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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1247). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## 2,2'-Biphenol Monohydrate

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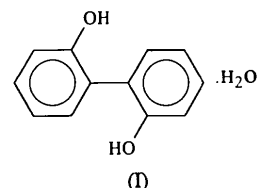
### Abstract

The structure of the title compound (2,2'-biphenyldiol monohydrate, C<sub>12</sub>H<sub>10</sub>O<sub>2</sub>·H<sub>2</sub>O) is stabilized by hydrogen bonds between the lattice water molecules and the 2,2'-biphenol molecules, resulting in two-dimensional networks.

### Comment

2,2'-Biphenol has attracted interest recently with regard to the synthesis of polynuclear transition metal complexes. 2,2'-Biphenoxide acts in both bidentate chelate (Coucouvani, Salifoglou, Kanatzidis, Simopoulos &

Papaefthymiou, 1984) and tri- or tetradentate bridging modes (Schake, Schmitt, Conti, Streib, Huffman, Hendrickson & Christou, 1991; Goldberg, Caneschi & Lippard, 1993). In an attempt to prepare lanthanoid(III) complexes containing 2,2'-biphenol or 2,2'-biphenoxide ligands, we obtained the title compound, (I).



All bond lengths and angles in (I) are comparable to related values reported in the literature (Allen *et al.*, 1987). The C(6)—C(7) bond between the two aromatic rings is significantly longer [1.491 (3) Å] than the C—C bonds within each ring. This is in agreement with the fact that, similar to the 2,2'-biphenoxide ligands in their metal complexes, the two aromatic rings in 2,2'-biphenol are not coplanar, but have a dihedral angle of 67.6(1)° between them. It is noteworthy that the hydroxyl groups are *trans* with respect to one another, which is different to the *cis* relationship found for the 2,2'-biphenoxide ligand in its metal complexes (Schake *et al.*, 1991; Goldberg, Caneschi & Lippard,

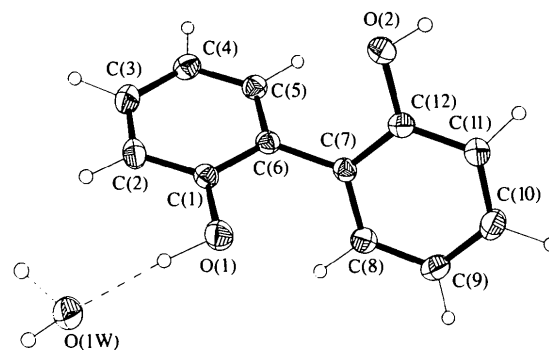


Fig. 1. The structure of 2,2'-biphenol monohydrate showing 30% probability displacement ellipsoids.

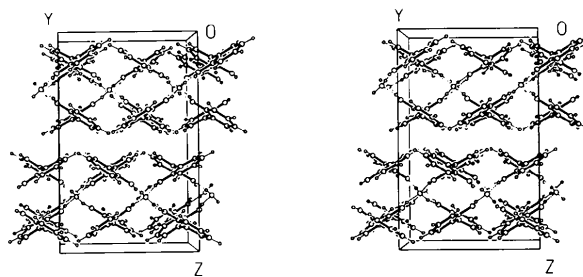


Fig. 2. The molecular packing showing the hydrogen bonding in the crystal lattice.

1993). The structure is consolidated by hydrogen bonds between the lattice water molecules and the hydroxyl O atoms. Each O(1W) water molecule forms two donor and two acceptor hydrogen bonds with the hydroxyl O(1) and O(2) atoms, with O...O distances ranging from 2.884 (2) to 3.160 (2) Å. The biphenol molecules are thus linked by hydrogen bonding through water molecules into two-dimensional networks perpendicular to the *c* axis.

## Experimental

To an aqueous solution of betaine (3 mmol) was added an aqueous solution (1 ml) of Eu(NO<sub>3</sub>)<sub>3</sub> (1 mmol). The mixture was heated to 323 K and stirred for 5 min. A methanolic solution (4 ml, 70%) of 2,2'-biphenol (2 mmol) was slowly added with stirring, then the resulting solution was adjusted to pH 3.5 and allowed to stand in air. Colourless block-shaped crystals were obtained after a week.

### Crystal data

C<sub>12</sub>H<sub>10</sub>O<sub>2</sub>·H<sub>2</sub>O

*M<sub>r</sub>* = 204.22

Orthorhombic

*Pbca*

*a* = 9.8080 (10) Å

*b* = 11.591 (2) Å

*c* = 17.8600 (10) Å

*V* = 2030.4 (4) Å<sup>3</sup>

*Z* = 8

*D<sub>x</sub>* = 1.336 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Mo *Kα* radiation

$\lambda$  = 0.71073 Å

Cell parameters from 24

reflections

$\theta$  = 8–12°

$\mu$  = 0.096 mm<sup>-1</sup>

*T* = 293 (2) K

Prismatic

0.35 × 0.30 × 0.26 mm

Colourless

### Data collection

Siemens *P4* diffractometer

$\omega$  scans

Absorption correction:

semi-empirical *via*  $\psi$  scan (Kopfmann & Huber, 1968)

*T<sub>min</sub>* = 0.951, *T<sub>max</sub>* = 0.987

2828 measured reflections

1452 independent reflections

978 observed reflections

[*I* > 2σ(*I*)]

*R<sub>int</sub>* = 0.0305

$\theta_{\max}$  = 24.99°

*h* = -11 → 0

*k* = -13 → 13

*l* = -13 → 0

3 standard reflections

monitored every 120

reflections

intensity decay: 0.015%

### Refinement

Refinement on *F*<sup>2</sup>

*R*(*F*) = 0.0474

*wR*(*F*<sup>2</sup>) = 0.1422

*S* = 1.022

1452 reflections

136 parameters

H atoms riding for C—H and located and fixed for O—H

$w = 1/[\sigma^2(F_o^2) + (0.077P)^2 + 0.4291P]$

where  $P = (F_o^2 + 2F_c^2)/3$

( $\Delta/\sigma$ )<sub>max</sub> = 0.004

$\Delta\rho_{\max} = 0.224 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\min} = -0.211 \text{ e } \text{Å}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
O(1)	0.1490 (2)	0.24179 (14)	0.31236 (10)	0.0472 (6)
O(2)	-0.1370 (2)	0.51137 (14)	0.31176 (10)	0.0471 (6)
C(1)	0.1847 (2)	0.3400 (2)	0.35099 (14)	0.0348 (7)
C(2)	0.3183 (2)	0.3781 (2)	0.3543 (2)	0.0451 (8)
C(3)	0.3500 (3)	0.4788 (2)	0.3929 (2)	0.0488 (8)
C(4)	0.2482 (3)	0.5426 (2)	0.4266 (2)	0.0449 (8)
C(5)	0.1148 (2)	0.5043 (2)	0.42273 (14)	0.0384 (7)
C(6)	0.0804 (2)	0.4017 (2)	0.38611 (14)	0.0328 (7)
C(7)	-0.0618 (2)	0.3563 (2)	0.38754 (14)	0.0322 (7)
C(8)	-0.0922 (2)	0.2556 (2)	0.42796 (15)	0.0411 (7)
C(9)	-0.2236 (3)	0.2124 (2)	0.4312 (2)	0.0462 (8)
C(10)	-0.3273 (3)	0.2700 (2)	0.3940 (2)	0.0469 (8)
C(11)	-0.2998 (2)	0.3693 (2)	0.3539 (2)	0.0416 (8)
C(12)	-0.1681 (2)	0.4122 (2)	0.35108 (15)	0.0355 (7)
O(1W)	0.3797 (2)	0.12406 (13)	0.24765 (10)	0.0484 (6)

Table 2. Selected geometric parameters (Å, °)

O(1)—C(1)	1.377 (3)	C(7)—C(12)	1.390 (3)
O(1)···O(1W)	2.884 (2)	C(7)—C(8)	1.405 (3)
O(2)—C(12)	1.381 (3)	C(8)—C(9)	1.384 (4)
C(1)—C(2)	1.384 (3)	C(9)—C(10)	1.386 (4)
C(1)—C(6)	1.397 (3)	C(10)—C(11)	1.382 (3)
C(2)—C(3)	1.390 (4)	C(11)—C(12)	1.385 (3)
C(3)—C(4)	1.380 (4)	O(1W)···O(2')	2.915 (2)
C(4)—C(5)	1.383 (3)	O(1W)···O(2'')	3.064 (2)
C(5)—C(6)	1.399 (3)	O(1W)···O(1 <sup>W</sup> )	3.160 (2)
C(6)—C(7)	1.491 (3)		
O(1)—C(1)—C(2)	121.8 (2)	C(12)—C(7)—C(8)	118.0 (2)
O(1)—C(1)—C(6)	117.5 (2)	C(12)—C(7)—C(6)	121.9 (2)
C(2)—C(1)—C(6)	120.7 (2)	C(8)—C(7)—C(6)	120.1 (2)
C(1)—C(2)—C(3)	120.0 (2)	C(9)—C(8)—C(7)	121.3 (2)
C(4)—C(3)—C(2)	120.3 (2)	C(8)—C(9)—C(10)	119.2 (2)
C(3)—C(4)—C(5)	119.4 (2)	C(11)—C(10)—C(9)	120.5 (2)
C(4)—C(5)—C(6)	121.6 (2)	C(10)—C(11)—C(12)	120.0 (2)
C(1)—C(6)—C(5)	117.9 (2)	O(2)—C(12)—C(11)	121.6 (2)
C(1)—C(6)—C(7)	120.8 (2)	O(2)—C(12)—C(7)	117.4 (2)
C(5)—C(6)—C(7)	121.2 (2)	C(11)—C(12)—C(7)	121.0 (2)

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

Dispersion corrections and absorption coefficients were taken from *International Tables for Crystallography* (Vol. C, 1992).

Data collection: *SHELXTL/PC* (Sheldrick, 1990a). Cell refinement: *SHELXTL/PC*. Data reduction: *SHELXTL/PC*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990b). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SK1012). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## A New Cyclophane

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### Abstract

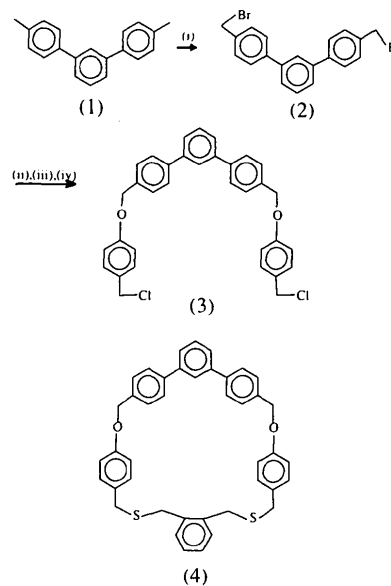
The X-ray diffraction studies of 9,25-dioxa-3,31-dithiaheptacyclo[31.4.0.2<sup>5,8</sup>.2<sup>11,14</sup>.1<sup>15,19</sup>.2<sup>20,23</sup>.2<sup>26,29</sup>]hexatetraconta-1(33),5,7,11,13,15,17,20,22,26,28,34,36,38,40,42(19),43,45-octadecaene, C<sub>42</sub>H<sub>36</sub>O<sub>2</sub>S<sub>2</sub>·3H<sub>2</sub>O, shows a distorted cyclic conformation with a hydrophobic cavity of size 8.56 × 8.55 Å<sup>2</sup> in the solid state. The compound exists as a trihydrate and the water molecules form a triangular cage caught inside the cavity. The molecules are held together by van der Waals interactions.

### Comment

Cyclophanes have received considerable attention in recent years as macrocyclic hosts for a variety of guest molecules (Odashima, Itai, Iitaka & Koga 1980; Diederich, 1991; Philip & Stoddart, 1991; Vogtle, 1992). The molecule possesses a non-collapsible rigid cavity, which gives the molecule a precise cavity size. The X-ray analysis of a cyclophane that has face-to-face arene rings is reported by Chiu, Hart & Ward (1993) and another cyclophane containing a 1,5,2,4,6,8-dithia-tetrazocine ring system is reported by Ho & Pascal (1994). The present paper reports the X-ray structure of a new cyclophane.

The scheme is based on a *m*-terphenyl framework (1), which can be obtained by the tandem aryne sequence (Hart & Ghosh, 1988). The dibromide (2)

was prepared from (1). Dichloride (3) was prepared from the dibromide (2) using *p*-hydroxymethylbenzoate. Coupling of dichloride (3) with *o*-xylene- $\alpha,\alpha'$ -dithiol under high dilution techniques in the presence of KOH in benzene–ethanol gave the title compound (4) (m.p. 473 K, 70%).



- (i) NBS (2 eq.), CCl<sub>4</sub>, Bz<sub>2</sub>O<sub>2</sub>,  $\Delta$   
(ii) *p*-Hydroxymethylbenzoate (2.1 eq.), K<sub>2</sub>CO<sub>3</sub>/DMF  
(iii) LAH/inf.  $\Delta$   
(iv) SOCl<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, Py  
(v) Benzene-Ethanol/KOH

(1)

Even though the crystals were obtained from chloroform, three water molecules were revealed during structure solution. These molecules would have been trapped during synthesis of the compound and exhibit high temperature factors.

Bond lengths and angles around the cyclophane molecule are normal. The bond lengths of S—C<sub>sp<sup>3</sup></sub> vary from 1.78 (1) to 1.81 (1) Å and C—S—C angles are 100.9 (5) and 101 (4)°. These values agree with the average values obtained for different structures (Allen *et al.*, 1987). The S3···S31 distance is 4.398 (3) Å.

The conformation of the molecule starting from the bond C1—C2 is *g<sup>-</sup>g<sup>-</sup>ag<sup>-</sup>asasgaasaaaagasag<sup>-</sup>ggasaa-gag<sup>-</sup>s*. The torsion angles on the two halves of the molecule C1—C33—C32—S31, C33—C1—C2—S3 [−80.9 (10) and −78.9 (10)°] and C8—O9—C10—C11, C26—O25—C24—C23 [69.8 (10) and 71.1 (10)°] indicate an approximate mirror symmetry but the torsion angles C2—S3—C4—C5 and C32—S31—C30—C29 [−171.4 (10) and 84.2 (10)°] negate this. The bond C2—S3 is in a *gauche* orientation and C32—S31 in the opposite arm is in a *trans* orientation.

The phenyl rings on the opposite arms A [C5—C6—C7—C8—C45—C46] and B' [C20—C21—C22—C23—C40—C41] are inclined at an angle 38.3 (3)° to