

Table 1. Selected geometric parameters (\AA , $^\circ$)

O1—C1	1.199 (2)	C9—C10	1.513 (2)
O2—C1	1.321 (2)	C10—C11	1.518 (2)
O3—C24	1.237 (1)	C11—C12	1.513 (2)
N1—C19	1.333 (2)	C12—C13	1.513 (2)
N1—C23	1.336 (2)	C13—C14	1.515 (2)
N2—C24	1.331 (2)	C14—C15	1.511 (2)
C1—C2	1.498 (2)	C15—C16	1.510 (2)
C2—C3	1.508 (2)	C16—C17	1.511 (3)
C3—C4	1.519 (2)	C17—C18	1.494 (3)
C4—C5	1.512 (2)	C19—C20	1.384 (2)
C5—C6	1.515 (2)	C20—C21	1.388 (2)
C6—C7	1.513 (2)	C20—C24	1.489 (2)
C7—C8	1.514 (2)	C21—C22	1.377 (2)
C8—C9	1.506 (2)	C22—C23	1.376 (2)
C19—N1—C23	118.0 (1)	C12—C13—C14	114.1 (1)
O1—C1—O2	122.4 (1)	C13—C14—C15	114.0 (2)
O1—C1—C2	125.7 (1)	C14—C15—C16	114.7 (2)
O2—C1—C2	111.8 (1)	C15—C16—C17	114.1 (2)
C1—C2—C3	115.7 (1)	C16—C17—C18	114.4 (2)
C2—C3—C4	111.6 (1)	N1—C19—C20	123.3 (1)
C3—C4—C5	114.9 (1)	C19—C20—C21	117.9 (1)
C4—C5—C6	113.4 (1)	C19—C20—C24	118.99 (10)
C5—C6—C7	114.6 (1)	C21—C20—C24	123.1 (1)
C6—C7—C8	114.6 (1)	C20—C21—C22	119.1 (1)
C7—C8—C9	114.5 (1)	C21—C22—C23	119.0 (1)
C8—C9—C10	114.5 (1)	N1—C23—C22	122.7 (1)
C9—C10—C11	114.4 (1)	O3—C24—N2	122.0 (1)
C10—C11—C12	114.3 (1)	O3—C24—C20	120.67 (10)
C11—C12—C13	114.2 (1)	N2—C24—C20	117.32 (9)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
O2—H1...N1	1.02 (1)	1.67 (1)	2.693 (1)	174 (1)
N2 ⁱ —H41 ⁱ ...O3	0.96 (1)	1.98 (1)	2.939 (1)	172 (1)
N2 ⁱⁱ —H42 ⁱⁱ ...O3	0.94 (1)	2.04 (2)	2.904 (1)	153 (1)

Symmetry codes: (i) $-1 - x, -y, -z$; (ii) $x, y, z - 1$.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *MULTAN88* (Debaerdemaeker *et al.*, 1988). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1032). Services for accessing these data are described at the back of the journal.

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6,6'-Dimethylbiphenyl-2,2'-dicarboxylic Acid (6,6'-Dimethyldiphenic Acid)

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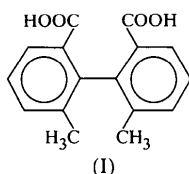
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Abstract

The title compound, $\text{C}_{16}\text{H}_{14}\text{O}_4$, crystallized in the centrosymmetric space group $P2_1/c$ with a single molecule in the asymmetric unit. The two carboxyl H atoms are ordered and are involved in hydrogen bonds whose $\text{O}_a \cdots \text{O}_a$ distances are 2.660 (2) and 2.641 (2) \AA . Each of the hydrogen bonds forms a cyclic hydrogen-bonded dimer about a center of symmetry. Thus, each molecule is linked to two others to form a chain. The structure comprises two sets of such chains linked, not by conventional hydrogen bonds, but by one significantly attractive $\text{C—H} \cdots \text{O}$ interaction. The intramolecular dihedral angle between the ring planes (twist angle) is 84.9 (1)°. The dihedral angles between the carboxyl-group planes and the planes of the rings to which they are attached are 36.7 (1) and 21.4 (1)°. A number of comparisons are made with the structure of the 'parent' compound, biphenyl-2,2'-dicarboxylic acid.

Comment

This report on 6,6'-dimethylbiphenyl-2,2'-dicarboxylic acid, (I), is one of a series on hydrogen bonding in biphenylcarboxylic acids which includes biphenyl-



3-carboxylic acid, 2-hydroxybiphenyl-3-carboxylic acid and biphenyl-2-carboxylic acid (Blackburn *et al.*, 1996; Dobson & Gerkin, 1996, 1998). The title acid crystallized in the centrosymmetric space group $P2_1/c$ with a single molecule in the asymmetric unit. The refined molecule is shown in Fig. 1 together with the numbering scheme. Each of the carboxyl H atoms is ordered and is involved in a hydrogen bond. Each hydrogen bond forms a cyclic hydrogen-bonded dimer about a center of symmetry, thus linking each molecule directly to two others to form a chain. The structure comprises two sets of such chains not cross-linked by conventional hydrogen bonds. Geometric details of the two hydrogen bonds are given in Table 2. The results of hydrogen-bond graph-set analysis (Bernstein *et al.*, 1995) are given in Table 3. Each of the two sets of $C_2^2(18)[R_2^2(8)]$ chains propagates in the **b** direction. The chains are cross-linked by a single significant C—H...O interaction [C5—H5...O2ⁱⁱⁱ: H...O 2.62, C...O 3.587 (2) Å and C—H...O 168°; symmetry code: (iii) $x, \frac{1}{2} - y, \frac{1}{2} + z$]. These C—H...O interactions themselves form chains which propagate in the **c** direction and link molecules of space group symmetry types 1 and 4, or 2 and 3.

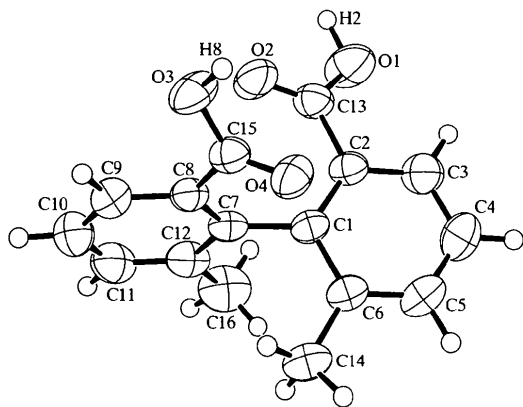


Fig. 1. ORTEPII (Johnson, 1976) drawing of 6,6'-dimethylbiphenyl-2,2'-dicarboxylic acid showing the numbering scheme. Displacement ellipsoids are drawn for 50% probability for all atoms except H atoms, for which they have been set artificially small.

In the title structure, the benzene rings are nearly planar; the maximum deviation of the ring C atoms from the best-fit plane describing them is 0.012 (2) Å, and the average deviation is 0.007 (4) Å for each of the

rings. The intramolecular dihedral angle between these ring planes, the so-called twist angle, is 84.9 (1)°. Since the dihedral angle between the planes of the C1—C6 (or C7—C12) rings of the two non-parallel sets of molecules is 84.0 (1)°, all the ring planes are either parallel or almost perpendicular to one another. The dihedral angle between the carboxyl-group plane (C13, O1, O2) and its ring plane is 36.7 (1)°, and that between the second carboxyl-group plane (C15, O3, O4) and its ring plane is 21.4 (1)°.

A packing diagram drawn to emphasize the structural features described above (Fig. 2) also shows that the structure is layered, with the layers stacked along **b** and connected by the hydrogen bonds. Contrarily, the C—H...O interactions link molecules only within such layers.

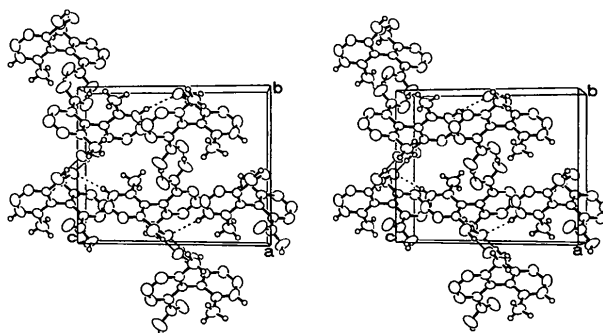


Fig. 2. ORTEPII (Johnson, 1976) packing diagram of the title acid. Displacement ellipsoids are drawn for 50% probability for all atoms except H atoms, for which they have been set artificially small. Hydrogen bonds are shown as fine solid lines, the C—H...O interactions as dashed lines. Excepting H5, which is involved in the C—H...O interaction and also serves to identify the C1—C6 ring, ring-H atoms have been omitted for clarity. The cell origin is at the lower right rear corner.

Of particular interest for comparison is the structure of biphenyl-2,2'-dicarboxylic acid (diphenic acid) as determined by Fronczek *et al.* (1987). While that structure was also assigned in $P2_1/c$, there are two molecules (denoted *A* and *B*) in its asymmetric unit. Although, as for the title compound, each *A* and *B* molecule forms two hydrogen-bonded cyclic dimers, these do not occur about centers of symmetry in that structure. Various parameters for the diphenic acid *A* and *B* molecules and the title molecule are listed for comparison in Table 4. While the twist angles are quite similar, the dihedral angles between the carboxyl-group planes and the ring planes are substantially larger in the title acid than in diphenic acid. Fronczek *et al.* (1987) note that diphenic acid is quite unusual among 2,2'-substituted biphenyls in having the C2—C1—C7—C8 torsion angle greater than 90° (*anti* conformation); the present acid differs from it in having the more common *syn* conformation.

Distances and angles of special interest in the title molecule are given in Tables 1 and 4; all distances and angles fall within normal ranges. The closest intermolecular approaches in this structure, excluding pairs of atoms in groups hydrogen bonded to each other, are between O2 and H5^{iv}, and are 0.08 Å less than the sum of the corresponding Bondi (1964) van der Waals radii [symmetry code: (iv) $x, \frac{1}{2} - y, -\frac{1}{2} + z$]. All other closest approaches exceed the sums of the corresponding Bondi radii.

Experimental

6,6'-Dimethylbiphenyl-2,2'-dicarboxylic acid was obtained from a sample in the chemical collection of Dr M. S. Newman as a colorless column which was cut to provide the experimental sample. An early synthesis is described by Bell (1934); see also Karnes *et al.* (1965).

Crystal data

$C_{16}H_{14}O_4$
 $M_r = 270.28$
 Monoclinic
 $P2_1/c$
 $a = 8.945(1) \text{ \AA}$
 $b = 11.472(1) \text{ \AA}$
 $c = 14.649(2) \text{ \AA}$
 $\beta = 106.36(1)^\circ$
 $V = 1442.4(3) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.245 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 11.7\text{--}17.4^\circ$
 $\mu = 0.084 \text{ mm}^{-1}$
 $T = 296 \text{ K}$
 Cut column
 $0.35 \times 0.31 \times 0.27 \text{ mm}$
 Colorless

Data collection

Rigaku AFC-5S diffractometer
 ω scans
 Absorption correction: none
 3539 measured reflections
 3332 independent reflections
 1738 reflections with
 $I > 2\sigma_I$

$R_{\text{int}} = 0.025$
 $\theta_{\text{max}} = 27.56^\circ$
 $h = 0 \rightarrow 11$
 $k = 0 \rightarrow 14$
 $l = -19 \rightarrow 18$
 6 standard reflections every 150 reflections
 intensity decay: 8.9%

Refinement

Refinement on F^2
 $R(F) = 0.052$
 $wR(F^2) = 0.084$
 $S = 1.61$
 3332 reflections
 190 parameters
 H atoms: see below
 $w = 1/\sigma^2(F^2)$
 $(\Delta/\sigma)_{\text{max}} < 0.01$

$\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.38 \text{ e \AA}^{-3}$
 Extinction correction:
 Zachariasen (1963, 1968)
 Extinction coefficient:
 $4.8(8) \times 10^{-7}$
 Scattering factors from
 Stewart *et al.* (1965) (H)
 and Creagh & McAuley
 (1992) (C, O)

Table 1. Selected geometric parameters (\AA , $^\circ$)

O1—C13	1.315(2)	O3—C15	1.302(2)
O2—C13	1.225(2)	O4—C15	1.220(2)
O1—C13—O2	121.9(2)	O3—C15—O4	122.1(2)
O1—C13—C2	114.2(2)	O3—C15—C8	114.6(2)
O2—C13—C2	123.9(2)	O4—C15—C8	123.3(2)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
O1—H1 ⁱ ···O2 ⁱ	1.01(3)	1.66(3)	2.660(2)	176(2)
O3—H8 ⁱⁱ ···O4 ⁱⁱ	1.02(3)	1.62(3)	2.641(2)	178(2)

Symmetry codes: (i) $2 - x, -y, 1 - z$; (ii) $2 - x, 1 - y, 1 - z$.

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

	(a)	(b)
(a)	$R_2^2(8)$	$C_2^2(18)[R_2^2(8)]$
(b)		$R_2^2(8)$

Table 4. Various geometric parameters ($^\circ$, \AA) for the A and B molecules of biphenyl-2,2'-dicarboxylic acid (diphenic acid) and for the title acid

The angular values for diphenic acid have been calculated from the published data via PLATON (Spek, 1990).

	Diphenic A†	Diphenic B†	(I)
Biphenyl twist angle	71.3(1)	83.6(1)	84.9(1)
Carboxyl group 1 to ring 1 dihedral angle	13.6(2)	3.2(2)	36.7(1)
Carboxyl group 2 to ring 2 dihedral angle	6.2(2)	11.3(2)	21.4(1)
Torsion angle C2—C1—C7—C8	-119.3(2)	-106.3(3)	-88.4(2)
$O_{d,1}\cdots O_{a,1}$ distance	2.655(1)	2.811(1)	2.660(2)
$O_{d,2}\cdots O_{a,2}$ distance	2.612(1)	2.553(1)	2.641(2)

† Fronczek *et al.* (1987).

Scan widths were $(1.40 + 0.35\tan\theta)^\circ$ in ω , with a background/scan time ratio of 0.5. The data were corrected for Lorentz and polarization effects. A linear decay correction was applied. 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 and the H atoms were then refined isotropically. Refined ring C—H distances ranged from 0.94(2) to 0.99(2) Å, methyl C—H distances from 0.85(2) to 1.00(2) Å, and methyl H—C—H angles from 104(2) to 108(2)°. Ring and methyl H atoms were then made canonical, with C—H = 0.98 Å and $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the attached C atom. The carboxyl H atoms were not made canonical; the refined O—H distances are given in Table 2. The maximum effect of extinction is 3.3% of F_o for 110. The maximum positive residual peak is located $\sim 0.5 \text{ \AA}$ from C12 and the maximum negative peak is located $\sim 0.1 \text{ \AA}$ from C2.

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: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: TEXSAN. Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: TEXSAN and PLATON (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1132). Services for accessing these data are described at the back of the journal.

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