

## 4'-Hydroxybiphenyl-4-carbonitrile

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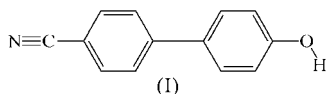
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The title compound,  $C_{13}H_9NO$ , crystallizes with four molecules in the asymmetric unit. Each of the four crystallographically independent molecules forms a chain parallel to the  $a$  axis with symmetry-equivalent molecules. These chains are held together by similar  $O-H\cdots NC$  hydrogen bonds, with approximately linear  $O-H\cdots N$  angles and significantly bent  $H\cdots N-C$  angles. The four different molecules are related by strong elements of pseudosymmetry. To better describe the pseudosymmetry, the structure has been reported in the non-standard space group  $C\bar{1}$ .

## Comment

Many 4,4'-disubstituted biphenyls have similar packing patterns. The dimethyl (Casalone *et al.*, 1969), dichloro (Brock *et al.*, 1978) and dibromo (Kronebusch *et al.*, 1976*b*; Mohamed *et al.*, 2003) compounds are isomorphous, with the molecules lined up end-to-end *via*  $X\cdots X$  contacts. The bromofluoro (Gleason *et al.*, 1991) compound is the same, with  $Br\cdots F$  contacts. The bromocyno (Kronebusch *et al.*, 1976*a*) and iodocyno (Britton & Gleason, 1991) compounds differ only in that there are  $X\cdots N$  interactions. Otherwise the packing is the same. The unit cell for the methylcyano compound (Haase *et al.*, 1992) suggests that this is isomorphous with the bromocyno and iodocyno compounds, but the details of the structure have not been determined. The cyanoethynyl compound (Langley *et al.*, 1998) has a similar arrangement, with molecules forming chains with  $CCH\cdots N$  interactions but with different side-to-side packing of the chains. In the dicyano compound (Britton & Young, 2003), the chains are tilted so that there can be antiparallel  $CN\cdots NC$  interactions.



The structure of the title compound, (I), has been determined in order to examine the effect of the expected  $OH\cdots NC$  interaction on the packing. An approximately linear molecular packing arrangement, similar to those in the 4,4'-biphenyls, seemed likely, but this would make it difficult to form the approximately linear  $O-H\cdots NC$  interactions that appear to be favored in this type of hydrogen bond, as shown

in *ortho*-, *meta*- and *para*-hydroxybenzoinitrile [Beswick *et al.* (1996), Britton (2004) and Higashi & Osaki (1977), respectively].

There are four molecules in the asymmetric unit. The anisotropic displacement ellipsoids and atom labeling for molecule *A* are shown in Fig. 1. The ellipsoids and the labeling are similar for molecules *B*, *C* and *D*. The bond lengths and angles agree among the four molecules within experimental error and are all normal. As is common, the exocyclic angles at the OH-bound C atoms are unequal; the angles *cis* to the hydroxy H atoms average  $123.0(3)^\circ$ , and those *trans* average  $117.4(4)^\circ$ . This difference is presumably due to  $H\cdots H$  repulsion. The corresponding angles in 4,4'-biphenyldiol are  $122.1(1)$  and  $117.8(1)^\circ$  (Jackisch *et al.*, 1990). The torsion angles in molecules *A–D* of (I) are  $31.8(1)$ ,  $37.0(1)$ ,  $36.4(1)$  and  $38.2(1)^\circ$ , respectively. The central axes of the molecules are bent. Fig. 2 shows molecule *A* viewed normal to the least-squares plane through atoms N14A, C13A, C1A, C4A, C7A, C10A and O15A; the next molecule in the chain [at  $(1+x, y, z)$ ] is also shown. The seven atoms are close to being planar, but as can be seen, the molecule is bowed in the plane. This bowing is such that it tends to bring both the  $O-H\cdots N$  and the  $H\cdots NC$  interactions closer to linearity. In the molecule shown, the angle between the C10A–O15A direction and the C13A–N14A direction is  $8.9(1)^\circ$ . The other three molecules are similar in arrangement, with corresponding angles of  $10.2^\circ$  (*B*),  $8.6^\circ$  (*C*) and  $12.2^\circ$  (*D*).

In order to simplify the discussion of the pseudosymmetry and to make the molecular chains lie parallel to an axis, the conventional unit cell [ $a = 10.604(3)$  Å,  $b = 11.826(3)$  Å,  $c = 18.005(5)$  Å,  $\alpha = 103.10(1)^\circ$ ,  $\beta = 100.23(1)^\circ$  and  $\gamma = 109.80(1)^\circ$ ] was converted by the matrix  $\bar{1}10/112/100$  to the cell in  $C\bar{1}$  reported in the experimental data.

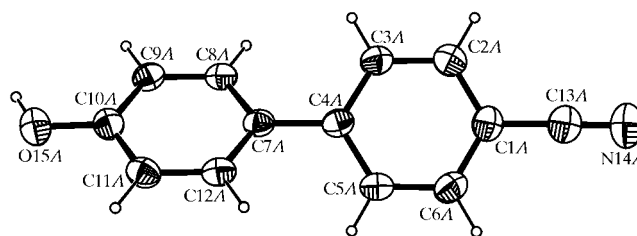


Figure 1

Molecule *A* of (I), with displacement ellipsoids shown at the 50% probability level. Molecules *B*, *C* and *D* have similar labeling and ellipsoids.

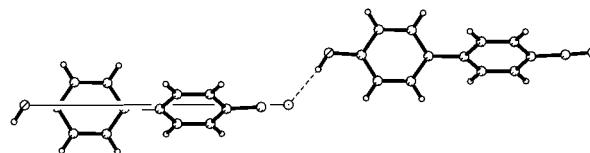


Figure 2

A view of a segment of the chain formed by molecule *A*, viewed normal to the mean plane through the central backbone of the molecule. A straight line connects the O and N atoms of the molecule on the left to make the bending more apparent. The bending is such that it pulls both the  $C-N\cdots H$  and the  $N\cdots H-O$  angles closer to linear.

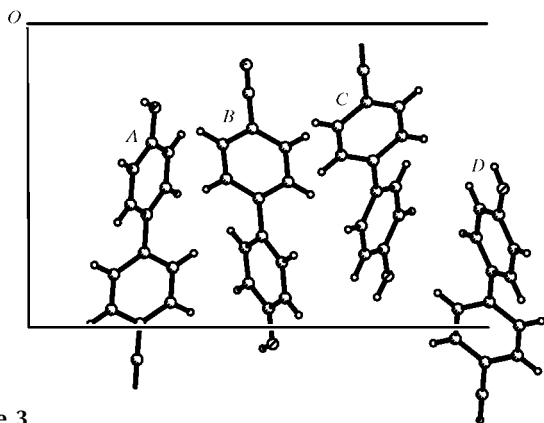
The packing is shown in Figs. 3 and 4; one asymmetric unit is shown in Fig. 3, and two asymmetric units related by an inversion center at  $(\frac{3}{4}, \frac{1}{4}, \frac{1}{2})$  are shown in Fig. 4. The four independent molecules are all aligned approximately parallel to the  $a$  axis [the deviations based on the intramolecular  $N \cdots O$  directions are  $10.2(1)$ ,  $10.4(1)$ ,  $10.1(1)$  and  $10.0(1)^\circ$  for molecules  $A$ ,  $B$ ,  $C$  and  $D$ , respectively]. The molecules form chains held together by  $O-H \cdots NC$  hydrogen bonds. The geometric data for these hydrogen bonds are given in Table 1, where they are compared with similar bonds in  $o$ -,  $m$ - and  $p$ -hydroxybenzotrile. The hydrogen bonds in the latter compounds are all almost completely linear for the  $O-H \cdots NC$  groups, which is the ideal arrangement for such bonds. In (I), the bonds are not ideal; while still close to linear at  $O-H \cdots N$ , they are bent at  $H \cdots NC$ . This arrangement is presumably a consequence of the difficulty in forming an efficient packing with the linear arrangement. The bending does not appear to affect the  $O \cdots N$  distances significantly.

The packing between chains involves six  $C-H \cdots N$  contacts with  $H \cdots N$  distances between 2.6 and 2.8 Å, and 37  $C-H \cdots C(\text{ring})$  contacts with  $H \cdots C$  distances between 2.8 and 3.1 Å. These contacts are important to the packing but none is remarkably short. This aspect of the packing in biphenyls has been discussed at length by Masunov *et al.* (1992).

Also evident, particularly in Fig. 4, is the pseudosymmetry relating the four crystallographically independent molecules. Such supersymmetry has been discussed extensively by Zorky and co-workers (see, among others, Zorky, 1996; Belsky *et al.*, 1995; Zorky & Dashevskaya, 1992, 1993). Zorky & Dashevskaya (1992, 1993), in particular, describe an example of  $Z' = 4$  that is close to that reported here.

The first hint of the pseudosymmetry can be found if we look at the coordinates of the molecular centers of the four molecules, *viz.*  $A$  at (0.724, 0.127, -0.009),  $B$  at (0.606, 0.251, 0.250),  $C$  at (0.470, 0.376, 0.491) and  $D$  at (0.899, 0.502, 0.750). While the  $x$  coordinates show no particular relationship, the  $y$  coordinates are at, and differ by, approximately integral multiples of  $b/8$ , and the  $z$  coordinates are at, and differ by, approximately integral multiples of  $c/4$ .

There are six kinds of pseudosymmetry elements present: (1) screw axes parallel to  $b$ , which relate  $A \leftrightarrow B$  and  $C \leftrightarrow D$ ;



**Figure 3**

A view along  $c$  of the asymmetric unit. The vertical axis is shown from  $O$  to  $a$ ; the horizontal axis is shown from  $O$  to  $b/2$ .

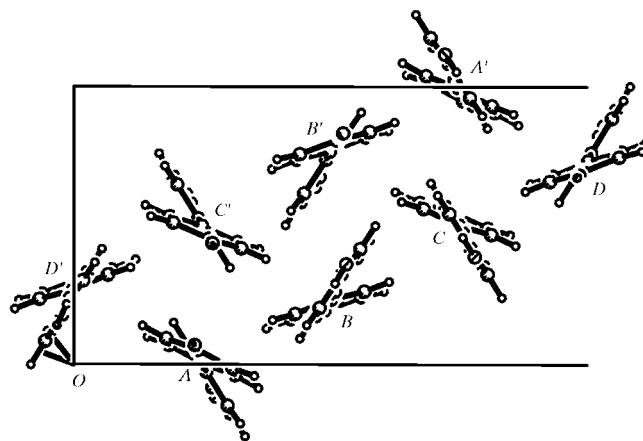
(2) screw axes parallel to  $a$ , which relate  $A \leftrightarrow C'$ ,  $B \leftrightarrow D'$ ,  $C \leftrightarrow A'$  and  $D \leftrightarrow B'$ ; (3) screw axes perpendicular to the  $ab$  plane, which relate  $A \leftrightarrow D'$ ,  $B \leftrightarrow C'$ ,  $C \leftrightarrow B'$  and  $D \leftrightarrow A'$ ; (4) glide planes perpendicular to  $b$ , which relate  $A \leftrightarrow B'$ ,  $B \leftrightarrow A'$ ,  $C \leftrightarrow D'$  and  $D \leftrightarrow C'$ ; (5) glide planes perpendicular to  $a$ , which relate  $A \leftrightarrow C$  and  $B \leftrightarrow D$ ; (6) glide planes parallel to the  $ab$  planes, which relate  $A \leftrightarrow D$  and  $B \leftrightarrow C$ . Glide planes 4, 5 and 6 are related, respectively, to the three screw axes 1, 2 and 3 by the real inversion center at  $(\frac{3}{4}, \frac{1}{4}, \frac{1}{2})$ . The pseudo-screw axes are all twofold. Details of the pseudosymmetry elements are included in the CIF in the section `_geom_special_details`.

It should be emphasized that the pseudosymmetry element directions are only approximately correct. The  $C$ -centered triclinic cell was chosen to simplify the discussion of the pseudosymmetry, but the  $\alpha$  and  $\gamma$  angles differ from  $90^\circ$  and these differences have been ignored. For each of the pairs of molecules, the best overlap has been determined using the program *OFIT* in *SHELXTL* (Sheldrick, 1997), and the r.m.s. deviations are given in Table 2, where they are compared with the r.m.s. deviations determined from the pseudosymmetry elements described above. As can be seen, the agreement is poorer, as would be expected, but still satisfactory.

The related compound 4-cyano-4'-ethynylbiphenyl (Langley *et al.*, 1998), in which the  $-OH$  group has been replaced with ethynyl ( $-C_2H$ ), also occurs in a triclinic cell with four molecules in the asymmetric unit, and with all the molecules close to parallel to each other and forming chains with their own kind held together by  $C_2H \cdots NC$  hydrogen bonds. However, in this case, there are no significant pseudosymmetrical relationships among the molecules.

4-Chloro-2-hydroxybiphenyl (Lehmler *et al.*, 2002), which is less closely related, also has a triclinic unit cell with four molecules in the asymmetric unit. In this case, the four independent molecules form cyclic tetrameric units rather than chains. Again, there are no significant pseudosymmetrical relationships among the molecules.

It is not clear why (I) should show so much pseudosymmetry while the closely related 4-cyano-4'-ethynylbiphenyl,



**Figure 4**

A view along  $a$  of the asymmetric unit shown in Fig. 3, plus the molecules related by a center of symmetry at  $(\frac{3}{4}, \frac{1}{4}, \frac{1}{2})$ . The vertical axis is shown from  $O$  to  $c$ ; the horizontal axis is shown from  $O$  to  $b/2$ .

which also has  $Z'$  equal to 4, shows none. Kitaigorodskii (1970) has pointed out that having  $Z'$  greater than 1 gives more degrees of freedom and therefore can increase the packing efficiency, but this explanation does not address the question of why some structures show pseudosymmetry and others with the same  $Z'$  do not.

## Experimental

Recrystallization was carried out from acetone, benzene/acetone, methylene chloride/acetone and carbon tetrachloride/acetone. The first three gave similar crystals; the last gave crystals of a distinctly different plate-like habit, but all proved to have the same cell dimensions.

### Crystal data

$C_{13}H_9NO$	$Z = 16$
$M_r = 195.21$	$D_x = 1.305 \text{ Mg m}^{-3}$
Triclinic, $C\bar{1}$	Mo $K\alpha$ radiation
$a = 12.936 (3) \text{ \AA}$	Cell parameters from 3725 reflections
$b = 33.696 (8) \text{ \AA}$	$\theta = 2.5\text{--}27.5^\circ$
$c = 10.604 (3) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$\alpha = 90.35 (1)^\circ$	$T = 174 (2) \text{ K}$
$\beta = 120.67 (1)^\circ$	Elongated octahedron, colorless
$\gamma = 89.60 (1)^\circ$	$0.50 \times 0.35 \times 0.30 \text{ mm}$
$V = 3975.5 (17) \text{ \AA}^3$	

### Data collection

Siemens SMART area-detector diffractometer	$R_{\text{int}} = 0.025$
$\omega$ scans	$\theta_{\text{max}} = 27.0^\circ$
22 798 measured reflections	$h = -16 \rightarrow 16$
8628 independent reflections	$k = -42 \rightarrow 42$
6872 reflections with $I > 2\sigma(I)$	$l = -13 \rightarrow 13$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.023P)^2 + 4.96P]$
$R[F^2 > 2\sigma(F^2)] = 0.055$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.119$	$(\Delta/\sigma)_{\text{max}} = 0.014$
$S = 1.12$	$\Delta\rho_{\text{max}} = 0.20 \text{ e \AA}^{-3}$
8628 reflections	$\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$
558 parameters	Extinction correction: <i>SHELXTL</i>
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.00031 (6)

**Table 1**

Distances and angles ( $\text{\AA}$ ,  $^\circ$ ) in O—H...NC hydrogen bonds.

H	N	O—H	O—H...N	H...N	H...N—C	O...N	Ref
H15A	N14A <sup>i</sup>	0.89	166	1.97	134	2.843 (2)	<i>a</i>
H15B	N14B <sup>ii</sup>	0.92	168	1.97	134	2.877 (2)	<i>a</i>
H15C	N14C <sup>ii</sup>	0.91	162	1.96	137	2.843 (2)	<i>a</i>
H15D	N14D <sup>i</sup>	0.92	161	1.94	139	2.828 (3)	<i>a</i>
H1	N2	0.91	167	1.92	174	2.820 (5)	<i>b</i>
H6	N1	0.88	170	1.97	166	2.839 (5)	<i>b</i>
H9	N8	0.94	174	1.91	170	2.847 (2)	<i>c</i>
H1A	N21B	0.92	173	1.88	170	2.795 (2)	<i>d</i>
H1B	N21A	0.91	172	1.90	158	2.798 (2)	<i>d</i>

Symmetry codes: (i)  $-1+x, y, z$ ; (ii)  $1+x, y, z$ . References: (a) 4-hydroxy-4'-cyanobiphenyl (this work); (b) 4-hydroxybenzoxazole (Higashi & Osaki, 1977); (c) 3-hydroxybenzoxazole (Britton, 2004); (d) 2-hydroxybenzoxazole (Beswick *et al.*, 1996).

In order to simplify the discussion of the pseudosymmetry and to make the molecular chains lie parallel to an axis, the conventional

**Table 2**

R.m.s. deviations ( $\text{\AA}$ ) between pseudosymmetrically related molecules.

Molecules	Best r.m.s. <sup>†</sup>	Pseudosymmetry r.m.s. <sup>‡</sup>
<i>A, B</i>	0.053	0.085
<i>A, C</i>	0.038	0.068
<i>A, D</i>	0.072	0.080
<i>B, C</i>	0.034	0.057
<i>B, D</i>	0.031	0.059
<i>C, D</i>	0.050	0.057

<sup>†</sup> Based on the comparison using *OFIT* in *SHELXTL* (Sheldrick, 1997); these are the best matches that can be obtained between each pair of molecules. <sup>‡</sup> Based on the pseudosymmetry elements described in the text; these elements are constrained to be parallel or perpendicular to unit-cell directions.

unit cell [ $a = 10.604 (3) \text{ \AA}$ ,  $b = 11.826 (3) \text{ \AA}$ ,  $c = 18.005 (5) \text{ \AA}$ ,  $\alpha = 103.10 (1)^\circ$ ,  $\beta = 100.23 (1)^\circ$  and  $\gamma = 109.80 (1)^\circ$ ] was converted by the matrix  $110/112/100$  to the cell in  $C\bar{1}$  reported in the experimental data.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1069). Services for accessing these data are described at the back of the journal.

## References

- Belsky, V. K., Zorkaya, O. N. & Zorky, P. M. (1995). *Acta Cryst.* **A51**, 473–481.
- Beswick, C., Kubicki, M. & Coddling, P. W. (1996). *Acta Cryst.* **C52**, 3171–3173.
- Britton, D. (2004). *Acta Cryst.* **E60**, o1513–o1514.
- Britton, D. & Gleason, W. B. (1991). *Acta Cryst.* **C47**, 2127–2131.
- Britton, D. & Young, V. G. Jr (2003). *Acta Cryst.* **E59**, o1849–o1851.
- Brock, C. P., Kuo, M.-S. & Levy, H. A. (1978). *Acta Cryst.* **B34**, 981–985.
- Bruker (2002). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Casalone, G., Mariani, C., Mugnoli, A. & Simonetta, M. (1969). *Acta Cryst.* **B25**, 1741–1750.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Gleason, W. B., Brostrom, M., Etter, M. C. & Johnson, R. B. (1991). *Acta Cryst.* **C47**, 1473–1476.
- Haase, W., Loub, J. & Paulus, H. (1992). *Z. Kristallogr.* **202**, 7–16.
- Higashi, T. & Osaki, K. (1977). *Acta Cryst.* **B33**, 607–609.
- Jackisch, M. A., Fronczek, F. R., Geiger, C. C., Hale, P. S., Daly, W. H. & Botler, L. G. (1990). *Acta Cryst.* **C46**, 919–922.
- Kitaigorodskii, A. I. (1970). *Adv. Struct. Res.* **3**, 173–247.
- Kronebusch, P., Gleason, W. B. & Britton, D. (1976a). *Cryst. Struct. Commun.* **5**, 17–20.
- Kronebusch, P., Gleason, W. B. & Britton, D. (1976b). *Cryst. Struct. Commun.* **5**, 839–842.
- Langley, P. J., Hullinger, J., Thaimattam, R. & Desiraju, G. R. (1998). *New J. Chem.* pp. 1307–1309.
- Lehmle, H.-J., Robertson, L. W., Parkin, S. & Brock, C. P. (2002). *Acta Cryst.* **B58**, 140–147.
- Masunov, A. E., Grishchenko, S. I. & Zorky, P. M. (1992). *Russ. J. Phys. Chem.* **66**, 23–30.
- Mohamed, A. K., Auner, N. & Bolte, M. (2003). *Acta Cryst.* **E59**, o476–o477.
- Sheldrick, G. M. (1997). *SHELXTL*. Version 5. Bruker AXS Inc., Madison, Wisconsin, USA.
- Zorky, P. M. (1996). *J. Mol. Struct.* **374**, 9–28.
- Zorky, P. M. & Dashevskaya, E. E. (1992). *Russ. J. Phys. Chem.* **66**, 35–42.
- Zorky, P. M. & Dashevskaya, E. E. (1993). *Acta Chim. Hung.* **130**, 247–259.