

Cyclic water pentamer in a tape-like structure†

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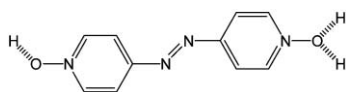
A novel water tape consisting of fused cyclic water pentamers has been observed in a supramolecular compound.

Water clusters have been intensively investigated both experimentally and theoretically due to their important relevance to biological systems and chemical processes.¹ Their structural information holds considerable promise for achieving a more accurate description of the properties of bulk water at a molecular level. A variety of water clusters including tetramers,² hexamers,^{3–5} octamers^{6,7} and decamers⁸ found in a number of crystal hosts have been structurally characterized and display different configurations. Many infinite 1D^{9,10} and 2D^{11–14} water morphologies consisting of the basic cyclic water ring units have also been assembled. These polymeric water morphologies, which structurally lie in between water clusters and bulk water, have physical properties very closely associated with those of bulk water. Without doubt, the above studies have significantly advanced the understanding of water structures and provided novel structural aspects of water and new insights into water with implications for biological environments.

Of particular interest is the water pentamer, which appears in large water clusters, liquid water, the surfaces of proteins and DNA. Theoretical calculations predict a cyclic quasi-planar ring structure as the most stable form for water trimer, tetramer and pentamer clusters, while the low-energy structures of larger clusters have 3D cage-like conformations.^{15,16} Curiously, in contrast to the frequently observed even-membered water ring morphologies such as (H₂O)_n (*n* = 4, 6, 8, 10, 12 and 18) in solid state complexes, the odd-membered water rings are rarely reported.¹⁷

With recognition of the strong capability of O,O'-bifunctional 4-pyridyl spacers to form hydrogen bonds with water molecules in supramolecular chemistry and crystal engineering,¹⁸ we observed two novel water morphologies in the solid state complexes bpedo·2H₂O and bpedo·5H₂O (bpedo = *trans*-bis(4-pyridyl)ethylene dioxide) very recently.¹⁴ The latter contains a water layer made up of twelve-membered rings and shows great resemblance with ice I_h. This promising water structure promotes us to further explore the hydrate structure of bpedo's analogue *trans*-4,4'-azopyridine dioxide (apdo, Scheme 1), which has similar geometry with bpedo. It turns out that a novel water tape consisting of fused cyclic water pentamers has been found in the solid state compound apdo·4H₂O **1**. This is a rare observation of water pentamers in crystalline hydrates.¹⁹

Single-crystal X-ray diffraction analysis revealed that **1** crystallizes in a polar space group *Pca*2₁ and contains one apdo and four water molecules in an asymmetric unit.‡ The hydrogen bonding association of water molecules leads to the formation of a cyclic pentamer consisting of one O1W, two symmetry-related O2W and



Scheme 1

O3W, whose conformation is similar to cyclopentane with one water molecule raising up above the plane formed by the other four oxygens (Fig. 1a). The geometric parameters of the pentamer are summarized in Table S1 (see ESI†). The water pentamer topology described here is in agreement with the puckered ring achieved from both experimental and theoretical studies by Liu, Saykally and coworkers.²⁰ However, the bent angle of the pentamer in **1** is 52.2°, which is considerably larger than that of the discrete pentamer (*ca.* 20°). The difference may be attributed to the influence of surrounding environments. The O···O distances within the pentamer range from 2.706(3) to 2.918(3) Å, which are well comparable with the values obtained from the *ab initio* calculations (2.73 (DFT) to 2.9 Å (HF)).²¹ This provides evidence to confirm that the same cyclic geometry of the water pentamer established for the isolated cluster also occurs in condensed phase environments.

Adjacent pentamers are fused together by sharing one edge, forming a one-dimensional water tape along the [001] direction (Fig. 1b). The O···O distance of the shared edge is 2.918(3) Å, significantly longer than others. The average O···O distance within the tape is 2.819 Å (90 K) or 2.842 Å (276 K), which is very close to the corresponding value of 2.85 Å found in liquid water,²² indicating a great structural resemblance to liquid water. The average O···O distance of 2.812 Å within apdo·4D₂O is unaffected after deuteration of water tapes. As molecular dynamics simulations suggest that water pentagons are a dominant topology in liquid water,²³ our water tapes, in this sense, may mimic the behavior of bulk water.

Additional O4W water molecules are bonded to the unshared water molecules (O1W) within the tapes as hydrogen bond acceptors to decorate the tapes (Fig. 1b). The dangling water molecules are located at the same side of the water tape, forming a groove. Adjacent decorated water tapes are arranged in an alternate up-and-down fashion such that one end of the apdo linker

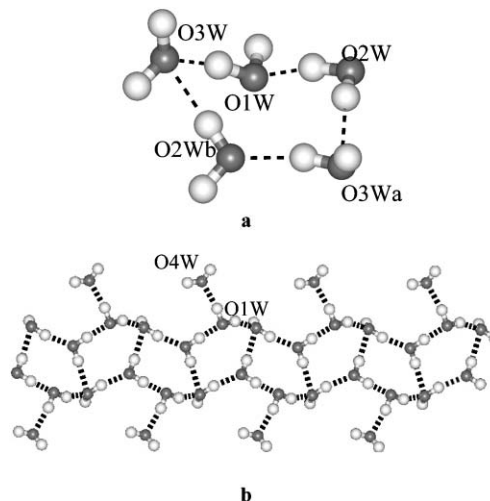


Fig. 1 a) Representation of the cyclic water pentamer observed in **1**. b) Hydrogen bonding association of water molecules into extended tapes with dangling water molecules.

† Electronic supplementary information (ESI) available: experimental details. See <http://www.rsc.org/suppdata/cc/b4/b404364b/>

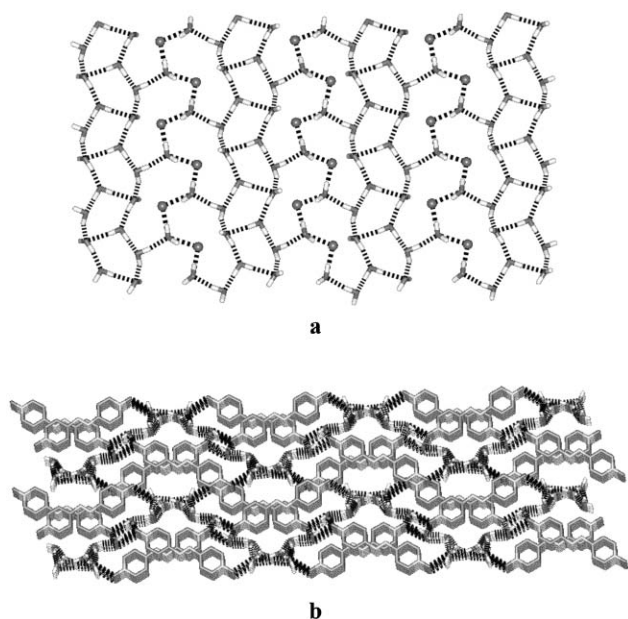


Fig. 2 a) Top view of the layer formed by water tapes and apdo linkers in **1**. For clarity, only the bridging oxygen atoms of apdo linker are drawn. b) Packing diagram of lamellar layer.

bridges the dangling water molecules belonging to different tapes, leading to a two dimensional highly puckered sheet in the a - c plane (Fig. 2a). The remaining end of the apdo linker is monodentately hydrogen-bonded to a free hydrogen from water molecule O3W on the third water tape within the sheet (Fig. 2b). Thus, water tapes are held together through an asymmetric μ_3 -hydrogen bonded apdo (Scheme 1), which might be responsible for the polarity of compound **1**. The apdo molecules reside in the groove of the water layers and neighboring apdo bridges from different layers are interweaved with one another at an intersecting angle of 129.6° with significant $\pi \cdots \pi$ interactions between pyridine rings and azo groups (interplanar distance of 3.18 \AA), giving rise to a lamellar layer (Fig. 2b). The adjacent lamellar layers have significant C-H \cdots O interactions (C \cdots O = 3.081 \AA ; C-H \cdots O = 161.4°) between the singly hydrogen bonded O atom of apdo and the pyridine rings of apdo from the adjacent layer, generating a three dimensional network.

Interestingly, apdo and bpedo facilitate distinct water aggregates, though they have essentially the same structural characters. The present finding of water tapes as well as the previous observation of water chains^{14,24} and layers¹⁴ demonstrates that pyridine oxide compounds are indeed good promoters to induce the aggregation of water molecules.

In conclusion, a novel water tape consisting of cyclic water pentamers anchored within a pyridine dioxide moiety has been structurally characterized. The observation of great consistence of geometry and structural parameters between our pentamer and the already established cyclic geometry of the isolated water pentamer provides important solid state evidence which supports the cyclic puckered ring geometry of the water pentamer. Given the importance of pentamer-like patterns of water in solvation of hydrophobic solutes, in the structures of clathrate hydrates and in biological macromolecules, the novel water tapes may provide insight into the nature of aqueous solvation, the structure and behaviors of bulk water and implication in living systems.

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Notes and references

‡ Crystal data for apdo-4H₂O **1** at 90 K: C₁₀H₁₆N₄O₆, $M = 288.27$, orthorhombic, $Pca2_1$, $a = 21.519(3)$, $b = 9.5841(9)$, $c = 6.5759(5) \text{ \AA}$, $U = 1356.2(2) \text{ \AA}^3$, $Z = 4$, $D_c = 1.412 \text{ Mg m}^{-3}$, $\mu = 0.117 \text{ mm}^{-1}$, $F(000) = 608$, $\text{GoF} = 0.960$. $R1$ and $wR2$ are 0.0550 and 0.1230, respectively, for 246 parameters and 2651 reflections [$I > 2\sigma(I)$]. For **1** at 276 K: C₁₀H₁₆N₄O₆, $M = 288.27$, orthorhombic, $Pca2_1$, $a = 21.52(2)$, $b = 9.645(7)$, $c = 6.643(6) \text{ \AA}$, $U = 1379(2) \text{ \AA}^3$, $Z = 4$, $D_c = 1.388 \text{ Mg m}^{-3}$, $\mu = 0.116 \text{ mm}^{-1}$, $F(000) = 608$, $\text{GoF} = 0.964$. $R1$ and $wR2$ are 0.0766 and 0.1925, respectively, for 246 parameters and 1385 reflections [$I > 2\sigma(I)$]. For apdo-4D₂O at 90 K: C₁₀H₈D₈N₄O₆, $M = 296.32$, orthorhombic, $Pca2_1$, $a = 21.483(3)$, $b = 9.593(2)$, $c = 6.570(1) \text{ \AA}$, $U = 1354.1(3) \text{ \AA}^3$, $Z = 4$, $D_c = 1.454 \text{ Mg m}^{-3}$, $\mu = 0.118 \text{ mm}^{-1}$, $F(000) = 608$, $\text{GoF} = 1.010$. $R1$ and $wR2$ are 0.0589 and 0.1442, respectively, for 246 parameters and 2367 reflections [$I > 2\sigma(I)$]. CCDC numbers 227242–227244. See <http://www.rsc.org/suppdata/cc/b4/b404364b/> for crystallographic data in cif format.

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