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2-[(2-Acetoxybenzoyl)oxy]benzoic acid

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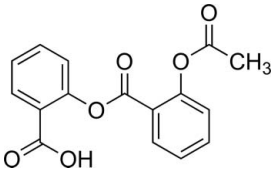
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.002 Å; R factor = 0.033; wR factor = 0.080; data-to-parameter ratio = 11.6.

The title compound, $C_{16}H_{12}O_6$, is a common impurity of *ortho*-acetylsalicylic acid (aspirin). The benzene rings form a dihedral angle of 81.9 (1)° while the acetyl and carboxyl groups form dihedral angles of 74.0 (1) and 26.4 (2)°, respectively, with the benzene rings to which they are bound. In the crystal, molecules are linked by pairs of O—H···O hydrogen bonds between the carboxyl groups, forming inversion dimers.

Related literature

For background literature concerning the crystallization and crystal structure of aspirin, see: Bond *et al.* (2007, 2011). For a discussion of the pharmacological effects of acetylsalicylsalicylic acid, see: Bundgaard (1974). For related structures, see: Greener *et al.* (2000); Cox *et al.* (2000); Iqbal *et al.* (2007).



Experimental

Crystal data

$C_{16}H_{12}O_6$
M_r = 300.26
Monoclinic, $P2_1/c$
a = 9.6314 (5) Å
b = 7.7548 (3) Å
c = 18.0763 (8) Å
β = 95.572 (2)°
V = 1343.73 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 150 K
0.40 × 0.20 × 0.02 mm

Data collection

Bruker Nonius X8 APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.887, T_{max} = 0.998
15807 measured reflections
2367 independent reflections
1868 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.080
S = 1.04
2367 reflections
204 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5···O6^{i}	0.86 (1)	1.81 (1)	2.6660 (16)	176 (2)

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

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

We are grateful to the Danish Natural Science Research Council and the Carlsberg Foundation for provision of the X-ray equipment.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FY2058).

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supplementary materials

Acta Cryst. (2012). E**68**, o2108 [doi:10.1107/S1600536812026475]

2-[(2-Acetoxybenzoyl)oxy]benzoic acid

Katarzyna A. Solanko and Andrew D. Bond

Comment

Acetylsalicylsalicylic acid is a condensation (dehydration) product of acetylsalicylic acid (aspirin) and salicylic acid, and is a common impurity in commerical aspirin samples. Its pharmacological effects have been examined by Bundgaard (1974), and it has been suggested that the compound is a potentially immunogenic substance involved in the development of allergic reactions to aspirin.

Experimental

The compound was prepared by acetylation of salicylsalicylic acid (purchased from Alfa Aesar) using acetic anhydride. 0.02 mol of salicylsalicylic acid was mixed with 0.01 mol of acetic anhydride with addition of 10% NaOH (5 ml) and *ca* 50 ml ice. The reactants were stirred for *ca* 2 h and the reaction was monitored by thin-layer chromotography. When the reaction was complete, the white solid was filtered and recrystallized from ethanol (yield 90%).

Refinement

H atoms bound to C atoms were placed geometrically and allowed to ride during refinement with C—H = 0.95 (aromatic) or 0.98 Å (methyl) and with U_{iso}(H) = 1.2 (aromatic) or 1.5U_{eq}(C) (methyl). The H atom bound to O5 was located in a difference Fourier map and refined with an isotropic displacement parameter, with the O—H distance restrained to 0.85 (1) Å.

Computing details

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT* (Bruker, 2010); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

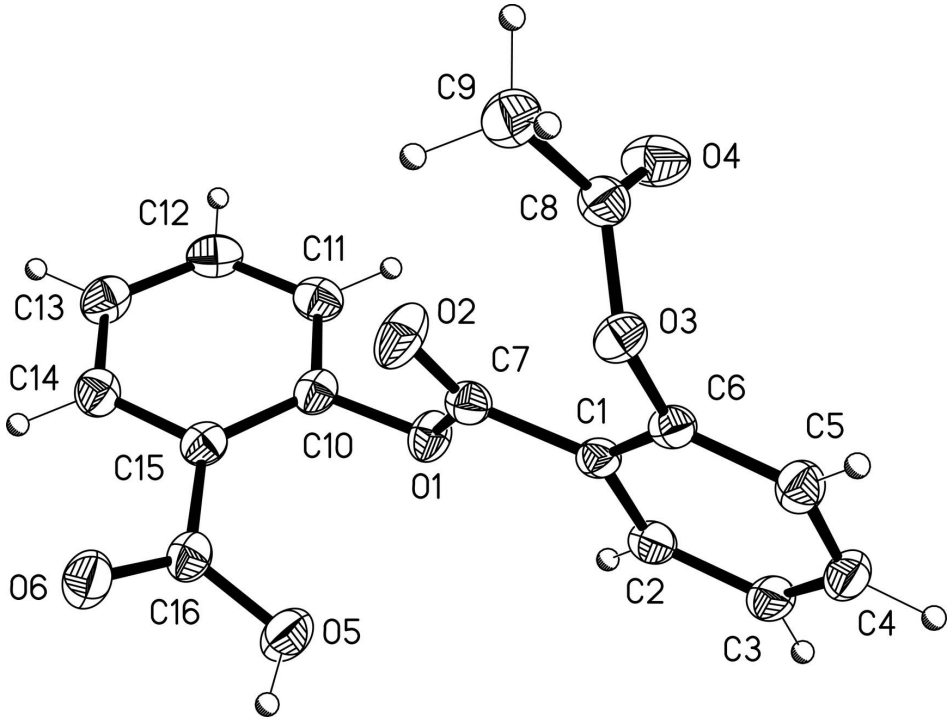

Figure 1

Molecular structure showing displacement ellipsoids at the 50% probability level for non-H atoms.

2-[(2-Acetoxybenzoyl)oxy]benzoic acid

Crystal data

$C_{16}H_{12}O_6$
$M_r = 300.26$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 9.6314\ (5)$ Å
$b = 7.7548\ (3)$ Å
$c = 18.0763\ (8)$ Å
$\beta = 95.572\ (2)°$
$V = 1343.73\ (11)$ Å^3
$Z = 4$
$F(000) = 624$
$D_x = 1.484$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5582 reflections
$\theta = 2.9–25.0°$
$\mu = 0.12$ mm^{-1}
$T = 150$ K
Lath, colourless
0.40 × 0.20 × 0.02 mm

Data collection

Bruker Nonius X8 APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.887$, $T_{max} = 0.998$
15807 measured reflections
2367 independent reflections
1868 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 25.1°$, $\theta_{min} = 3.6°$
$h = -11\rightarrow11$
$k = -9\rightarrow9$
$l = -21\rightarrow20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.080$
$S = 1.04$
2367 reflections
204 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0341P)^2 + 0.473P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.25601 (10)	0.66416 (13)	0.32136 (5)	0.0262 (3)
O2	0.38752 (12)	0.75630 (15)	0.42277 (7)	0.0369 (3)
O3	0.62427 (10)	0.57401 (13)	0.46447 (5)	0.0245 (3)
O4	0.69302 (12)	0.76366 (15)	0.38150 (6)	0.0367 (3)
O5	0.07707 (13)	0.52229 (15)	0.41146 (6)	0.0373 (3)
H5	0.052 (3)	0.451 (3)	0.4443 (11)	0.082 (8)*
O6	0.00116 (13)	0.70903 (14)	0.49167 (6)	0.0351 (3)
C1	0.45005 (15)	0.49405 (19)	0.36384 (8)	0.0212 (3)
C2	0.40413 (16)	0.3714 (2)	0.31037 (8)	0.0249 (4)
H2A	0.3206	0.3914	0.2791	0.030*
C3	0.47842 (16)	0.2217 (2)	0.30243 (9)	0.0281 (4)
H3A	0.4461	0.1398	0.2656	0.034*
C4	0.59942 (17)	0.1906 (2)	0.34767 (9)	0.0296 (4)
H4A	0.6494	0.0863	0.3426	0.036*
C5	0.64823 (16)	0.3111 (2)	0.40048 (8)	0.0263 (4)
H5A	0.7320	0.2903	0.4314	0.032*
C6	0.57436 (15)	0.46175 (19)	0.40792 (8)	0.0213 (3)
C7	0.36674 (15)	0.6510 (2)	0.37434 (8)	0.0232 (4)
C8	0.67024 (15)	0.7322 (2)	0.44426 (9)	0.0266 (4)
C9	0.68674 (17)	0.8504 (2)	0.50933 (9)	0.0331 (4)
H9A	0.7316	0.9574	0.4953	0.050*
H9B	0.7447	0.7949	0.5501	0.050*
H9C	0.5948	0.8768	0.5254	0.050*
C10	0.17065 (15)	0.8088 (2)	0.32687 (8)	0.0236 (4)
C11	0.18395 (16)	0.9407 (2)	0.27723 (9)	0.0283 (4)

H11A	0.2497	0.9319	0.2415	0.034*
C12	0.10136 (16)	1.0862 (2)	0.27940 (9)	0.0305 (4)
H12A	0.1091	1.1765	0.2445	0.037*
C13	0.00762 (16)	1.1002 (2)	0.33224 (9)	0.0303 (4)
H13A	−0.0480	1.2009	0.3343	0.036*
C14	−0.00502 (16)	0.9675 (2)	0.38195 (9)	0.0273 (4)
H14A	−0.0691	0.9784	0.4185	0.033*
C15	0.07431 (15)	0.81807 (19)	0.37966 (8)	0.0234 (3)
C16	0.04899 (16)	0.6788 (2)	0.43270 (9)	0.0258 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0273 (6)	0.0265 (6)	0.0240 (6)	0.0042 (5)	−0.0015 (5)	−0.0055 (5)
O2	0.0365 (7)	0.0319 (7)	0.0394 (7)	0.0092 (5)	−0.0106 (5)	−0.0158 (6)
O3	0.0298 (6)	0.0216 (6)	0.0218 (5)	−0.0006 (5)	0.0007 (4)	−0.0024 (5)
O4	0.0456 (7)	0.0353 (7)	0.0296 (7)	−0.0121 (6)	0.0064 (5)	0.0006 (5)
O5	0.0572 (8)	0.0227 (7)	0.0343 (7)	0.0042 (6)	0.0154 (6)	0.0015 (5)
O6	0.0490 (7)	0.0281 (7)	0.0299 (6)	0.0074 (5)	0.0123 (5)	0.0022 (5)
C1	0.0256 (8)	0.0192 (8)	0.0196 (8)	−0.0030 (6)	0.0066 (6)	0.0000 (6)
C2	0.0259 (8)	0.0258 (9)	0.0235 (8)	−0.0048 (7)	0.0047 (6)	−0.0016 (7)
C3	0.0339 (9)	0.0233 (9)	0.0284 (9)	−0.0048 (7)	0.0097 (7)	−0.0078 (7)
C4	0.0372 (9)	0.0212 (9)	0.0322 (9)	0.0034 (7)	0.0125 (8)	−0.0008 (7)
C5	0.0297 (8)	0.0254 (9)	0.0246 (8)	0.0025 (7)	0.0056 (7)	0.0011 (7)
C6	0.0269 (8)	0.0203 (8)	0.0175 (8)	−0.0032 (6)	0.0062 (6)	−0.0006 (6)
C7	0.0230 (8)	0.0235 (8)	0.0233 (8)	−0.0025 (6)	0.0025 (7)	−0.0007 (7)
C8	0.0227 (8)	0.0262 (9)	0.0303 (9)	−0.0005 (7)	0.0004 (7)	−0.0002 (7)
C9	0.0333 (9)	0.0316 (10)	0.0341 (9)	−0.0021 (7)	0.0019 (7)	−0.0074 (8)
C10	0.0221 (7)	0.0239 (9)	0.0235 (8)	0.0008 (6)	−0.0042 (6)	−0.0055 (7)
C11	0.0274 (8)	0.0316 (10)	0.0253 (8)	−0.0048 (7)	−0.0001 (7)	−0.0007 (7)
C12	0.0326 (9)	0.0275 (9)	0.0299 (9)	−0.0044 (7)	−0.0052 (7)	0.0059 (7)
C13	0.0288 (9)	0.0249 (9)	0.0356 (10)	0.0045 (7)	−0.0044 (7)	0.0019 (8)
C14	0.0232 (8)	0.0287 (9)	0.0293 (8)	0.0022 (7)	−0.0003 (7)	−0.0015 (7)
C15	0.0231 (8)	0.0234 (8)	0.0228 (8)	−0.0009 (6)	−0.0032 (6)	−0.0024 (7)
C16	0.0250 (8)	0.0248 (9)	0.0271 (9)	0.0035 (7)	−0.0002 (7)	−0.0026 (7)

Geometric parameters (Å, º)

O1—C7	1.3662 (18)	C5—C6	1.381 (2)
O1—C10	1.3998 (18)	C5—H5A	0.950
O2—C7	1.1995 (18)	C8—C9	1.488 (2)
O3—C8	1.3659 (19)	C9—H9A	0.980
O3—C6	1.3923 (18)	C9—H9B	0.980
O4—C8	1.2013 (18)	C9—H9C	0.980
O5—C16	1.3090 (19)	C10—C11	1.375 (2)
O5—H5	0.86 (1)	C10—C15	1.396 (2)
O6—C16	1.2242 (18)	C11—C12	1.383 (2)
C1—C6	1.395 (2)	C11—H11A	0.950
C1—C2	1.397 (2)	C12—C13	1.381 (2)
C1—C7	1.480 (2)	C12—H12A	0.950

C2—C3	1.378 (2)	C13—C14	1.379 (2)
C2—H2A	0.950	C13—H13A	0.950
C3—C4	1.378 (2)	C14—C15	1.391 (2)
C3—H3A	0.950	C14—H14A	0.950
C4—C5	1.385 (2)	C15—C16	1.480 (2)
C4—H4A	0.950		

C7—O1—C10	115.71 (11)	C8—C9—H9A	109.5
C8—O3—C6	117.58 (11)	C8—C9—H9B	109.5
C16—O5—H5	108.2 (16)	H9A—C9—H9B	109.5
C6—C1—C2	117.99 (14)	C8—C9—H9C	109.5
C6—C1—C7	121.35 (13)	H9A—C9—H9C	109.5
C2—C1—C7	120.63 (14)	H9B—C9—H9C	109.5
C3—C2—C1	120.84 (15)	C11—C10—C15	121.20 (14)
C3—C2—H2A	119.6	C11—C10—O1	117.20 (13)
C1—C2—H2A	119.6	C15—C10—O1	121.59 (14)
C2—C3—C4	120.23 (15)	C10—C11—C12	119.87 (14)
C2—C3—H3A	119.9	C10—C11—H11A	120.1
C4—C3—H3A	119.9	C12—C11—H11A	120.1
C3—C4—C5	120.08 (14)	C13—C12—C11	120.00 (15)
C3—C4—H4A	120.0	C13—C12—H12A	120.0
C5—C4—H4A	120.0	C11—C12—H12A	120.0
C6—C5—C4	119.63 (15)	C14—C13—C12	119.82 (15)
C6—C5—H5A	120.2	C14—C13—H13A	120.1
C4—C5—H5A	120.2	C12—C13—H13A	120.1
C5—C6—O3	117.13 (13)	C13—C14—C15	121.24 (14)
C5—C6—C1	121.20 (14)	C13—C14—H14A	119.4
O3—C6—C1	121.54 (13)	C15—C14—H14A	119.4
O2—C7—O1	121.63 (14)	C14—C15—C10	117.83 (14)
O2—C7—C1	126.80 (14)	C14—C15—C16	117.59 (13)
O1—C7—C1	111.55 (12)	C10—C15—C16	124.57 (14)
O4—C8—O3	121.91 (14)	O6—C16—O5	122.61 (14)
O4—C8—C9	127.32 (15)	O6—C16—C15	121.59 (14)
O3—C8—C9	110.77 (13)	O5—C16—C15	115.77 (13)

C6—C1—C2—C3	1.1 (2)	C6—O3—C8—O4	−14.2 (2)
C7—C1—C2—C3	−177.36 (13)	C6—O3—C8—C9	166.09 (12)
C1—C2—C3—C4	0.3 (2)	C7—O1—C10—C11	104.36 (15)
C2—C3—C4—C5	−1.2 (2)	C7—O1—C10—C15	−76.66 (17)
C3—C4—C5—C6	0.6 (2)	C15—C10—C11—C12	0.3 (2)
C4—C5—C6—O3	176.69 (13)	O1—C10—C11—C12	179.32 (13)
C4—C5—C6—C1	0.9 (2)	C10—C11—C12—C13	1.2 (2)
C8—O3—C6—C5	115.45 (14)	C11—C12—C13—C14	−1.1 (2)
C8—O3—C6—C1	−68.76 (17)	C12—C13—C14—C15	−0.6 (2)
C2—C1—C6—C5	−1.7 (2)	C13—C14—C15—C10	2.0 (2)
C7—C1—C6—C5	176.74 (13)	C13—C14—C15—C16	−177.04 (14)
C2—C1—C6—O3	−177.31 (12)	C11—C10—C15—C14	−1.9 (2)
C7—C1—C6—O3	1.1 (2)	O1—C10—C15—C14	179.14 (13)
C10—O1—C7—O2	0.9 (2)	C11—C10—C15—C16	177.09 (14)

C10—O1—C7—C1	179.84 (11)	O1—C10—C15—C16	−1.8 (2)
C6—C1—C7—O2	−6.4 (2)	C14—C15—C16—O6	−25.3 (2)
C2—C1—C7—O2	172.01 (15)	C10—C15—C16—O6	155.67 (15)
C6—C1—C7—O1	174.74 (12)	C14—C15—C16—O5	152.75 (14)
C2—C1—C7—O1	−6.87 (18)	C10—C15—C16—O5	−26.3 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5···O6^{i}	0.86 (1)	1.81 (1)	2.6660 (16)	176 (2)

Symmetry code: (i) −*x*, −*y*+1, −*z*+1.