



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

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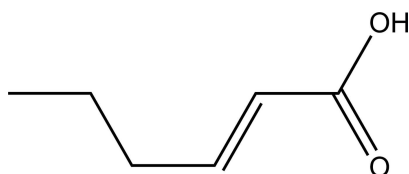
The crystal structure of the title compound, C₆H₁₀O₂, an α,β -unsaturated carboxylic acid, displays carboxylic acid inversion dimers linked by pairs of O—H...O hydrogen bonds. The packing is characterized by layers of acid dimers. All the non-H atoms of the (*E*)-hex-2-enoic acid molecule lie almost in the same plane (r.m.s. deviation for the non-H atoms = 0.018 Å).

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

CCDC reference: 1059596

1. Related literature

For the synthesis of unsaturated α,β -carboxylic acids including the title compound, see: Shabtai *et al.* (1981); Lee *et al.* (1990); Zhang *et al.* (2010). For crystal structure determinations of related unsaturated carboxylic acids, see, for acrylic acid: Higgs *et al.* (1963); Chatani *et al.* (1963); Boese *et al.* (1999); Oswald *et al.* (2011); see, for crotonic acid: Shimizu *et al.* (1974). For the structures of co-crystals containing the title compound, see: Aakeröy *et al.* (2003); Stanton & Bak (2008).



2. Experimental

2.1. Crystal data

C ₆ H ₁₀ O ₂	$c = 7.4967$ (3) Å
$M_r = 114.14$	$\alpha = 79.477$ (1)°
Triclinic, $P\bar{1}$	$\beta = 80.620$ (1)°
$a = 6.8556$ (3) Å	$\gamma = 63.654$ (1)°
$b = 6.9894$ (3) Å	$V = 315.12$ (2) Å ³

$Z = 2$
Mo $K\alpha$ radiation
 $\mu = 0.09$ mm⁻¹

$T = 150$ K
 $0.45 \times 0.41 \times 0.31$ mm

2.2. Data collection

Bruker APEXII CCD
diffractometer
Absorption correction: multi-scan
(SADABS; Bruker, 2014)
 $T_{\min} = 0.91$, $T_{\max} = 0.97$

5046 measured reflections
1518 independent reflections
1399 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.013$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.092$
 $S = 1.09$
1518 reflections
78 parameters

H atoms treated by a mixture of
independent and constrained
refinement
 $\Delta\rho_{\max} = 0.34$ e Å⁻³
 $\Delta\rho_{\min} = -0.16$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1...O2 ⁱ	0.918 (19)	1.721 (19)	2.6343 (9)	173.3 (17)

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

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: HB7405).

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supporting information

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

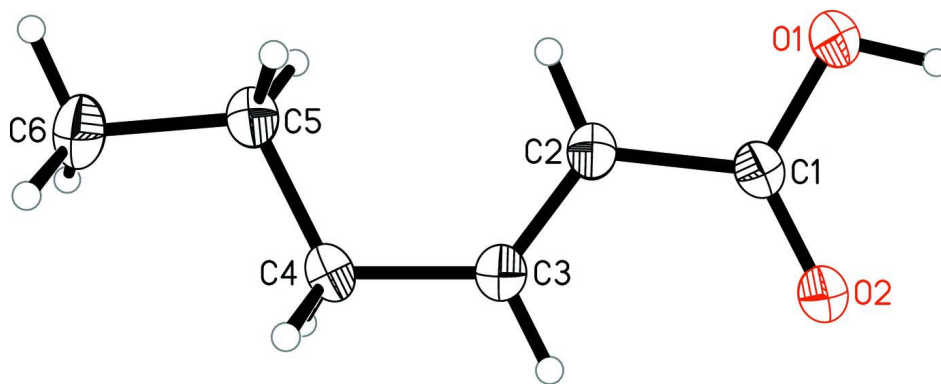
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S1. Synthesis and crystallization

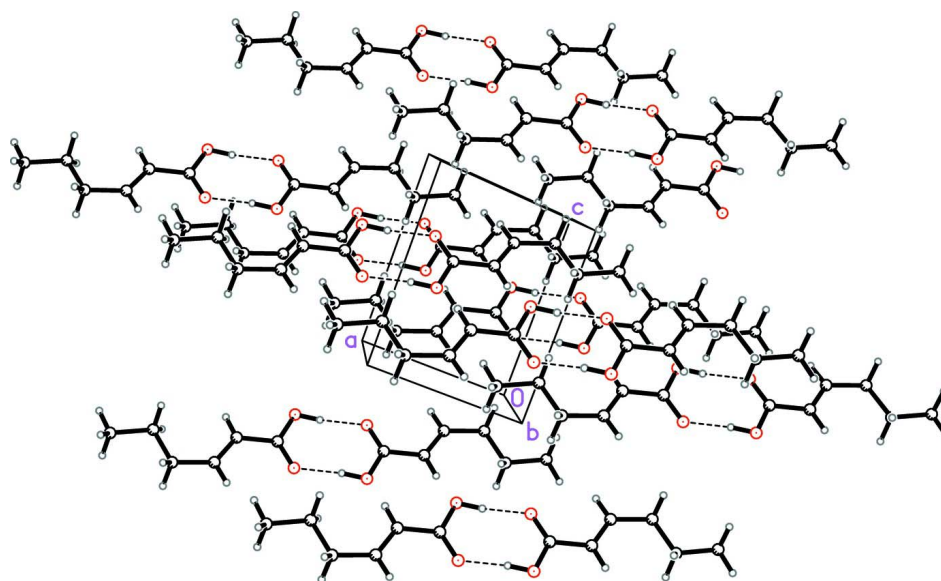
Malonic acid (24.8 g, 237.8 mmol, 1 eq) was dissolved in dry pyridine (37.6 g, 475.7 mmol, 2 eq) at room temperature in a three-necked flask equipped with a magnetic stir bar and a reflux condenser under a mild flow of argon. Butyraldehyde (17.2 g, 237.8 mmol, 1 eq) was then added in one portion and the resulting clear solution was further stirred for 72 h at room temperature under argon. Afterwards, the resulting light yellow to orange solution was brought to an acidic pH value by adding phosphoric acid at 0°C (42.5 wt.-%, 582.7 mmol, 2.45 eq). The resulting two layers were extracted three times with 150 ml portions of ethyl acetate and reduced to a volume of ca. 150 ml. To remove impurities from the aldol condensation the raw acid was converted into the corresponding sodium salt by addition of an aqueous solution of sodium carbonate (18.9 g, 178.4 mmol, 0.75 eq in 200 ml). After stirring for 30 minutes the water phase was separated und extracted three times with 150 ml portions of ethyl acetate. The water phase was then acidified with concentrated hydrochloric acid (35.2 g, 356.7 mmol, 1.5 eq), the organic phase was separated and the water phase was again extracted three times with 150 ml portions of ethyl acetate. The combined organic phases were dried over Na₂SO₄ and evaporated to dryness under diminished pressure. The resulting raw product was further purified by distillation *in vacuo* yielding the product in purity >99% (GC). mp. 32°C. ¹H NMR (400MHz, CDCl₃): δ = 12.13 (br s, 1H, OH); 7.08 (dt, ³J = 15.6 Hz, ³J = 7.0 Hz, 1H, -CH-); 5.82 (dt, ³J = 15.6 Hz, ⁴J = 1.6 Hz, 1H, -CH-); 2.23-2.17 (m, 2H, -CH₂-); 1.49 (ps-sext, J = 7.4 Hz, 2H, -CH₂-); 0.93 (t, ³J = 7.6 Hz, 3H, -CH₃-). ¹³C NMR (100MHz, CDCl₃): δ = 172.59 (CO); 152.33 (CH); 120.95 (CH); 34.40 (CH₂); 21.25 (CH₂); 13.72 (CH₃). MS (EI, 70eV): *m/z* = 114 (M⁺, 10), 99 (27), 81 (11), 73 (70), 71 (12), 69 (16), 68 (52), 67 (14), 57 (11), 55 (43), 53 (28), 51 (13), 50 (11), 45 (53), 43 (24), 42 (47), 41 (64), 40 (24), 39 (100), 38 (20), 29 (44). HRMS (ESI-TOF/MS): calculated for C₆H₁₀O₂ (M⁺) 114.06753, found 114.06768. Elemental analysis for C₆H₁₀O₂ % (calc.): C 63.13 (63.14); H 8.84 (8.83). Colourless prisms 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 freely. All other 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.

**Figure 1**

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

**Figure 2**

Packing diagram showing O—H...O hydrogen bonding.

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

Crystal data

$C_6H_{10}O_2$

$M_r = 114.14$

Triclinic, $P\bar{1}$

$a = 6.8556$ (3) Å

$b = 6.9894$ (3) Å

$c = 7.4967$ (3) Å

$\alpha = 79.477$ (1)°

$\beta = 80.620$ (1)°

$\gamma = 63.654$ (1)°

$V = 315.12$ (2) Å³

$Z = 2$

$F(000) = 124$

$D_x = 1.203$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3906 reflections

$\theta = 2.8$ – 28.9 °

$\mu = 0.09$ mm⁻¹

$T = 150$ K

Prism, colourless

$0.45 \times 0.41 \times 0.31$ 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)

$T_{\min} = 0.91$, $T_{\max} = 0.97$

5046 measured reflections

1518 independent reflections

1399 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.013$

$\theta_{\max} = 28.0^\circ$, $\theta_{\min} = 2.8^\circ$

$h = -9 \rightarrow 8$

$k = -9 \rightarrow 9$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.092$

$S = 1.09$

1518 reflections

78 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 0.0656P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.34 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.16 \text{ e } \text{\AA}^{-3}$

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 ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.25416 (11)	0.27334 (11)	0.55896 (10)	0.03153 (19)
H1	0.105 (3)	0.340 (3)	0.585 (2)	0.065 (5)*
O2	0.16993 (10)	0.55854 (11)	0.34602 (9)	0.02998 (19)
C1	0.30580 (14)	0.39036 (14)	0.41827 (12)	0.0232 (2)
C2	0.54014 (14)	0.29972 (14)	0.35596 (12)	0.0245 (2)
H2	0.6366	0.1656	0.4144	0.029*
C3	0.61808 (14)	0.40324 (14)	0.21920 (12)	0.0246 (2)
H3	0.5155	0.5375	0.1661	0.030*
C4	0.84965 (14)	0.33135 (15)	0.13986 (12)	0.0261 (2)
H4A	0.8960	0.4454	0.1455	0.031*
H4B	0.8554	0.3186	0.0095	0.031*
C5	1.01424 (15)	0.12084 (15)	0.22844 (13)	0.0286 (2)
H5A	0.9700	0.0049	0.2245	0.034*
H5B	1.0148	0.1327	0.3579	0.034*
C6	1.24357 (16)	0.06180 (18)	0.13358 (15)	0.0354 (2)
H6A	1.2465	0.0372	0.0084	0.053*
H6B	1.3469	-0.0695	0.1996	0.053*
H6C	1.2850	0.1796	0.1316	0.053*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0231 (3)	0.0305 (4)	0.0339 (4)	−0.0104 (3)	0.0043 (3)	0.0036 (3)
O2	0.0214 (3)	0.0309 (4)	0.0305 (4)	−0.0086 (3)	0.0022 (3)	0.0022 (3)
C1	0.0228 (4)	0.0254 (4)	0.0228 (4)	−0.0121 (3)	0.0011 (3)	−0.0045 (3)
C2	0.0201 (4)	0.0247 (4)	0.0266 (4)	−0.0086 (3)	0.0007 (3)	−0.0033 (3)
C3	0.0215 (4)	0.0254 (4)	0.0252 (4)	−0.0091 (3)	−0.0004 (3)	−0.0032 (3)
C4	0.0229 (4)	0.0295 (4)	0.0253 (4)	−0.0128 (4)	0.0030 (3)	−0.0021 (3)
C5	0.0229 (4)	0.0294 (5)	0.0310 (5)	−0.0106 (4)	0.0015 (3)	−0.0029 (4)
C6	0.0222 (4)	0.0390 (5)	0.0417 (6)	−0.0102 (4)	0.0029 (4)	−0.0102 (4)

Geometric parameters ($\text{\AA}$, $^\circ$)

O1—C1	1.3141 (11)	C4—H4A	0.9900
O1—H1	0.918 (19)	C4—H4B	0.9900
O2—C1	1.2259 (11)	C5—C6	1.5214 (13)
C1—C2	1.4699 (12)	C5—H5A	0.9900
C2—C3	1.3243 (13)	C5—H5B	0.9900
C2—H2	0.9500	C6—H6A	0.9800
C3—C4	1.4900 (12)	C6—H6B	0.9800
C3—H3	0.9500	C6—H6C	0.9800
C4—C5	1.5142 (13)		
C1—O1—H1	107.1 (11)	C5—C4—H4B	108.2
O2—C1—O1	122.73 (8)	H4A—C4—H4B	107.3
O2—C1—C2	123.58 (8)	C4—C5—C6	111.81 (8)
O1—C1—C2	113.69 (8)	C4—C5—H5A	109.3
C3—C2—C1	120.65 (8)	C6—C5—H5A	109.3
C3—C2—H2	119.7	C4—C5—H5B	109.3
C1—C2—H2	119.7	C6—C5—H5B	109.3
C2—C3—C4	126.86 (8)	H5A—C5—H5B	107.9
C2—C3—H3	116.6	C5—C6—H6A	109.5
C4—C3—H3	116.6	C5—C6—H6B	109.5
C3—C4—C5	116.56 (7)	H6A—C6—H6B	109.5
C3—C4—H4A	108.2	C5—C6—H6C	109.5
C5—C4—H4A	108.2	H6A—C6—H6C	109.5
C3—C4—H4B	108.2	H6B—C6—H6C	109.5
O2—C1—C2—C3	2.65 (14)	C2—C3—C4—C5	−1.89 (14)
O1—C1—C2—C3	−177.75 (8)	C3—C4—C5—C6	178.77 (8)
C1—C2—C3—C4	−179.32 (8)		

Hydrogen-bond geometry ($\text{\AA}$, $^\circ$)

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
O1—H1 $\cdots$ O2 ⁱ	0.918 (19)	1.721 (19)	2.6343 (9)	173.3 (17)

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