

## 2,4-Bis[1-(4-hydroxyphenyl)-1-methyl-ethyl]phenol: a three-dimensional framework built from O—H···O hydrogen bonds

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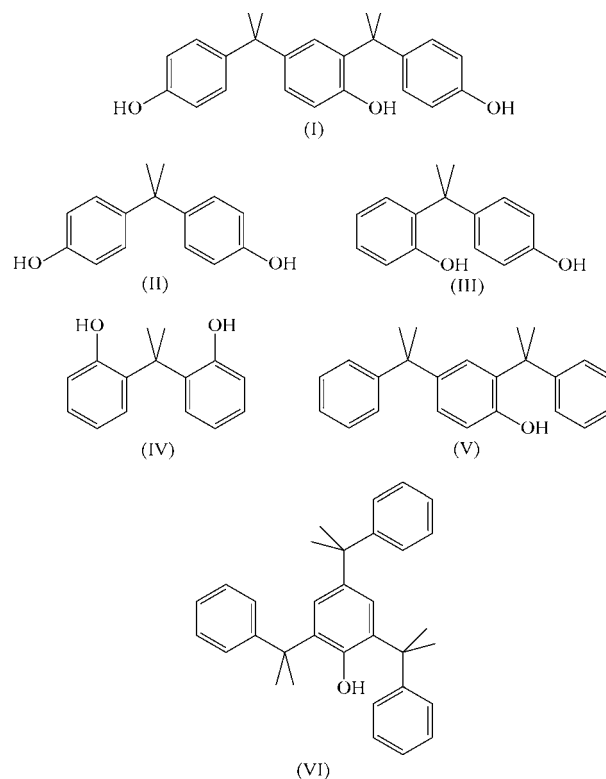
In the crystal structure of the title compound,  $C_{24}H_{26}O_3$ , (I), there are three different O—H···O hydrogen bonds, which individually form chains of  $C(10)$ ,  $C(12)$  and  $C(16)$  types. The combined effect of all these hydrogen bonds is the formation of a three-dimensional network, which is additionally stabilized by a single intermolecular C—H··· $\pi$  interaction. The significance of this study lies in the comparison drawn between the molecular structure of (I) and those of several of its analogues, which shows a close similarity in the almost perpendicular orientation of the benzene rings.

### Comment

The present investigation is a continuation of our work on the structural study of compounds formed as by-products during the industrial production of 4,4'-isopropylidenediphenol (commonly referred to as bisphenol-A or *p,p*-BPA), (II). In previous papers, the structures of two such by-products, *i.e.* 2,4'-isopropylidenediphenol [*o,p*-BPA; Cambridge Structural Database (CSD; Allen, 2002) refcode GALCAY (Rozycka-Sokolowska *et al.*, 2005)], (III), and 2,2'-isopropylidenediphenol [*o,o*-BPA; CSD refcode UCOFIC (Rozycka-Sokolowska *et al.* 2006)], (IV), were reported. Now, the structure of a third by-product, *i.e.* 2,4-bis[1-(4-hydroxyphenyl)-1-methyl-ethyl]phenol (commonly referred to as BPX-1), (I), is reported. We note that the 2,4-bis( $\alpha,\alpha$ -dimethylbenzyl)phenol skeleton also occurs in WOBROU (Bryan, 2000), (V), and VACKUF (Kurashev *et al.*, 1986), (VI), while (I) may be treated as a (4-hydroxyphenyl)isopropyl derivative of (II) (CEGYOC02; Okada, 1996) or of (III), sharing structural features with these two isomers of BPA.

Compound (I) is constructed around a benzene ring (C10–C15) which has (4-hydroxyphenyl)isopropyl substituents at positions 2 and 4 and a hydroxy substituent at position 1 (Fig. 1). This ring and the two benzene rings belonging to the former substituents, *i.e.* the C1–C6 and C19–C24 rings, are

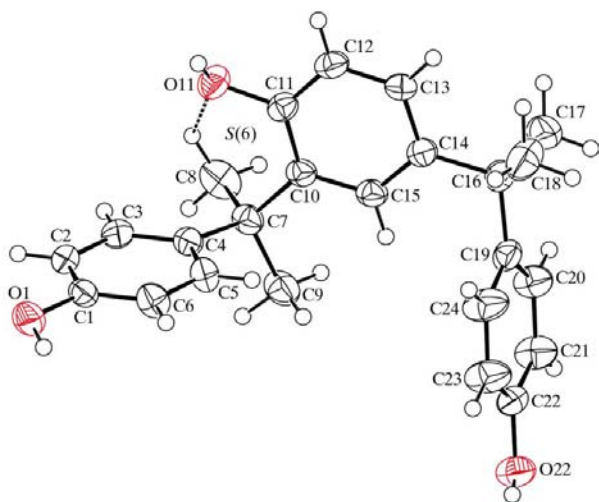
planar, with largest deviations from planarity of  $-0.008$  (2),  $0.013$  (2) and  $0.011$  (2) Å for atoms C4, C11 and C22, respectively. Similar to the case of the three isomers of isopropylidenediphenol, each hydroxy O atom attached to the benzene ring is nearly coplanar with it. Namely, atom O22 lies only  $0.017$  (2) Å above the plane of the C19–C24 ring, while atoms O1 and O11 lie  $0.037$  (2) and  $0.001$  (2) Å below the planes formed by atoms C1–C6 and C10–C15, respectively. The dihedral angles between the least-squares plane defined by the C atoms of the central benzene ring (C10–C15) and the C1–C6 and C19–C24 planes are  $87.2$  (1) and  $82.4$  (1)°, respectively, while the latter two planes are inclined at an angle of  $82.8$  (1)° to one another. As can be seen in Fig. 1, there is one weak intramolecular C—H···O hydrogen bond, which links methyl atom C8 *via* H8A with hydroxy atom O11 and generates an  $S(6)$  graph-set motif (Bernstein *et al.*, 1995). The noncoplanar practically perpendicular orientation of the benzene rings belonging to the molecule of (I) and the presence of an intramolecular C—H···O hydrogen bond with such a graph-set descriptor are in agreement with the structures observed for compounds (III)–(VI).



The crystal structure of (I) contains three strong nearly linear O—H···O hydrogen bonds (Table 1) which connect each molecule to six others. These interactions result in the formation of a continuous three-dimensional framework, which can be analyzed in terms of three independent one-dimensional substructures, each generated by one of the O—H···O hydrogen bonds.

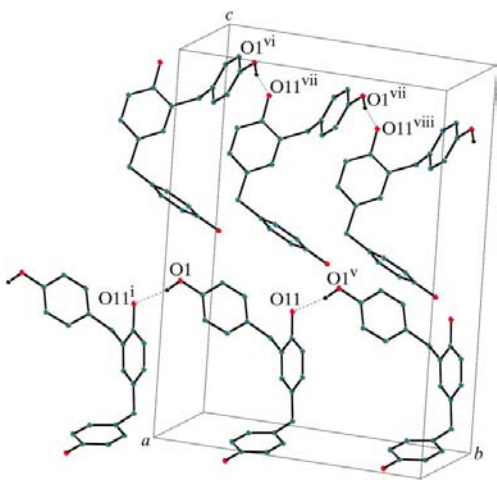
In the first substructure, atom O1 in the molecule at  $(x, y, z)$  acts as a hydrogen-bond donor *via* H1 to atom O11 belonging to the molecule at  $(x + \frac{1}{2}, y - \frac{1}{2}, z)$ , so forming a  $C(10)$  chain

running parallel to the  $[\bar{1}10]$  direction (Fig. 2). Two chains of this type pass through each unit cell, parallel to  $[\bar{1}10]$  and  $[110]$ , where the component molecules are related by the  $c$ -glide plane at  $y = \frac{1}{2}$ . In the second substructure, hydroxy atom O11 acts as a hydrogen-bond donor *via* H11 to atom O22 belonging to the molecule at  $(x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2})$ , so forming a zigzag  $C(12)$  chain (Fig. 3) which runs parallel to the  $[101]$  direction and is built from molecules related by the  $c$ -glide plane at  $y = \frac{1}{4}$ . The third substructure is generated by an O—H...O hydrogen bond that links hydroxy atom O22 at  $(x, y, z)$  *via* H22 with hydroxy atom O1 belonging to the molecule at



**Figure 1**

A view of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. The dashed line depicts the intramolecular hydrogen bond forming a pattern with the  $S(6)$  descriptor. H atoms are drawn as spheres of arbitrary radii.

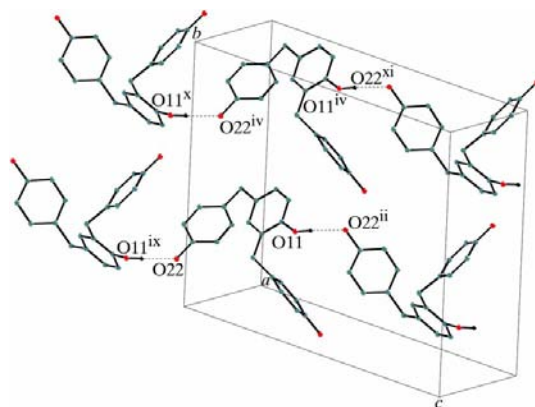


**Figure 2**

Part of the crystal structure of (I), showing the formation of two antiparallel hydrogen-bonded  $C(10)$  chains along the  $[110]$  and  $[110]$  directions. The C atoms of methyl groups and all H atoms not involved in the hydrogen-bond motifs have been omitted for clarity. [Symmetry codes: (i)  $x + \frac{1}{2}, y - \frac{1}{2}, z$ ; (v)  $x - \frac{1}{2}, y + \frac{1}{2}, z$ ; (vi)  $x - 1, -y, z + \frac{1}{2}$ ; (vii)  $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (viii)  $x, 1 - y, z + \frac{1}{2}$ .]

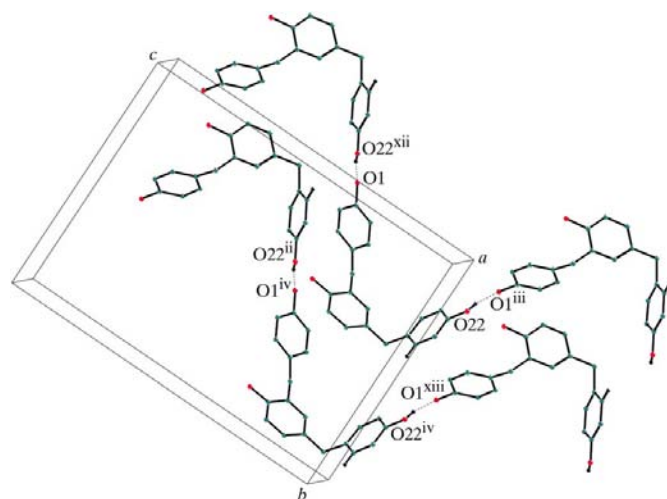
$(x, -y, z - \frac{1}{2})$ , so generating a zigzag  $C(16)$  chain (Fig. 4). This chain runs along the  $[001]$  direction and comprises molecules related by the  $c$ -glide plane at  $y = 0$ . Two parallel  $C(12)$  and two parallel  $C(16)$  chains pass through each unit cell.

The combined effect of the  $C(10)$ ,  $C(12)$  and  $C(16)$  chains parallel to the  $[110]$  and  $[\bar{1}10]$ ,  $[101]$ , and  $[001]$  directions, respectively, is sufficient to generate the continuous three-dimensional network. This network is additionally stabilized by a weak  $C-H \cdots \pi$  interaction, which connects aromatic atom C12 at  $(x, y, z)$  *via* atom H12 with the centroid of the C1–C6 benzene ring ( $Cg1$ ) of the molecule at  $(x + \frac{1}{2}, y + \frac{1}{2}, z)$  (Fig. 5 and Table 1).



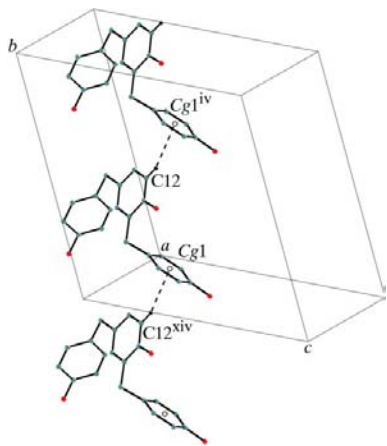
**Figure 3**

Part of the crystal structure of (I), showing the formation of two parallel hydrogen-bonded  $C(12)$  chains along the  $[101]$  direction. The C atoms of methyl groups and all H atoms not involved in the hydrogen-bond motifs have been omitted for clarity. [Symmetry codes: (ii)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (iv)  $x + \frac{1}{2}, y + \frac{1}{2}, z$ ; (ix)  $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (x)  $x, -y + 1, z - \frac{1}{2}$ ; (xi)  $x + 1, -y + 1, z + \frac{1}{2}$ .]



**Figure 4**

Part of the crystal structure of (I), showing the formation of two parallel hydrogen-bonded  $C(16)$  chains along the  $[001]$  direction. The C atoms of methyl groups and all H atoms not involved in the hydrogen-bond motifs have been omitted for clarity. [Symmetry codes: (ii)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (iii)  $x, -y, z - \frac{1}{2}$ ; (iv)  $x + \frac{1}{2}, y + \frac{1}{2}, z$ ; (xii)  $x, -y, z + \frac{1}{2}$ ; (xiii)  $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ .]



**Figure 5**  
Part of the crystal structure of (I), showing the intermolecular C—H... $\pi$  interaction. The C atoms of methyl groups and all H atoms not involved in this interaction have been omitted for clarity. [Symmetry codes: (iv)  $x + \frac{1}{2}, y + \frac{1}{2}, z$ ; (xiv)  $x - \frac{1}{2}, y - \frac{1}{2}, z$ .]

## Experimental

The sample of (I) was obtained from the Institute of Heavy Organic Synthesis (Kedzierzyn-Kozle, Poland). A crystal suitable for X-ray diffraction measurement was grown by slow evaporation of an ethanol solution at a constant temperature of 279 K.

### Crystal data

$C_{24}H_{26}O_3$	$V = 1977.76 (11) \text{ \AA}^3$
$M_r = 362.45$	$Z = 4$
Monoclinic, $Cc$	Mo $K\alpha$ radiation
$a = 6.2143 (2) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$b = 15.3978 (5) \text{ \AA}$	$T = 290 (2) \text{ K}$
$c = 20.7130 (7) \text{ \AA}$	$0.30 \times 0.27 \times 0.07 \text{ mm}$
$\beta = 93.729 (3)^\circ$	

### Data collection

Oxford Diffraction Xcalibur-3 CCD diffractometer	2469 independent reflections
7160 measured reflections	1729 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.027$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.082$	$\Delta\rho_{\text{max}} = 0.12 \text{ e \AA}^{-3}$
$S = 1.08$	$\Delta\rho_{\text{min}} = -0.11 \text{ e \AA}^{-3}$
2469 reflections	
305 parameters	
2 restraints	

All aromatic H atoms were positioned geometrically and constrained to ride on their parent atoms, with C—H distances of 0.93  $\text{\AA}$  and with  $U_{\text{iso}}(\text{H})$  values of  $1.2U_{\text{eq}}(\text{C})$ . H atoms of hydroxy and methyl groups were located in difference maps and refined isotro-

**Table 1**

Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ ).

Cg1 is the centroid of the C1—C6 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 $\cdots$ O11 <sup>i</sup>	0.92 (3)	1.91 (3)	2.813 (3)	166 (3)
O11—H11 $\cdots$ O22 <sup>ii</sup>	0.87 (4)	1.95 (4)	2.813 (3)	177 (4)
O22—H22 $\cdots$ O1 <sup>iii</sup>	0.89 (4)	1.88 (4)	2.756 (3)	167 (3)
C8—H8A $\cdots$ O11	1.03 (3)	2.31 (3)	2.987 (4)	122 (2)
C12—H12 $\cdots$ Cg1 <sup>iv</sup>	0.93	2.74	3.564 (3)	148

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

pically, giving O—H distances in the range 0.87 (4)–0.92 (3)  $\text{\AA}$  and C—H distances in the range 0.94 (4)–1.03 (4)  $\text{\AA}$ . In the absence of significant resonant scattering, the Flack (1983) parameter was indeterminate (Flack & Bernardinelli, 2000) and the Friedel equivalent reflections were merged prior to the final refinement.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2008).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3195). Services for accessing these data are described at the back of the journal.

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