

## 5,5'-Bis(hydroxymethyl)-3,3'-dimethoxybiphenyl-2,2'-diol with a new three-dimensional 3-modal topology of synthons

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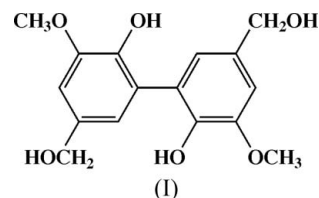
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The title lignin model compound, C<sub>16</sub>H<sub>18</sub>O<sub>6</sub>, resides on a twofold axis parallel with the *b* axis, with the mid-point of the internal C—C(−*x* + 1, *y*, −*z* +  $\frac{1}{2}$ ) bond located on the twofold axis. The *exo* angles between the methoxy groups and the benzene rings deviate significantly from the expected value of 120° [125.15 (7) and 114.27 (6)°]. A 12-coordinated 3-modal three-dimensional net with a new topology was identified on the synthon level. A comparison of the flexibility of related *o,o'*-disubstituted biphenyl derivatives and biphenyl is presented, with the angles between the ring planes in substituted biphenyls found to be in the range 40–70°.

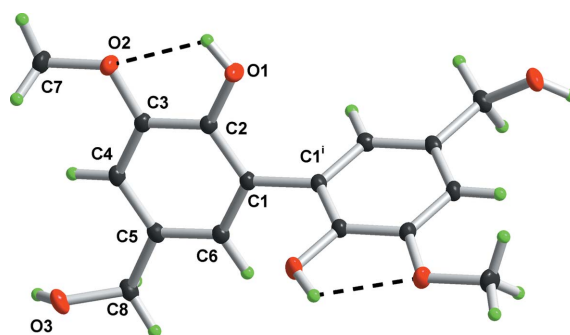
### Comment

The title compound, (I), is a lignin model compound representative of a type of biphenyl structure in lignins (Ralph *et al.*, 2004). The present study is aiming at an elucidation of the structure and conformation of phenolic structural elements of this type. A perspective drawing and the atom-numbering of (I) are shown in Fig. 1 and selected geometric parameters are given in Table 1. The molecule is located with the mid-point of the C1—C1<sup>i</sup> bond [symmetry code: (i) −*x* + 1, *y*, −*z* +  $\frac{1}{2}$ ] on a twofold axis parallel with the *b* axis. A striking deformation in (I) is the deviation of the O2—C3—C2 and O2—C3—C4 angles from 120° (Table 1). Such deformation was observed earlier by, for example, Lundquist *et al.* (1987) and Gallagher *et al.* (2001). There is an intramolecular hydrogen bond between the methoxy O atom and the adjacent hydroxy group (Fig. 1 and Table 2). There are also two strong intermolecular hydrogen bonds of O—H...O type present in the crystal structure of (I); geometric details of these hydrogen bonds are given in Table 2. On the first-level graph-set, as defined by Bernstein *et al.* (1995) and Grell *et al.* (1999), an *S*(5) string is formed by the intramolecular hydrogen bond, while both

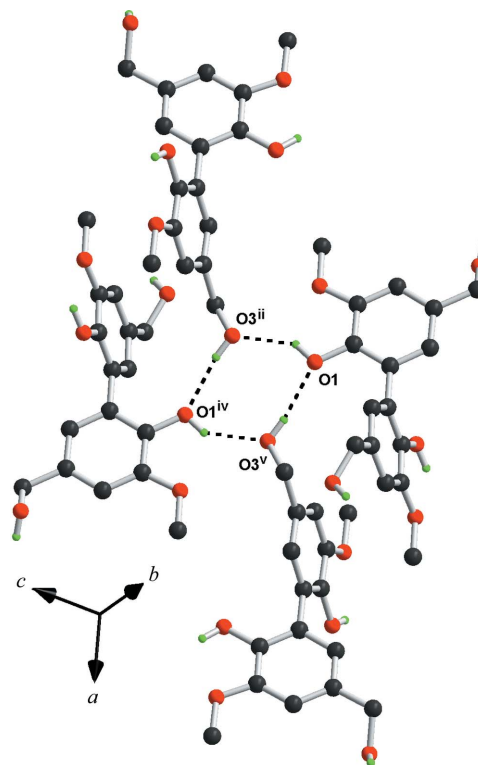
intermolecular hydrogen bonds form *C*(8) and *C*(9) chains. On the second-level graph-set, *R*<sub>4</sub><sup>4</sup>(8) rings are formed by the two intermolecular hydrogen bonds (Fig. 2).



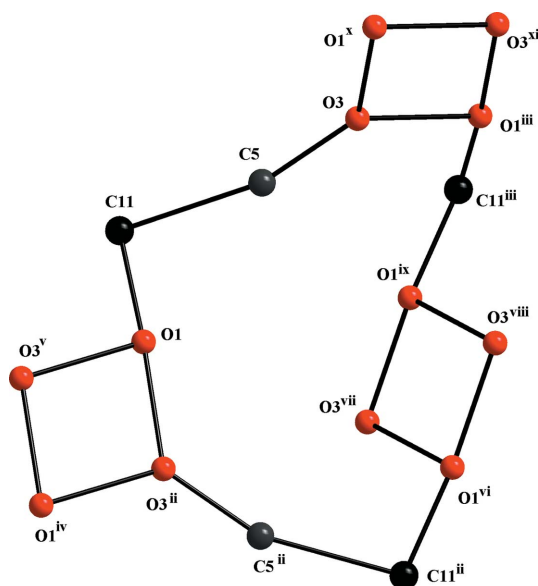
Due to the symmetry of the molecule of (I) and the arrangement in the unit cell, an infinite three-dimensional



**Figure 1**  
A perspective drawing of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Intramolecular hydrogen bonds are shown as dashed lines. [Symmetry code: (i) −*x* + 1, *y*, −*z* +  $\frac{1}{2}$ .]



**Figure 2**  
The hydrogen-bond pattern (dashed lines) in the structure of (I), showing the directed four-membered co-operative hydrogen bonds. H atoms not involved in the hydrogen-bonding pattern have been omitted for clarity. [Symmetry codes: (ii) −*x* +  $\frac{1}{2}$ , −*y* +  $\frac{1}{2}$ , *z* +  $\frac{1}{2}$ ; (iv) 1 − *x*, −*y*, 1 − *z*; (v) *x* +  $\frac{1}{2}$ , *y* −  $\frac{1}{2}$ , −*z* +  $\frac{1}{2}$ .]



**Figure 3**

A representation of the new topology in (I), showing the 12-coordinated 3-modal part of the three-dimensional framework. C11 is the mid-point of the C1—C1' bond. [Symmetry codes: (i)  $-x + 1, y, -z + \frac{1}{2}$ ; (ii)  $-x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (iii)  $x - \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (iv)  $1 - x, -y, 1 - z$ ; (v)  $x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (vi)  $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ ; (vii)  $x, -y + 1, z + \frac{1}{2}$ ; (viii)  $-x, y, -z + \frac{1}{2}$ ; (ix)  $-x + \frac{1}{2}, y + \frac{1}{2}, z$ ; (x)  $-x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (xi)  $-x, -y + 1, -z$ .]

framework is built, with a body-centred cubic (**bcu**) topology, using the nomenclature of the Reticular Chemistry Structural Resource (RCSR) database (O'Keeffe *et al.*, 2008). We contracted the molecular residues to synthons, defined by O1, C11 (the mid-point of the C1—C1' bond), C5 and O3, and a 12-coordinated 3-modal three-dimensional net with a new topology was identified using the program *TOPOS* (Blatov *et al.*, 2000; Blatov & Shevchenko, 2010). This new topology, denoted **vla1**, has a point (Schläfli) symbol for the net of  $(12^3)(4;12^2)_2$ . This means that each synthon is connected with 11 other synthons through symmetry-related molecules (Fig. 3).

The crystal structures of a number of lignin model compounds of the biphenyl type have been reported in the literature (Brunow *et al.*, 1995; Karhunen *et al.*, 1996; Xi *et al.*, 1996; Ferreira *et al.*, 1998; Roblin *et al.*, 2000). Compound (I) is phenolic and only one structurally related compound with phenolic groups has been examined previously, namely 5,5'-bis[(2-hydroxy-3-methoxy-5-methylphenyl)methyl]-3,3'-dimethoxy-2,2'-biphenyldiol (Xi *et al.*, 1996). In these two compounds, there are hydrogen bonds between the hydroxy and methoxy O atoms. In biphenyls *o,o'*-disubstituted with hydroxy groups lacking adjacent methoxy groups (Bedford *et al.*, 2003; Wang *et al.*, 1983; Bocelli *et al.*, 1999; Xi *et al.*, 1996; Byrne *et al.*, 1998), hydrogen bonds are formed between the hydroxy groups.

The angle between the aromatic rings is flexible in the structures of *o,o'*-disubstituted biphenyl derivatives; for (I) it is 68.88 (2)°. In Table 3, the angles between the aromatic rings and selected torsion angles are presented for a series of such compounds. The nonderivatized biphenyl molecule is planar in crystal structures at room temperature, but libration around

the long axis of the molecule suggests a statistically centrosymmetric arrangement (Charbonneau & Delugeard, 1977). At 41 K, crystals of biphenyl undergo a structural phase transition to an intermediate phase called phase II, and at 21 K another phase III is formed. Surprisingly, Cailleau *et al.* (1979) found the angle between the rings to be 10.2° for crystals of phase III, which was later correctly attributed to the existence of a modulated structure by Baudour & Sanquer (1983). In crystal structures where biphenyl is cocrystallized with other molecules or complexes as a solvent, the angle between the rings is dependent on the type and strength of the interactions, with a maximum value of 50.8° for a dichromium complex (Van Order *et al.*, 1987).

## Experimental

Compound (I) was prepared according to the method of Adler & Hernestam (1955) (m.p. 458–459 K; Adler & Hernestam reported m.p. 460–463 K under quick heating). Crystals of (I) were obtained by recrystallization from an acetone–ethanol (1:1 v/v) mixture.

### Crystal data

$C_{16}H_{18}O_6$	$V = 1412.54 (12) \text{ \AA}^3$
$M_r = 306.30$	$Z = 4$
Orthorhombic, <i>Pbcn</i>	Mo $K\alpha$ radiation
$a = 12.4911 (6) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$b = 8.5100 (4) \text{ \AA}$	$T = 153 \text{ K}$
$c = 13.2883 (7) \text{ \AA}$	$0.35 \times 0.20 \times 0.15 \text{ mm}$

### Data collection

Siemens SMART CCD area-detector diffractometer	23325 measured reflections
Absorption correction: multi-scan ( <i>SADABS</i> ; Sheldrick, 2003)	2621 independent reflections
$T_{\min} = 0.594, T_{\max} = 0.984$	2150 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.046$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	112 parameters
$wR(F^2) = 0.116$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{\max} = 0.55 \text{ e \AA}^{-3}$
2621 reflections	$\Delta\rho_{\min} = -0.22 \text{ e \AA}^{-3}$

H atoms were refined isotropically while their positions were constrained to ideal geometry using an appropriate riding model, with C—H = 0.95–0.99 Å. For methyl groups, O—C—H angles (109.5°) were kept fixed, while the torsion angle was allowed to refine with the starting positions based on the circular Fourier synthesis averaged using the local threefold axis. For the hydroxy groups, the O—H distances (0.84 Å) and C—O—H angles (109.5°) were kept fixed, while the torsion angles were allowed to refine with the starting

**Table 1**

Selected geometric parameters (Å, °).

O1—C2	1.3690 (9)	O3—C8	1.4339 (10)
O2—C7	1.4255 (10)	C1—C1 <sup>i</sup>	1.4893 (14)
C2—C1—C1 <sup>i</sup>	121.09 (7)	O2—C3—C4	125.15 (7)
C6—C1—C1 <sup>i</sup>	119.78 (7)	O2—C3—C2	114.27 (6)
O1—C2—C1	119.63 (7)	C6—C5—C4	119.04 (7)
O1—C2—C3	120.79 (7)	C6—C5—C8	120.05 (7)

Symmetry code: (i)  $-x + 1, y, -z + \frac{1}{2}$ .

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...O2	0.84	2.22	2.6720 (9)	114
O1—H1...O3 <sup>ii</sup>	0.84	2.03	2.7489 (8)	144
O3—H3...O1 <sup>iii</sup>	0.84	2.09	2.9138 (9)	168

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

positions based on the circular Fourier synthesis. The highest positive peaks in the residual electron-density map with absolute values higher than that of the minimum peak,  $-0.22 \text{ e } \text{Å}^{-3}$ , ranging from 0.23 to  $0.55 \text{ e } \text{Å}^{-3}$ , are located in the middle of the bonds and represent the  $\sigma$  electrons.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINTE* (Bruker, 2003); data reduction: *SAINTE* and *SADABS* (Sheldrick, 2003); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3249). Services for accessing these data are described at the back of the journal.

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**Table 3**

Torsion angles C(O)—C—C—C(O) [C2—C1—C1<sup>i</sup>—C2<sup>i</sup> in (I)] and C(H)—C—C—C(H) [C6—C1—C1<sup>i</sup>—C6<sup>i</sup> in (I)] (°), and angle *A* between the aromatic rings (°) for (I) and related compounds.

In the Remarks column, BP = biphenolic and NP = nonphenolic.

Compound (CSD refcode)	Reference	Remarks	C(O)—C—C—C(O)	C(H)—C—C—C(H)	<i>A</i>
(I)	This work	BP	114.43 (8)	108.33 (8)	68.88 (2)
AJAPUW	<i>a</i>	BP	53.96	47.95	51.52
CIPXII	<i>b</i>	BP	49.04	41.98	44.86
MEBMIP	<i>c</i>	BP	−55.18	−49.49	52.77
MEBMOV	<i>c</i>	BP	−46.49	−41.09	43.81
TECQOH	<i>d</i>	BP	62.10	63.16	62.12
TECQOH	<i>d</i>	BP	−61.73	−61.22	61.47
NUTSUQ	<i>e</i>	BP	−51.39	−45.75	48.65
MAYFEX	<i>f</i>	NP	65.86	64.45	65.11
TUGVUM	<i>g</i>	NP	−53.41	−48.04	50.87
NOZZUX	<i>h</i>	NP	−63.35	−57.09	60.15
NOZZUX	<i>h</i>	NP	−115.39	−115.34	65.09
NOZZOR	<i>h</i>	NP	−62.85	−56.41	59.42
ZIZDIV	<i>i</i>	NP	120.70	119.49	59.83
ZIZDOB	<i>i</i>	NP	128.82	125.23	53.10
ZIZDOB	<i>i</i>	NP	−123.74	−120.36	59.10

References: (a) Bedford *et al.* (2003); (b) Wang *et al.* (1983); (c) Bocelli *et al.* (1999); (d) Xi *et al.* (1996); (e) Byrne *et al.* (1998); (f) Roblin *et al.* (2000); (g) Karhunen *et al.* (1996); (h) Ferreira *et al.* (1998); (i) Brunow *et al.* (1995). For the Cambridge Structural Database (CSD), see: Allen (2002).

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