

## ORGANIC COMPOUNDS

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## Hydrogen bonding in 4,4',6,6'-tetramethylbiphenyl-2,2'-dicarboxylic acid

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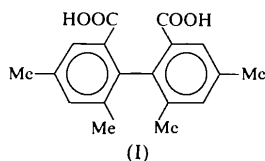
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### Abstract

The title compound, C<sub>18</sub>H<sub>18</sub>O<sub>4</sub>, crystallizes in the centrosymmetric space group  $P2_1/c$ , with two molecules in the asymmetric unit. Each of the four independent carboxylic H atoms is ordered, and each participates in hydrogen bonding. The O<sub>D</sub>...O<sub>A</sub> distances in the hydrogen bonds are 2.598 (3), 2.608 (3), 2.652 (3) and 2.641 (3) Å. Two cyclic hydrogen-bonded dimers are found, neither occurring about a center of symmetry; each, however, occurs about a pseudo-center. Numerous hydrogen-bonded chains, all propagating along [010], are also present. The biphenyl twist angles are 88.4 (2) and 87.5 (2)°. Structural comparisons are made with the structures of the 'parent' compound, diphenic acid, and its 4,4'- and 6,6'-dimethyl derivatives.

### Comment

This report on 4,4',6,6'-tetramethylbiphenyl-2,2'-dicarboxylic acid, (I), is one of a series on hydrogen bonding in biphenyl carboxylic acids, and follows reports on the 6,6'- and 4,4'-dimethylbiphenyl-2,2'-dicarboxylic acids (Gerkin, 1998*a,b*). The title acid crystallizes in



the centrosymmetric space group  $P2_1/c$ , with two molecules, (IA) and (IB), in the asymmetric unit. The refined asymmetric unit is shown in Fig. 1, together with the numbering scheme. Each of the four carboxylic H atoms is ordered and each participates in a unique hydrogen bond. Geometric details of the four hydrogen bonds are given in Table 2. The results of hydrogen-bond graph-set analysis (Bernstein *et al.*, 1995) are given in Table 3

for the first- and basic second-level graph sets. Among the second-level graphs, the two  $R_2^2(8)$  patterns, cyclic hydrogen-bonded dimers (neither, of course, disposed about a center of symmetry), are the most apparent in the packing diagram, Fig. 2. The dimers do occur, however, about pseudo-centers. Thus, for example, the point [0.246 (6), 0.002 (14), 0.132 (7)] is a pseudo-center for all the non-H atoms of an *A* and *B* molecule. The greatest distance of the midpoint between corresponding *A* and *B* atoms from this pseudo-center is 0.44 Å; the average value is 0.2 (1) Å. The remaining second-level graphs are chains, all with descriptor  $C_2^2(18)$  and all propagating in the [010] direction. To clarify the chaining in this structure, consider first the chain involving hydrogen bonds *a* and *b* (Table 2) which includes the home-base *A* molecule: this *A* molecule (of space group symmetry type 1) is preceded, and followed, in the *ab* chain by *B* molecules of symmetry type 2, which in turn are preceded and followed by *A* molecules of symmetry type 1, and so on. This can accordingly be designated as an *A1–B2* chain. Moreover, the identical *A* and *B* molecules are also connected by the other three sets of chains given in Table 3, namely, *ad*, *bc* and *cd*. Thus, there are four distinguishable *A1–B2* chains involving the home-base *A* molecule. Similarly, there are *A2–B1*, *A3–B4* and *A4–B3* types of chains, yielding a grand total of 16 distinguishable chains. There are no hydrogen-bond connections among chains of types *A1–B2*, *A2–B1*, *A3–B4* and *A4–B3*. There are three C—H...O interactions for which the H...O distance is less than the corresponding Bondi (1964) van der Waals radius sum. Their geometric parameters are given in Table 2. These interactions partially crosslink chains of the four types just delineated: the only types of chains not directly linked *via* the tabulated C—H...O interactions are *A1–B2* and *A4–B3*, and *A2–B1* and *A3–B4*.

In this structure, the benzene rings are very nearly planar: the maximum deviation of any of the ring *C* atoms from the best-fit planes describing them is 0.012 (4) Å, while the average deviation is 0.005 (4) Å. The intramolecular dihedral angle between the benzene ring planes (the biphenyl twist angle) is 88.4 (2)° for the *A* molecule and 87.5 (2)° for the *B* molecule. Since, further, the dihedral angle between the two sets of non-parallel C1–C6 ring planes is 75.4 (1)° for the *A* molecules and 71.0 (1)° for the *B* molecules, all the benzene ring planes are either parallel or roughly perpendicular to one another. This structural feature is apparent in Fig. 2. The dihedral angles between the carboxyl group planes and the associated ring planes are 16.9 (4) and 13.9 (4)° for the *A* molecule, and 14.1 (4) and 14.2 (4)° for the *B* molecule. Thus, the carboxyl groups are roughly coplanar with the rings to which they are attached, a feature that is also apparent in Fig. 2.

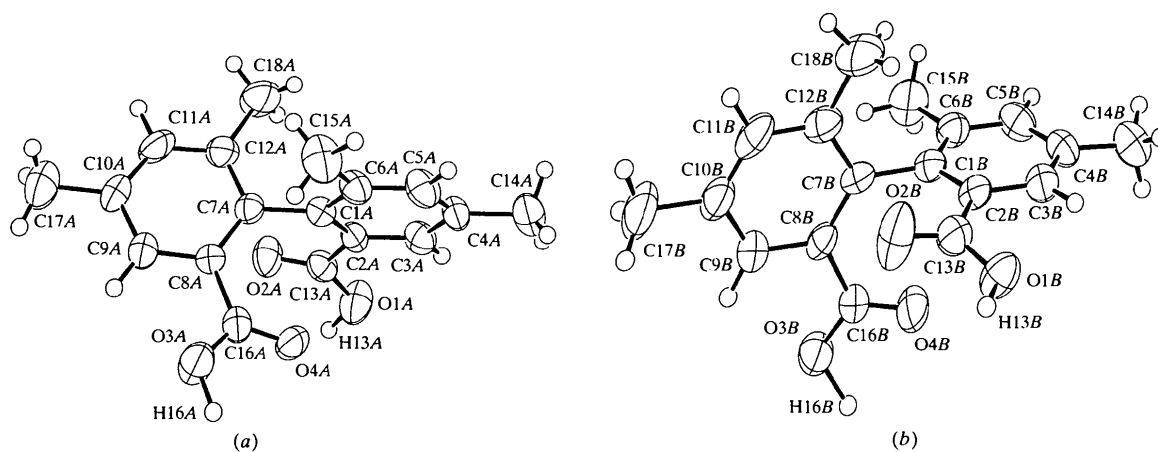


Fig. 1. ORTEPII (Johnson, 1976) drawing of the title acid showing (a) molecule *A* and (b) molecule *B*, with the atom-numbering scheme. Displacement ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small.

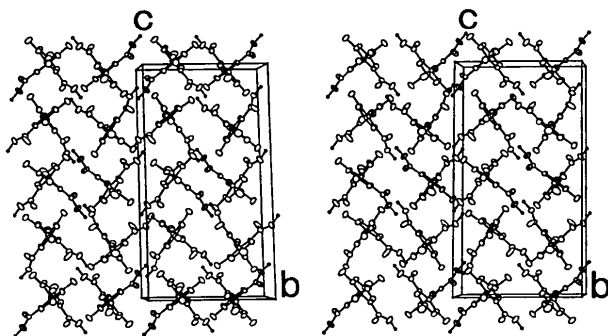


Fig. 2. ORTEPII (Johnson, 1976) packing diagram of (I) viewed down the *a* axis. H atoms have been omitted for clarity, except for carboxylic H atoms. Displacement ellipsoids are drawn at 20% probability for all atoms except H, for which they have been set artificially small. Atoms O1A and O2A are depicted with principal (as well as enveloping) ellipsoids, for ease of distinguishing *A* and *B* molecules.

Structural comparisons of particular interest involve the structures of the 'parent' acid, diphenic acid (Fronczek *et al.*, 1987), and of 4,4'- and 6,6'-dimethylbiphenyl-2,2'-dicarboxylic acid (Gerkin, 1998*a,b*). As anticipated on a steric basis, the twist angles of (IA) and (IB) are in closest agreement with that of the 6,6'-dimethyl analog [84.9(1)°], which also has four substituents on the C atoms *ortho* to the phenyl-phenyl bond. With respect to the dihedral angles between the planes of the carboxyl groups and the planes of the rings to which they are attached, (IA) and (IB) are less similar to the 6,6'- analog than to either the 4,4'- analog or diphenic acid itself; indeed, however, (IA) and (IB) are most similar to each other. The inter-ring torsion angles C2—C1—C7—C8 are 95.5(5) and -87.1(5)° for (IA) and (IB), respectively. Thus, as do the diphenic acid *A* and *B* molecules, (IA) has the unusual *anti* conforma-

tion, while (IB), as do the 4,4'- and 6,6'- analogs, has the *syn* conformation, which is the more common for 2,2'-substituted biphenyls (Fronczek *et al.*, 1987). With respect to  $O_D \cdots O_A$  distances in this group of molecules, both the largest value [2.811(1) Å] and the smallest [2.553(1) Å] are observed for the diphenic acid *B* molecule, the remaining 11 values lying between 2.722(2) and 2.584(2) Å.

Comparing further aspects of the structures of diphenic acid, the 6,6'-dimethyl analog, the 4,4'-dimethyl analog and (I), we note that  $Z' = 2, 1, 1.5$  and 2, respectively. In all these structures, eight-membered cyclic hydrogen-bonded dimers are formed, but only in the 6,6'-dimethyl analog do the dimers occur about centers.

Distances and angles of special interest are given in Table 1; all distances and angles fall within normal ranges. The closest intermolecular approaches in this structure, excluding pairs of atoms in carboxyl groups hydrogen bonded to each other, occur between C15A and H11B<sup>v</sup> [symmetry code: (v) = 1 - *x*, 1 - *y*, -*z*], and between O3B and H15A2<sup>vi</sup> [symmetry code: (vi) 1 + *x*,  $\frac{3}{2} - y$ ,  $\frac{1}{2} + z$ ], and are 0.06 Å less than the sums of the corresponding Bondi (1964) van der Waals radii.

Biphenyl twist angles in molecules with four H atoms bonded to the C atoms *ortho* to the phenyl-phenyl bond are discussed by Brock & Minton (1989), who report that the distribution of twist angles for such molecules has its maximum at approximately 37°, with a subsidiary maximum near 0°.

## Experimental

4,4',6,6'-Tetramethylbiphenyl-2,2'-dicarboxylic acid was obtained as a large colorless crystal from a sample in the chemical collection of Dr M. S. Newman. This crystal was cut to

provide the experimental sample. A synthesis is described by Karnes *et al.* (1965).

#### Crystal data

$C_{18}H_{18}O_4$   
 $M_r = 298.34$   
 Monoclinic  
 $P2_1/c$   
 $a = 13.658 (1) \text{ \AA}$   
 $b = 11.388 (1) \text{ \AA}$   
 $c = 22.178 (2) \text{ \AA}$   
 $\beta = 106.951 (8)^\circ$   
 $V = 3299.5 (6) \text{ \AA}^3$   
 $Z = 8$   
 $D_x = 1.201 \text{ Mg m}^{-3}$   
 $D_m$  not measured

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 25 reflections  
 $\theta = 13.1\text{--}15.7^\circ$   
 $\mu = 0.079 \text{ mm}^{-1}$   
 $T = 296 \text{ K}$   
 Cut column  
 $0.38 \times 0.27 \times 0.15 \text{ mm}$   
 Colorless

#### Data collection

Rigaku AFC-5S diffractometer  
 $\omega$  scans  
 Absorption correction: none  
 8334 measured reflections  
 7620 independent reflections  
 2417 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$   
 $\theta_{\text{max}} = 27.56^\circ$   
 $h = 0 \rightarrow 17$   
 $k = 0 \rightarrow 14$   
 $l = -28 \rightarrow 27$   
 6 standard reflections every 150 reflections  
 intensity decay: 5.5%

#### Refinement

Refinement on  $F^2$   
 $R(F) = 0.074$   
 $wR(F^2) = 0.097$   
 $S = 1.21$   
 7620 reflections  
 414 parameters  
 H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma(F^2)]^2$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.69 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.73 \text{ e \AA}^{-3}$   
 Extinction correction: Zachariasen (1963, 1968)  
 Extinction coefficient:  $3.8 (1) \times 10^{-7}$   
 Scattering factors from Stewart *et al.* (1965) (H) and Creagh & McAuley (1992) (C, O)

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

O1A—C13A	1.306 (4)	O1B—C13B	1.294 (4)
O2A—C13A	1.234 (4)	O2B—C13B	1.231 (4)
O3A—C16A	1.299 (4)	O3B—C16B	1.295 (4)
O4A—C16A	1.228 (4)	O4B—C16B	1.217 (4)
O1A—C13A—O2A	122.7 (3)	O1B—C13B—O2B	121.5 (4)
O1A—C13A—C2A	114.8 (3)	O1B—C13B—C2B	116.7 (4)
O2A—C13A—C2A	122.5 (4)	O2B—C13B—C2B	121.8 (4)
O3A—C16A—O4A	122.0 (4)	O3B—C16B—O4B	120.7 (4)
O3A—C16A—C8A	115.1 (3)	O3B—C16B—C8B	116.5 (3)
O4A—C16A—C8A	122.9 (4)	O4B—C16B—C8B	122.8 (4)

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

D—H...A	D—H	H...A	D...A	D—H...A
O1A—H13A...O2B <sup>i</sup>	1.17 (5)	1.43 (5)	2.598 (3)	175 (4)
O3A—H16A...O4B <sup>ii</sup>	1.03 (5)	1.58 (5)	2.608 (3)	172 (4)
O1B—H13B...O2A <sup>ii</sup>	1.12 (5)	1.54 (5)	2.652 (3)	172 (4)
O3B—H16B...O4A <sup>i</sup>	1.25 (5)	1.40 (5)	2.641 (3)	172 (4)
C14A—H14A3...O1B <sup>iii</sup>	0.98	2.66	3.592 (4)	159
C15A—H15A2...O3B <sup>iii</sup>	0.98	2.64	3.532 (4)	151
C17B—H17B3...O1A <sup>iv</sup>	0.98	2.66	3.599 (5)	160

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

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

	a	b	c	d
a	D	$C_2^2(18)$	$R_2^2(8)$	$C_2^2(18)$
b		D	$C_2^2(18)$	$R_2^2(8)$
c			D	$C_2^2(18)$
d				D

Scan widths were  $(1.50 + 0.35\tan\theta)^\circ$  in  $\omega$ , with a background/scan time-ratio of 0.5. The data were corrected for Lorentz and polarization effects. 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. We note that the data set is rather weak, but the reason is unknown. Difference Fourier methods were used to locate initial H-atom positions, which were then refined isotropically. H atoms bonded to C atoms were then made canonical, with C—H = 0.98  $\text{\AA}$  and  $U_{\text{iso}} = 1.2U_{\text{eq}}$  of the attached C atom. At least two H atoms of each methyl group were refined before the methyl group H atoms were made canonical. The refined O—H distances are given in Table 2. Since some of these distances substantially exceed 0.98  $\text{\AA}$ , hydrogen-bond angles were recalculated with H atoms fixed at 0.98  $\text{\AA}$  from the donors along the D—H direction determined in the final least-squares fit; however, the largest change in angle this produced is  $1^\circ$ , considerably less than the s.u. of the best-fit value. Accordingly, the refined H positions were used throughout Table 2 for O—H...O angles. It is noteworthy that the top peaks in the final difference map do not occur in positions which could be considered as possible alternative locations for the carboxylic H atoms; thus, these H atoms are regarded as definitely ordered, although the O—H distances are greater than 0.98  $\text{\AA}$ . This interpretation is further supported by the observed C—O distances. The maximum effect of extinction is 10.6% of  $F_o$  for 10 $\bar{2}$ . The maximum positive residual peak is located  $\sim 2.1 \text{ \AA}$  from C14B; the maximum negative peak is located  $\sim 2.1 \text{ \AA}$  from C15A.

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).

We acknowledge with pleasure our use of the departmental X-ray crystallographic facility, which is supervised by staff crystallographer Dr J. C. Gallucci. The diffractometer system was purchased with funds provided in part by an NIH grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1167). Services for accessing these data are described at the back of the journal.

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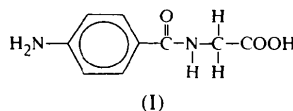
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[*Z. Kristallogr.* (1993), **207**, 53–58] and with the structure of the parent molecule, hippuric acid.

### Comment

This study of 4-aminohippuric acid, (I), is one of a series on hydrogen bonding in amino-substituted cyclic carboxylic acids which includes 4-aminoquinoline-2-carboxylic acid monohydrate (Burd *et al.*, 1997), and 3-aminopyrazine-2-carboxylic acid, 2-aminonicotinic acid and 3-aminopyrazole-4-carboxylic acid (Dobson & Gerkin, 1996, 1997, 1998). Although a structure of (I) has been reported by Chakrabarti & Dattagupta (1993) (hereafter, CD), the H atoms were not refined and the s.u.'s of most metrical parameters appeared large, although no specific experimental difficulties were cited. The present interest is, *via* a structure redetermination, to determine and describe the hydrogen bonding more precisely and more fully than did the previous study.



The title acid crystallized in the non-centrosymmetric space group  $P2_12_12_1$  with one molecule in the asymmetric unit, in agreement with CD; the cell edges are in moderate agreement with CD, the greatest difference being 0.06 Å in the *b* edge (present indexing). The refined molecule and the numbering scheme are shown in Fig. 1. In this molecule, there are three potential hydrogen-bond donors (O1, N1 and N2) with four potential hydrogen-bonding H atoms (H1, H1N1, H1N2 and H2N2), and five potential hydrogen-bond acceptors (O1, O2, O3, N1 and N2). Four hydrogen bonds in fact occur (in agreement with CD); these involve all the potential donors and their H atoms, but only the three O atoms of the five potential acceptors just cited. The H atoms in these bonds are ordered, and proton transfer from the carboxyl group to the amino group does not occur in this structure. Hydrogen-bond geometrical parameters are given in Table 2. Overall, the angular geometries in particular are not in good agreement with those reported by CD: in the order given in Table 2, these angles are 164 (2) *versus* 142, 173 (2) *versus* 170, 163 (2) *versus* 130, and 167 (2) *versus* 154°, respectively; moreover, in each case, the angle found in the present study is larger. The results of hydrogen-bond graph-set analysis (Bernstein *et al.*, 1995) for the first- and basic second-level graphs for these four bonds (labelled *a–d*, for this purpose, in the same order as Table 2) are given in Table 3. Cyclic hydrogen-bonded dimers are not formed; through second-level graphs, only chain patterns occur. In the order of their occurrence in Table 3, these chains propagate along **a**, **b**, **a, b**, **c**, **c, b**, **a** and **a**, and gen-

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## Hydrogen bonding in 4-aminohippuric acid

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### Abstract

The title acid, C<sub>9</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>, crystallized in the non-centrosymmetric space group  $P2_12_12_1$  with one molecule in the asymmetric unit. Four hydrogen bonds occur whose donor–acceptor distances are: O1···O3 2.630 (2), N1···O3 3.090 (2), N2···O1 3.099 (2), and N2···O2 3.022 (2) Å, and whose angles fall in the range 163 (2)–173 (2)°. The H atoms in these bonds are ordered. Cyclic hydrogen-bonded dimers are not formed; through second-level graphs, only hydrogen-bonded chains occur. These form a strongly three-dimensional array of hydrogen bonds. The dihedral angle between the core plane and the carboxyl plane is 54.8 (2)°, and between the core plane and the plane of the amino group, 34 (1)°. The structure is compared with a previous determination by Chakrabarti & Dattagupta