A Triphenylphoshine Oxide−Water Aggregate Facilitates an Exceptionally Short C−H···O Hydrogen Bond

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The concept that C−H···O interactions exist as significant secondary interactions, and occasionally the dominant interaction,[1] in molecular solids is now well established.[2] It is acknowledged that the shorter C−H···O contacts generally possess similar properties to N−H···O and O−H···O hydrogen bonds, albeit with lower bond energies and longer intermolecular distances, with the nature of the interaction being heavily dependent on the structural and chemical characteristics of the C−H donor group and the oxygen acceptor. Some of the shortest C−H···O intermolecular contacts arise from acidic C−H protons, such as those in terminal alkynes.[3] Triphenylphosphine oxide (TPPO) (**1**) has been widely exploited[4] in crystal engineering,[5] particularly with regard to the design of hydrogen-bonded cocrystals, because of the presence of a strongly polarized hydrogen-bond acceptor (P=O) coupled with the fact that the protons on the phenyl rings are poor hydrogen-bond donors. Recently, short C−H···O contacts (H···O distances 1.99−2.05 Å) have been reported[6] in the structure of a complex of triphenylsilylacetylene (Ph₃Si−C≡C−H) and **1**.

In this paper, we report an exceptionally short and linear C−H···O contact between 1,4-diethynylbenzene (**2**) and a water molecule in the solid state. The water molecule is also hydrogen bonded through O−H···O interactions to two molecules of TPPO, and we propose that the polarizing effect on the water oxygen is responsible for creating an enhanced hydrogen-bond acceptor.

Crystals of [**1**₄·**2**·2H₂O] were obtained by slow evaporation of a 4:1 solution of TPPO (obtained from Aldrich) and **2** (prepared by a modified literature procedure[7]) in benzene. In the crystal structure,[8] (Figure 1) both of the alkyne functionalities of a molecule of **2** participate in short C−H···O contacts (H···O and C···O distances 1.96 and 3.02 Å, respectively, C−H···O angle 169.3°) with a water molecule which is simultaneously hydrogen bonded to two TPPO molecules. The O−H···O(P) contacts are almost equivalent with H···O distances of 1.85 and 1.77 Å and O−H···O angles of 161° and 168°, respectively. This (TPPO)₂−water aggregate[9] enhances the hydrogen-bond acceptor strength of the water oxygen by the polarization of
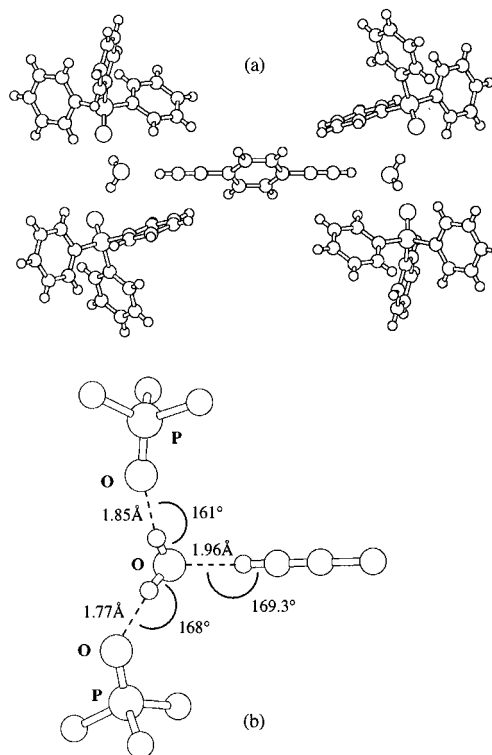

Figure 1. (a) The interaction of one molecule of **2** with two molecules of water in the crystal structure of [**1**₄·**2**·2H₂O]. (b) The detailed intermolecular contacts between **1**, **2** and water in the [**1**₄·**2**·2H₂O] aggregate. For clarity, the phenyl rings have been omitted. The O−H and alkyne C−H bond lengths were normalized at 0.98 and 1.07 Å, respectively, in accordance with standard values derived from neutron diffraction data.

the O−H bonds of the water molecule, thus creating a more negative electrostatic potential surface around the oxygen atom of the water. Ab initio quantum mechanical calculations[10] at the HF/6-31G(d,p) level using trimethylphosphine oxide as a model system for TPPO show that the minimum electrostatic surface potential around the oxygen atom for uncomplexed water (−46.6 kcal mol⁻¹) is made significantly more negative (−66.0 kcal mol⁻¹) by complexation with two molecules of trimethylphosphine oxide.

The C−H···O interaction of a terminal alkyne with water is a rare motif: we are aware of only two other structures[11] containing such a motif with the shorter[11a] H···O distance being 2.09 Å. A comparison, using the Cambridge Structural Database,[12] of our C−H···O contact with all other intermo-

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(8) Crystal data for [**1**₄·**2**·2H₂O] at 296(2) K: [C₈₂H₇₀P₄O₆], M = 1275.26 g mol⁻¹, triclinic space group $P\bar{1}$ a = 9.7929(8) Å, b = 20.9698(15) Å, c = 8.8836(6) Å, α = 101.143(3)°, β = 102.256(4)°, γ = 86.064(2)°, V = 1748.4(2) Å³, Z = 1, D_c = 1.211 g cm⁻³, no. of unique reflections = 5626, goodness of fit = 1.126, R = 0.048, wR_2 = 0.112.

(9) The interaction of a water molecule with the oxygen atoms of two R₃P=O groups is evident in crystal structures reported previously, although in these cases the water molecule does not participate in very short C−H···O contacts (shortest H···O distance 2.30 Å: Ramm, M.; Costisella, B. *Acta Crystallogr., Sect C* **1996**, *52*, 2305−2306). The structure reported here also has no other strong intermolecular interactions involving the molecule donating the C−H proton. This fact supports the view that this C−H···O contact is likely to be a true attractive interaction rather than a forced close contact resulting from other more dominant intermolecular interactions.

(10) Geometry optimisation calculations were performed using GAMESS (Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347). The version of GAMESS dated November 22, 1995 was used for all calculations). The fully optimized geometries were then used as the input coordinates for the calcluation of the electrostatic potential surface using SPARTAN (Wavefunction Inc., Irvine, CA, 1995; Version 4.1.1).

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lecular C−H···O short contacts[13] between organic molecules shows that only 62 other H···O distances are shorter than 1.97 Å from a total of ca. 1100 shorter than 2.20 Å. There is, however, a need for caution when interpreting[14] such data since stronger intermolecular interactions between a pair of molecules can force C−H···O contacts to be closer than their ideal equilibrium positions, to the extent that the interactions may actually be repulsive. This is partly reflected in the poor distance−angle correlation (i.e., few of these short contacts are close to linear) of the 62 short C−H···O contacts discussed above, for which only 10 have C−H···O angles greater than 160°.

The strength of the C≡C−H···OH$_2$ interaction reported here can be assessed by IR spectroscopy (Figure 2). In principle, the C−H···O interaction weakens the C−H bond and thus shifts the alkyne C−H stretching vibration to a lower frequency. The difference (denoted $\Delta v_{\equiv C-H}$) between the "free" alkyne C−H stretching frequency[15] (3308 cm^{-1}, determined for a solution of **2** in CCl$_4$) and the hydrogen-bonded alkyne C−H stretching frequency in the [**1**$_4$·**2**·2H$_2$O] crystal structure (3106 cm^{-1}) gives a qualitative indication of the strength of C−H···O interaction. In this system, the $\Delta v_{\equiv C-H}$ of 202 cm^{-1} is the largest reported[16] for a terminal alkyne and represents further evidence that this C−H···O interaction is comparable in many respects to traditional "strong" hydrogen-bonding interactions such as N−H···O and O−H···O.

The C−H···O interaction reported here demonstrates that the polarizing effect of a strong hydrogen-bond acceptor (TPPO) upon a molecule of water can be exploited to transform the properties of a motif that is associated with weak hydrogen bonds to one which is characteristic of stronger conventional

Figure 2. The terminal alkyne C−H stretching region in IR spectra for (a) dilute solution of **2** in CCl$_4$ and (b) [**1**$_4$·**2**·2H$_2$O] in the solid state (KBr disk). Values of the C−H stretching frequency are given in the text. The broad peak at > 3300 cm^{-1} in (b) arises from the water O−H stretching vibration.

hydrogen bonds. We are currently developing the concepts discussed in this paper by investigating the design and exploitation of phosphine oxide receptors for water, together with the development of spectroscopic techniques for the characterization of C−H···O interactions.

Supporting Information Available: Tables of crystallographic data for [**1**$_4$·**2**·2H$_2$O] (9 pages). See any current masthead page for ordering and Internet access instructions.

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(13) The search criteria (CDS dated 2/28/97) were error and disorder free organic only structures with *R* factors less than 10%; 1118 C−H···O contacts with H···O distances less than 2.20 Å were found, of which 93% were longer than 2.00 Å.

(14) Jeffrey, G. A. *An Introduction to the Hydrogen Bond*; Oxford University Press, Inc.: New York, 1997; pp 96−97.

(15) Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FTIR spectrometer at ambient temperature. Solid state spectra were obtained as KBr disks. Spectra were also recorded as a mull in hexachloro-1,3-butadiene to discount the possibility of polymorphic interference. Solution spectra (concentration approximately 2 mM) were recorded in CCl$_4$ in an Aldrich demountable liquid cell kit with a path length of 0.5 mm. All spectra were recorded at a resolution of 2 cm^{-1}.

(16) The previous largest reported $\Delta v_{\equiv C-H}$ red shift (180 cm^{-1}) is for the presumed O=P−C≡C−H···O=P interactions in dibutyl(ethynyl)-phosphine oxide (Lutz, B.; van der Maas, J.; Kanters, J. A. *J. Mol. Struct.* **1994**, *325*, 203−214) whereas the largest reported shift for a known crystal structure is 149 cm^{-1} for a Ph$_3$Si−C≡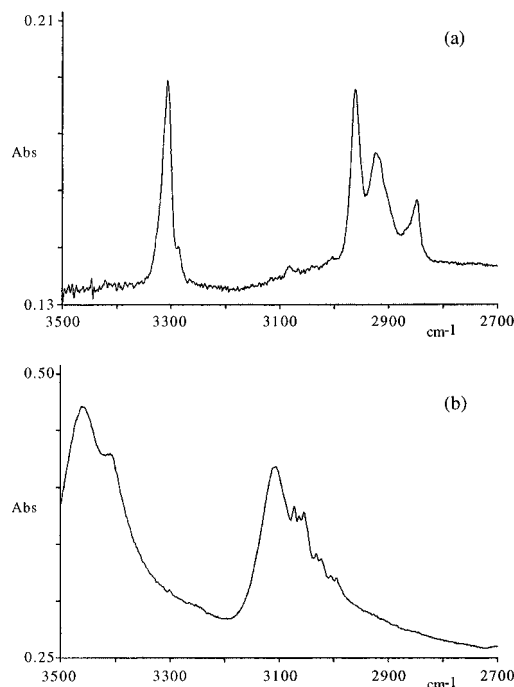C−H···O=PPh$_3$ interaction (ref 6).