



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

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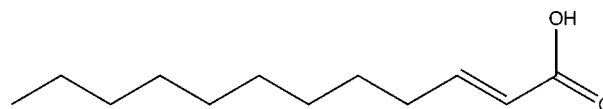
The crystal structure of (*E*)-dodec-2-enoic acid, C₁₂H₂₂O₂, an α,β -unsaturated carboxylic acid with a melting point (295 K) near room temperature, is characterized by carboxylic acid inversion dimers linked by pairs of O—H...O hydrogen bonds. The carboxylic acid group and the following three carbon atoms of the chain of the (*E*)-dodec-2-enoic acid molecule lie almost in one plane (r.m.s. deviation for the four C atoms and two O atoms = 0.012 Å), whereas the remaining carbon atoms of the hydrocarbon chain adopt a nearly fully staggered conformation [moduli of torsion angles vary from 174.01 (13) to 179.97 (13)°].

Keywords: crystal structure; hydrogen bonding; dimer; unsaturated carboxylic acid; fatty acid.

CCDC reference: 1407997

1. Related literature

For the synthesis of unsaturated α,β -carboxylic acids including the title compound by adapted routes established by Knoevenagel (1898) and Doebner (1902), see: Shabtai *et al.* (1981). For crystal structure determinations of related α,β -unsaturated carboxylic acids, see, for acrylic acid: Higgs *et al.* (1963), Chatani *et al.* (1963), Boese *et al.* (1999), or Oswald *et al.* (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); see, for (*E*)-undecen-2-enoic acid: Sonneck *et al.* (2015). For structures of co-crystals containing (*E*)-hex-2-enoic acid, see: Aakeröy *et al.* (2003), or Stanton & Bak (2008).



2. Experimental

2.1. Crystal data

C ₁₂ H ₂₂ O ₂	$\gamma = 102.3158 (19)^\circ$
$M_r = 198.29$	$V = 606.96 (4) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 4.6475 (2) \text{ \AA}$	Cu $K\alpha$ radiation
$b = 5.4169 (2) \text{ \AA}$	$\mu = 0.56 \text{ mm}^{-1}$
$c = 24.7041 (10) \text{ \AA}$	$T = 150 \text{ K}$
$\alpha = 91.547 (2)^\circ$	$0.44 \times 0.30 \times 0.12 \text{ mm}$
$\beta = 91.788 (2)^\circ$	

2.2. Data collection

Bruker APEXII CCD diffractometer	12048 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2014)	2117 independent reflections
$T_{\min} = 0.80, T_{\max} = 0.94$	1964 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.026$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$	129 parameters
$wR(F^2) = 0.131$	H-atom parameters constrained
$S = 1.13$	$\Delta\rho_{\max} = 0.29 \text{ e \AA}^{-3}$
2117 reflections	$\Delta\rho_{\min} = -0.23 \text{ e \AA}^{-3}$

Table 1
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	0.84	1.80	2.6319 (15)	170

Symmetry code: (i) $-x + 1, -y + 3, -z$.

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: SHELXL2014/7 (Sheldrick, 2015); molecular graphics: SHELXL2014/7; software used to prepare material for publication: SHELXL2014/7.

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7452).

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supporting information

Acta Cryst. (2015). E71, o528–o529 [doi:10.1107/S2056989015011937]

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

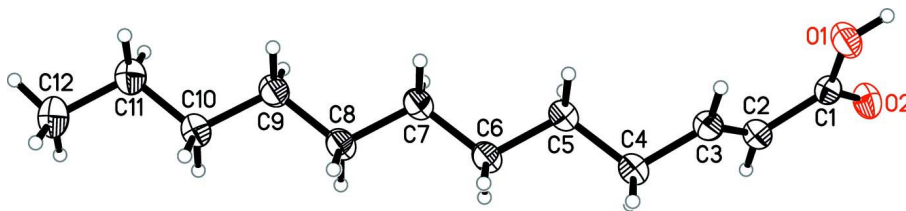
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S1. Synthesis and crystallization

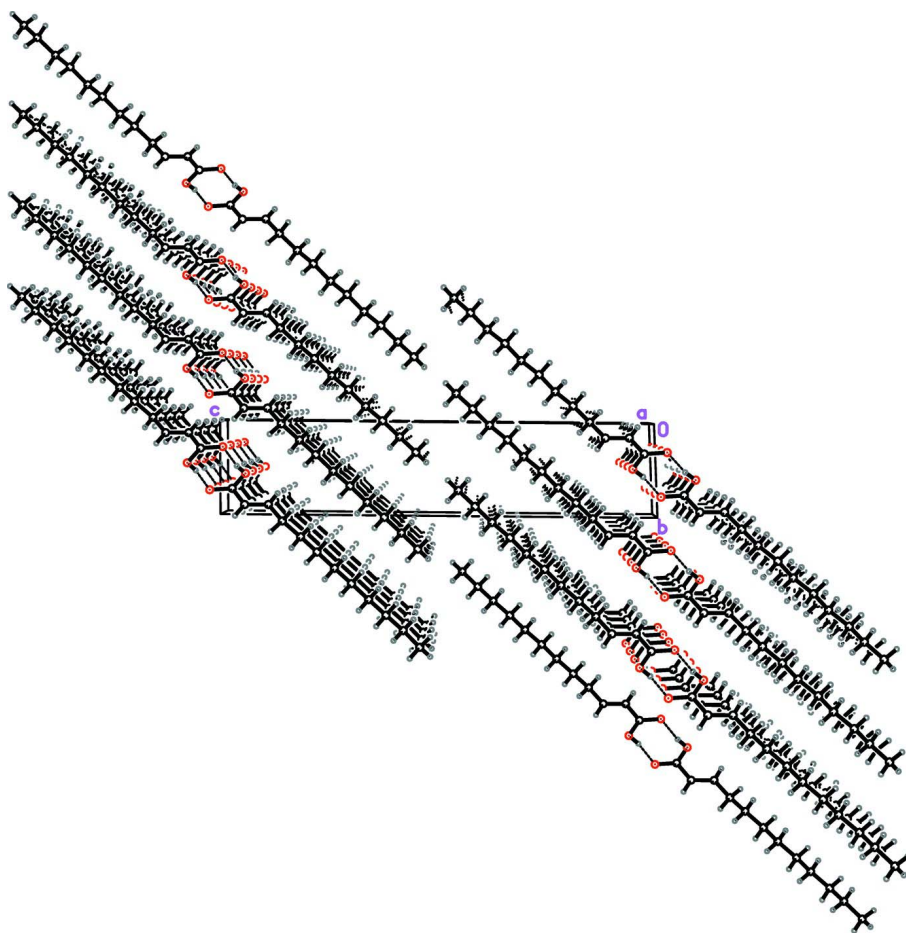
Malonic acid (25.0 g, 240.2 mmol, 1.0 eq) is dissolved in dry pyridine (38.0 g, 480.5 mmol, 2.0 eq) at room temperature in a three-necked flask equipped with a magnetic stir bar and a reflux condenser under a mild flow of argon. Decanal (37.5 g, 240.2 mmol, 1.0 eq) is then added in one portion and the resulting clear solution is further stirred for 72 h 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, 600.6 mmol, 2.5 eq). The resulting two layers are extracted three times with 150 mL 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 150 mL 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. 22 °C. ¹H NMR (400 MHz, CDCl₃): δ = 12.15 (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-); 1.50-1.42 (m, 2H, -CH₂-); 1.32-1.24 (m, 12H, 6x -CH₂-); 0.90-0.86 (m, 3H, -CH₃-). ¹³C NMR (100 MHz, CDCl₃): δ = 172.53 (CO); 152.68 (CH); 120.76 (CH); 32.47 (CH₂); 32.02 (CH₂); 29.61 (CH₂), 29.52 (CH₂), 29.43 (CH₂); 29.29 (CH₂); 28.02 (CH₂); 22.81 (CH₂); 14.23 (CH₃). MS (EI, 70eV): *m/z* = 198 (M⁺, 0), 99 (16), 98 (12), 97 (17), 96 (14), 95 (11), 86 (17), 84 (18), 83 (16), 82 (12), 81 (20), 73 (34), 71 (13), 70 (15), 69 (21), 68 (18), 67 (20), 57 (29), 56 (22), 55 (47), 54 (11), 53 (20), 45 (14), 43 (70), 42 (19), 41 (100), 40 (14), 39 (52), 29 (58). HRMS (ESI-TOF/MS): calculated for C₁₂H₂₂O₂ ([M-H]⁻) 197.1547, found 197.15481. Elemental analysis for C₁₂H₂₂O₂ % (calc.): C 72.53 (72.68); H 11.24 (11.18). Suitable single crystals were grown by slow evaporation of an ethanolic solution at -30 °C over one week.

S2. Refinement

H atoms were placed in idealized positions with d(C—H) = 0.95 Å (CH), 0.99 Å (CH₂), 0.98 Å (CH₃) and refined using a riding model with *U*_{iso}(H) fixed at 1.2 *U*_{eq}(C) for CH and CH₂ and 1.5 *U*_{eq}(C) for CH₃. The carboxylic acid group was assigned by examining the C—O distances and H1 was placed using the AFIX 147 instruction (d(O—H) = 0.84 Å, *U*_{iso}(H) fixed at 1.5 *U*_{eq}(O)).

**Figure 1**

Molecular structure of the title compound with atom labelling and displacement ellipsoids drawn at 50% probability level.

**Figure 2**

Packing diagram showing intermolecular hydrogen bonding.

(*E*)-dodec-2-enoic acid

Crystal data

$C_{12}H_{22}O_2$

$M_r = 198.29$

Triclinic, $P\bar{1}$

$a = 4.6475(2) \text{ \AA}$

$b = 5.4169(2) \text{ \AA}$

$c = 24.7041(10) \text{ \AA}$

$\alpha = 91.547(2)^\circ$

$\beta = 91.788(2)^\circ$

$\gamma = 102.3158(19)^\circ$

$V = 606.96(4) \text{ \AA}^3$

$Z = 2$

$F(000) = 220$

$D_x = 1.085 \text{ Mg m}^{-3}$
 Cu $K\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$
 Cell parameters from 6666 reflections
 $\theta = 3.6\text{--}66.9^\circ$

$\mu = 0.56 \text{ mm}^{-1}$
 $T = 150 \text{ K}$
 Plate, colourless
 $0.44 \times 0.30 \times 0.12 \text{ mm}$

Data collection

Bruker APEXII CCD
 diffractometer
 Radiation source: microfocus
 Multilayer monochromator
 Detector resolution: $8.3333 \text{ pixels mm}^{-1}$
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2014)
 $T_{\min} = 0.80$, $T_{\max} = 0.94$

12048 measured reflections
 2117 independent reflections
 1964 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\max} = 66.0^\circ$, $\theta_{\min} = 3.6^\circ$
 $h = -5 \rightarrow 5$
 $k = -6 \rightarrow 6$
 $l = -29 \rightarrow 29$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.131$
 $S = 1.13$
 2117 reflections
 129 parameters
 0 restraints

Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0529P)^2 + 0.282P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.29 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.23 \text{ e \AA}^{-3}$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.7187 (3)	1.2963 (3)	0.03952 (6)	0.0277 (4)
C2	0.8819 (3)	1.1356 (3)	0.06965 (6)	0.0314 (4)
H2	0.9763	1.0250	0.0497	0.038*
C3	0.9029 (3)	1.1384 (3)	0.12290 (6)	0.0306 (4)
H3	0.8092	1.2517	0.1421	0.037*
C4	1.0622 (4)	0.9777 (3)	0.15566 (7)	0.0332 (4)
H4A	1.2230	1.0881	0.1778	0.040*
H4B	1.1523	0.8714	0.1309	0.040*
C5	0.8573 (3)	0.8076 (3)	0.19299 (6)	0.0303 (4)
H5A	0.7510	0.9129	0.2148	0.036*
H5B	0.7090	0.6858	0.1706	0.036*
C6	1.0184 (3)	0.6615 (3)	0.23115 (6)	0.0304 (4)
H6A	1.1303	0.5606	0.2094	0.036*
H6B	1.1618	0.7832	0.2545	0.036*
C7	0.8121 (4)	0.4855 (3)	0.26692 (6)	0.0311 (4)
H7A	0.6701	0.3631	0.2435	0.037*
H7B	0.6985	0.5865	0.2882	0.037*

C8	0.9696 (4)	0.3400 (3)	0.30579 (6)	0.0313 (4)
H8A	1.0830	0.2386	0.2846	0.038*
H8B	1.1115	0.4622	0.3293	0.038*
C9	0.7607 (4)	0.1648 (3)	0.34138 (7)	0.0333 (4)
H9A	0.6186	0.0429	0.3178	0.040*
H9B	0.6474	0.2664	0.3626	0.040*
C10	0.9160 (4)	0.0181 (3)	0.38039 (7)	0.0341 (4)
H10A	1.0257	-0.0866	0.3592	0.041*
H10B	1.0612	0.1398	0.4035	0.041*
C11	0.7074 (4)	-0.1519 (4)	0.41657 (8)	0.0432 (4)
H11A	0.5556	-0.2675	0.3936	0.052*
H11B	0.6057	-0.0462	0.4393	0.052*
C12	0.8622 (5)	-0.3083 (4)	0.45332 (8)	0.0495 (5)
H12A	0.9605	-0.4159	0.4311	0.074*
H12B	0.7169	-0.4145	0.4755	0.074*
H12C	1.0089	-0.1952	0.4770	0.074*
O1	0.5999 (3)	1.4499 (2)	0.06736 (5)	0.0374 (3)
H1	0.5041	1.5251	0.0464	0.056*
O2	0.7029 (3)	1.2789 (2)	-0.01126 (4)	0.0363 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0262 (7)	0.0246 (8)	0.0319 (8)	0.0035 (6)	0.0022 (6)	0.0044 (6)
C2	0.0306 (8)	0.0301 (8)	0.0352 (9)	0.0100 (7)	0.0022 (6)	0.0046 (6)
C3	0.0274 (8)	0.0291 (8)	0.0358 (9)	0.0071 (6)	0.0010 (6)	0.0042 (6)
C4	0.0309 (8)	0.0359 (9)	0.0347 (9)	0.0110 (7)	-0.0009 (6)	0.0067 (7)
C5	0.0300 (8)	0.0306 (8)	0.0318 (8)	0.0104 (7)	-0.0016 (6)	0.0032 (6)
C6	0.0294 (8)	0.0295 (8)	0.0334 (8)	0.0095 (7)	-0.0032 (6)	0.0030 (6)
C7	0.0311 (8)	0.0301 (8)	0.0335 (8)	0.0102 (7)	-0.0021 (6)	0.0033 (6)
C8	0.0311 (8)	0.0301 (8)	0.0342 (8)	0.0098 (7)	-0.0023 (6)	0.0040 (7)
C9	0.0327 (8)	0.0335 (9)	0.0347 (9)	0.0096 (7)	-0.0019 (7)	0.0051 (7)
C10	0.0351 (9)	0.0342 (9)	0.0347 (9)	0.0109 (7)	-0.0010 (7)	0.0061 (7)
C11	0.0415 (10)	0.0459 (11)	0.0433 (10)	0.0103 (8)	0.0025 (8)	0.0147 (8)
C12	0.0554 (12)	0.0499 (11)	0.0450 (11)	0.0127 (9)	0.0035 (9)	0.0192 (9)
O1	0.0442 (7)	0.0364 (7)	0.0367 (6)	0.0193 (5)	0.0013 (5)	0.0060 (5)
O2	0.0453 (7)	0.0357 (7)	0.0307 (6)	0.0143 (5)	-0.0012 (5)	0.0053 (5)

Geometric parameters (Å, °)

C1—O2	1.2543 (19)	C7—H7B	0.9900
C1—O1	1.2881 (19)	C8—C9	1.524 (2)
C1—C2	1.473 (2)	C8—H8A	0.9900
C2—C3	1.316 (2)	C8—H8B	0.9900
C2—H2	0.9500	C9—C10	1.524 (2)
C3—C4	1.496 (2)	C9—H9A	0.9900
C3—H3	0.9500	C9—H9B	0.9900
C4—C5	1.527 (2)	C10—C11	1.518 (2)

C4—H4A	0.9900	C10—H10A	0.9900
C4—H4B	0.9900	C10—H10B	0.9900
C5—C6	1.525 (2)	C11—C12	1.523 (2)
C5—H5A	0.9900	C11—H11A	0.9900
C5—H5B	0.9900	C11—H11B	0.9900
C6—C7	1.522 (2)	C12—H12A	0.9800
C6—H6A	0.9900	C12—H12B	0.9800
C6—H6B	0.9900	C12—H12C	0.9800
C7—C8	1.524 (2)	O1—H1	0.8400
C7—H7A	0.9900		
O2—C1—O1	123.37 (14)	H7A—C7—H7B	107.7
O2—C1—C2	119.24 (14)	C9—C8—C7	113.34 (13)
O1—C1—C2	117.38 (13)	C9—C8—H8A	108.9
C3—C2—C1	122.91 (15)	C7—C8—H8A	108.9
C3—C2—H2	118.5	C9—C8—H8B	108.9
C1—C2—H2	118.5	C7—C8—H8B	108.9
C2—C3—C4	125.30 (15)	H8A—C8—H8B	107.7
C2—C3—H3	117.4	C8—C9—C10	113.76 (13)
C4—C3—H3	117.4	C8—C9—H9A	108.8
C3—C4—C5	112.03 (13)	C10—C9—H9A	108.8
C3—C4—H4A	109.2	C8—C9—H9B	108.8
C5—C4—H4A	109.2	C10—C9—H9B	108.8
C3—C4—H4B	109.2	H9A—C9—H9B	107.7
C5—C4—H4B	109.2	C11—C10—C9	113.50 (14)
H4A—C4—H4B	107.9	C11—C10—H10A	108.9
C6—C5—C4	113.32 (13)	C9—C10—H10A	108.9
C6—C5—H5A	108.9	C11—C10—H10B	108.9
C4—C5—H5A	108.9	C9—C10—H10B	108.9
C6—C5—H5B	108.9	H10A—C10—H10B	107.7
C4—C5—H5B	108.9	C10—C11—C12	113.18 (15)
H5A—C5—H5B	107.7	C10—C11—H11A	108.9
C7—C6—C5	113.10 (13)	C12—C11—H11A	108.9
C7—C6—H6A	109.0	C10—C11—H11B	108.9
C5—C6—H6A	109.0	C12—C11—H11B	108.9
C7—C6—H6B	109.0	H11A—C11—H11B	107.8
C5—C6—H6B	109.0	C11—C12—H12A	109.5
H6A—C6—H6B	107.8	C11—C12—H12B	109.5
C6—C7—C8	113.85 (13)	H12A—C12—H12B	109.5
C6—C7—H7A	108.8	C11—C12—H12C	109.5
C8—C7—H7A	108.8	H12A—C12—H12C	109.5
C6—C7—H7B	108.8	H12B—C12—H12C	109.5
C8—C7—H7B	108.8	C1—O1—H1	109.5
O2—C1—C2—C3	-178.37 (15)	C5—C6—C7—C8	-179.36 (13)
O1—C1—C2—C3	1.9 (2)	C6—C7—C8—C9	179.97 (13)
C1—C2—C3—C4	179.24 (14)	C7—C8—C9—C10	179.96 (13)
C2—C3—C4—C5	-120.08 (17)	C8—C9—C10—C11	178.76 (14)

C3—C4—C5—C6	-174.01 (13)	C9—C10—C11—C12	176.92 (15)
C4—C5—C6—C7	-178.05 (13)		

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O1—H1...O2 ⁱ	0.84	1.80	2.6319 (15)	170

Symmetry code: (i) $-x+1, -y+3, -z$.