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2-Biphenylol revisited

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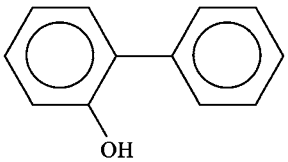
The substantially disordered structure of 2-biphenylol [Perrin *et al.* (1987). *Acta Cryst.* C**43**, 980–982; Kapon & Reisner (1988). *Acta Cryst.* C**44**, 2039] has been reinvestigated as a function of temperature. The structure was determined at 305, 294, 145 and 90 K; crystals were taken to the lowest temperature both rapidly and slowly (0.1 K min^{-1}). The results of the previous room-temperature study were confirmed and no important structural change was found down to 90 K. Comparisons with structures known for other simple 2- and 2,2′-substituted biphenyl derivatives suggest that the molecular stacks found for 2-biphenylol are probable for related molecules. The disorder in 2-biphenylol allows the formation of some O—H···O bonds, but packing efficiency is a more important factor in this structure than is hydrogen bonding.

1. Introduction

The structure of 2-biphenylol (Perrin *et al.*, 1987) is unusual for its high space-group symmetry (*Fdd*2; Kapon & Reisner, 1988), its extensive disorder (hydroxyl group in four positions) and the apparent absence of any intermolecular O—H···O or O—H···π bonding.[1] Perrin *et al.* (1987) did mention that ‘some intermolecular bonds are formed occasionally between O atoms with different numbering’. A close look at the structure suggested that one of the two types of disorder might make possible some O—H···O bonds if there were short-range order in the orientations of molecules related by the translation **c** (see Figs. 1 and 2). In the years since the structure of 2-biphenylol was first investigated low-temperature systems have become the norm and CCD diffractometers that allow recording of the non-Bragg scattering have become common. We wondered whether we could find a phase transition to an ordered structure at low temperatures or see diffuse scattering indicative of short-range order.



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[1] Perrin *et al.* (1987) claimed to have found intramolecular O—H···π bonds, but did not give many details. We are skeptical.

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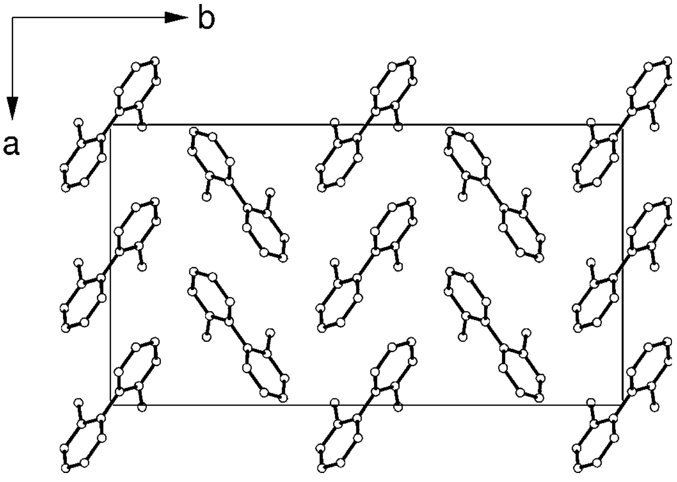

Figure 1
Packing diagram of 2-biphenylol showing the herringbone arrangement of the molecular stacks that are centered on twofold axes parallel to **c**. None of the atoms of the minor constituent are shown and all H atoms have been left out. The occupancy factors of the two O atoms shown are equal, but their sum is only a little larger than 3/4.

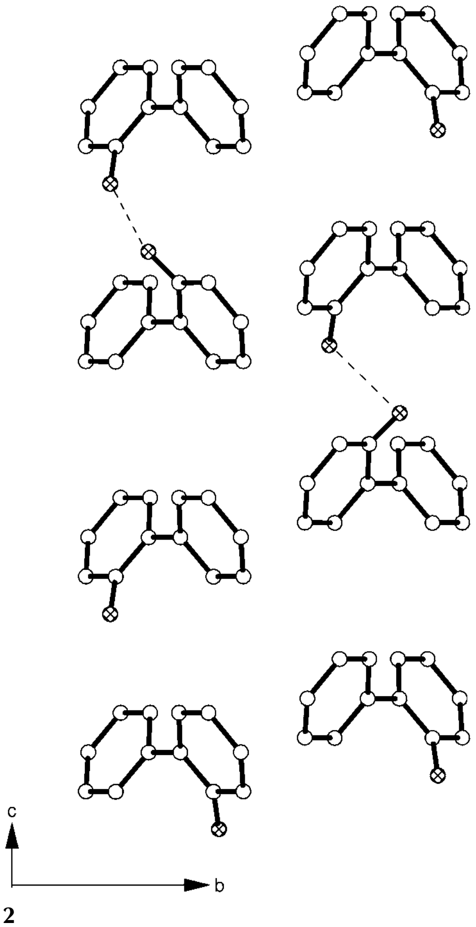

Figure 2
Diagram showing the possible positions of the hydroxyl groups within parts of two molecular stacks. If a hydroxyl group is in one of the less probable positions it might form an O—H···O bond with a hydroxyl group in either of the more probable positions, although the distances and angles (see text) suggest that a bond to an O atom on the same 'side' of the stack (as in the right-hand side of the drawing) is more probable. The H atoms have been omitted from the drawing for clarity.

2. Experimental

2.1. Initial crystallographic experiments

Crystals grow from hydrocarbon solvents as colorless needles that are elongated along **c**; the most prominent faces belong to the form {110}. Over a period of weeks the crystals develop a pinkish color, probably as a result of surface oxidation. Data were initially collected at 294 and 145 K. Nine different scan sets were made in each case so that the 'redundant' reflections in a set would correspond to a variety of paths of the reciprocal-lattice points through the sphere of reflection; on average each unique reflection was measured nine times at each temperature. This redundancy and variety ensured that the synthetic 'precession pictures' made with the *PRECESSION* routine of the program suite *COLLECT* (Nonius, 2000) would be of good quality. Experimental details can be found in Table 1.[2]

We looked for information about possible short-range correlations in the regions between the Bragg peaks. After the orientation matrix had been determined (Otwinowski & Minor, 1997), the data in the frames were transformed using the *PRECESSION* routine in *COLLECT* (Nonius, 2000) to give undistorted views of slices $nk\ell$, $hn\ell$ and hkn, $n = 0$–3, of the reciprocal lattice. We scrutinized these pictures in the hope of finding significant diffuse scattering or hints of reflections corresponding to a larger or lower-symmetry unit cell, but we were disappointed. The background scattering was clearly lower at 145 K than at 294 K and the pattern extended to higher scattering angles at the lower temperature, but the projections showed little other than small symmetric Bragg peaks. The pictures are unremarkable. We found two or three weak features that could correspond to breaking of the *F*-centering, but these features are likely to be Renninger (or multi-beam) reflections.

Refinements began from coordinates archived in the Cambridge Structural Database (Allen, 2002; hereafter, the CSD). Since 2-biphenylol crystallizes in the space group *Fdd*2 (No. 43) with $Z' = 8/16 = 1/2$, the molecules must lie on twofold axes around which the hydroxyl group must be disordered. A second type of disorder exchanges the 2 and 6 positions of each phenyl ring some of the time (see Fig. 3). There are then four possible positions of the hydroxyl group with occupancy factors that have been reported to be 0.4, 0.4, 0.1 and 0.1 at room temperature (Perrin *et al.*, 1987; Kapon & Reisner, 1988).

Refinement of the structure using a single phenyl ring and two O-atom positions with occupancy factors of *ca* 0.4 and 0.1 gave satisfactory agreement factors ($R_1 = 0.039$ at 145 K) and reasonable atomic displacement ellipsoids, but also gave a C—O distance (1.16 Å) for the minor O-atom position that is *ca* 0.30 Å too short. We concluded that the exact position of the

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[2] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS5004). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

	305 K	294 K	145 K	90 K
Crystal data				
Chemical formula	$C_{12}H_{10}O$	$C_{12}H_{10}O$	$C_{12}H_{10}O$	$C_{12}H_{10}O$
M_r	170.20	170.20	170.20	170.20
Cell setting, space group	Orthorhombic, *Fdd*2	Orthorhombic, *Fdd*2	Orthorhombic, *Fdd*2	Orthorhombic, *Fdd*2
a, b, c (Å)	12.871 (3), 23.939 (5), 5.8870 (12)	12.874 (2), 23.940 (3), 5.8880 (10)	12.8820 (10), 23.533 (2), 5.7815 (8)	12.875 (3), 23.416 (5), 5.7500 (12)
V (Å^3)	1813.9 (6)	1814.7 (5)	1752.7 (3)	1733.5 (6)
Z	8	8	8	8
D_x (Mg m^{-3})	1.246	1.246	1.290	1.304
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	605	5983	6063	587
θ range (°)	1.0–27.5	1.0–27.5	1.0–27.5	1.0–27.5
μ (mm^{-1})	0.08	0.08	0.08	0.08
Temperature (K)	305 (2)	294 (2)	145 (2)	90.0 (2)
Crystal form, color	Rod, colorless	Rod, colorless	Rod, colorless	Rod, colorless
Crystal size (mm)	0.40 × 0.30 × 0.20	0.25 × 0.10 × 0.08	0.25 × 0.10 × 0.08	0.40 × 0.30 × 0.20
Data collection				
Diffractometer	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD
Data collection method	ω scans at fixed $\chi = 55°$	ω scans at fixed $\chi = 55°$	ω scans at fixed $\chi = 55°$	ω scans at fixed $\chi = 55°$
Absorption correction	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)
$T_{\min}$	0.970	0.981	0.980	0.968
$T_{\max}$	0.985	0.994	0.994	0.984
No. of measured, independent and observed reflections	1005, 1005, 557	1018, 1018, 889	969, 969, 935	964, 964, 931
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.050	0.021	0.027	0.033
$\theta_{\max}$ (°)	27.5	27.5	27.5	27.5
Range of h, k, l	$-16 \Rightarrow h \Rightarrow 16$ $-29 \Rightarrow k \Rightarrow 30$ $-7 \Rightarrow l \Rightarrow 7$	$-16 \Rightarrow h \Rightarrow 16$ $-30 \Rightarrow k \Rightarrow 29$ $-7 \Rightarrow l \Rightarrow 7$	$-16 \Rightarrow h \Rightarrow 16$ $-30 \Rightarrow k \Rightarrow 29$ $-7 \Rightarrow l \Rightarrow 7$	$-16 \Rightarrow h \Rightarrow 16$ $-29 \Rightarrow k \Rightarrow 30$ $-7 \Rightarrow l \Rightarrow 7$
Refinement				
Refinement on	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.045, 0.133, 0.96	0.033, 0.081, 1.04	0.027, 0.065, 1.12	0.030, 0.074, 1.08
No. of reflections	1005	1018	969	964
No. of parameters	90	90	90	90
H-atom treatment	Constrained to parent site	Constrained to parent site	Constrained to parent site	Constrained to parent site
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.074P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 0.2808P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0266P)^2 + 0.8287P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2 + 1.5151P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.001	0.001	0.003	0.001
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.12, −0.12	0.07, −0.08	0.11, −0.09	0.13, −0.12
Extinction method	*SHELXL*	*SHELXL*	*SHELXL*	*SHELXL*
Extinction coefficient	0.011 (2)	0.0145 (17)	0.0156 (13)	0.0104 (14)

Computer programs used: *COLLECT* (Nonius, 2000), *SCALEPACK* (Otwinowski & Minor, 1997), *DENZO-SMN* (Otwinowski & Minor, 1997), *SHELXS*97 (Sheldrick, 1994), *SHELXL*97 (Sheldrick, 1997), *XP in Siemens SHELXTL* (Sheldrick, 1994), *SHELX*97-2 (Sheldrick, 1997) and local procedures.

phenyl ring depends on the position of the hydroxyl substituent.[3]

Several disorder models were investigated. Eventually we chose to include two complete phenyl rings in the asymmetric unit with occupancy factors that sum to one. Since the average separation of overlapping C atoms is 0.30 (1) Å at 294 K and 0.32 (1) Å at 145 K, it was necessary to impose a variety of constraints and restraints during the least-squares cycles (*SHELXL*97; Sheldrick, 1997). The geometries of the phenyl rings were restrained with the instructions SAME, DFIX and FLAT; the target distance $d_{\rm C-C}$ within the rings was 1.40 (2) Å. The displacement parameters for overlapping C atoms were set equal (six EADP instructions) and the instruction DELU was included. The minor O atom (occupancy < 0.15) was refined isotropically. The number of restraints reported by *SHELXL*97 was 57. This model does not give precise or accurate interatomic distances (the inappropriate averaging around the twofold axis of chemically

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[3] Perrin *et al.* (1987) came to the same conclusion, but restrained-refinement programs that allow more complicated descriptions of disorder were not available to them. Kapon & Reisner (1988), who were primarily interested in revising the space group from *Cc* to *Fdd*2, did not discuss the C—O distances.

different rings means that determination of accurate distances is impossible), but it does show (see Fig. 3) how the ring is shifted when the O atom is moved from one side of a ring to the other (*i.e.* from the 2 to the 6 position). The $C_{ar}—H$ protons were included in calculated positions.

When the refinements were nearly complete we looked to see if there was any sign of the hydroxyl proton. For both the 145 and 294 K structures the highest peak in the final difference map ($0.17\ e\ Å^{-3}$ at 145 K; $0.12\ e\ Å^{-3}$ at 294 K) was located such that the O—H distance and C—O—H angle for the major O position were very close to the values expected; the location of the peak can be seen in Fig. 3. The H atom for the major position was therefore included in the final refinement cycles with an occupancy factor equal to that of the attached O atom; the C—C—O—H torsion angle was allowed to vary. Removing this H atom from the model raises the final agreement factors R_1 and wR_2 to 0.030 and 0.076 at 145 K and to 0.034 and 0.092 at 294 K (compare with values in Table 1). The remaining features in the difference maps are very small (see Table 1) and the peaks found are located at bond centers.

2.2. Further crystallographic experiments

After the installation of a CRYOCOOL-LN2 low-temperature system (CRYO Industries of America, Manchester, NH) that allowed slow cooling under computer control, as well as substantially reduced $N_2(l)$ consumption at the lowest termperatures, we returned to this problem. Data were collected at 90.0 (2) K for one crystal that was flash cooled and for two crystals that were cooled from room temperature at 0.1 K $\min^{-1}$ (*i.e.* 34 h total from 295 to 90 K). The 90 K entry in Table 1 is for one of the slow-cooled crystals. The 'precession pictures' calculated from the two sets of data collected at 90 K show no unusual features.

Data were also collected at 305 (2) K, which is *ca* 25 K below the melting point of the crystal, to see if the four occupancy factors might become more equal above room temperature. During data collection at 305 K the crystal shrank by *ca* 20%, presumably because of sublimation, during the hour required for rapid data collection. The resulting intensity changes were absorbed in the standard frame-to-frame scaling process and so required no special correction. It proved impossible to collect data at or above 310 K.

2.3. NMR experiments

An attempt was made at the Max Planck Institute for Polymer Research at the University of Mainz to measure the solid-state NMR spectra of 2-biphenylol to see what the rate of ring flipping within a crystal might be. Unfortunately, the combination of a long spin-lattice relaxation time ($T_1 \simeq 25$ s), poor ^1H chemical shift resolution and a low melting point (fast magic-angle spinning causes local heating) made a successful experiment impossible.

2.4. Database searches

Searches of the Cambrige Structural Database, CSD (Allen, 2002), used the November 2002 (5.24) release and also the updates of February, April and July 2003. Structures were viewed and analyzed with the program *Mercury* (Bruno *et al.*, 2002).

3. Results

3.1. Thermal contraction of the unit cell

The cell contraction between 294 and 90 K is substantial (volume change of −4.5%), but unremarkable. The contraction is split nearly evenly between **b** and **c** (−2.2 and −2.3%; see Fig. 4), while the length of **a** remains essentially constant. The cell constants at 90 K for the slow-cooled crystals were all about 0.05% smaller than for the flash-cooled crystal, but otherwise the change in cooling rate seemed to have had little effect.

3.2. Molecular geometry

The results of previous authors (Perrin *et al.*, 1987) were confirmed. The average dihedral angle around $C1—C1^i$ [(i) $\frac{1}{2} - x, \frac{1}{2} - y, z$] is 56 (1)° at 294, 145 and 90 K if the two major sites are considered. The corresponding angle for the minor sites is 57 (1)° and for the major–minor site combination is 58 (1)°.

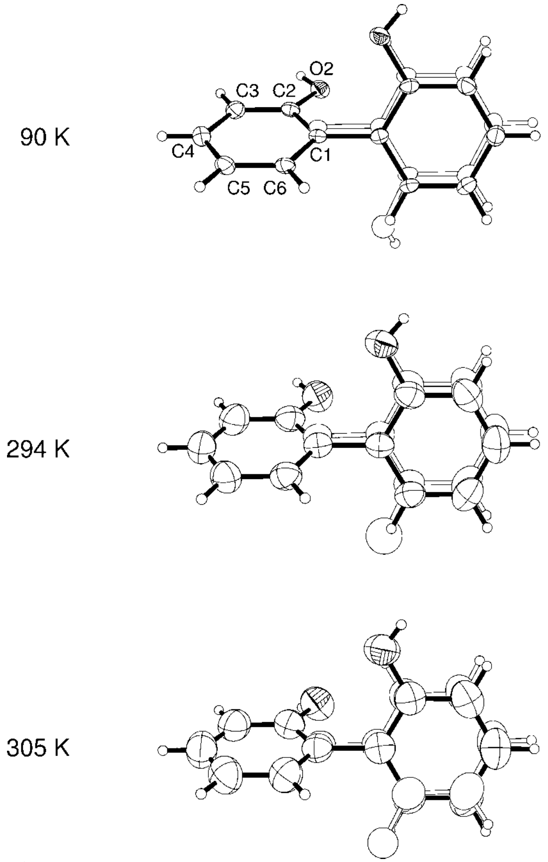

Figure 3
Perspective drawing of 2-biphenylol at 90 K (top), 294 K (middle) and 305 K (bottom); the shapes of the ellipsoids of the non-H atoms correspond to 50% probability contours of atomic displacement. Most of one ring of the minor component has been omitted. The atom-numbering scheme is the same at all temperatures.

We found no important change in the disorder when the structure was cooled from 294 to 145 K; the sum of the occupancies of the two major sites is 0.775 (5) at 294 K and 0.783 (5) at 145 K. The same occupancy-factor sum at 90 K is 0.777 (6) for the flash-cooled crystal and 0.811 (6) and 0.813 (7) for the slow-cooled crystals. At 305 K the corresponding value is 0.80 (1).

The atomic displacement ellipsoids (see Fig. 3) shrink as expected (Dunitz *et al.*, 1988) as the temperature decreases.

3.3. Possibility of O—H···O hydrogen bonding

There are four distinct possibilities for the formation of O—H···O bonds. First, an O atom at a major site can interact with O atoms at either of the two minor sites of a molecule related by the translation (0,0,−1) (see the two molecular stacks shown in Fig. 2). Second, for each of these two possibilities either the hydroxyl at the major site or the hydroxyl at the minor site may be the proton donor. The O···O distances at 90 K are 2.40 Å for the arrangement shown in the stack on the left of Fig. 2 and 2.97 Å for the arrangement shown on the right, but there is so much inappropriate averaging in the space group *Fdd*2 that the O···O distances might well be under- or overestimated by several 0.1 Å. The C—O···O angles are 147 and 154° for the shorter O···O distance, and 92 and 100° for the longer O···O distance (in each case the angle for the higher-occupancy hydroxyl group as the proton donor is given first). Since the C—O—H angle is *ca* 100°, the longer O···O distance could give an approximately linear O—H···O group. The O—H···O angle for the shorter distance would have to be substantially smaller and would therefore be rather unfavorable. If O—H···O bonds are formed, they are probably like those shown in the stack on the right of Fig. 2.

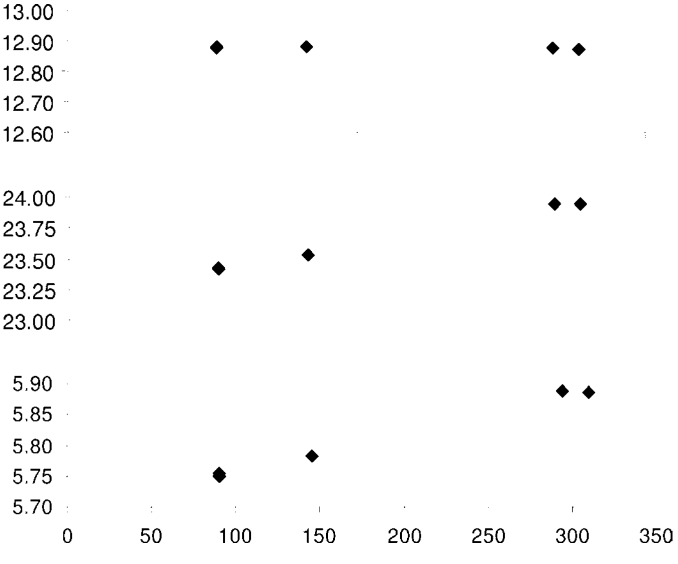

Figure 4
Graphs showing the change in cell constants with temperature. Scale divisions are approximately 1% of the cell length. The three sets of values shown for 90 K are so similar that they cannot be distinguished.

If the distribution of the hydroxyl groups among the possible sites were optimized for the formation of O—H···O bonds, then each of the O atoms at a minor site and a third of the O atoms at a major site would be either proton donors or proton acceptors. [An occupancy factor of 1/4:3/4 has been assumed because the observed value at 294 K is 0.775 (5).] If the distribution were so optimized then half of the molecules would participate in O—H···O bonds. Perfect correlation would also mean that the most favorable of the O—H···O arrangements would always be possible. If the distribution of the hydroxyl groups were random, then only 75% of the O atoms at the minor sites would interact with an O atom at a major site and half of the O—H···O interactions would have to have the less favorable of the two possible geometries (see Fig. 2). Finally, it must be noted that there is a chance, unlikely as it might seem, that the distribution is optimized to prevent O—H···O interactions.

3.4. Other types of hydrogen bonds

The best candidates for C—H···O bonds are the interactions C3—H3···O2^{i} (H···O 2.63 Å; C—H···O 167° at 90 K), C5′—H5′···O2^{i} [2.42 Å; 163°; (i) $x+\frac{3}{4}-1=x-\frac{1}{4}$, $-y+\frac{1}{4}$, $z+\frac{3}{4}-1=z-\frac{1}{4}$] and C6′—H6′···O2′^{ii} [2.51 Å; 170°; (ii) $\frac{1}{2}-x, \frac{1}{2}-y, z-1$]. None of these seems likely to be structure determining.

We doubt that intermolecular O—H···π interactions are important. The O2—H2 bond points in the general direction of C4 and C4′, and one of the distances is at least a little short [O2···H4^{iii} 2.53 Å; O2···H4′^{iii} 2.74 Å; (iii) $x+\frac{1}{4}$, $-y+\frac{1}{4}$, $z-\frac{3}{4}$], but the O2—H2 bond points outside of the H atoms attached to the C_6 ring.

It is possible that the position of H2, which is reasonably certain from the stucture solution and refinement, is determined by an identifiable intermolecular interaction. On the other hand, the C2—H2 bond may simply point in the observed direction because that is the direction within the stacks in which there is the most space.

3.5. Related structures

3.5.1. *Fdd*2 structures. Five other simple biphenyls crystallize in the *Fdd*2, $Z' = \frac{1}{2}$, pattern found for 2-biphenylol (refcode FIFMAI0); these five are 2-fluorobiphenyl (YUYXIZ), 2,2′-difluorobiphenyl (PUGPIQ), 2,2′-dichlorobiphenyl (DCLBIP), decafluorobiphenyl (DECFDP01 and DECFDP01), and 2,2′,4,4′-tetraaminobiphenyl (BUWCAX01). Two other closely related molecules [9,10-dihydro-4,5-dimethoxyphenanthrene (FIXWIS01) and its 4,5-bis(trifluoromethyl) analogue (FIXWEO)[4]] also crystallize in this pattern. This *Fdd*2 structure type appears to be very favorable for the close packing of significantly twisted biphenyl fragments with *ortho* substituents; the importance of the stacking interactions along **c** in 2-biphenylol is demonstrated clearly by the crystal morphology (crystals are elongated along **c**; see §2).

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[4] A 9,10-dihydrophenanthrene ring system can be viewed as a biphenyl fragment with a C_2H_4 bridge between *ortho* positions on the two rings.

Packing density seems to be the determining factor in this structure type; in only three of these eight structures would important intermolecular interactions between the substituents be anticipated: The 2-hydroxy derivative would be expected to make O—H···O or O—H···π bonds, and the 2,2′,4,4′-tetraamino derivative would probably be expected to make N—H···N bonds. The 2,2′-dichloro derivative might be expected to show Cl···Cl contacts (Desiraju & Parthasarathy, 1989). The 2-hydroxy, 2,2′,4,4′-tetraamino and 2,2′-dichloro derivatives probably crystallize all in this pattern because it allows dense packing and because the desirable interactions between substituents can be realised to some degree.[5]

The much larger molecule 1,2,3,4,1′,2′,3′,4′-octaphenylbiphenyl (PUTVUV) also crystallizes in this same *Fdd*2 packing arrangement.

The 2-fluorobiphenyl and 2-biphenylol structures must be disordered because the molecules are located on a twofold rotation axis, but have only one *ortho* substituent. This required disorder adds $RT(0.5\ln0.5 + 0.5\ln0.5) = -RT\ln2 = -1.7\ \text{kJ mol}^{-1}$ to the free energy at 298 K of the 2-fluoro derivative if the random occupation of sites is assumed. This *TS* term compensates for the energy associated with the empty space at one of the two disorder sites. The difference in size between an H and F atom is not very large so that the disorder in the 2-fluorobiphenyl is not surprising. The difference in size between an H atom and an OH group must be, however, substantially larger.

The 2-biphenylol structure has additional disorder so that the one substituent is found in all four *ortho* positions rather than in just two. Using occupancy factors of 3/8, 3/8, 1/8 and 1/8, which are close to the values determined experimentally at 294 K, we estimate the *TS* term for this structure to be $RT[2(1/8)\ln(1/8) + 2(3/8)\ln(3/8)] = -3.1\ \text{kJ mol}^{-1}$ if occupation is random and less if it is not. Since the 2-biphenylol structure is the only one of the eight *Fdd*2 structures that shows this second type of disorder, it probably occurs because it allows the formation of O—H···O bonds. If so, then why is the occupation of all four sites not equal, in which case the RT term would be $-RT\ln4 = -3.4\ \text{kJ mol}^{-1}$?

3.5.2. Other structures. We located the structures of nine other biphenyls that have simple substituents in at least one *ortho* position and H atoms in all other positions.[6] Two of these [2,2′-diaminobiphenyl (DABIPH) and biphenyl-2,2′-dicarbonylchloride (BPHCOY10)] also form stacks around twofold axes in the solid state, but crystallize in *C*2/*c* with $Z' = 1/2$ rather than in *Fdd*2. The change from a polar to a centrosymmetric space group means that the stacks point in both directions. The formation of N—H···N bonds in DABIPH (there is an N···N contact of 3.11 Å across an inversion center) may responsible for the change in symmetry. The 1:1 compound of biphenyl and perfluorobiphenyl (BPPFBP) also crystallizes in the *C*2/*c*, $Z' = \frac{1}{2}$ pattern. A third simple biphenyl [2-(2′-hydroxyphenyl)benzyl alcohol (KOHJIA)] forms stacks that are linked by interstack O—H···O bonds, but the symmetry is reduced from *C*2/*c* to *Cc* because of the size difference between the —OH and —CH_2OH substituents. The related heterocycle 2,2′-bipyridine-1,1′-dioxide (NARFER) also crystallizes in the *C*2/*c*, $Z' = 1/2$ pattern, as does 1,1′-binaphthyl (BINAPH01).

No stacks are found for the remaining six biphenyls. The crystallization of biphenyl-2-carboxylic acid (NOZVIH) in a different arrangment is no surprise because the packing unit is a hydrogen-bonded dimer rather than the individual molecule. Stacks are absent in 2,2′-dibromo- (HIQQON) and 2,2′-diodobiphenyl (PIPROV) because the contacts *X*···*X* (and maybe *X*···H—C) are determining in these isostructural crystals. The reasons for the absence of stacks are less clear in the cases of 2-nitro- (LESYEN), 2,2′-dinitro- (ZZZJPA01) and 2,2′-dimethylaminobiphenyl (KAHRAM), although the size of the substituents may play a role.

4. Discussion

The puzzle of this structure is the absence of a good set of O—H···O or possibly O—H···π bonds. Usually such bonds are formed, even if packing efficiency is sacrificed (*cf.* H_2O).

4.1. Packing arrangement

Stacking of 2′- and 2,2′-substituted biphenyls is expected because stacking is the best way for these propeller-shaped molecules to fill space. If the 2 and 2′ substituents are the same the stacks might be expected to lie on twofold rotational axes because about half of molecules that can lie on such axes do (Pidcock *et al.*, 2003). If the 2 and 2′ substituents are not identical, but are not too different in size, then disorder across a C_2 axis is unremarkable because the substituents do not affect the van der Waals surface of the stack much and because the disorder provides free-energy $RT\ln2$ to compensate for the energy associated with the void at the position of the smaller substituent. If the molecular C_2 axis is lost the space group becomes *Fd*, which is an alternate setting of *Cc*. Apparently, the additional rotations and displacements allowed in *Cc* but not in *Fdd*2 do not lower the energy of 2-biphenylol enough to offset the loss of entropy associated with the disorder.

The resulting *Fdd*2 structure is polar, but the addition of an inversion center to give *Fddd* would destroy the stacks. The addition of a twofold axis along the long molecular axis would not change the space group.

In the related *C*2/*c*, $Z' = \frac{1}{2}$, structure type observed for another group of simple biphenyls the packing of the stacks is different. The herringbone packing of the stacks that is visible in Fig. 1 is absent.

4.2. Interstack interactions

The shortest intermolecular interactions between the stacks are across the *d* glide located at, *e.g.*, $y = 1/8$. The region

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[5] The intramolecular Cl···Cl distance in 2,2′-dichlorobiphenyl is 3.42 Å (*i.e.* 0.18 Å less than the sum of the van der Waals radii) and the C—Cl···Cl—C torsion angle is 81°.

[6] Structures of 2-chloro-, 2-bromo-, 2-iodo-, 2-methyl-, 2,2′-dimethyl-, 2-methoxy- and 2,2′-dimethoxybiphenyl are not yet in the CSD, perhaps because most have melting points well below 308 K.

around C3 in one ring interacts with the hydroxyl group of the next molecule (see in Fig. 1). It is possible that these interactions (see above) are attractive, but it also seems possible that they are not. Contraction with cooling in the **b** and **c** directions is large (see Fig. 4) but the length of the **a** axis is effectively constant. If the C3—H3···O2 contact (see above) is favorable, then the C5′—H5′···O2 contact appears to be more favorable, in which case more complete disorder, rather than the partial disorder observed, might be expected.

4.3. Disorder within the stacks

The existence of a second type of disorder, which places the hydroxyl group at the 6 and 6′ positions as well as at the 2 and 2′ positions, is unique to the 2-biphenylol structure. Since the disorder type is unusual it suggests the presence of special interactions, which are most likely to be O—H···O bonds.

Since the van der Waals surface of the stack is changed little by the second type of disorder no correlation of adjacent stacks is necessary. The fraction of O—H···O bonds within a stack can be quite high, even in the absence of long-range order. The C-atom displacements associated with the change of position of the OH group are *ca* 0.3 Å, *i.e.* similar in size to the thermal displacements at room temperature (see Fig. 3), so there are few consequences of the switch other than the change in hydrogen bonding.

4.4. Changes with temperature

Changes in the degree of disorder with temperature require flips of the phenyl rings around the C1—C4 axis. Since these motions are known to occur in solids (see Fattah *et al.*, 1993) it seemed possible that a change in the structure would be seen with temperature, especially if the crystal were cooled very slowly. The joint occupancy factor for the 2 and 2′ sites is 0.775 (5) at 294 K and 0.783 (5) at 145 K, with an average of 0.812 (6) at 90 K for the two slow-cooled crystals [0.811 (6) and 0.813 (7)]. The difference between the first and second values is not significant, but is consistent with the differences between the second and third [0.029 (8)], and first and third [0.037 (8)]. The occupancy factor for the major sites seems to be increasing as the temperature is lowered. The possibility that the occupancy factors at low temperature would be higher if the crystals had been grown at low temperature cannot be ruled out. The disorder observed may have been ‘frozen-in’.

If the degree of O—H···O bonding decreases slightly with cooling, it must be that the considerable contaction of the unit cell makes the 0.3 Å C-atom displacements associated with the disorder unfavorable. In the end, the drive for packing efficiency seems to be more important than the drive to form O—H···O bonds.

4.5. Melting points

The melting point of unsubstituted biphenyl (BIPHEN) is 342–345 K. The melting points of 2-biphenylol (FIFMAI), 3-biphenylol (no structure in the CSD) and 4-biphenylol (BOPSAA) are 330–332, 349–351 and 438–440 K. The melting point of 2,2′-biphenyldiol (NUTSUQ), which forms one intermolecular O—H···O bond per molecule, is 381–383 K. [All melting points were taken from the Aldrich (2003) catalog.] The addition of a 2-hydroxy substituent to biphenyl lowers the melting point by *ca* 12 K, probably because the substituent requires that the molecule be substantially twisted and so makes the molecule harder to pack densely. The lowering of the melting point upon substitution argues against the formation of good O—H···O bonds.

5. Summary

Structural results obtained previously (Perrin *et al.*, 1987; Kapon & Reisner, 1988) are confirmed. Molecules of 2-biphenylol crystallize in an *Fdd*2 packing arrangement of molecular stacks typical of symmetrically substituted 2,2′-biphenyls. The 2/2′ disorder in 2-biphenylol is the same as observed in the corresponding fluoro derivative. The additional 2/6 (and 2′/6′) disorder is unique to 2-biphenylol and so suggests that some O—H···O bonds are present. As the temperature is lowered the crystal contracts substantially in two directions (including the stack axis) and the disorder of the 2- and 6- (and 2′- and 6′-) positions decreases slightly. The drive for efficient packing in this compound overcomes the drive for the formation of O—H···O bonds, especially as the temperature is lowered.

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