H Bonds in Chains of Water Molecules

Structure of a Self-Assembled Chain of Water Molecules in a Crystal Host**

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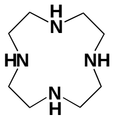
Some of the properties of water are considered "anomalous".[1–3] Although hydrogen-bonding interactions and their fluctuations are known to determine the properties of water, the major obstacle to fully comprehend its behavior has been the complexity of correctly describing the interactions between water molecules.[1–4] The diversity of the cooperative association of the water molecules is attested by a large number of polymorphic forms of ice.[5–7] The key to understanding the behavior of water is precise structural data of various hydrogen-bonded water networks in diverse environments. It is this realization that has prompted extensive investigations of water structures in recent years.[1–18]

As it is possible to obtain precise information on the nature of cooperative association of a small collection of water molecules, various water clusters have been studied theoretically and experimentally.[2–4,8–11] These studies have revealed a quasiplanar cyclic structure for the trimer, tetramer and pentamer. Although 3D structures have been theoretically predicted and experimentally observed for the hexamer and higher water clusters, a quasiplanar hexamer has also been reported.[11] Recent studies have led to the characterization of several water clusters in various crystal hosts at room temperature.[12–18] Notable among these are hexamers,[14–16] octamers[12,17] and a decamer.[13] While these studies have significantly advanced our understanding of the structure of several "discrete" water clusters, very little is known of how these clusters link themselves to form a larger network of water molecules. Herein, we report the structure of a highly ordered infinite chain of water molecules found in a crystal host at room temperature. It is shown that the chain consists of cyclic water tetramers linked by two bridging water molecules. We believe that the water structure demonstrated herein brings to light yet another novel mode of the cooperative association of water molecules. This discovery is helpful in improving the modeling of some of the unexplained properties of water, and understanding better the structure and behavior of water molecules in biological systems.

Organic compounds with functional moieties that are present in biological molecules can help stabilize various water topologies in environments resembling those in living systems.[19] Taking this fact into consideration, we have examined the crystal structure of the supramolecular assembly of 1,4,7,10-tetraazacyclododecane **1** and the water molecules within.[19] The X-ray crystallographic study[20] reveals that the supramolecular assembly is the result of cooperative hydrogen-bonding interactions between water molecules, and between water molecules and organic molecules. The crystal-packing diagram (Figure 1 a) shows that the organic molecules in the crystal are stacked one on top of the other along the crystallographic *c* axis, and are associated with



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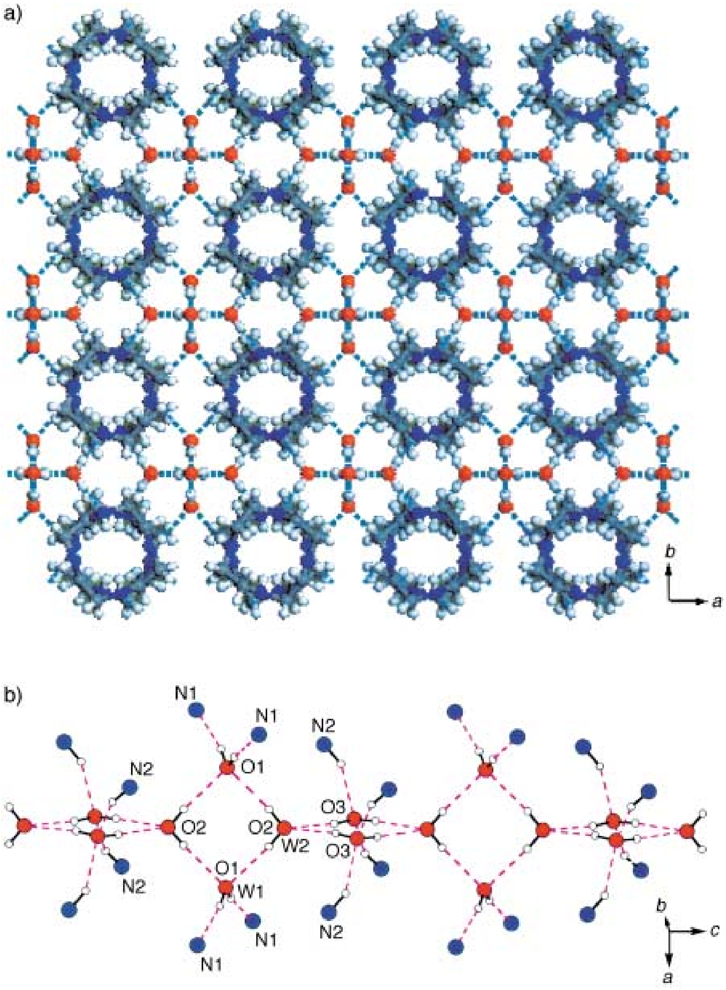

Figure 1. a) Packing diagram of the supramolecular system viewed along the crystallographic *c* axis. Carbon: gray; oxygen: red; nitrogen: blue; hydrogen: white; H bonds: dashed blue lines. The water clusters that are seen in the center of the organic molecules are not connected to each other along the crystallographic *a* or *b* axis but are H bonded to the NH groups of the adjacent organic moieties and the infinite water chain is formed only along the *c* axis. b) Hydrogen-bonding motif of the self-assembled chain of water molecules. Nitrogen: blue; H bonds: dashed purple lines. Selected bond lengths and angles are provided in Table 1.

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neighboring water molecules through N–H···O and O–H···N hydrogen-bonding interactions.

The hydrogen-bonding association leads to the formation of an infinite chain of water molecules along the *c* axis (Figure 1b). The chain consists of cyclic water tetramers formed by two types of water molecules, W1 and W2, the corresponding oxygen atoms of which are represented by O1 and O2. The individual tetrameric clusters are bridged along the *c* axis by two water molecules of type W3[21] that lie in a plane perpendicular to that containing the four water molecules forming the tetramer. Each water molecule involved in the formation of the infinite chain is hydrogen bonded to four neighboring molecules in an almost-tetrahedral arrangement. While W2 is hydrogen bonded to four other water molecules, W1 and W3 are involved in forming two O–H···N and N–H···O hydrogen bonds, respectively, with the neighboring organic moiety in addition to forming two hydrogen bonds with W2 water molecules. The oxygen atoms involved in the formation of the cyclic tetramer lie in a plane. It may appear from Figure 1b that the chain is formed by "corner-sharing tetramers", where the successive tetrameric units lie in two perpendicular planes. However, we consider "bridged tetramers" is a more appropriate description of the chain than the former description, because of the following observations: The distance between two O2 atoms forming the tetramer is 3.968(2) Å, while that separating the O2 atoms of the successive tetramers is significantly larger, 4.923(2) Å along the *c* axis. The O···O hydrogen-bonding distance is measured to be 2.896(2) Å in the tetramer while that involved in the bridging is 3.004(2) Å. The data presented in Table 1 also suggest that the hydrogen-bonding interaction of W1 with the surrounding amino moieties, O1–H···N, is significantly stronger than the interaction of W3, N–H···O3. These structural parameters imply that one of the three types of water molecules, W3, is held less tightly in the lattice compared to the other two.

Table 1: Selected bond lengths and bond angles associated with the chain of water molecules.

D–H···A	D–H [Å]	H···A [Å]	D···A [Å]	D-H-A [°]
O2–H···O1	0.83(2)	2.07(2)	2.896(2)	172(3)
O3–H···O2	0.93(2)	2.08(3)	3.004(2)	172(2)
O1–H···N1	0.87(2)	1.97(2)	2.8383(17)	170(2)
N2–H···O3	0.897(18)	2.401(18)	3.1871(19)	146.4(14)

D = donor atom, A = acceptor atom.

Tetrameric clusters of water molecules were investigated theoretically and experimentally.[22,23] Both theoretical calculations and vibration rotation tunneling spectroscopy of the water tetramer in the gas phase indicated a quasiplanar cyclic structure, in which each water molecule forms two hydrogen bonds; one as a donor and the other as an acceptor. The free hydrogen available with each water molecule alternates above and below the plane. Assuming an S_4 symmetry for the tetramer, the average O–H···O bond length in this tetramer was estimated to be 2.79 Å.[23] Interestingly, the hydrogen-bonding motif of the water tetramer in the self-assembled system presented herein, in which each water molecule is involved in the formation of four hydrogen bonds, is very different from that theoretically predicted or experimentally observed in the gas phase. This difference is because of the influence of the surrounding organic moieties and nearby water molecules. What is even more interesting is the manner in which tetrameric water clusters are self-assembled in the form of an infinite chain. We believe that this motif of association of the water molecules has not even been speculated previously.

In summary, we have characterized a novel water structure in an organic molecular host. The structure reported herein demonstrates that tetrameric water clusters can be important constituents of a water chain. As water molecules play a crucial role in contributing to the stability and function of the biological assemblies, and because the details of the water structures in channels, in energy-transducing proteins, and in enzymes are largely unknown,[24–26] the present finding may provide insight into the hydrogen-bonding motif of the aqueous environments in living systems and help unravel the mechanism of proton conduction in living systems.

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[19] The chosen molecule contains several secondary NH groups that mimic those present in biological systems (see for example, *Water and Biological Macromolecules* (Ed.: E. Westhoff), CRC Press, Boca Raton, FL, **1993**.

[20] Crystal data for **1**$\cdot 3\,H_2O$: Single crystals were grown from a toluene solution of **1**. The X-ray data were collected on an Enraf-Nonius Mach 3 single-crystal diffractometer that uses graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) by ω-scan method. Unit cell parameters were determined by least squares fit of 25 reflections having 2θ values in the range 18–21°.The structure was solved by direct methods and refined by least squares procedures on F^2 using SHELX-97 (G. M. Sheldrick, Program for the solution and refinement of crystal structures, University of Göttingen, Germany, **1997**) package. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the methylene groups were included in the structure factor calculation at idealized positions by using a riding model, but not refined. The hydrogen atoms of the water molecules and the amino moieties were located from the difference Fourier transform and refined isotropically. Crystal dimension: $0.68 \times 0.48 \times 0.40$ mm; $T = 298(2)$ K; orthorhombic, *Ccca;* $a = 16.658(2)$, $b = 16.908(5)$ and $c = 8.891(4)$ Å, $V = 2504.3(12)$ Å^3, $Z = 8$, $\rho_{\text{calc}} = 1.201\ \text{g cm}^{-3}$, $2\theta_{\max} = 27.95°$; 1713 reflections collected of which 1514 were unique; $R_1 = 0.0404$, $wR_2 = 0.0900$ for $I > 2\sigma(I)$; residual electron density: 0.155 and -0.175 e Å^{-3}. Even though a crystal structure of **1** was previously reported (J. H. Reibenspies, *Acta Crystallogr. Sect. C* **1992**, *48*, 1717), the arrangement of the water molecules in the crystal lattice was never examined. Moreover, the present crystallographic data show that ours is an improved structure that allows determination of the location of the water-hydrogen atoms more precisely. CCDC-195982 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 CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[21] The corresponding oxygen atoms are representated as O3 in Figure 1 b.

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