First example of cooperative O–H···C≡C–H···Ph hydrogen bonding: crystalline 7-ethynyl-6,8-diphenyl-7*H*-benzocyclohepten-7-ol

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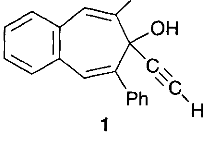
In the crystalline title compound, molecular dimers are joined by a system of interconnected O–H···C≡C–H and C≡C–H···Ph hydrogen bonds for which IR spectra indicate considerable strength; this hydrogen-bond configuration has not been observed previously.

It is generally accepted that acidic C–H groups may act as weak hydrogen-bond donors,[1] and that π-bond moieties like C=C, C≡C, Ph or heteroarenes may act as weak hydrogen-bond acceptors.[2] In some cases, the terminal alkynyl group was even found to donate and accept hydrogen bonds simultaneously,[2,3] O–H···C≡C–H···O. Interactions between weak donors and weak acceptors have been studied in various systems,[4] but the degree to which they parallel conventional hydrogen bonding is rather unclear. Recently, we showed that short contacts between the acidic C–H donor C≡C–H and π-acceptors have the structural and IR-spectroscopic characteristics of hydrogen bonds,[5,6] very similar to, for example, C–H···O interactions. In the present communication,† we report the first example of an interconnected hydrogen-bond system O–H···C≡C–H···Ph, which is found in the crystalline title compound, **1**.‡

The crystal structure of **1**§ contains two symmetry-independent molecules. Since they have very similar conformations,¶ the molecular structure and the atomic numbering scheme is shown only for one, Fig. 1. The central cycloheptadiene ring is in a boat conformation; the hydroxy group is in an equatorial and the ethynyl group in an axial position with respect to the ring; the phenyl rings are positioned almost perpendicular to each other. The lone-pair region of the hydroxy group is engaged in two intramolecular contacts with the phenyl rings, and is therefore sterically hindered to form short intermolecular contacts. In the crystal lattice, the two symmetry-independent molecules form a dimer (Fig. 2), which is held together by an unexpected system of weak hydrogen bonds: the hydroxy groups do not form hydrogen bonds with other hydroxy groups (as is the normal case), but point at the triple bonds of the alkynyl residues (geometry in Table 1).|| The ethynyl residues form short contacts with phenyl rings of the neighbouring molecules. For both types of contacts, the geometries are indicative of weak hydrogen bonding: for the O–H···C≡C contacts, the H···C distances are between 2.41 and 2.51 Å with even shorter distances to the centre of the triple bond. For the C≡C–H···Ph contacts, the individual H···C distances cover the relatively wide range 2.64–3.25 Å, but the distances to the aromatic centroids are shorter than any of the H···C separations (Table 1).



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To see whether the described contacts actually are hydrogen bonds, the IR absorption spectra were recorded for crystals and solutions in CCl_4.†† The results (Table 2) show the typical spectral shifts indicative of weak hydrogen bonding:[3,5,7] the alkynyl C–H stretching frequency $\nu_{\equiv C-H}$ in the crystal is reduced by $\Delta\nu$ −46 cm^{-1} compared to the 'free' alkynyl group

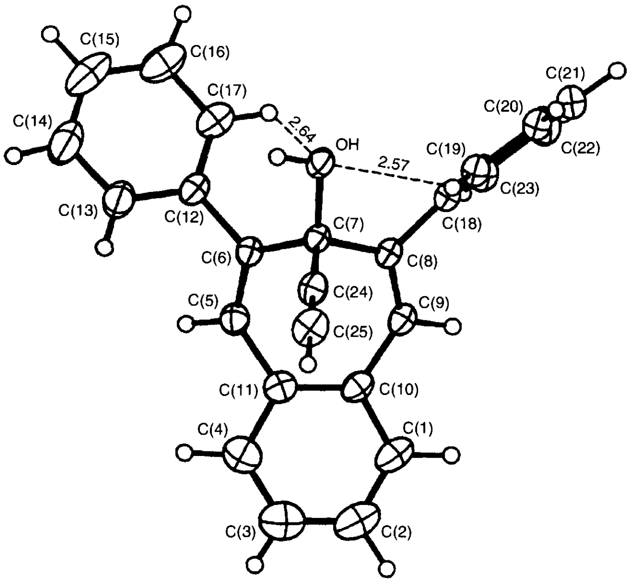

Fig. 1 Molecular structure and atomic numbering scheme of **1** (molecule A; the conformation of molecule B is almost identical). Displacement ellipsoids are drawn at the 30% probability level.

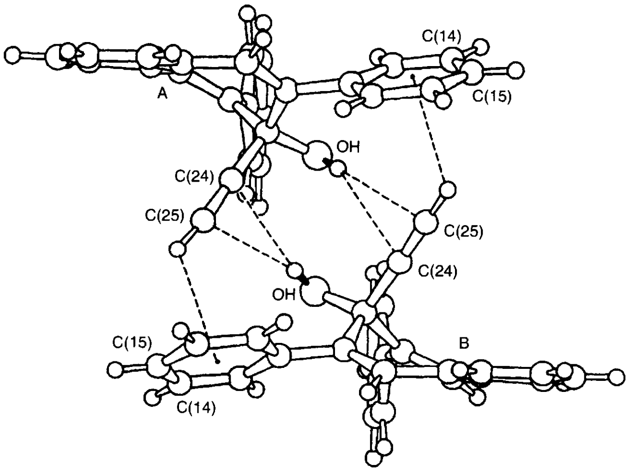

Fig. 2 The dimer of molecules A and B and the intermolecular hydrogen bonds

in the CCl_4 solution; similar spectral downshifts are typically observed for the better investigated C≡C–H···O hydrogen bonds.[7] When recorded at liquid-nitrogen temperature, owing to sharpening of the bands, a slight splitting of the $\nu_{\equiv C-H}$ band is observed (Table 2); this reflects that owing to the symmetry independence of molecules A and B, the two C≡C–H···Ph interactions are non-equivalent. Particularly interesting is the behaviour of the OH stretching frequency. Even in CCl_4 solution, it is shifted by about -17.5 cm^{-1} from the normal values *ca.* 3607.5 cm^{-1} for free tertiary equatorial α-ethynyl alcohols.[8] This indicates that in apolar solution, the O–H group forms a weak hydrogen-bond like intramolecular interaction with one of the phenyl groups, which are the only acceptors that are sterically available (similar shifts of ν_{O-H} occur with intramolecular O–H···C≡C interactions in apolar solvents).[9] In the crystal, ν_{O-H} is reduced by *ca.* -98 cm^{-1} from the value for free O–H. This is a shift comparable to the 'long end' of conventional O–H···O hydrogen bonds,[10] indicating an appreciable strength of this O–H···π interaction.

The above results leave no doubt that the molecular dimers in crystalline **1** are held together by interconnected hydrogen bonds of the cooperative arrangement O–H···C≡C–H···Ph. This hydrogen-bond configuration has not been reported before (and the Cambridge Structural Database contains no comparable entry), adding a new variant to what modes of intermolecular interactions one must be prepared to find in the solid state.

This study was supported by the Deutsche Forschungsgemeinschaft (T. S. by Sa 196/25-1, M. T. by Ta 189/1-1 and Ta 189/1-2) and by the Research Network 'Molecular Recognition and Complexity' of the European Union (ERB-CHRX-CT94-0469). T. S. is on leave from the Max-Delbrück-Centrum für Molekulare Medizin, Forschungsgruppe Kristallographie (Professor U. Heinemann), Robert Rössle Strasse 10), 13122 Berlin, Germany.

Table 1 Geometry of the hydrogen bonds (Å,°) M = centroid of the π acceptors (for normalized H-positions with C–H 1.09 Å, O–H 0.98 Å). Left numbers correspond to contacts donated by molecule A, right numbers to contacts donated by molecule B

	H···C	X···C	X–H···C
O–A/B–H···C(24)B/A	2.50/2.50	3.29/3.40	138/152
···C(25)B/A	2.41/2.51	3.32/3.44	154/159
···M–B/A	2.38/2.43	3.25/3.37	147/159
C(25)A/B–H···C(12)B/A	3.25/3.18	3.57/3.58	100/102
···C(13)B/A	2.94/2.98	3.46/3.55	109/113
···C(14)B/A	2.65/2.72	3.52/3.62	136/140
···C(15)B/A	2.64/2.65	3.66/3.68	155/158
···C(16)B/A	2.93/2.88	3.76/3.71	132/133
···C(17)B/A	3.20/3.13	3.71/3.66	109/110
···M–B/A	2.59/2.58	3.34/3.36	124/127

Table 2 Stretching wavenumbers†† in cm^{-1}

Sampling	ν_{O-H}	$\nu_{\equiv C-H}$
Dilute solution in CCl_4 at room temp.	3590.1[a]	3311.2
Crystal (in KBr) at room temp.	3509.8	3265.4, 3270.8(sh)
Crystal (in KBr) at 98 K	3501.8	3256.2, 3260.3

[a] For tertiary 'non-shielded' α-ethynyl alcohols, HC≡C–CR(OH)–R′, ν_{O-H} values in CCl_4 are typically in the range 3611–3606.5 cm^{-1}.[8]

Footnotes

† Part 4 of the Series 'Weak Hydrogen Bonding'. Part 3: see Ref. 6.

‡ *Synthesis of* **1**: analogous to the title compound of Ref. 6. Starting material 6,8-diphenyl-7*H*-benzocyclohepten-7-one, **2**.[11] (*i*) Addition of –C≡C–SiMe$_3$ at C^7 by reaction with HC≡C–SiMe$_3$, *n*-buthyllithium, yields 7-(trimethylsilylethynyl)-6,8-diphenyl-7*H*-benzocyclohepten-7-ol **3**; (*ii*) deletion of SiMe$_3$ by treatment of **3** (MeOH) with 1 mol dm^{-3} KOH yields **1**.

§ *Crystal data* for **1**: 7-Ethynyl-6,8-diphenyl-7*H*-benzocyclohepten-7-ol ($C_{25}H_{18}O$, M = 334.4). Crystallization from H_2O–hexane, monoclinic, space group $P2_1/n$; a = 16.478(3), b = 10.475(1), c = 21.620(6) Å, β = 98.97(4) °, U = 3686(1) Å^3, Z = 8, D_c = 1.21 g cm^{-3}. Enraf-Nonius CAD4 diffractometer, room temperature, Ni-filtered Cu-Kα X-rays, ω–2θ scan mode, $\lambda/2 \sin \theta_{max}$ = 0.89 Å, 0.65 × 0.40 × 0.15 mm^3 crystal, 5453 unique reflections, 4702 with $F^2 > 2\sigma(F^2)$, no absorption correction. Structure solution and refinement with standard methods (SIR92 and SHELXL93); H-atoms refined isotropically. Final R = 0.036 (for observed reflections), $wR(F^2)$ = 0.116 (for all reflections). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/42.

¶ Conformational differences between the symmetry-independent molecules A and B respectively: the torsion angles within the cycloheptadiene ring vary by < 1.5 °. The torsion angles (°) defining the orientation of the phenyl rings are: C(7)–C(6)–C(12)–C(13) −123.0(2), −123.9(1); C(7)–C(8)–C(18)–C(19) 55.1(2), 56.6(2). The dihedral angles (°) between the phenyl planes are 82.8(1), 83.2(1)°. We thank a referee for calculating the parameters of the pseudo-twofold axis relating the independent molecules: X/a = 0.99(2), Y/b = 0.384(5), parallel to z, translation −0.018(4).

‖ Within the dimer, the hydroxy groups approach closely to an O···O distance of 3.10 Å, with H···O distances of 2.91, 2.70 Å and O–H···O angles of 92, 105 ° for H(A) and H(B), respectively. This might be taken as an indication of very weak hydrogen bonding. Since the arrangement is associated with a short repulsive H···H contact of 2.48 Å, however, it is unclear whether it has actually a net cohesive character.

†† FTIR instrumentation: Mattson Research Series spectrophotometer equipped with a DTGS detector; Specac P/N 21.000 variable-temperature cell. Scanning parameters: region 4000–500 cm^{-1}, resolution 2 cm^{-1}, 64 scans and triangular apodization.

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Received, 8th January 1996; Com. 6/00178E