Synthesis and Molecular Structures of the Lowest Melting Odd- and Even-Numbered α,β-Unsaturated Carboxylic Acids—(*E*)-Hept-2-Enoic Acid and (*E*)-Oct-2-Enoic Acid

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Abstract: The molecular structures of the two lowest melting odd- and even-numbered α,β-unsaturated carboxylic acids—(*E*)-hept-2-enoic acid (**C7**) and (*E*)-oct-2-enoic acid (**C8**)—are herein reported. The title compounds were crystallized by slow evaporation of ethanolic solutions at -30 °C. **C7** crystallizes in the triclinic space group $P\overline{1}$ with two molecules in the unit cell and **C8** in the monoclinic space group $C2/c$ with eight molecules in the unit cell. The unit cell parameters for **C7** are: $a = 5.3049(2)$ Å, $b = 6.6322(3)$ Å, $c = 11.1428(5)$ Å, $\alpha = 103.972(3)°$, $\beta = 97.542(3)°$, $\gamma = 90.104(3)°$, and $V = 376.92(3)$ Å^3 (T = 150(2) K). The unit cell parameters for **C8** are: $a = 19.032(10)$ Å, $b = 9.368(5)$ Å, $c = 11.520(6)$ Å, $\beta = 123.033(11)°$, and $V = 1721.80(16)$ Å^3 (T = 200(2) K).

Keywords: X-ray crystal structure; hydrogen bond; dimer; unsaturated carboxylic acid

1. Introduction

Essential fatty acids have attracted much interest in food, health, and nutrition sciences due to their role in biological processes especially for humans [1–4]. Oleic acid, (*Z*)-octadec-9-enoic acid, and linoleic acid, (9*Z*,12*Z*)-9,12-octadecadienoic acid, respectively, can be found, for example, in meat and milk products, nuts, olives, and oils. Increasing the number of double bonds within the alkyl chain leads to a melting point decrease and hence yields liquids at ambient conditions, which is an especially important property of polyunsaturated fatty acids [5]. Derivatives of the title compounds—(*E*)-hept-2-enoic acid (**C7**) and (*E*)-oct-2-enoic acid (**C8**)—exhibit interesting occurrences and properties. For example, they can be found as active compounds in beetles' sexual pheromones [6,7], as part of siderophores in bacteria [8,9], as an anti-osteoporotic [10], or as phytotoxic substances [11], respectively.

Crystal structure determinations of α,β-unsaturated carboxylic acids have been known from the literature in the cases of acrylic acid (**C3**) [12–15] and crotonic acid (**C4**) [16] for more than 40 years, but the crystal structures of other members of α,β-unsaturated carboxylic acids, namely, (*E*)-pent-2-enoic acid (**C5**) [17], (*E*)-hex-2-enoic acid (**C6**) [18], (*E*)-non-2-enoic acid (**C9**), (*E*)-dec-2-enoic acid (**C10**) [19], (*E*)-undec-2-enoic acid (**C11**) [20], and (*E*)-dodec-2-enoic acid (**C12**) [21], respectively, have just recently been reported. In addition, two crystal structure determinations of co-crystals containing **C6** are also known [22,23]. In comparison, a complete set of crystal structures of the corresponding saturated carboxylic acids (propionic acid to pentadecanoic acid) is also available from the literature [24–28]. In this contribution, we report on the synthesis, characterization, and crystal structure determinations of the two missing and lowest melting odd- and even-numbered members

of the series of α,β-unsaturated carboxylic acids—(*E*)-hept-2-enoic acid (**C7**) and (*E*)-oct-2-enoic acid (**C8**)—respectively, which complete the series of crystal structure data from **C3** to **C12**.

2. Results and Discussion

2.1. Synthesis and Melting Points

The synthesis of α,β-unsaturated carboxylic acids has been known for more than 130 years, when Schneegans reported on the synthesis of nonenoic acid via the reaction of heptanal, sodium acetate, and acetic anhydride in 1885 [29]. More than 20 years later, Harding and Weizmann reported on the correct molecular formula of the received (*E*)-non-2-enoic acid in 1910 [30]. The syntheses of the two α,β-unsaturated carboxylic acids **C7** and **C8** were conducted by an adapted condensation reaction of malonic acid and the appropriate aldehyde at room temperature in high yields and purities as depicted in Scheme 1 [31–34] (see Experimental Section for details).

R = *n*Butyl, *n*Pentyl
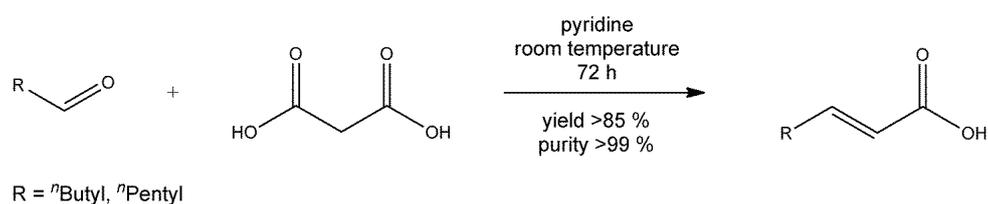
Scheme 1. Reaction sequence for the synthesis of the two title compounds—**C7** and **C8**.

The title compounds exhibit low melting points, which lie below room temperature (**C7**: −11 °C; **C8**: 10 °C). As expected, crystallographic data of these structures have not yet been reported to date due to difficulties in crystallizing and analyzing. From the complete series of trans-α,β-unsaturated carboxylic acids, a melting point alternation for even- and odd-numbered trans-α,β-unsaturated carboxylic acids from **C3** to **C16** can be found as for most homologous chemical series. For comparison, in the case of saturated carboxylic acids, from hexanoic acid to pentadecanoic acid, this effect was traced back to crystal density variations [24]. This correlation was not detected in the present case for trans-α,β-unsaturated carboxylic acids from **C3** to **C16**.

The melting point alternation for the series of trans-α,β-unsaturated carboxylic acids **C3** to **C16** based on melting points known from the literature and this work is depicted in Figure 1 [17–21,35–40]. It is clear that **C7** has the lowest melting point within the series of odd-numbered carboxylic acids, whereas **C8** exhibits the lowest melting point within the series of even-numbered carboxylic acids, respectively. Crystallographic density of **C7** is significantly higher than that of **C8**, whereas the melting point of **C7** is remarkably lower than that of **C8**, which is in contrast to the most homologous chemical series, e.g., for saturated carboxylic acids.
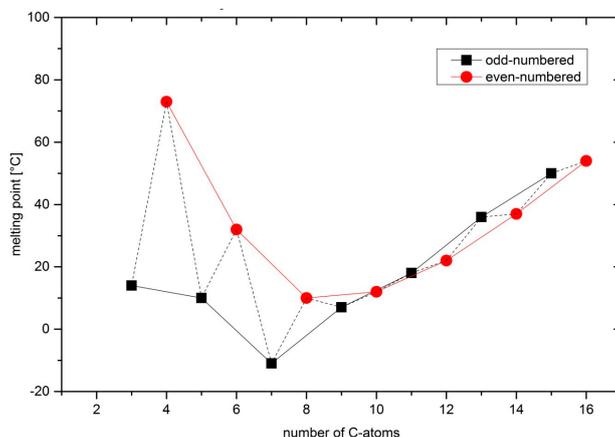
Figure 1. Melting point alternation of trans-α,β-unsaturated carboxylic acids in the series **C3** to **C16**.

2.2. Crystal Structures

Molecular structures of linked acid dimers of the title compounds with pairs of O–H···O hydrogen bonds are shown in Figures 2 and 3, respectively, with an atom-labeling scheme and displacement thermal ellipsoids at the 50% probability level. Crystal and instrumental parameters of the crystal structure determinations of **C7** and **C8** can be found in Table 1.
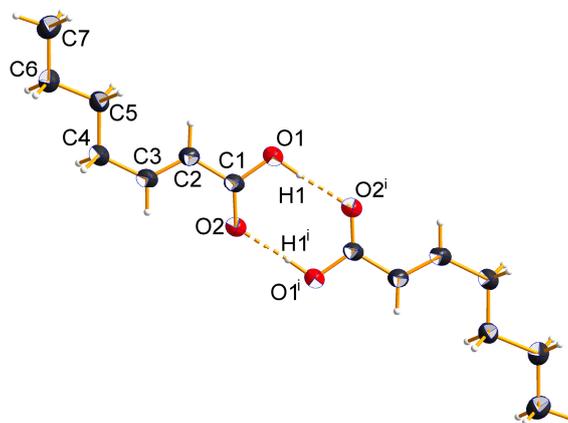
Figure 2. View of acid dimer molecules in the crystal of **C7** showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.
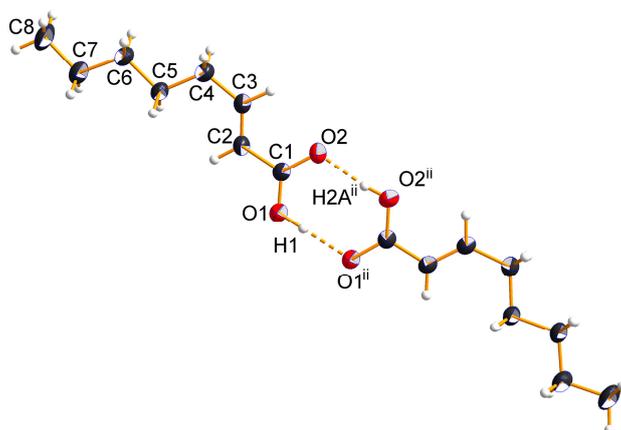
Figure 3. View of acid dimer molecules in the crystal of **C8** showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Selected bond lengths and angles are summarized in Table 2. **C7** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell, whereas **C8** crystallizes in the monoclinic space group $C2/c$ with eight molecules in the unit cell. Trans-α,β-unsaturated carboxylic acids in the series **C3**–**C12** crystallize either in orthorhombic (**C3**: *Ibam*) [12–15], monoclinic (**C4**: $C2/c$; **C9**: $P2_1/c$) [16,19], or triclinic (**C5**, **C6**, **C10**, **C11**, **C12**: $P\bar{1}$) [17–21] space groups. The title compounds show no exceptional behavior and crystallize in these known space groups (**C7**: $P\bar{1}$; **C8**: $C2/c$). Bond lengths and angles in **C7** and **C8** closely resemble values found in other α,β-unsaturated carboxylic acids [12–23]. The bond length C1–C2 is in accordance with reported C(sp^2)–C(sp^2) single bonds incorporated in carboxylic systems (**C7**: 1.4672(15) Å; **C8**: 1.4712(19) Å; ref.: 1.475 Å [41]). The bond lengths C2–C3 show characteristic values for C(sp^2)–C(sp^2) trans-configured double bonds (**C7**: 1.3240(15) Å; **C8**: 1.3140(20) Å; ref.: 1.312 Å [41]). The crystal structures of **C7** and **C8** are characterized by carboxylic acid dimers linked by pairs of O–H···O hydrogen bonds. Interestingly, the hydrogen-bonded dimer in **C7** is connected by inversion (O1···O2), whereas **C8** exhibits a hydrogen-bonded dimer built up by

a mirror plane (O1···O1 and O2···O2). Views of the packing of acid dimer layers in **C7** and **C8** are depicted in Figures 4 and 5, respectively.

Table 1. Crystal data and structure refinement for **C7** and **C8**.

Compound	C7	C8
Chemical formula	$C_7H_{12}O_2$	$C_8H_{14}O_2$
Formula weight	128.17	142.19
Crystal system	triclinic	monoclinic
a	5.3049(2) Å	19.032(10) Å
b	6.6322(3) Å	9.368(5) Å
c	11.1428(5) Å	11.520(6) Å
α	103.972(3)°	90°
β	97.542(3)°	123.033(11)°
γ	90.104(3)°	90°
Unit cell volume	376.92(3) Å^3	1721.8(16) Å^3
Temperature	150(2) K	200(2) K
Space group	$P\bar{1}$	$C2/c$
Z (Z')	2 (1)	8 (1)
μ	0.661 mm^{-1}	0.077 mm^{-1}
No. of reflections measured	5233	13812
No. of independent reflections	1325	1883
R_{int}	0.0194	0.0293
Final R_1 values ($I > 2\sigma(I)$)	0.0299	0.0433
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0837	0.1071
Final R_1 values (all data)	0.0328	0.0634
Final $wR(F^2)$ values (all data)	0.0861	0.1238
Goodness of fit on F^2	1.068	1.047
Density	1.129 g/cm^3	1.097 g/cm^3

Table 2. Selected atom distances (Å) and angles (°) for **C7** and **C8**.

Compound	C7	C8
Atoms	Distance	Distance
C1–O1	1.3178(12)	1.2655(18)
C1–O2	1.2265(12)	1.2644(18)
C1–C2	1.4672(15)	1.4712(19)
C2–C3	1.3240(15)	1.3140(20)
C3–C4	1.4905(15)	1.4920(20)
average C–C (*alkyl chain*)	1.519	1.519
H-bonds in:	D–H···A	D···A
C7	O1–H1···O2^i	2.637
C8	O1–H1···O1^{ii}	2.651 [#]
	O2–H2A···O2^{ii}	2.595 [#]
Atoms	Angle	Angle
O1–C1–O2	122.91(9)	122.36(13)
O1–C1–C2	113.37(9)	118.88(12)
O2–C1–C2	123.71(9)	118.76(13)
C1–C2–C3	121.41(9)	121.69(13)
C2–C3–C4	126.47(9)	127.87(13)
H-bonds in:	D–H···A	Angle
C7	O1–H1···O2^i	176.8
C8	O1–H1···O1^{ii}	177.3 [#]
	O2–H2A···O2^{ii}	171.7 [#]
Symmetry codes:	(i) −*x*, −*y*, −*z*	
	(ii) −*x*, *y*, −*z* + 2.5	

Note: [#] suffered from disorder.
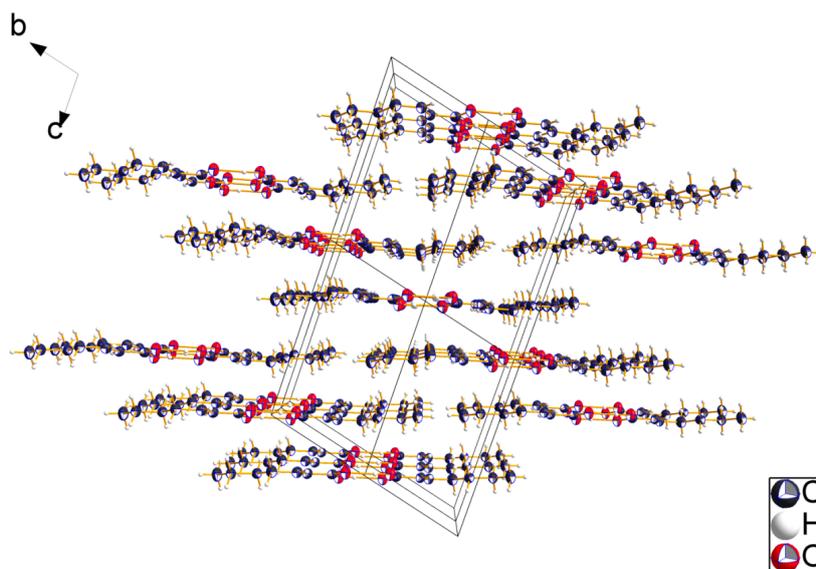
Figure 4. View of the packing of acid dimer layers in the crystal of **C7** along the crystallographic *a* axis.
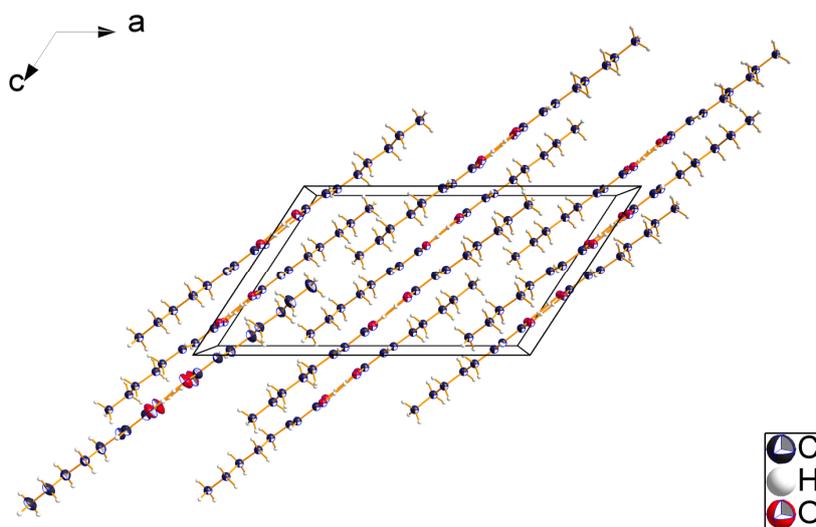
Figure 5. View of the packing of acid dimer molecules in the crystal of **C8** along the crystallographic *b* axis.

All non-hydrogen atoms of **C7** and **C8** lie nearly in one plane with a mean deviation from the best plane defined by these atoms of 0.02 Å in **C7** and 0.03 Å in **C8**. In **C7**, C6 exhibits the largest deviation from that plane (0.033(1) Å), whereas this is observed for O2 with 0.056(1) Å in **C8**, respectively. For **C8**, the carboxyl group is affected by disorder. Equal C–O bond distances were obtained (C1–O1: 1.2655(18), C1–O2 1.2644(18) Å), which indicates that there is a half mirrored overlay by a single and a double bond for C1–O1 and C1–O2, respectively. This could not be further resolved reasonably by applying a splitting model and geometric restraints. The initial geometry of the carboxyl group was retained, and two hydrogen atoms (H1 and H2A) are therefore present, each only half occupied (O1–H1: 0.90(4), O2–H2A: 0.84(4) Å). Only one orientation is shown in each case for Figure 3.

3. Experimental Section

3.1. General Considerations

NMR spectra were recorded on a AV300 or AV400 spectrometer (Bruker, Billerica, MA, USA) and chemical shifts of the ^{1}H, and ^{13}C spectra were reported in parts per million (ppm) using the solvent shifts for ^{1}H and ^{13}C as internal standard (CDCl$_3$: ^{1}H δ = 7.26, ^{13}C δ = 77.0). Elemental analysis for C and H was performed on a Microanalysator TruSpec CHNS device (LECO Corporation, Saint Joseph, MI, USA). MS spectra were determined by electron spray ionization using a Electron Finnigan MAT 95-XP mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). Melting points were determined by cyclic differential scanning calorimetry (DSC) using a DSC823^e device (Mettler-Toledo GmbH, Gießen, Germany) in the range of −50 °C to 50 °C with a heating rate of 10 K/min (2 cycles, N$_2$ atmosphere, Al crucible). All melting points are peak temperatures.

3.2. Materials

All chemicals were used as received without further drying or purification unless otherwise noted. *n*-pentanal, *n*-hexanal, and malonic acid were purchased from ABCR (purity >98%).

3.3. General Synthesis and Crystallization of α,β-Unsaturated Carboxylic Acids

Malonic acid (25.0 g, 240.2 mmol, 1.0 eq) was 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. The appropriate aldehyde (240.2 mmol, 1.0 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 %, 138.5 g, 600.6 mmol, 2.5 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 *in vacuo*. To remove impurities from aldol condensation the raw acid was 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 min, the water phase was separated and extracted three times with 150-mL portions of ethyl acetate. The water phase was then acidified with concentrated hydrochloric acid (37.0 wt %, 35.5 g, 360.4 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 Na$_2$SO$_4$ and evaporated to dryness under diminished pressure. The resulting raw product was further purified by distillation *in vacuo*, yielding the product with a purity of >99% (GC).

The two purified and liquid unsaturated carboxylic acids crystallize spontaneously during storage in a refrigerator at −30 °C as compact polycrystalline materials. Suitable single crystals for X-ray investigations were obtained by slow evaporation of the solvent from ethanolic solutions of each compound at −30 °C over two weeks in small open GC vials.

(E)-hept-2-enoic acid (**C7**). M. p. −11 °C (lit. –12 °C−−11 °C) [42]; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 12.20 (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–); 2.26–2.20 (m, 2H, –CH$_2$–); 1.49–1.41 (m, 2H, –CH$_2$–); 1.39–1.30 (m, 2H, –CH$_2$–); 0.91 (t, ^3J = 7.2 Hz; 3H, –CH$_3$–). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 172.59 (CO); 152.61 (CH); 120.79 (CH); 32.12 (CH$_2$); 30.09 (CH$_2$); 22.33 (CH$_2$); 13.90 (CH$_3$). MS (EI, 70eV): *m/z* = 128 (M$^+$, 3), 110 (10), 99 (37), 87 (11), 86 (18), 82 (12), 81 (14), 73 (68), 71 (11), 69 (14), 68 (47), 67 (15), 57 (15), 56 (46), 55 (41), 54 (14), 53 (33), 52 (11), 51 (22) 50 (14), 45 (51), 43 (58), 42 (23), 41 (100), 40 (19), 39 (98), 38 (21), 29 (51). HRMS (ESI-TOF/MS): calculated for C$_7$H$_{12}$O$_2$ ([M – H]$^-$) 127.07645, found 127.07660. Elemental analysis for C$_7$H$_{12}$O$_2$% (calc.): C 65.58 (65.60); H 9.58 (9.44).

(E)-oct-2-enoic acid (**C8**): M. p. 10 °C (lit. 2 °C–6 °C) [43,44]; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 11.83 (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–); 2.25–2.19 (m, 2H, –CH$_2$–); 1.51–1.43 (m, 2H, –CH$_2$–); 1.34–1.27 (m, 4H, 2x –CH$_2$–); 0.91–0.86 (m, 3H,

$-CH_3-$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.56 (CO); 152.66 (CH); 120.78 (CH); 32.41 (CH_2); 31.43 (CH_2); 27.68 (CH_2); 22.54 (CH_2); 14.06 (CH_3). MS (EI, 70eV): m/z = 142 (M^+, 0), 99 (20), 96 (20), 87 (11), 86 (22), 82 (22), 81 (11), 73 (54), 71 (12), 70 (37), 69 (13), 68 (33), 67 (22), 57 (20), 56 (18), 55 (57), 54 (12), 53 (23), 51 (12), 45 (45), 43 (27), 42 (29), 41 (100), 40 (20), 39 (98), 29 (89). HRMS (ESI-TOF/MS): calculated for $C_8H_{14}O_2$ ($[M - H]^-$) 141.0921, found 141.09201. Elemental analysis for $C_8H_{14}O_2$% (calc.): C 65.50 (65.57); H 9.97 (9.92).

3.4. Crystal Structure Determinations

Data were collected on a Bruker Kappa APEX II Duo diffractometer [45]. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (SHELXL-2014) on F^2 with the SHELXTL software package [46,47]. Data were corrected for absorption effects using the multi-scan method (SADABS) [48]. All non-hydrogen atoms were refined anisotropically. For **C7**, H1 could be found from the difference Fourier map and was refined freely. For **C8** the carboxyl group is affected by disorder, which is apparent in equal C–O bond lengths. This could not be further resolved reasonably by applying a splitting model and geometric restraints. H1 and H2A are found from the difference Fourier map and were refined with U_{iso}(H) fixed at 1.5 U_{eq}(O) and site occupancy factors of 0.5. All other H atoms were placed in idealized positions with d(C–H) = 0.95 Å (CH), 0.99 Å (CH_2), 0.98 Å (CH_3) and refined using a riding model with U_{iso}(H) fixed at 1.2 U_{eq}(C) for CH and CH_2 and 1.5 U_{eq}(C) for CH_3. Crystal data, data collection, and refinement parameters are collected in Table 1. The DIAMOND program package was used for graphical representations [49]. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre—CCDC-1475066 for *(E)*-hept-2-enoic acid (**C7**), and CCDC-1475065 for *(E)*-oct-2-enoic acid (**C8**). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk.

4. Conclusions

The crystal and molecular structures of *(E)*-hept-2-enoic acid (**C7**) and *(E)*-oct-2-enoic acid (**C8**) exhibiting the lowest melting points for odd- and even-numbered homologues within the series of α,β-unsaturated carboxylic acids are reported. By analogy to other known crystal structures of this class of substances, **C7** and **C8** are characterized by carboxylic acid dimers linked by pairs of O–H···O hydrogen bonds.

Author Contributions: Study conception and design: Tim Peppel, Marcel Sonneck, Anke Spannenberg, Sebastian Wohlrab; acquisition of data: Tim Peppel, Marcel Sonneck, Anke Spannenberg; analysis and interpretation of data: Tim Peppel, Marcel Sonneck, Anke Spannenberg; the drafting of the manuscript: Tim Peppel, Marcel Sonneck, Anke Spannenberg, Sebastian Wohlrab; critical revision: Tim Peppel, Anke Spannenberg, Sebastian Wohlrab.

Conflicts of Interest: The authors declare no conflict of interest.

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