

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1498). Services for accessing these data are described at the back of the journal.

References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Blackburn, A. C., Dobson, A. J. & Gerkin, R. E. (1996). *Acta Cryst.* **C52**, 409–411.
- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Burd, C. J., Dobson, A. J. & Gerkin, R. E. (1997). *Acta Cryst.* **C53**, 602–605.
- Creagh, D. C. & McAuley, W. J. (1992). *International Tables for Crystallography*, Vol. C, pp. 219–222. Kluwer Academic Publishers, Dordrecht.
- Dobson, A. J. & Gerkin, R. E. (1996). *Acta Cryst.* **C52**, 1512–1514.
- Dobson, A. J. & Gerkin, R. E. (1997). *Acta Cryst.* **C53**, 1427–1429.
- Dobson, A. J. & Gerkin, R. E. (1998). *Acta Cryst.* **C54**, 253–256.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7–2. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.
- Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.
- Zachariasen, W. H. (1968). *Acta Cryst.* **A24**, 212–216.

Acta Cryst. (1998). **C54**, 1885–1887

1-(*o*-Tolylmethyl)naphthalene-2-carboxylic Acid

ROGER E. GERKIN

Department of Chemistry, The Ohio State University,
Columbus, Ohio 43210, USA. E-mail: gerkin@chemistry.
ohio-state.edu

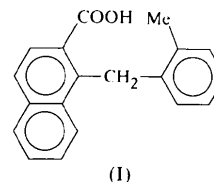
(Received 20 March 1998; accepted 7 July 1998)

Abstract

The title acid, C₁₉H₁₆O₂, crystallized in space group *P*1̄. In this structure, a hydrogen bond of the 'cyclic dimer' type is formed about a center of symmetry. The O_{donor}...O_{acceptor} distance is 2.647 (1) Å. The carboxylic H and O atoms are ordered. The dihedral angle between the best-fit naphthalene plane and the carboxylic acid group plane is 11.1 (2)°.

Comment

This study is one of a continuing series on hydrogen bonding in carboxylic acids. 1-(*o*-Tolylmethyl)naphthalene-2-carboxylic acid, (1), crystallized in space group *P*1̄. The refined molecule is shown in Fig. 1, which also presents the numbering scheme. The single type of hydrogen bond forms a cyclic dimer about a center of symmetry, as shown in Fig. 2. Geometric details of the hydrogen bond are given in Table 1. The first-level graph-set descriptor (Bernstein *et al.*, 1995) is R₂²(8) and there are no higher-level graph sets.



The ten C atoms of the naphthalene core and the six C atoms of the benzene ring lie very nearly in planes, the maximum deviations of an atom from the best-fit planes through them being 0.016 (1) and 0.003 (1) Å, respectively, while the average deviations are 0.010 (4) and 0.002 (1) Å, respectively. The dihedral angle between the naphthalene plane and the benzene plane is 79.76 (5)°. The dihedral angle between the naphthalene plane and the plane of the carboxy group is 11.1 (2)°; this value may be compared with that of 1.4 (5)° for naphthalene-2-carboxylic acid (Fitzgerald & Gerkin, 1993).

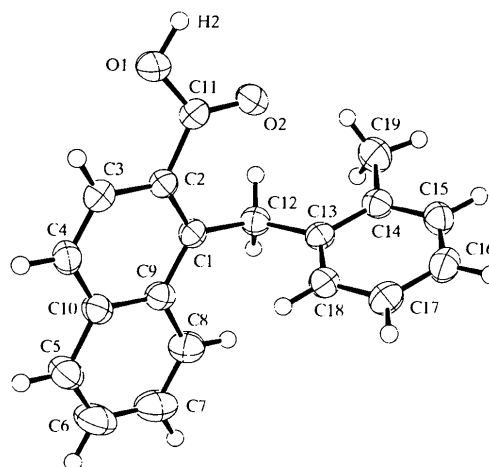


Fig. 1. ORTEPII (Johnson, 1976) diagram of 1-(*o*-tolylmethyl)naphthalene-2-carboxylic acid, showing the molecular numbering scheme. Displacement ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small.

Distances and angles of special interest are given in Table 1. All intramolecular distances and angles fall within normal ranges. Whereas in naphthalene-2-carboxylic acid, the carboxylic H atom is disordered to

a significant degree, both at room temperature and at 153 K (Blackburn *et al.*, 1996), in the title molecule it is ordered. In all three cases, however, the carboxylic O atoms are ordered, the largest principal axes of their displacement ellipsoids being nearly normal to the carboxy group planes.

The packing of the title acid is shown in Fig. 2. An interesting feature of the packing arrangement is that aromatic rings whose planes are parallel do not lie directly over each other; instead, they are in every case separated by some other portion of a molecule or simply offset from each other. Thus, no π - π interaction can occur. The closest intermolecular approaches, excluding pairs of atoms in hydrogen-bonded carboxy groups, are between C17 and H7ⁱⁱ [symmetry code: (ii) $1 + x, y, z$] and are 0.06 Å greater than the corresponding sum of the Bondi (1964) van der Waals radii.

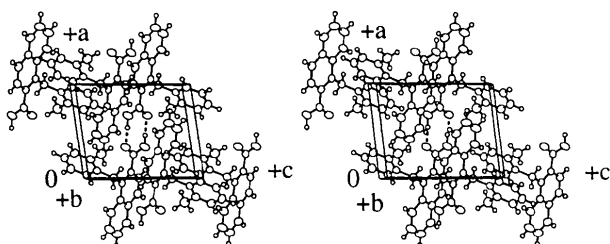


Fig. 2. ORTEP (Johnson, 1976) stereoview of the title acid. Displacement ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small. Hydrogen bonds are shown as dashed lines.

Experimental

1-(*o*-Tolylmethyl)naphthalene-2-carboxylic acid was obtained from the chemical collection of Dr M. S. Newman as a colorless prism. This was cut to provide the experimental sample. While Newman's synthetic scheme is unknown, a synthesis of the closely related compound 1-(phenylmethyl)naphthalene-2-carboxylic acid is given by Smith *et al.* (1981).

Crystal data

C ₁₉ H ₁₆ O ₂	Mo <i>K</i> α radiation
<i>M_r</i> = 276.33	λ = 0.7107 Å
Triclinic	Cell parameters from 25 reflections
<i>P</i> 1	θ = 12.8–17.5°
<i>a</i> = 7.831 (1) Å	μ = 0.078 mm ⁻¹
<i>b</i> = 9.9159 (8) Å	<i>T</i> = 296 K
<i>c</i> = 10.2115 (5) Å	Cut prism
α = 113.128 (7)°	0.38 × 0.23 × 0.23 mm
β = 91.309 (7)°	Colorless
γ = 103.504 (6)°	
<i>V</i> = 703.2 (1) Å ³	
<i>Z</i> = 2	
<i>D_x</i> = 1.305 Mg m ⁻³	
<i>D_m</i> not measured	

Data collection

Rigaku AFC-5S diffractometer
ω/2θ scans
Absorption correction: none
3491 measured reflections
3251 independent reflections
2444 reflections with $I > 2\sigma(I)$
R_{int} = 0.010

θ_{max} = 27.56°
h = 0 → 10
k = -12 → 12
l = -13 → 13
6 standard reflections
every 150 reflections
intensity variation: ±1.5%
(average maximum relative intensity)

Refinement

Refinement on *F*²
R(*F*) = 0.043
wR(*F*²) = 0.056
S = 2.53
3251 reflections
195 parameters
H atoms: see below
w = 1/σ²(*F*²)
(Δ/σ)_{max} < 0.01

Δρ_{max} = 0.26 e Å⁻³
Δρ_{min} = -0.21 e Å⁻³
Extinction correction:
Zachariasen (1963, 1968)
Extinction coefficient:
36 (1) × 10⁻⁷
Scattering factors from
Stewart *et al.* (1965) (H)
and Creagh & McAuley
(1992) (C, O)

Table 1. Selected geometric and hydrogen-bonding parameters (Å, °)

O1—C11	1.320 (1)	O2—C11	1.217 (1)	
O1—C11—O2	121.6 (1)	O2—C11—C2	124.6 (1)	
O1—C11—C2	113.8 (1)			
<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H2...O2 ⁱ	1.00 (2)	1.65 (2)	2.647 (1)	176 (1)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Scan widths were $(1.60 + 0.35\tan\theta)^\circ$ in ω, with a background/scan time ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment indicated space group *P*1 or *P*1̄ (No. 1 or 2). *P*1 was given initial preference and, since refinement proceeded well, it was adopted. Difference Fourier methods were used to locate the initial H-atom positions; the H atoms were then refined isotropically, yielding C—H distances ranging from 0.96 (2) to 1.01 (2) Å. Subsequently, all but the carboxylic H atom were made canonical, with a C—H distance of 0.98 Å and *U*_{iso} = 1.2*U*_{eq} of the associated C atom. The carboxylic H atom, H2, was refined isotropically; the O—H distance is given in Table 1. The maximum effect of extinction was 9.5% of *F*_o for 121̄. The maximum positive residual peak was located approximately midway between C1 and C12; the maximum negative peak was located ~0.6 Å from C19.

Data collection: *MSCI/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCI/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: *ORTEP* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

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

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.

References

- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Blackburn, A. C., Fitzgerald, L. J. & Gerkin, R. E. (1996). *Acta Cryst. C* **52**, 2862–2864.
- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Creagh, D. C. & McAuley, W. J. (1992). *International Tables for X-ray Crystallography*, Vol. C, pp. 219–222. Dordrecht: Kluwer.
- Fitzgerald, L. J. & Gerkin, R. E. (1993). *Acta Cryst. C* **49**, 1952–1958.
- Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7-2. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Sheldrick, G. M. (1985). *SHELXS86*. In *Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, Oxford University Press.
- Smith, J. G., Welankiwar, S. S., Chu, N. G., Lai, E. H. & Sondheimer, S. J. (1981). *J. Org. Chem.* **46**, 4658–4662.
- Spek, A. L. (1990). *Acta Cryst. A* **46**, C-34.
- Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3174–3187.
- Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.
- Zachariasen, W. H. (1968). *Acta Cryst. A* **24**, 212–216.

Acta Cryst. (1998). **C54**, 1887–1889

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

ROGER E. GERKIN

Department of Chemistry, The Ohio State University,
Columbus, Ohio 43210, USA. E-mail: gerkin@chemistry.
ohio-state.edu

(Received 18 May 1998; accepted 14 July 1998)

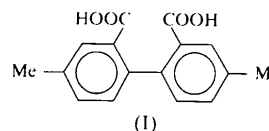
Abstract

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

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)



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

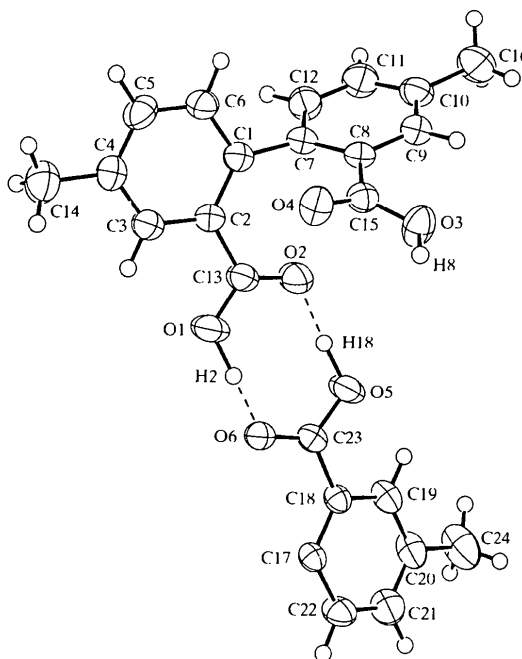


Fig. 1. ORTEP (Johnson, 1976) drawing of the asymmetric unit in the title structure, showing our numbering scheme. Displacement ellipsoids are drawn for 50% probability for non-H atoms; circles of arbitrary small radius depict H atoms. The intra-unit hydrogen bonds are shown by dashed lines.