

First Neutron Diffraction Analysis of an O–H··· π Hydrogen Bond: 2-Ethynyladamantan-2-ol

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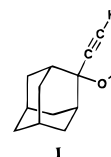
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Abstract: The neutron diffraction analysis of crystals of 2-ethynyladamantan-2-ol (**I**) provides confirmation of the presence of an unusual O–H··· π hydrogen bond, together with more common O–H···O and C–H···O bonds, as proposed previously. This is first neutron analysis of an O–H··· π hydrogen bond, which is shown to be short and linear, with the O–H vector clearly directed towards the mid-point (X) of the triple bond (O···X = 3.221 Å, H···X = 2.258 Å, O–H···X = 179.0°) rather than toward either of the two alkyne carbon atoms. An exceptionally short and straight C–H···O bond is also present in the network which probably owes its characteristics to a cooperative effect with an O–H···O hydrogen bond. The three types of hydrogen bond in this crystal structure link molecules to form supramolecular synthons which are defined as spatial arrangements of intermolecular interactions which incorporate the geometrical and chemical recognition features of molecules.

Introduction

There has been considerable interest recently in various types of weak hydrogen bonds in the context of crystal engineering, molecular recognition, and supramolecular chemistry.¹ Bonds of the types C–H···O and C–H···N have been well-studied,² these studies leading in turn to investigations of other types of weak bonds; for example, O–H··· π , N–H··· π , C–H··· π , O–H···M, N–H···M, M–H···O, and C–H···M³ (M = metal). Investigations of these novel hydrogen bonds typically employ one (or both) of the following techniques: (i) searches of the Cambridge Structural Database (CSD)⁴ for structures in which such bonds might be present and/or (ii) experimental characterization of unusual hydrogen bond types via single crystal X-ray or, ideally, single crystal neutron diffraction analysis.^{1a} Neutron diffraction is superior in this context because it yields precise hydrogen atom positions. This paper describes the neutron diffraction analysis of 2-ethynyladamantan-1-ol, **I**, a structure which contains a network of O–H···O, C–H···O and unusual O–H··· π hydrogen bonds.^{5,6}



Earlier X-ray studies of **I**⁵ indicated the presence of two symmetry independent molecules (denoted as **A** and **B**) linked by an O–H···O bond. In addition it was suggested that the O–H group of molecule **A** was involved in an intramolecular O–H··· π bond with the adjacent alkynic group. No other unusually short intermolecular interactions were reported. In a more recent infrared (IR) study of **I**⁶ it was stated that the O–H group in molecule **A** forms an intermolecular O–H··· π bond with the alkynic group of an inversion-related molecule, **A'**, resulting in the formation of “dimers”. It was also reported that there is an intermolecular C–H···O bond between the

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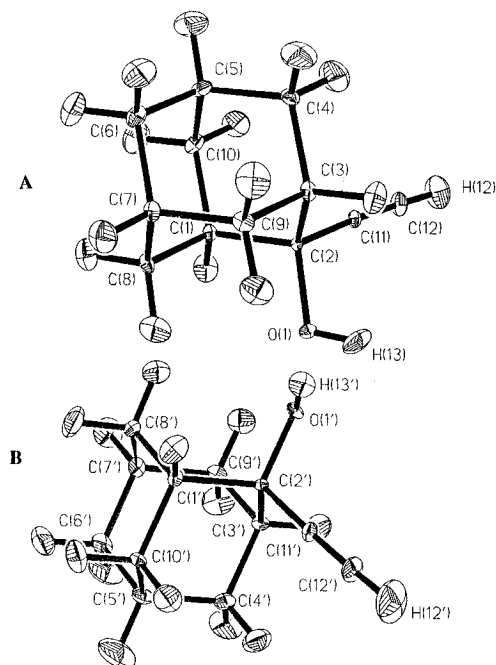


Figure 1. A 50% probability thermal ellipsoid plot of **I**.

alkynic group of **A** and the O–H group of an adjacent molecule **B'** which was overlooked in the original X-ray analysis.⁵ We therefore undertook a low temperature single crystal neutron diffraction study of **I** in order to confirm the unusual hydrogen bond network proposed⁶ and to provide a definitive geometrical description of the O–H $\cdots\pi$ hydrogen bond present.

Experimental Section

Crystals suitable for neutron diffraction analysis were grown from light petroleum.⁷ Neutron data were collected at the pulsed neutron source ISIS using the time-of-flight single crystal Laue diffractometer, SXD. The time-of-flight Laue diffraction (tofLD) technique allows the measurement of a fully resolved three-dimensional volume of reciprocal space in a single measurement, or frame. This is achieved by combining the time-of-flight technique available at a pulsed neutron source, by which the arrival time of each neutron at the detector gives a measure of its wavelength, with the use of large area position-sensitive detectors (PSDs). Collection of a complete structure factor set in this diffraction geometry consists of the accumulation of a series of such frames, each collected with a stationary crystal and detector arrangement.

In the present experiment, two PSDs, each of $192 \times 192 \text{ mm}^3$ active area, in $3 \text{ mm} \times 3 \text{ mm}$ pixels, were used. These were situated with their centers at $2\theta = 55^\circ$, $\sim 190 \text{ mm}$ from the sample (low angle detector), and $2\theta = 125^\circ$, $\sim 160 \text{ mm}$ from the sample (high angle detector). There is thus a very large angle subtended at the sample by both detectors.

The crystal, of dimension $3 \times 2 \times 1.5 \text{ mm}^3$ was mounted on a two-circle orienter (ϕ, χ) in a Displex closed cycle refrigerator (CCR) helium cryostat, on the single crystal diffractometer SXD at the ISIS spallation neutron source.⁸ The data were collected at a temperature of 100 ± 1

(7) We thank Professor J. A. Kanters, University of Utrecht, for a gift of compound **I**. The compound is prepared from adamantanone. An anhydrous THF solution of adamantanone (4.51 g, 30.0 mmol, in 50 mL) was slowly added to a stirred and cooled (15°C) suspension of the sodium acetylide in xylene (11–15%, 40 mL, 110–150 mmol), for 1 h under nitrogen. The mixture was stirred for 18 h at room temperature and for 1 h at 70°C . Then it was cautiously diluted first with water (50 mL) and then with ether (30 mL) while being cooled with ice. The mixture was acidified with 50% H_2SO_4 , the organic layer was separated, and the aqueous layer extracted with ether ($3 \times 20 \text{ mL}$). The combined organic layer and extracts were washed with saturated aqueous sodium chloride and then dried with Na_2SO_4 . Finally, the solvent was evaporated under reduced pressure to give compound **I** as a white solid (5.30 g, mp $102\text{--}104^\circ \text{C}$).

K, the computer-controlled temperature being measured by a Rh–Fe thermocouple site around 10 mm from the sample at the CCR head.

Data were collected in 47 frames from each detector, at a series of ϕ and χ angles to give good coverage of reciprocal space. The wavelength range used was $0.5\text{--}5 \text{ \AA}$. The nature of the data collection is such that different $\sin \theta/\lambda$ values are reached in different parts of the detector. Typical frame exposure times were around 3–4 h, resulting in several hundred observed reflections in each detector. This data collection method, and the large degree of overlap between frames collected at different times, leads to a large overdetermination of equivalent reflections in the data set. It is clear from the normalization and merging procedure that there is no measurable change in the diffracting power of the crystal during the data collection.

With many reflections determined within each frame, determination and refinement of the UB matrix was straightforward. Each three-dimensional data histogram was searched for peaks, and these were indexed using the UB matrix. The final cell dimensions were determined using reflections taken from a wide range of data frames, while for peak integration, a local UB matrix refined for each frame was used.

The peaks were integrated using a profile fitting approach based on the known analytical shape of the reflections in the time-of-flight direction, well understood from the characteristics of the ISIS source and moderator. The function used was a Gaussian convoluted with a decaying exponential function, which is found to reproduce the peak shape well. The variable parameters in this fit are the Gaussian height and width and the time constant of the exponential, all of which vary with time-of-flight. This method is found to be both sensitive and reliable in the integration of both strong and weak peaks. It should be noted that reflections for which this profile fitting procedure failed after four attempts on different integration windows were excluded from the data set, thus resulting in a somewhat reduced occurrence of very weak or “unobserved” peaks in the final data set.

The reflection intensities were normalized to the incident beam profile using the incoherent scattering from a polycrystalline vanadium sample. Semiempirical absorption corrections were also applied at this stage, using the vanadium and sample scattering. The resulting intensities were reduced to structure factors, giving a data set of 12 628 reflections. These data were used in the CCSL⁹ least squares refinement program SFLSQ, to apply a variable wavelength extinction correction based on the Becker–Coppens formalism¹⁰ using a Gaussian model with one variable parameter, the mosaic spread.

The resulting corrected structure factors were merged and subject to initial refinements in the GSAS program.¹¹ The 12 628 observed data yielded 3503 unique merged reflections ($R_{\text{merg}} = 0.056$) to be used in the final refinements.^{12,13}

Structure Analysis and Discussion

The crystal structure of **I** was found to contain all three hydrogen bonds predicted on the basis of the X-ray crystallographic and spectroscopic evidence.^{5,6} A comparison of the geometrical parameters of these with the parameters obtained in the original X-ray study⁵ is given in Table 1. The primary structural motif is the supramolecular synthon,^{1c} **II** which is a tetrameric loop comprised of O–H \cdots O and C–H \cdots O bonds in alternating **A** and **B** molecules. This tetrameric loop synthon is illustrated in Figure 2. the motif is translated along [100] to

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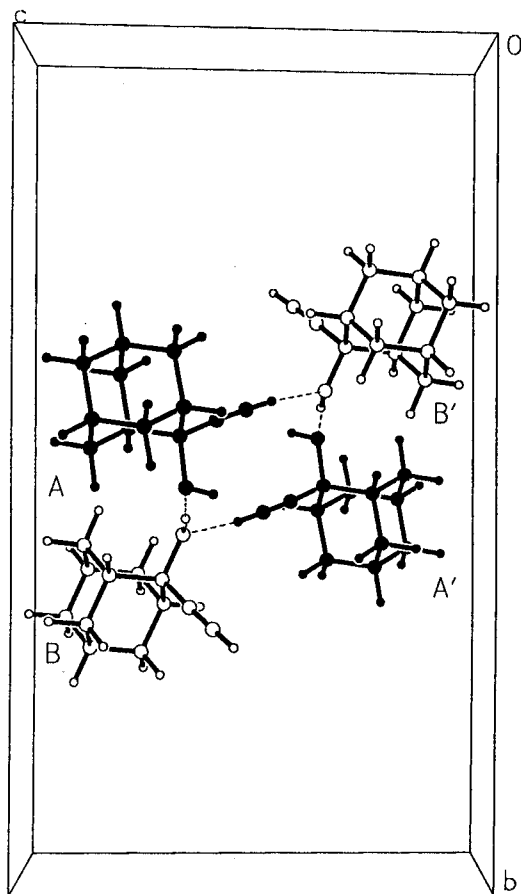
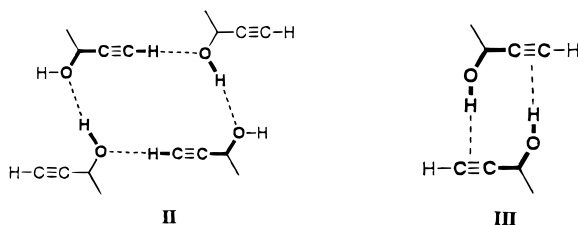


Figure 2. View along [100] of the tetrameric loop synthon, **II** which is comprised of O—H···O and C—H···O hydrogen bonds between alternating **A** and **B** molecules.

generate O—H··· π hydrogen bonds between the **A** molecules, as shown in Figure 3. These O—H··· π hydrogen bonds form the dimer synthon, **III** confirming the earlier IR findings.⁶



This is the first O—H··· π bond to be analyzed by neutron diffraction and so its geometry was carefully scrutinized. The bond is short and linear with the O—H group clearly directed towards the midpoint (X) of the triple bond (2.258 Å, 179.0°)

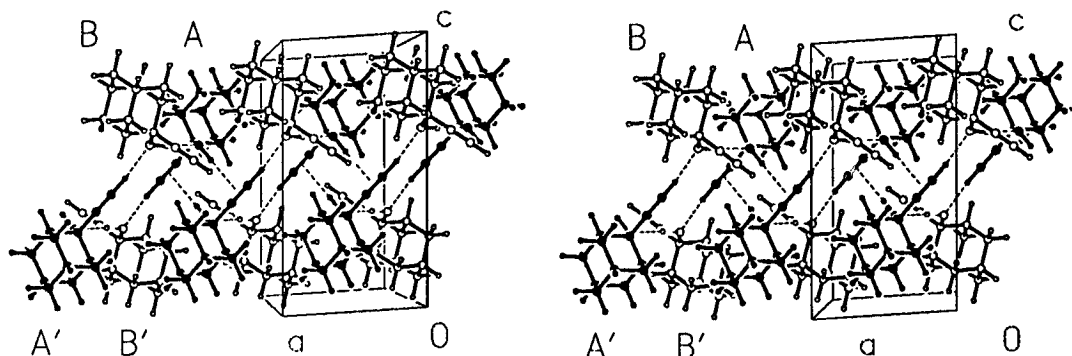


Figure 3. Stereoview along [010] of the translation of synthon **II** along [100] to generate O—H··· π bonds between **A** molecules.

Table 1. Comparison of X-ray and Neutron Derived Geometries of the Hydrogen Bonds Present in the Crystal Structure of 2-Ethynyladamantan-2-ol

		X-ray ⁵	neutron
O ₁ —H ₁₃ ···O ₁	O···O	2.84 Å	2.813(5) Å
	H···O	2.06 Å	1.845(8) Å
	O—H···O	143°	175.9(6)°
C ₁₂ —H ₁₂ ^a ···O ₁	C···O	3.18 Å	3.135(5) Å
	H···O	2.23 Å	2.070(8) Å
	C—H···O	171°	173.3(6)°
O ₁ —H ₁₃ ^b ··· π	O···C ₁₁	3.35 Å	3.326(5) Å
	H···C ₁₁	2.35 Å	2.384(8) Å
	O—H···C ₁₁	160°	166.5(6)°
	O···C ₁₂	3.25 Å	3.227(5) Å
	H···C ₁₂	2.25 Å	2.294(9) Å
	O—H···C ₁₂	163°	163.6(5)°
	O···X	3.25 Å	3.221 Å
H···X	2.22 Å	2.258 Å	
O—H···X	169°	179.0°	

^a Symmetry transformations used to generate equivalent atoms: $-x, -y+1, -z+1$. ^b $-x+1, -y+1, -z+1$.

rather than towards either of the two alkyne carbon atoms (2.384(8) Å, 166.5(6)°; 2.294(9) Å, 163.6(5)°). Comparison of the neutron and X-ray derived geometries shows that this preference of the O—H group to point towards the triple bond midpoint is unequivocally shown only in the neutron analysis.

The C—H···O bond present in the structure of **I** is also an exceptional short and linear example of the type (2.070(8) Å, 173.3(6)°). A search for short C—H···O bonds in neutron derived structures, using the CSD,⁴ located only 17 H···O contacts of less than 2.250 Å. The bond present in **I** is longer than only one of these (CSD refcode METHYM01;¹⁴ 2.045 Å, 170.9°), and it is shorter and considerably more linear than the next shortest contact (CSD refcode VALREF;¹⁵ 2.123 Å, 150.3°). A careful examination of all 17 of these short C—H···O bonds revealed that each possesses one or more of the following structural features: (i) a very acidic C—H group,^{2b} (ii) the oxygen atom present as an anion,^{2k} and (iii) the C—H···O bond lies within a cooperative network.^{1a,b} In the present case, factors (i) and (iii) are seen to operate. The cooperativity effect in synthon **II** leads to a very short C—H···O bond which seems to gain in strength at the expense of the O—H···O bond (1.845(8) Å). The strength of the C—H···O bond is also indicated by a lengthening of alkyne C—H bond in molecule **A** compared with the same bond in molecule **B**, which is not involved in hydrogen bonding (1.070(8) Å cf. 1.045(12) Å).

All three types of hydrogen bond originate from the H—O—C—C≡C—H fragment. Molecule **A** (black in Figures 2 and 3) utilizes all of the donors (C—H, O—H) and acceptors (O—H, —C≡C—) in this fragment. Molecule **B** (white in Figures 2 and 3) utilizes only its O—H group, as both an O—H···O donor and as a C—H···O acceptor. A search of the CSD⁴ for the

fragment $\text{H}-\text{O}-\text{C}-\text{C}\equiv\text{C}-\text{H}$ resulted in 77 hits. Of these, 58 were found to contain $\text{C}-\text{H}\cdots\text{O}$ bonds of the type found in **I**, and seven were found to contain $\text{O}-\text{H}\cdots\text{O}$ bonds, but only three structures were located in which an $\text{O}-\text{H}\cdots\pi$ bond was implicated. These three are the title compound,⁵ a steroid (CSD refcode MNPREY¹⁶), and a heterocyclic steroid, danazole (CSD refcode YAPZEU^{3c}). In all three cases, the $\text{O}-\text{H}\cdots\pi$ bonds occur within cooperative networks, again indicating that such cooperativity is often necessary in the stabilization of networks constituted of weak hydrogen bonds.

Conclusions

In summary, this study shows the following: (i) clear evidence of an $\text{O}-\text{H}\cdots\pi$ hydrogen bond in terms of neutron diffraction analysis; (ii) that such a hydrogen bond when directed

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toward a $-\text{C}\equiv\text{C}-$ bond, points at the center of the bond rather than at either of the alkynic carbon atoms; (iii) the presence of a very short and straight $\text{C}-\text{H}\cdots\text{O}$ hydrogen bond which owes its distinctive characteristics to a cooperative effect involving an $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond; (iv) that these patterns of hydrogen bonds can be described in terms of supramolecular synthons which are defined as spatial arrangements of intermolecular interactions which incorporate the geometrical and chemical recognition features of molecules.

Supporting Information Available: Tables of crystal data, positional parameters, bond lengths and angles, and displacement parameters (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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