

Weak hydrogen bonding. Part 3.¹ A benzyl group accepting equally strong hydrogen bonds from O–H and C–H donors: 5-ethynyl-5H-dibenzo[*a,d*]cyclohepten-5-ol

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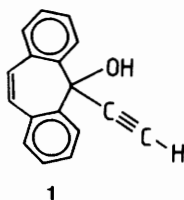
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In the crystal structure of the title compound, one of the benzyl groups accepts hydrogen bonds from a hydroxy and an ethynyl group, one to each face of the ring. For both hydrogen bonds, energies around $-1.3 \text{ kcal mol}^{-1}$ have been calculated. The bond donated by the hydroxy group has unusual geometry and is directed almost linearly at a C atom with $\text{H} \cdots \text{C} = 2.36 \text{ \AA}$.

Introduction

It has long been known from spectroscopic experiments that aromatic moieties may accept hydrogen bond type interactions,² which are usually called 'X–H $\cdots \pi$ hydrogen bonds'. However, these weak hydrogen bonds were for a long time regarded as exotic and of little general importance. Only in recent years have their structural properties attracted greater interest. In the gas phase, where hydrogen bonded dimers are formed free of steric strain, distances of the donor X to the aromatic midpoint M were found to be 3.35 Å for X–H = water,³ 3.59 Å for X = ammonia⁴ and 3.62 Å for X–H = HCl.⁵ For the dimer water–benzene, a binding energy around 1.8 kcal mol⁻¹ and a very flat potential were found;³ the latter results in a soft geometry of the interaction (1 cal = 4.184 J). For the crystalline state, several examples of O–H $\cdots \pi(\text{Bz})$ hydrogen bonds are documented.^{6,7} In biological systems, N–H $\cdots \pi(\text{Bz})$ interactions are of particular importance.^{8,9} Even acidic C–H groups may donate hydrogen-bond type interactions to aromatic moieties.^{1b}

In the present study, we have investigated the intermolecular interactions in crystalline 5-ethynyl-5H-dibenzo[*a,d*]cyclohepten-5-ol, **1**, using crystallographic, IR-spectroscopic and computational techniques.



In classical terms,¹⁰ one should expect hydrogen bonds to be formed between the strongest donor and the strongest acceptor in the structure; in **1**, this would result in cooperative interactions O–H \cdots O–H \cdots O–H. However, we find a complex system of different types of weak hydrogen bonds and $\pi \cdots \pi$ interactions, in particular of X–H $\cdots \pi(\text{Bz})$ hydrogen bonds, whereas O–H \cdots O hydrogen bonds are not formed.

Results

Molecular structure

The molecular structure of **1** as observed in the crystal structure is shown in Fig. 1. The central cycloheptene ring adopts a boat

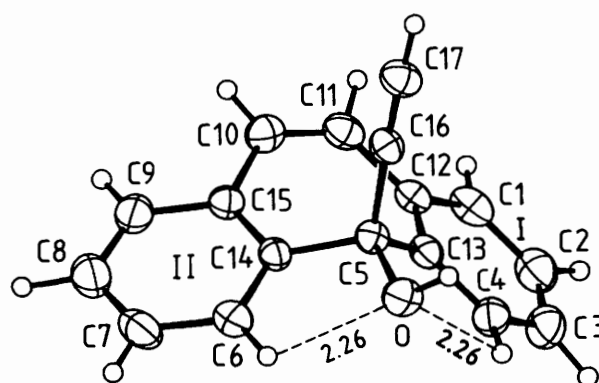


Fig. 1 Molecular structure and atomic numbering scheme of 5-ethynyl-5H-dibenzo[*a,d*]cyclohepten-5-ol (displacement ellipsoids drawn at the 30% probability level)

conformation, the substituent hydroxy group is equatorial and the ethynyl group is in an axial position with respect to this ring. The two benzyl groups (I, II) form a dihedral angle of 51.1°. The overall shape of the molecule therefore is arched with the ethynyl group projecting perpendicularly from the convex side. The hydroxy group is involved in short intramolecular contacts with two benzyl H-atoms ($\text{H} \cdots \text{O} = 2.26 \text{ \AA} \dagger$), which cover the larger part of the oxygen lone-pair region. Only a fraction of the lone-pair region remains sterically accessible for intermolecular interactions.

Crystal structure

In the crystal lattice, dimers are formed in which molecules related by the inversion centre of the space group contact with their concave faces, Fig. 2. This is associated with parallel $\pi \cdots \pi$ interactions of benzyl group II (interplanar distance 3.55 Å, lateral shift 1.36 Å, centroid–centroid distance 3.80 Å). Furthermore, there is a relatively short contact from benzyl group II to benzyl group I of the other molecule in the dimer (C8–H \cdots C4' with $\text{H} \cdots \text{C} = 2.88 \text{ \AA}$). The outer surface of the dimer is characterised by the two projecting ethynyl residues and the sterically shielded hydroxy groups.

[†] Geometry of the intramolecular C–H \cdots O contacts: H4 \cdots O and H6 \cdots O = 2.26 Å; C4 \cdots O = 2.72 and C6 \cdots O = 2.65 Å; angle at H = 104° and 101° for H4 and H6, respectively (for normalised H-positions).

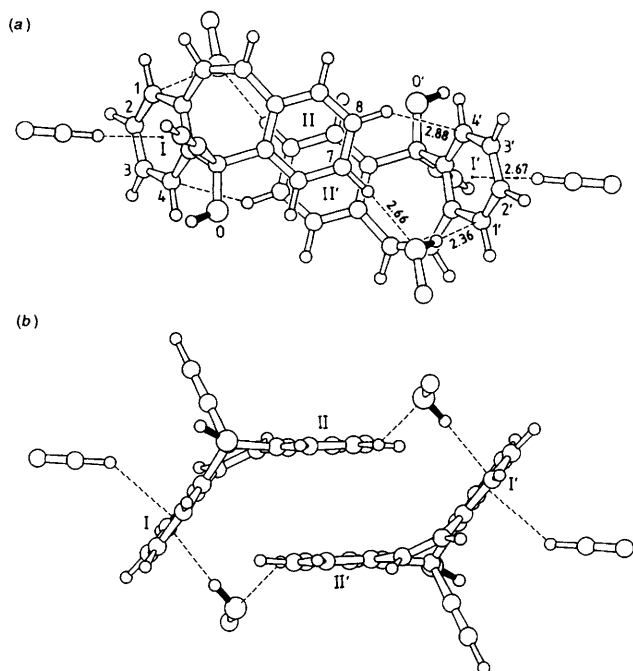


Fig. 2 Molecular dimer and the accepted hydrogen bonds. (a) Projection on the plane of benzyl group II. (b) Projection perpendicular to benzyl group II. To show the direction of the hydrogen bonds accepted by the benzyl group, the bond donated by O-H is drawn to a C atom, whereas the one donated by C≡C-H is drawn to the aromatic centroid.

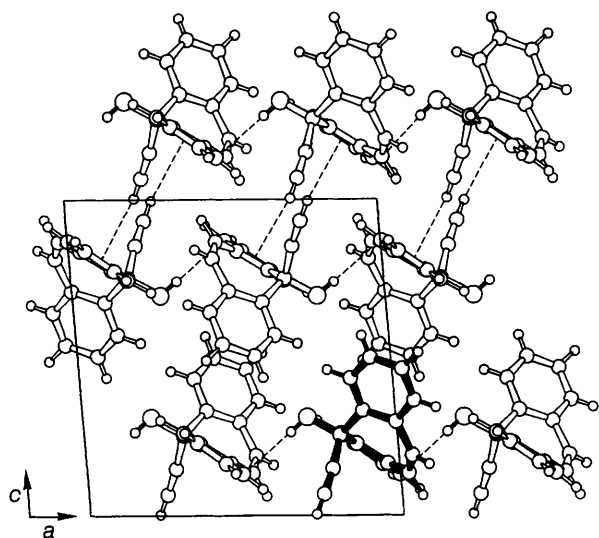


Fig. 3 Crystal packing in projection on the *a,c*-plane. Only the dominant C-H... π and O-H...C contacts are shown by dashed lines; C-H...O contacts omitted for clarity. In this projection, there appear to be dimers linked by mutual -C≡C-H... π interactions; actually, however, the molecules involved in this interaction form infinite chains in the direction of the crystallographic *b*-axis (*i.e.* the projection axis).

The arrangement of the dimers in the crystal lattice is shown in Fig. 3. Surprisingly, the hydroxy and the ethynyl groups do not donate X-H...O or X-H... π (C≡C) interactions, but satisfy their hydrogen bond donor potentials by intermolecular contacts to benzyl group I (also shown in Fig. 2). The geometry of these interactions is shown in detail in Fig. 4 (relevant numerical data in Table 1). The ethynyl residue points almost directly at the midpoint M of the aromatic group: the six relevant H...C separations fall into the narrow range 2.92–3.13 Å and the H...M separation of 2.67 Å is significantly shorter than any of the H...C distances. This is the typical geometry of a C≡C-H... π (Bz) hydrogen bond.^{1b} The hydroxy

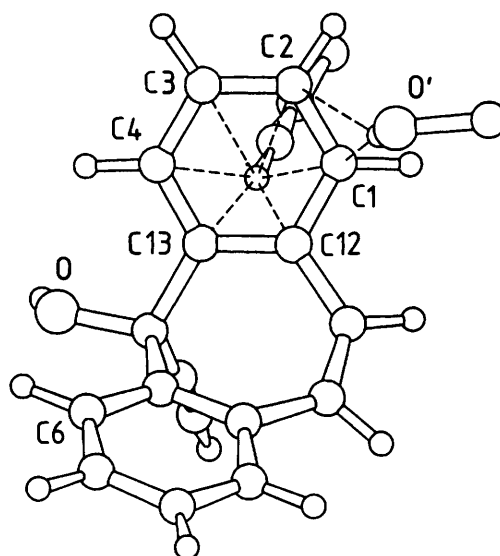


Fig. 4 Hydrogen bonds accepted by benzyl group I shown in projection on the aromatic plane

Table 1 Geometry of the hydrogen bonds accepted by benzyl group I in Å and degrees; M = benzyl centroid (for normalised H-positions based on bond lengths C-H = 1.08 Å and O-H = 0.98 Å)

	H...C	O...C	O-H...C
O-H...C1	2.36	3.34	176
...C2	2.70	3.60	153
...C3	3.55	4.35	140
...C4	4.07	4.85	139
...C13	3.88	4.69	141
...C12	3.05	3.93	150
...M	3.02	3.92	153
	H...C	C...C	C-H...C
C17-H...C1	2.93	3.68	127
...C2	3.05	3.65	116
...C3	3.13	3.83	123
...C4	3.06	3.98	144
...C13	2.94	4.00	169
...C12	2.92	3.91	152
...M	2.67	3.59	143

group contacts the other face of the benzyl group in a very different geometry: the O-H bond points almost linearly at an individual C atom (C1) with H...C = 2.36 Å and an angle at H of 176°. This interaction is associated with a short H...H contact, (O)H...H1 = 2.39 Å. The second shortest H...C contact is to C2, 2.70 Å, and all other H...C distances are > 3 Å, Table 1. This is an unusual geometry which contrasts with the face-on O-H... π (Bz) hydrogen bonds reported earlier.⁷

As mentioned above, the hydroxy group is sterically shielded by intramolecular contacts to C4-H and C6-H (Fig. 1). The remaining acceptor potential is only poorly satisfied by two long intermolecular C-H...O contacts with H...O separations of 2.66 and 2.70 Å, respectively ‡ (not shown in Fig. 4). These are very weak interactions, so that in this crystal structure, O-H accepts only much weaker hydrogen bonds than benzyl group I. The alkynyl group C≡C-H accepts only one long intermolecular contact from C11-H with H...C17 = 2.76 Å and H...C16 = 3.16 Å, which is also a very weak interaction (not shown in Fig. 3).

‡ Geometry of the intermolecular C-H...O contacts: C7-H...O: H...O = 2.66, C...O = 3.62 Å, angle at H = 149°, symm. = 1.5 - x, y - 0.5, 1 - z. C9-H...O: H...O = 2.70, C...O = 3.47 Å, angle at H = 130°, symm. = x + 0.5, -0.5 - y, z (for normalised H-positions).

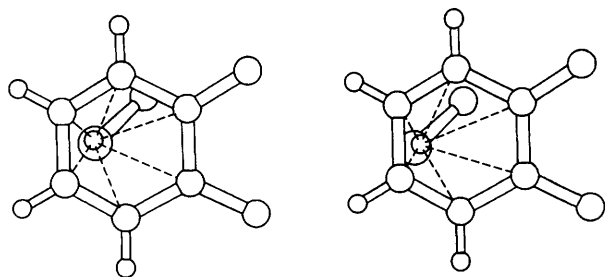


Fig. 5 Two symmetry-independent O–H... π hydrogen bonds in crystalline **2**.¹⁴ For acceptor molecule A (left), the individual H...C distances are in the range 2.32–2.92 Å, the H...M distance is 2.27 Å and the O–H...M angle is 161°. For acceptor molecule B (right), the H...C distances are in the range 2.39–3.12 Å, the H...M distance is 2.38 Å and the O–H...M angle is 170°.

IR spectrum

In order to verify the bonding nature of the X–H... π (Bz) contacts, the IR spectra were recorded for crystals and a dilute solution in CCl₄. In both spectra, the O–H and \equiv C–H stretching vibrations show sharp and distinct bands (for ν_{X-H} values, see Experimental section). The wavenumber shifts for crystals compared to apolar solution are -61 cm^{-1} for ν_{O-H} and -41 cm^{-1} for $\nu_{\equiv C-H}$. These spectral downshifts clearly indicate hydrogen bonding interactions of O–H and \equiv C–H.² Similar shifts of $\nu_{\equiv C-H}$ were observed in our previous study on \equiv C–H... π hydrogen bonds^{1b} (*cf.* for typical \equiv C–H...O hydrogen bonds,^{11,12} the downshift of $\nu_{\equiv C-H}$ is in the range 20–100 cm^{-1} ; for typical O–H...O hydrogen bonds,² the downshift of ν_{O-H} is 100 to several hundreds of cm^{-1}).

Quantum chemical calculations

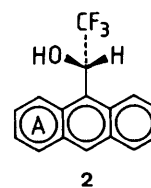
The energies of the intermolecular contacts discussed above were estimated by quantum chemical calculations in the same way as in the previous study^{1b} (*ab initio* molecular orbital calculations on suitable polyatomic models with ≤ 30 atoms using the program¹³ GAUSSIAN 92/DFT).

(a) Isolated contacts (dimers). Interaction energies were calculated for dimers with the same contact geometry as observed in the crystal structure. The O–H...C interaction was approximated by a dimer MeOH–benzene, yielding a bond energy of $-1.3\text{ kcal mol}^{-1}$. The \equiv C–H... π interaction was approximated by a dimer propyne–benzene, also yielding an energy of $-1.3\text{ kcal mol}^{-1}$ (very similar values were previously obtained for propyne–Bz dimers in other geometries^{1b}). The long C7–H...O contact shown in Fig. 2 ($\text{H}\cdots\text{O} = 2.66\text{ \AA}$) was approximated by a dimer benzene–MeOH, yielding a bond energy of only $-0.15\text{ kcal mol}^{-1}$, which is barely significant. Finally, the parallel $\pi\cdots\pi$ interaction was approximated by a benzene dimer to yield $-0.71\text{ kcal mol}^{-1}$.

(b) Cooperative patterns. The hydrogen bond pattern shown in Fig. 2 might possess some weak cooperative properties due to mutual polarisation of the involved groups. In a cooperative hydrogen bond arrangement, the total binding energy is significantly larger than the sum of bond energies of isolated contacts. This effect was clearly detected in calculations on interconnected interactions like \equiv C–H... \equiv C–H... π (Ph), where at least some of the groups involved act simultaneously as donor and acceptor.^{1b} In the present case, however, this effect did not show up in the calculations: for the trimer MeOH–Bz–propyne in the geometry of the O–H...Bz...H–C \equiv C arrangement (Fig. 2), we calculate a total bond energy of $-2.6\text{ kcal mol}^{-1}$ and for the trimer Bz–MeOH–Bz in the geometry of the C–H...O–H...Bz arrangement (Fig. 2), we calculate $-1.45\text{ kcal mol}^{-1}$. In both cases, these are the

sums of the individual bond energies. This means that on the present level of approximation, (i) the long C–H...O–H contact is too weak to enhance the strength of the O–H...C interaction significantly and (ii) the two hydrogen bonds accepted by the benzyl group can be regarded as independent interactions.

(c) Energy of face-on O–H... π (Bz) hydrogen bonds. In the present crystal structure, the O–H...Bz contact is not directed more or less at the centroid of the aromatic ring, but almost directly at a C atom and is furthermore associated with a (presumably repulsive) short H...H contact. More typical are face-on O–H...Bz hydrogen bonds, which were observed in several crystal structures (*e.g.* refs. 6, 7, 14–17). In most of the earlier examples, the interactions are intramolecular, *i.e.* associated with steric strain, or there are ions involved (anionic acceptor molecules), so that they cannot be directly compared with the present case. However, beautiful examples for intermolecular face-on O–H...Bz interactions in an uncharged compound were reported for (*S*)-2,2,2-trifluoro-1-(9-anthryl)ethanol, **2**, by Rzepa and co-workers.¹⁴ For this



crystal structure,[§] the geometries of two symmetry-independent O–H...Bz interactions are shown in Fig. 5 (geometrical data in the figure legend). In these contacts, the shortest H...C distances are similar as in the present structure, but the O–H bonds point at least roughly at the aromatic centroid and the H-atom is in relatively short contact with all benzyl C-atoms. Also, there are no short H...H contacts. Therefore, one can expect higher binding energies than in the title structure, and actually, we calculate energies of $-2.0\text{ kcal mol}^{-1}$ and $-2.4\text{ kcal mol}^{-1}$ for acceptors A and A', respectively. This is almost one half of the energy of a typical O–H...O hydrogen bond.

Discussion

The hydrogen bond acceptor potentials of benzyl groups and other aromatic moieties are usually underestimated, although X–H... π (Bz) hydrogen bonds have been observed in many crystal structures. The present crystal structure provides the first example of a benzyl group that accepts simultaneously two symmetry-independent hydrogen bonds of similar strengths. One of these is donated by a hydroxy and the other one by an ethynyl group. Quantum chemical calculations suggest bond energies around $-1.3\text{ kcal mol}^{-1}$ for both interactions, *i.e.* about one-third to one-quarter of the energy of conventional O–H...O hydrogen bonds. The IR downshift of ν_{X-H} and the calculated binding energies are similar to those usually reported for \equiv C–H...O hydrogen bonds. Since for steric reasons no O–H...O interactions are formed in the structure,[¶] the X–

[§] Atomic coordinates retrieved from the Cambridge Structural Database,¹⁹ reference code SOCLIF.

[¶] Note in response to referee's comment. In classical views,¹⁰ the organisation of a hydrogen bond arrangement follows laws of hierarchy and of competition: the strongest donor in a structure tends to hydrogen bond with the strongest acceptor, the second strongest donor bond with the second strongest acceptor, *etc.* Of **1**, by far the strongest donor is O–H, the second strongest is \equiv C–H and the $>$ C–H donors are rather weak.²⁰ The strongest acceptor is O–H, whereas the π -acceptors Bz, \equiv C and C=C are weak, C=C presumably being the weakest. Therefore, one should expect that in crystalline **1**, cooperative O–H...O–H...O–H hydrogen bonds are formed, which satisfy the dual donor/acceptor potential of the hydroxy group. For such O–

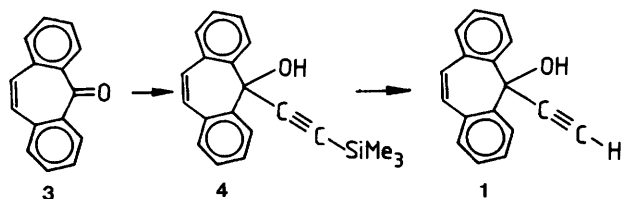
H... π (Bz) units are the strongest intermolecular forces in the crystal.

The geometries of the two X-H... π (Bz) interactions are strikingly different from each other. The one donated by the ethynyl group points approximately towards the aromatic centroid M, with the H...M distance significantly shorter than all individual H...C distances. In contrast, the interaction donated by the hydroxy group is significantly off-centred and points directly towards one of the C atoms. This supports gas-phase results³ that the hydrogen bond acceptor directionality of aromatic moieties is extremely soft, and allows considerably different hydrogen bond geometries with not much of a difference in bond energy. || This means that X-H... π (Bz) interactions can be easily and freely adjusted within the framework of other crystal packing forces. However, quantum chemical computations indicate that the face-on X-H... π (Bz) hydrogen bonds are somewhat stronger than off-centre bonds directed at individual C atoms. This is supported by the observation that the face-on bonds occur more frequently in crystal structures than the off-centre arrangements.

Experimental

Synthesis of the title compound

The title compound **1** was prepared starting from 5*H*-dibenzo[*a,d*]cyclohepten-5-one, **3**, following Scheme 1. All



Scheme 1

operations were performed in an atmosphere of dry argon using Schlenk and vacuum techniques. Solvents were dried by standard methods and distilled prior to use. NMR spectra were recorded on a Bruker AM 270 (270 MHz) instrument. IR spectra were taken on a Perkin-Elmer 983 instrument. Elemental analyses (C, H, N) were performed on a Heraeus CHN-rapid elemental analyser. Mass spectra (EI, 70 eV) were recorded on a Varian MAT 711 instrument.

H...O interactions, bond energies are typically around 4–5 kcal mol⁻¹. Since then no more O acceptors are available, the C \equiv C–H group should form hydrogen bonds with one of the second strongest acceptors, either C \equiv C–H...C=C or C \equiv C–H...Bz, with bond energies around 1–2 kcal mol⁻¹.^{1b} The other C–H donors should play only a marginal role. We found this hierarchy obeyed in a number of related crystal structures,^{1b} but in **1**, it is obviously severely disabled. This is presumably due to the steric shielding of O–H and to the complicated shape of the molecule, which prevents the effective O–H...O–H hydrogen bonding observed in the earlier study (and also prevents possible C \equiv C–H...O–H interactions). Instead, O–H must resort to the second strongest acceptor available, Bz, which is also the acceptor for C \equiv C–H. As a result, only weak hydrogen bonds are formed, none of which is clearly dominant over the others. We refrain from speculations as to which of the intermolecular interactions contributes in which way to molecular association. Generally, crystal packing results from the interplay of all intermolecular forces (hydrogen bonds, π ... π , van der Waals, etc.) and it is usually very difficult or even impossible to quantify the role of a particular contributor. This is particularly true if, as in the present case, a large number of weak interactions of similar strengths are formed.

|| Note in response to referee's comments. The theoretical understanding of X–H... π hydrogen bonding is very unsatisfactory, although it is more or less accepted that they are primarily electrostatic interactions. There are major uncertainties concerning the directionality behaviour, distance dependence, energetics, cooperativity, polarisation, etc., which cannot be explained by individual crystal structure analyses.

(a) **5-Trimethylsilylethynyl-5*H*-dibenzo[*a,d*]cyclohepten-5-ol, **4**.** A solution of trimethylsilylacetylene (4 cm³, 28 mmol) in 60 cm³ of THF was treated with butyllithium (10.5 cm³; 2.5 mol dm⁻³ in hexane; 26 mmol) at –78 °C. After stirring for 10 min, the solution was allowed to warm up to room temperature. After recooling to –78 °C a solution of **3**, (commercial, Aldrich; 5 g, 24 mmol) in 40 cm³ of THF was added dropwise. Stirring was continued at low temperature for 20 min and at room temperature for an additional 30 min. Water (20 cm³) was added followed by anhydrous potassium carbonate until the aqueous solution became pasty. The organic phase was decanted and the aqueous layer was washed with 2 \times 20 cm³ of diethyl ether. The combined organic phase was dried over sodium sulfate and filtered. Removal of the solvent under reduced pressure gave **4** as a white solid (5.5 g, 75%). ¹H NMR (270 MHz, CDCl₃) 8.06 (d, 2 H, CH), 7.44–7.22 (m, 6 H, CH), 7.13 (s, 2 H, C=CH), 3.00 (s, 1 H, OH) and 0.20 (s, 9 H, SiCH₃).

(b) **5-Ethynyl-5*H*-dibenzo[*a,d*]cyclohepten-5-ol, **1**.** A solution of **4** (5 g, 16 mmol) in 50 cm³ of methanol was treated with aq. KOH (16 cm³; 1 mol dm⁻³). After stirring for 1 h methanol was removed under reduced pressure and the aqueous phase was extracted with 5 \times 50 cm³ of diethyl ether. The organic phase was dried over sodium sulfate and filtered. Evaporation of the solvent and recrystallisation from diethyl ether–hexane at –26 °C gave **1** as large, prismatic colourless crystals (3.2 g, 84%) (Calc. for C₁₇H₁₂O: C, 87.90; H, 5.21. Found: C, 87.3; H, 5.07%). ¹H NMR (270 MHz, CDCl₃) 8.07 (d, 2 H, CH), 7.46–7.27 (m, 6 H, CH), 7.17 (s, 2 H, C=CH), 3.04 (s, 1 H, OH) and 2.64 (s, 1 H, C \equiv CH); ¹³C{¹H} NMR (CDCl₃, 67.89 MHz) 139.5, 132.4, 131.3, 129.1, 128.2, 127.1 (Ar-C) 123.7 (HC=CH), 84.7 (COH), 73.7 (C \equiv CH) and 72.1 (C \equiv CH); ν (KBr)/cm⁻¹ 3548 (O–H), 3269 (\equiv C–H) and 2102 (C \equiv C); ν (CCl₄)/cm⁻¹ 3609 (O–H), 3310 (\equiv C–H) and 2110 (C \equiv C).

Crystallography

X-Ray diffraction data for **1** were measured on an Enraf-Nonius Turbo-CAD4 diffractometer [FR571 rotating anode X-ray generator, Ni-filtered Cu-K α radiation with $\lambda = 1.542$ Å, crystal size 0.35 \times 0.25 \times 0.20 mm³, ω -scan mode, $\lambda/2 \sin \theta_{\max} = 0.89$ Å, 1714 unique reflections of which 1640 have $F_o > 2\sigma(F_o)$, room temperature]. The space group is monoclinic $P2_1/a$ with $a = 11.991(2)$, $b = 8.356(1)$, $c = 12.105(3)$ Å, $\beta = 94.62(3)^\circ$, $V = 1208.8(4)$ Å³, $Z = 4$, $D_c = 1.28$ g cm⁻³. The structure was solved with direct methods and refined with standard techniques,¹⁸ final $R = 0.049$ [anisotropic refinement for non-H atoms and isotropic refinement for H atoms, refinement against F for reflections with $F_o > 2\sigma(F_o)$, no absorption correction]. ††

Computations

Quantum-chemical calculations were performed in the *ab initio* MO LCAO SCF (HF + MP2) approximation using the GAUSSIAN 92/DFT routine package.¹³ Hydrogen bond energies and atomic partial charges were calculated using the 6-31G** basis set and by taking into account the BSSE (basis set superposition error) by means of the MASSAGE option of the program (hardware: CRAY Y-MP4D/464 of the Konrad-Zuse-Zentrum, Berlin).

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†† Atomic coordinates, displacement parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. For details, see Instruction to Authors, Issue 1.

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Note added in proof: an O-H... π (Bz) hydrogen bond with an edge-on geometry similar to that in **1** was found in 2-(2,4,6-trimethylphenyl)adamantan-2-ol by J. Baron, J. A. Kanters, E. T. G. Lutz, J. H. van der Maas, A. Schouten and M. Wierzejewska-Hnat (*J. Mol. Struct.*, 1990, **222**, 305) with a spectral downshift of $\nu_{\text{O-H}}$ 65 cm^{-1} .

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