. https://coilink.org/20.500.12592/1kh2egj

[4] Wang, G., Jing, S., Liu, G., & Gao, X. (2020). Review on the synthesis and properties of the energetic compound containing boron. *Current Organic Chemistry*, *24*(10), 1097-1107. https://doi.org/10.2174/1385272824999200516180719

[5] Zeng, X., Li, N., & Jiao, Q. (2018). Carbon-free energetic materials: Computational study on nitro-substituted BN-cage molecules with high heat of detonation and stability. *RSC Advances*, *8*, 14654-14662. https://doi.org/10.1039/C7RA13476B

[6] Li, Y., Hao, J., Liu, H., Lu, S., & Tse, J. S. (2015). High-energy density and superhard nitrogen-rich B-N compounds. *Physical Review Letters*, *115*, 105502. https://doi.org/10.1103/PhysRevLett.115.105502

[7] Bettinger, H. F., Kar, T., & Sánchez-García, E. (2009). Borazine and benzene homo- and heterodimers. *The Journal of Physical Chemistry A*, *113*(14), 3353-3359. https://doi.org/10.1021/jp808173h

[8] Ina, L. M., & Ball, D. W. (2017). Density functional theory calculations on nitrated boroxines as possible high energy-density materials. *Ohio Journal of Science*, 117(2). https://doi.org/10.18061/ojs.v117i2.5298

[9] Zagorac, J., Fonovic, M., Djukic, M. B., Butulija, S., Prikhna, T., & Zagorac, D. (2024). Structural properties of full-scope AlN/BN compounds investigated using ab initio calculations. *Procedia Structural Integrity*, *54*, 453-459. https://doi.org/10.1016/j.prostr.2024.01.106

[10] Verma, K., & Viswanathan, K. S. (2017). The borazine dimer: The case of a dihydrogen bond competing with a classical hydrogen bond. *Physical Chemistry Chemical Physics*, *19*, 19067-19074. https://doi.org/10.1039/C7CP04056C

[11] Verma, K., & Viswanathan, K. S. (2018). A tale of two structures: The stacks and Ts of borazine and benzene hetero and homo dimers. *ChemistrySelect*, *3*(3), 864-873. https://doi.org/10.1002/slct.201703005

[12] Kawahara, S., Tsuzuki, S., & Uchimaru, T. (2003). Ab initio calculation of interaction nature of borazine ($B_3N_3H_6$) dimer. *Journal of Chemical Physics*, *119*, 10081-10087. https://doi.org/10.1063/1.1616914

[13] Stewart, J. J. P. (1989). Optimization of parameters for semiempirical methods I. Method. *Journal of Computational Chemistry*, *10*, 209-220. https://doi.org/10.1002/jcc.540100208

[14] Stewart, J. J. P. (1989). Optimization of parameters for semiempirical methods II. Application. *Journal of Computational Chemistry*, *10*, 221-264. https://doi.org/10.1002/jcc.540100209

[15] Leach, A. R. (1997). *Molecular modeling* (2nd ed.). Essex: Longman.

[16] Fletcher, P. (1990). *Practical methods of optimization* (1st ed.). New York: Wiley.

[17] Kohn, W., & Sham, L. (1965). Self-consistent equations including exchange and correlation effects. *Physical Review*, *140*, A1133-A1138. https://doi.org/10.1103/PhysRev.140.A1133

[18] Parr, R. G., & Yang, W. (1989). *Density functional theory of atoms and molecules* (1st ed.). London: Oxford University Press.

[19] Cramer, C. J. (2004). *Essentials of computational chemistry* (2nd ed.). Chichester, West Sussex: Wiley.

[20] Young, D. C. (2001). *Computational chemistry*. New York: Wiley.

[21] Becke, A. D. (1988). Density-functional exchange-energy approximation with correct asymptotic behavior. *Physical Review A*, *38*, 3098-3100. https://doi.org/10.1103/PhysRevA.38.3098

[22] Vosko, S. H., Wilk, L., & Nusair, M. (1980). Accurate spin-dependent electron liquid correlation energies for local spin density calculations: A critical analysis. *Canadian Journal of Physics*, *58*, 1200-1211. https://doi.org/10.1139/p80-159

[23] Lee, C., Yang, W., & Parr, R. G. (1988). Development of the Colle-Salvetti correlation energy formula into a functional of the electron density. *Physical Review B*, *37*, 785-789. https://doi.org/10.1103/PhysRevB.37.785

[24] Wavefunction Inc. (2006). SPARTAN 06. Irvine, CA, USA.

[25] Gaussian 03, Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, Jr., J.A., Vreven, T., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrzewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Ortiz, J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Gonzalez, C., & Pople, J.A., Gaussian, Inc., Wallingford CT, 2004.

[26] Türker, L. (1999). AM1 treatment of cyclophanes with vinylic bridges. *Polycyclic Aromatic Compounds*, *13*, 25-31. https://doi.org/10.1080/10406639908020540

[27] Türker, L., & Gümüş, S. (2009). A theoretical study on some (1,4)cyclophanes. *Polycyclic Aromatic Compounds*, *29*(2), 103-122. https://doi.org/10.1080/10406630902861411

[28] Dewar, J. M. S. (1969). *The molecular orbital theory of organic chemistry*. New York: McGraw-Hill.

[29] Dewar, M. J. S., & Dougherty, R. C. (1975). *The PMO theory of organic chemistry*. New York: Plenum/Rosetta.

[30] Minkin, V. I., Glukhovtsev, M. N., & Simkin, B. Y. (1994). *Aromaticity and antiaromaticity: Electronic and structural aspects*. New York: Wiley.

[31] Schleyer, P. R., & Jiao, H. (1996). What is aromaticity? *Pure and Applied Chemistry*, *68*, 209-218. https://doi.org/10.1351/pac199668020209

[32] Schleyer, P. R. (2001). Introduction: Aromaticity. *Chemical Reviews*, *101*, 1115-1118. https://doi.org/10.1021/cr0103221

[33] Cyranski, M. K., Krygowski, T. M., Katritzky, A. R., & Schleyer, P. R. (2002). To what extent can aromaticity be defined uniquely? *Journal of Organic Chemistry*, *67*, 1333-1338. https://doi.org/10.1021/jo016255s

[34] Chen, Z., Wannere, C. S., Corminboeuf, C., Puchta, R., & Schleyer, P. von R. (2005). Nucleus independent chemical shifts (NICS) as an aromaticity criterion. *Chemical Reviews*, *105*(10), 3842-3888. https://doi.org/10.1021/cr030088

[35] Gershoni-Poranne, R., & Stanger, A. (2015). Magnetic criteria of aromaticity. *Chemical Society Reviews*, *44*(18), 6597-6615. https://doi.org/10.1039/C5CS00114E

[36] Dickens, T. K., & Mallion, R. B. (2016). Topological ring-currents in conjugated systems. *MATCH Communications in Mathematical and in Computer Chemistry*, *76*, 297-356.

[37] Stanger, A. (2010). Obtaining relative induced ring currents quantitatively from NICS. *Journal of Organic Chemistry*, *75*(7), 2281-2288. https://doi.org/10.1021/jo1000753

[38] Monajjemi, M., & Mohammadian, N. T. (2015). S-NICS: An aromaticity criterion for nano molecules. *Journal of Computational and Theoretical Nanoscience*, *12*(11), 4895-4914. https://doi.org/10.1166/jctn.2015.4458

[39] Schleyer, P. R., Maerker, C., Dransfeld, A., Jiao, H., & Hommes, N. J. R. E. (1996). Nucleus independent chemical shifts: A simple and efficient aromaticity probe. *Journal of the American Chemical Society*, *118*, 6317-6318. https://doi.org/10.1021/ja960582d

[40] Corminboeuf, C., Heine, T., & Weber, J. (2003). Evaluation of aromaticity: A new dissected NICS model based on canonical orbitals. *Physical Chemistry Chemical Physics*, *5*, 246-251. https://doi.org/10.1039/B209674A

[41] Stanger, A. (2006). Nucleus-independent chemical shifts (NICS): Distance dependence and revised criteria for aromaticity and antiaromaticity. *Journal of Organic Chemistry*, *71*(3), 883-893. https://doi.org/10.1021/jo051746o

[42] Chen, Z., Wannere, C.S., Corminboeuf, C., Puchta, R., & Schleyer, P.R. (2005). Nucleus independent chemical shifts (NICS) as an aromaticity criterion. *Chemical Reviews*, *105*(10), 3842-3888. https://doi.org/10.1021/cr030088+

[43] Báez-Grez, R., & Pino-Rios, R. (2022). The hidden aromaticity in borazine. *RSC Advances*, *12*, 7906-7910. https://doi.org/10.1039/D1RA06457F

[44] Wavefunction Inc. (2005). *SPARTAN: Molecular modeling in physical chemistry*. Irvine, CA, USA.

[45] Ferguson, L. N. (1969). *The modern structural theory of organic chemistry*. New Delhi: Prentice-Hall of India.

[46] Fleming, I. (1976). *Frontier orbitals and organic reactions*. London: Wiley.

[47] Anslyn, E. V., & Dougherty, D. A. (2006). *Modern physical organic chemistry*. Sausalito, CA: University Science Books.