Table 2. *Hydrogen-bonding geometry (Å, °)*

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1$A$—H16$A$···O3$A^{i}$ | 0.86 (3) | 1.87 (3) | 2.726 (3) | 171 (3) |
| O2$A$—H17$A$···O3$B^{ii}$ | 0.83 (2) | 1.96 (2) | 2.787 (2) | 173 (3) |
| O3$A$—H18$A$···O2$B^{iii}$ | 0.74 (2) | 1.96 (2) | 2.697 (3) | 170 (3) |
| O1$B$—H16$B$···O1$A^{iv}$ | 0.77 (2) | 2.00 (2) | 2.764 (3) | 171 (3) |
| O2$B$—H17$B$···O2$A$ | 0.80 (2) | 1.94 (2) | 2.737 (3) | 175 (3) |
| O3$B$—H18$B$···O1$B^{v}$ | 0.89 (2) | 1.80 (2) | 2.687 (3) | 175 (3) |

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

Table 3. *First- and basic second-level graph-set descriptors involving hydrogen bonds designated (a) to (f) in the order given in Table 2*

| | (*a*) | (*b*) | (*c*) | (*d*) | (*e*) | (*f*) |
|---|---|---|---|---|---|---|
| (*a*) | $C(8)$ | $D_2^2(10)$ | $D_3^3(13)$ | $D_2^2(4)$ | $D_2^2(9)$ | — |
| (*b*) | | $D$ | $R_4^4(32)$ | $C_2^2(16)$ | $R_4^4(20)$ | $D_3^3(11)[R_2^2(16)]$ |
| (*c*) | | | $D$ | $C_2^2(16)$ | $C_2^2(10)$ | $D_3^3(17)[R_2^2(16)]$ |
| (*d*) | | | | $D$ | $C_2^2(16)$ | $D_3^3(13)[R_2^2(16)]$ |
| (*e*) | | | | | $D$ | $D_3^3(19)[R_2^2(16)]$ |
| (*f*) | | | | | | $R_2^2(16)$ |

Fourier difference methods were used to locate initial H-atom positions for all but one of the methyl H atoms; the H atoms were then refined isotropically. Subsequently, all H atoms except the hydroxyl H atoms were made canonical, with a C—H distance of 0.98 Å and isotropic displacement parameters fixed at 1.2 times those of the attached C atoms. The hydroxyl H atoms were refined isotropically. When the model with two molecules as the asymmetric unit converged, the maximum residual difference peak indicated methyl group disorder in the C10*A* group. The maximum residual peak was assigned as C51*A* and the populations of C10*A* and C51*A* were refined together with the six coordinates, anisotropic displacement components for C10*A* and an isotropic displacement factor for C51*A*. Taking into consideration the relatively small occupancy of C51*A*, 0.183, the geometry at the refined C51*A* atom is reasonable: C9*A*—C51*A* 1.35 (2) Å and C3*A*—C9*A*—C51*A* 122.3 (7)°. Due to the relatively small occupancy of C51*A*, no attempt was made to model its H atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

The authors thank Dr Kurt Loening for help with nomenclature and Dr J. C. Gallucci for help of various sorts. The diffractometer was purchased with funds provided in part by an NIH grant.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1397). Services for accessing these data are described at the back of the journal.

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# Biphenyl-2-carboxylic Acid: a Layered Structure

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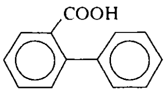
## Abstract

The title acid, $C_{13}H_{10}O_2$, crystallized in the centrosymmetric space group $P2_1/c$ with four molecules in the asymmetric unit. These four molecules form two pairs of cyclic hydrogen-bonded dimers of the usual sort, but these are not formed about centers of symmetry. The $O_{donor}\cdots O_{acceptor}$ distances in these hydrogen bonds are 2.660 (3), 2.638 (3), 2.676 (3) and 2.634 (3) Å. The carboxylic H atoms and the carboxylic O atoms are ordered. The biphenyl twist angles range from 46.5 (2) to 52.5 (2)°. The dihedral angles between the carboxyl group planes and the planes of the rings to which they are attached range from 43.6 (3) to 50.9 (3)°. In the two latter respects, this structure differs appreciably from the structures of the other two biphenyl monocarboxylic acids. The structure is layered parallel to the *ab* plane.

## Comment

This report on biphenyl-2-carboxylic acid, (I), is one of a series on hydrogen bonding in aromatic carboxylic acids. It follows reports on biphenyl-3-carboxylic acid (Blackburn *et al.*, 1996) and biphenyl-4-carboxylic acid (Brock *et al.*, 1984), and thus completes the structural determination of the series of biphenyl monocarboxylic acids. As in the previous studies, the dihedral angle between the phenyl planes is a matter of further interest in this study.



(I)

The title acid crystallized in the centrosymmetric space group $P2_1/c$ with four molecules in the asymmetric unit. These four molecules form two pairs of cyclic hydrogen-bonded dimers of the usual sort, but these are not formed about centers of symmetry. Fig. 1 presents these dimers together with the labeling scheme. Geometric details of the hydrogen bonds are given in Table 2. Although the O1*B*—H13*B* distance appears unrealistically large, none of the top 25 electron-density difference peaks lies near O1*B* (so no alternative assignment of an H atom near O1*B* is possible), nor does any lie near O2*A* (which would suggest the possibility of a disordered H atom); since, moreover, the C13*B*—O1*B*—H13*B* angle, 115 (1)°, is normal, H13*B* along with the other carboxylic H atoms is modeled as ordered. Each of the eight carboxylic O atoms has the axis of its largest principal displacement tensor component nearly normal to the plane of its carboxyl group, as expected for ordered carboxylic O atoms. In terms of graph-set analysis of hydrogen bonds (Bernstein *et al.*, 1995), the first-level graph-set descriptors are *DDDD*, while the second-level descriptors are both $R_2^2(8)$. There are no graph sets of higher level.

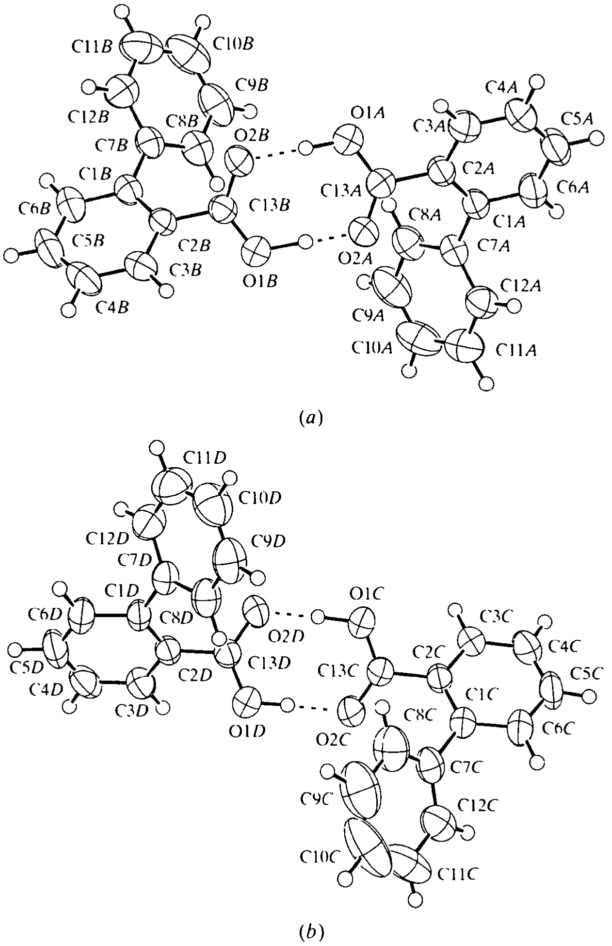


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the four crystallographically inequivalent biphenyl-2-carboxylic acid molecules in the two sets of hydrogen-bonded dimers making up the title structure, together with the numbering scheme: (*a*) the *A–B* dimer and (*b*) the *C–D* dimer. Hydrogen bonds are depicted as dashed lines. Displacement ellipsoids are drawn at 50% probability for non-H atoms and H atoms are shown as small spheres.

The eight phenyl rings of the four independent molecules are closely planar: the maximum deviation of any phenyl C atom from the best-fit plane describing that phenyl group is 0.012 (3) Å, while the largest average deviation of the six phenyl C atoms from the best-fit plane describing them is 0.006 (3) Å. The four phenyl rings carrying the carboxyl substituents depart slightly more from planarity than do the four unsubstituted rings. Table 3 presents the intramolecular dihedral angles for the four sets of molecules. The intramolecular dihedral angles between the phenyl-ring planes (the so-called twist angles), which range from 46.5 (2) to 52.5 (2)°, may be compared with those observed in biphenyl-3-carboxylic acid at 296 K [31.78 (8)°] and biphenyl-4-carboxylic acid [28.7 (2)–35.7 (2)°]. It should be noted that the latter two substances, unlike the title substance, have four H atoms *ortho* to the phenyl–phenyl bond and that the distribution of twist angles for such molecules has its maximum at ~37°, with a subsidiary maximum near 0° (Brock & Minton, 1989). In the title substance, the dihedral angles between the carboxyl-group planes and the planes of the rings to which they are attached range from 43.6 (3) to 50.9 (3)° and are thus in striking contrast to the corresponding values observed for biphenyl-3- and biphenyl-4-carboxylic acids, all four of which are less than 10°.

The intermolecular dihedral angles between phenyl-ring planes, for rings each carrying a carboxyl group, lie in moderately small ranges near 0 [0.7 (2)–23.6 (2)] or 90° [78.2 (2)–82.9 (2)°]; moreover, the corresponding values for unsubstituted rings lie in narrower ranges near 0 [1.6 (2)–7.1 (2)] or 90° [84.4 (2)–87.7 (2)°]. This disposition of the phenyl rings, and the attendant geometrical effects, are illustrated in the packing diagram (Fig. 2).

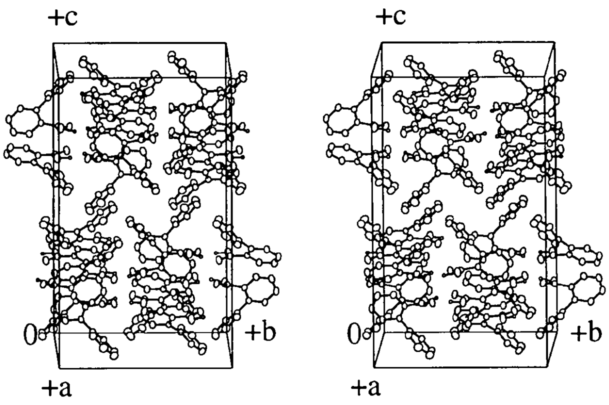


Fig. 2. *ORTEP*II (Johnson, 1976) packing diagram of biphenyl-2-carboxylic acid. For clarity, all ring H atoms have been omitted and displacement ellipsoids are drawn at 25% probability for non-H atoms. Other H atoms are shown as small spheres.

An important characteristic of this structure is that it is layered, with the layers parallel to the *ab* plane, as shown in Fig. 3. Whereas in many carboxylic acid structures the hydrogen bonds link molecules into strong three-dimensional arrays, here no hydrogen bonds link molecules along, or near, the **c** direction. The occurrence of such unbonded layers leads to the inference that crystals of this phase should cleave readily parallel to the *ab* plane.

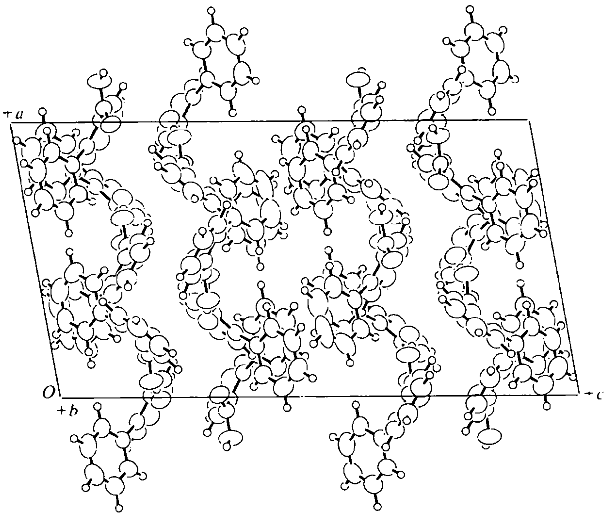


Fig. 3. *ORTEP*II (Johnson, 1976) packing diagram displaying the layered structure of biphenyl-2-carboxylic acid. Displacement ellipsoids are drawn at 50% probability for non-H atoms and H atoms are shown as small spheres.

Among a number of structures of nitro-substituted biphenyl-2-carboxylic acids, that of 4,4′-dinitrobiphenyl-2-carboxylic acid (Popova *et al.*, 1990) appears most appropriate for comparisons with the title acid, along with the structure of 2-butyl-1-[(2′-carboxybiphenyl-4-yl)methyl]-4-chloro-5-(hydroxymethyl)imidazole (Bradbury *et al.*, 1992). In these two substituted acids, the biphenyl core intramolecular dihedral angles are 57.9 and 62.9°, respectively, while those in the title acid range from 46.5 (2) to 52.5 (2)°; the dihedral angles between the carboxyl-group planes and the attached phenyl-ring planes are 34.0 and 32.5°, respectively, while those of the title acid range from 43.6 (3) to 50.9 (3)°. Thus, the title acid configurations lie closer to those of the two substituted acids than to those of biphenyl-3- or biphenyl-4-carboxylic acid. The title acid and these two substituted acids differ in that the acid OH groups are, respectively, *anti* and *syn* to the phenyl–phenyl bonds.

Distances and angles of special interest in the title structure are given in Table 1. Among the 56 intramolecular C—C distances in this structure, the C9—C10 distance in molecule *C*, 1.339 (7) Å, differs the most from the closest corresponding distance in the other three molecules, 1.365 (6) Å; it should also be noted that C9*C* and C10*C* have the largest, and very substantial, displacement parameters among the non-H atoms. The closest intermolecular approaches, excluding pairs of atoms within directly hydrogen-bonded groups, are between H4*A* and H4*B*$^{i}$ [symmetry code: (i) $x, -1+y, z$] and between C2*A* and H3*B*$^{ii}$ [symmetry code: (ii) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$] and fall short of the corresponding van der Waals radii sums (Bondi, 1964) by 0.17 and 0.16 Å, respectively.

## Experimental

Biphenyl-2-carboxylic acid was obtained as a white crystalline powder from Janssen Chim. This solid was loaded into a glass tube which was then flushed with nitrogen, sealed and passed through an air-core Bridgman furnace, similar to that described by Sherwood & Thomson (1960). The experimental sample was cut from the resulting boule.

*Crystal data*

$C_{13}H_{10}O_2$
$M_r$ = 198.22
Monoclinic
$P2_1/c$
$a$ = 12.861 (2) Å
$b$ = 14.328 (2) Å
$c$ = 23.929 (2) Å
$\beta$ = 99.784 (11)°
$V$ = 4345 (1) Å$^3$
$Z$ = 16
$D_x$ = 1.212 Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda$ = 0.71073 Å
Cell parameters from 25 reflections
$\theta$ = 10.4–12.8°
$\mu$ = 0.081 mm$^{-1}$
$T$ = 296 K
Cut plate
0.38 × 0.38 × 0.30 mm
Colorless

*Data collection*

AFC-5*S* diffractometer
$\omega$ scans

$R_{int}$ = 0.021
$\theta_{max}$ = 27.56°

Absorption correction: none
10 900 measured reflections
10 039 independent reflections
3366 reflections with $I > 2\sigma(I)$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 18$
$l = -31 \rightarrow 30$
6 standard reflections every 150 reflections intensity decay: 3.79%

*Refinement*

Refinement on $F^2$
$R(F) = 0.052$
$wR(F^2) = 0.137$
$S = 1.12$
10 038 reflections
701 parameters
All H atoms refined
$w = 1/\sigma^2(F^2)$
$(\Delta/\sigma)_{\max} < 0.01$
$\Delta\rho_{\max} = 0.45$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.46$ e Å$^{-3}$
Extinction correction: none
Scattering factors from Stewart *et al.* (1965) (H) and Creagh & McAuley (1992) (C, O)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| O1*A*—C13*A* | 1.283 (3) | O1*C*—C13*C* | 1.283 (3) |
| O2*A*—C13*A* | 1.237 (3) | O2*C*—C13*C* | 1.248 (3) |
| O1*B*—C13*B* | 1.286 (3) | O1*D*—C13*D* | 1.282 (3) |
| O2*B*—C13*B* | 1.236 (3) | O2*D*—C13*D* | 1.239 (3) |
| O1*A*—C13*A*—O2*A* | 123.1 (3) | O1*C*—C13*C*—O2*C* | 122.8 (3) |
| O1*A*—C13*A*—C2*A* | 115.3 (3) | O1*C*—C13*C*—C2*C* | 116.2 (3) |
| O2*A*—C13*A*—C2*A* | 121.6 (3) | O2*C*—C13*C*—C2*C* | 121.0 (3) |
| C13*A*—O1*A*—H13*A* | 115 (2) | C13*C*—O1*C*—H13*C* | 117 (2) |
| O1*B*—C13*B*—O2*B* | 123.4 (3) | O1*D*—C13*D*—O2*D* | 123.4 (3) |
| O1*B*—C13*B*—C2*B* | 114.9 (3) | O1*D*—C13*D*—C2*D* | 114.8 (3) |
| O2*B*—C13*B*—C2*B* | 121.7 (3) | O2*D*—C13*D*—C2*D* | 121.8 (3) |
| C13*B*—O1*B*—H13*B* | 115 (1) | C13*D*—O1*D*—H13*D* | 115 (2) |

Table 2. *Hydrogen-bonding geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1*A*—H13*A*···O2*B* | 1.05 (5) | 1.63 (5) | 2.660 (3) | 166 (4) |
| O1*B*—H13*B*···O2*A* | 1.23 (5) | 1.41 (5) | 2.638 (3) | 177 (4) |
| O1*C*—H13*C*···O2*D* | 1.11 (5) | 1.56 (5) | 2.676 (3) | 174 (4) |
| O1*D*—H13*D*···O2*C* | 1.03 (5) | 1.61 (5) | 2.634 (3) | 174 (4) |

Table 3. *Dihedral angles (°) within the four sets of title molecules*

| Molecule | C1-phenyl to C7-phenyl | C1-phenyl to carboxyl | C7-phenyl to carboxyl |
|---|---|---|---|
| *A* | 51.1 (2) | 43.6 (3) | 53.8 (4) |
| *B* | 48.7 (2) | 50.9 (3) | 51.8 (3) |
| *C* | 52.5 (2) | 45.4 (3) | 53.5 (4) |
| *D* | 46.5 (2) | 50.2 (4) | 51.8 (4) |

Scan widths were $(1.60 + 0.35\tan\theta)^\circ$ in $\omega$, with a background/scan time-ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and centrosymmetric intensity statistics indicated space group $P2_1/c$ (No. 14); since refinement proceeded well it was adopted. Difference-Fourier methods were used to locate the initial H-atom positions. The 36 refined C—H distances ranged from 0.87 (3) to 1.05 (3) Å, with a mean value 0.98 Å; the refined O—H distances are given in Table 2. The extinction coefficient was predicted to be negative and was therefore not included in the refinement. In later stages of the refinement, the single reflection with $\Delta F/\sigma(F) > 10$, *i.e.* 102, was excluded from the least-squares refinement. The maximum positive residual peak was located ~0.7 Å from C1*C*, and the maximum negative peak was located ~1.1 Å from C12*D* and 1.2 Å from C7*D*.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

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