Neutron Diffraction Study of Aromatic Hydrogen Bonds: 5-Ethynyl-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol at 20 K

THOMAS STEINER,[a]* SAX A. MASON[b] AND MATTHIAS TAMM[c]

[a]*Institut für Kristallographie, Freie Universität Berlin, Takustrasse 6, D-14195 Berlin, Germany,* [b]*Institut Laue-Langevin, BP 156, 38042 Grenoble CEDEX 9, France,* and [c]*Institut für Anorganische und Analytische Chemie, Freie Universität Berlin, Fabeckstrasse 34-36, D-14195 Berlin, Germany. E-mail: steiner@chemie.fu-berlin.de*

Abstract

The neutron diffraction crystal structure of the title compound, $C_{17}H_{12}O$, was determined at 20 K. One of the benzyl groups accepts intermolecular hydrogen bonds from a hydroxyl and an ethynyl group, one to each face of the ring. The bond donated by the hydroxyl group points almost linearly to an aromatic C atom with a H···C separation of 2.339 (6) Å. The bond donated by the ethynyl group points to the aromatic midpoint *M* with a H···*M* separation of 2.587 (5) Å. The average acetylenic C—H bond length determined by low-temperature neutron diffraction is only 1.062 (6) Å, appreciably shorter than observed for chemically different C—H bonds.

1. Introduction

In recent years much effort has been made to characterize the structural features of hydrogen bonds with π-acceptors ($\pi = C\equiv C$, $C=C$, phenyl rings Ph *etc.*). For Ph acceptors these interactions are often termed 'aromatic hydrogen bonds'. Only a few examples can be given of the numerous X-ray crystallographic studies on X—H···π bonds of the types O—H···Ph (Aubry, Protas, Moreno-Gonzalez & Marraud, 1977), O—H···C≡C and O—H···C=C (Viswamitra, Radhakrishnan, Bandekar & Desiraju, 1993), O—H···Cp (Glidewell, Klar, Lightfoot, Zakaria & Ferguson, 1996), N—H···Ph (Bakshi *et al.*, 1994), Cl—H···Ph (Deeg & Mootz, 1993), Cl—H···C≡C (Mootz & Deeg, 1992), C—H···Ph and C—H···C≡C (Steiner, Starikov, Amado & Teixeira-Dias, 1995), and C—H···C=C (Lutz, Kanters, van der Maas, Kroon & Steiner, 1997). On the whole, these studies indicate an extremely soft geometry of the X—H···π hydrogen bond. For O—H···Ph interactions, crystal structures are reported where O—H points more or less to the midpoint of the Ph acceptor (*e.g.* Aubry, Protas, Moreno-Gonzales & Marraud, 1977; Rzepa, Webb, Slawin & Williams, 1991), but there are also very off-centred arrangements where O—H apparently points to a particular aromatic

C—C bond of the Ph acceptor (*e.g.* Nakatsu, Yoshioka, Kunimoto, Kinugasa & Ueji, 1978) or even to an individual C atom (*e.g.* Steiner, Starikov & Tamm, 1996). Similarly, in O—H···C≡C hydrogen bonds, O—H was found pointing to the C≡C midpoint (*e.g.* Steiner, Tamm, Lutz & van der Maas, 1996), but also to one of the two C atoms (*e.g.* Viswamitra, Radhakrishnan, Bandekar & Desiraju, 1993).

Analyzing hydrogen-bond geometries taken from X-ray diffraction data is not without problems (for O—H···O bonds, see *e.g.* Jeffrey & Saenger, 1991). Since in a hydrogen bond the H-atom vibration amplitude increases dramatically with the decreasing strength of the interaction (Eriksson & Hermansson, 1983), the exact location of the H atom in O—H···π interactions is even more problematic than for O—H···O bonds. In practice, the most important atomic position in the coordinate set, *i.e.* H(O), is often the least reliably determined one. Therefore, it would be highly desirable to analyze X—H···π interactions from neutron diffraction data which supply the H-atom positions precisely. Unfortunately, only two neutron crystal structures of X—H···π hydrogen bonds have been determined so far: 2-ethynyladamantan-2-ol, with an O—H···C≡C hydrogen bond (Allen *et al.*, 1996), and orthorhombic acetylene, with C—H···C≡C interactions (McMullan, Kvick & Popelier, 1992).

In this contribution we report a neutron diffraction study of aromatic hydrogen bonds. The system under study is 5-ethynyl-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (1). The occurrence of O—H···Ph and C≡C—H···Ph hydrogen bonding in this compound has previously been
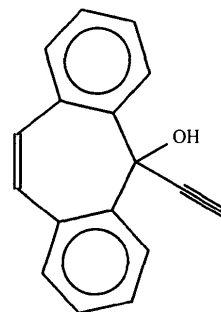
discussed using X-ray data diffraction and IR spectroscopic data, and quantum chemical calculations (Steiner, Starikov & Tamm, 1996). The structure contains no conventional hydrogen bonds.

2. Experimental

Compound (1) was prepared as reported previously (Steiner, Starikov & Tamm, 1996). When reproducing crystallization under the reported conditions, *i.e.* growing crystals from ether–*n*-hexane at 247 K or other temperatures <273 K, it was found that normally two crystal forms appear in the same batch, small crystals which are stable at ambient conditions, and possess the unit-cell constants as reported, and very large crystals which decay within minutes if taken from the solvent. Large crystals of the stable form were eventually obtained by slow cooling of a hot concentrated solution in 2-propanol.

A slightly irregular plate-like single crystal of dimensions $0.49 \times 1.28 \times 1.48$ mm^3, volume 0.93 mm^3, was glued to an Al pin and sealed in a Displex cryo-refrigerator (Archer & Lehmann, 1986) on the D19 thermal-beam neutron diffractometer at the high-flux reactor of the Institut Laue–Langevin (ILL), Grenoble. This instrument is equipped with a $4 \times 64°$ position-sensitive detector (Thomas *et al.*, 1983). The crystal was indexed at room temperature and then cooled to 20 K at 2° min^{-1}, while monitoring the strong $\bar{2}01$ reflection. Some 1519 reflections were then measured at $\lambda = 0.9557(2)$ Å, mostly with ω scans in equatorial geometry, to a 2θ value of 54° (standard ILL programs *Hklgen* and *Mad*). Three standard reflections were monitored approximately every 12 h and showed no significant variation. The wavelength was then changed to $\lambda = 1.3135(2)$ Å in order to increase the neutron flux on the sample for the higher-angle reflections and a further 1433 reflections were measured to a 2θ value of 100.4°, with some overlap for scaling. The same 3 standard reflections, now monitored every ~6 h, again showed no significant variation. The unit-cell dimensions were determined from the angular positions of 757 strong reflections at 1.3135(2) Å, with γ values between 13 and 100° (standard ILL program *Rafd*19). Bragg intensities were integrated in three dimensions using the ILL program *Retreat* (Wilkinson, Khamis, Stansfield & McIntyre, 1988). The intensities were then corrected for attenuation by the cylidrical heat shields and by the crystal itself using the program *D19abs*, based on the ILL version of the CCSL system (Matthewman, Thompson & Brown, 1982). The analytical absorption correction yielded transmission values of $T_{min} = 0.7845$, $T_{max} = 0.9092$ at $\lambda = 1.3135$ Å and $T_{min} = 0.8260$, $T_{max} = 0.9255$ at $\lambda = 0.9557$ Å. Scaling of the two data sets was

Table 1. *Experimental details*

Crystal data	
Chemical formula	$C_{17}H_{12}O$
Chemical formula weight	232.28
Cell setting	Monoclinic
Space group	$P2_1/a$
a (Å)	11.8097 (9)
b (Å)	8.2776 (7)
c (Å)	12.0030 (10)
β (°)	94.951 (4)
V (Å^3)	1169.0 (2)
Z	4
D_x (Mg m^{-3})	1.320
Radiation type	Thermal–neutron
Wavelength (Å)	0.9557 (2) and 1.3135 (2)
No. of reflections for cell parameters	757
θ range (°)	6.9–50.4
μ (mm^{-1})	At $\lambda = 0.9557$ Å: 0.159; at $\lambda = 1.3135$ Å: 0.192
Temperature (K)	20
Crystal form	Prisma
Crystal size (mm)	1.48 × 1.28 × 0.49
Crystal color	Light brown
Data collection	
Diffractometer	D19 of the ILL (see text)
Data collection method	Area detector
Absorption correction	Analytical
T_{min}	0.78
T_{max}	0.91
No. of measured reflections	2952
No. of independent reflections	1939
No. of observed reflections	1551
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.0348
θ_{max} (°)	50.30
$\sin(\theta/\lambda)_{max}$ (Å^{-1})	0.586
Range of h, k, l	$-13 \rightarrow h \rightarrow 13$
	$-8 \rightarrow k \rightarrow 9$
	$-13 \rightarrow l \rightarrow 7$
No. of standard reflections	3
Frequency of standard reflections	Every 12 and 6 h
Refinement	
Refinement on	F^2
Minimalization	Sum of $w\Delta F^2$
$R[F^2 > 2\sigma(F^2)]$	0.0483
$wR(F^2)$	0.1207
S	1.065
No. of reflections used in refinement	1914
No. of parameters used	271
H-atom treatment	All H-atom parameters refined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0524P)^2 + 6.2121P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	<0.001
Source of atomic scattering factors	Sears (1984)
Computer programs	
Structure refinement	*SHELXL93* (Sheldrick, 1993)
Molecular graphics	*ORTEPII* (Johnson, 1976)

based on 112 overlap reflections, yielding an R_{scale} value of 0.040.

Atomic coordinates of the room-temperature X-ray structure were used as the starting model. Neutron scattering lengths were taken from Sears (1984). Refinement with standard methods (Sheldrick, 1993) proceeded smoothly; unrestrained anisotropic refinement converged with $R = 0.048$ (for observed

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O	0.7162 (2)	0.0610 (3)	0.3086 (2)	0.0089 (5)
C1	0.9991 (2)	0.3650 (2)	0.1280 (2)	0.0096 (4)
C2	0.9471 (2)	0.5058 (2)	0.1624 (2)	0.0096 (4)
C3	0.8579 (2)	0.4954 (3)	0.2301 (2)	0.0110 (4)
C4	0.8181 (2)	0.3446 (2)	0.2604 (2)	0.0094 (4)
C5	0.8157 (2)	0.0381 (2)	0.2531 (2)	0.0068 (4)
C6	0.8676 (2)	−0.1133 (2)	0.4345 (2)	0.0097 (4)
C7	0.9370 (2)	−0.2189 (2)	0.5006 (2)	0.0112 (4)
C8	1.0377 (2)	−0.2752 (2)	0.4634 (2)	0.0107 (4)
C9	1.0699 (2)	−0.2226 (2)	0.3605 (2)	0.0092 (4)
C10	1.0475 (2)	−0.0672 (2)	0.1881 (2)	0.0084 (4)
C11	1.0291 (2)	0.0717 (2)	0.1310 (2)	0.0086 (4)
C12	0.9625 (2)	0.2110 (2)	0.1625 (2)	0.0069 (4)
C13	0.86790 (15)	0.2029 (2)	0.2258 (2)	0.0061 (4)
C14	0.8988 (2)	−0.0631 (2)	0.3300 (2)	0.0077 (4)
C15	1.0026 (2)	−0.1151 (2)	0.2933 (2)	0.0078 (4)
C16	0.7844 (2)	−0.0520 (2)	0.1478 (2)	0.0081 (4)
C17	0.7493 (2)	−0.1238 (2)	0.0645 (2)	0.0087 (5)
H(O)	0.6533 (5)	0.0744 (7)	0.2567 (5)	0.0315 (10)
H1	1.0687 (4)	0.3726 (6)	0.0740 (4)	0.0268 (10)
H2	0.9776 (4)	0.6225 (5)	0.1357 (4)	0.0266 (10)
H3	0.8186 (4)	0.6054 (5)	0.2585 (4)	0.0256 (9)
H4	0.7461 (4)	0.3370 (5)	0.3104 (4)	0.0224 (9)
H6	0.7874 (4)	−0.0714 (6)	0.4624 (4)	0.0254 (9)
H7	0.9091 (4)	−0.2579 (6)	0.5811 (4)	0.0294 (10)
H8	1.0913 (4)	−0.3596 (6)	0.5138 (4)	0.0293 (10)
H9	1.1496 (4)	−0.2673 (6)	0.3316 (4)	0.0280 (10)
H10	1.1091 (4)	−0.1510 (5)	0.1572 (4)	0.0236 (9)
H11	1.0768 (4)	0.0916 (5)	0.0586 (4)	0.0241 (9)
H17	0.7179 (5)	−0.1845 (7)	−0.0100 (4)	0.0358 (12)

reflections). Final fractional atomic coordinates are given in Table 2.†

3. Results and discussion

3.1. *General*

Upon cooling to 20 K the unit-cell dimensions reduce almost isotropically, indicating that there are only marginal shifts of the molecules with respect to each other (Table 3). Therefore, very close similarity of the room-temperature and 20 K crystal structures of (1) can be expected. In fact, the overall molecular structure (Fig. 1) and the crystal packing (Fig. 2) at 20 K are virtually the same as at room temperature. Therefore, only characteristics of the molecular conformation and the crystal packing need to be mentioned here, which are relevant to the hydrogen bonds discussed below. The molecule is arch-shaped, with the ethynyl group projecting perpendicularly from the convex side. The hydroxyl group is in an equatorial position and is engaged in two intramolecular C—H···O contacts which shield the larger part of the lone pair from forming intermolecular interactions; therefore, it cannot

Table 3. *Reduction of the unit cell upon cooling to 20 K*

δ = relative difference of room temperature and 20 K values [δ = 100 × ($x_{20\,K}$ − x_{RT})/x_{RT}]. Room-temperature (RT) data from Steiner, Starikov & Tamm (1996).

	Room-temperature value	δ (%)
a (Å)	11.991 (2)	−1.51 (2)
b (Å)	8.356 (1)	−0.94 (2)
c (Å)	12.105 (3)	−0.84 (3)
β (°)	94.62 (3)	0.35 (3)
V (Å^3)	1208.8 (4)	−3.29 (4)

act as an acceptor of O—H···O hydrogen bonds (selected data on the molecular conformation is given in the legend of Fig. 1).

3.2. *The aromatic hydrogen bonds*

In the crystal lattice, the hydroxyl group forms an intermolecular contact with a benzyl group of a neighboring molecule and the other face of this benzyl group is engaged in a short contact to the ethynyl group of a different neighbor, Fig. 2. The other benzyl group is engaged in face-to-face and edge-to-face π-stacking interactions with a neighboring molecule (described in the X-ray study). The hydrogen-bond nature of both X—H···Ph contacts has been shown from IR spectroscopic data: at room temperature the O—H stretching frequency ν_{OH} is reduced by 61 cm^{-1} compared with a solution in CCl$_4$, and the ethynyl C—H stretching frequency ν_{CH} is reduced by 41 cm^{-1} (Steiner, Starikov & Tamm, 1996). Both values are indicative for weak but significant hydrogen bonding. Quantum chemical calculations (*ab initio* molecular orbital) estimated for both produce bond energies around −5.4 kJ mol^{-1}.

The geometry of these interactions is shown in detail in Fig. 3 and geometrical parameters are listed in Table 4. The ω angles given in Table 4 are defined as the angle
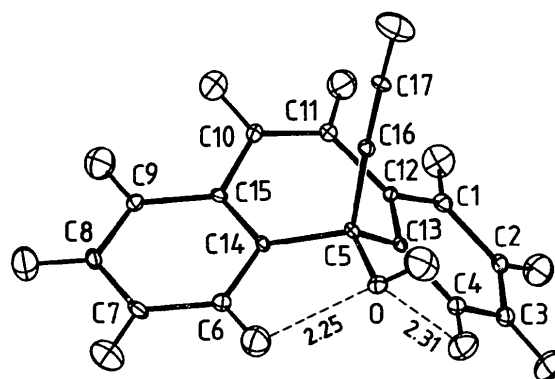

Fig. 1. Molecular structure of (1) at 20 K; displacement ellipsoids are drawn at the 50% probability level. Only C and O atoms are labeled. Selected geometrical data: Angle between least-squares planes of the benzyl groups: 50.38 (7)°. Geometry of the intramolecular C—H···O contacts: H4···O 2.312 (5), H6···O 2.247 (5), C4···O 2.723 (3), C6···O 2.663 (3) Å; C4—H···O 100.3 (3), C6—H···O 100.1 (3)°. Torsion angle defining the O—H orientation: C16—C5—O—H −33.7 (5)°.

Table 4. *Geometry of the aromatic hydrogen bonds*
($\overset{\circ}{A}$,°); M = aromatic midpoint

C—H···X	H···C	O/C···C	O/C—H···C	ω(H)	ω(O/C)
O—H···C1^i	2.339 (6)	3.270 (3)	174.4 (5)		
O—H···C2^i	2.680 (6)	3.539 (3)	153.4 (5)		
O—H···C3^i	3.523 (6)	4.280 (3)	139.9 (4)		
O—H···C4^i	4.020 (6)	4.752 (3)	137.7 (4)		
O—H···C13^i	3.832 (6)	4.585 (3)	139.8 (4)		
O—H···C12^i	3.012 (6)	3.835 (3)	147.9 (5)		
O—H···M^i	2.979 (6)	3.832 (3)	152.6 (4)	41.7	35.3
C17—H···C1^{ii}	2.848 (5)	3.575 (3)	125.7 (4)		
C17—H···C2^{ii}	3.001 (6)	3.586 (3)	115.2 (4)		
C17—H···C3^{ii}	3.097 (6)	3.783 (3)	123.0 (4)		
C17—H···C4^{ii}	3.009 (6)	3.921 (3)	144.2 (4)		
C17—H···C13^{ii}	2.855 (5)	3.909 (3)	170.8 (5)		
C17—H···C12^{ii}	2.822 (5)	3.791 (3)	151.5 (4)		
C17—H···M^{ii}	2.587 (5)	3.494 (3)	142.8 (5)	6.8	8.6

Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z$; (ii) $\frac{3}{2} - x, y - \frac{1}{2}, -z$.

between the normal of the Ph plane and the X···M line (I). An atom X placed exactly 'above' the Ph midpoint is characterized by $\omega = 0°$. The numerical data in essence verify the X-ray study, aside from the expected hydrogen-bond shortening due to cooling. The ethynyl group is placed roughly above the Ph midpoint M with $\omega(H) = 6.8°$ and $\omega(C) = 8.6°$ and points to M. The distances of the ethynyl H atom to the six individual C atoms are in the narrow range 2.848–3.097 Å (range
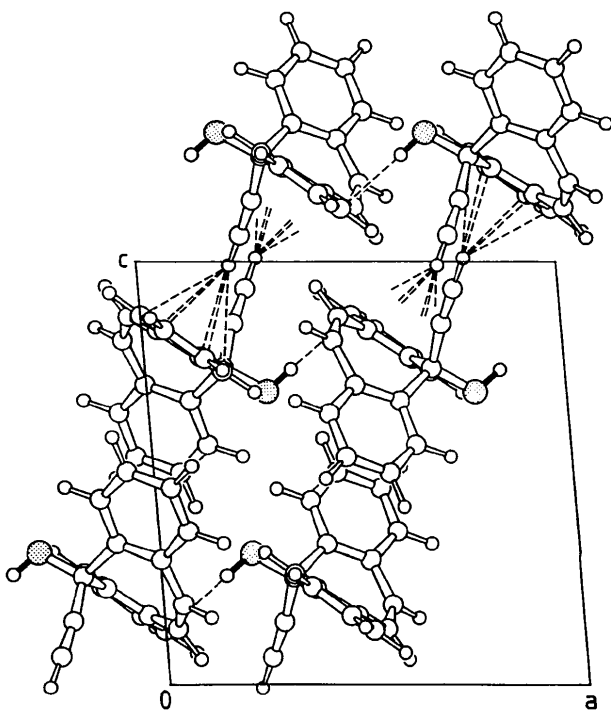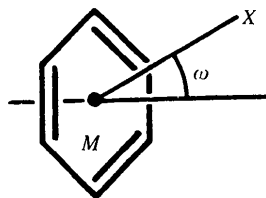
Table 5. *X—H bond distances ($\overset{\circ}{A}$)*

O—H	0.934 (8)	C7—H	1.096 (5)
C1—H	1.092 (5)	C8—H	1.090 (4)
C2—H	1.088 (4)	C9—H	1.096 (4)
C3—H	1.091 (4)	C10—H	1.093 (4)
C4—H	1.084 (4)	C11—H	1.088 (4)
C6—H	1.088 (5)	C17—H	1.064 (5)

(I)

width 0.249 Å) and the distance to the midpoint is shorter than that to any of the C atoms [H···M = 2.587 (5) Å]. This is close to ideal geometry, which allows interaction of the C≡C—H donor with the entire aromatic π-electron cloud.

(a)

(b)

Fig. 2. Crystal packing in projection on the x, z plane. O—H···Ph and C≡C—H···Ph hydrogen bonds are indicated by dashed lines. O atoms are drawn shaded. Note that the molecules linked by C≡C—H···Ph interactions are related by the 2_1 screw axis and therefore form a chain in the y direction.
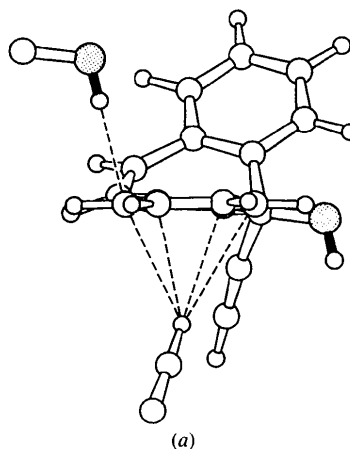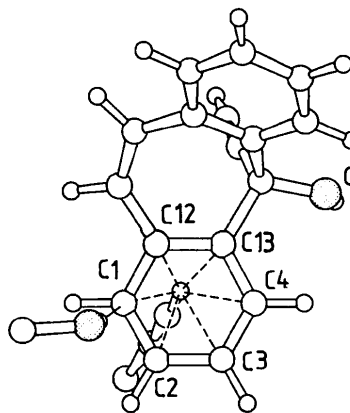
Fig. 3. The O—H···Ph and C≡C—H···Ph hydrogen bonds shown in projections (a) onto the Ph plane and (b) perpendicular to the Ph plane. O atoms are drawn shaded.

Table 6. Csp^1—H bond distances d_{CH} (Å) determined by single crystal neutron diffraction at low temperature

Compound	T (K)	d_{CH}	C≡H—H interaction	Reference
(1)	20	1.064 (5)	C—H···Ph bond	This work
2-Ethynyladamantan-2-ol	100	1.070 (8)	C—H···O bond	Allen *et al.* (1996)
2-Ethynyladamantan-2-ol	100	1.045 (12)	'Free'	Allen *et al.* (1996)
Acetylene, deuterated†	15	1.070 (5)	C—H···C≡C bond	McMullan *et al.* (1992)
Acetylene, deuterated‡	143	1.036 (3)	'Free'	McMullan *et al.* (1992)

† Orthorhombic phase.   ‡ Cubic phase; McMullan *et al.* (1992) note that d_{CH} is heavily affected by thermal vibration effects and question the reliability of d_{CH}; therefore, data of this kind given by McMullan *et al.* (1992) for nondeuterated acetylene is not shown here.

The geometry of the O—H···Ph interaction is very different: O—H does not reside above the center of the Ph group, but is very off-centered with $\omega(H) = 41.7°$ and $\omega(O) = 35.3°$. The O—H vector points almost linearly to the C1 atom of the Ph group with H···C1 = 2.339(6) Å and O—H···C1 = 174.4(5)°. The other H···C distances and also the distance to the Ph midpoint are much longer (H···C 2.339–4.020 Å, range width 1.681 Å). Furthermore, the O—H···Ph interaction is associated with a short H···H contact, H(O)···H1 = 2.371(8) Å, which is presumably repulsive. This is clearly a very unfavorable geometry for an aromatic hydrogen bond, resulting in the relatively low bond energy of −5.4 kJ mol^{-1} calculated for the room-temperature data, which must be compared with values < −8.4 kJ mol^{-1} for face-on geometries. The weakness of the O—H···Ph bond is reflected in a short covalent O—H bond length of 0.934(8) Å (not corrected for thermal vibration effects). In conventional hydrogen bonds, O—H is typically >0.95 Å; see *e.g.* Steiner & Saenger (1994).

3.3. C—H bond lengths

The C—H bond lengths as obtained in refinement are listed in Table 5. The mean length of the ten Csp^2—H bonds is 1.091 (1) Å and no individual value deviates more than 2σ from the mean. The ethynyl Csp^1—H bond is significantly shorter, 1.064(5) Å. For comparison, the few Csp^1—H bond lengths available from low-temperature single crystal neutron diffraction data are given in Table 6. These bond lengths are affected to differing degrees by thermal vibration (shortening) and hydrogen-bonding effects (lengthening), so that they can be compared only with reservation. The value for the cubic phase of deuterated acetylene was questioned by the original authors because of strong thermal vibrations and should therefore not be used as a reference value. The mean of the other four data is 1.062(6) Å, representing a preliminary value for the low-temperature neutron-determined 'normal' Csp^1—H bond length. Even though the data quantity is very small and the data set is chemically inhomogeneous, this value indicates that the Csp^1—H bond length is systematically shorter than the C—H bond lengths of chemically different C types. For comparison,

examples are given for mean values in low-temperature neutron data ($T < 30$ K): 1.085(1) Å for 345 Csp^2—H bonds in (CC)C—H systems; 1.088(1) Å for 312 Csp^3—H bonds in C—Me; 1.100(1) Å for 100 Csp^3—H bonds in (CC)CH$_2$ systems; 1.105(2) Å for 29 Csp^3—H bonds in (CCO)C—H systems (compiled by Steiner & Saenger, 1993).

4. Conclusions

In this study the geometries of two aromatic hydrogen bonds are reliably determined. In one, a C≡C—H donor points more or less to the midpoint of a Ph acceptor, thereby interacting with the entire π-electron cloud. In the other bond a hydroxyl group points to an individual C atom, which is an unfavorable geometry. Therefore, the bond energy of the O—H···Ph interaction is comparable to that of the C≡C—H···Ph bond, despite the much larger donor strength of O—H.

There are views in the literature that an aromatic hydrogen bond X—H···Ph requires that the X atom is placed above the Ph face and the X—H vector is oriented more or less at the center of the aromatic moiety; if this is not the case the arrangement should not deserve the name 'aromatic hydrogen bond'. In alternative views, aromatic hydrogen bonds are attributed very pronounced conformational variability, and off-centered geometries are regarded as nothing but somewhat less favorable cases. The present study clearly supports the latter view: the existence of a very off-centered O—H···Ph contact in (1) is confirmed; its bonding nature has previously been shown from IR spectroscopic data. There is no reason why contacts of this type should not be regarded as 'hydrogen bonds'.

Note added in proof. After submission of this paper, a relevant neutron diffraction study of aromatic hydrogen bonds in aminophenols was published: Allen, F. H., Hoy, V. J., Howard, J. A. K., Thalladi, V. R.,

Desiraju, G. R., Wilson, C. C. & McIntyre, G. J. (1997). *J. Am. Chem. Soc.* **119**, 3477-3480.

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