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4-Acetylbenzoic acid: hydrogen bonding and packing in a simple aromatic ε-keto acid

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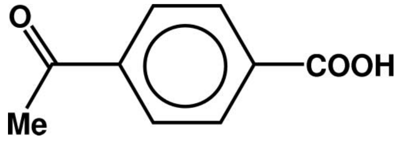
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.051; wR factor = 0.156; data-to-parameter ratio = 11.0.

The title compound, $C_9H_8O_3$, adopts a conformation in which both substituents lie nearly coplanar with the ring. Asymmetric units aggregate by centrosymmetric carboxyl pairing. Close offset stacking of rings in parallel planes creates intermolecular C···C π–π contacts of 3.322 (3) and 3.352 (3) Å, with an accompanying C···O π–π contact of 3.147 (3) Å and similarly close interactions between O atoms and aromatic π systems. One close intermolecular C—H···O contact is also present.

Related literature

For related literature, see: Borthwick (1980); Steiner (1997).



Experimental

Crystal data

$C_9H_8O_3$
M_r = 164.15
Monoclinic, $P2_1/c$
a = 5.3887 (3) Å
b = 4.9490 (3) Å
c = 28.1011 (16) Å
β = 95.478 (4)°
V = 746.00 (7) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 0.93 mm^{-1}
T = 100 (2) K
0.35 × 0.18 × 0.05 mm

Data collection

Bruker SMART CCD APEXII area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.738, T_{max} = 0.957
3378 measured reflections
1226 independent reflections
992 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.156
S = 1.12
1226 reflections
111 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3A···O2^{i}	0.84	1.79	2.618 (2)	170
C5—H5···O3^{ii}	0.95	2.53	3.375 (2)	148

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x-1, y+1, z$.

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2004); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

HWT is grateful to Professor Gree Loober Spoog for helpful consultations. The authors acknowledge support by NSF–CRIF grant No. 0443538.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2466).

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supplementary materials

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4-Acetylbenzoic acid: hydrogen bonding and packing in a simple aromatic ε-keto acid

R. A. Lalancette, M. H. Malak and **H. W. Thompson**

Comment

Our study of solid-state H-bonding patterns in ketocarboxylic acids has employed several examples of fundamentally simple systems to explore the minimum requirements for various H-bonding modes. Among such compounds is the title aromatic.

Fig. 1 shows the asymmetric unit. Although rotations are formally possible about three of its C—C bonds, the two most consequential are suppressed by conjugative coplanarity requirements, while methyl rotation should have only very slight effects on the packing. Full conjugation requires both carbonyl groups to lie very close to the ring plane, with the acetyl group (O1, C8, C4, C9) and the carboxyl (O2, O3, C7, C1) defining planes whose dihedral angles are respectively 6.75 (16) and 0.46 (16)° relative to the plane of the ring carbons and generating a ketone-*versus*-carboxyl dihedral angle of 7.03 (18)°. Although the tiitle compound is inherently achiral, this creates a conformational chirality to which the rotational conformation of the methyl contributes further; for the methyl H nearest the ring plane, the torsion angle H9A—C9···C5—H5 = 14.8°.

The C—O bond lengths and C—C—O angles conform to values typical for highly ordered dimeric carboxyls (Borthwick, 1980) and no significant averaging by disorder is observed [O2—C7 = 1.241 (3) & O3—C7 = 1.306 (2) Å; O2—C7—C1 = 121.46 (19) & O3—C7—C1 = 115.46 (17)°].

Fig. 2 illustrates the packing of the chosen cell, in which asymmetric units associate as H-bonded centrosymmetric dimers whose two halves lie in planes separated by 0.231 Å. Two sets of these dimers, screw-related and centered at 1/2,1/2,1/2 and at 1/2,0,0, lie in planes whose dihedral angle is 84.79 (5)°. Dimers of each type stack translationally in planes separated by 0.583 (3) & 3.337 (3) Å. The former arrangement involves a molecular offset to the side, without ring overlap but close enough to create several relatively short C—H···O intermolecular approaches (Steiner, 1997). These include one H···O contact of 2.53 Å (between H5 and O3), plus another three that lie narrowly (2.61–2.62 Å) beyond the range normally accepted for these close contacts (2.60 Å). For the larger interplanar separation, the offset is only half a molecule each in both length and width, creating close intermolecular sp^2 contacts of 3.147 (3) Å (C7···O2), 3.352 (3) Å (C2···C8) and 3.322 (3) Å (C5···C7). This arrangement does not involve pi-stacking of the rings themselves, but places both O1 and O3 over adjacent aromatic ring-centers at distances of 3.506 (3) & 3.313 (3) Å to the respective centroids. All of these presumably represent attractive pi interactions.

Experimental

The title compound was purchased from Acros Organics/Fisher Scientific, Springfield, NJ, USA, and recrystallized from acetic acid, mp 483 K. Typically for carboxyl-paired keto acids, the solid-state (KBr) infrared spectrum features a broad asymmetric absorption at 1683 cm^{-1} for both C=O functions; in $CHCl_3$ solution this peak is seen at 1689 cm^{-1}.

Refinement

All H atoms were found in electron density difference maps. The O—H was constrained to an idealized position with distance fixed at 0.84 Å and $U_{iso}(H) = 1.5U_{eq}(O)$. The methyl H atoms were put in ideally staggered positions with C—H distances of 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$. The aromatic C—Hs were placed in geometrically idealized positions and constrained to ride on their parent C atoms with C—H distances of 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

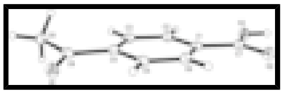

Fig. 1. The asymmetric unit with displacement ellipsoids shown at the 30% probability level.

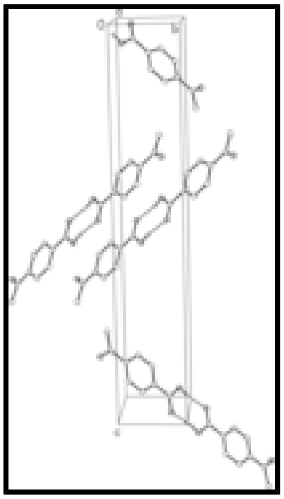

Fig. 2. A partial packing diagram, showing the centrosymmetric dimerization of the asymmetric unit. For clarity all carbon-bound H atoms have been removed. Displacement ellipsoids are shown at the 30% probability level.

4-Acetylbenzoic acid

Crystal data

$C_9H_8O_3$	$F_{000} = 344$
$M_r = 164.15$	$D_x = 1.462$ Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: 483 K
Hall symbol: -P 2ybc	Cu $K\alpha$ radiation $\lambda = 1.54178$ Å
$a = 5.3887 (3)$ Å	Cell parameters from 3385 reflections
$b = 4.9490 (3)$ Å	$\theta = 3.2–68.0°$
$c = 28.1011 (16)$ Å	$\mu = 0.93$ mm^{-1}
$\beta = 95.478 (4)°$	$T = 100 (2)$ K
$V = 746.00 (7)$ Å^3	Thin platelet, colourless
$Z = 4$	0.35 × 0.18 × 0.05 mm

Data collection

Bruker SMART CCD APEXII area-detector	1226 independent reflections

diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 100(2)$ K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2001)

$T_{\min} = 0.738$, $T_{\max} = 0.957$

3378 measured reflections

992 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\max} = 68.0°$

$\theta_{\min} = 3.2°$

$h = -5 \rightarrow 6$

$k = -5 \rightarrow 5$

$l = -32 \rightarrow 33$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.051$

$wR(F^2) = 0.156$

$S = 1.12$

1226 reflections

111 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0946P)^2 + 0.1889P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.27$ e Å^{-3}

$\Delta\rho_{\min} = -0.29$ e Å^{-3}

Extinction correction: none

Special details

Experimental. crystal mounted on cryoloop using Paratone-N

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.3411 (4)	0.9939 (4)	0.41921 (8)	0.0224 (5)
O1	−0.0882 (3)	1.7124 (3)	0.31732 (6)	0.0304 (5)
C2	0.4809 (4)	1.0345 (4)	0.38039 (8)	0.0234 (5)
H2	0.6238	0.9265	0.3769	0.028*
O2	0.2903 (3)	0.7448 (3)	0.48987 (5)	0.0261 (4)
C3	0.4105 (4)	1.2319 (4)	0.34710 (8)	0.0238 (5)
H3	0.5077	1.2615	0.3211	0.029*
O3	0.6124 (3)	0.6451 (3)	0.44821 (6)	0.0271 (4)

H3A	0.6426	0.5338	0.4706	0.041*
C4	0.1981 (4)	1.3887 (4)	0.35118 (8)	0.0223 (5)
C5	0.0586 (4)	1.3456 (4)	0.39016 (8)	0.0237 (5)
H5	−0.0861	1.4512	0.3933	0.028*
C6	0.1298 (4)	1.1511 (4)	0.42392 (8)	0.0239 (5)
H6	0.0351	1.1242	0.4504	0.029*
C7	0.4130 (4)	0.7837 (4)	0.45532 (8)	0.0220 (5)
C8	0.1112 (4)	1.6002 (4)	0.31530 (8)	0.0235 (5)
C9	0.2724 (4)	1.6640 (5)	0.27578 (8)	0.0261 (5)
H9A	0.2179	1.8349	0.2605	0.039*
H9B	0.2575	1.5187	0.2520	0.039*
H9C	0.4466	1.6801	0.2891	0.039*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0226 (11)	0.0189 (11)	0.0252 (12)	−0.0021 (8)	0.0004 (8)	−0.0039 (9)
O1	0.0247 (9)	0.0333 (9)	0.0333 (10)	0.0056 (7)	0.0035 (6)	0.0043 (7)
C2	0.0202 (11)	0.0216 (11)	0.0282 (12)	0.0001 (8)	0.0019 (8)	−0.0036 (9)
O2	0.0267 (9)	0.0258 (9)	0.0262 (8)	0.0028 (6)	0.0054 (6)	0.0013 (6)
C3	0.0218 (12)	0.0242 (12)	0.0259 (11)	−0.0024 (8)	0.0050 (8)	−0.0028 (9)
O3	0.0262 (9)	0.0266 (9)	0.0291 (9)	0.0070 (6)	0.0046 (6)	0.0038 (6)
C4	0.0217 (11)	0.0202 (11)	0.0246 (11)	−0.0025 (8)	−0.0002 (8)	−0.0030 (8)
C5	0.0187 (11)	0.0231 (12)	0.0291 (12)	0.0003 (8)	0.0020 (8)	−0.0020 (9)
C6	0.0233 (11)	0.0242 (11)	0.0248 (12)	−0.0007 (8)	0.0049 (9)	−0.0020 (8)
C7	0.0205 (11)	0.0183 (10)	0.0270 (11)	−0.0018 (8)	0.0008 (8)	−0.0050 (8)
C8	0.0222 (11)	0.0213 (11)	0.0266 (11)	−0.0013 (8)	−0.0004 (8)	−0.0048 (9)
C9	0.0257 (12)	0.0261 (12)	0.0262 (12)	0.0015 (8)	0.0012 (9)	0.0035 (9)

Geometric parameters (Å, °)

C1—C6	1.395 (3)	O3—H3A	0.8400
C1—C2	1.398 (3)	C4—C5	1.402 (3)
C1—C7	1.479 (3)	C4—C8	1.497 (3)
O1—C8	1.216 (3)	C5—C6	1.380 (3)
C2—C3	1.381 (3)	C5—H5	0.9500
C2—H2	0.9500	C6—H6	0.9500
O2—C7	1.241 (3)	C8—C9	1.507 (3)
C3—C4	1.396 (3)	C9—H9A	0.9800
C3—H3	0.9500	C9—H9B	0.9800
O3—C7	1.306 (2)	C9—H9C	0.9800
C6—C1—C2	119.9 (2)	C5—C6—C1	119.98 (19)
C6—C1—C7	119.33 (18)	C5—C6—H6	120.0
C2—C1—C7	120.73 (19)	C1—C6—H6	120.0
C3—C2—C1	119.8 (2)	O2—C7—O3	123.1 (2)
C3—C2—H2	120.1	O2—C7—C1	121.46 (19)
C1—C2—H2	120.1	O3—C7—C1	115.46 (17)
C2—C3—C4	120.79 (19)	O1—C8—C4	120.59 (19)

C2—C3—H3	119.6	O1—C8—C9	120.8 (2)
C4—C3—H3	119.6	C4—C8—C9	118.56 (19)
C7—O3—H3A	109.5	C8—C9—H9A	109.5
C3—C4—C5	119.0 (2)	C8—C9—H9B	109.5
C3—C4—C8	122.62 (19)	H9A—C9—H9B	109.5
C5—C4—C8	118.41 (19)	C8—C9—H9C	109.5
C6—C5—C4	120.5 (2)	H9A—C9—H9C	109.5
C6—C5—H5	119.7	H9B—C9—H9C	109.5
C4—C5—H5	119.7		

C6—C1—C2—C3	0.6 (3)	C7—C1—C6—C5	−179.16 (19)
C7—C1—C2—C3	−179.96 (19)	C6—C1—C7—O2	−0.3 (3)
C1—C2—C3—C4	−1.3 (3)	C2—C1—C7—O2	−179.8 (2)
C2—C3—C4—C5	1.0 (3)	C6—C1—C7—O3	179.80 (19)
C2—C3—C4—C8	−178.4 (2)	C2—C1—C7—O3	0.4 (3)
C3—C4—C5—C6	−0.1 (3)	C3—C4—C8—O1	172.2 (2)
C8—C4—C5—C6	179.4 (2)	C5—C4—C8—O1	−7.3 (3)
C4—C5—C6—C1	−0.5 (3)	C3—C4—C8—C9	−5.8 (3)
C2—C1—C6—C5	0.3 (3)	C5—C4—C8—C9	174.73 (19)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3A···O2^{i}	0.84	1.79	2.618 (2)	170
C5—H5···O3^{ii}	0.95	2.53	3.375 (2)	148

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) *x*−1, *y*+1, *z*.

Fig. 1

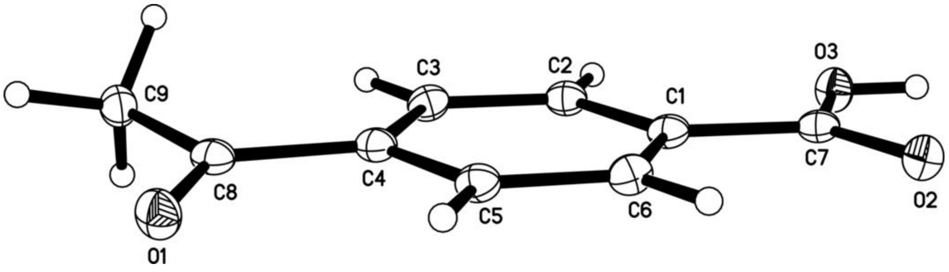

Fig. 2