

Research Article

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Sequential Hexagonal Water Sheets in 2,5-Thiophenediboroic Acid Layers

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Abstract: The crystal structure of 2,5-thiophenediboroic acid (tdba) tetrahydrate is reported here. The water molecules constitute a hexagonal sheet, which is embedded in between the layers of tdba. Such hexagonal water sheet is templated by the boronic acid moieties through O-H...O hydrogen bonds. The supramolecular assemblies of this type with discrete solvent cluster might provide pre-model to understand the solute-solvent interactions in the solution media.

Keywords: diboroic acid, self assembly, hexagonal water sheet, crystal structure.

1. INTRODUCTION

Solvent evaporation method is a classic and an elegant process, often utilized for the preparation of organic supramolecular assemblies in the form of crystalline materials.¹⁻⁵ In this method, during the process of self assembly of the solute molecules, sometimes, solvent molecule(s) from the pool also include into the resultant molecular solids.⁶⁻¹⁰ The number of solvent molecules would be included in such molecular solids varies depending upon the availability of interaction sites in that molecular assemblies.¹¹⁻¹⁵ Further, whatsoever the number of solvent molecules included in the molecular solid, it is apparent that, the exact bulk property of the liquid solvent could not be revealed. However, solvent molecules with discrete cluster formation embedded in the molecular solids might provide a preliminary idea about the behaviour of the solute molecules in the solution, especially their interaction with solvent molecules.

Water inclusion in molecular ensembles sometimes is a cursory, because of its small size and maximum of four hydrogen bonding sites.¹⁶⁻²⁰ Further, in general, the viability of water inclusion would be higher for the molecular assemblies with unequal number of hydrogen bonding donors and acceptors.²¹ For instance, carboxylates include water at ease as compared to carboxylic acids.²²⁻²⁷ Towards revealing the formation of cluster of water in molecular solids, depending upon the availability of hydrogen bonding groups in the host molecules, two simple terephthalate salts, tetraethylammonium terephthalate hexahydrate (**1**) and bis(2-amino-4-methylpyridinium) terephthalate tetrahydrate (**2**) were taken as representative examples randomly.^{28,29} Both the salts possess terephthalate ion with different counter

cation of different hydrogen bonding abilities. The arrangement of water in the molecular complexes is shown in Figure 1. The terephthalate ions of **1** interact to all six water molecules and constitute a sheet structure as shown in Figure 1a. However, the counter cation without any

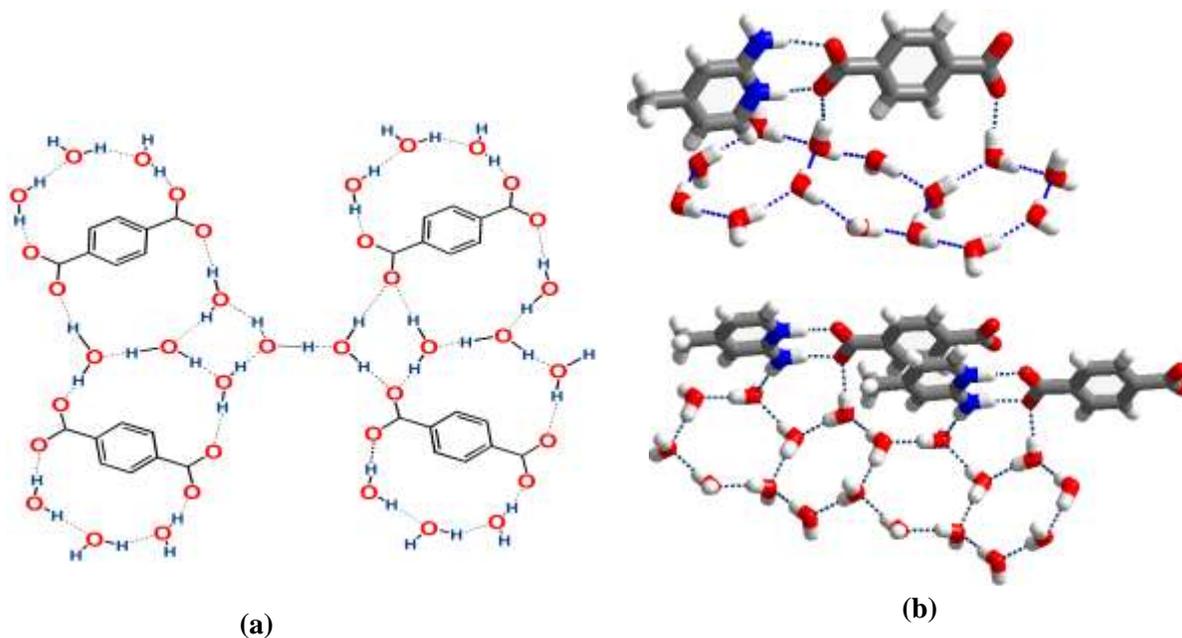


Figure 1. Interaction of water molecules in the molecular assemblies of a) terephthalate-water cluster in tetraethylammonium terephthalate b) 2-aminotoluidinium terephthalate with hexagonal water tape.

hydrogen bonding groups forms a separate layer of its own through van der Waals interactions.²⁸ In case of **2**, the counter cation, 2-amino-4-methylpyridinium ion, with hydrogen bonding donor groups interacts to the terephthalate ion through $N-H...O/N^+-H...O^-$ dimeric hydrogen bonds with $R_2^2(8)$ hydrogen bonding geometry. As a result, the water molecules included in the molecular assembly of **2** form a discrete cluster as a hexagonal ribbon (Figure 1b). Thus, suitable hydrogen bonding groups in **2** direct the formation of discrete water cluster and, although, such cluster is not present in **1** even with six water molecules. Extension of the water cluster of **2** from ribbon to a sheet or any other higher order water cluster might give a pre-model to understand the water-solute interaction in aqueous medium as the large water cluster might provide a precise data compared to the small one. In this regard, a hint could be taken from the supramolecular assembly of **2**, for the extension of its hexagonal water ribbon to at least a hexagonal sheet. For that we have reasoned to extend the parallelly arranged $R_2^2(8)$ dimeric unit, 2-amino-4-methylpyridinium-terephthalate, which templates the hexagonal water ribbon, to any higher order supramolecular pattern such as chain. Such higher order supramolecular ensemble might template higher order water clusters and in case of chain, it would be a hexagonal water sheet. Although, many supramolecular chain with $R_2^2(8)$ hydrogen bonding geometry would be invoked as a template, phenylenediboronic acid (pdba) with diboronic acid group³⁰ complies this surmise with the formation of hexagonal water sheet embedded in its supramolecular assembly. Thus, towards preparation of hexagonal water sheet mediated by diboronic acid, we have succeeded with 2,5-thiophenediboronic acid which might assist in understanding the solute-water interactions in the aqueous media as discussed below.

2. EXPERIMENTAL SECTION

2.1 Synthesis of tdba.4H₂O

Good quality crystals of tdba.4H₂O were obtained using the slow evaporation method by dissolving 25mg of tdba in 10 mL of 1:1 ratio mixture of methanol and water.

2.2 X-ray Structure Determination

Good quality single crystals of tdba.4H₂O were carefully selected using Leica microscope and glued to a glass fibre using an adhesive (cyanoacrylate). The crystal is smeared in the adhesive solution to prevent decomposition. The intensity data were collected on a Bruker single-crystal X-ray diffractometer, equipped with an APEX detector. Subsequently, the data were processed using the Bruker suite of programs (SAINT), and the convergence was found to be satisfactory with good R_{ini} parameters. Absorption corrections were applied using SADABS package. The structure determination by direct methods and refinements by least-squares methods on F^2 were performed using the SHELXTL-PLUS package.³¹ The processes were smooth without any complications. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms are treated isotropically. All the intermolecular interactions were computed using PLATON.³² All packing diagrams are generated using Diamond software.³³

3. RESULTS AND DISCUSSION

Crystallization of 2,5-thiophenediboronic acid from methanol/water (1:1) gave a platelet crystals suitable for single crystal X-ray diffraction analysis and the structural data³⁴ reveals inclusion of four water molecules with respect to tdba. The two boronic acid groups in tdba show the syn-anti conformation as observed for many other boronic acids,³⁵⁻⁴¹ however, with rare cisoid conformation. The tdba molecules interact with each other through a typical $R_2^2(8)$ dimeric O-H...O hydrogen bonding pattern as shown in Figure 2a. Four water molecules of each connected to the two boronic acid groups of tdba on both sides through O-H...O hydrogen bonds (Figure 2b). Further, the molecular assembly in three dimension shows stacked sheet structure of alternate layers of tdba and water molecules (Figure 3a) which resembles the structure of pdba.4H₂O.

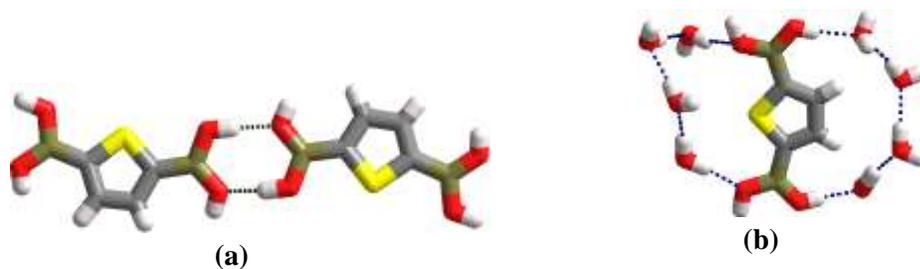


Figure 2. a) Boronic acid interaction through $R_2^2(8)$ dimeric O-H...O hydrogen bonding pattern. b) Connected boronic acid groups of tdba by water molecules through O-H...O hydrogen bonds.

The tdba molecules form a chain structure in its layer utilizing O-H...O dimeric hydrogen bonds. Such chains interact laterally through B- π interactions with the distance of $\sim 3.4 \text{ \AA}$ (Figure 3b). The water cluster shows a hexagonal sheet arrangement along the crystallographic b direction as shown in Figure 4a. The boronic acid chains are arranged parallel to each other in the water sheet (Figure 4b).

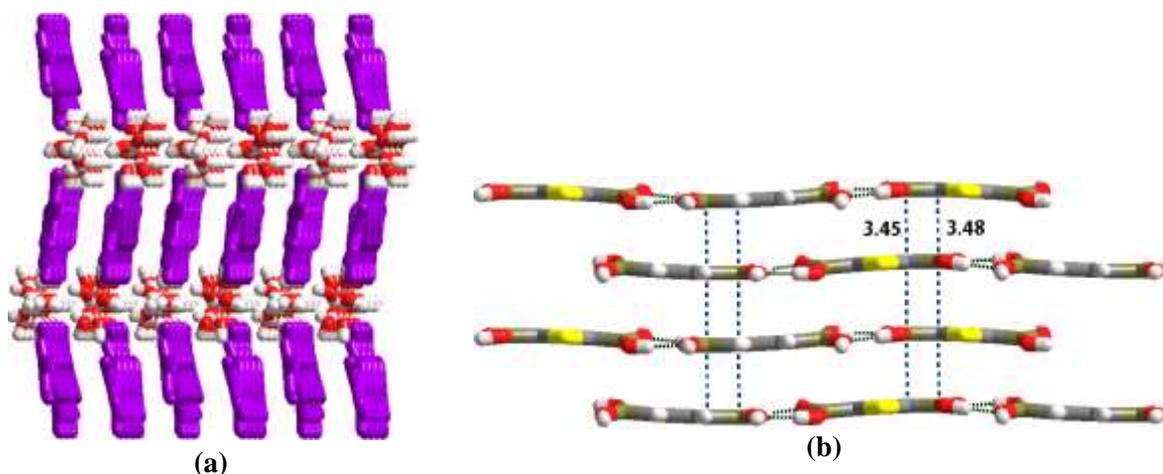


Figure 3. a) Alternate sheets of tdba and hexagonal water sheet in tdba.4H₂O. b) Typical sheet structure of tdba with B- π interactions.

The hexagonal water sheet constitutes two different six-membered rings with twist-boat and half chair conformation as shown in Figure 4c. The bond length between the oxygen of water molecules in the water sheet shows a range of 2.753-2.878 Å with average of 2.805 Å, and the tetrahedral angles are in the range of 85.7° to 130.6° with deviation of ~21° from the ideal tetrahedral angle. Such large deviation in bond angle and bond length infers the awkward sheet structure because of the flexible nature of the hydrogen bonds.

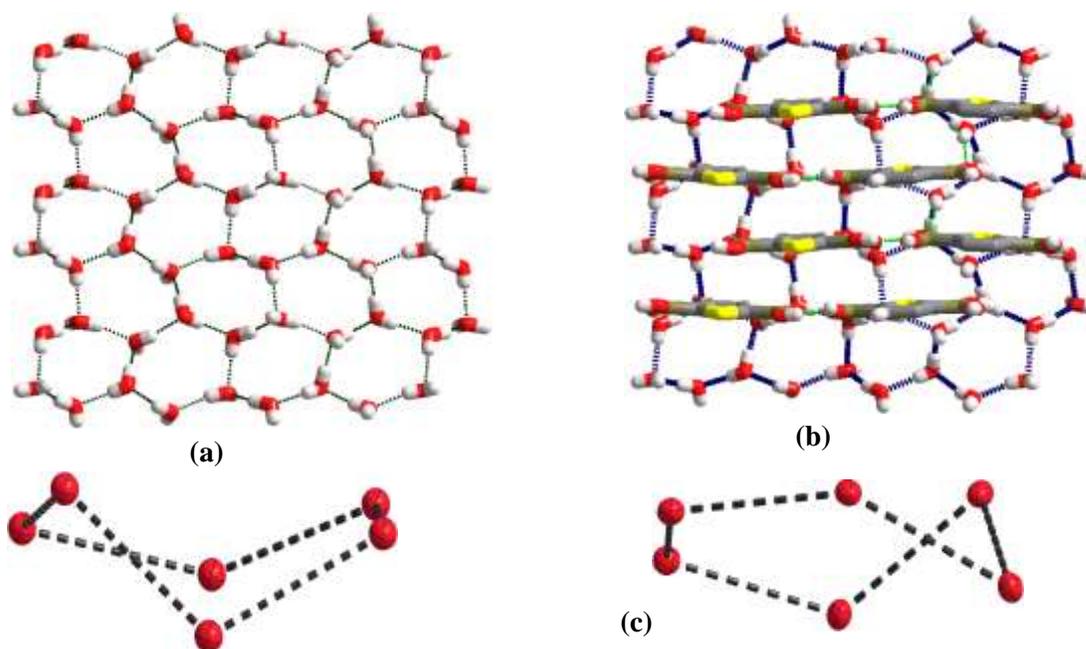


Figure 4. a) The hexagonal water sheet arrangement in tdba.4H₂O. b) Perpendicular stacking arrangement of tdba with respect to the water sheet. c) Twist-boat and half-chair conformations of the hexagonal rings of the hexagonal water sheet of tdba.4H₂O.

Further analysis of the hexagonal water sheet shows a helical pattern of water molecules running along *a* direction. The helices are running opposite to each other and are connected as shown in Figure 5a. Apart from that, as the hydrogen atoms in water molecules are refined reasonably, the flow of hydrogen bonding from donor to acceptor in the hexameric rings are analysed as shown in Figure 5b. The six membered ring with half chair conformation shows the hydrogen bonding flow throughout the ring as circular. However, the hexamer with twist-boat conformation shows two opposite flow of hydrogen bonds. Further, the neighbours of the respective hexamer rings show the opposite hydrogen bonding flow either as circular or half circle (Figure 5b).

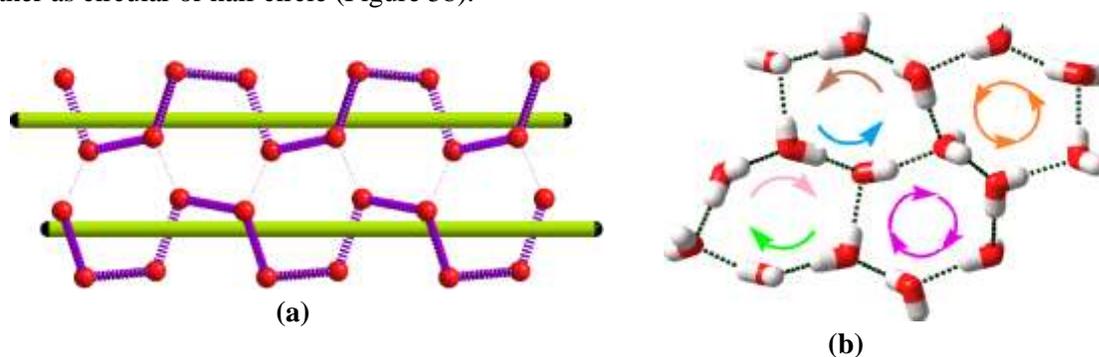


Figure 5. a) Helical arrangement of water in the hexagonal water sheet. b) Flow of hydrogen bonding the hexameric ring of water sheet.

It is important to compare the $\text{pdba} \cdot 4\text{H}_2\text{O}$ and $\text{tdba} \cdot 4\text{H}_2\text{O}$ molecular assemblies, as both of them form nearly similar sandwich molecular assemblies in three dimension. Such comparison might provide the similar/dissimilar features between the molecular assemblies to understand the influence of the diboronic acid in the formation of such supramolecular assemblies. In this respect, both the boronic acids include four water molecules with respect to their stoichiometric ratio and the boronic acid groups adapt syn-anti conformation. However, the two boronic acid groups of *tdba* and *pdba* possess the cisoid and transoid conformations respectively. Such conformational change in the boronic acids, although, does not affect the primary interaction of water molecules as both boronic acid group of the diboronic acids connected through four water molecules on each side of the molecule. In spite of such similar molecular recognition pattern, notable differences were also observed; the placement of boronic acid chain on the water sheet is different as shown in Figure 6, where *pdba* chain run diagonally along the water sheet, however, the *tdba* chain run parallelly along the *c* direction of the *ac* plane sheet.

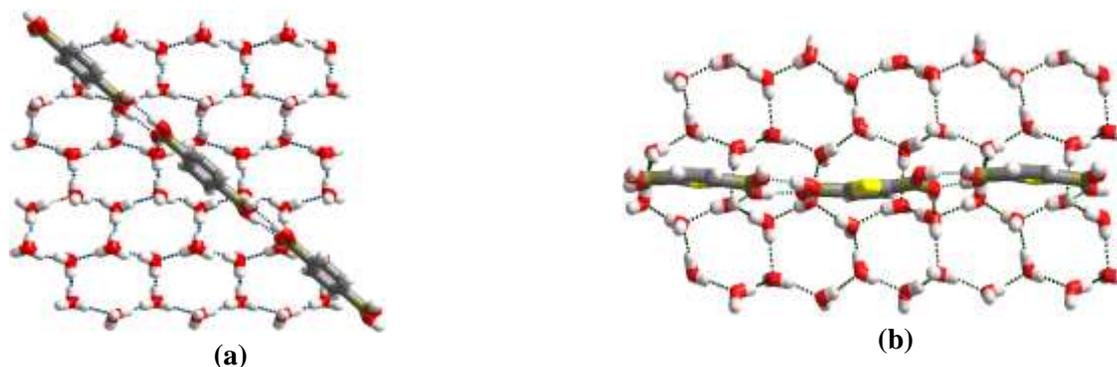


Figure 6. a) Arrangement of boronic acid tapes on the hexagonal water sheet a) $\text{pdba} \cdot 4\text{H}_2\text{O}$. b) $\text{tdba} \cdot 4\text{H}_2\text{O}$.

Apart from that, the boronic acid chain of pdba tilted 67.39° to the plane of water cluster; however, for tdba it is 73.65° . Further, the boronic acid groups constitute a straight chain in pdba, however, a slight zig-zag pattern for tdba due to its molecular skeleton (Figure 7). Such an arrangement might have result into the variation in the hexagonal water cluster assemblies of tdba.4H₂O, where the rings possesses different conformation such as twist-boat and half-chair conformation with respect to chair and boat conformation observed in pdba.4H₂O.



Figure 7. Chain structure of diboronic acid with $R_2^2(8)$ hydrogen bonding pattern a) pdba b)tdba

Interestingly, within the diboronic acid (tdba.4H₂O and pdba.4H₂O) mediated hexagonal water sheet, a major difference observed is the arrangement of diboronic acid molecules on the water sheet assembly as shown in Figure 6, and such change is result into a different template effect in spreading the water molecules in two dimensions. In spite of such different packing arrangements of the supramolecular assemblies of tdba.4H₂O and pdba.4H₂O, the interaction of boronic acids to the water sheet is almost same. Thus, both the boronic acids might behave similar in the aqueous solution with little variation. It would be interesting to analyse other organic assemblies containing varied host molecules with discrete hexagonal water sheet. Such analysis of variable behaviour of different host molecule to the water sheet might provide valuable information for the behaviour of the organic molecules in the aqueous media. For that purpose, there are five organic molecular assemblies possessing the hexagonal water sheet, including the boronic acid tetrahydrates are discussed here,^{30,42,43} and they are classified into two groups; one with the ratio of 1:4 ratio of solute and water (group I), and the other with 1:2 ratio (group II). In the group I molecular ensembles, the host molecules interact to the water sheet through both of their hydrogen bonding donor and acceptor groups. However, the host molecules in the second group interact to the water sheet only through the hydrogen bonding acceptors. Interestingly in all the molecular assemblies only the axial hydrogen bonding sites are involved in the interaction with the solute molecules and the equatorial sites involved in extending the water sheet in its plane (Figure 8)

As a result, the molecular skeleton of the host molecules are pushed away orthogonally from the polar water sheet not below than 65° from the plane of water sheet. Further, the host molecules in the first group form interaction to each water molecules in the hexameric ring, however, only three molecules are involved in hydrogen bonding to the solute molecules in the second group as shown in Figure 8 (Table 1).

Thus, a four centred tetrahedral hydrogen bonding is observed for all the water molecules in the first groups, however, water molecules which do not interact to the solute molecules involved in three centred bond for the second group which is utilized only to extend the water sheet (Figure 8). The dumped hydrogen bonding sites of such water molecules are because of the close proximity of the hydrophobic group substituted on the host molecule as shown in Figure 9.

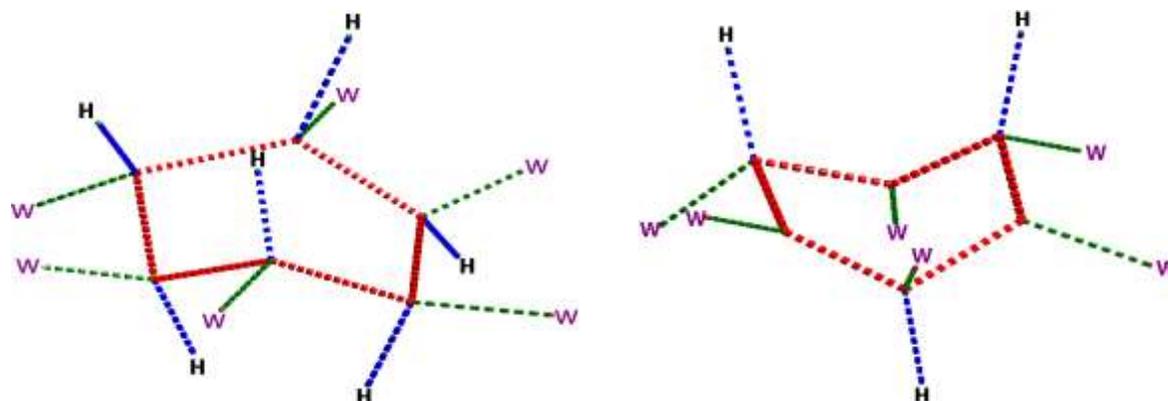


Figure 8. Typical interaction of water molecules in the hexamer of a) group I and b) group II.

Table 1. Direction of the hydrogen bonding pattern of the water to the solute molecules.

Sl.No.	Compound	Hydrogen bonding interaction of water to the host molecules in a hexameric ring					
		✓	✓	✓	✓	✓	✓
1	2,3-Diaminophenazine.4H ₂ O	✓	✓	✓	✓	✓	✓
2	2,5-Thiophenediboronic acid.4H ₂ O	✓	✓	✓	✓	✓	✓
3	1,4-Phenylenediboronic acid.4H ₂ O	✓	✓	✓	✓	✓	✓
4	bis(dimethylamino)squaraine.2H ₂ O	✓	X	✓	X	✓	X
5	Dimethyladenine.2H ₂ O	✓	X	✓	X	✓	X

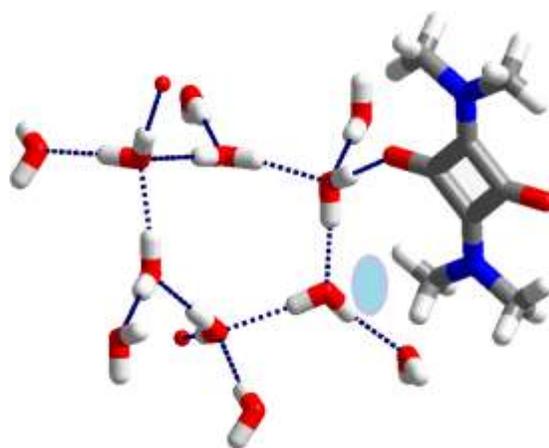


Figure 9. Hydrophobic effect of methyl group of bis(dimethylamino)squaraine.2H₂O near to the water molecule to deactivate the hydrogen bonding ability of the water molecule.

4. CONCLUSION

The crystal structure of tdba.4H₂O reveals the template effect of the diboronic acid moiety to obtain a hexagonal water sheet as observed in the case of pdba.4H₂O. The different molecular skeleton of

these boronic acids templates varied hexagonal water sheet arrangement in their resultant assemblies. Further, the boronic acids chains with $R_2^2(8)$ hydrogen bonding pattern are arranged differently on the hexagonal water sheet. However, the basic molecular interactions between the water sheet assemblies and the boronic acids are nearly the same. Thus, these diboronic acids might behave almost same in the aqueous medium with little differences. Further, evaluation of the interaction of the boronic acids to the hexagonal water sheet shows deflection of the host molecules to the polar water sheet due to the hydrophobic effect. Such an observation is also noted in other reported molecular assemblies with discrete hexagonal water sheet. Apart from that, although the molecular skeleton of the host molecule is arranged orthogonal to the water sheet, the substituted hydrophobic groups on the host molecules which are forced to proximate the water sheet dumps one of the hydrogen bonding sites of water in the water sheet. Thus, these different behaviours of host molecules to the water sheet in terms of their interactions might provide valuable information about the water-solute interaction in the aqueous media.

ACKNOWLEDGMENT

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SUPPORTING INFORMATION AVAILABLE

X-ray data in CIF format, this information is available free of charge via the Internet at <http://pubs.acs.org>.

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The authors declare no conflict of interest

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