Tetrahedron Letters 51 (2010) 6901–6905

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

$-B(OH)_2$ versus –OH in supramolecular synthesis: molecular complexes of 4-hydroxyphenylboronic acid with aza-donor compounds

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ARTICLE INFO

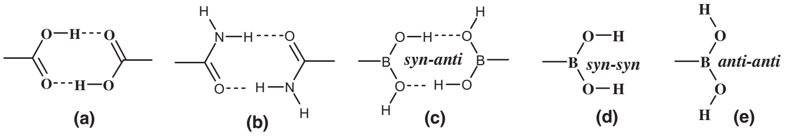
Article history:
Received 28 September 2010
Revised 18 October 2010
Accepted 24 October 2010
Available online 30 October 2010

Keywords:
Boronic acid
Co-crystallization
Molecular recognition
Hydrogen bonds

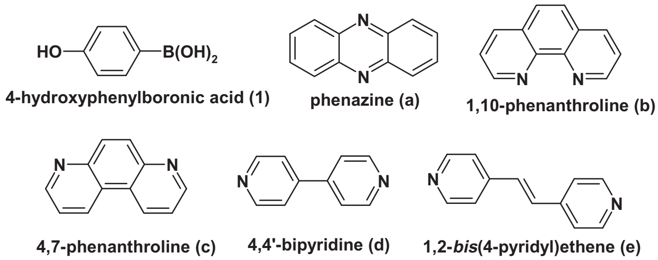
ABSTRACT

$-B(OH)_2$ moiety forms interactions with aza-donor compounds as much as –OH does, as derived from the supramolecular assemblies of 4-hydroxyphenylboronic acid with aza-donor compounds demonstrating for the first time, a comparative study of $-B(OH)_2$ versus –OH.

In supramolecular synthesis, recognition between the complimentary functional groups is a key factor for the evaluation of influence of noncovalent interactions in the formation of specific architectures.[1–4] In this process, in recent times, boronic acids, with general formula $R-B(OH)_2$, have been well considered to be of potential co-crystal formers,[5,6] as much as other well known organic entities with functional groups like –COOH, $-CONH_2$, –OH, etc.,[7–9] especially due to the ability of the $-B(OH)_2$ functionality



Scheme 1.



reactants	products
1 + (a)	1a
1 + (b)	1b
1 + (c)	1c
1 + (d)	1d
1 + (e)	1e & 1e'

Chart 1.

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doi:10.1016/j.tetlet.2010.10.126

to form a variety of hydrogen bonds through different conformations, identified as *syn–anti*, *syn–syn,* and *anti–anti*, as depicted in Scheme 1.

Also, competitive nature of $-B(OH)_2$, in the presence of functional groups like –COOH, was well explored.[6a–c] However, studies related to the efficacy of $-B(OH)_2$ versus –OH, in supramolecular synthesis are apparently not known although $-B(OH)_2$ is known to have affinity toward pyridyl *N*-atoms, as similar to –OH moiety, with the formation of O–H···N hydrogen bonds, as observed in some co-crystals of boronic acids with aza compounds.[5a,10] Thus, we considered co-crystallization studies of 4-hydroxyphenylboronic acid, which have both –OH and $-B(OH)_2$ moieties, with some aza-donor compounds, as listed in Chart 1, having pyridyl *N*-atoms at different positions and we report, herein, the salient features of these structural assemblies.

Co-crystallization of 4-hydroxyphenylboronic acid, **1**, with phenazine gave a 1:1 complex, **1a**,[11] in the form of a layered structure. Within a typical layer, both the co-crystal formers interact with each other through O–H···N hydrogen bonds (H···N, 1.81 Å), established between –OH group of **1** and pyridyl *N*-atoms of phenazine, which is further complimented by C–H···N (H···N, 2.70 Å) hydrogen bonds, yielding a quartet network, as shown in Figure 1a. Thus, $-B(OH)_2$ moiety did not interact directly with phenazine, but formed O–H···O (H···O, 1.91 Å) hydrogen bonds, as shown in Figure 1b, connecting the adjacent ensembles of quartets shown in Figure 1a, in the three dimensional packing (see the Fig. 1c).

Nevertheless, in the co-crystals of **1** with 1,10-phenanthroline,[11] the complimentary molecules recognize each other through the formation of O–H···N hydrogen bonds (H···N, 1.92 Å) exclusively formed by $-B(OH)_2$ moiety with hetero *N*–atom of phenanthroline. Indeed, the boronic acid, **1** adopts *syn–syn* conformation and glue to both the *N*-atoms on phenanthroline (Fig. 2a).

Further, as observed for $-B(OH)_2$ in complex **1a**, the –OH group in complex **1b** is involved in the formation of O–H···O (H···O, 1.89 Å) hydrogen bonds that are involved in the aggregation of the ensembles as shown in Figure 2b in the form of crinkled tapes, which, in turn, are packed in three dimensional arrangement such that phenanthroline molecules are sandwiched between the layers of molecule **1**.

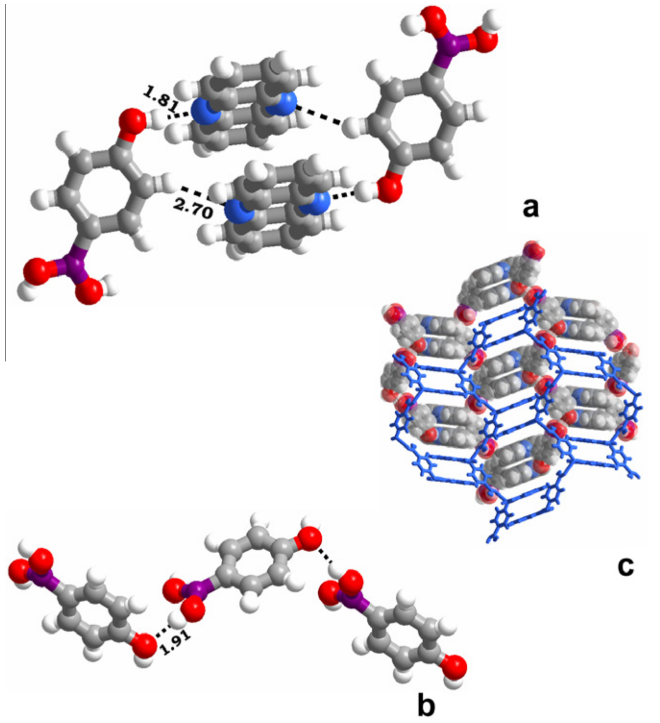

Figure 1. (a) Recognition pattern between the co-crystal formers 4-hydroxyphenylboronic acid and phenazine in **1a**; (b) O–H···O hydrogen bonds formed by $-B(OH)_2$ moieties; (c) packing of molecules in three dimensional arrangement in the complex **1a**.

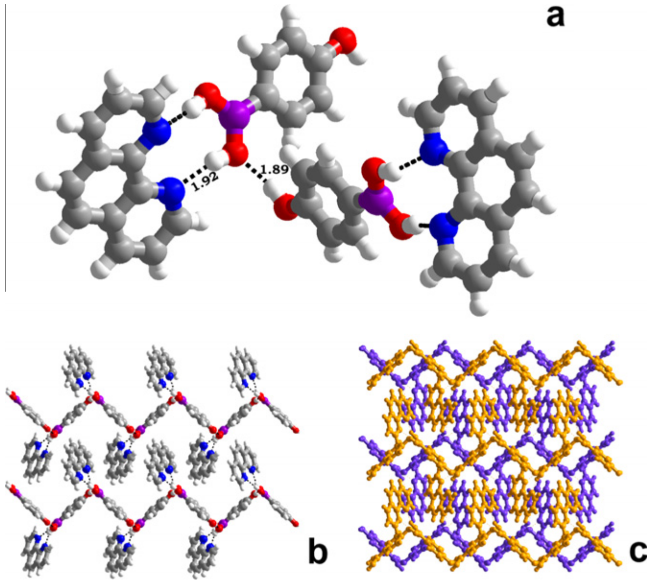

Figure 2. (a) Recognition pattern observed between 1,10-phenanthroline and the molecules of **1**, in the complex **1b**; (b) infinite tapes of boronic acid **1** held together by O–H···O hydrogen bonds in the co-crystals of **1b**; (b) Sandwich structure in the crystal lattice of complex, **1b**.

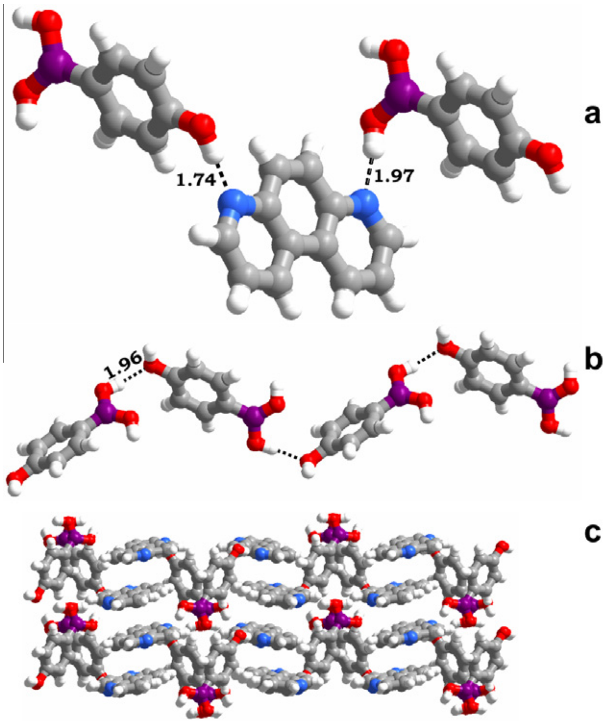

Figure 3. (a) Recognition pattern observed between, the boronic acid, **1** and 4,7-phenanthroline in the co-crystal, **1c**; (b) intermolecular interactions formed by $-B(OH)_2$ with the neighboring molecules; (c) packing of molecules in crystal lattice.

Thus, it is apparent that –B(OH)$_2$ and –OH on **1** show exactly opposite trends in the formation of complexes of **1** with phenazine and 1,10-phenanthroline. In contrast, in the complex of **1** and 4,7-phenanthroline (an analog of 1,10-phenanthroline with just changing positions of *N*-atoms), **1c**, both –OH and –B(OH)$_2$ are involved in the formation of recognition patterns with the aza-donor molecules.

In complex, **1c**,[11] although recognition between the constituents is through O–H···N hydrogen bonds, as noted in **1a** and **1b**, but they are formed due to the interaction of both –B(OH)$_2$ (H···N, 1.97 Å) and –OH (H···N, 1.74 Å) with the aza-donor compounds, as shown in Figure 3a. Further, –B(OH)$_2$ exist in *syn–anti* conformation as observed in **1a**. Such ensembles, however, further interact with each other through O–H···O hydrogen bonds (H···O, 1.96 Å), formed between –B(OH)$_2$ and –OH moieties (Fig. 3b), exactly as observed in **1a** and **1b**. Such an aggregation ultimately packs, in the crystal lattice, in the form of ladders, with rods being formed by **1** while phenanthroline molecules act as rungs (Fig. 3c).

It is apparent from the structural analysis of **1a**–**1c** that, both –B(OH)$_2$ and –OH show predominance in the formation of a specific assembly, depending upon the position of *N*-atoms on the aza-donors. Since, only the rigid aza-donors have been used in **1a**–**1c**, the study is extended to other pyridyl ligands with conformational flexibility, to explore its impact on the affinity of –B(OH)$_2$ and –OH toward the aza-donors. Thus, co-crystallization experiments of **1**, carried out with 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethene, are discussed, herein.

Surprisingly, in co-crystals, **1d**,[11] of 4,4′-bipyridine (*bpy*) with **1**, an intriguing asymmetric unit is observed with a total of fifteen molecules comprising of three symmetry independent units of co-crystal formers in 3:2 ratio. It is noteworthy to mention that molecules of **1** exist in *syn–syn* as well as *syn–anti* conformations. Interestingly, three distinct ensembles of six molecular units, with each being formed by association of each of three molecules of aza and **1**, are held together by O–H···N and C–H···O hydrogen bonds (Fig. 4a). Complete characteristics of the hydrogen bonds are listed in Table S1, ESI†. In a detailed analysis of recognition features, it is apparent that in each ensemble both the conformations of –B(OH)$_2$ and –OH moiety show affinity toward *bpy* simultaneously. For example, –B(OH)$_2$ in *syn–syn* conformation forms two O–H···N hydrogen bonds with two *bpy* molecules while –B(OH)$_2$ in *syn–anti* conformation forms one O–H···N hydrogen bond with another *bpy* molecule. Similarly –OH moiety interacts with those aza-donor molecules hold by **1** through –B(OH)$_2$, through single O–H···N hydrogen bond. Ultimately, the ensembles are held together by the O–H···O and C–H...O hydrogen bonds formed between –B(OH)$_2$ and –OH moieties, leading to the formation of a ladder structure, as shown in Figure 4b.

However, an exciting feature is observed in the co-crystals of **1** with 1,2-bis(4-pyridyl)ethene, as two different types of crystals were obtained, depending upon the composition of the co-crystal formers in the reaction mixture. The crystals, thus, obtained are labeled **1e** and **1e’** for the complexes of 1:2 and 1:1, respectively.[11] Structure determination reveals that both the complexes are

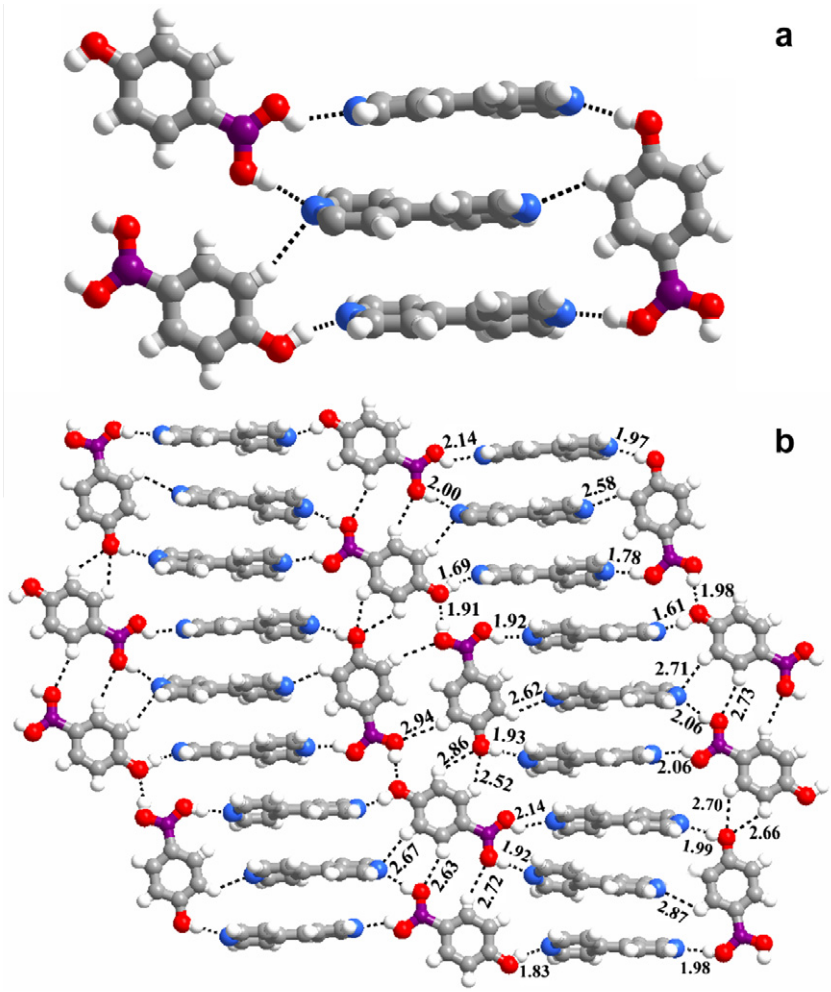

Figure 4. (a) Recognition pattern of –B(OH)$_2$ and –OH moieties with *bpy* molecules, in the complex **1d**. (b) Arrangement of molecules in the form of ladder-type architecture in complex, **1d**.

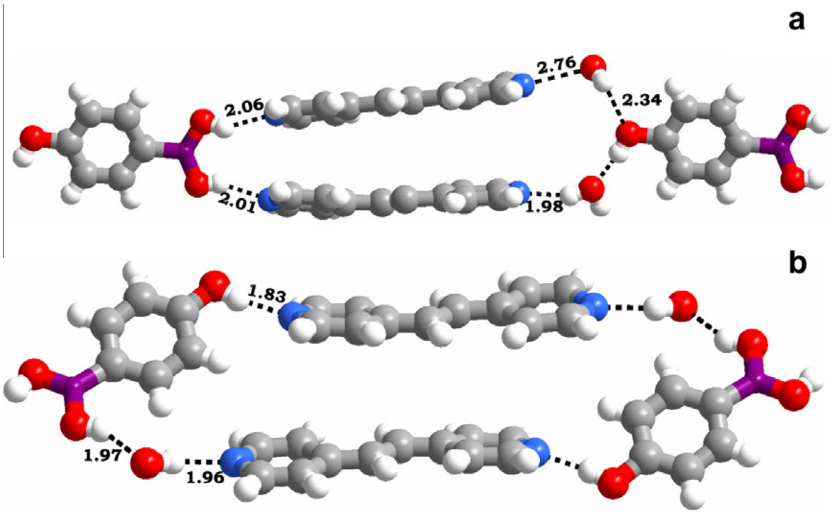

Figure 5. Network of intermolecular interactions formed by –B(OH)$_2$ and –OH in (a) **1e** and (b) **1e**′.

hydrates.[12] –B(OH)$_2$ moiety adopts *syn*–*syn* and *syn*–*anti* conformations in **1e** and **1e**′, respectively. Thus, as observed in **1b**, the *syn*–*syn* mediated –B(OH)$_2$ moiety in **1e** directly interacts with the aza-donor compounds through O–H···N (H···N, 2.06, 2.01 Å) hydrogen bonds. However, the –OH moiety is involved in the formation of O–H···O (H···O, 2.34 Å) hydrogen bonds with water molecules, which in turn interact with aza-donor molecules that are being connected to the molecules of **1** through –B(OH)$_2$ moiety.

Similarly, in the complex **1e**′, wherein the –B(OH)$_2$ moiety shows *syn*–*anti* conformation, the –OH moiety is connected to aza-donor through O–H···N (H···N, 1.83 Å) hydrogen bond, while –B(OH)$_2$ moiety establish interaction with water molecule, which are further connected to the aza-donors as shown in Figure 5b.

It is noteworthy to mention that the involvement of water with –OH and –B(OH)$_2$ in **1e** and **1e**′, respectively, as shown in Figure 5, clearly demonstrates the unique role being played by –B(OH)$_2$ and –OH, independent of each other, in the formation of molecular complexes **1e** and **1e**′. Thus, **1e** and **1e**′ may be grouped along with **1b** and **1a**, respectively.

In conclusion, the study of assemblies, **1a**–**1e** and **1e**′ reveals that –B(OH)$_2$ influence the formation of distinct co-crystals, as much as –OH does, despite the fact that the hydrogen bonds formed by –OH are relatively stronger than the ones being formed by –B(OH)$_2$. In fact, formation of different molecular complexes, **1e** and **1e**′ demonstrate the real competitive nature of the –B(OH)$_2$. Thus, utilization of –B(OH)$_2$ in the supramolecular synthesis does not limit to the mimic of –COOH and –CONH$_2$ but also can be employed as equivalent of –OH moiety as well.

Acknowledgment

We thank the Department of Science and Technology (DST) for the financial support.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.10.126.

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11. Crystal data (**1a**) $C_{18}H_{15}BN_2O_3$, monoclinic, $P2_1/n$, $a = 8.405(5)$, $b = 23.225(12)$, $c = 9.102(5)$ Å, $\beta = 115.18(9)°$, $V = 1607.9(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.341$ g cm^{-3}, $\mu = 0.089$ mm^{-1}, $2\theta_{max} = 56.84$, λ(Mo Kα) = 0.71073 Å, $T = 273(2)$ K, 9414 total reflections $R_1 = 0.0613$, and $wR_2 = 0.1386$ for 3699 reflections ($I > 2\sigma(I)$), CCDC 742753. Compound (**1b**) $C_{18}H_{15}BN_2O_3$, monoclinic, $P2_1/c$, $a = 12.435(3)$, $b = 10.941(3)$, $c = 12.177(3)$ Å, $\beta = 108.18(1)°$, $V = 1574.0(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.342$ g cm^{-3}, $\mu = 0.091$ mm^{-1}, $2\theta_{max} = 50.04$, λ(Mo Kα) = 0.71073 Å, $T = 293(2)$ K, 10432 total reflections $R_1 = 0.0525$ and $wR_2 = 0.1648$ for 2772 reflections ($I > 2\sigma(I)$), CCDC 742750. Compound (**1c**) $C_{18}H_{15}BN_2O_3$, $P2_1/n$, $a = 7.229(1)$, $b = 20.718(4)$, $c = 11.036(2)$ Å, $\beta = 107.58(5)°$, $V = 1575.7(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.341$ g cm^{-3}, $\mu = 0.091$ mm^{-1}, $2\theta_{max} = 55.00$, λ(Mo Kα) = 0.71073 Å, $T = 293(2)$ K, 11590 total reflections, $R_1 = 0.0660$ and $wR_2 = 0.0738$ for 2858 reflections ($I > 2\sigma(I)$), CCDC 742752. Compound (**1d**) $C_{42}H_{38}B_2N_6O_6$, $P\bar{1}$, $a = 13.960(9)$, $b = 17.186(11)$, $c = 25.222(16)$ Å, $\alpha = 92.64(1)$, $\beta = 100.65(1)$, $\gamma = 111.18(1)°$, $V = 5503.0(6)$ Å^3, Z = 2, $\rho_{calcd} = 1.346$ g cm^{-3}, $\mu = 0.091$ mm^{-1}, $2\theta_{max} = 51.20$, λ(Mo Kα) = 0.71073 Å, $T = 298(2)$ K, 53346 total reflections, $R_1 = 0.0962$ and $wR_2 = 0.2674$ for 19893 reflections ($I > 2\sigma(I)$), CCDC 742751. Compound (**1e**) $C_{30}H_{31}BN_4O_5$, orthorhombic, *Pbca*, $a = 14.153(5)$, $b = 18.023(6)$, $c = 22.549(6)$ Å, $V = 5751.0(3)$ Å^3, Z = 8, $\rho_{calcd} = 1.224$ g cm^{-3}, $\mu = 0.085$ mm^{-1}, $2\theta_{max} = 46.52$, λ(Mo Kα) = 0.71073 Å, $T = 293(2)$ K, 11295 total reflections, $R_1 = 0.1631$ and $wR_2 = 0.2348$ for 4066 reflections ($I > 2\sigma(I)$), CCDC 745865. Compound (**1e′**) $C_{18}H_{18}BN_2O_4$, triclinic, $P\bar{1}$, $a = 9.269(6)$, $b = 9.322(7)$, $c = 11.591(8)$ Å, $\alpha = 90.80(2)$, $\beta = 104.90(2)$, $\gamma = 112.48(2)°$, $V = 887.2(1)$ Å^3, Z = 2, $\rho_{calcd} = 1.266$ g cm^{-3}, $\mu = 0.089$ mm^{-1}, $2\theta_{max} = 50.56$, λ(Mo Kα) = 0.71073 Å, $T = 293(2)$ K, 6675 total reflections, $R_1 = 0.1642$ and $wR_2 = 0.3867$ for 3194 reflections ($I > 2\sigma(I)$), CCDC 745866.
12. The *R*-factors for **1e** and **1e′** are found to be higher than the other structures, **1a**–**1d**, but the authenticity of the homogeneity is established by powder patterns as given in Supplementary data (Fig. S1, ESI†)