Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1403). Services for accessing these data are described at the back of the journal.

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angles are 68.1 (1) and 64.6 (1)°. The dihedral angles between the benzene-ring planes and the planes of the carboxyl groups attached to them are 0.7 (3), 23.3 (2) and 18.4 (2)°. Structural comparisons are made with the 'parent' compound, diphenic acid, and with the isomeric compound, 6,6'-dimethylbiphenyl-2,2'-dicarboxylic acid.

Comment

This report on 4,4'-dimethylbiphenyl-2,2'-dicarboxylic acid, (I), is one of a series on hydrogen bonding in biphenyl carboxylic acids, and follows reports on biphenyl-3-carboxylic acid (Blackburn *et al.*, 1996), biphenyl-2-carboxylic acid (Dobson & Gerkin, 1998)

(I)

and the isomer, 6,6'-dimethylbiphenyl-2,2'-dicarboxylic acid (Gerkin, 1998). Compound (I) crystallized in the centrosymmetric space group C2/c with 1.5 molecules in the asymmetric unit. The refined asymmetric unit is shown in Fig. 1 together with the numbering scheme. Three hydrogen bonds occur in this structure, and in each the H atom is ordered. Geometric details are given in Table 2. Each of the hydrogen bonds participates in an eight-membered cyclic dimer arrangement, and

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Hydrogen-Bonded Trimers in 4,4'-Dimethylbiphenyl-2,2'-dicarboxylic Acid

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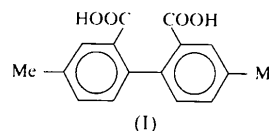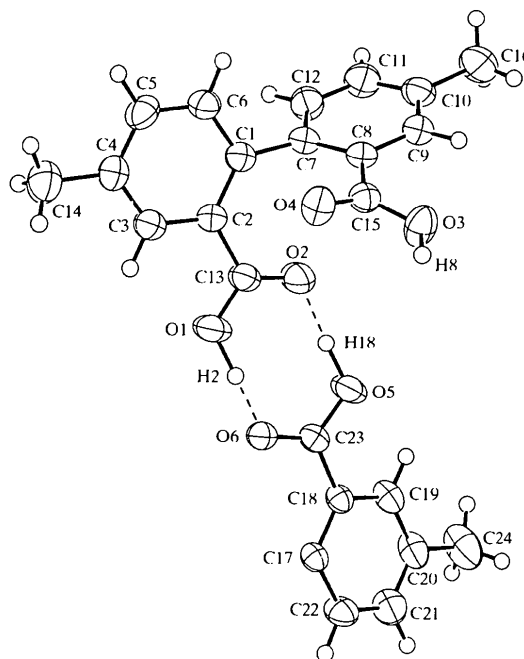
Abstract

The title acid, $C_{16}H_{14}O_4$, crystallized in the centrosymmetric space group C2/c with 1.5 molecules in the asymmetric unit. Each of the three independent carboxylic H atoms is ordered, and each participates in hydrogen bonding. The $O_D \cdots O_A$ distances in the hydrogen bonds are 2.584 (2), 2.647 (2) and 2.722 (2) Å. Three sets of cyclic dimer hydrogen bonds are formed within and between two asymmetric units, linking them into molecular trimers. The trimers lie on twofold axes which bisect the central C—C bond of one molecule and the COOH dimer connecting the other two. The two biphenyl twist

Fig. 1. *ORTEPII* (Johnson, 1976) drawing of the asymmetric unit in the title structure, showing our numbering scheme. Displacement ellipsoids are drawn for 50% probability for non-H atoms; circles of arbitrary small radius depict H atoms. The intra-unit hydrogen bonds are shown by dashed lines.

three such cyclic dimers are formed within and between two asymmetric units. The result is molecular trimers bound by three sets of cyclic dimer hydrogen bonds, as shown in Fig. 2. The trimers lie on twofold axes which bisect the central C—C bond of one molecule and the COOH dimer connecting the other two. Results of hydrogen-bond graph set analysis (Bernstein *et al.*, 1995) involving the three hydrogen bonds, which are labeled *a–c* in the order given in Table 2, are given in Table 3 for the first- and basic second-level graph sets. The tabulation shows that, consistent with the trimeric arrangement described above, only rings and finite patterns occur.
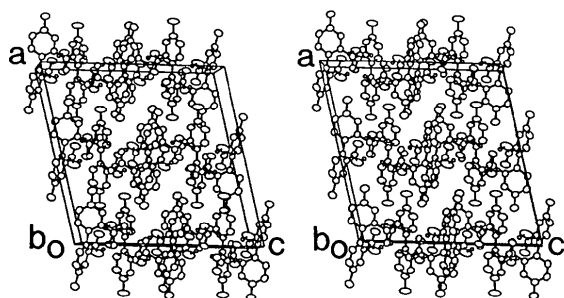

Fig. 2. *ORTEP*II (Johnson, 1976) packing diagram of (I). Displacement ellipsoids are drawn for 50% probability for non-H atoms; circles of arbitrary small radius depict H atoms. For clarity, H atoms not involved in hydrogen bonding are omitted.

In this structure the three independent benzene rings are very nearly planar: the maximum deviations of the ring-C atoms from the best-fit planes describing them are 0.007 (2), 0.014 (2) and 0.017 (2) Å, while the average deviations are 0.004 (2), 0.010 (5) and 0.010 (4) Å. The dihedral angle between the planes of the C1–C6 and C7–C12 rings [which comprise what can be designated as the (*IA*) molecule] is 68.1 (1)° (the biphenyl twist angle). Similarly, the dihedral angle between the planes of the C17–C22 ring and the C17^i– C22^i [symmetry code: (i) $1 - x$, y, $\frac{1}{2} - z$] ring [which comprise the (*IB*) molecule] is 64.6 (1)°. These values may be compared with the values 71.3 (1), 83.6 (1) and 84.9 (1)° found for the *A* and *B* molecules in the 'parent' compound, diphenic acid, and for the isomeric 6,6'-dimethylbiphenyl-2,2'-dicarboxylic acid, respectively (Fronczek *et al.*, 1987; Gerkin, 1998). The dihedral angles between the planes of the three independent benzene rings in (I) and the planes of their attached carboxyl groups are 0.7 (3) and 23.3 (2)° for (*IA*) and 18.4 (2)° (twice) for (*IB*). These values are neither closely similar to, nor radically different from, the corresponding values for the three comparison molecules cited above. The inter-ring torsion angles, C2—C1—C7—C8 and C18—C17—C17^i—C18^i, are −73.1 (3) and −71.8 (4)°, respectively. Thus, molecules (*IA*) and (*IB*), like the 6,6'-isomeric molecule but unlike

the two 'parent' compound molecules (*A* and *B*), have the *syn* conformation, which is the more common for 2,2'-substituted biphenyls.

In addition to illustrating the trimeric molecular arrangement, Fig. 2 makes obvious a second feature of this structure, namely, the orientation of the long axes of all the molecules near the *a* direction of the unit cell.

Distances and angles of special interest in molecules (*IA*) and (*IB*) are given in Table 1. All distances and angles apparently fall within normal ranges. It is of interest to note that the pairs of plane angles made by the ring-to-ring bonds and the bonds adjacent to them which terminate at the carboxyl-substituted C atoms (C7—C1—C2 and analogs) are substantially larger than the remaining pairs (which terminate at H-carrying C atoms) (C7—C1—C6 and analogs), and that the agreement between these values for the present molecules and for the diphenic acid molecules is quite good: the average values here are 126.8 (6) *versus* 115.6 (6)°, while for diphenic acid they are 124.8 (1) *versus* 116.7 (1)°. Consistent with a steric origin for this difference, the respective values for the 6,6'-dimethyl isomer (in which the H-carrying C atoms are replaced by CH_3-substituted C atoms) show a smaller difference: 122.8 (3) *versus* 118.3 (7)°. The closest intermolecular approaches in this structure, excluding pairs of atoms in groups hydrogen-bonded to each other, occur between O5 and H24C^{ii} [symmetry code: (ii) $\frac{3}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$] and are 0.14 Å less than the corresponding Bondi (1964) van der Waals radius sum.

Experimental

4,4'-Dimethylbiphenyl-2,2'-dicarboxylic acid, whose synthesis is described by Newman & Lilje (1979), was obtained from a crystalline sample in Dr M. S. Newman's chemical collection as a colorless rod. This was cut to provide the experimental sample.

Crystal data

$C_{16}H_{14}O_4$	Mo $K\alpha$ radiation
$M_r = 270.28$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$C2/c$	reflections
$a = 18.955 (2)$ Å	$\theta = 13.4–17.2°$
$b = 12.143 (1)$ Å	$\mu = 0.086$ mm^{-1}
$c = 18.773 (2)$ Å	$T = 296$ K
$\beta = 103.739 (6)°$	Cut rod
$V = 4197.3 (6)$ Å^3	$0.42 \times 0.38 \times 0.31$ mm
$Z = 12$	Colorless
$D_x = 1.283$ Mg m^{-3}	
D_m not measured	

Data collection

AFC-5S diffractometer	$h = 0 \rightarrow 24$
ω scans	$k = 0 \rightarrow 15$
Absorption correction: none	$l = -24 \rightarrow 23$

5234 measured reflections
4852 independent reflections
2841 reflections with
$I > 2.0\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 27.56°$

6 standard reflections
every 150 reflections
intensity variation $\pm3.6\%$
(average maximum
relative intensity)

Refinement

Refinement on F^2
$R(F) = 0.057$
$wR(F^2) = 0.094$
$S = 1.79$
4850 reflections
283 parameters
H atoms treated by a
mixture of independent
and constrained refinement

$w = 1/\sigma^2(F^2)$
$(\Delta/\sigma)_{max} = <0.01$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}
Extinction correction: none
Scattering factors from
Stewart *et al.* (1965) for
H and Creagh & McAuley
(1992) for C, O

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

O1—C13	1.270 (2)	O5—C23	1.284 (2)
O2—C13	1.232 (2)	O6—C23	1.241 (2)
O3—C15	1.308 (2)	C1—C7	1.498 (3)
O4—C15	1.233 (2)	C17—C17^i	1.498 (3)
C1—C2—C13	123.4 (2)	O3—C15—C8	115.1 (2)
C3—C2—C13	116.9 (2)	O4—C15—C8	122.6 (2)
C7—C8—C15	121.2 (2)	C17—C18—C23	121.7 (2)
C9—C8—C15	118.4 (2)	C19—C18—C23	118.5 (2)
O1—C13—O2	121.2 (2)	O5—C23—O6	122.2 (2)
O1—C13—C2	115.2 (2)	O5—C23—C18	117.2 (2)
O2—C13—C2	123.5 (2)	O6—C23—C18	120.6 (2)
O3—C15—O4	122.3 (2)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H2$\cdots$O6	1.13 (3)	1.45 (3)	2.584 (2)	173 (3)
O3—H8$\cdots$O4^i	1.08 (3)	1.57 (3)	2.647 (2)	172 (3)
O5—H18$\cdots$O2	1.12 (4)	1.61 (4)	2.722 (2)	173 (3)

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

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

	a	b	c
a	$D_2^2(12)$	$R_3^3(27)[R_2^2(8)]$	$D_2^2(14)[R_2^2(8)]$
b		$R_2^2(8)$	$R_3^3(27)[R_2^2(8)]$
c			$D_2^2(12)$

Scan widths were $(1.50 + 0.35\tan\theta)°$ in ω, 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 $C2/c$ (No. 15); since refinement proceeded well it was adopted. Fourier difference methods were used to locate initial H-atom positions, and the H atoms were then refined isotropically. Refined C—H distances ranged from 0.92 (3) to 1.01 (3) Å, with a mean value of 0.97 (3) Å. Subsequently, all H atoms except carboxylic-H atoms were made canonical with C—H = 0.98 Å and $U_{iso} = 1.2U_{eq}$ of the attached C atom. Refined O—H distances are given in Table 2.

The extinction coefficient was predicted to be negative in late stages of refinement and was thus not included in the model. However, two intense low-angle reflections (200 and 020), whose intensities were very substantially lower than the calculated values in late stages of refinement, were excluded from the final fit. The maximum positive residual peak is located ~1.1 Å from O1; the maximum negative peak is located ~0.3 Å from O1.

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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