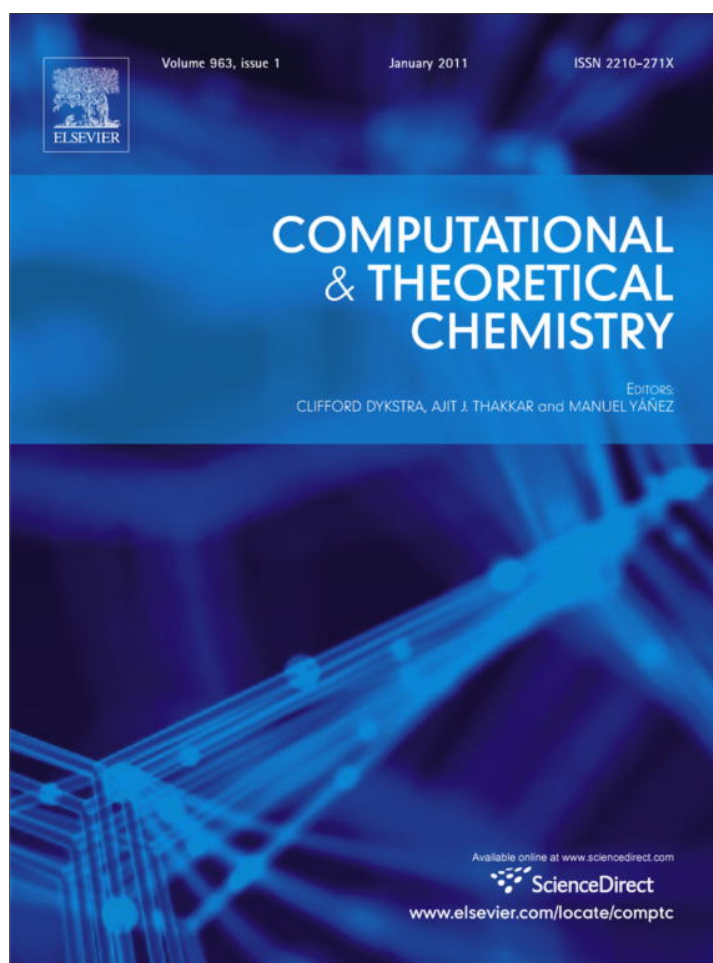


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journal homepage: www.elsevier.com/locate/comptcShort range interactions in molecular complexes of 1,4-benzenediboronic acid with aromatic *N*-oxidesRupam Sarma^a, Pradip K. Bhattacharyya^b, Jubaraj B. Baruah^{a,*}^a Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781 039, Assam, India^b Department of Chemistry, Arya Vidyapeeth College, Guwahati 781 016, Assam, India

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ABSTRACT

Energy of the molecular complexes of 1,4-benzenediboronic acid with different aromatic *N*-oxides (PNO, pyridine-*N*-oxide; QNO, quinoline-*N*-oxide; IQNO, isoquinoline-*N*-oxide; and BPNO, 4,4'-bipyridine-*N,N'*-dioxide) are determined by density-functional theory (using B3LYP and BHandH functionals) and MP2 calculations using the 6-31++G(d) basis set. The optimized structures derived from different ways of hydrogen bonds are compared with the solid state structures obtained experimentally. Two types of orientations, type-1 and type-2, primarily contributing to the hydrogen bond between *N*-O and O-H groups in the molecular complexes are identified and the energy differences between them are compared. The energy differences are in the range of 3–6 kcal/mol. The role of C-H...O interactions contributing to the stability of different hydrogen bond motifs are described. The study on HOMO and LUMO in the cases of the molecular complexes clearly depicts existence of three types of B- π interactions, namely η^2 , η^3 (both B- π -aromatic) and B... π (N=O) interactions.

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1. Introduction

The formation of molecular complexes is governed by hydrogen bonds and other allied interactions [1–3]. Different types of theoretical parameters like molecular orbital, charge on atoms, bond order, etc are commonly employed to correlate reactivity and stability of molecular systems [4]. The density functional theory (DFT) has been employed successfully to study of hydrogen bonding patterns in different types of molecular systems [5–7]. Boronic acids find applications in the fields of synthetic organic chemistry [8], biochemistry [9] and sensors [10]. Due to its structural similarity with carboxylic acids, boronic acids have been widely employed for generation of supramolecular assemblies. Accordingly, numbers of literatures are available on homo-molecular and hetero-molecular assemblies of boronic acids [11]. Among them, the 1,4-benzenediboronic acid (BDBA) is of special interest. The presence of the two B(OH)₂ units makes it a better node for construction of supramolecular architectures. The BDBA possesses a number of hydrogen bonding modes as illustrated in Scheme 1 to form supramolecular assemblies.

Such assemblies can be reorganized by interactions with guest molecules that are capable of forming relatively stronger hydrogen bonds over the existing ones. For this purpose an aromatic *N*-oxide can be of choice, as they are capable of forming strong hydrogen bond with boronic acids [12]. The presence of the partially negative

oxygen atom on aromatic *N*-oxides makes them suitable hydrogen bond acceptor but complicity arises due to numbers of possible hydrogen bonding modes some of which are shown in Scheme 2.

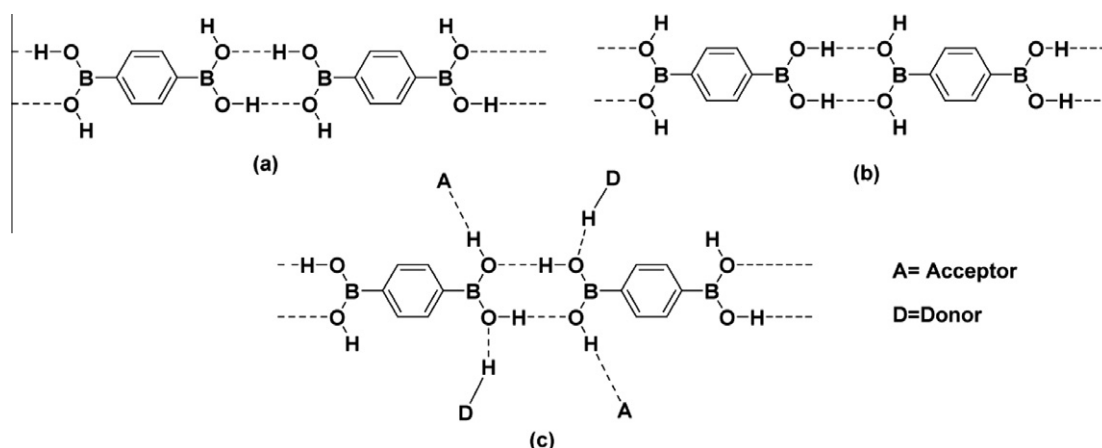
Thus, it is necessary to identify the preferential patterns of hydrogen bonding through a theoretical approach. Further interest on aromatic *N*-oxides has flourished because of their practical impact on biological activity [13]. Weak interactions between different active groups such as a *N*-oxo and a carboxylic or boronic acid (*N*-O...H, O-H...O interactions etc.) do have influence on properties like recognition, solubility or permeability through a medium etc. Thus, we have carried out a theoretical study to make a correlation of weak interactions in molecular complexes formed between some aromatic *N*-oxides and 1,4-benzenediboronic acid that are listed in Chart 1.

2. Computational details

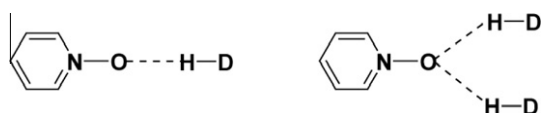
DFT calculations: DFT and MP2 methods are used to observe the strength of hydrogen bonds. The initial coordinates are taken from the geometries obtained from the single crystal X-ray diffraction data. B3LYP and BHandH functionals are used in the DFT calculations [14]. We have used 6-31++G(d) basis set as it is found to be sufficient to predict reliable properties for hydrogen-bonded systems in gas phase [15,16]. The 1:1 molecular complexes are optimized using the B3LYP functional and compared with structures obtained experimentally. Single point calculations on the molecular complexes of different B composition viz. 1:1 to 1:4 are performed using B3LYP and BHandH functional. Although the results

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Scheme 1. Different types of hydrogen bonded interactions among phenylboronic acid molecules.



Scheme 2. Linear and bifurcated hydrogen bonds of *N*-oxides with donor.

obtained by using B3LYP functional do not support the interactions observed experimentally in a few molecular complexes, the results from BHandH calculations agree well with the experimental findings. The consistency of the results of BHandH/6-31++G(d) level calculations are further supported by MP2/6-31++G(d) level of calculations. All calculations are performed using Gaussian03 program [17]. The frequencies of the species are calculated and the optimized geometries are confirmed to be local minima. The counterpoise (CP) correction is incorporated from the basis set superposition error (BSSE) using the Boys and Bernardi procedure in order to correct for the interaction energies [18,19], which were found to be in the range 1–4 kcal/mol.

To express the strength of the hydrogen bonded systems, we have used the term *interaction energy* (interaction energy ΔE_{AB} between two species A and B is defined as $\Delta E_{AB} = E_{AB} - (E_A + E_B)$, where E_{AB} is the energy of the molecular complex, E_A energy of species A and E_B is the energy of species B).

3. Results and discussion

The present study involves the following aspects of molecular complexes of 1,4-benzenediboronic acid and aromatic *N*-oxides such as PNO, QNO, IQNO and BPNO in gas phase. Our observations are divided in five sections.

1. Optimized structures of the hydrogen bonded systems and relevance to their crystal structure.
2. Strength of the type-1 and type-2 interactions.
3. Strength of the hydrogen bonds in different molecular complexes.
4. Energy separations between HOMO-LUMO in the molecular complexes.
5. Interactions between the HOMO of the aromatic *N*-oxides and LUMO of the acid to establish the feasibilities of B- π interactions.

The choice on the system is based on the possible comparison to get realistic picture of the structural features of molecular complexes formed between 1,4-benzenediboronic acid and aromatic *N*-oxide molecules such as PNO, QNO, IQNO and BPNO [11b].

3.1. Optimized structures of the hydrogen bonded systems and relevance to their crystal structure

We have optimized the 1:1 structures of the molecular complexes (at B3LYP/6-31++G(d) level) of BDBA with four different aromatic *N*-oxides (PNO, QNO, IQNO and BPNO) and compared them with those obtained experimentally. From the crystal structures of the systems we have observed the formation of two different types of hydrogen bonds (with different bond length and bond angles) between the $-B(OH)_2$ and *N*-oxo synthons: type-1 and type-2 as shown in the Scheme 3. These orientations are observed for all the cases except BDBA-IQNO system.

The optimized structure of molecular complexes of BDBA and PNO as a representative case is shown in Fig. 1a. The optimized

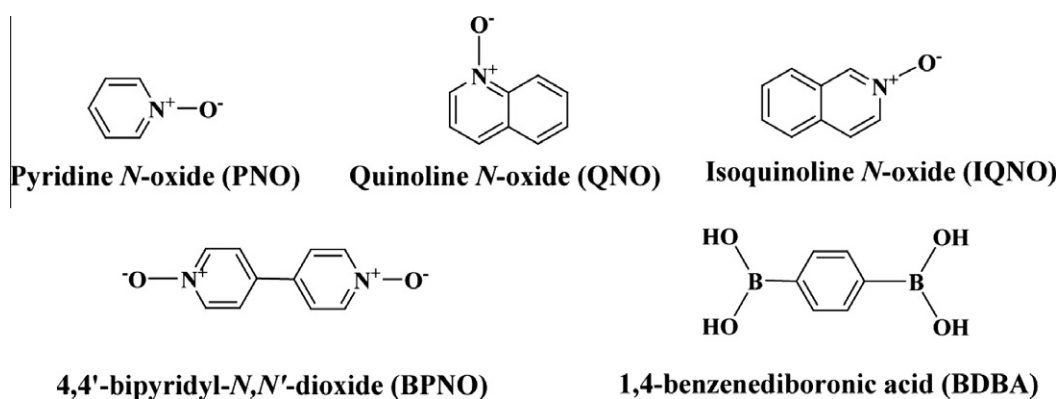
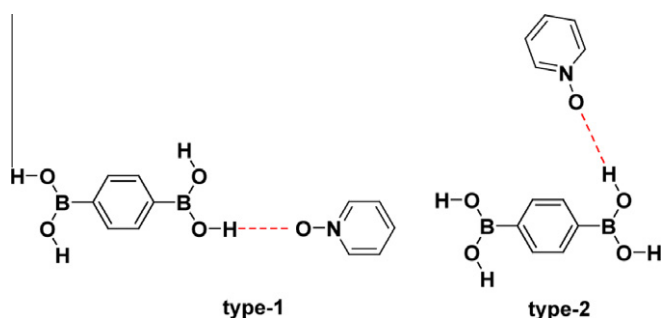


Chart 1. The aromatic *N*-oxides and 1,4-benzenediboronic acid that are studied.



Scheme 3. Two different types of hydrogen bonds between the $-B(OH)_2$ and N -oxo synthons.

structure is in good accord with the type-1 interaction in the crystal structure. The type-1 packing pattern, Fig. 1(b), shows the existence of an $O-H\cdots O$ interaction with $d_{D-H\cdots A}$ (Å), $O3-H4\cdots O21$, 1.91 and $\angle D-H\cdots A$ (°), $\angle O3-H4\cdots O21$, 158 and a secondary $C-H\cdots O$ interaction with $d_{D-H\cdots A}$ (Å), $C31-H32\cdots O1$, 2.35 and $\angle D-H\cdots A$ (°), $\angle C31-H32\cdots O1$, 164. The other packing pattern of the PNO molecule (type-2) leads to a structure having an $O-H\cdots O$ interaction with $d_{D-H\cdots A}$ (Å), $O11-H12\cdots O21$, 1.71 and $\angle D-H\cdots A$ (°), $\angle O11-H12\cdots O21$, 175 (Fig. 1(c)). Moreover there exist two more $C-H\cdots O$ interactions with $d_{D-H\cdots A}$ (Å), $C15-H16\cdots O21$, 2.47; $\angle D-H\cdots A$ (°), $\angle C15-H16\cdots O21$, 161 and $d_{D-H\cdots A}$ (Å), $C23-H24\cdots O11$, 2.59; $\angle D-H\cdots A$ (°), $\angle C23-H24\cdots O11$, 131.

Similar calculations are performed in the case of molecular complexes of BDBA with QNO and BPNO (refer to supplementary data). The optimized geometries of the 1:1 molecular complexes corroborate well with the experimentally determined structures. However, an interesting difference is observed between

the optimized and the structure obtained experimentally of the 1:1 molecular complex of BDBA and BPNO. In case of the optimized structure the two aromatic rings of the 4,4'-bipyridyl- N,N' -dioxide molecule is not exactly coplanar but remains twisted making an angle of 31° with each other, however, this twisting is absent in the crystal structures (refer to Supplementary material) [11b].

3.2. Strength of the type-1 and type-2 interactions

To compare the energies of these two types of orientations (scheme 3) in each of the cases except BDBA-IQNO system, we have performed single point calculations at different levels of theory. The results obtained from B3LYP/6-31++G(d) level of calculations (refer to Supplementary material) do not agree with the interactions observed experimentally and hence we have performed the calculations using the BHandH functional which is used for study hydrogen bond interactions [20a]. Further to this such calculations are used for narrating weak interactions such as π - π interactions in molecular complexes [20b,c]. In present study also the BHandH/6-31++G(d) level of calculations agree well with the experimental findings. The results obtained from BHandH/6-31++G(d) calculations are further supported by MP2/6-31++G(d) level calculations. The comparative energies of the 1:1 molecular complexes in their type-1 and type-2 orientations are shown in Table 1. It is observed that the order of interaction energy in case of type-1 orientation at MP2/6-31++G(d) level is BDBA-QNO < BDBA-BPNO \ll BDBA-PNO (Table 1), whereas in type-2 orientation this order changes to BDBA-BPNO < BDBA-QNO \ll BDBA-PNO. Comparison shows that in each of the cases, the type-2 orientation is energetically more favorable as compared to the type-1 orientation. This difference in the stability can be accounted for by the short range interaction parameters available in each of the

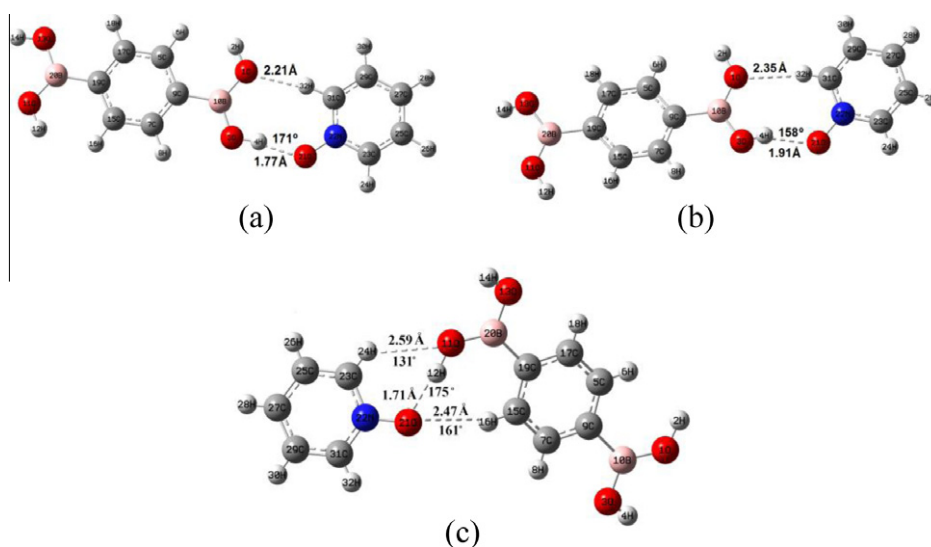


Fig. 1. (a) Optimized structure of 1:1 molecular complex of BDBA and PNO, (b) and (c) structures of 1:1 molecular complex in type-1 and type-2 packing patterns respectively.

Table 1

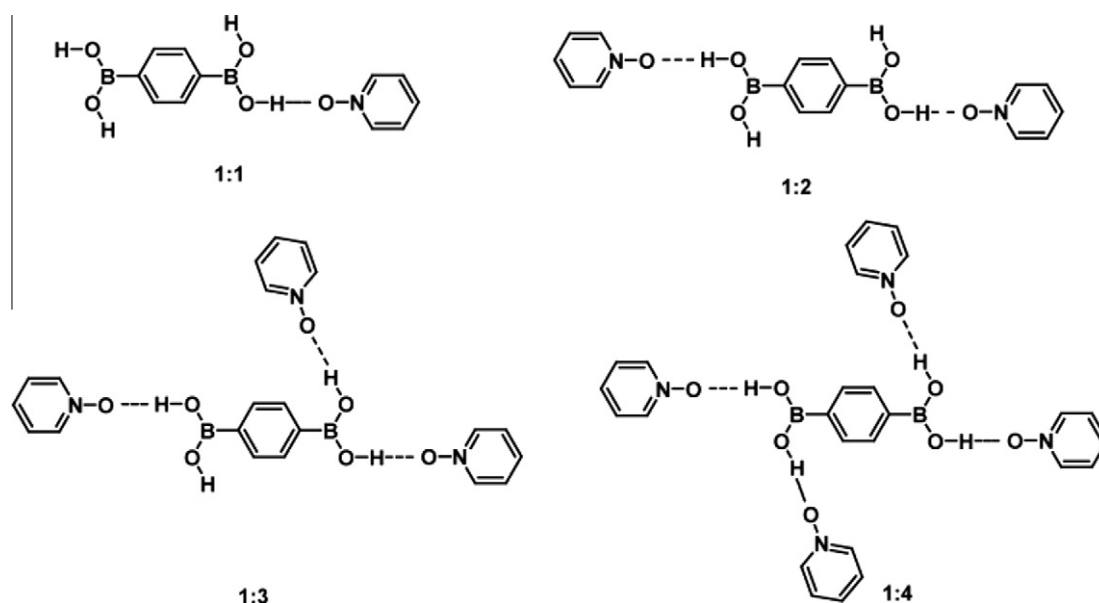
BSSE corrected interaction energies (in kcal/mol) in type-1 and type-2 orientations at BHandH/6-31++G(d) and MP2/6-31++G(d) levels of theory.

Molecular complex	type-1		type-2	
	BHandH/6-31++G(d)	MP2/6-31++G(d)	BHandH/6-31++G(d)	MP2/6-31++G(d)
BDBA-QNO	-8.91	-6.20	-12.63	-11.40
BDBA-BPNO	-9.53	-7.63	-12.41	-10.55
BDBA-PNO	-38.81	-36.86	-49.00	-43.59

Table 2

BSSE corrected interaction energies (in kcal/mol) of different molecular systems at BHandH/6-31++G(d) and MP2/6-31++G(d) levels.

Molecular complex	BHandH /6-31++G(d)				MP2/6-31++G(d)			
	1:1	1:2	1:3	1:4	1:1	1:2	1:3	1:4
BDBA-IQNO	-9.57	-18.99	-30.78	-41.83	-7.22	-14.25	-33.51	-46.76
BDBA-QNO	-8.20	-16.19	-24.09	-37.19	-6.20	-12.20	-22.58	-31.75
BDBA-BPNO	-12.41	-24.07	-29.83	-35.73	-10.55	-19.97	-25.84	-30.76
BDBA-PNO	-18.81	-21.73	-38.11	-53.42	-36.86	-44.28	-57.05	-68.97

**Scheme 4.** Orientations of 1:1, 1:2, 1:3 and 1:4 molecular complexes considered for single point calculations.

different packing patterns. In 1:1 molecular complex between BDBA and PNO, the type-1 orientation provides space for one O–H...O and one C–H...O interaction. In contrast, the type-2 orientation ends up with one O–H...O and two C–H...O interactions. Moreover, the D–H...A distances for type-2 orientation are found to be shorter than the type-1 counterpart. The same is true for BDBA-QNO and BDBA-BPNO molecular complexes.

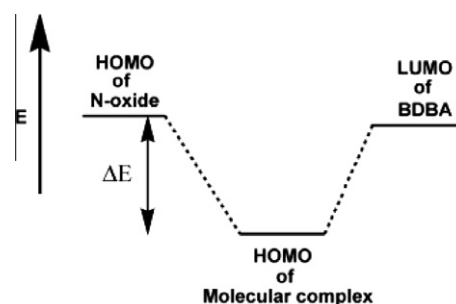
In both the type-1 and type-2 orientations, BDBA-PNO molecular complex exhibit exceptionally high values of interaction energies and this can be accounted for comparatively smaller size of the PNO molecule and hence less steric congestion. The absence of steric congestion in BDBA-PNO molecular complex allow strong interactions with shorter O–H...O distance (1.91 nm in type-1 and 1.71 in type-2, compared to >2.0 nm in other complexes).

3.3. Strength of the hydrogen bonding

We have considered the orientations found in the crystal structures of the molecular complexes and performed single point calculations at BHandH/6-31++G(d) and MP2/6-31++G(d) level of theory. The interaction energies of 1:1, 1:2, 1:3 and 1:4 molecular systems are shown in Table 2. The orientations considered to calculate the interaction energies of the different complexes are illustrated in Scheme 4 by taking BDBA-PNO as an example.

The calculated energies tabulated in Table 2 shows consistency in results and clearly depict strong attractive interactions between the components of the molecular complexes. While systematically moving from 1:1 to 1:4 complex, it is expected that the interaction energies should also increase proportionally as the number of H-bond increases. However, the increment in the energy values is non-uniform. This happens as the number of aromatic N-oxide in-

creases around the BDBA molecule during formation of 1:1 through 1:4 complexes, the steric congestion increases. This increase in the steric congestion, in turn, forces the molecules to re-adjust among them at the cost of some amount of interaction energy which is decided by the structural features associated with the acceptor N-oxide.

**Fig. 2.** Schematic presentation for energy separation of HOMO and LUMO during formation of molecular complexes.**Table 3**The energy of separation ΔE (in kcal/mol) obtained from single point calculation at MP2/6-31++G(d) level of theory.

Molecular complex	ΔE
BDBA-IQNO	-4.65
BDBA-QNO	-8.75
BDBA-BPNO	-4.70
BDBA-PNO	-5.91

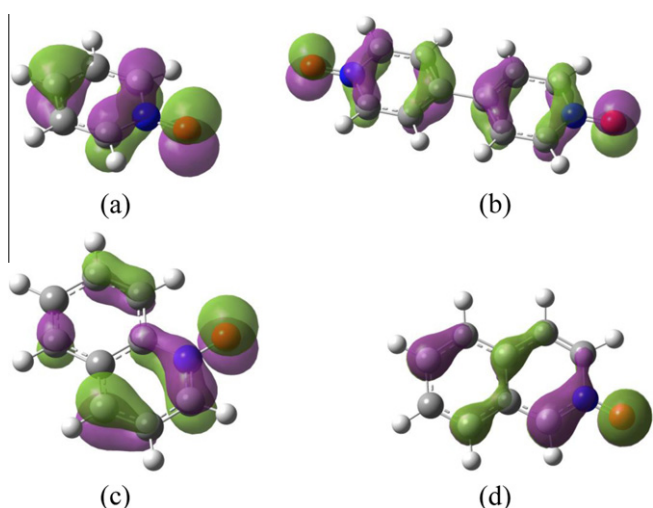


Fig. 3. HOMO of (a) PNO molecule, (b) BPNO molecule, (c) QNO molecule, (d) IQNO molecule.

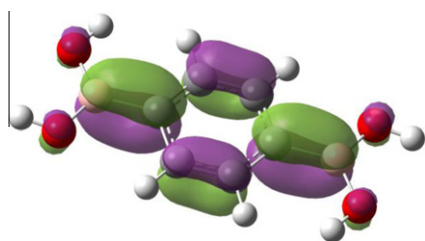


Fig. 4. LUMO of 1,4-benzenediboric acid.

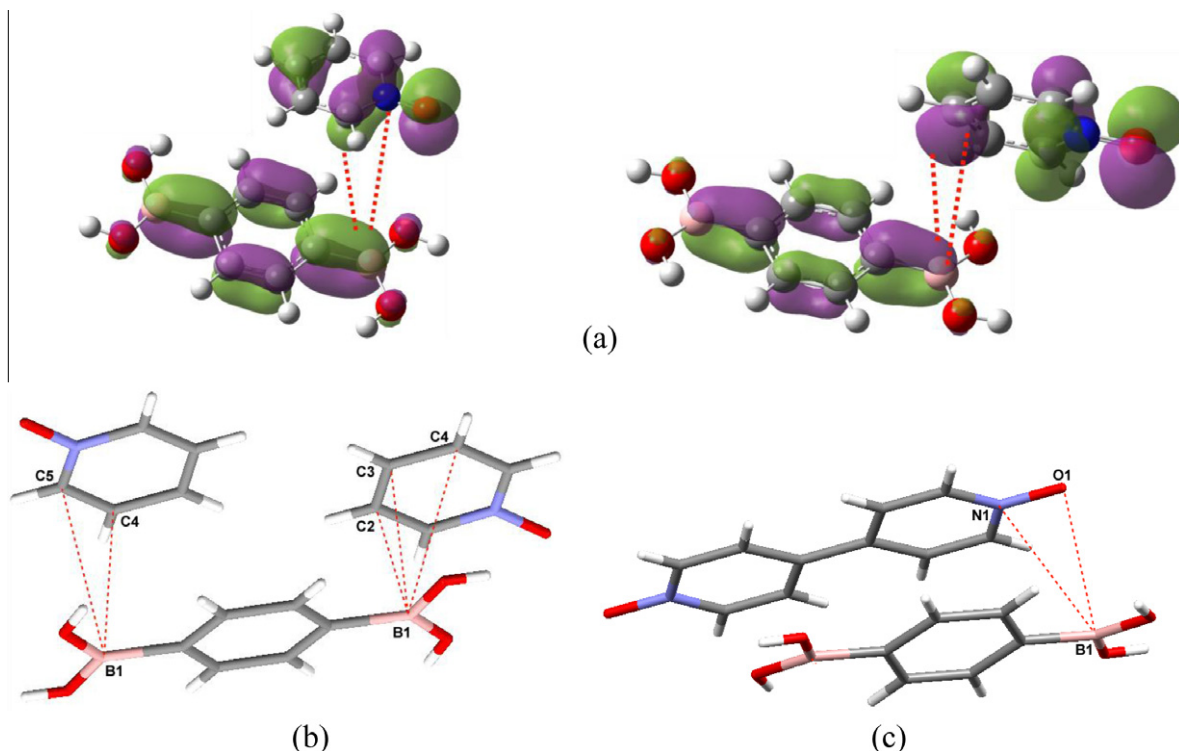


Fig. 5. (a) HOMO–LUMO perspective of the B– π interactions in the case the BDBA–PNO molecular complex; B– π interactions between BDBA and (b) PNO, (c) BPNO in their molecular complexes observed experimentally.

In case of BDBA–IQNO the isoquinoline *N*-oxide molecules are in parallel orientation to each other, are less sterically hindered and hence the increase in interaction energy is somewhat proportionate.

3.4. Energy separations between HOMO–LUMO in the molecular complexes

In a synergic effect of $B + HA \rightleftharpoons BHA$ type (where $B = N$ -oxide; $HA = BDBA$) of hydrogen bonding interactions, intermolecular hydrogen bond formation favors when the HOMO of the BHA has lower energy than the HOMO of B or LUMO of HA [21]. To observe such energy of separation $\Delta E (= E_{HOMO,BHA} - E_{HOMO,B})$ as shown in Fig. 2, single point calculation on the geometry obtained from crystal structures of each individual species namely B and BHA were performed.

The ΔE values for the different molecular complexes are shown in Table 3, which clearly shows that the energy of HOMO of the molecular complexes is lower than the energy of the HOMO of the *N*-oxides and the energy of LUMO of the BDBA. This indicates that hydrogen bond formation is favorable in all cases.

3.5. Interactions between the HOMO of the aromatic *N*-oxides and LUMO of the acid to establish the feasibilities of B– π interactions

The HOMO of the electron donor (H-acceptor) and LUMO of the electron acceptor (H-donor) plays important role during the formation of hydrogen bonds [21]. During formation of molecular complex the HOMO of the aromatic *N*-oxides and LUMO of BDBA are involved. The HOMO of the four *N*-oxides are shown in Fig. 3 and the LUMO of 1,4-benzenediboric acid are shown in Fig. 4.

It can be easily seen from Fig. 3 that in all four examples the HOMO is associated with the O atoms and some portion spreading over the aromatic N–C bond. This depicts that the O atom can act

as an electron donor. Hence, it readily participates in hydrogen bonding. The LUMO of 1,4-benzenediboronic acid is quite symmetric, it spreads over the B–C and C–C bond of the ring (Fig. 4).

A careful look on the HOMO of the PNO and BPNO shows that the HOMO is symmetrically distributed over the aromatic ring, whereas, in case of QNO and IQNO the HOMO is less symmetric. This symmetric arrangement of the HOMO of PNO and BPNO explains the B– π interactions of PNO or BPNO with BDBA molecule. In fact such B– π interaction is clearly observed, experimentally in the molecular complexes of BDBA with both PNO and BPNO [11b]. In the case of BDBA–PNO molecular complex one η^2 and one η^3 types of B– π (aromatic) interactions are observed; similar interactions are also depicted experimentally [11b]. The perspective of HOMO–LUMO for the occurrence of B– π interaction in the case the BDBA–PNO molecular complex is shown in Fig. 5(a) whereas Fig. 5(b) shows the experimentally observed interactions. Similarly, in the case of BDBA–BPNO molecular complex a B– π (N=O) interaction is observed as shown in Fig. 5(c).

4. Conclusion

In conclusion we have shown that depending on the orientation of the hydrogen atoms of B–OH bond there are two different types of hydrogen bonding orientations operative in the formation of molecular complexes between 1,4-benzenediboronic acid and aromatic *N*-oxides. There exist significant differences in the interaction energies of the different 1:1 molecular complexes of BDBA and aromatic *N*-oxides in the two different orientations type-1 and type-2. Comparison between the interaction energies of molecular complexes having different composition reveals an increasing order on moving from 1:1 towards 1:4. However, the non-uniformity in the increase in energies in different molecular complexes with respect to composition may be accounted for by the steric factors involved. The orientations of the HOMOs of aromatic *N*-oxides and the LUMO of BDBA clearly depict the existence of B– π interactions in the BDBA–PNO and BDBA–BPNO molecular complexes. A generalized approach to understand weak interaction in molecular complexes of 1,4-benzenediboronic acid with aromatic *N*-oxides is brought forward.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.comptc.2010.10.020.

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