Corrections for Lorentz and polarization effects were applied, but not for absorption or decay. The structure was solved by Patterson synthesis and Fourier methods, and refined by full-matrix least-squares techniques on F using modified weights.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: modified *SDP* (Frenz, 1988).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PT1027). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Biphenyl-3-carboxylic Acid at 296 and 203 K

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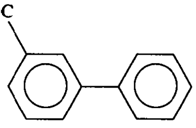
(*Received 4 December 1995; accepted 11 March 1996*)

Abstract

In biphenyl-3-carboxylic acid, $C_{13}H_{10}O_2$, hydrogen bonding is of the cyclic-dimer type about a center of symmetry. The carboxyl H atom is ordered. The dihedral angle between the planar phenyl rings is 31.78 (8)° at 296 K and 31.27 (6)° at 203 K. The data show that the larger-than-average magnitudes of the displacement parameters of the carboxylic O atoms are due to thermal motion rather than static disorder.

Comment

The present study of biphenyl-3-carboxylic acid, (I), is part of a series of studies on hydrogen bonding in carboxylic acids. In this case, the value of the dihedral angle between the phenyl rings is also a matter of interest.



(I)

The hydrogen bonding is of the cyclic-dimer type about a center of symmetry (Fig. 1 and Table 5). The C—O and O—H distances found in the carboxyl group (Table 2) are entirely consistent with an ordered carboxylic H atom.

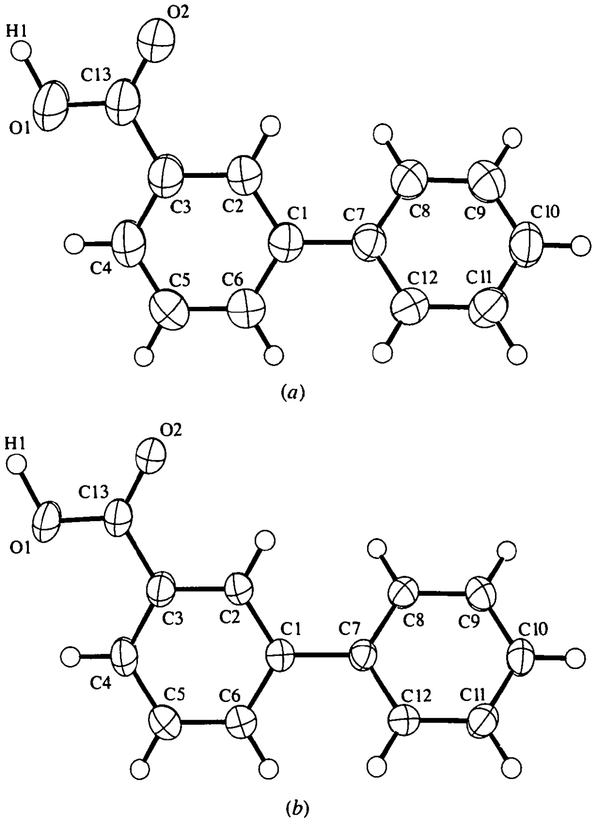


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the biphenyl-3-carboxylic acid molecule (*a*) at 296 and (*b*) at 203 K, showing the atomic numbering schemes. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H atoms for which they have been set artificially small.

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Each of the phenyl rings is closely planar; the atoms of ring C1–C6 deviate by an average of 0.003 Å from the best-fit plane through them [for both the room-temperature structure (RT) and the low-temperature structure (LT)], while the corresponding value for the atoms of ring C7–C12 is 0.005 Å (for both RT and LT). The dihedral angle between these planes is 31.78 (8)° for RT and 31.27 (6)° for LT. These results may be compared with those for another biphenyl monocarboxylic acid, biphenyl-4-carboxylic acid, determined at room temperature. There are three independent molecules in this structure, for which the dihedral angles are 28.7 (2), 35.7 (2) and 32.2 (2)° (Brock, Blackburn & Haller, 1984). They may be further compared with results for a similarly substituted biphenyl, 3-nitrobiphenyl, determined at room temperature. This structure contains two independent molecules and we calculate the dihedral angles to be 26.5 (3) and 25.2 (3)° from the data of Rajnikant, Watkin & Tranter (1995).

The carboxyl group and the phenyl ring to which it is attached are virtually coplanar in (I), the dihedral angles between these planes being 3.1 (3) for RT and 3.2 (2)° for LT. The corresponding angles in biphenyl-4-carboxylic acid are 5.0, 8.6 and 9.1° (Brock, Blackburn & Haller, 1984), and the corresponding angles in 3-nitrobiphenyl between the nitro group plane and the plane of the phenyl ring to which it is attached we calculate as 7.4 (4) and 3.7 (7)° from the data of Rajnikant, Watkin & Tranter (1995).

Owing to the somewhat larger-than-average magnitudes of the displacement parameters of the carboxyl O atoms in RT, the possibility of disorder was considered. LT was then determined in an attempt to resolve this question. If it is assumed that both temperatures are sufficiently high for the crystals to be in the high-temperature limit for thermal displacement, the ratio of B_{eq} values should be equal to the ratio of the absolute temperatures, 203/296 = 0.686 (see, for example, Dunitz, Schomaker & Trueblood, 1988). The ratios of B_{eq}(LT) to B_{eq}(RT) were evaluated for atoms O1 and O2, and also, for comparison, for atoms C4 and C13. These ratios are 0.685, 0.706, 0.672 and 0.688, respectively. The combined RT and LT data thus support the interpretation that the O atoms behave in a similar manner to the C atoms and that the O atoms are subject to large thermal motions rather than to static disorder.

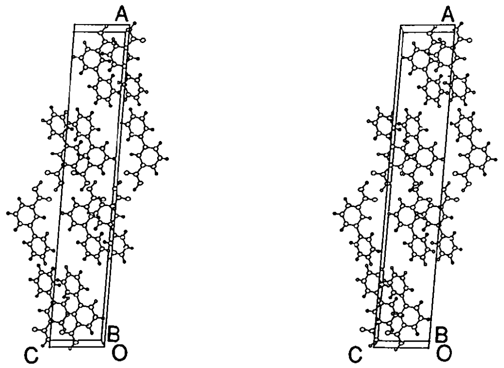

Fig. 2. An *ORTEP*II (Johnson, 1976) packing diagram of biphenyl-3-carboxylic acid at 203 K. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H atoms for which they have been set artificially small.

Excluding atoms involved in hydrogen bonding, the closest intermolecular approaches fall short of the corresponding van der Waals radii (Bondi, 1964) sums by distances between 0.10 and 0.18 Å, and involve atoms O1, O2 and C6 of a given molecule with atoms H4, H5 and H8 of three other molecules.

A potential orthorhombic cell based on vectors 201, 010 and 001 can be dismissed as coincidental since a *c*-axis photo failed conspicuously to manifest mirror symmetry.

Experimental

Biphenyl-3-carboxylic acid was synthesized by standard methods from 3-bromobiphenyl (Aldrich Chemical Company) *via* the Grignard reagent and solid CO_2. The raw product was twice dissolved in aqueous NaOH, treated with Norit-A decolorizing carbon, filtered and acidified with hydrochloric acid to produce crystalline biphenyl-3-carboxylic acid. The final mixture was filtered and the product air dried. The resulting dry acid was dissolved in ethyl acetate. Slow evaporation of the solvent at room temperature produced crystals from which the experimental samples were cut.

(I) at 296 K (RT)

Crystal data

$C_{13}H_{10}O_2$
M_r = 198.22
Monoclinic
*C*2/*c*
a = 41.121 (2) Å
b = 7.039 (2) Å
c = 7.085 (2) Å
β = 94.90 (1)°
V = 2043.2 (9) Å^3
Z = 8
D_x = 1.289 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 15.0–17.3°
μ = 0.081 mm^{-1}
T = 296 K
Cut block
0.42 × 0.31 × 0.27 mm
Colorless

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: none
2566 measured reflections
2531 independent reflections
1340 observed reflections [$I > 3\sigma(I)$]
R_{int} = 0.013

θ_{max} = 27.50°
$h = 0 \rightarrow 53$
$k = 0 \rightarrow 9$
$l = -9 \rightarrow 9$
6 standard reflections monitored every 150 reflections intensity variation: ±2.1% (average maximum)

Refinement

Refinement on F
$R = 0.044$
$wR = 0.056$
$S = 1.98$
1340 reflections
141 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = <0.01$
$\Delta\rho_{\max} = 0.17$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}

Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: $39\,(2) \times 10^{-7}$
Atomic scattering factors from Stewart, Davidson & Simpson (1965) for H atoms and Cromer & Waber (1974) for C and O atoms

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for RT*

$U_{\rm iso}$ for H1; $U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	$U_{\rm iso}/U_{\rm eq}$
O1	0.99092 (4)	0.2659 (4)	−0.0160 (3)	0.1027 (7)
O2	0.95870 (4)	0.2753 (3)	−0.2808 (2)	0.0872 (6)
C1	0.87573 (4)	0.2376 (3)	0.0200 (3)	0.0453 (5)
C2	0.90291 (5)	0.2562 (3)	−0.0819 (3)	0.0509 (6)
C3	0.93437 (5)	0.2541 (3)	0.0093 (3)	0.0542 (6)
C4	0.93888 (5)	0.2355 (4)	0.2039 (3)	0.0639 (7)
C5	0.91198 (6)	0.2180 (4)	0.3072 (3)	0.0662 (8)
C6	0.88102 (5)	0.2181 (3)	0.2154 (3)	0.0557 (6)
C7	0.84209 (4)	0.2399 (3)	−0.0757 (3)	0.0427 (5)
C8	0.83452 (5)	0.3458 (3)	−0.2399 (3)	0.0526 (6)
C9	0.80286 (5)	0.3521 (3)	−0.3233 (3)	0.0580 (7)
C10	0.77847 (5)	0.2519 (3)	−0.2475 (3)	0.0557 (6)
C11	0.78566 (5)	0.1443 (3)	−0.0878 (3)	0.0545 (6)
C12	0.81698 (5)	0.1373 (3)	−0.0031 (3)	0.0496 (6)
C13	0.96267 (5)	0.2666 (4)	−0.1058 (3)	0.0649 (7)
H1	1.0110 (9)	0.278 (5)	−0.103 (5)	0.20 (2)

Table 2. *Selected geometric parameters (Å, °) for RT*

C1—C2	1.388 (3)	C7—C12	1.393 (3)
C1—C6	1.390 (3)	C8—C9	1.383 (3)
C1—C7	1.488 (2)	C9—C10	1.372 (3)
C2—C3	1.396 (3)	C10—C11	1.373 (3)
C3—C4	1.382 (3)	C11—C12	1.375 (3)
C4—C5	1.383 (3)	C3—C13	1.479 (3)
C5—C6	1.379 (3)	C13—O1	1.276 (2)
C7—C8	1.395 (3)	C13—O2	1.238 (2)
C2—C1—C6	117.6 (2)	C7—C8—C9	120.5 (2)
C2—C1—C7	121.4 (2)	C8—C9—C10	120.6 (2)
C6—C1—C7	121.0 (2)	C9—C10—C11	119.5 (2)
C1—C2—C3	120.9 (2)	C10—C11—C12	120.5 (2)
C2—C3—C4	120.2 (2)	C7—C12—C11	121.1 (2)
C3—C4—C5	119.4 (2)	C2—C3—C13	119.1 (2)
C4—C5—C6	119.9 (2)	C4—C3—C13	120.7 (2)
C1—C6—C5	122.0 (2)	C3—C13—O1	116.8 (2)
C1—C7—C8	121.2 (2)	C3—C13—O2	120.8 (2)
C1—C7—C12	121.0 (2)	O1—C13—O2	122.4 (2)
C8—C7—C12	117.7 (2)	C13—O1—H1	115 (2)

(I) at 203 K (LT)

Crystal data

$C_{13}H_{10}O_2$
$M_r = 198.22$
Monoclinic
$C2/c$
$a = 41.065\,(3)$ Å
$b = 6.965\,(3)$ Å
$c = 7.051\,(3)$ Å
$\beta = 94.83\,(2)^\circ$
$V = 2009.5\,(12)$ Å^3
$Z = 8$
$D_x = 1.310$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15.4–17.7^\circ$
$\mu = 0.082$ mm^{-1}
$T = 203$ K
Cut prism
$0.39 \times 0.39 \times 0.34$ mm
Colorless

Data collection

Rigaku AFC-5S diffractometer
ω scans
Absorption correction: none
2535 measured reflections
2500 independent reflections
1513 observed reflections $[I > 3\sigma(I)]$
$R_{\rm int} = 0.013$

$\theta_{\max} = 27.50^\circ$
$h = 0 \rightarrow 53$
$k = 0 \rightarrow 9$
$l = -9 \rightarrow 9$
6 standard reflections monitored every 150 reflections intensity variation: ±2.2% (average maximum)

Refinement

Refinement on F
$R = 0.039$
$wR = 0.049$
$S = 1.79$
1513 reflections
141 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = <0.01$
$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}

Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: $2.2\,(7) \times 10^{-7}$
Atomic scattering factors from Stewart, Davidson & Simpson (1965) for H atoms and Cromer & Waber (1974) for C and O atoms

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for LT*

$U_{\rm iso}$ for H1; $U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	$U_{\rm iso}/U_{\rm eq}$
O1	0.99099 (3)	0.2678 (3)	−0.0143 (2)	0.0731 (5)
O2	0.95872 (3)	0.2790 (2)	−0.2821 (2)	0.0597 (4)
C1	0.87548 (4)	0.2377 (2)	0.0207 (2)	0.0310 (4)
C2	0.90275 (4)	0.2578 (3)	−0.0818 (2)	0.0347 (4)
C3	0.93425 (4)	0.2552 (3)	0.0090 (2)	0.0370 (4)
C4	0.93877 (4)	0.2345 (3)	0.2054 (3)	0.0432 (5)
C5	0.91177 (4)	0.2152 (3)	0.3087 (2)	0.0443 (5)
C6	0.88069 (4)	0.2160 (3)	0.2177 (2)	0.0376 (5)
C7	0.84183 (4)	0.2397 (2)	−0.0754 (2)	0.0293 (4)
C8	0.83419 (4)	0.3477 (3)	−0.2401 (2)	0.0353 (5)
C9	0.80241 (4)	0.3540 (3)	−0.3250 (2)	0.0390 (5)
C10	0.77785 (4)	0.2529 (3)	−0.2480 (2)	0.0371 (4)
C11	0.78518 (4)	0.1427 (3)	−0.0872 (2)	0.0362 (5)
C12	0.81665 (4)	0.1360 (2)	−0.0013 (2)	0.0326 (4)
C13	0.96262 (4)	0.2688 (3)	−0.1057 (3)	0.0447 (5)
H1	1.0117 (7)	0.276 (4)	−0.110 (4)	0.13 (1)

Table 4. *Selected geometric parameters (Å, °) for LT*

C1—C2	1.390 (2)	C7—C12	1.398 (2)
C1—C6	1.396 (2)	C8—C9	1.390 (2)
C1—C7	1.487 (2)	C9—C10	1.378 (2)
C2—C3	1.394 (2)	C10—C11	1.381 (2)
C3—C4	1.389 (2)	C11—C12	1.381 (2)
C4—C5	1.384 (2)	C3—C13	1.476 (2)
C5—C6	1.379 (2)	C13—O1	1.283 (2)
C7—C8	1.397 (2)	C13—O2	1.243 (2)
C2—C1—C6	117.8 (1)	C7—C8—C9	120.8 (1)
C2—C1—C7	121.4 (1)	C8—C9—C10	120.4 (2)
C6—C1—C7	120.9 (1)	C9—C10—C11	119.4 (1)
C1—C2—C3	121.1 (1)	C10—C11—C12	120.7 (2)
C2—C3—C4	120.0 (2)	C7—C12—C11	120.8 (1)
C3—C4—C5	119.3 (1)	C2—C3—C13	119.5 (1)
C4—C5—C6	120.4 (2)	C4—C3—C13	120.5 (1)
C1—C6—C5	121.4 (2)	C3—C13—O1	116.7 (2)
C1—C7—C8	121.2 (1)	C3—C13—O2	120.7 (1)
C1—C7—C12	120.9 (1)	O1—C13—O2	122.6 (2)
C8—C7—C12	117.9 (1)	C13—O1—H1	113 (1)

Table 5. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
RT				
O1—H1···O2^{i}	1.08 (4)	1.55 (4)	2.623 (2)	174 (3)
LT				
O1—H1···O2^{i}	1.13 (3)	1.49 (3)	2.614 (2)	174 (2)

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

Scan widths were $(1.45 + 0.35 \tan\theta)^\circ$ in ω (RT) and $(1.50 + 0.35 \tan\theta)^\circ$ in ω (LT), with background to scan time ratios of 0.5. The data were corrected for Lorentz and polarization effects. For each of the crystals, the Laue group assignment, systematic absences and intensity statistics consistent with centrosymmetry indicated space group *C2/c* and since refinement proceeded well, it was adopted in each case. Fourier difference methods were used to locate the H-atom positions. Full-matrix least-squares refinement was performed. In the later stages of refinement, ring H atoms were made canonical: C—H = 0.98 Å and $U_{iso} = 1.2U_{eq}$ of the attached atom. The carboxyl H atom was refined isotropically. For the crystal of RT, the maximum effect of extinction was 57% of F_o for 020 and for the crystal of LT, it was 7.6% of F_o for 020.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structures: *MITHRIL* (Gilmore, 1983); program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

It is a pleasure to acknowledge the partial support provided to AJD by a National Needs Fellowship. We thank Dr J. C. Gallucci for help of various sorts. The diffractometer was purchased with funds provided in part by an NIH grant.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1218). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 2323–2326

N-Saccharinperacetic Acid Monohydrate and *N*-Saccharinpentanoic Acid Monohydrate

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(Received 5 December 1995; accepted 15 March 1996)

Abstract

Hydrogen bonds involving water molecules dominate the crystal structures of *N*-saccharinperacetic acid monohydrate (3-oxo-2*H*-1,2-benzisothiazole-2-peroxyethanoic acid 1,1-dioxide monohydrate, $C_9H_7NO_6S.H_2O$) and *N*-saccharinpentanoic acid monohydrate (3-oxo-2*H*-1,2-benzisothiazole-2-pentanoic acid 1,1-dioxide monohydrate, $C_{12}H_{13}NO_5S.H_2O$). In both structures, molecules are held together by these hydrogen bonds to form two-dimensional blocks. Interdigitation of saccharin groups between adjacent blocks completes the three-dimensional structure.

Comment

As part of a general comparative study of the hydrogen-bond networks formed in organic carboxylic acids and peracids, we have previously reported on the crystal structures of a number of *N*-saccharin acids (Feeder & Jones, 1994*a*) and *N*-saccharin peracids (Feeder & Jones, 1994*b*). We report here the structures of *N*-saccharinperacetic acid monohydrate, (I), and *N*-saccharinpentanoic acid monohydrate, (II). With these structures it has been possible to characterize the structural features relating to the additional hydrogen-bonding provided by the water molecules.

The bond lengths and angles within the saccharin groups are similar to those found for the series of *N*-saccharin acids (Feeder & Jones, 1994*a*) and *N*-saccharin peracids (Feeder & Jones, 1994*b*), as well as