Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: none
7078 measured reflections
2781 independent reflections
2337 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$
$\theta_{\rm max} = 25.88°$
$h = -6 \rightarrow 6$
$k = -15 \rightarrow 16$
$l = -16 \rightarrow 16$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.120$
$S = 1.130$
2781 reflections
217 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2 + 0.1482P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.136$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.117$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.025 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C1—N6	1.330 (2)	C3—N4	1.342 (2)
C1—N2	1.3541 (19)	N4—C5	1.360 (2)
N2—C3	1.343 (2)	C5—N6	1.370 (2)
N6—C1—N2	128.17 (14)	C3—N4—C5	113.71 (13)
C3—N2—C1	111.93 (13)	N4—C5—N6	124.86 (14)
N4—C3—N2	127.82 (14)	C1—N6—C5	113.43 (13)

H atoms were located by difference Fourier synthesis. Whereas the H atoms bonded to nitrogen were refined isotropically, the others were refined with fixed individual displacement parameters [$U(\rm H) = 1.2U_{\rm eq}(\rm C)$] using a riding model with C—H(secondary) = 0.97 Å or C—H(aromatic) = 0.93 Å.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1354). Services for accessing these data are described at the back of the journal.

References

Allen, F. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
Dueholm, K. L., Egholm, M., Behrens, C., Christensen, L., Hansen, H. F., Vulpius, T., Petersen, K. H., Berg, R. H., Nielsen, P. E. & Buchardt, O. (1994). *J. Org. Chem.* **59**, 5767–5773.
Egholm, M., Buchardt, O., Nielsen, P. E. & Berg, R. H. (1992). *J. Am. Chem. Soc.* **114**, 1895–1897.
Nielsen, P. E. (1996). *Perspect. Drug Discov. Des.* **4**, 76–84.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1995). *SMART* and *SAINT. Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sommer, A. (1998). PhD thesis, University of Frankfurt, Germany.

Acta Cryst. (1999). C**55**, 1306–1308

2-(*p*-Toluoyl)benzoic acid

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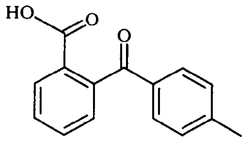
(*Received 22 April 1999; accepted 4 May 1999*)

Abstract

The title compound, $C_{15}H_{12}O_3$, crystallizes as a centrosymmetric dimer hydrogen bonded *via* the carboxylic acid groups. The carboxylic acid group is nearly coplanar with the adjacent aromatic ring, which is almost perpendicular to the tolyl ring. In contrast to all comparable *o*-benzoylbenzoic acid structures retrieved from the Cambridge Structural Database, the torsion angle between the carbonyl group linking both aromatic rings and the phenyl ring carrying the carboxylic acid group is less than 90°, resulting in a shorter distance between the two carbonyl O atoms.

Comment

Substituted 2-benzoylbenzoic acids, such as the title compound, (I), are starting materials for the synthesis of 2,3-dihydrothiazolo[2,3-*a*]isoindol-5(9b*H*)-ones, compounds that inhibit reverse transcriptase of the human immune deficiency virus 1 (HIV-1) (Mertens *et al.*, 1993). The antiviral activity of these compounds depends on the substituent on the phenyl ring. 2-(*p*-Toluoyl)benzoic acid leads to a compound with an IC_{50} value of 0.77 µ*M*. The X-ray structure determination of (I) was carried out in order to elucidate the molecular conformation and the mode of hydrogen bonding.



(I)

The molecule consists of two substituted phenyl rings linked by a carbonyl group. The dihedral angle between the two aromatic rings is 89.86 (8)°. The carboxylic acid group is nearly coplanar with the adjacent aromatic ring, the dihedral angle between the two moieties being 5.2 (4)°. The carbonyl group is almost coplanar with the tolyl ring [O1—C1—C11—C16 16.3 (4)°], but it is nearly perpendicular [O1—C1—C21—C22 80.3 (3)°] to the other aromatic ring. As a result, the two C—C bonds adjacent to the carbonyl group display significantly different lengths, because conjugation of the π-system is possible for the carbonyl group and the tolyl ring, but disrupted for the carbonyl group and the benzoic acid moiety. The orientation of the carboxyl group with respect to the substituent in the *ortho* position is such that the hydroxyl O222 atom is *trans* to the *ortho*-C21 atom of the aromatic ring. Since the absolute value of the C1—C21—C22—C221 torsion angle is less than 90°, the carbonyl O221 atom of the carboxylic acid group is closer to the central carbonyl O1 atom than it is to the pivot C11 atom of the tolyl ring.

Compound (I) crystallizes as pairs of centrosymmetric carboxyl dimers, a motif that is common for benzoic acids (Leiserowitz, 1976). The central carbonyl group is not involved in hydrogen bonding; short contacts (less than 3 Å) from O1 to hydrogen are listed in Table 2.

A search of the Cambridge Structural Database (Allen & Kennard, 1993; Version 5.16 of October 1998) for *o*-benzoylbenzoic acid derivatives yields four comparable structures: 2-benzoylbenzoic acid (Delettre, 1969; Lalancette *et al.*, 1990), 2-(3-bromo-4-chlorobenzoyl)-benzoic acid (Popov *et al.*, 1994), 2-benzoylbenzoic acid monohydrate (Lalancette *et al.*, 1990) and 2-(3-chloro-4-hydroxybenzoyl)benzoic acid (Skrzat, 1980). These molecules display the following features similar to the title compound: (i) in all of them, the bond between the central carbonyl C atom and the benzoic acid aromatic ring is longer than the other C—C single bond; (ii) the carboxyl group shows the same orientation with respect to the *ortho* substituent of the aromatic ring; and (iii) the torsion angle between the central carbonyl group and the phenyl ring not carrying the carboxyl group ranges from 14 to 18°. With regard to the hydrogen-bond pattern of these structures, 2-(3-chloro-4-hydroxybenzoyl)benzoic acid is a special case because it contains a hydroxyl group (involved in hydrogen bonding) in a *para* position with respect to the benzoyl group. Thus, no carboxyl dimers are observed, but the remaining three molecules crystallize as hydrogen-bonded carboxyl dimers. In 2-benzoylbenzoic acid monohydrate, the dimers move apart by an additional 2.45 Å to accommodate insertion of a bridging water molecule. In contrast to the title compound, the bond between the central carbonyl group and the benzoic acid phenyl ring is oriented in a rotational sense that provides a greater separation of the two carbonyl O atoms within the same molecule. The absolute value of the corresponding torsion angle ranges from 103.2° in 2-(3-bromo-4-chlorobenzoyl)benzoic acid to 116.8° in 2-benzoylbenzoic acid monohydrate.

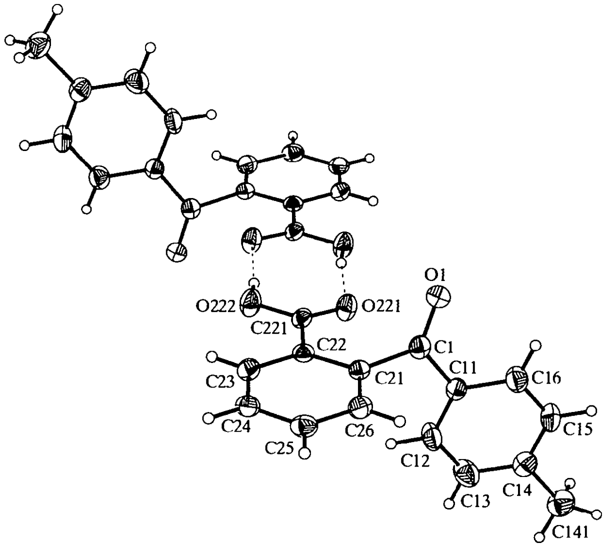


Fig. 1. Perspective view of the title compound as a hydrogen-bonded dimer, with the atom numbering for only one symmetry-independent molecule shown. Displacement ellipsoids are shown at the 50% probability level.

Experimental

A solution of phthalic acid anhydride (12.59 g, 0.085 mol) and toluene (44.12 ml, 0.55 mol) was cooled to 273 K. After addition of $AlCl_3$ (25.32 g, 0.19 mol), the mixture was stirred for 10 min at this temperature and then for 3 h at 363 K. For work-up, the solution was poured into 100 ml water containing 25 g ice. After removing the solvent, the title compound was obtained by hydrodistillation. Single crystals were obtained by slow evaporation from ethyl acetate.

Crystal data

$C_{15}H_{12}O_3$
$M_r = 240.25$
Monoclinic
$P2_1/c$
$a = 11.124\,(2)$ Å
$b = 14.780\,(3)$ Å
$c = 7.129\,(1)$ Å
$\beta = 93.17\,(3)°$
$V = 1170.3\,(4)$ Å^3
$Z = 4$
$D_x = 1.364$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 3050 reflections
$\theta = 1–25°$
$\mu = 0.095$ mm^{-1}
$T = 173\,(2)$ K
Plate
0.30 × 0.18 × 0.10 mm
Colourless

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.972$, $T_{\max} = 0.991$
21 945 measured reflections
2584 independent reflections

1428 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.084$
$\theta_{\max} = 27.10°$
$h = -14 \rightarrow 14$
$k = -18 \rightarrow 18$
$l = -9 \rightarrow 9$
72 standard reflections
frequency: 1200 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.128$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.238$ e Å^{-3}
$\Delta\rho_{\min} = -0.239$ e Å^{-3}

$S = 1.032$
2584 reflections
166 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0422P)^2 + 0.5211P]$ where $P = (F_o^2 + 2F_c^2)/3$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.025 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C1—O1	1.220 (3)	C22—C221	1.493 (3)
C1—C11	1.485 (3)	C221—O221	1.238 (3)
C1—C21	1.525 (3)	C221—O222	1.299 (3)
O1—C1—C11	122.6 (2)	O221—C221—O222	123.9 (2)
O1—C1—C21	118.6 (2)	O221—C221—C22	121.2 (2)
C11—C1—C21	118.5 (2)	O222—C221—C22	114.9 (2)
O1—C1—C11—C12	−164.3 (2)	O1—C1—C21—C22	80.3 (3)
O1—C1—C11—C16	16.3 (4)	C21—C22—C221—O221	5.1 (4)
O1—C1—C21—C26	−94.0 (3)	C23—C22—C221—O222	4.7 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O222—H222···O221^{i}	0.84	1.79	2.628 (2)	172
C141—H14*C*···O1^{ii}	0.98	2.57	3.512 (3)	160
C23—H23···O1^{iii}	0.95	2.64	3.326 (3)	130
C141—H14*A*···O1^{iv}	0.98	2.83	3.712 (3)	150

Symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $2 - x, 1 - y, 2 - z$; (iv) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$.

All H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [$U(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C_{methyl}})$, $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ or $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{O})$] using a riding model with C—H(methyl) = 0.98, C—H(aromatic) = 0.95 or O—H = 0.84 Å. The methyl group attached to the aromatic ring was allowed to rotate about its local threefold axis, and the torsion angle about the C—O bond of the hydroxyl group was also refined.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1357). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
Delettre, J. (1969). *C. R. Acad. Sci. Ser. C*, **269**, 103–104.
Lalancette, R. A., Vanderhoff, P. A. & Thomson, H. W. (1990). *Acta Cryst.* C**46**, 1682–1686.
Leiserowitz, L. (1976). *Acta Cryst.* B**32**, 775–802.
Mertens, A., Zilch, H., König, B., Schäfer, W., Poll, T., Kampe, W., Seidel, H., Leser, U. & Leinert, H. (1993). *J. Med. Chem.* **36**, 2526–2535.
Popov, S. I., Kopylova, T. M., Andrievsky, A. M., Medvedev, S. V. & Yatsenko, A. V. (1994). *Zh. Org. Khim.* **30**, 266–272.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction of Area Detector Data*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1995). *SMART* and *SAINT. Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Skrzat, Z. (1980). *Pol. J. Chem.* **54**, 795–799.

Acta Cryst. (1999). C**55**, 1308–1310

4-Iodopyridine, a structure with very short nitrogen–iodine contacts

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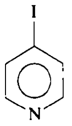
(*Received 22 January 1999; accepted 20 April 1999*)

Abstract

The title compound, C_5H_4IN, crystallizes in the polar space group *Fdd*2 with imposed twofold symmetry (through the N atom and the C—I group). The C—I bond length is 2.100 (5) Å (2.106 Å after libration correction). The molecules are arranged in chains parallel to the polar *z* axis, with very short intermolecular N···I contacts of 2.988 (5) Å.

Comment

We are interested in secondary bonding in halogenopyridines (Jones & Freytag, 1999). We report here the crystal structure of a 4-iodopyridine, (I). As far as we are aware, this is the first reported structure of 4-iodo-substituted pyridine or of any simple (monosubstituted) iodopyridine.



(I)

The title compound crystallizes in the polar space group *Fdd*2 with half a molecule in the asymmetric unit (Fig. 1); atoms I, N and C3 lie on a twofold axis. The bond lengths within the molecule [C—N 1.337 (5), C—C 1.387 Å (mean value)] display no significant differences from those in pyridine [C—N 1.336, C—C 1.379 Å (mean values)] (Mootz & Wussow, 1981). A rigid body libration correction (Schomaker & Trueblood,

Acta Crystallographica Section C
ISSN 0108-2701 © 1999