organic papers

# Ethyl 2-(2-formylphenoxy)ethanoate–ethyl 2-(2-carboxyphenoxy)ethanoate [0.682 (7)/0.318 (7)]

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Key indicators

Single-crystal X-ray study
$T = 120$ K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.039
wR factor = 0.097
Data-to-parameter ratio = 9.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title cocrystal, $0.682C_{11}H_{12}O_4 \cdot 0.318C_{11}H_{12}O_5$, the carboxylic acid constituent shows an intramolecular O—H···(O,O) hydrogen bond.

Comment

The title compound, (I)/(II) (Fig. 1), is a cocrystal of a substituted benzaldehyde and benzoic acid that arose unexpectedly during our studies of novel cyclization reactions (Williamson *et al.*, 2005). Auto-oxidation reactions of benzaldehydes, probably proceeding *via* a radical mechanism, have been known for many years (Mulcahy & Watt, 1952).
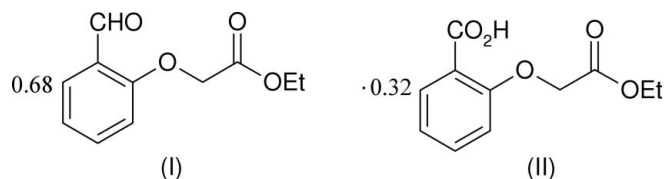
Except for the aldehyde –H and carboxylic acid –OH groups, all the atoms in (I)/(II) are equivalent and overlap in the cocrystal, and the geometric parameters for (I)/(II) may be regarded as normal (Allen *et al.*, 1987). Compound (II) displays a bifurcated intramolecular O—H···(O,O) bond (Table 1). The fact that (II) prefers (or is forced) to form this intramolecular interaction may help to explain why the aldehyde and acid are able to crystallize together.

Two short intermolecular C—H···O interactions occur in the cocrystal (Table 1). For the C6—H6···O1[i] bond (see Table 1 for symmetry code), the O atom of the aldehyde/carboxylic acid C=O group serves as one of the acceptors. Thus, regardless of the identity of an individual molecule (aldehyde or acid), an infinite (along [010]) $C(6)$ chain (Bernstein *et al.*, 1995) generated by the 2_1 screw axis is established. There are no π–π stacking interactions observed in this cocrystal; the minimum separation of the centroids of the benzene rings of nearby molecules is greater than 4.8 Å.

Experimental

A dry two-necked flask was charged with NaH (0.360 g, 15 mmol), which had been washed with dry petrol (3 × 1 ml). Dry dimethylformamide (40 ml) was added and the suspension cooled to 273 K. Salicylaldehyde (1.220 g, 1.06 ml, 10 mmol) was added, and the solution stirred for 20 min. Ethyl bromoacetate (2.12 g, 1.20 ml, 11 mmol) was added in one portion. The solution was allowed to warm to room temperature and was then stirred for 1 h. H₂O (60 ml) was added, followed by extraction with Et₂O (3 × 50 ml). The organic fractions were combined, washed with saturated brine (75 ml) and

dried over MgSO$_4$, and the solvent was removed *in vacuo*. Chromatography, eluting with 20% EtOAc in hexane, collecting the fraction with R_f = 0.22, yielded the desired product as an oil, which crystallized slowly at room temperature (1.90 g, 91%; m.p. 333–337 K). Analysis: C$_{11}$H$_{12}$O$_4$ requires: C 63.45, H 5.81%; found C 61.80, H, 5.72%. IR (KBr, ν_{max}, cm^{-1}): 2954.0 (Ar), 2843.3 [C=O (aldehyde)], 1740.3 [C=O (ester)], 1695.9 [C=O (aldehyde)].

Recrystallization from EtOH did not succeed immediately. However, colourless needles were obtained upon slow (7 d) evaporation of an ethanol solution. It is likely that auto-oxidation occurred at this stage to yield the final cocrystal of (I)/(II).

Crystal data

0.682C$_{11}$H$_{12}$O$_4$·0.318C$_{11}$H$_{12}$O$_5$	V = 1045.41 (8) Å^3
M_r = 213.29	Z = 4
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
a = 4.8119 (2) Å	μ = 0.11 mm^{-1}
b = 13.8528 (6) Å	T = 120 (2) K
c = 15.6831 (7) Å	0.42 × 0.25 × 0.08 mm

Data collection

Nonius KappaCCD area-detector diffractometer	9977 measured reflections
	1419 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)	1129 reflections with $I > 2\sigma(I)$
T_{min} = 0.957, T_{max} = 0.993	R_{int} = 0.046

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039	157 parameters
$wR(F^2)$ = 0.098	H-atom parameters constrained
S = 1.06	$\Delta\rho_{max}$ = 0.19 e Å^{-3}
1419 reflections	$\Delta\rho_{min}$ = −0.23 e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2$\cdots$O3	0.99	1.70	2.497 (5)	134
O2—H2$\cdots$O4	0.99	2.50	3.395 (5)	151
C6—H6$\cdots$O1^i	0.95	2.56	3.504 (3)	174
C8—H8$B\cdots$O4^{ii}	0.99	2.43	3.354 (3)	155

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

Anomalous dispersion was negligible and Friedel pairs were merged before refinement. The molecules of (I) and (II) are achiral, and thus the observed non-centrosymmetric space group must arise from a packing effect. After initial modelling as the expected aldehyde [compound (I)], very high residuals ($wR > 0.40$) and a large difference peak near atom C1 resulted. Modelling the crystal structure as compound (II) also resulted in very high residuals, and unreasonable U^{ij} values for atom O2. Refinement as a cocrystal of (I) + (II) (occupancies of the –O2—H2 and –H1 groups/atoms attached to atom C1 refined with their sum constrained to unity) rapidly converged to a physically plausible result with low residuals.

The C11 methyl group is disordered over two positions of equal occupancy [refined value for the first component = 0.50 (3)]. The O-bound H atom was located in a difference map and refined as riding, with U_{iso}(H) = 1.2U_{eq}(O). All C-bound H atoms were placed in
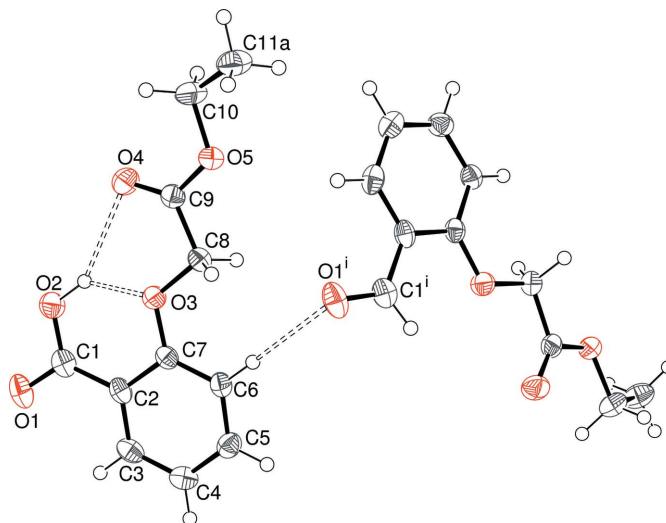
Figure 1
The structures of two molecules in the cocrystal, with one represented as the acid, (II), and one as the aldehyde, (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radius. Hydrogen bonds are indicated by double-dashed lines. Only one disorder component of the C11 methyl group is shown. (Symmetry code as in Table 1.)

calculated positions, with C—H = 0.95–0.99 Å, and refined as riding, with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C).

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997), and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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supporting information

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$M_r = 213.29$	$D_x = 1.355$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 1430 reflections
$a = 4.8119$ (2) Å	$\theta = 2.9–27.5°$
$b = 13.8528$ (6) Å	$\mu = 0.11$ mm^{-1}
$c = 15.6831$ (7) Å	$T = 120$ K
$V = 1045.41$ (8) Å^3	Slab, colourless
$Z = 4$	$0.42 \times 0.25 \times 0.08$ mm

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Radiation source: fine-focus sealed tube	1419 independent reflections
Graphite monochromator	1129 reflections with $I > 2\sigma(I)$
ω and φ scans	$R_{int} = 0.046$
Absorption correction: multi-scan (SADABS; Bruker, 2003)	$\theta_{max} = 27.5°$, $\theta_{min} = 3.9°$
$T_{min} = 0.957$, $T_{max} = 0.993$	$h = -6 \rightarrow 5$
	$k = -17 \rightarrow 13$
	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difmap and geom
$R[F^2 > 2\sigma(F^2)] = 0.039$	H-atom parameters constrained
$wR(F^2) = 0.098$	$w = 1/[\sigma^2(F_o^2) + (0.0559P)^2 + 0.0632P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	
1419 reflections	$(\Delta/\sigma)_{max} < 0.001$
157 parameters	$\Delta\rho_{max} = 0.19$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.23$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: SHELXL97 (Sheldrick, 1997), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
	Extinction coefficient: 0.031 (6)

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.3059 (5)	0.92120 (16)	0.70792 (15)	0.0331 (5)	
H1	0.4298	0.9021	0.7520	0.040*	0.682 (7)
C2	0.0918 (5)	0.85223 (14)	0.67935 (13)	0.0279 (5)	
C3	−0.0628 (5)	0.87175 (16)	0.60610 (14)	0.0326 (5)	
H3	−0.0302	0.9299	0.5756	0.039*	
C4	−0.2616 (5)	0.80823 (17)	0.57725 (15)	0.0342 (6)	
H4	−0.3644	0.8221	0.5270	0.041*	
C5	−0.3106 (5)	0.72371 (17)	0.62229 (14)	0.0325 (5)	
H5	−0.4472	0.6796	0.6023	0.039*	
C6	−0.1631 (5)	0.70251 (15)	0.69608 (13)	0.0279 (5)	
H6	−0.2014	0.6452	0.7272	0.033*	
C7	0.0399 (4)	0.76560 (15)	0.72365 (13)	0.0257 (5)	
C8	0.1580 (5)	0.66534 (15)	0.84300 (13)	0.0276 (5)	
H8A	0.1944	0.6077	0.8074	0.033*	
H8B	−0.0354	0.6621	0.8643	0.033*	
C9	0.3585 (4)	0.66947 (15)	0.91613 (13)	0.0276 (5)	
C10	0.4839 (6)	0.5919 (2)	1.04427 (16)	0.0456 (7)	
H10A	0.5094	0.6564	1.0703	0.055*	
H10B	0.6683	0.5650	1.0294	0.055*	
C11A	0.324 (3)	0.5233 (10)	1.1055 (6)	0.046 (2)	0.50 (3)
H11A	0.4306	0.5151	1.1582	0.068*	0.50 (3)
H11B	0.2988	0.4604	1.0780	0.068*	0.50 (3)
H11C	0.1419	0.5512	1.1188	0.068*	0.50 (3)
C11B	0.449 (6)	0.5058 (10)	1.0888 (11)	0.065 (5)	0.50 (3)
H11D	0.5727	0.5053	1.1385	0.098*	0.50 (3)
H11E	0.4948	0.4514	1.0514	0.098*	0.50 (3)
H11F	0.2559	0.5003	1.1078	0.098*	0.50 (3)
O1	0.3320 (3)	1.00164 (11)	0.67838 (12)	0.0434 (5)	
O2	0.4619 (10)	0.9054 (4)	0.7772 (3)	0.037 (2)	0.318 (7)
H2	0.4288	0.8436	0.8074	0.045*	0.318 (7)
O3	0.1994 (3)	0.75114 (10)	0.79483 (9)	0.0306 (4)	
O4	0.5400 (3)	0.72816 (12)	0.92481 (11)	0.0384 (4)	
O5	0.3060 (3)	0.59732 (10)	0.96963 (9)	0.0321 (4)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0332 (12)	0.0300 (12)	0.0360 (12)	0.0012 (10)	0.0098 (11)	−0.0001 (10)
C2	0.0286 (11)	0.0231 (10)	0.0319 (11)	0.0051 (9)	0.0095 (9)	−0.0015 (10)
C3	0.0343 (12)	0.0319 (12)	0.0316 (12)	0.0089 (10)	0.0067 (10)	0.0057 (10)
C4	0.0314 (12)	0.0395 (13)	0.0316 (11)	0.0059 (11)	0.0005 (10)	0.0045 (10)
C5	0.0274 (11)	0.0344 (12)	0.0357 (12)	−0.0015 (11)	−0.0010 (10)	−0.0042 (10)
C6	0.0271 (11)	0.0235 (10)	0.0330 (11)	−0.0008 (9)	0.0027 (10)	0.0001 (9)
C7	0.0261 (11)	0.0240 (11)	0.0271 (11)	0.0053 (9)	0.0039 (9)	−0.0013 (9)
C8	0.0277 (11)	0.0257 (11)	0.0296 (11)	0.0018 (10)	0.0022 (9)	0.0016 (9)
C9	0.0235 (10)	0.0280 (11)	0.0314 (11)	0.0047 (10)	0.0017 (10)	−0.0015 (9)
C10	0.0481 (15)	0.0493 (15)	0.0395 (14)	0.0060 (13)	−0.0176 (12)	0.0030 (13)
C11A	0.043 (5)	0.061 (5)	0.033 (3)	−0.003 (4)	−0.007 (4)	0.009 (3)
C11B	0.089 (12)	0.050 (5)	0.057 (6)	−0.013 (6)	−0.040 (7)	0.016 (4)
O1	0.0448 (10)	0.0260 (8)	0.0595 (11)	−0.0027 (8)	0.0151 (10)	0.0015 (8)
O2	0.033 (3)	0.034 (3)	0.045 (4)	−0.008 (2)	−0.002 (2)	0.008 (2)
O3	0.0330 (9)	0.0288 (8)	0.0300 (8)	−0.0045 (7)	−0.0035 (7)	0.0051 (6)
O4	0.0288 (9)	0.0407 (9)	0.0456 (9)	−0.0056 (8)	−0.0043 (8)	0.0014 (8)
O5	0.0359 (9)	0.0298 (8)	0.0306 (8)	0.0015 (7)	−0.0069 (7)	0.0017 (7)

Geometric parameters (Å, º)

C1—O1	1.213 (3)	C8—H8A	0.9900
C1—O2	1.339 (5)	C8—H8B	0.9900
C1—C2	1.475 (3)	C9—O4	1.201 (3)
C1—H1	0.9500	C9—O5	1.329 (3)
C2—C3	1.395 (3)	C10—C11B	1.392 (11)
C2—C7	1.409 (3)	C10—O5	1.452 (3)
C3—C4	1.377 (3)	C10—C11A	1.555 (10)
C3—H3	0.9500	C10—H10A	0.9900
C4—C5	1.388 (3)	C10—H10B	0.9900
C4—H4	0.9500	C11A—H11A	0.9800
C5—C6	1.389 (3)	C11A—H11B	0.9800
C5—H5	0.9500	C11A—H11C	0.9800
C6—C7	1.380 (3)	C11B—H11D	0.9800
C6—H6	0.9500	C11B—H11E	0.9800
C7—O3	1.369 (3)	C11B—H11F	0.9800
C8—O3	1.422 (2)	O2—H2	0.9903
C8—C9	1.500 (3)		
O1—C1—O2	113.7 (3)	O4—C9—O5	125.2 (2)
O1—C1—C2	123.5 (2)	O4—C9—C8	125.47 (19)
O2—C1—C2	122.2 (3)	O5—C9—C8	109.36 (17)
O1—C1—H1	117.9	C11B—C10—O5	112.2 (5)
C2—C1—H1	118.6	C11B—C10—C11A	26.8 (9)
C3—C2—C7	118.5 (2)	O5—C10—C11A	103.7 (4)
C3—C2—C1	119.8 (2)	C11B—C10—H10A	125.6

C7—C2—C1	121.7 (2)	O5—C10—H10A	111.0
C4—C3—C2	121.2 (2)	C11A—C10—H10A	111.0
C4—C3—H3	119.4	C11B—C10—H10B	84.4
C2—C3—H3	119.4	O5—C10—H10B	111.0
C3—C4—C5	119.3 (2)	C11A—C10—H10B	111.0
C3—C4—H4	120.3	H10A—C10—H10B	109.0
C5—C4—H4	120.3	C10—C11A—H11A	109.5
C4—C5—C6	121.0 (2)	C10—C11A—H11B	109.5
C4—C5—H5	119.5	H11A—C11A—H11B	109.5
C6—C5—H5	119.5	C10—C11A—H11C	109.5
C7—C6—C5	119.3 (2)	H11A—C11A—H11C	109.5
C7—C6—H6	120.4	H11B—C11A—H11C	109.5
C5—C6—H6	120.4	C10—C11B—H11D	109.5
O3—C7—C6	124.01 (18)	C10—C11B—H11E	109.5
O3—C7—C2	115.30 (19)	H11D—C11B—H11E	109.5
C6—C7—C2	120.7 (2)	C10—C11B—H11F	109.5
O3—C8—C9	106.51 (17)	H11D—C11B—H11F	109.5
O3—C8—H8A	110.4	H11E—C11B—H11F	109.5
C9—C8—H8A	110.4	C1—O2—H2	116.0
O3—C8—H8B	110.4	C7—O3—C8	118.48 (17)
C9—C8—H8B	110.4	C9—O5—C10	115.81 (18)
H8A—C8—H8B	108.6		
O1—C1—C2—C3	10.7 (3)	C1—C2—C7—O3	0.7 (3)
O2—C1—C2—C3	−179.3 (3)	C3—C2—C7—C6	−1.3 (3)
O1—C1—C2—C7	−170.1 (2)	C1—C2—C7—C6	179.48 (19)
O2—C1—C2—C7	0.0 (4)	O3—C8—C9—O4	−8.5 (3)
C7—C2—C3—C4	0.0 (3)	O3—C8—C9—O5	172.12 (16)
C1—C2—C3—C4	179.2 (2)	C6—C7—O3—C8	1.0 (3)
C2—C3—C4—C5	0.5 (3)	C2—C7—O3—C8	179.79 (18)
C3—C4—C5—C6	0.3 (3)	C9—C8—O3—C7	−179.91 (17)
C4—C5—C6—C7	−1.6 (3)	O4—C9—O5—C10	0.8 (3)
C5—C6—C7—O3	−179.22 (18)	C8—C9—O5—C10	−179.85 (18)
C5—C6—C7—C2	2.1 (3)	C11B—C10—O5—C9	−169.3 (15)
C3—C2—C7—O3	179.91 (18)	C11A—C10—O5—C9	163.9 (6)

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O2—H2⋯O3	0.99	1.70	2.497 (5)	134
O2—H2⋯O4	0.99	2.50	3.395 (5)	151
C6—H6⋯O1[i]	0.95	2.56	3.504 (3)	174
C8—H8B⋯O4[ii]	0.99	2.43	3.354 (3)	155

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