



Short range interactions in molecular complexes of 1,4-benzenediboronic acid with aromatic *N*-oxides

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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.

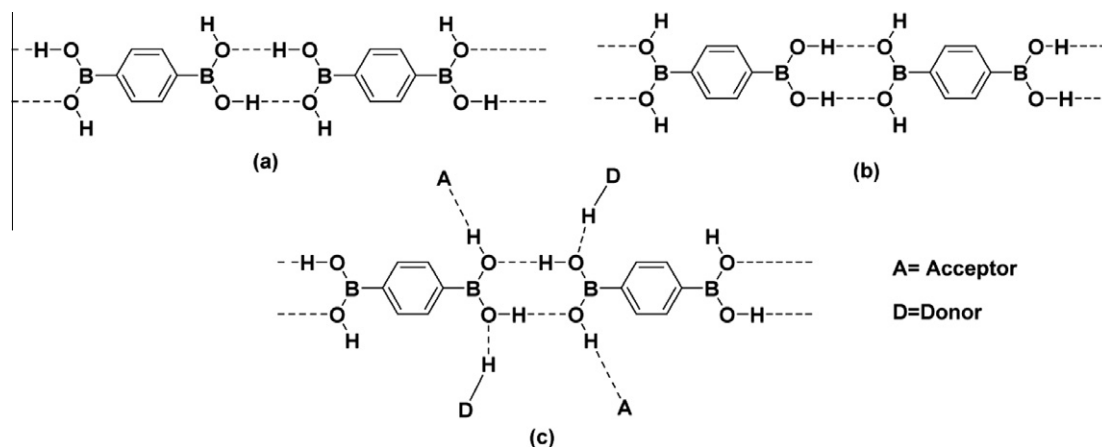
Thus, it is necessary to identify the preferential patterns of hydrogen bonding through a theoretical approach. Further interest on aromatic *N*-oxides has flourished because of their practical impact on biological activity [13]. Weak interactions between different active groups such as a *N*-oxo and 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

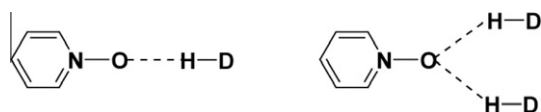
DFT calculations: DFT and MP2 methods are used to observe the strength of hydrogen bonds. The initial coordinates are taken from the geometries obtained from the single crystal X-ray diffraction data. B3LYP and BHandH functionals are used in the DFT calculations [14]. We have used 6-31++G(d) basis set 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 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

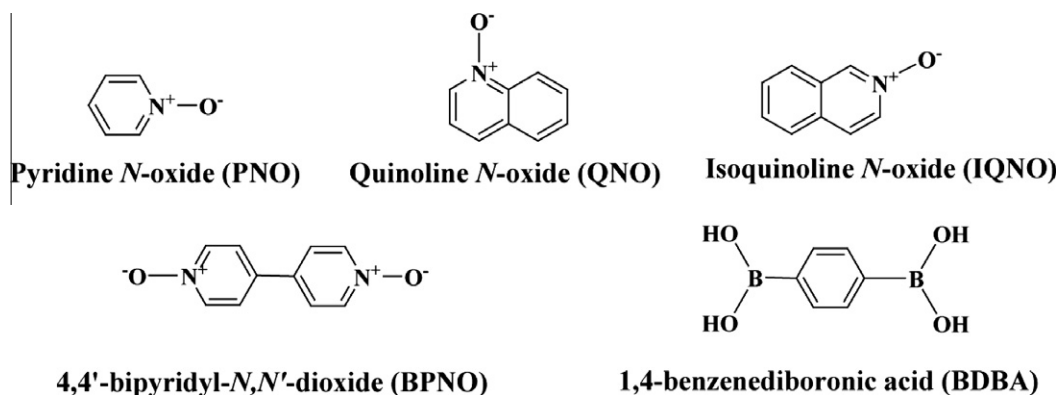


Chart 1. The aromatic *N*-oxides and 1,4-benzenediboronic acid that are studied.

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