



The π - π Stacking Interaction of Azaborine and Some of its Derivatives: A Quantum Mechanical Study

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Derivatives of azaborine *viz.*, diazaborines, borazine and pseudoborazine, but interestingly all of them are not purely aromatic. The sequence of aromaticity of some azaborine and its derivatives were given as azaborine > diazaborine > pseudoborazine > borazine. Also they have different ring bond distances as B-B, N-N and B-N. Due to their difference in properties of aromaticity and structure, the π - π stacking interaction was also very interesting and quite different from the normal aromatic systems. Quantum mechanical, MP2 method is quite useful for determining the π - π stacking interaction in different azaborine dimers and its derivatives for eclipsed and staggered stacked conformations. Stacked models of azaborine derivatives with intermolecular rotations also shows different interaction energies.

Keywords: Azaborine, Borazine, Aromaticity, MP2 methods, π - π Stacking.

INTRODUCTION

Wiberg proposed "inorganic benzene" for borazine on the basis of the fact that all the B-N bond lengths in borazine are equivalent which is the main criterion of aromaticity for hydrocarbons and also the number of π -electrons is the same as in benzene [1]. However, aromaticity in azaborine, diazaborine, borazine and pseudoborazine is lower than benzene due to the difference in electronegativity between boron and nitrogen [2]. Generally, aromaticity of such molecule is studied on the basis of structural, reactivity, magnetic and energetic criteria. However, these criteria are likely to strongly diverge from each other in case of inorganic heterocycles [3]. Usually, the aromaticity of inorganic heterocyclic compounds are found to be associated with the aromatic stabilization energy (ASE) [4]. The computed ASE of benzene (92.5-150.6 kJ mol⁻¹) is higher than that of borazine (41.8-46.4 kJ mol⁻¹). Hence, this energy criteria shows that the borazine is less aromatic than that of benzene [5-7]. Fernandez and Frenking on the basis of energy decomposition analysis concluded that the degree of aromaticity in borazine is small, which is supported by Fernandez *et al.* [8] and Islas *et al.* [9] by using electron localization function (ELF) analysis. In borazine, delocalization of π -electrons are comparatively reduced than benzene due to the large difference in electronegativity between boron (2.0) and nitrogen (3.0), which means

that π -electron clouds are more localized on nitrogen atoms [10-12]. Because of the polarity of B-N bonds, the reactivity pattern of borazine is different from benzene [10,11]. Recently a new magnetic criterion is suggested by Schleyer *et al.* [13] and Jug [14], which is known as nucleus independent chemical shift (NICS) is used to probe the degree of aromaticity in planar rings. It's definition is the negative of magnetic shielding which is computed at the centre of ring [13,14]. The smaller negative NICS value for borazine (-3.2) in comparison to that of benzene (-10.7) indicates that aromaticity of borazine is much lower than that of benzene [15]. There has always been an interest in the molecules where a HC-CH group is substituted by a HB-NH group which gives an isoelectronic molecule having a B-N bond [16]. Of these, the most important molecules are azaborine (1,2-dihydro-1,2-azaborine) which is obtained by the replacement of one CH-CH group by one HN-BH group or diazaborines obtained by the replacement of two CH-CH groups by two HN-BH groups and borazine or pseudoborazine obtained by the replacement of three CH-CH groups [17,18]. Though experimentally borazine has been known since 1926; 1,2-dihydro-1,2-azaborine was prepared in 2008 by Liu and Marder [16] and then investigated by other authors [7,19-21].

Stacking interaction in borazine homodimer: Among various non-covalent interactions, the π - π stacking interactions are prominent in crystal packing and also plays an important

role in molecular recognition processes [22]. The π - π stacking interaction in the benzene dimer has been widely studied and it is concluded that dispersion interaction is the main source of attraction in homogeneous π - π interaction [23]. Borazine and benzene are isoelectronic analogue of each other and hence is also known as inorganic benzene. Borazine has amphoteric π -electron system, *i.e.* it has both electron rich p -orbital (on N atoms) and electron deficient p -orbital (on B atoms). So, in homo-stacking dimer of borazine charge transfer (CT) interaction can be seen [24]. Though borazine homodimer has the π - π interaction of unique nature and also has important industrial applications, no study on the molecular interaction property has been reported in a borazine homodimer. The symmetry of the geometry of borazine monomer is D_{3h} which is in agreement with various computational investigations [25]. A total of four stationary points could be identified in borazine which are sandwich (S), parallel displaced (PD) and two T-forms named as T_{1N} and T_{1Nrot} (Fig. 1). The minima on the potential energy surface corresponding to S, PD and the two T forms differ in the relative orientation of borazine ring. Upon dimerization the geometries of the individual borazine molecules slightly changes. In the two T-forms, the N-H bonds which points towards the π -face of other borazine ring are found to be slightly elongated and the corresponding borazine rings have highest deformation energy compared to the monomer. The order of energy of isomers (*i.e.* $S > PD > T_{1N} > T_{1Nrot}$) of dimers featuring the most favourable B---N intermolecular interactions and obtained using MP2 method does not change since higher order correlation are used [26].

Due to lower symmetry and reduced aromaticity, we were interested in studying the π - π stacking interaction in borazine and its effect in the change in bond distance and bond angles of azaborine derivatives.

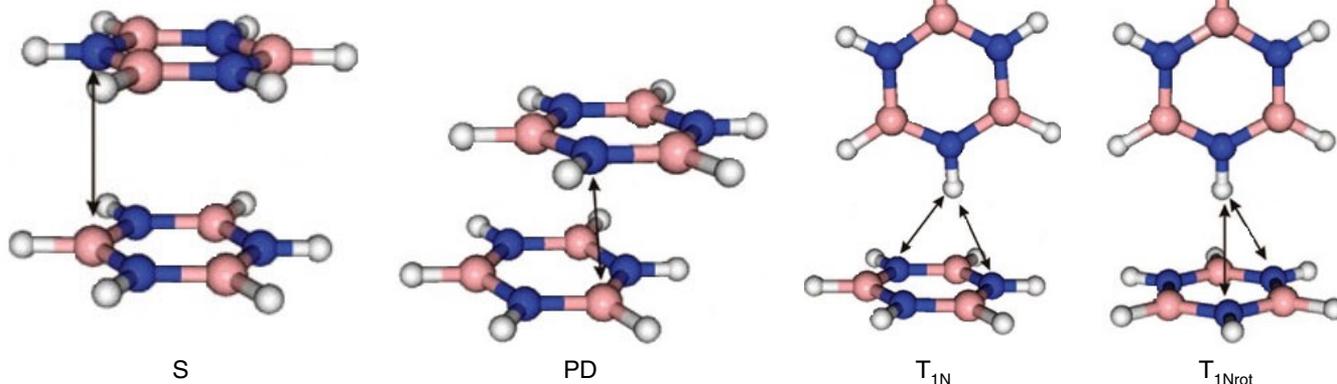


Fig. 1. Interaction modes in borazine homodimer (a) sandwich (S), (b) parallel-displaced (PD), (c) T_{1N} and (d) T_{1Nrot}

COMPUTATIONAL METHODS

All optimized geometries were used for constructing various stacked models of azaborine isomers using *JoinMolecule* package of software. In addition, Arguslab was also used to visualize and observe the different stacked models. For studying the long range non-covalent interaction such as π - π interaction, quantum mechanical *ab initio* method is most reliable one. All the stacked models have been computed by using MP2 method with GaussView5.0 and Gaussian09 software. The geometries were optimized by using the MP2/6-311++G(d,p) basis set and same basis set was used for the calculation of single point energy.

Azaborine dimers can be directly stacked like sandwich structure with different intermolecular rotations, but in present observations only 0° , 60° , 120° and 180° rotations were considered, which shows the preferable interactions among them (Fig. 2). Here, 0° intermolecular rotation can be considered as eclipsed and rest of them are considered as staggered conformations. The π - π stacking interaction energies for the stacked dimeric models can be calculated by the following equation:

$$\text{Interaction energy} = E_{\text{stacked}} - 2E_{\text{single}}$$

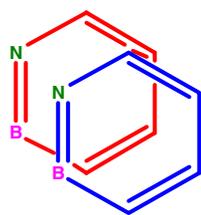
where E_{stacked} = single point energy of stacked azaborine molecule and E_{single} = single point energy of single unstacked azaborine molecule. All the calculations were computed by using Gaussian09 [27].

RESULTS AND DISCUSSION

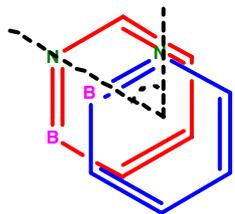
In present work, we have investigated the π - π stacking interaction of azaborine and its derivatives (Table-1). Although π - π stacking interaction is very common in purely aromatic

TABLE-1
LIST OF AZABORINE AND ITS DERIVATIVES ALONG WITH THEIR AROMATICITY

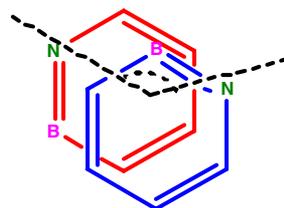
Names	Stacked models	Aromaticity
Azaborine (BZ1)	BZ1-BZ1	Most aromatic
Diazaborine1 (BZ2)	BZ2-BZ2	Much more aromatic than pure borazine
Diazaborine2 (BZ3)	BZ3-BZ3	Much more aromatic than pure borazine
Diazaborine 3 (BZ4)	BZ4-BZ4	Much more aromatic than pure borazine
Diazaborine 4 (BZ5)	BZ5-BZ5	Much more aromatic than pure borazine
Diazaborine 5 (BZ6)	BZ6-BZ6	Much more aromatic than pure borazine
Borazine (BZ7)	BZ7-BZ7	Weakly aromatic/non aromatic
Pseudoborazine (BZ8)	BZ8-BZ8	More aromatic than pure borazine



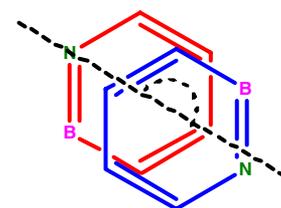
0°



60°

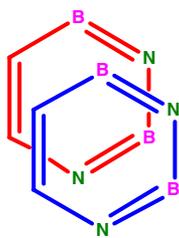


120°

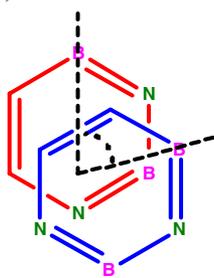


180°

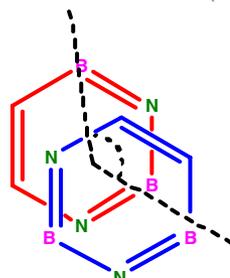
(a) Intermolecular rotation for stacked azaborine molecule (BZ1)



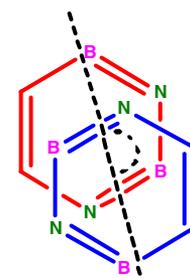
0°



60°

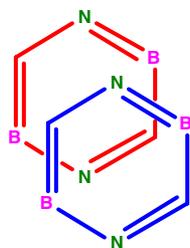


120°

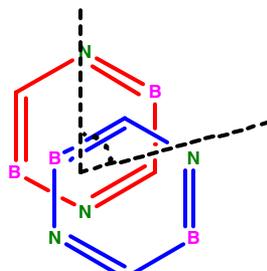


180°

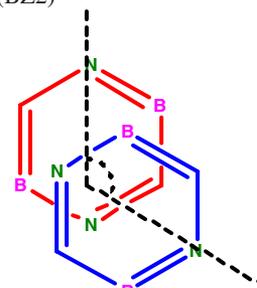
(b) Intermolecular rotation for stacked diazaborine 1 molecule (BZ2)



0°



60°

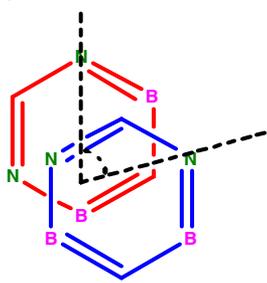


120°

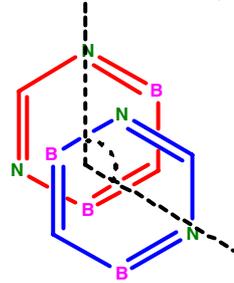
(c) Intermolecular rotation for stacked diazaborine 2 molecule (BZ3)



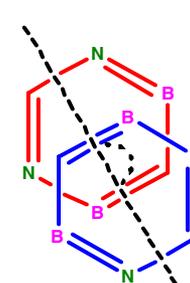
0°



60°

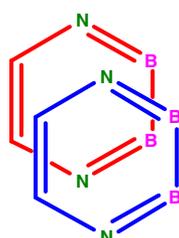


120°

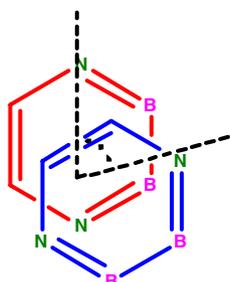


180°

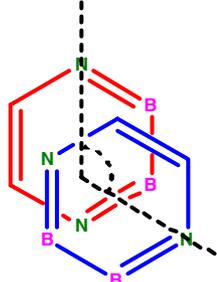
(d) Intermolecular rotation for stacked diazaborine 3 molecule (BZ4)



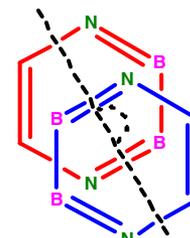
0°



60°

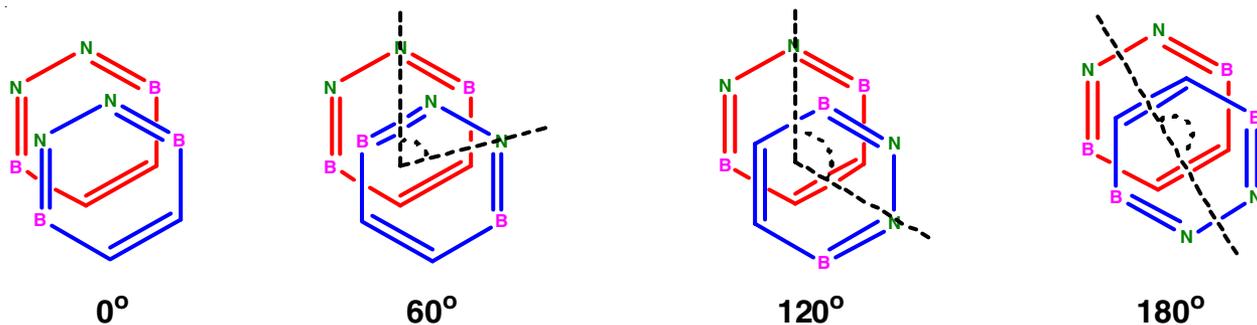


120°

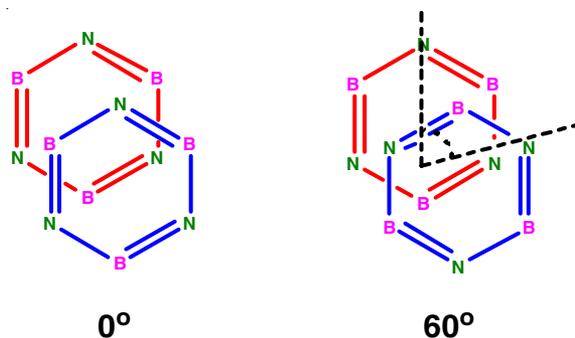


180°

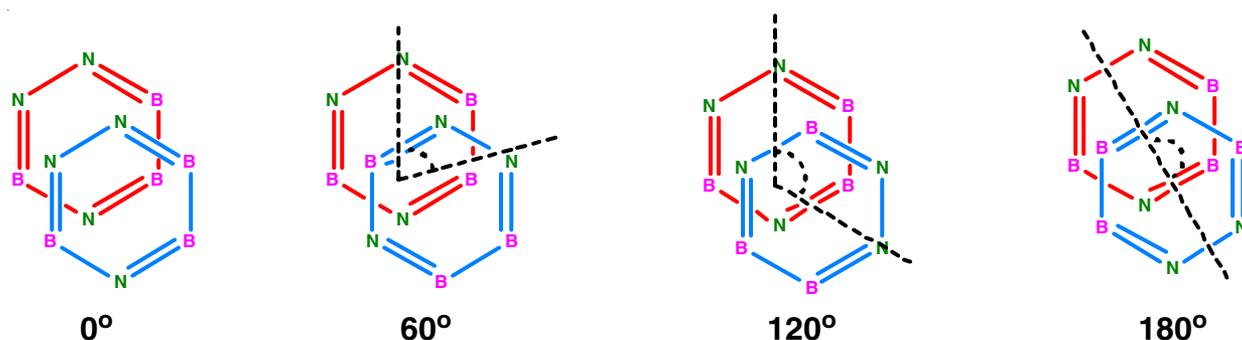
(e) Intermolecular rotation for stacked diazaborine 4 molecule (BZ5)



(f) Intermolecular rotation for stacked diazaborine 5 molecule (BZ6)



(g) Intermolecular rotation for stacked borazine molecule (BZ7)



(h) Intermolecular rotation for stacked pseudoborazine molecule (BZ8)

Fig. 2. Intermolecular rotations for azaborine and its derivatives

system, but this investigation also revealed that it is taking place also in weakly aromatic and non-aromatic system, such as azaborine and its derivatives (Table-1). Moreover, there might be a difference in stacking energy of purely aromatic and non-aromatic system. Initially, all the molecules were optimized by using Gaussian 09 program code and then the π - π stacking interactions of azaborine and its derivatives have been studied for different intermolecular rotations in gas phase (Fig. 3). The stacked models were prepared by placing one azaborine ring parallelly over the other ring. The internal separation between the azaborine molecule is kept constant and it was 3.6 Å, which gives the most favoured staking interaction between two azaborine rings. Then the ring has been horizontally shifted along either X, Y or Z-axis (from positive to negative direction), keeping the other ring at a constant position, to get the most favoured minimized stacked model. Here, the horizontal shifting for the stacked model was investigated along X-axis from -3 to +3 Å.

The single-point MP2 calculations with 6-311++G(d,p) basis set have been found useful in describing the stability of stacked azaborine and its derivatives. It is well known that if the π - π stacking interaction energy for a stacked model is found to be more negative then it gives the most stable stacked structure. The relative changes of the interaction energies of different stable stacked models of azaborine and some of its derivatives are shown in Table-2. From the interaction energy plot *i.e.* interaction energy (kcal/mol) *vs.* horizontal shifting (Å), it has been observed that there appears at least one minima at one end of the plot. The point at minima always gives more negative interaction energy value, which represents the most stable stacked model (Fig. 4a-h). On the other hand, the less negative or positive interaction energy values in the plot gives more repulsion in the stacked model and the stability such stacked model is also very less than that of other models.

The computed interaction energies for stacked models of MP2 levels of calculations are summarized in Table-2. The series

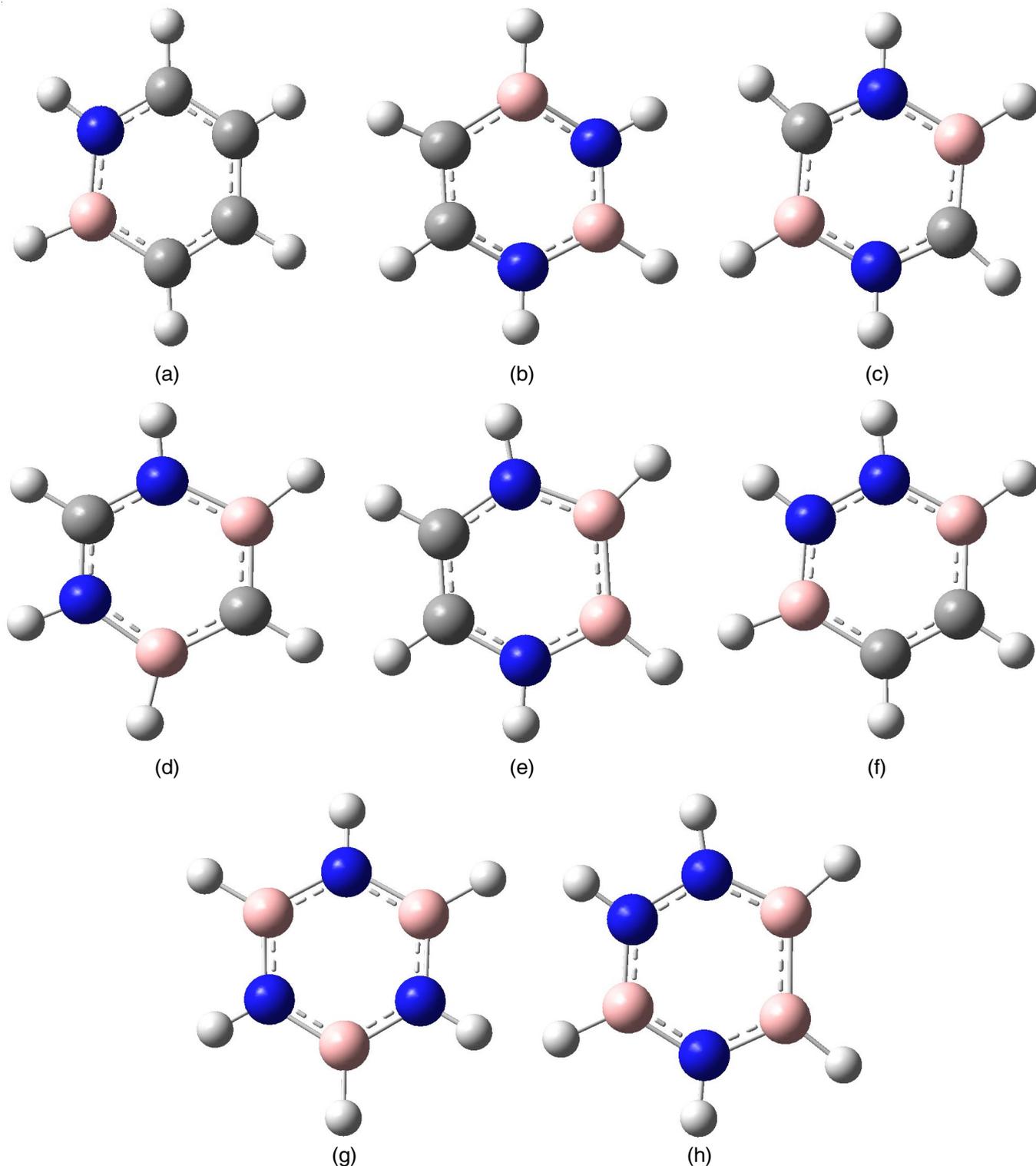


Fig. 3. Optimized models of azaborine and its derivatives (a) azaborine (BZ1), (b) diazaborine 1 (BZ2), (c) diazaborine 2 (BZ3), (d) diazaborine 3 (BZ4), (e) diazaborine 4 (BZ5) (f) diazaborine 5 (BZ6), (g) borazine (BZ7) and (h) pseudoborazine (BZ8)

of results could provide prior necessity of dispersion forces for the stabilization of these stacked molecules. The results of MP2 level of theories reflect the extent of dispersion energies accounted in all these calculations. Indeed, the electron correlations included in MP2 level with diffused function in the basis set could estimate more negative interaction energies, where an increase of diffuse function in the basis set provides

little change in the interaction energies. It may be noted that the difference of interaction energies obtained from MP2/6-311++G(d,p) calculations was significantly large.

Herein, the eclipsed stacked models of azaborine and its derivatives was taken as intermolecular rotation 0° , where there was no intermolecular rotation taking place in the stacked model. Among all the stacked models of azaborine and its derivatives

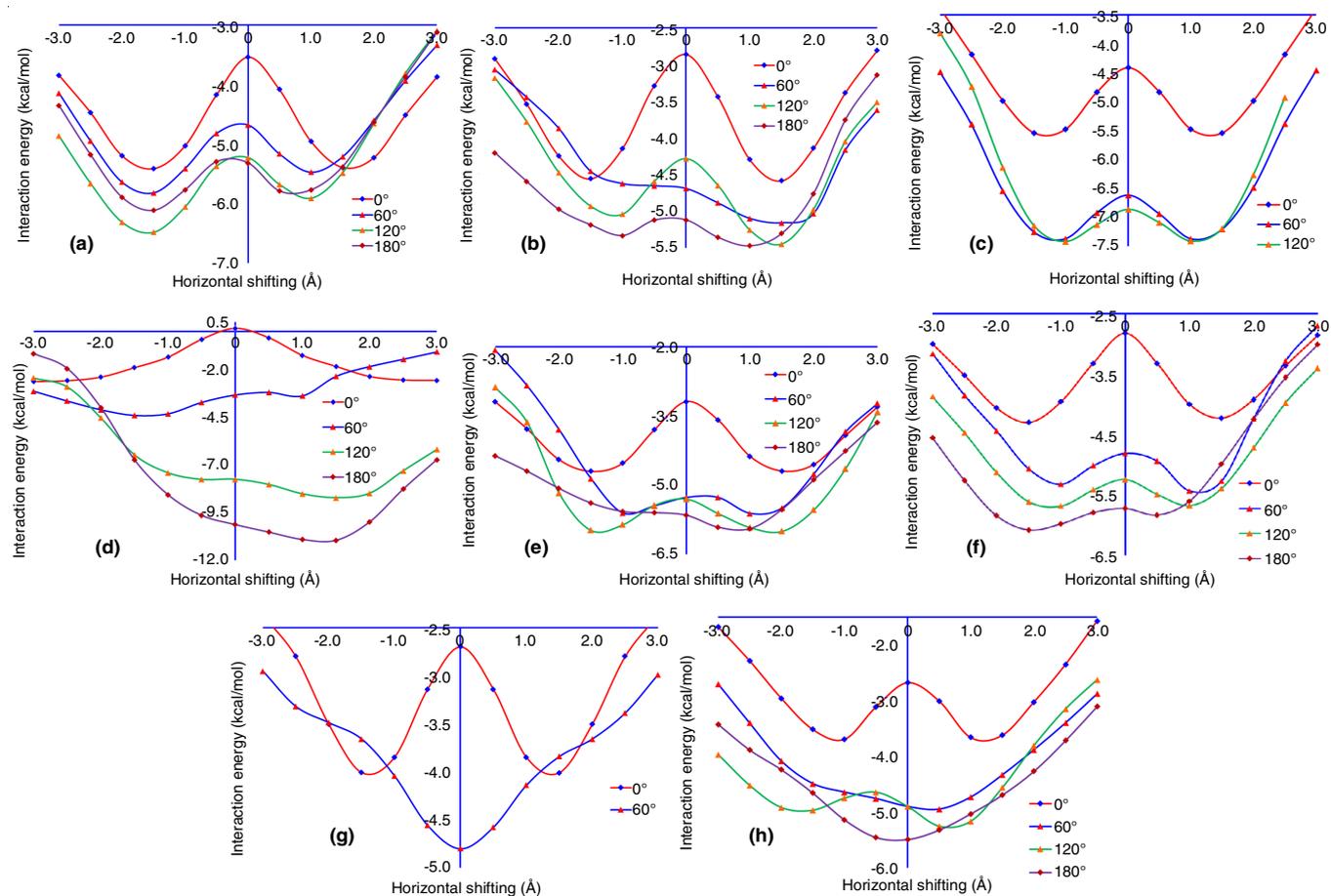


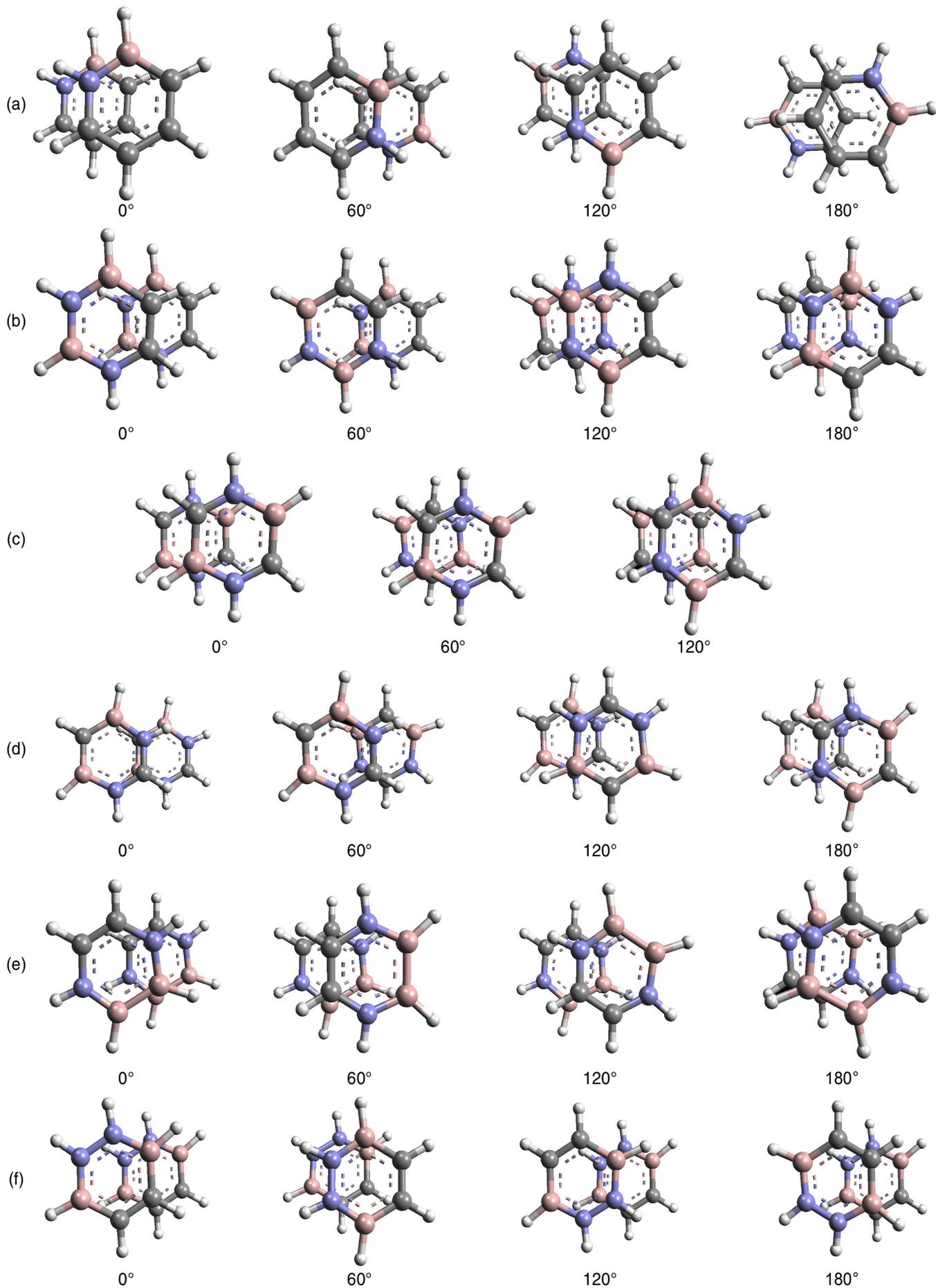
Fig. 4. Interaction energy plot for (a) BZ1-BZ1, (b) BZ2-BZ2, (c) BZ3-BZ3, (d) BZ4-BZ4, (e) BZ5-BZ5, (f) BZ6-BZ6, (g) BZ7-BZ7, and (h) BZ8-BZ8 stacked models at different intermolecular rotations

Stacked models	Interaction energies (kcal/mol)			
	Intermolecular rotation (°)			
	0°	60°	120°	180°
BZ1-BZ1	-5.42	-5.82	-6.48	-6.12
BZ2-BZ2	-4.60	-5.16	-5.45	-5.48
BZ3-BZ3	-5.55	-7.37	-7.42	–
BZ4-BZ4	-2.40	-4.40	-8.71	-10.95
BZ5-BZ5	-4.70	-5.62	-6.00	-5.95
BZ6-BZ6	-4.30	-5.43	-5.68	-6.08
BZ7-BZ7	-4.01	-4.80	–	–
BZ8-BZ8	-3.67	-4.95	-5.26	-5.49

for their eclipsed conformations (0°), it has been observed that the π - π stacking interaction energy of BZ3 dimer was found to be the most negative value *i.e.* -5.55kcal/mol (Table-2). The more negative stacking interaction energy value represents the most stable conformation and effective calculation of electron-electron correlation and dispersion forces. The minima of the interaction energy plots stacked models shows the most favoured and stable geometry for BZ3 as shown in Fig. 5c. On the other hand, the stacking interaction energy of BZ4 stacked dimer was found to be less negative and considered as the least stable eclipsed conformation as shown in Fig. 5d. For all the stacked models of azaborine and its derivatives, it has been observed

that the interactions energy plot was totally different for all the azaborine stacked models. The sequence of stability of the stacked models of azaborine and its derivatives with eclipsed conformations (0°) is shown as: BZ4-BZ4 < BZ8-BZ8 < BZ7-BZ7 < BZ6-BZ6 < BZ2-BZ2 < BZ5-BZ5 < BZ1-BZ1 < BZ3-BZ3.

It is well known that the π - π stacking interaction for eclipsed and staggered models are quite different, therefore the π - π stacking interactions of staggered stacked models for azaborine and its derivatives were also investigated at different intermolecular rotation 60°, 120° and 180°. It has been observed that the staggered conformation for π - π stacking interaction is always found more stable than that of eclipsed conformations. This is due to the minimum repulsive forces between the hetero atoms (B and N) of monomer in the staggered stacked model than that of the eclipsed conformation. Among all the staggered conformation of azaborine derivatives, π - π stacking interaction energy of BZ4 dimer was found to be the most negative value (-10.95 kcal/mol) at 180° intermolecular rotation (Table-2). As discussed above, more negative π - π stacking interaction energy value represents the most stable conformation which gives effective calculation of electron-electron correlation and dispersion forces. Again, in the interaction energy plot of stacked models, a global minimum in the plot has been observed. This minimum of interaction energy plot of stacked models results the most favoured and stable conformation for stacked models



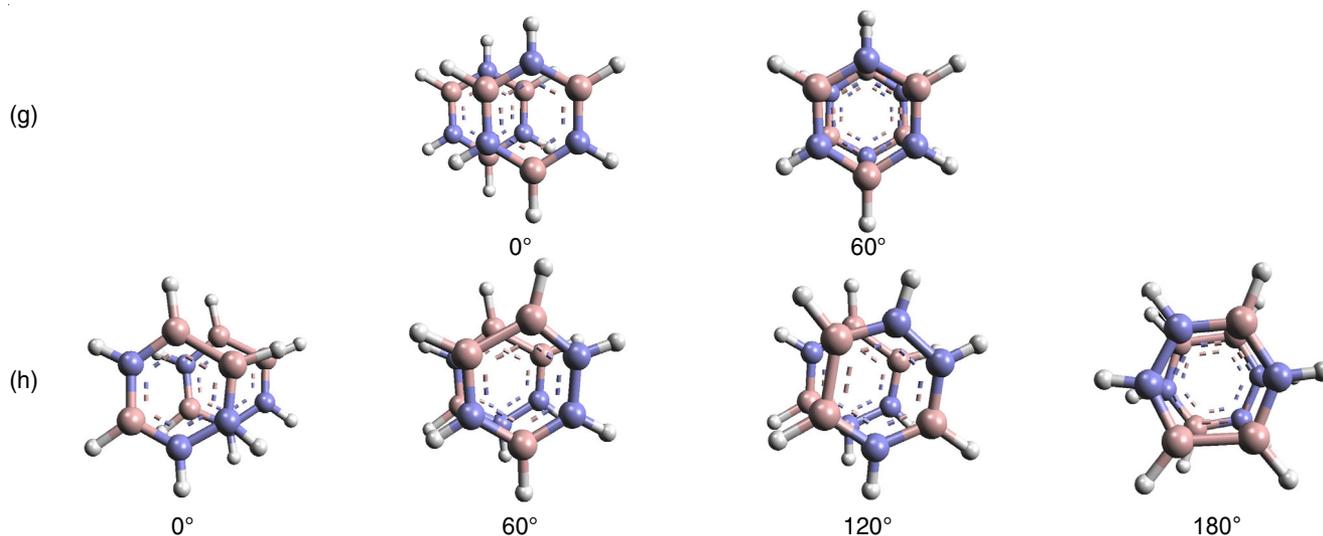


Fig. 5. Minimized stacked models for (a) BZ1-BZ1, (b) BZ2-BZ2, (c) BZ3-BZ3, (d) BZ4-BZ4, (e) BZ5-BZ5, (f) BZ6-BZ6, (g) BZ7-BZ7, and (h) BZ8-BZ8 staking interactions

(Fig. 4a-h). For all the stacked dimer models, it has been observed that in eclipsed and staggered conformations when no horizontal shifting is taking place the interaction energy for the stacked model gives less negative value *i.e.* the maxima in the interaction energy plot (Fig. 4a-h). It happens due to the repulsion between the hetero atoms (B and N) of the rings in the stacked model. But interestingly, some significant change in borazine (BZ7) stacked system has also observed. The staggered conformation with 60° intermolecular rotation for borazine stacked dimer without any horizontal shifting shows minima in the interaction energy plot, which gives the most stable conformation (Fig. 4g). It happens because at 60° intermolecular rotation, the electronegative N atom of one borazine molecule is placed just above on the electropositive B atom of other borazine molecule in the stacked model which shows a strong interaction between N and B atoms of borazine dimer and gives more negative interaction energy value (Fig. 5g and Table-2).

The sequence of stability of the π - π stacking interactions in azaborine dimers and its derivatives with respect to different intermolecular rotation is given below:

- π - π stacking in BZ1 dimer: $0^\circ < 60^\circ < 180^\circ < 120^\circ$
- π - π stacking in BZ2 dimer: $0^\circ < 60^\circ < 120^\circ \sim 180^\circ$
- π - π stacking in BZ3 dimer: $0^\circ < 60^\circ < 120^\circ$
- π - π stacking in BZ4 dimer: $0^\circ < 60^\circ < 120^\circ < 180^\circ$
- π - π stacking in BZ5 dimer: $0^\circ < 60^\circ < 120^\circ \sim 180^\circ$
- π - π stacking in BZ6 dimer: $0^\circ < 60^\circ < 120^\circ < 180^\circ$
- π - π stacking in BZ7 dimer: $0^\circ < 60^\circ$
- π - π stacking in BZ8 dimer: $0^\circ < 60^\circ < 120^\circ < 180^\circ$

From the above studies, it has been observed that staggered conformation for stacked model always gives the most stable stacked conformations than that of eclipsed stacked conformations. In most of the azaborine derivatives, the π - π stacking interaction energy for staggered model increases with increase in intermolecular rotations from 0° to 180° , respectively (Table-2). On the other hand, in BZ2 and BZ5 stacked models the π - π stacking interaction energy increases with intermolecular rotation from 0° to 120° only, but further increase in intermolecular rotation (*i.e.* 180°) the π - π stacking interaction energy remains almost constant. Interestingly, BZ1 stacked model is only one

where the π - π stacking interaction energy is found to be more negative at 120° intermolecular rotation, it happens because of the unsymmetrical repulsion between the B and N atoms of the stacked model (Figs. 3a and 5a).

Conclusion

All azaborine derivatives are not purely aromatic and planer, since they have different B-N bond distances and B-N-B bond angles. Using quantum mechanical studies, it has been observed that they show better π - π stacking interaction in their dimeric form in gas phase. Among all the stacked models of azaborine dimer stacked systems in gas phase, it has been observed that the stacking interaction energies of azaborine model with an eclipsed conformation (with intermolecular rotation = 0°) is found to have the most negative value, *i.e.* -5.55 kcal/mol for BZ3 and gives the stable conformation. On the other hand, for staggered stacked models BZ4 gives the most stable conformation with minimum interaction value -10.95 kcal/mol.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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