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Ethyl (*E*)-4-(2-formylphenoxy)but-2-enoate

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.048
wR factor = 0.126
Data-to-parameter ratio = 17.4

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

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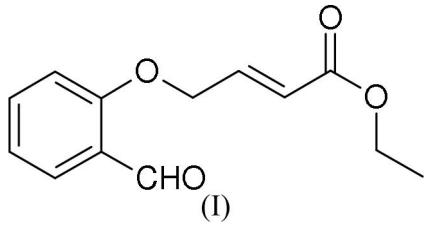
The molecule of the title compound, $C_{13}H_{14}O_4$, possesses normal geometric parameters. Its approximately planar conformation could be influenced by two intramolecular C—H···O interactions.

Comment

The title compound, (I), was prepared as a test substrate for an investigation into potential catalysts for the intramolecular Stetter reaction. The compound is well known and has been previously used in this context (Kerr *et al.*, 2002). In the present work, the synthesis used was that of Gong *et al.* (1998).



(I)

The molecule of compound (I) possesses normal geometric parameters (Table 1). The complete molecule is approximately planar (for the non-H atoms, the r.m.s deviation from the least-squares plane is 0.100 Å). This conformation might be stabilized by two intramolecular C—H···O interactions

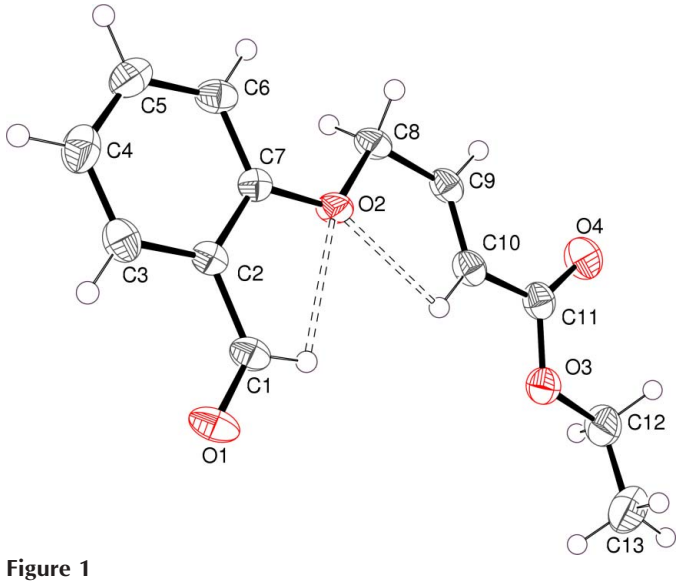


Figure 1
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small spheres of arbitrary radi. The possible C—H···O interactions are indicated by dashed lines.

(Fig. 1, Table 2). The acute O—H···O bond angles are consistent with the intramolecular nature of these putative bonds. The r.m.s. deviation from the mean plane for atoms C1, C2, C7, C8, C9, C10 and O2 is 0.043 Å [maximum deviation 0.1005 (11) Å for O2].

There are no π–π stacking or other weak intermolecular interactions in (I) and the crystal packing (Fig. 2) is controlled by van der Waals forces.

Experimental

A dry two-necked flask was charged with NaH (15 mmol, 360.4 mg). Dry dimethylformamide (40 ml) was added and the resulting suspension cooled to 273 K. Salicylaldehyde (10 mmol, 1.220 g, 1.06 ml) was added and the solution stirred for 20 min. Ethyl 4-bromocrotonate (11 mmol, 2.82 g, 2.01 ml) was added in one portion. The solution was then allowed to warm to room temperature and stirred for 1 h. Water (60 ml) was added, followed by extraction with Et_2O (3 × 50 ml). The combined organic phases were washed with saturated brine (75 ml), dried ($MgSO_4$) and the solvent removed. Chromatography of the resulting solid in 10% EtOAc in hexane allowed collection of the desired product (1.809 g, 77.2%), which was recrystallized from ethanol as colourless blocks or plates; m.p 342–344 K. Analysis, $C_{13}H_{14}O_4$ requires: C 66.66, H 6.02%; found: C 66.53, H 6.00%. Spectroscopic analysis: IR (KBr, ν_{max}, cm^{-1}): 2975.6 (Ar), 2902.4 (CH), 2859.5 (CHO), 1709.4 (CO_2Et), 1671 (CHO); ^{1}H NMR (250 MHz, $CDCl_3$, δ, p.p.m.); 10.5 (1H, *s*, CHO), 7.8 (1H, *d*, *J* = 8 Hz, Ph), 7.6 (1H, *t*, *J* = 8 Hz, Ph), 7.0 (3H, *m*), 6.2 (1H, *d*, *J* = 15 Hz, CH—CO_2Et), 4.8 (2H, *s*, CH_2), 4.2 (2H, *q*, *J* = 7 Hz, CH_2), 1.3 (3H, *t*, *J* = 8 Hz, Me); ^{13}C NMR (250 MHz, $CDCl_3$, δ, p.p.m.) 189.3 (CHO), 165.8 (CO_2Et), 160.2, 141.2, 135.9, 128.8, 125.1, 122.5, 121.4, 112.5, 66.8 (CH_2), 60.7 (CH_2), 14.2 (Me); MS (ESI$^+$): calculated: *m*/*z* 252.1230; found: 252.1232 [*M*+NH_4^+].

Crystal data

$C_{13}H_{14}O_4$
M_r = 234.24
Monoclinic, $P2_1/c$
a = 10.6759 (6) Å
b = 6.9487 (4) Å
c = 16.4346 (6) Å
β = 102.164 (3)°
V = 1191.81 (11) Å^3
Z = 4
D_x = 1.305 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 2702 reflections
θ = 2.9–27.5°
μ = 0.10 mm^{-1}
T = 120 (2) K
Plate, colourless
0.46 × 0.27 × 0.09 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
T_{min} = 0.957, T_{max} = 0.993
10 415 measured reflections
2712 independent reflections
1830 reflections with $I > 2\sigma(I)$
R_{int} = 0.052
θ_{max} = 27.5°
h = −13 → 13
k = −8 → 8
l = −17 → 21

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.126
S = 1.02
2712 reflections
156 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.059P)^2 + 0.2428P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.036 (5)

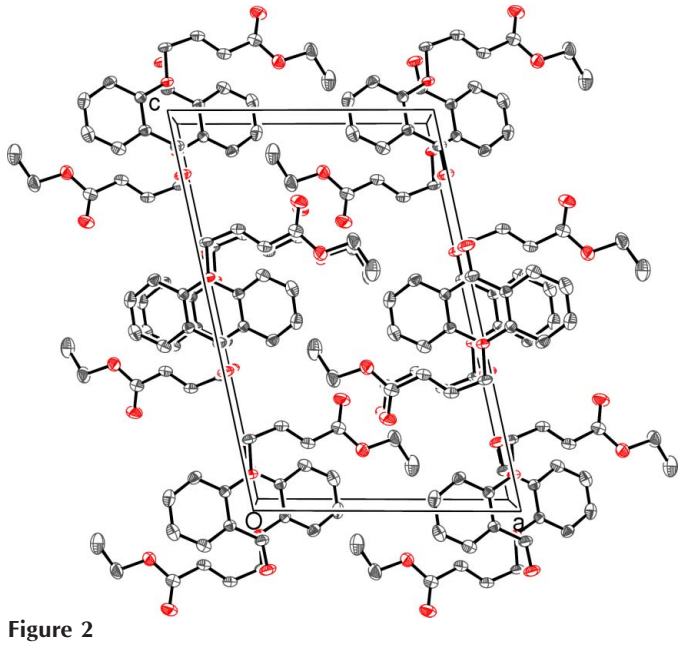


Figure 2
The unit-cell packing in (I), viewed down [010]. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

Table 1
Selected torsion angles (°).

O1—C1—C2—C7	179.50 (15)	O2—C8—C9—C10	5.2 (2)
C1—C2—C7—O2	−1.2 (2)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O2	0.95	2.39	2.7353 (17)	101
C10—H10···O2	0.95	2.38	2.7221 (19)	101

All H atoms were placed in calculated positions, with C—H distances in the range 0.95–0.99 Å, and refined as riding on their carrier atoms, 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: *DENZO* (Otwinowski & Minor 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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References

Bruker (2003). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Gong, Y., Najdi, S., Olmstead, M. M. & Kurth, M. J. (1998). *J. Org. Chem.* **63**, 3081–3086.
Kerr, M. S., Read de Alaniz, J. & Rovis, T. (2002). *J. Am. Chem. Soc.* **124**, 10298–10299.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

supporting information

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Crystal data

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Hall symbol: -P 2ybc
$a = 10.6759\ (6)$ Å
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$\beta = 102.164\ (3)°$
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$D_x = 1.305$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2702 reflections
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$T = 120$ K
Plate, colourless
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Data collection

Nonius KappaCCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (SADABS; Bruker, 2003)
$T_{min} = 0.957$, $T_{max} = 0.993$
10415 measured reflections
2712 independent reflections
1830 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.2°$
$h = -13\rightarrow13$
$k = -8\rightarrow8$
$l = -17\rightarrow21$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.126$
$S = 1.02$
2712 reflections
156 parameters
0 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.059P)^2 + 0.2428P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}
Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.036 (5)

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}
C1	0.00191 (16)	0.2643 (2)	0.41727 (9)	0.0290 (4)
H1	0.0776	0.2147	0.4520	0.035*
C2	−0.10653 (15)	0.3112 (2)	0.45585 (9)	0.0241 (4)
C3	−0.21906 (16)	0.3879 (2)	0.40804 (10)	0.0323 (4)
H3	−0.2253	0.4080	0.3501	0.039*
C4	−0.32119 (17)	0.4351 (3)	0.44321 (11)	0.0381 (5)
H4	−0.3973	0.4875	0.4101	0.046*
C5	−0.31130 (17)	0.4051 (3)	0.52753 (11)	0.0362 (4)
H5	−0.3817	0.4367	0.5520	0.043*
C6	−0.20042 (16)	0.3297 (2)	0.57726 (10)	0.0305 (4)
H6	−0.1947	0.3112	0.6352	0.037*
C7	−0.09813 (14)	0.2818 (2)	0.54104 (9)	0.0236 (4)
C8	0.03522 (15)	0.1948 (3)	0.67211 (8)	0.0283 (4)
H8A	−0.0271	0.1052	0.6886	0.034*
H8B	0.0236	0.3234	0.6953	0.034*
C9	0.16789 (16)	0.1254 (2)	0.70449 (9)	0.0283 (4)
H9	0.1922	0.1012	0.7626	0.034*
C10	0.25501 (16)	0.0942 (2)	0.65988 (9)	0.0288 (4)
H10	0.2332	0.1142	0.6014	0.035*
C11	0.38551 (17)	0.0292 (2)	0.69836 (10)	0.0311 (4)
C12	0.59362 (17)	−0.0211 (3)	0.67090 (12)	0.0457 (5)
H12A	0.6030	−0.1177	0.7161	0.055*
H12B	0.6441	0.0943	0.6926	0.055*
C13	0.63992 (19)	−0.1017 (3)	0.59849 (14)	0.0503 (5)
H13A	0.7313	−0.1328	0.6154	0.075*
H13B	0.6273	−0.0066	0.5535	0.075*
H13C	0.5917	−0.2188	0.5790	0.075*
O1	0.00079 (12)	0.28500 (18)	0.34378 (6)	0.0387 (4)
O2	0.01446 (10)	0.20508 (16)	0.58333 (6)	0.0282 (3)
O3	0.45966 (11)	0.02940 (18)	0.64209 (7)	0.0357 (3)
O4	0.42190 (13)	−0.01633 (19)	0.77059 (7)	0.0443 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0347 (9)	0.0324 (10)	0.0205 (7)	−0.0045 (7)	0.0075 (7)	−0.0014 (7)

C2	0.0274 (8)	0.0226 (8)	0.0223 (7)	−0.0051 (7)	0.0053 (6)	−0.0022 (7)
C3	0.0352 (10)	0.0300 (10)	0.0291 (8)	−0.0030 (8)	0.0009 (7)	0.0018 (7)
C4	0.0293 (10)	0.0337 (11)	0.0481 (10)	0.0018 (8)	0.0010 (8)	0.0012 (8)
C5	0.0289 (9)	0.0320 (10)	0.0499 (11)	−0.0005 (8)	0.0135 (8)	−0.0059 (8)
C6	0.0344 (9)	0.0309 (10)	0.0287 (8)	−0.0063 (8)	0.0120 (7)	−0.0061 (7)
C7	0.0236 (8)	0.0224 (9)	0.0247 (8)	−0.0033 (6)	0.0047 (6)	−0.0022 (6)
C8	0.0361 (9)	0.0341 (10)	0.0157 (7)	−0.0016 (7)	0.0076 (6)	−0.0009 (7)
C9	0.0373 (10)	0.0280 (9)	0.0185 (7)	−0.0023 (7)	0.0033 (7)	0.0008 (7)
C10	0.0355 (9)	0.0287 (9)	0.0203 (7)	−0.0017 (7)	0.0017 (7)	−0.0002 (7)
C11	0.0362 (9)	0.0262 (9)	0.0291 (8)	−0.0007 (8)	0.0030 (7)	0.0000 (7)
C12	0.0294 (10)	0.0546 (13)	0.0514 (11)	0.0102 (9)	0.0046 (8)	0.0161 (10)
C13	0.0383 (11)	0.0352 (11)	0.0798 (14)	0.0004 (9)	0.0179 (10)	−0.0046 (11)
O1	0.0498 (8)	0.0489 (8)	0.0196 (6)	−0.0085 (6)	0.0123 (5)	−0.0011 (5)
O2	0.0291 (6)	0.0408 (7)	0.0150 (5)	0.0039 (5)	0.0055 (4)	0.0008 (5)
O3	0.0308 (7)	0.0403 (8)	0.0353 (6)	0.0053 (5)	0.0052 (5)	0.0068 (5)
O4	0.0456 (8)	0.0540 (9)	0.0292 (7)	0.0084 (6)	−0.0010 (5)	0.0094 (6)

Geometric parameters (Å, º)

C1—O1	1.2138 (18)	C8—H8A	0.99
C1—C2	1.469 (2)	C8—H8B	0.99
C1—H1	0.95	C9—C10	1.318 (2)
C2—C3	1.395 (2)	C9—H9	0.95
C2—C7	1.399 (2)	C10—C11	1.474 (2)
C3—C4	1.377 (2)	C10—H10	0.95
C3—H3	0.95	C11—O4	1.2107 (19)
C4—C5	1.383 (3)	C11—O3	1.338 (2)
C4—H4	0.95	C12—O3	1.452 (2)
C5—C6	1.391 (2)	C12—C13	1.491 (3)
C5—H5	0.95	C12—H12A	0.99
C6—C7	1.390 (2)	C12—H12B	0.99
C6—H6	0.95	C13—H13A	0.98
C7—O2	1.3639 (18)	C13—H13B	0.98
C8—O2	1.4305 (16)	C13—H13C	0.98
C8—C9	1.485 (2)		
O1—C1—C2	124.04 (16)	C9—C8—H8B	110.1
O1—C1—H1	118.0	H8A—C8—H8B	108.4
C2—C1—H1	118.0	C10—C9—C8	125.85 (14)
C3—C2—C7	119.04 (14)	C10—C9—H9	117.1
C3—C2—C1	120.33 (14)	C8—C9—H9	117.1
C7—C2—C1	120.63 (14)	C9—C10—C11	121.70 (14)
C4—C3—C2	121.23 (15)	C9—C10—H10	119.1
C4—C3—H3	119.4	C11—C10—H10	119.1
C2—C3—H3	119.4	O4—C11—O3	124.30 (16)
C3—C4—C5	118.99 (16)	O4—C11—C10	125.43 (17)
C3—C4—H4	120.5	O3—C11—C10	110.26 (13)
C5—C4—H4	120.5	O3—C12—C13	107.47 (15)

C4—C5—C6	121.41 (16)	O3—C12—H12A	110.2
C4—C5—H5	119.3	C13—C12—H12A	110.2
C6—C5—H5	119.3	O3—C12—H12B	110.2
C7—C6—C5	119.11 (15)	C13—C12—H12B	110.2
C7—C6—H6	120.4	H12A—C12—H12B	108.5
C5—C6—H6	120.4	C12—C13—H13A	109.5
O2—C7—C6	124.26 (14)	C12—C13—H13B	109.5
O2—C7—C2	115.53 (13)	H13A—C13—H13B	109.5
C6—C7—C2	120.22 (15)	C12—C13—H13C	109.5
O2—C8—C9	108.23 (12)	H13A—C13—H13C	109.5
O2—C8—H8A	110.1	H13B—C13—H13C	109.5
C9—C8—H8A	110.1	C7—O2—C8	118.02 (12)
O2—C8—H8B	110.1	C11—O3—C12	117.39 (13)

O1—C1—C2—C3	−1.2 (3)	C1—C2—C7—C6	178.90 (15)
O1—C1—C2—C7	179.50 (15)	O2—C8—C9—C10	5.2 (2)
C7—C2—C3—C4	0.1 (2)	C8—C9—C10—C11	178.58 (15)
C1—C2—C3—C4	−179.18 (16)	C9—C10—C11—O4	6.4 (3)
C2—C3—C4—C5	−0.1 (3)	C9—C10—C11—O3	−172.88 (16)
C3—C4—C5—C6	0.4 (3)	C6—C7—O2—C8	−8.0 (2)
C4—C5—C6—C7	−0.7 (3)	C2—C7—O2—C8	172.08 (13)
C5—C6—C7—O2	−179.24 (15)	C9—C8—O2—C7	−174.39 (13)
C5—C6—C7—C2	0.7 (2)	O4—C11—O3—C12	−2.6 (3)
C3—C2—C7—O2	179.52 (14)	C10—C11—O3—C12	176.75 (15)
C1—C2—C7—O2	−1.2 (2)	C13—C12—O3—C11	153.40 (15)
C3—C2—C7—C6	−0.4 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O2	0.95	2.39	2.7353 (17)	101
C10—H10···O2	0.95	2.38	2.7221 (19)	101