



Crystal structure of (*E*)-undec-2-enoic acid

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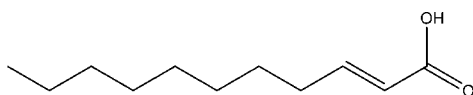
In the molecule of the title low-melting α,β -unsaturated carboxylic acid, $C_{11}H_{20}O_2$, the least-squares mean line through the octyl chain forms an angle of $60.10(13)^\circ$ with the normal to plane of the acrylic acid fragment (r.m.s. deviation = 0.008 \AA). In the crystal, centrosymmetrically related molecules are linked by pairs of $O-H\cdots O$ hydrogen bonds into dimers, forming layers parallel to the (041) plane.

Keywords: crystal structure; hydrogen bond; dimer; unsaturated carboxylic acid.

CCDC reference: 1401589

1. Related literature

For an adapted direct synthesis of the title compound following the procedure established by Knoevenagel (1898) and Doebner (1902), see: Bikulova *et al.* (1988); Kemme *et al.* (2010). For crystal structure determinations of related unsaturated α,β -carboxylic acids, see, for acrylic acid: Higgs & Sass (1963); Chatani *et al.* (1963); Boese *et al.* (1999); Oswald & Urquhart (2011); see, for crotonic acid: Shimizu *et al.* (1974); see, for (*E*)-pent-2-enoic acid: Peppel *et al.* (2015a); see, for (*E*)-hex-2-enoic acid: Peppel *et al.* (2015b). For structures of co-crystals containing (*E*)-hex-2-enoic acid, see: Aakeröy *et al.* (2003); Stanton & Bak (2008).



2. Experimental

2.1. Crystal data

$C_{11}H_{20}O_2$

$M_r = 184.27$

Triclinic, $P\bar{1}$
 $a = 4.6346(4) \text{ \AA}$
 $b = 5.4200(5) \text{ \AA}$
 $c = 22.7564(19) \text{ \AA}$
 $\alpha = 88.386(2)^\circ$
 $\beta = 88.357(2)^\circ$
 $\gamma = 78.340(2)^\circ$

$V = 559.46(8) \text{ \AA}^3$
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.07 \text{ mm}^{-1}$
 $T = 150 \text{ K}$
 $0.50 \times 0.41 \times 0.12 \text{ mm}$

2.2. Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2014)
 $T_{\min} = 0.87$, $T_{\max} = 0.99$

13660 measured reflections
 2687 independent reflections
 2317 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.134$
 $S = 1.10$
 2687 reflections
 122 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.33 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.24 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1-H1\cdots O2^i$	0.90 (2)	1.73 (2)	2.6244 (14)	172.2 (19)

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

Data collection: APEX2 (Bruker, 2014); cell refinement: SAINT (Bruker, 2013); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL2014 (Sheldrick, 2015); molecular graphics: SHELXL2014; software used to prepare material for publication: SHELXL2014.

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: RZ5160).

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supporting information

Acta Cryst. (2015). E71, o426–o427 [doi:10.1107/S2056989015009469]

Crystal structure of (*E*)-undec-2-enoic acid

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S1. Synthesis and crystallization

Malonic acid (25.0g, 240.2 mmol, 1.0 eq) is dissolved in dry pyridine (38.0g, 480.5mmol, 2.0 eq) at room temperature in a three-necked flask equipped with a magnetic stir bar and a reflux condenser under a mild flow of argon. Nonanal (34.2g, 240.2mmol, 1.0 eq) is then added in one portion and the resulting clear solution is further stirred for 72h at room temperature under argon. Afterwards, the resulting light yellow to orange solution is brought to an acidic pH value by adding phosphoric acid at 0 °C (42.5wt. %, 138.5 g, 600.6mmol, 2.5 eq). The resulting two layers are extracted three times with 150mL portions of ethyl acetate and reduced to a volume of ca. 150 mL *in vacuo*. To remove impurities from aldol condensation the raw acid is converted into the corresponding sodium salt by addition of an aqueous solution of sodium carbonate (20.4 g, 192.2 mmol, 0.8 eq in 200 mL). After stirring for 30 minutes the water phase is separated and extracted three times with 150 mL portions of ethyl acetate. The water phase is then acidified with concentrated hydrochloric acid (37.0wt. %, 35.5 g, 360.4 mmol, 1.5 eq), the organic phase is separated and the water phase is again extracted three times with 150mL portions of ethyl acetate. The combined organic phases are dried over Na₂SO₄ and evaporated to dryness under diminished pressure. The resulting raw product is further purified by distillation *in vacuo* yielding the product in purity >99% (GC). m.p. 18°C. ¹H NMR (400MHz, CDCl₃): δ = 12.24 (br s, 1H, OH); 7.09 (dt, ³J = 15.6 Hz, ³J = 7.0 Hz, 1H, -CH-); 5.82 (dt, ³J = 15.6 Hz, ⁴J = 1.6 Hz, 1H, -CH-); 2.26-2.19 (m, 2H, -CH₂-); 1.50-1.43 (m, 2H, -CH₂-); 1.33-1.24 (m, 10H, 5x -CH₂-); 0.91-0.85 (m, 3H, -CH₃-). ¹³C NMR (100MHz, CDCl₃): δ = 172.50 (CO); 152.69 (CH); 120.76 (CH); 32.47 (CH₂); 31.98 (CH₂); 29.48 (CH₂), 29.32 (CH₂), 29.29 (CH₂); 28.02 (CH₂); 22.79 (CH₂); 14.22 (CH₃). MS (EI, 70eV): *m/z* = 184 (M⁺, 0), 99 (15), 97 (12), 96 (11), 95 (11), 86 (17), 84 (17), 83 (17), 82 (17), 81 (16), 73 (36), 70 (17), 69 (25), 68 (20), 67 (19), 57 (37), 56 (20), 55 (46), 54 (12), 53 (23), 45 (22), 43 (60), 42 (20), 41 (100), 40 (14), 39 (57), 29 (62). HRMS (ESI-TOF/MS): calculated for C₁₁H₂₀O₂ ([M—H]⁻) 183.13905, found 183.13912. Elemental analysis for C₁₁H₂₀O₂ % (calc.): C 71.67 (71.70); H 10.83 (10.94). Suitable single crystals were grown by slow evaporation of an ethanolic solution at -30 °C over one week.

S2. Refinement

H1 could be found from the difference Fourier map and was refined with $U_{\text{iso}}(\text{H})$ fixed at $1.5 U_{\text{eq}}(\text{O})$. All other H atoms were placed in idealized positions with $d(\text{C—H}) = 0.95 \text{ \AA}$ (CH), 0.99 \AA (CH₂), 0.98 \AA (CH₃) and refined using a riding model with $U_{\text{iso}}(\text{H})$ fixed at $1.2 U_{\text{eq}}(\text{C})$ for CH and CH₂ and $1.5 U_{\text{eq}}(\text{C})$ for CH₃.

S3. Comment

The crystal structure of (*E*)-undec-2-enoic acid, C₁₁H₂₀O₂, an α,β -unsaturated carboxylic acid with a melting point near room temperature (m. p. 18°C), is characterized by acid dimers. The corresponding dimers are connected *via* intermolecular hydrogen bonds of the carboxylic groups C=O...H—O. The crystal packing of (*E*)-undec-2-enoic acid is described by layers of acid dimers parallel to the (0 4 1) plane which are featured by layers of polar headgroups and

hydrophobic hydrocarbon chains. The carboxylic group and the following three carbon atoms (C2, C3, C4) of the (*E*)-undec-2-enoic acid molecule lie in one plane (r.m.s. deviation = 0.008 Å), whereas the atoms of the hydrocarbon chain starting from C4 until C11 adopt a nearly fully staggered conformation.

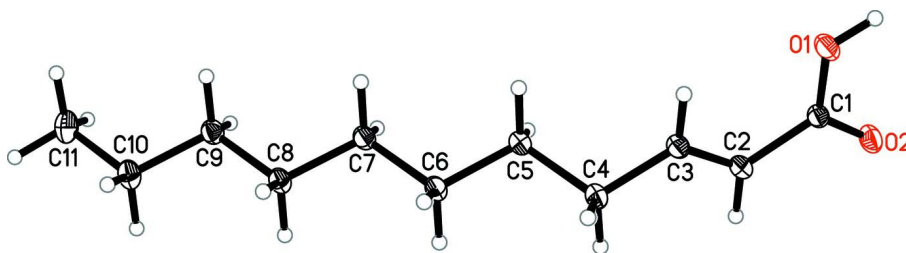


Figure 1

Molecular structure of the title compound with displacement ellipsoids drawn at 30% probability level.

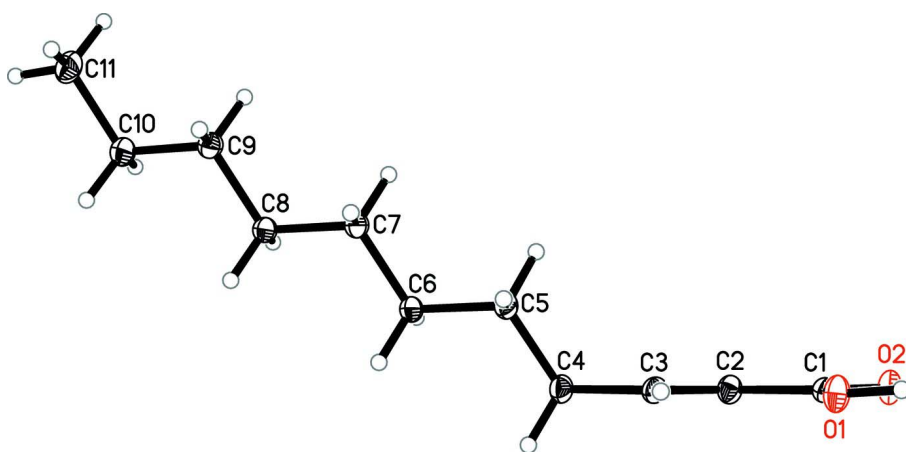


Figure 2

Side view of the molecular structure of the title compound (displacement ellipsoids drawn at 30% probability level).

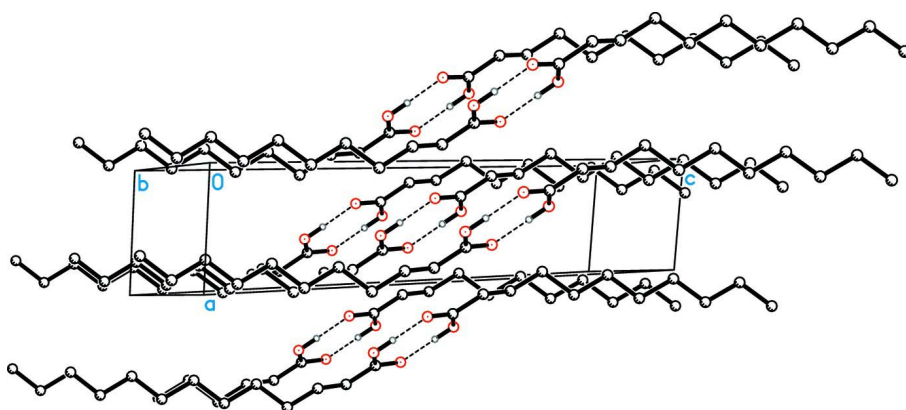


Figure 3

Packing diagram showing intermolecular O—H...O hydrogen bonds. Hydrogen atoms not involved in hydrogen bonding are omitted for clarity.

(E)-Undec-2-enoic acid*Crystal data*

$C_{11}H_{20}O_2$
 $M_r = 184.27$
 Triclinic, $P\bar{1}$
 $a = 4.6346$ (4) Å
 $b = 5.4200$ (5) Å
 $c = 22.7564$ (19) Å
 $\alpha = 88.386$ (2)°
 $\beta = 88.357$ (2)°
 $\gamma = 78.340$ (2)°
 $V = 559.46$ (8) Å³

$Z = 2$
 $F(000) = 204$
 $D_x = 1.094$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 7014 reflections
 $\theta = 2.7$ – 29.0 °
 $\mu = 0.07$ mm⁻¹
 $T = 150$ K
 Plate, colourless
 $0.50 \times 0.41 \times 0.12$ mm

Data collection

Bruker APEXII CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Detector resolution: 8.3333 pixels mm⁻¹
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2014)
 $T_{\min} = 0.87$, $T_{\max} = 0.99$

13660 measured reflections
 2687 independent reflections
 2317 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$
 $\theta_{\max} = 28.0$ °, $\theta_{\min} = 1.8$ °
 $h = -6 \rightarrow 6$
 $k = -7 \rightarrow 7$
 $l = -30 \rightarrow 30$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.134$
 $S = 1.10$
 2687 reflections
 122 parameters
 0 restraints

Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0544P)^2 + 0.245P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.33$ e Å⁻³
 $\Delta\rho_{\min} = -0.24$ 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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.7148 (3)	-0.2848 (2)	0.45696 (6)	0.0231 (3)
C2	0.8753 (3)	-0.1147 (2)	0.42422 (6)	0.0264 (3)
H2	0.9723	-0.0090	0.4457	0.032*
C3	0.8904 (3)	-0.1026 (2)	0.36643 (6)	0.0251 (3)
H3	0.7934	-0.2107	0.3457	0.030*
C4	1.0477 (3)	0.0674 (3)	0.33084 (6)	0.0278 (3)
H4A	1.2051	-0.0358	0.3066	0.033*
H4B	1.1418	0.1667	0.3576	0.033*
C5	0.8388 (3)	0.2471 (2)	0.29077 (6)	0.0247 (3)

H5A	0.7283	0.1481	0.2672	0.030*
H5B	0.6942	0.3622	0.3154	0.030*
C6	0.9983 (3)	0.4033 (2)	0.24928 (6)	0.0248 (3)
H6A	1.1150	0.4972	0.2728	0.030*
H6B	1.1374	0.2884	0.2236	0.030*
C7	0.7898 (3)	0.5893 (2)	0.21098 (6)	0.0249 (3)
H7A	0.6536	0.7060	0.2367	0.030*
H7B	0.6700	0.4953	0.1883	0.030*
C8	0.9460 (3)	0.7429 (2)	0.16835 (6)	0.0263 (3)
H8A	1.0691	0.8340	0.1910	0.032*
H8B	1.0792	0.6263	0.1421	0.032*
C9	0.7376 (3)	0.9326 (2)	0.13091 (6)	0.0267 (3)
H9A	0.6155	0.8415	0.1080	0.032*
H9B	0.6036	1.0487	0.1571	0.032*
C10	0.8949 (3)	1.0861 (3)	0.08881 (6)	0.0329 (3)
H10A	1.0269	0.9703	0.0622	0.039*
H10B	1.0190	1.1756	0.1116	0.039*
C11	0.6854 (4)	1.2777 (3)	0.05206 (7)	0.0392 (4)
H11A	0.5668	1.1901	0.0282	0.059*
H11B	0.7991	1.3723	0.0262	0.059*
H11C	0.5552	1.3943	0.0781	0.059*
O1	0.5924 (2)	-0.43092 (19)	0.42681 (4)	0.0323 (3)
O2	0.7045 (2)	-0.28190 (19)	0.51201 (4)	0.0320 (3)
H1	0.490 (5)	-0.520 (4)	0.4504 (9)	0.048*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0225 (6)	0.0211 (6)	0.0259 (6)	-0.0050 (5)	-0.0002 (5)	0.0019 (5)
C2	0.0270 (6)	0.0256 (6)	0.0288 (7)	-0.0111 (5)	-0.0007 (5)	0.0023 (5)
C3	0.0239 (6)	0.0227 (6)	0.0294 (7)	-0.0071 (5)	-0.0009 (5)	0.0031 (5)
C4	0.0263 (7)	0.0299 (7)	0.0282 (7)	-0.0093 (5)	0.0012 (5)	0.0064 (5)
C5	0.0245 (6)	0.0253 (6)	0.0255 (6)	-0.0084 (5)	0.0012 (5)	0.0022 (5)
C6	0.0242 (6)	0.0239 (6)	0.0267 (6)	-0.0065 (5)	0.0029 (5)	0.0030 (5)
C7	0.0243 (6)	0.0238 (6)	0.0269 (6)	-0.0065 (5)	0.0012 (5)	0.0023 (5)
C8	0.0255 (6)	0.0239 (6)	0.0292 (7)	-0.0052 (5)	0.0028 (5)	0.0039 (5)
C9	0.0271 (7)	0.0242 (6)	0.0288 (7)	-0.0058 (5)	0.0003 (5)	0.0030 (5)
C10	0.0353 (8)	0.0307 (7)	0.0318 (7)	-0.0059 (6)	0.0037 (6)	0.0064 (6)
C11	0.0485 (9)	0.0335 (8)	0.0338 (8)	-0.0053 (7)	-0.0004 (7)	0.0094 (6)
O1	0.0394 (6)	0.0321 (5)	0.0302 (5)	-0.0195 (4)	-0.0007 (4)	0.0029 (4)
O2	0.0413 (6)	0.0325 (5)	0.0253 (5)	-0.0157 (4)	0.0023 (4)	0.0032 (4)

Geometric parameters (Å, °)

C1—O2	1.2527 (16)	C7—C8	1.5219 (17)
C1—O1	1.2862 (16)	C7—H7A	0.9900
C1—C2	1.4717 (17)	C7—H7B	0.9900
C2—C3	1.3153 (19)	C8—C9	1.5207 (18)

C2—H2	0.9500	C8—H8A	0.9900
C3—C4	1.4942 (17)	C8—H8B	0.9900
C3—H3	0.9500	C9—C10	1.5173 (19)
C4—C5	1.5289 (18)	C9—H9A	0.9900
C4—H4A	0.9900	C9—H9B	0.9900
C4—H4B	0.9900	C10—C11	1.520 (2)
C5—C6	1.5239 (17)	C10—H10A	0.9900
C5—H5A	0.9900	C10—H10B	0.9900
C5—H5B	0.9900	C11—H11A	0.9800
C6—C7	1.5215 (17)	C11—H11B	0.9800
C6—H6A	0.9900	C11—H11C	0.9800
C6—H6B	0.9900	O1—H1	0.90 (2)
O2—C1—O1	123.41 (12)	C8—C7—H7A	108.8
O2—C1—C2	119.25 (11)	C6—C7—H7B	108.8
O1—C1—C2	117.34 (11)	C8—C7—H7B	108.8
C3—C2—C1	122.85 (12)	H7A—C7—H7B	107.7
C3—C2—H2	118.6	C9—C8—C7	113.76 (11)
C1—C2—H2	118.6	C9—C8—H8A	108.8
C2—C3—C4	125.24 (12)	C7—C8—H8A	108.8
C2—C3—H3	117.4	C9—C8—H8B	108.8
C4—C3—H3	117.4	C7—C8—H8B	108.8
C3—C4—C5	111.88 (11)	H8A—C8—H8B	107.7
C3—C4—H4A	109.2	C10—C9—C8	113.44 (11)
C5—C4—H4A	109.2	C10—C9—H9A	108.9
C3—C4—H4B	109.2	C8—C9—H9A	108.9
C5—C4—H4B	109.2	C10—C9—H9B	108.9
H4A—C4—H4B	107.9	C8—C9—H9B	108.9
C6—C5—C4	112.95 (11)	H9A—C9—H9B	107.7
C6—C5—H5A	109.0	C9—C10—C11	113.21 (13)
C4—C5—H5A	109.0	C9—C10—H10A	108.9
C6—C5—H5B	109.0	C11—C10—H10A	108.9
C4—C5—H5B	109.0	C9—C10—H10B	108.9
H5A—C5—H5B	107.8	C11—C10—H10B	108.9
C7—C6—C5	113.02 (11)	H10A—C10—H10B	107.8
C7—C6—H6A	109.0	C10—C11—H11A	109.5
C5—C6—H6A	109.0	C10—C11—H11B	109.5
C7—C6—H6B	109.0	H11A—C11—H11B	109.5
C5—C6—H6B	109.0	C10—C11—H11C	109.5
H6A—C6—H6B	107.8	H11A—C11—H11C	109.5
C6—C7—C8	113.71 (11)	H11B—C11—H11C	109.5
C6—C7—H7A	108.8	C1—O1—H1	110.8 (13)
O2—C1—C2—C3	-178.40 (13)	C4—C5—C6—C7	-177.83 (11)
O1—C1—C2—C3	1.88 (19)	C5—C6—C7—C8	-178.77 (11)
C1—C2—C3—C4	179.50 (12)	C6—C7—C8—C9	-178.82 (11)
C2—C3—C4—C5	-119.96 (15)	C7—C8—C9—C10	179.63 (11)
C3—C4—C5—C6	-173.87 (11)	C8—C9—C10—C11	-179.27 (12)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1—H1···O2 ⁱ	0.90 (2)	1.73 (2)	2.6244 (14)	172.2 (19)

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