"Weak" OH···πHydrogen Bonds in the Structures of Two Phenols

Piotr Kuś[a] and Peter G. Jones[b]

[a] Department of Chemistry, Silesian University, 9, Szkolna Street, 40-006 Katowice, Poland
[b] Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, D-38023 Braunschweig, Germany

Reprint requests to Dr. P. Kuś. E-mail: pkus@tc3.ich.us.edu.pl

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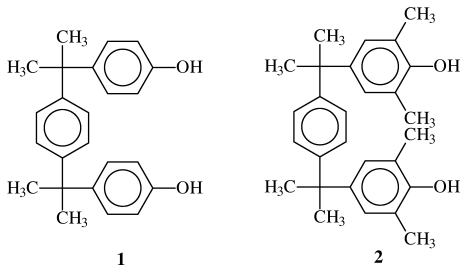
Crystallographic studies of α,α'-di(4-hydroxyphenyl)-1,4-diisopropylbenzene (**1**) and α,α'-di-(3,5-dimethyl-4-hydroxyphenyl)-1,4-diisopropylbenzene (**2**) were performed. Both compounds display the *anti* conformation. Compound **1** crystallizes as the 1:1 hydrate; the packing involves three classical hydrogen bonds and one non-classical OH···π bond. Both OH groups of **2** form non-classical OH···π hydrogen bonds to aromatic rings.

Key words: Phenol, Hydrogen Bond, Intermolecular Interaction, Crystal Structure, Supramolecular Chemistry

The occurrence of *intra*molecular hydrogen bonds of the type OH···π was confirmed, using IR spectroscopy, as long ago as the 1930's [1]. *Inter*molecular bonds of this nature became a subject of interest in the 1960's, whereby confirmation of their existence by crystallographic methods followed some thirty years later [2]. Such interactions are classified as one type of "weak" hydrogen bond, with a strong hydrogen bond donor (O-H) and a weak acceptor (the π-system).

The current paper describes OH···π interactions in the crystal structures of two bis-phenols, **1** and **2**. Their structures are shown in the Scheme. The two compounds were obtained using well-known methods described in the patent literature [3, 4].



Compound **1** can exist in two conformations: *anti* or *syn* (the Scheme shows the *syn* conformers). The structures were first established on the basis of NMR, UV and IR spectra, which however gave no clues as to the presence or otherwise of both isomers in the post-

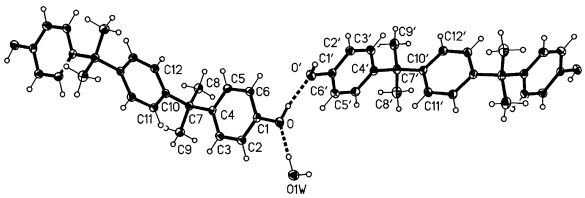


Fig. 1. The asymmetric unit of compound **1** (numbered), with the two independent molecules completed by inversion symmetry, showing two classical hydrogen bonds. Ellipsoids represent 50% probability levels.

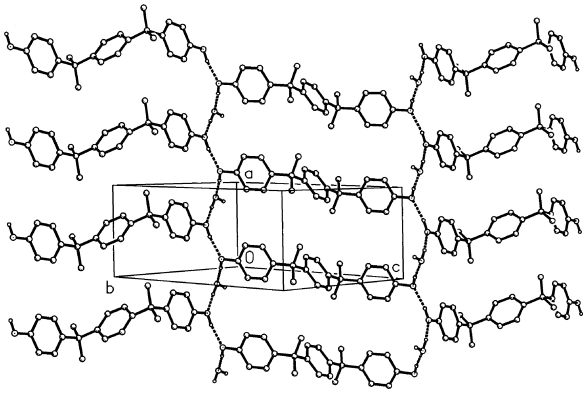


Fig. 2. Classical hydrogen bonding in compound **1** (hydrogen bonds shown as dashed lines; H atoms not involved in H bonding are omitted for clarity). View direction perpendicular to (011).

reaction mixture. This can only be confirmed, at least in the solid state, through crystallographic studies of the initial bis-phenol **1** and its ability to form cyclic

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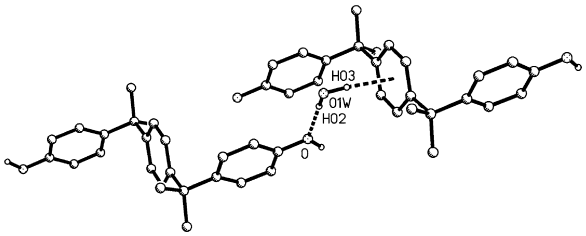

Fig. 3. The non-classical hydrogen bond from a water hydrogen to the centre of a phenyl ring in compound **1**.

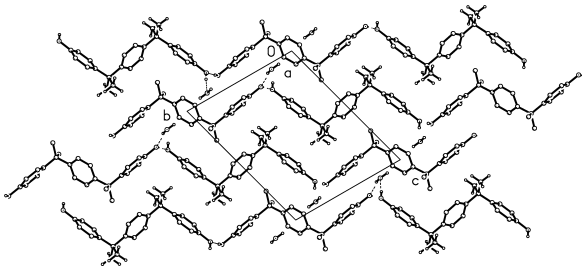

Fig. 4. Side-on projection (along the *x* axis) of neighbouring layers in **1**.

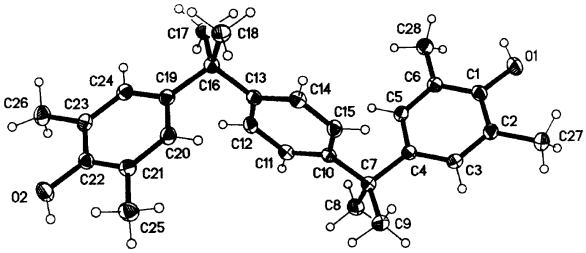

Fig. 5. The molecule of compound **2**. Ellipsoids represent 50% probability levels.

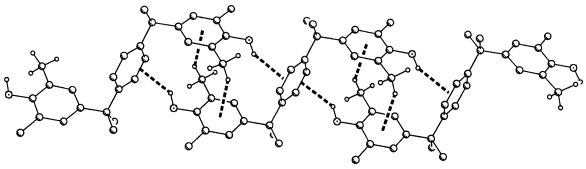

Fig. 6. The non-classical hydrogen bonding in **2**, linking the molecules parallel to the *x* axis.

compounds [5 – 9]. The occurrence of the stable *anti* conformer has been confirmed by a crystallographic study of the di-O-propyl derivative of compound **1** [6]. Here we report corresponding studies on compound **1** and its tetramethyl derivative [α,α'-bis(3,5-dimethyl-4-hydroxyphenyl)-1,4-diisopropylbenzene, **2**]. Compound **1**, however, was found to crystallize as a monohydrate, presumably having absorbed adventitious water.

Table 1. Crystallographic data collection, solution and refinement details for **1** and **2**.

Compound	**1** × H_2O	**2**
Formula	$C_{24}H_{28}O_3$	$C_{28}H_{34}O_2$
M_r[g/mol]	364.46	402.55
Crystal system	triclinic	monoclinic
Space group	$P(-1)$	$P2_1/c$
Cell dimensions [Å, °]: a	6.3484(6)	9.5948(6)
b	11.1770(11)	18.4855(12)
c	14.2379(12)	13.3212(11)
α	104.987(4)	90
β	92.591(4)	108.323(4)
γ	90.923(4)	90
V [Å^3]	974.50	2242.9
Z	2	4
$F(000)$	428	872
Crystal habit	Colourless tablet	Colourless, irregular
Crystal size [mm^3]	$0.45\times0.25\times0.15$	$0.40\times0.35\times0.25$
D_x [Mg/m^3]	1.242	1.192
$2\theta_{max}$ [°]	60	60
μ [mm^{-1}]	0.08	0.07
Temperature [K]	133	133
Measured reflections	11331	25265
Independent reflections	5606	6566
R_{int}	0.023	0.031
Parameters	264	287
S	1.05	1.05
$R1[F^2>2(F^2)]$	0.040	0.043
$wR2(F^2$, all refl.)	0.117	0.130
$\Delta\rho_{max}$ [eÅ^{-3}]	0.42	0.36

Table 2. Classical hydrogen bonds [Å and °] for compound **1**.

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
O-H(01)…O'	0.887(18)	1.833(18)	2.7111(10)	170.0(16)
O'-H(01')…O(1W)$^{\#1}$	0.888(16)	1.772(16)	2.6560(10)	173.5(14)
O(1W)-H(02)…O	0.884(18)	1.900(18)	2.7548(11)	162.2(16)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $x-1, y, z$.

Results and Discussion

The asymmetric unit in the structure of compound **1** consists of two independent half-molecules, both of which are extended to complete molecules by crystallographic inversion symmetry, and one molecule of water (Fig. 1).

Both molecules necessarily display the *anti* conformation; the interplanar angles from the central to the outer rings are 83° and 85°. The hydroxy groups and the water molecule are involved in three classical hydrogen bonds (Table 2), which link the residues to form corrugated layers parallel to (011) (Fig. 2).

It was, however, unexpected and striking that the potential hydrogen bond donor O-H03 was not involved in classical hydrogen bonds. Closer inspection showed that the layers are linked by a non-classical hydrogen

bond of the form OH···π from O-H03 to the centroid (Cent1) of the ring formed by C10-12 (and their inversion equivalents; Fig. 3).

The ring symmetry means that there are two such interactions, one on each side of the ring. With the O-H bond length normalised [10] to 0.98 Å, parameters for this interaction are H···Cent1 2.34 Å, O-H···Cent1 152°, operator $x,-1+y,z$. A search of the Cambridge Database [11] reveals few (*ca.* 10) examples of this type of interaction with reliable hydrogen positions of the water molecules, and the current structure appears to represent the shortest H···Cent distance yet recorded for a water hydrogen. Even shorter, charge-assisted, distances have however been established between other OH functions and tetraphenylborate anions [12].

Other ring centroids, Cent2 from C1-C6 and Cent3 from C1'-C6', are involved in C-H···π interactions involving methyl hydrogens: C8'-H8'2···Cent2 2.71 Å, 147°, operator $1-x,1-y,1-z$ and C9'-H9'1···Cent3 2.68 Å, 145°, operator $-x,1-y,1-z$ (C-H normalised to 1.08 Å [10]). These interactions can all be recognised in the side-on projection of neighbouring layers (Fig. 4).

The tetramethyl derivative of compound **1** [α,α'-di (3,5-dimethyl-4-hydroxyphenyl)-1,4-diisopropylbenzene **2**] forms cyclic tetraoxycyclophane structures, as does compound **1**, and with similar yields [13]. It crystallizes in an analogous *anti* conformation to that of **1** (Fig. 5).

Neither OH group of **2** participates in classical hydrogen bonding. Instead, both form non-classical OH···π hydrogen bonds to aromatic rings. However, there is a clear difference from the OH···π hydrogen bonds of **1**; the acceptors are better formulated with individual bonds, rather than the complete rings. The parameters (M = midpoint) are: O1-H01···($M_{C11-C12}$), H···M 2.42 Å, angle 143°, operator $1+x,y,z$; O2-H02···($M_{C14-C15}$), H···M 2.44 Å, angle 148°, operator $-1+x,y,z$. There is also a C-H···π interaction involving a methyl hydrogen: C28-H28C···Cent(C19-C24) 2.53 Å, 145°, operator $1+x,y,z$. The net effect (Fig. 6) is to link the molecules in chains parallel to the *x* axis.

Experimental Section

Compounds **1** and **2** were obtained as described in [3, 4]. Colourless single crystals were obtained by slow evaporation from a mixture of methanol (99%) and traces of pyridine (**1**), or from dichloromethane (after column chromatography) (**2**).

Data were registered on a Bruker SMART 1000 CCD diffractometer using Mo-K_α radiation. Structures were subjected to full-matrix least-squares refinement on F^2. Water and hydroxyl hydrogen atoms were refined freely. Methyl hydrogens were included as idealised rigid groups, with unambiguous starting positions from difference syntheses. Other hydrogens were included using a riding model.

Crystal data and details of refinement are given in Table 1. Data collection, cell refinement and data reduction: Bruker SMART 1000 CCD system [14]. Program used to solve structures: SHELXS-97 [15]. Program used to refine structures: SHELXL-97 [16]. Molecular graphics: Siemens XP [17]. Complete crystallographic data have been deposited at the Cambridge Crystallographic Data Centre under the numbers CCDC-227814 for **1**, and CCDC-227815 for **2**. Copies can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: Int.+1223-336-033; e-mail:deposit@ccdc.cam.ac.uk).

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