Water Chemistry

Modification of 2D Water That Contains Hexameric Units in Chair and Boat Conformations—A Contribution to the Structural Elucidation of Bulk Water**

*Patricia Rodríguez-Cuamatzi, Gabriela Vargas-Díaz, and Herbert Höpfl**

Given that water is the most abundant and cheapest solvent available for the development of new reagents and the study of chemical processes, it is not surprising that still the major part of research is related somehow to this substance. This fact is clearly also because water is nature's solvent, thus playing a fundamental role in almost all branches of natural sciences. In view of this relevance, it might be therefore somewhat surprising that there is still intensive research being carried out that concerns, among other aspects, the structure of this medium in the gaseous,[1–3] liquid[2–5] and solid state.[6–8] There are two factors that make the study of water difficult. The first factor is that the hydrogen bond between water molecules is highly flexible so that they can aggregate into a variety of small and medium-sized clusters, which form the basic units for the construction of larger 1D, 2D, and 3D structures including clathrates.[2–3,9] The second factor is that a series of low-energy, dynamic processes are occurring, at least in the gaseous and liquid phase.[1–3] The need for detailed knowledge of the hydrogen bonding and the rearrangement dynamics between water molecules distributed in two and three dimensions arises from the fact that these processes rule the anomalous physical and chemical properties of liquid and solid water,[3,4] the processes that occur at the ice–liquid, ice–air and liquid–air interfaces[10–12] as well as the interaction between water and solutes.[11]

From an experimental point of view, so far a significant progress has been made with respect to the structural characterization of discrete small[1–3,9,13–15] and medium-sized[16–18] water clusters $(H_2O)_n$ ($n = 2$–100) as well as the characterization of 1D aggregates such as chains and tapes.[19–21] However, only disperse information is available on 2D layers,[9,19–29] Many of these layers are sandwich inclusion structures, in which the 2D water sheets are composed either of puckered edge-sharing pentameric clusters or result from the combination of cyclic tetrameric, pentameric, hexameric and/or (very rarely) larger clusters.[9,21] Only a few structures that contain solely edge-sharing hexameric rings have been characterized so far by X-ray crystallography and, interestingly, the conformations of the water layers have been different in each case, being all-chair,[24] all-boat[25] or an intermediate of them.[26–29] Of these conformers, only that having an all-boat conformation[25] has a structural motif similar to the one found in ice I_h (Figure 1).[30] Although one of the structures has an all-chair conformation,[24] it is apparent that its configuration (all-*cis*) is different from the one found in ice I_h (all-*trans*).

We report herein on the structure of a 2D sheet of water molecules: 1) that in close analogy with ice I_h contains two different types of hydrogen-bonded hexameric rings, one with a chair and the other with a boat conformation, in which 2) all water molecules are involved in hydrogen bonds only, and which 3) have a clearly defined hydrogen-bonding system. We consider that the description of this structure is fundamental

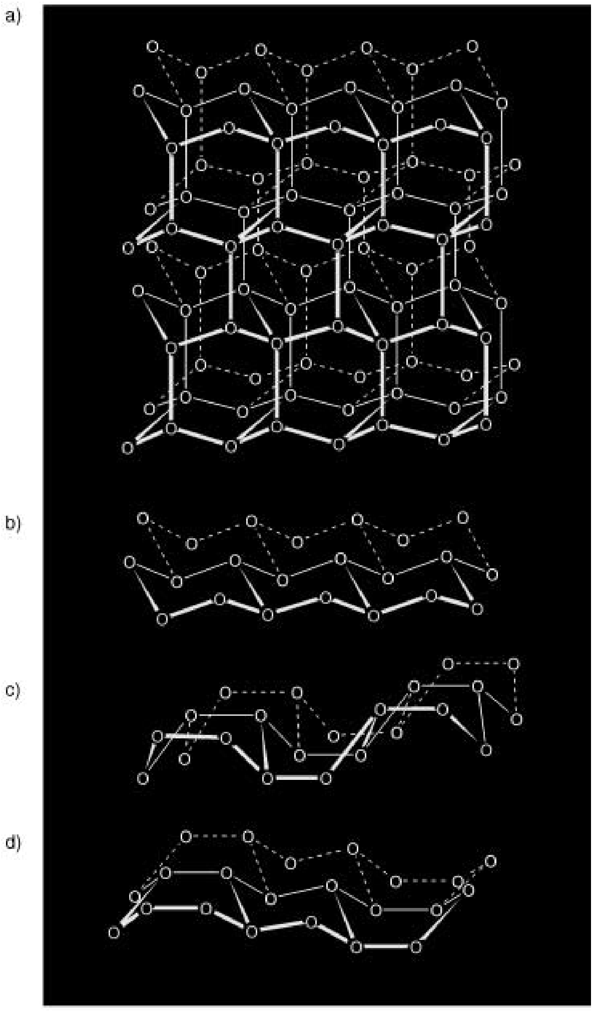


Figure 1. Comparison of the hydrogen bonding pattern found in 1,4-$[B(HO)_2]_2C_6H_4 \cdot 4\,H_2O$ with that of hexagonal ice I_h: a) 3D structure of hexagonal ice I_h; b) fragment of the structure of hexagonal ice I_h showing a 2D sheet with all hexameric rings in the chair conformation; c) fragment of the structure of hexagonal ice I_h showing a 2D sheet with all hexameric rings in the boat conformation (this pattern is also observed in the 2D water cluster described in reference [25]); d) 2D hydrogen-bonding pattern found for 1,4-$[B(HO)_2]_2C_6H_4 \cdot 4\,H_2O$ with hexameric rings that have both chair and boat conformations.

---

[*] P. Rodríguez-Cuamatzi, G. Vargas-Díaz, Dr. H. Höpfl
Centro de Investigaciones Químicas
Universidad Autónoma del Estado de Morelos
Av. Universidad 1001, C.P. 62210 Cuernavaca (Mexico)
Fax: (+52) 777-329-7997
E-mail: hhopfl@buzon.uaem.mx

[**] This work was supported by CONACyT. The authors thank Dr. L. Infantes for helpful comments.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200453957

to understanding better the chemical processes that occur at the surface of water or at an interface, since it is known that cyclic hexameric water clusters are present in liquid water,[3,4] participate in the solvatation process of surfactants[4] and are the only clusters found in the normal-pressure crystalline modifications of ice.[30]

Crystals of 1,4-$[B(HO)_2]_2C_6H_4{\cdot}4\,H_2O$ were obtained after recrystallization of 1,4-phenylenediboronic acid (pdba) in water.[31] The IR spectrum of the crystals recorded on KBr showed two relatively sharp bands at $\tilde{\nu} = 3292$ and $3408\ \text{cm}^{-1}$. To determine whether these bands represent the stretching modes of the water molecules, the stretching modes of the B–OH hydroxy groups, or both, a sample was heated at 250 °C for 2 h under vacuum to eliminate all water molecules from the crystal lattice. Since the IR spectra of the dried and hydrated samples were practically identical and considering that the stretching vibrations of hydrogen-bonded water molecules are generally weak and give rise to broad bands,[29] it was concluded that the water stretching modes are hidden below the vibrational frequencies of the B–OH hydroxy groups.

The asymmetric unit of the triclinic crystal lattice contains one pdba molecule and four water molecules (space group $P\bar{1}$). The pdba molecules are oriented in such a way that supramolecular $(\text{pdba})_n$ chains are generated through point reflection at crystallographic inversion centers (Figure 2a). These polymeric chains are held together by pairs of BO–H···O(H)B hydrogen bonds that have a hydrogen-bonding pattern similar to that found in carboxylic acid dimers.[32] This motif is commonly observed in molecules with phenylboronic acid groups.[33] The two boronic acid moieties in each pdba molecule are independent of each other, but have practically identical hydrogen-bonding geometries, O···O = 2.74 Å. The supramolecular chains are aligned parallel to each other, with neighboring chains being separated by a distance of 3.2 Å. To guarantee optimized π–π interactions, these chains are displaced with respect to each other. In the crystal-lattice layers of parallelly stacked diboronic acid chains are intercalated between 2D sheets of water molecules located in the *ac* plane of the crystal lattice (Figure 2b). The separation between the water layers is 8.5 Å. When viewed along axis *b*, the six-membered water rings are arranged in a distorted honeycomb-like manner (Figure 3a). Of the three independent cyclic water hexamers that are present in the crystal lattice (A, B, and C, Figure 3a), two of the rings (A and C) are each formed between only two crystallographically independent water molecules (O13 and O14 for ring A; O11 and O12 for ring C), and both rings have an inversion center and a chair conformation (Figure 3b). The third independent hexameric ring, B, is not located at a crystallographic symmetry center,

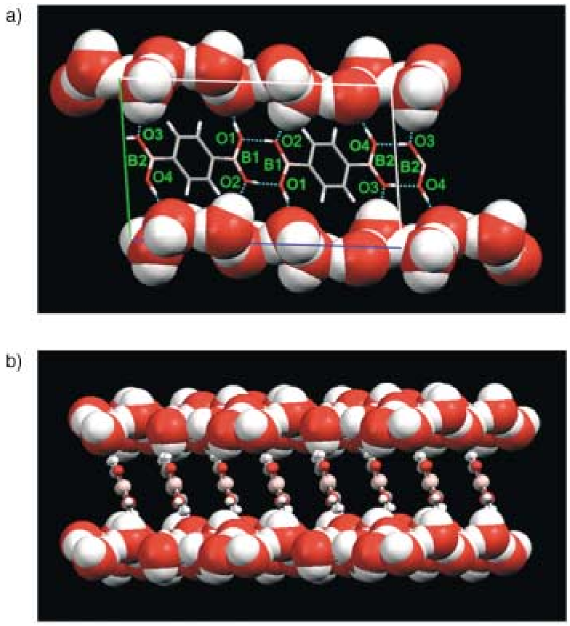


Figure 2. Fragment of the crystal lattice showing the intercalation of parallelly stacked supramolecular chains of pdba between two 2D-sheets of water: a) perspective view showing the dimeric units formed between the pdba molecules and the hydrogen bonding interactions to the water sheets; b) perspective view in direction of the supramolecular chains: grey, carbon; red, oxygen; pink, boron; white, hydrogen.

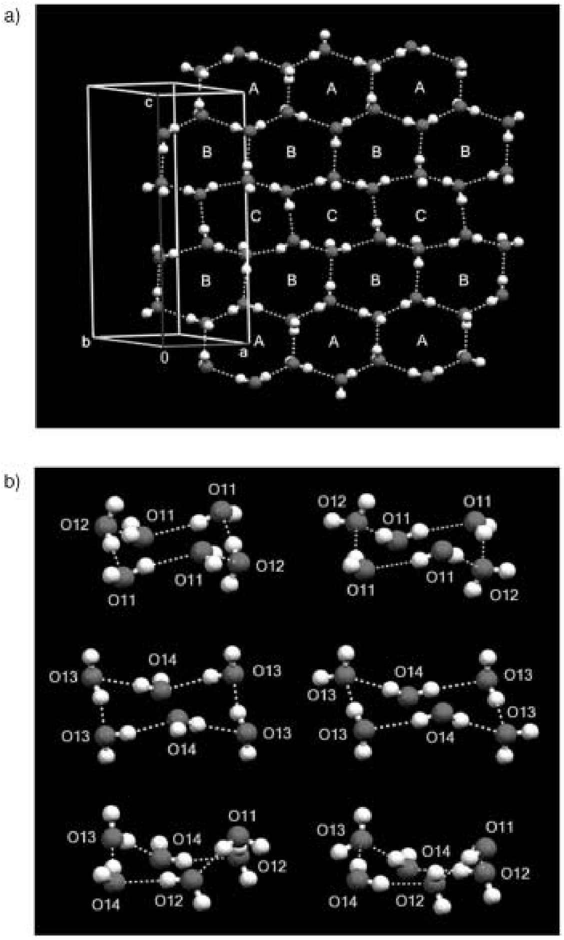


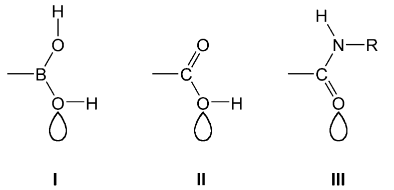
Figure 3. Ball-and-stick view of the 2D water sheet: a) presentation showing the overall hydrogen bonding interactions and the presence of three independent hexameric rings, which are arranged in tapes, which have alternately chair (A, C) and boat (B) conformation; b) view showing the conformations of the three independent hexameric rings with the two different hydrogen-bonding patterns observed in each. Top: rings C; Middle: rings A; Bottom: rings B. Gray, oxygen; white, hydrogen.

although it contains two O12 and two O14 oxygen atoms. Unexpectedly, this ring has a boat conformation, which can be seen also from Figure 3b. The O···O distances in the hydrogen bonds found in this supramolecular structure of water range from 2.77–2.85 Å, with an average value of 2.81 Å. For comparison, the O···O separations in ice I_h ($T = 60$ K) and liquid water are 2.75 and 2.85 Å, respectively.[9,30] The O···O···O bond angles vary from 92.8 to 122.2°, thus deviating only up to 16.7° from the ideal tetrahedral angle found in ice I_h.[30] The overall conformation of the 2D sheets of water molecules shown in Figure 1d results from the alternate combination of hexameric-ring tapes that have all-chair and all-boat conformations. This motif is different from those found in ice I_h (Figure 1a–c) and the water layers reported so far,[19–29] and it may be therefore considered as a new phase of 2D ice.

Of the four independent water molecules present in the crystal lattice, each molecule is involved in a maximum of four hydrogen bonds. For the formation of the 2D water layer, each water molecule must participate in three hydrogen-bonding interactions. This means that for every oxygen atom, one further hydrogen bond is available for an interaction with one of the four B–OH groups, thus giving an extended 3D hydrogen-bonding system. The interactions between the intercalating 2D water sheets and the guest molecules occur simultaneously above and below the plane (Figure 2). The O···O separations from the water sheets to the pdba molecules are 2.72–2.83 Å; therefore, the hydrogen-bonding interactions are slightly stronger than those in the interior of the 2D sheet (see above). It is important to notice that like in the all-chair and all-boat conformations outlined in Figure 1b and c, 50% of the interface water molecules can interact through a hydrogen bonding interaction with a substrate above the sheet and the other 50% with a substrate below that sheet. If one considers that the "ultimate" layer between bulk water and extended systems, such as hydrophilic and hydrophobic macromolecules or polymers, corresponds to the contact surface at which the chemical interactions between solvent and substrate take place, a detailed structural knowledge of these interfaces is essential for a more complete understanding of biochemical and pharmacological processes, surface chemistry, solvatation, etc.[10–12]

A detailed analysis of the hydrogen-bonding scheme in the water layers of $1,4\text{-}[B(HO)_2]_2C_6H_4\cdot 4\,H_2O$ shows that only the 2D hydrogen-bonding pattern shown in Figure 3a is present. As required by the space-group symmetry ($P\bar{1}$), this pattern has inversion centers, which causes the neighboring hydrogen-bonded rings of the same type (A, B, or C) to have two different motifs (Figure 3b). Because of these different motifs and since the inclined orientation of the pdba chains with respect to the 2D sheets causes a displacement of the hydrogen bonding patterns in neighboring water layers (by $|a|$ along axis a), in the final crystal structure, each water molecule is connected to three hydrogen atoms, of which the one directed to the B–OH group has an occupancy of 1.0 and the other two have an occupancy of 0.5.[31]

Since the hydrogen bonding system in 2D water layers is highly flexible, the 2D water sheet described herein may represent one of the possible structures for the surface of water or ice, especially in the presence of a macromolecular or polymeric system that has a spatial distribution of functional groups capable of hydrogen bonding in a similar way to pdba. This statement is not empty when one considers that the boronic acid moiety can be structurally related to biochemically important functional groups such as the carboxylic acid and carboxamide groups (Scheme 1).



Scheme 1. The spatial distribution of the functional groups capable of hydrogen bonding in the biochemically important carboxylic acid (**II**) and carboxamide (**III**) groups is similar to that of the boronic acid moiety (**I**).

Experimental Section

1,4-Phenylenediboronic acid was prepared according to a reported method.[34] Crystals suitable for X-ray crystallography were grown from water.

X-ray diffraction studies of crystals mounted in a sealed capillary that contained some mother liquor were carried out on a BRUKER-AXS APEX diffractometer with a CCD area detector ($\lambda_{K\alpha} = 0.71073$ Å, monochromator: graphite).[31] Frames were collected at $T = 293$ K by ω-rotation ($\Delta/\omega = 0.3°$) at 10 s per frame.[35] The measured intensities were reduced to F^2 and corrected for absorption with SADABS.[36] Structure solution, refinement, and data output were carried out with the SHELXTL-NT program.[37] Non-hydrogen atoms were refined anisotropically. C-H hydrogen atoms were placed in geometrically calculated positions by using a riding model. O–H hydrogen atoms were localized by difference Fourier maps and refined by fixing the bond length to 0.84 Å; the isotropic temperature factors were fixed to a value 1.5 times that of the oxygen atoms. Images were created with the MERCURY program.[38] Hydrogen-bonding interactions in the crystal lattice were calculated with PLATON.[39]

Received: February 6, 2004 [Z53957]

Keywords: boron · hydrogen bonds · structure elucidation · supramolecular chemistry · water chemistry

---

[1] U. Buck, F. Huisken, *Chem. Rev.* **2000**, *100*, 3863.
[2] F. N. Keutsch, R. J. Saykally, *Proc. Natl. Acad. Sci. USA* **2001**, *98*, 10533.
[3] R. Ludwig, *Angew. Chem.* **2001**, *113*, 1856; *Angew. Chem. Int. Ed.* **2001**, *40*, 1809.
[4] K. A. T. Silverstein, A. D. J. Haymet, K. A. Dill, *J. Am. Chem. Soc.* **1998**, *120*, 3166.
[5] T. Head-Gordon, G. Hura, *Chem. Rev.* **2002**, *102*, 2651.
[6] C. Lobban, J. L. Finney, W. F. Kuhs, *Nature* **1998**, *391*, 268.
[7] M. Koza, H. Schober, A. Tolle, F. Fujara, T. Hansen, *Nature* **1999**, *397*, 660.
[8] C. A. Tulk, C. J. Benmore, J. Urquidi, J. Neuefeind, B. Tomberli, P. A. Egelstaff, *Science* **2002**, *297*, 1320.
[9] G. A. Jeffrey in *An Introduction to Hydrogen Bonding*, Oxford University Press, New York, **1997**.

[10] L. F. Scatena, M. G. Brown, G. L. Richmond, *Science* **2001**, *292*, 908.

[11] S. Baldelli, C. Schnitzer, D. J. Campbell, M. J. Shultz, *J. Phys. Chem. B* **1999**, *103*, 2789.

[12] P. J. Rossky, *Nature* **2002**, *419*, 889.

[13] K. Liu, M. G. Brown, C. Carter, R. J. Saykally, J. K. Gregory, D. C. Clary, *Nature* **1996**, *381*, 501.

[14] R. N. Pribble, T. S. Zwier, *Science* **1994**, *265*, 75.

[15] K. Nauta, R. E. Miller, *Science* **2000**, *287*, 293.

[16] L. J. Barbour, G. W. Orr, J. L. Atwood, *Nature* **1998**, *393*, 671.

[17] A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, S. Roy, A. Berkle, *Angew. Chem.* **2002**, *114*, 3756; *Angew. Chem. Int. Ed.* **2002**, *41*, 3604.

[18] K. Raghuraman, K. K. Katti, L. J. Barbour, N Pillarsetty, C. L. Barnes, *J. Am. Chem. Soc.* **2003**, *125*, 6955.

[19] L. Infantes, S. Motherwell, *CrystEngComm* **2002**, *4*, 454.

[20] A. L. Gillon, N. Feeder, R. J. Davey, R. Storey, *Cryst. Growth Des.* **2003**, *3*, 663.

[21] C. Janiak, T. G. Scharmann, *J. Am. Chem. Soc.* **2002**, *124*, 14010.

[22] K. Koga, H. Tanaka, X. C. Zeng, *Nature* **2000**, *408*, 564.

[23] M. Morgenstern, J. Müller, T. Michely, G. Comsa, *Z. Phys. Chem. (Muenchen Ger.)* **1997**, *198*, 43.

[24] T. Dahl, *Acta Chem. Scand. Ser. B* **1987**, 379.

[25] K.-M. Park, R. Kuroda, T. Iwamoto, *Angew. Chem.* **1993**, *105*, 939; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 884.

[26] I. Goldberg, *J. Inclusion Phenom. Macrocyclic Chem.* **1984**, *1*, 349.

[27] T. Dahlems, D. Mootz, M. Schilling, *Z. Naturforsch. B* **1996**, *51*, 536.

[28] A. Albert, D. Mootz, *Z. Naturforsch. B* **1997**, *52*, 615.

[29] B. Lunelli, *Phys. Chem. Chem. Phys.* **1999**, *1*, 1469.

[30] W. F. Kuhs, M. S. Lehman, *J. Phys. Chem.* **1983**, *87*, 4312.

[31] Crystal data for $C_6H_8B_2O_4 \cdot 4H_2O$, $M_r = 237.81$, $0.11 \times 0.26 \times 0.54$ mm^3, triclinic, space group $P\bar{1}$, $a = 4.940(2)$, $b = 8.727(4)$, $c = 14.216(6)$ Å, $\alpha = 95.032(7)$, $\beta = 91.789(7)$, $\gamma = 101.485(7)°$, $V = 597.6(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.322$, $2\theta_{max} = 25$, 2096 independent reflections, $R_1 = 0.044$ for 1582 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.1336$ for all data, 193 parameters. CCDC-229392 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[32] L. Leiserowitz, *Acta Crystallogr. Sect. B* **1976**, *32*, 775.

[33] J.-H. Fournier, T. Maris, J. D. Wuest, W. Guo, E. Galoppini, *J. Am. Chem. Soc.* **2003**, *125*, 1002.

[34] I. G. C. Coutts, H. R. Goldschmid, O. C. Musgrave, *J. Chem. Soc. C* **1970**, 488.

[35] Bruker Analytical X-ray Systems, SMART: Bruker Molecular Analysis Research Tool, Version 5.618, **2000**.

[36] Bruker Analytical X-ray Systems. SAINT–NT, Version 6.04, **2001**.

[37] Bruker Analytical X-ray Systems, SHELXTL-NT, Version 6.10, **2000**.

[38] Cambridge Crystallographic Data Center, Mercury, Version 1.1.2, **2002**.

[39] PLATON, version 210103, A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C-34.