SUPPORTING INFORMATION (B307208H)

On the crystal structures and melting point alternation of the *n*-alkyl carboxylic acids

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S1. Crystallographic data for C_6–C_{15}

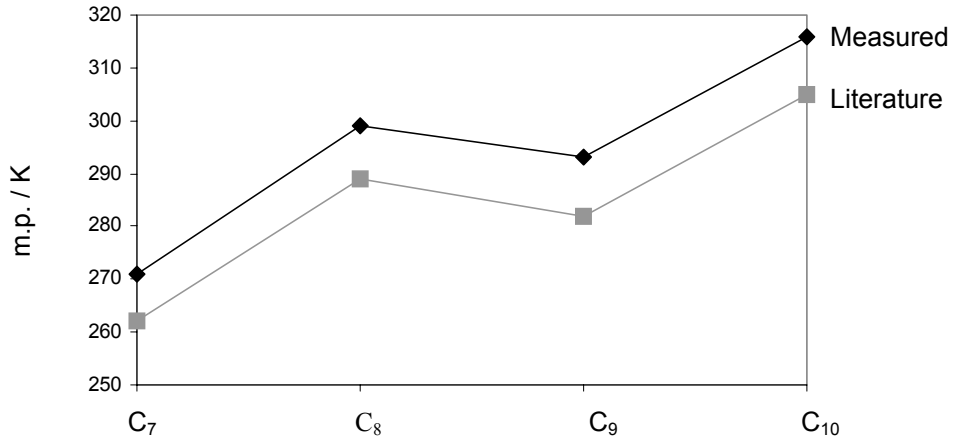
	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}
Formula	$C_6H_{12}O_2$	$C_7H_{14}O_2$	$C_8H_{16}O_2$	$C_9H_{18}O_2$	$C_{10}H_{20}O_2$	$C_{11}H_{22}O_2$	$C_{12}H_{24}O_2$	$C_{13}H_{26}O_2$	$C_{14}H_{28}O_2$	$C_{15}H_{30}O_2$
F.W.	116.16	130.18	144.21	158.23	172.26	186.29	200.31	214.34	228.36	242.39
T / K	240(2)	230(2)	170(2)	270(2)	170(2)	300(2)	270(2)	310(2)	270(2)	330(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$C2/c$	$P2_1/c$	$C2/c$
Z	4	4	4	4	4	4	4	8	4	8
a / Å	15.0180(15)	16.0089(15)	18.6641(11)	21.1130(3)	22.8440(16)	25.839(3)	27.563(2)	59.880(2)	31.559(3)	69.258(3)
b / Å	5.0236(5)	5.0764(4)	4.9756(3)	4.9188(6)	4.9612(3)	4.9123(4)	9.9627(3)	4.9425(2)	4.9652(5)	4.9556(2)
c / Å	9.9426(6)	10.1589(7)	9.5741(5)	10.1177(7)	9.3977(6)	10.0285(11)	9.5266(6)	9.8118(5)	9.4260(11)	9.7197(4)
α / º	90	90	90	90	90	90	90	90	90	90
β / º	106.549(5)	92.864(3)	95.774(2)	93.778(7)	93.559(4)	99.010(3)	98.006(2)	93.800(2)	94.432(4)	98.024(2)
γ / º	90	90	90	90	90	90	90	90	90	90
V / Å^3	719.04(11)	824.56(12)	884.59(9)	1048.45(15)	1063.02(12)	1257.2(2)	1290.41(15)	2897.5(2)	1472.6(3)	3303.3(2)
ρ_{calc} (gcm^{-3})	1.073	1.049	1.083	1.002	1.076	0.984	1.031	0.983	1.030	0.975
μ (Mo Kα)	0.079	0.075	0.076	0.069	0.072	0.065	0.068	0.064	0.066	0.062
2θ range (º)	4.10–24.95	4.02–25.42	4.24–27.44	3.87–23.37	4.20–27.53	3.99–18.04	4.17–22.45	4.09–18.70	3.89–22.51	3.57–18.00
Total data	4974	2970	6645	4082	8141	2909	5775	4645	3920	6196
Unique data	1233	1340	1923	1334	2242	859	1614	1094	1509	1141
R_{int}	0.0469	0.0369	0.0685	0.0595	0.1061	0.0669	0.0994	0.0810	0.0442	0.1036
$R1$ [$I > 2\sigma(I)$]	0.0504	0.0624	0.0701	0.0719	0.0925	0.0714	0.0671	0.0597	0.0564	0.0697
$wR2$ [all data]	0.1393	0.1855	0.1963	0.2205	0.2350	0.2063	0.1813	0.1770	0.1526	0.1889
S	1.05	1.05	1.16	1.10	1.09	1.10	1.19	1.08	1.12	1.12
CCDC No.	197245	197246	197247	197248	197249	197250	197251	197252	197253	198903

S2. Calibration of the temperature at the sample

All data were measured on the same instrument using the same N_2 cryostream, so that the *relative* data collection temperatures (relevant to the discussion of the isothermal density alternation) are as accurate as possible. The temperature measured at the cryostream nozzle differs slightly from the temperature at the sample. To calibrate the temperature on an absolute scale, the melting points of single crystals of heptanoic (C_7), octanoic (C_8), nonanoic (C_9) and decanoic acid (C_{10}) were measured, with the melting point judged to be the temperature at which the diffraction pattern was lost. Comparison with literature values suggest that a correction of *ca.* 10 K is appropriate in the range 270–320 K, *i.e.* the temperature at the sample is *ca*. 10 K less than that registered by the cryostream. In all cases, the temperature quoted is that derived at the sample.

Calibration measurements:

	Measured at nozzle (K)	Literature Value (K)	Δ (K)
C_7	271	262	-9
C_8	299	289	-10
C_9	293	282	-11
C_{10}	316	305	-11

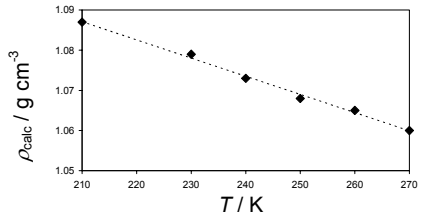


S3. Thermal variation of the unit-cell parameters and crystal density

Hexanoic acid (C_6)

T / K	*a* / Å	*b* / Å	*c* / Å	*β* / °	*V* / Å^3	ρ_{calc} / g cm^{-3}
210	14.989(2)	5.0298(6)	9.8588(10)	107.322(5)	709.5(2)	1.087
230	15.005(2)	5.0275(5)	9.9101(8)	106.899(4)	715.3(1)	1.079
240	15.018(2)	5.0236(5)	9.9426(6)	106.549(5)	719.0(1)	1.073
250	15.025(2)	5.0289(5)	9.9659(9)	106.419(4)	722.3(1)	1.068
260	15.027(2)	5.0239(6)	9.9921(10)	105.156(4)	724.5(2)	1.065

Unit-cell parameters only at 230 and 210 K. Full data set measured at 240 K.

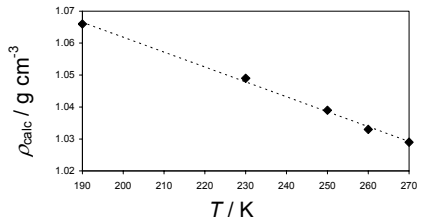


Dashed line shows least-squares best fit line through the data points
Density extrapolated to 270 K = **1.060 g cm^{-3}**

Heptanoic acid (C_7)

T / K	*a* / Å	*b* / Å	*c* / Å	*β* / °	*V* / Å^3	ρ_{calc} / g cm^{-3}
190	15.694(2)	5.1090(4)	10.1193(9)	91.881(3)	810.9(1)	1.066
230	16.009(2)	5.0764(4)	10.1589(7)	92.864(3)	824.6(1)	1.049
250	16.205(2)	5.0566(4)	10.1745(8)	93.682(3)	832.0(1)	1.039
260	16.299(3)	5.0534(6)	10.1898(11)	94.144(5)	837.1(2)	1.033

Unit-cell parameters only at 190 K Full data set measured at 230 K.



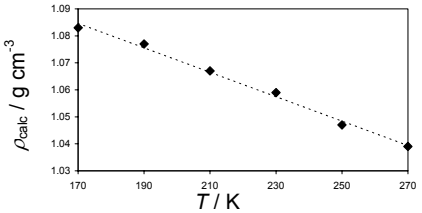
Dashed line shows least-squares best fit line through the data points
Density extrapolated to 270 K = **1.029 g cm^{-3}**

S3. Thermal variation of the unit-cell parameters and crystal density (cont.)

Octanoic acid (C_8)

[Providing comparison with extrapolation of hexanoic and heptanoic acid]

T / K	*a* / Å	*b* / Å	*c* / Å	*β* / º	*V* / Å^3	ρ_{calc} / g cm^{-3}
170	18.664(1)	4.9756(3)	9.5741(5)	95.774(2)	884.6(1)	1.083
190	18.685(4)	4.9761(7)	9.6225(13)	96.123(5)	889.6(2)	1.077
210	18.755(3)	4.9789(7)	9.6766(12)	96.594(5)	897.6(2)	1.067
230	18.801(3)	4.9734(6)	9.7483(11)	97.212(4)	904.3(2)	1.059
250	18.868(3)	4.9710(7)	9.8296(12)	97.916(5)	913.2(2)	1.047
270	18.960(4)	4.9608(7)	9.9232(13)	98.711(5)	922.6(3)	1.038



Dashed line shows least-squares best fit line through the data points
Density extrapolated to 270 K = **1.039 g cm^{-3}**
i.e. **the linear extrapolation gives a density comparable to the measured value**

Nonanoic acid (C_9)

T / K	*a* / Å	*b* / Å	*c* / Å	*β* / º	*V* / Å^3	ρ_{calc} / g cm^{-3}
270	21.113(3)	4.9188(6)	10.1177(7)	93.778(7)	1048.5(2)	1.002

Decanoic acid (C_{10})

T / K	*a* / Å	*b* / Å	*c* / Å	*β* / º	*V* / Å^3	ρ_{calc} / g cm^{-3}
270	23.10(3)	4.973(5)	9.716(7)	91.28(8)	1116(3)	1.025

Undecanoic acid (C_{11})

T / K	*a* / Å	*b* / Å	*c* / Å	*β* / º	*V* / Å^3	ρ_{calc} / g cm^{-3}
290	10.000(3)	4.916(1)	25.898(7)	99.401(8)	1256.1(5)	0.985
300	10.0285(11)	4.9123(4)	25.839(3)	99.010(3)	1257.2(2)	0.984

Linear extrapolation gives density at 270 K = **0.987 g cm^{-3}**

S3. Thermal variation of the unit-cell parameters and crystal density (cont.)

Dodecanoic acid (C_{12})

T / K	*a* / Å	*b* / Å	*c* / Å	*β* / º	*V* / Å^3	ρ_{calc} / g cm^{-3}
270	27.563(2)	4.9627(3)	9.5266(6)	98.006(2)	1290.4(2)	1.031

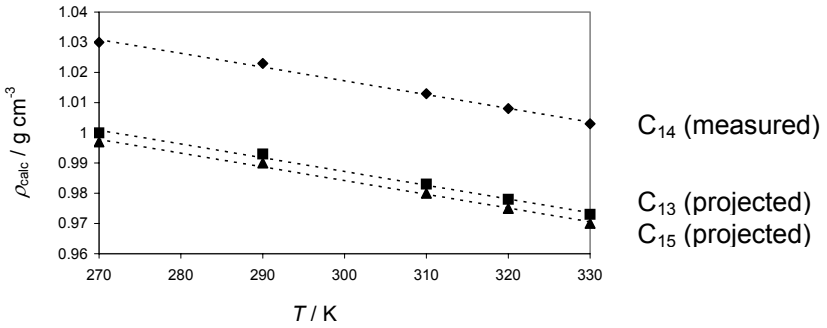
Tetradecanoic acid (C_{14})

T / K	*a* / Å	*b* / Å	*c* / Å	*β* / º	*V* / Å^3	ρ_{calc} / g cm^{-3}
270	31.559(3)	4.9652(5)	9.4260(11)	94.432(4)	1472.6(3)	1.030

S4. Estimation of the crystal density at 270 K for C_{13} and C_{15}

Predicted trend based on variable temperature measurements of the unit-cell parameters of tetradecanoic acid:

T / K	*a* / Å	*b* / Å	*c* / Å	*β* / °	*V* / Å^3	ρ_{calc} / g cm^{-3}
270	31.559(3)	4.9652(5)	9.4260(11)	94.432(4)	1472.6(3)	1.030
290	31.626(13)	4.957(1)	9.492(5)	95.055(12)	1482(1)	1.023
320	31.843(9)	4.946(1)	9.606(4)	96.202(10)	1504(1)	1.008
330	31.854(1)	4.942(1)	9.674(1)	96.708(1)	1512(1)	1.003



Shifting the linear plot so that $\rho = 0.983$ g cm^{-3} at 310 K (as measured for C_{13}), ρ may be estimated for C_{13} as **1.000 g cm^{-3}** at 270 K.

Shifting the linear plot so that $\rho = 0.975$ g cm^{-3} at 320 K (as measured for C_{15}), ρ may be estimated for C_{15} as **0.997 g cm^{-3}** at 270 K.

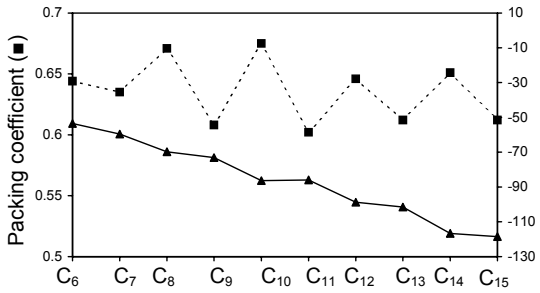
These extrapolations assume that the thermal variations of the *C*-centered structures of C_{13} and C_{15} are similar to those of the other structures, and should be considered as the best possible estimates.

S5. Packing coefficients and lattice binding energies

Lattice binding energies were calculated using the Dreiding 2.21 forcefield with default parameters (S. L. Mayo, B. D. Olafson, W. A. Goddard III, *J. Phys. Chem.* **1990**, 94, 8897), incorporating van der Waals and electrostatic terms. Hydrogen-bonded dimers were treated as discrete rigid entities. Atomic point charges were derived from the electrostatic potential, calculated using MOPAC-AM1. Values quoted are for minimized models within constrained unit cells. Molecular volumes are derived from the van der Waals surface.

	Molecular volume / Å^3	Unit-cell volume / Å^3	Packing coefficient	Lattice binding energy / kcal mol^{-1}
C_6	115.8	719.0	0.644	-53.52
C_7	130.8	824.6	0.635	-59.61
C_8	148.3	884.6	0.671	-69.73
C_9	159.5	1048.5	0.608	-73.11
C_{10}	179.4	1063.0	0.675	-86.37
C_{11}	189.1	1257.2	0.602	-85.92
C_{12}	208.3	1290.4	0.646	-98.79
C_{13}	221.8	2897.5	0.612	-101.47
C_{14}	239.8	1472.6	0.651	-116.67
C_{15}	252.7	3303.3	0.612	-118.46

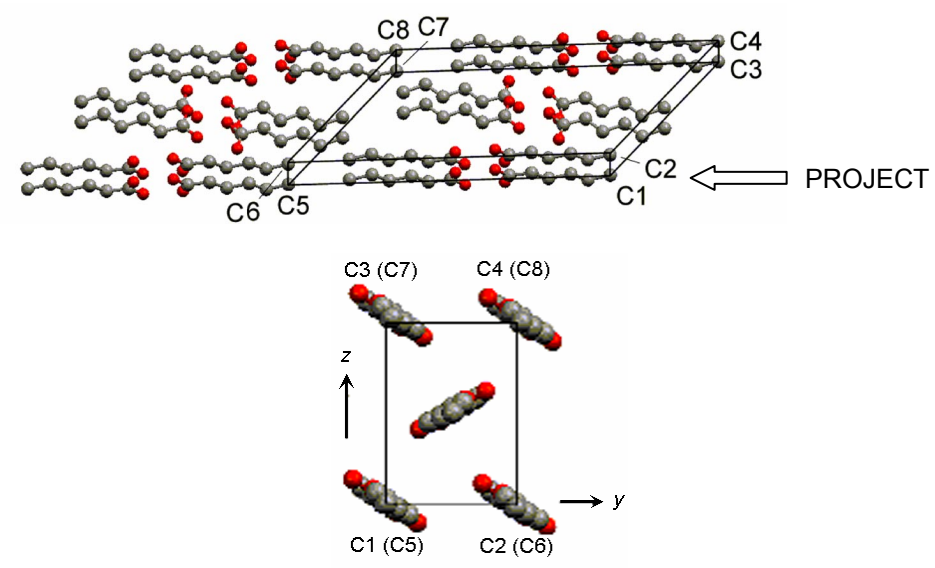
Note that these values are derived from the full data sets and are temperature-dependent to some degree.



The packing coefficients oscillate around *ca*. 0.630, with those of the odd acids systematically lower than those of the even acids. The lattice binding energies show an overall decrease (*i.e.* the structures become more stable), consistent with the steady increase in molecular weight and melting point. Superimposed on this general trend is an alternating trend, with the odd structures systematically less stable than the evens.
Both quantities mirror the alternation trend exhibited by the crystal density.

S6. Formal definitions of the orthogonal cells

The orthogonal cells are defined as described in the main text. Their dimensions are determined from the 3-dimensional coordinates of the 8 points that describe the repeating unit (a monoclinic cell in 3 dimensions). This cell is projected along C1–C5, and the resulting orthogonal coordinates are quoted in ångstroms relative to C1 at the origin.



[Even structure illustrated. For odd structures, orthogonal cell includes 2 bilayers]

Hexanoic acid (C_6):

	x / Å	*y* / Å	*z* / Å
C1	0	0	0
C2	0	5.0236	0
C3	6.987	0	7.074
C4	6.987	5.0236	7.074
C5	-20.235	0	0
C6	-20.235	5.0236	0
C7	-13.248	0	7.074
C8	-13.248	5.0236	7.074

a_o = 20.235 Å, b_o = 5.0236 Å, c_o = 7.074 Å

S6. Formal definitions of the orthogonal cells (cont.)

Heptanoic acid (C_7):

	x / Å	*y* / Å	*z* / Å
C1	0	0	0
C2	0	5.0764	0
C3	6.814	0	7.542
C4	6.814	5.0764	7.542
C5	-42.963	0	0
C6	-42.963	5.0764	0
C7	-36.149	0	7.542
C8	-36.149	5.0764	7.542

a_o = 42.963 Å, b_o = 5.0764 Å, c_o = 7.542 Å

Octanoic acid (C_8):

	x / Å	*y* / Å	*z* / Å
C1	0	0	0
C2	0	4.9756	0
C3	6.549	0	6.994
C4	6.549	4.9756	6.994
C5	-25.372	0	0
C6	-25.372	4.9756	0
C7	-18.823	0	6.994
C8	-18.823	4.9756	6.994

a_o = 25.372 Å, b_o = 4.9756 Å, c_o = 6.994 Å

Nonanoic acid (C_9):

	x / Å	*y* / Å	*z* / Å
C1	0	0	0
C2	0	4.9188	0
C3	6.254	0	7.952
C4	6.254	4.9188	7.952
C5	-53.601	0	0
C6	-53.601	4.9188	0
C7	-47.347	0	7.952
C8	-47.347	4.9188	7.952

a_o = 53.601 Å, b_o = 4.9188 Å, c_o = 7.952 Å

S6. Formal definitions of the orthogonal cells (cont.)

Decanoic acid (C_{10}):

	x / Å	*y* / Å	*z* / Å
C1	0	0	0
C2	0	4.9612	0
C3	6.234	0	7.032
C4	6.234	4.9612	7.032
C5	-30.470	0	0
C6	-30.470	4.9612	0
C7	-24.236	0	7.032
C8	-24.236	4.9612	7.032

a_o = 30.470 Å, b_o = 4.9612 Å, c_o = 7.032 Å

Undecanoic acid (C_{11}):

	x / Å	*y* / Å	*z* / Å
C1	0	0	0
C2	0	4.9123	0
C3	6.007	0	8.032
C4	6.007	4.9123	8.032
C5	-63.739	0	0
C6	-63.739	4.9123	0
C7	-57.732	0	8.032
C8	-57.732	4.9123	8.032

a_o = 63.739 Å, b_o = 4.9123 Å, c_o = 8.032 Å

Dodecanoic acid (C_{12}):

	x / Å	*y* / Å	*z* / Å
C1	0	0	0
C2	0	4.9627	0
C3	6.122	0	7.299
C4	6.122	4.9627	7.299
C5	-35.626	0	0
C6	-35.626	4.9627	0
C7	-29.504	0	7.299
C8	-29.504	4.9627	7.299

a_o = 35.626 Å, b_o = 4.9627 Å, c_o = 7.299 Å

S6. Formal definitions of the orthogonal cells (cont.)

Tridecanoic acid (C_{13}):

	x / Å	*y* / Å	*z* / Å
C1	0	0	0
C2	0	4.9425	0
C3	5.753	0	7.948
C4	5.753	4.9425	7.948
C5	-73.739	0	0
C6	-73.739	4.9425	0
C7	-67.986	0	7.948
C8	-67.987	4.9425	7.948

a_o = 73.739 Å, b_o = 4.9425 Å, c_o = 7.948 Å

Tetradecanoic acid (C_{14}):

	x / Å	*y* / Å	*z* / Å
C1	0	0	0
C2	0	4.9652	0
C3	5.983	0	7.285
C4	5.983	4.9652	7.285
C5	-40.715	0	0
C6	-40.715	4.9652	0
C7	-34.732	0	7.285
C8	-34.732	4.9652	7.285

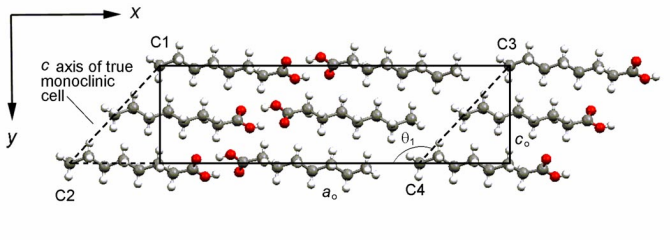
a_o = 40.715 Å, b_o = 4.9652 Å, c_o = 7.285 Å

Pentadecanoic acid (C_{15}):

	x / Å	*y* / Å	*z* / Å
C1	0	0	0
C2	0	4.9556	0
C3	5.616	0	7.933
C4	5.616	4.9556	7.933
C5	-89.639	0	0
C6	-84.023	4.9556	0
C7	-84.023	0	7.933
C8	-89.639	4.9556	7.933

a_o = 84.023 Å, b_o = 4.9556 Å, c_o = 7.933 Å

S7. Measurement of angle of methyl group interface to $a_o b_o$ plane (θ_1)



C1, C2, C3 and C4 define the $a_o c_o$ plane. All coordinates are orthogonal coordinates in ångstroms, projected onto the $a_o c_o$ plane. The angle of the methyl group interface to the $a_o b_o$ plane (θ_1) is derived from the scalar product of C1→C2 and C1→C3 (using only the x and z components).

Hexanoic acid (C_6):

	x / Å	z / Å
C1	0	0
C2	-6.987	7.074
C3	20.235	0
C4	13.247	7.074
C5	9.399	7.258
X1	4.700	3.629
X2	8.194	0.092

Vector C1→C3 =+ 20.235 x + 0.000 z
Vector C1→C2 = – 6.987 x + 7.074 z
Scalar product (C1→C3)·(C1→C2) = -141.386
= C1→C3 X1→X2 cos θ_1 = 201.1891 cos θ_1
cos θ_1 = -0.70275
Tilt angle θ_1 = 134.6°

S7. Measurement of angle of methyl group interface to $a_o b_o$ plane (θ_1) (cont.)

Heptanoic acid (C_7):

	x / Å	z / Å
C1	0	0
C2	-6.815	7.542
C3	42.963	0
C4	36.149	7.542
C5	33.129	7.576
X1	5.824	3.788
X2	9.231	0.017

Vector C1→C3 =+ 42.963 x + 0.000 z
Vector C1→C2 = – 6.815 x + 7.542 z
Scalar product (C1→C3)·(C1→C2) = -292.788
= C1→C3 X1→X2 cos θ_1 = 436.6800 cos θ_1
cos θ_1 = -0.67049
Tilt angle θ_1 = 132.1°

Octanoic acid (C_8):

	x / Å	z / Å
C1	0	0
C2	-6.549	6.994
C3	25.372	0
C4	18.822	6.994
C5	14.954	7.314
X1	7.477	3.657
X2	10.752	0.160

Vector C1→C3 =+ 25.372 x + 0.000 z
Vector C1→C2 = – 6.549 x + 6.994 z
Scalar product (C1→C3)·(C1→C2) = -166.167
= C1→C3 X1→X2 cos θ_1 = 243.1082 cos θ_1
cos θ_1 = -0.68351
Tilt angle θ_1 = 133.1°

S7. Measurement of angle of methyl group interface to $a_o b_o$ plane (θ_1) (cont.)

Nonanoic acid (C_9):

	x / Å	*z* / Å
C1	0	0
C2	-6.254	7.952
C3	53.601	0
C4	47.348	7.952
C5	44.136	7.808
X1	8.668	3.904
X2	11.795	-0.072

Vector C1→C3 =+ 53.601 *x* + 0.000 *z*
Vector C1→C2 = – 6.254 *x* + 7.952 *z*
Scalar product (C1→C3)·(C1→C2) = -335.255
= C1→C3 X1→X2 cos θ_1 = 542.3361 cos θ_1
cos θ_1 = -0.61817
Tilt angle θ_1 = 128.2°

Decanoic acid (C_{10}):

	x / Å	*z* / Å
C1	0	0
C2	-6.234	7.032
C3	30.470	0
C4	24.236	7.032
C5	20.327	7.417
X1	10.163	3.709
X2	13.280	0.193

Vector C1→C3 =+ 30.470 *x* + 0.000 *z*
Vector C1→C2 = – 6.234 *x* + 7.032 *z*
Scalar product (C1→C3)·(C1→C2) = -189.960
= C1→C3 X1→X2 cos θ_1 = 286.3842 cos θ_1
cos θ_1 = -0.66339
Tilt angle θ_1 = 131.6°

S7. Measurement of angle of methyl group interface to $a_o b_o$ plane (θ_1) (cont.)

Undecanoic acid (C_{11}):

	x / Å	*z* / Å
C1	0	0
C2	-6.009	8.032
C3	63.739	0
C4	57.733	8.032
C5	53.369	7.393
X1	11.327	3.904
X2	14.330	-0.111

Vector C1→C3 =+ 63.739 *x* + 0.000 *z*
Vector C1→C2 = – 6.009 *x* + 8.032 *z*
Scalar product (C1→C3)·(C1→C2) = -382.875
= C1→C3 X1→X2 cos θ_1 = 639.2114 cos θ_1
cos θ_1 = -0.59898
Tilt angle θ_1 = 126.8°

Dodecanoic acid (C_{12}):

	x / Å	*z* / Å
C1	0	0
C2	-6.122	7.299
C3	35.626	0
C4	29.502	7.299
C5	25.572	7.702
X1	12.786	3.851
X2	15.847	0.201

Vector C1→C3 =+ 35.626 *x* + 0.000 *z*
Vector C1→C2 = – 6.122 *x* + 7.299 *z*
Scalar product (C1→C3)·(C1→C2) = -218.083
= C1→C3 X1→X2 cos θ_1 = 339.3704 cos θ_1
cos θ_1 = -0.64261
Tilt angle θ_1 = 130.0°

S7. Measurement of angle of methyl group interface to $a_o b_o$ plane (θ_1) (cont.)

Tridecanoic acid (C_{13}):

	x / Å	*z* / Å
C1	0	0
C2	-5.750	7.948
C3	73.739	0
C4	67.989	7.948
C5	64.928	7.510
X1	14.029	3.756
X2	16.904	-0.219

Vector C1→C3 =+ 73.739 *x* + 0.000 *z*
Vector C1→C2 = – 5.750 *x* + 7.948 *z*
Scalar product (C1→C3)·(C1→C2) = -424.024
= C1→C3 X1→X2 cos θ_1 = 723.5134 cos θ_1
cos θ_1 = -0.58606
Tilt angle θ_1 = 125.9°

Tetradecanoic acid (C_{14}):

	x / Å	*z* / Å
C1	0	0
C2	-5.982	7.285
C3	40.715	0
C4	34.733	7.285
C5	30.809	7.726
X1	15.405	3.863
X2	18.396	0.221

Vector C1→C3 =+ 40.715 *x* + 0.000 *z*
Vector C1→C2 = – 5.982 *x* + 7.285 *z*
Scalar product (C1→C3)·(C1→C2) = -243.560
= C1→C3 X1→X2 cos θ_1 = 383.7769 cos θ_1
cos θ_1 = -0.63464
Tilt angle θ_1 = 129.4°

S7. Measurement of angle of methyl group interface to $a_o b_o$ plane (θ_1) (cont.)

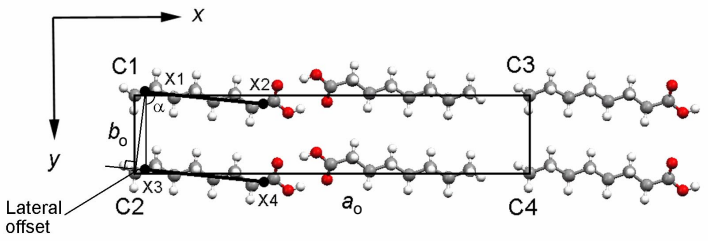
Pentadecanoic acid (C_{15}):

	x / Å	*z* / Å
C1	0	0
C2	-5.616	7.933
C3	84.023	0
C4	78.408	7.933
C5	75.310	7.418
X1	16.649	3.709
X2	19.457	-0.258

Vector C1→C3 =+ 84.023 *x* + 0.000 *z*
Vector C1→C2 = – 5.616 *x* + 7.933 *z*
Scalar product (C1→C3)·(C1→C2) = -471.856
= C1→C3 X1→X2 cos θ_1 = 816.6837 cos θ_1
cos θ_1 = -0.57777
Tilt angle θ_1 = 125.3°

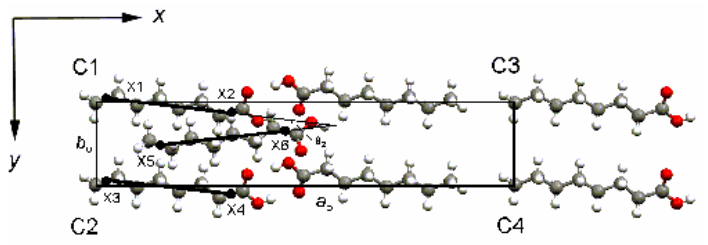
S8. PROJECTION ONTO a_ob_o:

(i) Measurement of lateral offset of acid dimers adjacent along b_o



C1, C2, C3 and C4 define the a_ob_o plane. All coordinates are orthogonal coordinates in ångstroms, projected onto the a_ob_o plane. The direction of propagation of each *n*-alkyl chain is taken as the vector between the centroids of the two terminal C–C bonds. X1→X2 and X3→X4 define adjacent molecules within a given bilayer in the a_ob_o plane. The angle between the vectors X1→X2 and X1→X3 is denoted α, and the lateral offset is then given by X1→X3 cos α.

(ii) Measurement of angle between *n*-alkyl chains projected in a_ob_o plane (θ_2)



C1, C2, C3 and C4 define the a_ob_o plane. All coordinates are orthogonal coordinates in ångstroms, projected onto the a_ob_o plane. The direction of propagation of each *n*-alkyl chain is taken as the vector between the centroids of the two terminal C–C bonds. X1→X2 and X3→X4 define adjacent molecules within a given bilayer in the a_ob_o plane. The angle between the vectors X5→X6 and X1→X2 (θ_2) expresses the rotation of adjacent a_ob_o layers around the c_o direction. In the *C* ' structures of C_7, C_9 and C_{11}, this angle is also the angle between alkyl chains in adjacent bilayers within the herringbone arrangement.

S8. PROJECTION ONTO a_ob_o (cont.)

Hexanoic acid (C_6):

	x / Å	*y* / Å
C1	0	0
C2	0	5.024
C3	20.235	0
C4	20.235	5.024
X1	0.707	-0.195
X2	5.645	0.687
X3	0.707	4.829
X4	5.645	5.711
X5	4.200	2.656
X6	9.138	1.774

Vector X1→X2 =+ 4.938 *x* + 0.882 *y*
Vector X1→X3 = + 0.000 *x* + 5.024 *y*
Scalar product (X1→X2)·(X1→X3) = 4.4312
= X1→X2 X1→X3 cos α = 25.2011 cos α
cos α = 0.175832
Lateral offset = 5.024 cos α = 0.88 Å

Vector X5→X6 = + 4.938 *x* – 0.882 *y*
Scalar product (X1→X2)·(X5→X6) = 23.6059
= X1→X2 X5→X6 cos θ_2 = 25.1618 cos θ_2
cos θ_2 = 0.938165
Angle between alkyl chains, θ_2 = 20.3°

S8. PROJECTION ONTO $a_o b_o$ (cont.)

Heptanoic acid (C_7):

	x / Å	*y* / Å
C1	0	0
C2	0	5.076
C3	42.963	0
C4	42.963	5.076
X1	0.531	-0.469
X2	6.714	-1.757
X3	0.531	4.609
X4	6.714	3.322
X5	15.156	0.783
X6	21.339	2.070

Vector X1→X2 =+ 6.183 *x* + 1.288 *y*
Vector X1→X3 = + 0.000 *x* + 5.076 *y*
Scalar product (X1→X2)·(X1→X3) = 6.5379
= X1→X2 X1→X3 cos α = 32.0586 cos α
cos α = 0.203936
Lateral offset = 5.076 cos α = 1.04 Å

Vector X5→X6 = + 6.183 *x* – 1.287 *y*
Scalar product (X1→X2)·(X5→X6) = 36.5731
= X1→X2 X5→X6 cos θ_2 = 39.8884 cos θ_2
cos θ_2 = 0.916886
Angle between alkyl chains, θ_2 = 23.5°

S8. PROJECTION ONTO $a_o b_o$ (cont.)

Octanoic acid (C_8):

	x / Å	*y* / Å
C1	0	0
C2	0	4.976
C3	25.372	0
C4	25.372	4.976
X1	0.681	-0.247
X2	8.209	0.566
X3	0.681	4.727
X4	8.209	5.540
X5	3.956	2.524
X6	11.484	1.711

Vector X1→X2 =+ 7.528 *x* + 0.813 *y*
Vector X1→X3 = + 0.000 *x* + 4.976 *y*
Scalar product (X1→X2)·(X1→X3) = 4.0497
= X1→X2 X1→X3 cos α = 37.6701 cos α
cos α = 0.107503
Lateral offset = 4.976 cos α = 0.53 Å

Vector X5→X6 = + 7.528 *x* – 0.813 *y*
Scalar product (X1→X2)·(X5→X6) = 56.0098
= X1→X2 X5→X6 cos θ_2 = 57.3318 cos θ_2
cos θ_2 = 0.976941
Angle between alkyl chains, θ_2 = 12.3°

S8. PROJECTION ONTO $a_o b_o$ (cont.)

Nonanoic acid (C_9):

	x / Å	*y* / Å
C1	0	0
C2	0	4.919
C3	53.601	0
C4	53.601	4.919
X1	0.562	0.379
X2	9.309	1.460
X3	0.562	-4.539
X4	9.309	-3.458
X5	3.689	-1.487
X6	12.436	-2.568

Vector X1→X2 =+ 8.747 *x* + 1.081 *y*
Vector X1→X3 = + 0.000 *x* + 4.919 *y*
Scalar product (X1→X2)·(X1→X3) = 5.3224
= X1→X2 X1→X3 cos α = 43.3544 cos α
cos α = 0.122764
Lateral offset = 4.919 cos α = 0.60 Å

Vector X5→X6 = + 8.747 *x* – 1.081 *y*
Scalar product (X1→X2)·(X5→X6) = 75.3414
= X1→X2 X5→X6 cos θ_2 = 77.6786 cos θ_2
cos θ_2 = 0.969912
Angle between alkyl chains, θ_2 = 14.1°

S8. PROJECTION ONTO $a_o b_o$ (cont.)

Decanoic acid (C_{10}):

	x / Å	*y* / Å
C1	0	0
C2	0	4.961
C3	30.470	0
C4	30.470	4.961
X1	0.660	-0.263
X2	10.739	0.433
X3	0.660	4.698
X4	10.739	5.394
X5	3.777	2.352
X6	13.856	1.656

Vector X1→X2 =+ 10.079 *x* + 0.696 *y*
Vector X1→X3 = + 0.000 *x* + 4.961 *y*
Scalar product (X1→X2)·(X1→X3) = 3.4536
= X1→X2 X1→X3 cos α = 50.1311 cos α
cos α = 0.06889
Lateral offset = 4.961 cos α = 0.34 Å

Vector X5→X6 = + 10.079 *x* – 0.696 *y*
Scalar product (X1→X2)·(X5→X6) = 101.1018
= X1→X2 X5→X6 cos θ_2 = 102.0707 cos θ_2
cos θ_2 = 0.990508
Angle between alkyl chains, θ_2 = 7.9°

S8. PROJECTION ONTO $a_o b_o$ (cont.)

Undecanoic acid (C_{11}):

	x / Å	*y* / Å
C1	0	0
C2	0	4.912
C3	63.739	0
C4	63.739	4.912
X1	0.578	0.319
X2	11.838	1.194
X3	0.578	-4.593
X4	11.838	-3.719
X5	3.581	-1.876
X6	14.841	-2.750

Vector X1→X2 =+ 11.260 *x* + 0.875 *y*
Vector X1→X3 = + 0.000 *x* + 4.912 *y*
Scalar product (X1→X2)·(X1→X3) = 4.2931
= X1→X2 X1→X3 cos α = 55.4755 cos α
cos α = 0.077387
Lateral offset = 4.912 cos α = 0.38 Å

Vector X5→X6 = + 11.260 *x* – 0.875 *y*
Scalar product (X1→X2)·(X5→X6) = 126.0220
= X1→X2 X5→X6 cos θ_2 = 127.5532 cos θ_2
cos θ_2 = 0.987996
Angle between alkyl chains, θ_2 = 8.9°

S8. PROJECTION ONTO $a_o b_o$ (cont.)

Dodecanoic acid (C_{12}):

	x / Å	*y* / Å
C1	0	0
C2	0	4.963
C3	35.626	0
C4	35.626	4.963
X1	0.659	-0.278
X2	13.310	0.400
X3	0.659	4.685
X4	13.310	5.363
X5	3.720	2.268
X6	16.371	1.590

Vector X1→X2 =+ 12.651 *x* + 0.678 *y*
Vector X1→X3 = + 0.000 *x* + 4.963 *y*
Scalar product (X1→X2)·(X1→X3) = 3.3599
= X1→X2 X1→X3 cos α = 62.8768 cos α
cos α = 0.05344
Lateral offset = 4.963 cos α = 0.27 Å

Vector X5→X6 = + 12.651 *x* – 0.678 *y*
Scalar product (X1→X2)·(X5→X6)
= 159.5881 = X1→X2 X5→X6 cos θ_2 = 160.5075 cos θ_2
cos θ_2 = 0.994272
Angle between alkyl chains, θ_2 = 6.1°

S8. PROJECTION ONTO $a_o b_o$ (cont.)

Tridecanoic acid (C_{13}):

	x / Å	*y* / Å
C1	0	0
C2	0	4.943
C3	73.739	0
C4	73.739	4.943
X1	0.602	0.288
X2	14.418	0.931
X3	0.602	-4.654
X4	14.418	-4.011
X5	3.477	-2.269
X6	17.293	-2.912

Vector X1→X2 =+ 13.816 *x* + 0.643 *y*
Vector X1→X3 = + 0.000 *x* + 4.943 *y*
Scalar product (X1→X2)·(X1→X3) = 3.17835
= X1→X2 X1→X3 cos α = 68.36641 cos α
cos α = 0.04649
Lateral offset = 4.943 cos α = 0.23 Å

Vector X5→X6 = + 13.816 *x* – 0.643 *y*
Scalar product (X1→X2)·(X5→X6) = 190.4684
= X1→X2 X5→X6 cos θ_2 = 191.2953 cos θ_2
cos θ_2 = 0.995677
Angle between alkyl chains, θ_2 = 5.3°

S8. PROJECTION ONTO $a_o b_o$ (cont.)

Tetradecanoic acid (C_{14}):

	x / Å	*y* / Å
C1	0	0
C2	0	4.965
C3	40.715	0
C4	40.715	4.965
X1	0.653	-0.277
X2	15.856	0.357
X3	0.653	4.688
X4	15.856	5.322
X5	3.644	2.225
X6	18.847	1.591

Vector X1→X2 =+ 15.203 *x* + 0.634 *y*
Vector X1→X3 = + 0.000 *x* + 4.965 *y*
Scalar product (X1→X2)·(X1→X3) = 3.1428
= X1→X2 X1→X3 cos α = 75.5433 cos α
cos α = 0.04160
Lateral offset = 4.965 cos α = 0.21 Å

Vector X5→X6 = + 15.203 *x* – 0.634 *y*
Scalar product (X1→X2)·(X5→X6) = 230.7293
= X1→X2 X5→X6 cos θ_2 = 231.5332 cos θ_2
cos θ_2 = 0.996504
Angle between alkyl chains, θ_2 = 4.8°

S8. PROJECTION ONTO $a_o b_o$ (cont.)

Pentadecanoic acid (C_{15}):

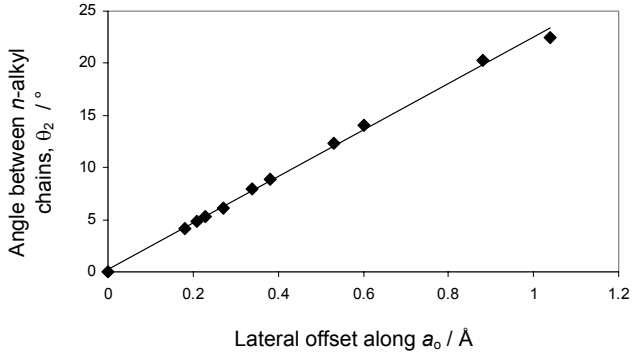
	x / Å	*y* / Å
C1	0	0
C2	0	4.956
C3	84.023	0
C4	84.023	4.956
X1	0.603	0.260
X2	16.984	0.857
X3	0.603	-4.696
X4	16.984	-4.099
X5	-2.205	-2.353
X6	14.176	-2.950

Vector X1→X2 =+ 16.381 *x* + 0.597 *y*
Vector X1→X3 = + 0.000 *x* + 4.956 *y*
Scalar product (X1→X2)·(X1→X3) = 2.96369
= X1→X2 X1→X3 cos α = 81.24327 cos α
cos α = 0.03648
Lateral offset = 4.956 cos α = 0.18 Å

Vector X5→X6 = + 16.381 *x* – 0.597 *y*
Scalar product (X1→X2)·(X5→X6) = 267.9808
= X1→X2 X5→X6 cos θ_2 = 268.6936 cos θ_2
cos θ_2 = 0.997347
Angle between alkyl chains, θ_2 = 4.2°

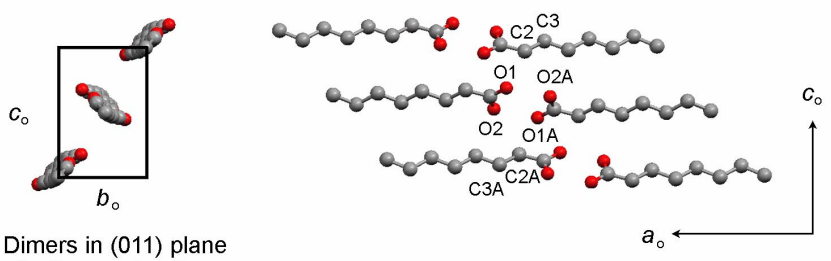
S8. PROJECTION ONTO $a_o b_o$ (cont.)

(iii) Correlation between the lateral offset in the $a_o b_o$ plane and θ_2



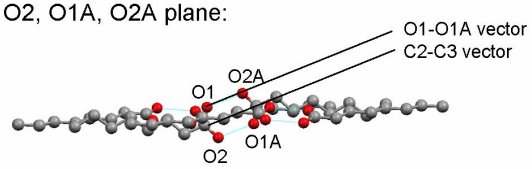
S9. Alignment of C_β–C_γ bond vectors relative to carboxyl groups in adjacent $a_o b_o$ planes

The plane of the carboxyl groups is defined by the four oxygen atoms of the two acid molecules that comprise a dimer (O1, O2, O1A, O2A). The atoms C2 and C3 (*i.e.* C_β and C_γ, respectively) are then considered in adjacent acid molecules. All atoms are projected onto the plane of the carboxyl group, and listed as orthogonal coordinates in ångstroms. The vectors O1→O2A and O2→O1A always parallel (they are related by center of inversion in the carboxyl group plane). The C-C bonds above and below plane are always parallel also (related by lattice translation along *b* and *c*). Thus, the relative alignment of the adjacent acid dimers is specified by a single angle between the vectors O1→O2A and C2→C3.



Dimers in (011) plane of orthogonal cell

Projection onto O1, O2, O1A, O2A plane:



S9. Alignment of C_β–C_γ bond vectors relative to carboxyl groups in adjacent $a_o b_o$ planes (cont.)

Hexanoic acid (C_6):

	x / Å	*y* / Å
O1	0	0
O2	2.191	0.367
O1A	1.885	2.993
O2A	-0.306	2.626
C2	0.541	1.338
C3	0.415	2.515
C2A	1.343	1.655
C3A	1.469	0.479

Vector O1→O2A = – 0.306 *x* + 2.626 *y*
Vector C2→C3 = – 0.126 *x* + 1.177 *y*
Scalar product (O1→O2A).(C2→C3) = 3.129
= O1→O2A C2→C3 cos θ = 3.129 cos θ
***i.e.* cos θ = 1. Vectors are parallel**

Heptanoic acid (C_7):

	x / Å	*y* / Å
O1	0	0
O2	2.167	0.468
O1A	1.778	3.083
O2A	-0.388	2.615
C2	0.624	1.260
C3	0.519	2.483
C2A	1.154	1.823
C3A	1.259	0.600

Vector O1→O2A = – 0.388 *x* + 2.615 *y*
Vector C2→C3 = – 0.105 *x* + 1.223 *y*
Scalar product (O1→O2A).(C2→C3) = 3.239
= O1→O2A C2→C3 cos θ = 3.245 cos θ
Angle between vectors = 3.5°

S9. Alignment of C_β–C_γ bond vectors relative to carboxyl groups in adjacent $a_o b_o$ planes (cont.)

Octanoic acid (C_8):

	x / Å	*y* / Å
O1	0	0
O2	2.224	-0.071
O1A	2.284	2.566
O2A	0.060	2.636
C2	0.773	1.291
C3	0.738	0.114
C2A	1.511	1.274
C3A	1.546	2.452

Vector O1→O2A =+ 0.060 *x* + 2.636 *y*
Vector C2→C3 = – 0.035 *x* – 1.177 *y*
Scalar product (O1→O2A).(C2→C3) = – 3.105
= O1→O2A C2→C3 cos θ = 3.105 cos θ
i.e. **cos θ = –1. Vectors are parallel**

Nonanoic acid (C_9):

	x / Å	*y* / Å
O1	0	0
O2	2.197	0.323
O1A	1.928	2.955
O2A	-0.270	2.632
C2	1.505	1.724
C3	1.599	0.486
C2A	0.423	1.231
C3A	0.329	2.468

Vector O1→O2A =– 0.270 *x* + 2.632 *y*
Vector C2→C3 = + 0.094 *x* – 1.238 *y*
Scalar product (O1→O2A).(C2→C3) = – 3.284
= O1→O2A C2→C3 cos θ = 3.285 cos θ
Angle between vectors = 1.5°

S9. Alignment of C_β–C_γ bond vectors relative to carboxyl groups in adjacent $a_o b_o$ planes (cont.)

Decanoic acid (C_{10}):

	x / Å	*y* / Å
O1	0	0
O2	2.217	-0.155
O1A	2.348	2.470
O2A	0.131	2.625
C2	1.508	1.118
C3	1.456	-0.037
C2A	0.840	1.352
C3A	0.892	2.507

Vector O1→O2A =+ 0.131 *x* + 2.625 *y*
Vector C2→C3 = – 0.052 *x* – 1.155 *y*
Scalar product (O1→O2A).(C2→C3) = – 3.039
= O1→O2A C2→C3 cos θ = 3.039 cos θ
i.e. **cos θ = –1. Vectors are parallel**

Undecanoic acid (C_{11}):

	x / Å	*y* / Å
O1	0	0
O2	2.209	0.215
O1A	2.029	2.858
O2A	-0.180	2.643
C2	1.568	1.593
C3	1.622	0.366
C2A	0.461	1.265
C3A	0.407	2.493

Vector O1→O2A =– 0.180 *x* + 2.643 *y*
Vector C2→C3 = + 0.054 *x* – 1.227 *y*
Scalar product (O1→O2A).(C2→C3) = – 3.253
= O1→O2A C2→C3 cos θ = 3.254 cos θ
Angle between vectors = 1.4°

S9. Alignment of C_β–C_γ bond vectors relative to carboxyl groups in adjacent $a_o b_o$ planes (cont.)

Dodecanoic acid (C_{12}):

	x / Å	*y* / Å
O1	0	0
O2	2.213	0.176
O1A	2.065	2.801
O2A	-0.148	2.625
C2	0.652	1.296
C3	0.713	0.132
C2A	1.413	1.505
C3A	1.352	2.670

Vector O1→O2A =– 0.148 *x* + 2.625 *y*
Vector C2→C3 = + 0.061 *x* – 1.164 *y*
Scalar product (O1→O2A).(C2→C3) = – 3.064
= O1→O2A C2→C3 cos θ = 3.064 cos θ
i.e. **cos θ = –1. Vectors are parallel**

Tridecanoic acid (C_{13}):

	x / Å	*y* / Å
O1	0	0
O2	2.214	0.107
O1A	2.124	2.736
O2A	-0.090	2.628
C2	0.601	1.325
C3	0.585	2.513
C2A	1.523	1.411
C3A	1.539	0.223

Vector O1→O2A =– 0.090 *x* + 2.628 *y*
Vector C2→C3 = – 0.016 *x* + 1.188 *y*
Scalar product (O1→O2A).(C2→C3) = 3.1235
= O1→O2A C2→C3 cos θ = 3.1242 cos θ
Angle between vectors = 1.2°

S9. Alignment of C_β–C_γ bond vectors relative to carboxyl groups in adjacent $a_o b_o$ planes (cont.)

Tetradecanoic acid (C_{14}):

	x / Å	*y* / Å
O1	0	0
O2	2.218	-0.180
O1A	2.370	2.441
O2A	0.152	2.622
C2	1.536	1.054
C3	1.467	-0.107
C2A	0.834	1.388
C3A	0.903	2.549

Vector O1→O2A =+ 0.152 *x* + 2.622 *y*
Vector C2→C3 = – 0.069 *x* – 1.161 *y*
Scalar product (O1→O2A).(C2→C3) = – 3.055
= O1→O2A C2→C3 cos θ = 3.055 cos θ
i.e. **cos θ = –1. Vectors are parallel**

Pentadecanoic acid (C_{15}):

	x / Å	*y* / Å
O1	0	0
O2	2.219	-0.040
O1A	2.252	2.593
O2A	0.034	2.633
C2	0.716	1.282
C3	0.710	0.082
C2A	1.537	1.311
C3A	1.543	2.511

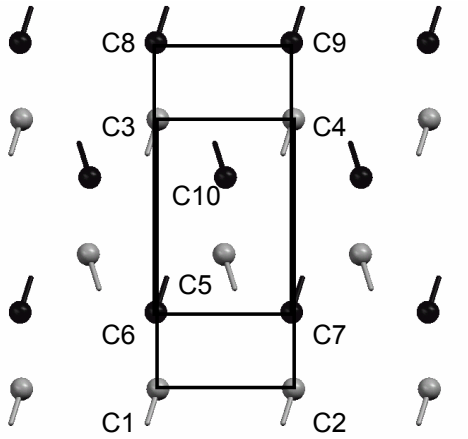
Vector O1→O2A =+ 0.034 *x* + 2.633 *y*
Vector C2→C3 = – 0.006 *x* – 1.200 *y*
Scalar product (O1→O2A).(C2→C3) = – 3.1598
= O1→O2A C2→C3 cos θ = 3.1599 cos θ
Angle between vectors = 0.4°

S10. Projection of the terminal C–C bond vectors onto the methyl group interface (the *bc* plane) (cont.)

Hexanoic acid (C_6):

	x / Å	*y* / Å	*z* / Å
C1	0	0	0
C2	0	5.0236	0
C3	0	0	9.943
C4	0	5.0236	9.943
C5	0	2.461	4.971
C6	-2.608	-0.051	2.835
C7	-2.608	4.973	2.835
C8	-2.608	-0.051	12.778
C9	-2.608	4.973	12.778
C10	-2.608	2.512	7.807
C1A	0.744	-0.390	-1.257
C2A	0.744	4.634	-1.257
C3A	0.744	-0.390	8.685
C4A	0.744	4.637	8.685
C5A	0.744	2.851	3.714
C6A	-3.353	0.339	4.093
C7A	-3.353	5.363	4.093
C8A	-3.353	0.339	14.035
C9A	-3.353	5.363	14.035
C10A	-3.353	2.122	9.064

[Fractional y coordinate = 0.490]



Origin shift in ångstroms in *bc* plane = C1→C6 = – 0.051 *y* + 2.835 *z*
bc cell = 5.0236 Å x 9.943 Å
Thus, origin shift in FRACTIONAL coordinates in the *bc* plane = (– 0.010, 0.285)

Magnitude of C1→C1A vector projected in *bc* plane = C1→C1A
= (– 0.390 *y* – 1.257 *z*) = **1.316 Å**

C–C vectors projected in *bc* plane: C1→C1A = – 0.390 *y* – 1.257 *z*
C5→C5A = + 0.390 *y* – 1.257 *z*
Scalar product (C1→C1A).(C5→C5A) = 1.4279 = C1→C1A C5→C5A $\cos \phi_1$
Thus, angle between C–C bond vectors projected in *bc* plane (ϕ_1) = 34.5°

Scalar product (C1→C1A).$(C1\rightarrow C1A)_{proj}$ = 1.7321
= C1→C1A $(C1\rightarrow C1A)_{proj}$ $\cos \phi_2$
Thus, angle between C–C bond vectors and *bc* plane (ϕ_2) = 29.5°

Volume of parallelpiped defined by C1→C2, C1→C3 and C1→C6 =
Magnitude of scalar triple product (C1→C6).[(C1→C2)×(C1→C3)]
= V_{Me}**(1) = 130.3 Å^3**

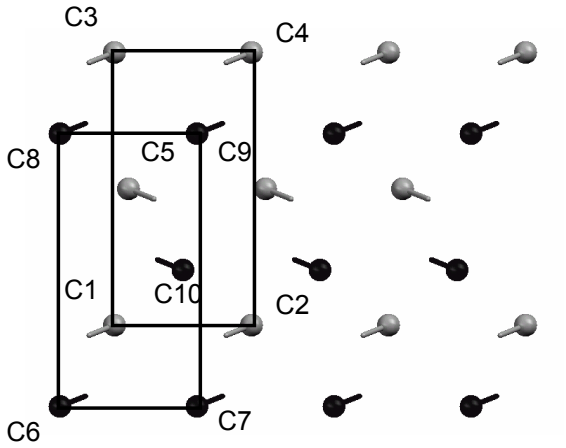
Volume of parallelpiped defined by C1A→C2A, C1A→C3A and C1A→C6A =
Magnitude of scalar triple product (C1A→C6A).[(C1A→C2A)×(C1A→C3A)]
= V_{Me}**(2) = 204.6 Å^3**

S10. Projection of the terminal C–C bond vectors onto the methyl group interface (the *bc* plane) (cont.)

Heptanoic acid (C_7):

	x / Å	*y* / Å	*z* / Å
C1	0	0	0
C2	0	5.079	0
C3	0	0	10.164
C4	0	5.079	10.164
C5	0	0.527	5.082
C6	-2.217	-2.013	-3.032
C7	-2.217	3.066	-3.032
C8	-2.217	-2.012	7.132
C9	-2.217	3.067	7.132
C10	-2.217	2.540	2.050
C1A	1.093	-0.939	-0.375
C2A	1.093	4.140	-0.375
C3A	1.093	-0.939	9.789
C4A	1.093	4.140	9.789
C5A	1.093	1.467	4.706
C6A	-3.310	-1.072	-2.656
C7A	-3.310	4.007	-2.656
C8A	-3.310	-1.072	7.508
C9A	-3.310	4.007	7.508
C10A	-3.310	1.600	2.425

[Fractional y coordinate = 0.104]



Origin shift in ångstroms in *bc* plane = C1→C6 = – 2.013 *y* – 3.032 *z*
bc cell = 5.079 Å x 10.164 Å
Thus, origin shift in FRACTIONAL coordinates in the *bc* plane = (– 0.396, – 0.298)

Magnitude of C1→C1A vector projected in *bc* plane = C1→C1A
= (– 0.939 *y* – 0.375 *z*) = **1.011 Å**

C–C vectors projected in *bc* plane: C1→C1A = – 0.939 *y* – 0.375 *z*
C5→C5A = + 0.939 *y* – 0.375 *z*
Scalar product (C1→C1A).(C5→C5A) = – 0.7417 = C1→C1A C5→C5A $\cos \phi_1$
Thus, angle between C–C bond vectors projected in *bc* plane (ϕ_1) = 136.4 = 43.6°

Scalar product (C1→C1A).(C1→C1A)$_{proj}$ = 1.0223
= C1→C1A (C1→C1A)$_{proj}$ $\cos \phi_2$
Thus, angle between C–C bond vectors and *bc* plane (ϕ_2) = 47.2°

Volume of parallelpiped defined by C1→C2, C1→C3 and C1→C6 =
Magnitude of scalar triple product (C1→C6).[(C1→C2)×(C1→C3)]
= V_{Me}**(1) = 114.4 Å^3**

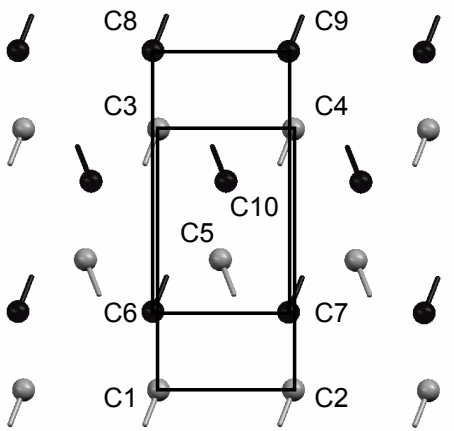
Volume of parallelpiped defined by C1A→C2A, C1A→C3A and C1A→C6A =
Magnitude of scalar triple product (C1A→C6A).[(C1A→C2A)×(C1A→C3A)]
= V_{Me}**(2) = 227.3 Å^3**

S10. Projection of the terminal C–C bond vectors onto the methyl group interface (the *bc* plane) (cont.)

Octanoic acid (C_8):

	x / Å	*y* / Å	*z* / Å
C1	0	0	0
C2	0	4.9756	0
C3	0	0	9.574
C4	0	4.9756	9.574
C5	0	2.281	4.787
C6	-2.616	-0.207	2.880
C7	-2.616	4.769	2.880
C8	-2.616	-0.206	12.454
C9	-2.616	4.769	12.454
C10	-2.616	2.488	7.666
C1A	0.667	-0.498	-1.262
C2A	0.667	4.477	-1.263
C3A	0.667	-0.498	8.312
C4A	0.667	4.478	8.312
C5A	0.667	2.779	3.524
C6A	-3.283	0.291	4.142
C7A	-3.283	5.267	4.142
C8A	-3.283	0.292	13.716
C9A	-3.283	5.267	13.716
C10A	-3.283	1.990	8.929

[Fractional y coordinate = 0.458]



Origin shift in ångstroms in *bc* plane = C1→C6 = – 0.207 *y* + 2.880 *z*
bc cell = 4.9756 Å x 9.574 Å
Thus, origin shift in FRACTIONAL coordinates in the *bc* plane = (– 0.042, 0.301)

Magnitude of C1→C1A vector projected in *bc* plane = C1→C1A
= (– 0.498 *y* – 1.262 *z*) = **1.357 Å**

C–C vectors projected in *bc* plane: C1→C1A = – 0.498 *y* – 1.262 *z*
C5→C5A = + 0.497 *y* – 1.262 *z*
Scalar product (C1→C1A).(C5→C5A) = 1.3459 = C1→C1A C5→C5A $\cos\phi_1$
Thus, angle between C–C bond vectors projected in *bc* plane (ϕ_1) = 43.1°

Scalar product (C1→C1A).$(C1\rightarrow C1A)_{proj}$ = 1.8406
= C1→C1A $(C1\rightarrow C1A)_{proj}$ $\cos\phi_2$
Thus, angle between C–C bond vectors and *bc* plane (ϕ_2) = 26.2°

Volume of parallelpiped defined by C1→C2, C1→C3 and C1→C6 =
Magnitude of scalar triple product (C1→C6).[(C1→C2)×(C1→C3)]
= V_{Me}**(1) = 124.6 Å^3**

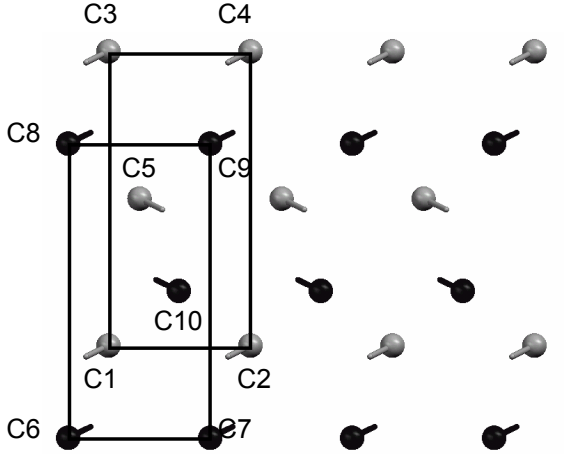
Volume of parallelpiped defined by C1A→C2A, C1A→C3A and C1A→C6A =
Magnitude of scalar triple product (C1A→C6A).[(C1A→C2A)×(C1A→C3A)]
= V_{Me}**(2) = 188.1 Å^3**

S10. Projection of the terminal C–C bond vectors onto the methyl group interface (the *bc* plane) (cont.)

Nonanoic acid (C_9):

	x / Å	*y* / Å	*z* / Å
C1	0	0	0
C2	0	4.9188	0
C3	0	0	10.118
C4	0	4.9188	10.118
C5	0	1.107	5.059
C6	-2.614	-1.352	-3.187
C7	-2.614	3.567	-3.187
C8	-2.614	-1.352	6.931
C9	-2.614	3.567	6.931
C10	-2.614	2.459	1.872
C1A	1.127	-0.759	-0.386
C2A	1.127	4.160	-0.386
C3A	1.127	-0.759	9.732
C4A	1.127	4.160	9.732
C5A	1.127	1.866	4.673
C6A	-3.740	-0.593	-2.800
C7A	-3.740	4.326	-2.800
C8A	-3.740	-0.593	7.317
C9A	-3.740	4.325	7.317
C10A	-3.740	1.701	2.258

[Fractional y coordinate = 0.225]



Origin shift in ångstroms in *bc* plane = C1→C6 = – 1.352 *y* – 3.187 *z*
bc cell = 4.9188 Å x 10.118 Å
Thus, origin shift in FRACTIONAL coordinates in the *bc* plane = (– 0.275, – 0.315)

Magnitude of C1→C1A vector projected in *bc* plane = C1→C1A
= (– 0.759 *y* – 0.386 *z*) = **0.852 Å**

C–C vectors projected in *bc* plane: C1→C1A = – 0.759 *y* – 0.386 *z*
C5→C5A = + 0.759 *y* – 0.386 *z*
Scalar product (C1→C1A).(C5→C5A) = – 0.4271 = C1→C1A C5→C5A $\cos \phi_1$
Thus, angle between C–C bond vectors projected in *bc* plane (ϕ_1) = 126.1° = 53.9°

Scalar product (C1→C1A).(C1→C1A)$_{proj}$ = 0.7251
= C1→C1A (C1→C1A)$_{proj}$ $\cos \phi_2$
Thus, angle between C–C bond vectors and *bc* plane (ϕ_2) = 52.9°

Volume of parallelpiped defined by C1→C2, C1→C3 and C1→C6 =
Magnitude of scalar triple product (C1→C6).[(C1→C2)×(C1→C3)]
= V_{Me}**(1) = 130.1 Å^3**

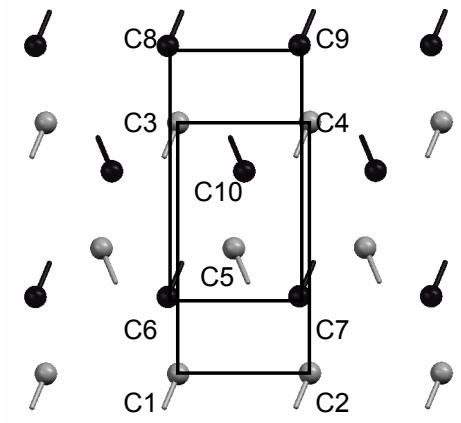
Volume of parallelpiped defined by C1A→C2A, C1A→C3A and C1A→C6A =
Magnitude of scalar triple product (C1A→C6A).[(C1A→C2A)×(C1A→C3A)]
= V_{Me}**(2) = 242.2 Å^3**

S10. Projection of the terminal C–C bond vectors onto the methyl group interface (the *bc* plane) (cont.)

Decanoic acid (C_{10}):

	x / Å	*y* / Å	*z* / Å
C1	0	0	0
C2	0	4.9612	0
C3	0	0	9.398
C4	0	4.9612	9.398
C5	0	2.089	4.699
C6	-2.670	-0.391	2.882
C7	-2.670	4.570	2.882
C8	-2.670	-0.392	12.280
C9	-2.670	4.569	12.280
C10	-2.670	2.480	7.581
C1A	0.653	-0.525	-1.254
C2A	0.653	4.436	-1.253
C3A	0.653	-0.526	8.144
C4A	0.653	4.436	8.144
C5A	0.653	2.614	3.445
C6A	-3.323	0.134	4.136
C7A	-3.323	5.095	4.136
C8A	-3.323	0.133	13.533
C9A	-3.323	5.094	13.533
C10A	-3.323	1.955	8.834

[Fractional y coordinate = 0.421]



Origin shift in ångstroms in *bc* plane = C1→C6 = – 0.391 *y* + 2.882 *z*
bc cell = 4.9612 Å x 9.398 Å
Thus, origin shift in FRACTIONAL coordinates in the *bc* plane = (– 0.079, 0.307)

Magnitude of C1→C1A vector projected in *bc* plane = C1→C1A
= (– 0.525 *y* – 1.254 *z*) = **1.359 Å**

C–C vectors projected in *bc* plane: C1→C1A = – 0.525 *y* – 1.254 *z*
C5→C5A = + 0.525 *y* – 1.254 *z*
Scalar product (C1→C1A).(C5→C5A) = 1.2969 = C1→C1A C5→C5A cos ϕ_1
Thus, angle between C–C bond vectors projected in *bc* plane (ϕ_1) = 45.4°

Scalar product (C1→C1A).(C1→C1A)$_{proj}$ = 1.8475
= C1→C1A (C1→C1A)$_{proj}$ cosϕ_2
Thus, angle between C–C bond vectors and *bc* plane (ϕ_2) = 25.7°

Volume of parallelpiped defined by C1→C2, C1→C3 and C1→C6 =
Magnitude of scalar triple product (C1→C6).[(C1→C2)×(C1→C3)]
= V_{Me}**(1)= 124.5 Å^3**

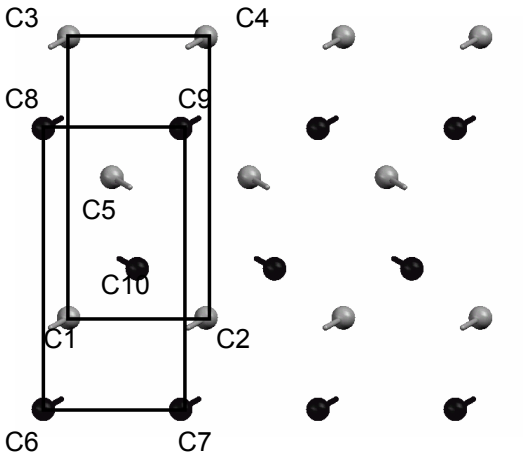
Volume of parallelpiped defined by C1A→C2A, C1A→C3A and C1A→C6A =
Magnitude of scalar triple product (C1A→C6A).[(C1A→C2A)×(C1A→C3A)]
= V_{Me}**(2)= 185.4 Å^3**

S10. Projection of the terminal C–C bond vectors onto the methyl group interface (the *bc* plane) (cont.)

Undecanoic acid (C_{11}):

	x / Å	*y* / Å	*z* / Å
C1	0	0	0
C2	0	4.9123	0
C3	0	0	10.029
C4	0	4.9123	10.029
C5	0	1.556	5.014
C6	-2.702	-0.899	-3.270
C7	-2.702	4.013	-3.270
C8	-2.702	-0.890	6.758
C9	-2.702	4.012	6.758
C10	-2.702	2.456	1.744
C1A	1.175	-0.638	-0.358
C2A	1.175	4.275	-0.358
C3A	1.175	-0.638	9.670
C4A	1.175	4.274	9.670
C5A	1.175	2.194	4.656
C6A	-3.877	-0.262	-2.912
C7A	-3.877	4.651	-2.912
C8A	-3.877	-0.262	7.117
C9A	-3.877	4.650	7.117
C10A	-3.877	1.818	2.103

[Fractional y coordinate = 0.317]



Origin shift in ångstroms in *bc* plane = C1→C6 = – 0.899 *y* – 3.270 *z*
bc cell = 4.9123 Å x 10.029 Å
Thus, origin shift in FRACTIONAL coordinates in the *bc* plane = (– 0.183, – 0.326)

Magnitude of C1→C1A vector projected in *bc* plane = C1→C1A
= (– 0.638 *y* – 0.358 *z*) = **0.732 Å**

C–C vectors projected in *bc* plane: C1→C1A = – 0.638 *y* –0.358 *z*
C5→C5A = + 0.638 *y* – 0.358 *z*
Scalar product (C1→C1A).(C5→C5A) = –0.2789 = C1→C1A C5→C5A cos ϕ_1
Thus, angle between C–C bond vectors projected in *bc* plane (ϕ_1) = 121.4° = 58.6°

Scalar product (C1→C1A).(C1→C1A)$_{proj}$ = 0.5352
= C1→C1A (C1→C1A)$_{proj}$ cos ϕ_2
Thus, angle between C–C bond vectors and *bc* plane (ϕ_2) = 58.1°

Volume of parallelpiped defined by C1→C2, C1→C3 and C1→C6 =
Magnitude of scalar triple product (C1→C6).[(C1→C2)×(C1→C3)]
= V_{Me}**(1) = 133.1 Å^3**

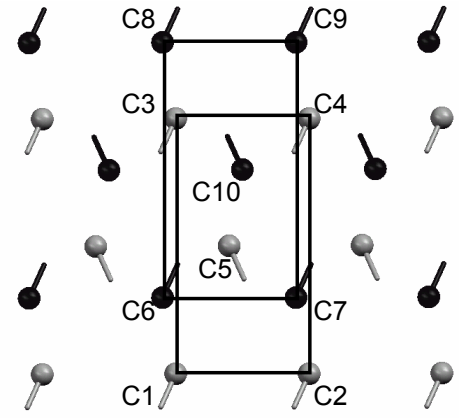
Volume of parallelpiped defined by C1A→C2A, C1A→C3A and C1A→C6A =
Magnitude of scalar triple product (C1A→C6A).[(C1A→C2A)×(C1A→C3A)]
= V_{Me}**(2) = 248.9 Å^3**

S10. Projection of the terminal C–C bond vectors onto the methyl group interface (the *bc* plane) (cont.)

Dodecanoic acid (C_{12}):

	x / Å	*y* / Å	*z* / Å
C1	0	0	0
C2	0	4.9627	0
C3	0	0	9.527
C4	0	4.9627	9.527
C5	0	1.990	4.763
C6	-2.752	-0.491	2.835
C7	-2.752	4.471	2.835
C8	-2.752	-0.492	12.361
C9	-2.752	4.471	12.361
C10	-2.752	1.926	8.828
C1A	0.688	-0.555	-1.230
C2A	0.688	4.408	-1.230
C3A	0.688	-0.556	8.297
C4A	0.688	4.407	8.297
C5A	0.688	2.545	3.533
C6A	-3.441	0.064	4.065
C7A	-3.441	5.026	4.065
C8A	-3.441	0.063	13.591
C9A	-3.441	5.026	13.591
C10A	-3.441	2.479	9.082

[Fractional y coordinate = 0.401]



Origin shift in ångstroms in *bc* plane = C1→C6 = – 0.491 *y* + 2.835 *z*
bc cell = 4.9627 Å x 9.527 Å
Thus, origin shift in FRACTIONAL coordinates in the *bc* plane = (– 0.099, 0.298)

Magnitude of C1→C1A vector projected in *bc* plane = C1→C1A
= (– 0.555 *y* – 1.230 *z*) = **1.349 Å**

C–C vectors projected in *bc* plane: C1→C1A = – 0.555 *y* – 1.230 *z*
C5→C5A = + 0.555 *y* – 1.230 *z*
Scalar product (C1→C1A).(C5→C5A) = 1.2049 = C1→C1A C5→C5A cos ϕ_1
Thus, angle between C–C bond vectors projected in *bc* plane (ϕ_1) = 48.6°

Scalar product (C1→C1A).(C1→C1A)$_{proj}$ = 1.8209
= C1→C1A (C1→C1A)$_{proj}$ cosϕ_2
Thus, angle between C–C bond vectors and *bc* plane (ϕ_2) = 27.0°

Volume of parallelpiped defined by C1→C2, C1→C3 and C1→C6 =
Magnitude of scalar triple product (C1→C6).[(C1→C2)×(C1→C3)]
= V_{Me}**(1) = 130.1 Å^3**

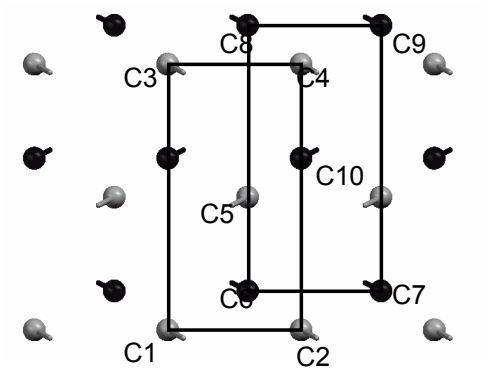
Volume of parallelpiped defined by C1A→C2A, C1A→C3A and C1A→C6A =
Magnitude of scalar triple product (C1A→C6A).[(C1A→C2A)×(C1A→C3A)]
= V_{Me}**(2) = 195.2 Å^3**

S10. Projection of the terminal C–C bond vectors onto the methyl group interface (the *bc* plane) (cont.)

Tridecanoic acid (C_{13}):

	x / Å	*y* / Å	*z* / Å
C1	0	0	0
C2	0	4.9425	0
C3	0	0	9.812
C4	0	4.9425	9.812
C5	0	2.962	4.906
C6	-2.737	2.962	1.439
C7	-2.737	6.905	1.439
C8	-2.737	2.962	11.250
C9	-2.737	6.905	11.250
C10	-2.737	4.943	6.344
C1A	1.268	0.577	-0.302
C2A	1.268	5.520	-0.302
C3A	1.268	0.577	9.510
C4A	1.268	5.520	9.510
C5A	1.268	2.385	4.604
C6A	-4.005	2.385	1.740
C7A	-4.005	7.328	1.740
C8A	-4.005	2.385	11.552
C9A	-4.005	7.328	11.552
C10A	-4.005	5.520	6.646

[Fractional y coordinate = 0.599]



Origin shift in ångstroms in *bc* plane = C1→C6 = + 2.962 *y* + 1.439 *z*
bc cell = 4.9425 Å x 9.812 Å
Thus, origin shift in FRACTIONAL coordinates in the *bc* plane = (0.599, 0.147)

Magnitude of C1→C1A vector projected in *bc* plane = C1→C1A
= (+ 0.577 *y* – 0.302 *z*) = **0.651 Å**

C–C vectors projected in *bc* plane: C1→C1A = + 0.577 *y* – 0.302 *z*
C5→C5A = – 0.577 *y* – 0.302 *z*
Scalar product (C1→C1A).(C5→C5A) = – 0.2417 = C1→C1A C5→C5A $\cos \phi_1$
Thus, angle between C–C bond vectors projected in *bc* plane (ϕ_1) = 124.8° = 55.2°

Scalar product (C1→C1A).$(C1\rightarrow C1A)_{proj}$ = 0.4241
= C1→C1A $(C1\rightarrow C1A)_{proj}$ $\cos \phi_2$
Thus, angle between C–C bond vectors and *bc* plane (ϕ_2) = 62.8°

Volume of parallelpiped defined by C1→C2, C1→C3 and C1→C6 =
Magnitude of scalar triple product (C1→C6).[(C1→C2)×(C1→C3)]
= V_{Me}**(1) = 132.7 Å^3**

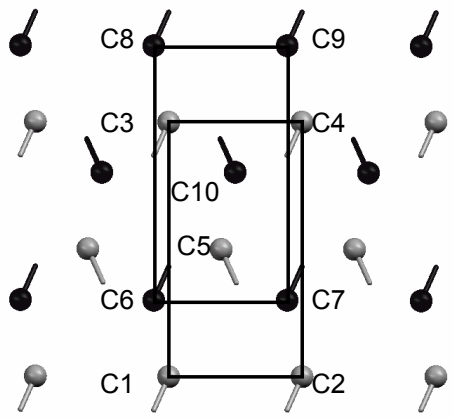
Volume of parallelpiped defined by C1A→C2A, C1A→C3A and C1A→C6A =
Magnitude of scalar triple product (C1A→C6A).[(C1A→C2A)×(C1A→C3A)]
= V_{Me}**(2) = 255.7 Å^3**

S10. Projection of the terminal C–C bond vectors onto the methyl group interface (the *bc* plane) (cont.)

Tetradecanoic acid (C_{14}):

	x / Å	*y* / Å	*z* / Å
C1	0	0	0
C2	0	4.9652	0
C3	0	0	9.426
C4	0	4.9652	9.426
C5	0	1.947	4.713
C6	-2.752	-0.535	2.831
C7	-2.752	4.430	2.831
C8	-2.752	-0.536	12.257
C9	-2.752	4.430	12.257
C10	-2.752	2.482	7.544
C1A	0.677	-0.555	-1.235
C2A	0.677	4.410	-1.235
C3A	0.677	-0.555	8.191
C4A	0.677	4.410	8.191
C5A	0.677	2.502	3.478
C6A	-3.429	0.020	4.067
C7A	-3.429	4.985	4.067
C8A	-3.429	0.019	13.493
C9A	-3.429	4.984	13.493
C10A	-3.429	1.927	8.779

[Fractional y coordinate = 0.392]



Origin shift in ångstroms in *bc* plane = C1→C6 = – 0.535 *y* + 2.831 *z*
bc cell = 4.9652 Å x 9.426 Å
Thus, origin shift in FRACTIONAL coordinates in the *bc* plane = (– 0.108, 0.300)

Magnitude of C1→C1A vector projected in *bc* plane = C1→C1A
= (– 0.555 *y* – 1.235 *z*) = **1.354 Å**

C–C vectors projected in *bc* plane: C1→C1A = – 0.555 *y* – 1.235 *z*
C5→C5A = + 0.555 *y* – 1.235 *z*
Scalar product (C1→C1A).(C5→C5A) = 1.2172 = C1→C1A C5→C5A cos ϕ_1
Thus, angle between C–C bond vectors projected in *bc* plane (ϕ_1) = 48.4°

Scalar product (C1→C1A).(C1→C1A)$_{proj}$ = 1.8333
= C1→C1A (C1→C1A)$_{proj}$ cos ϕ_2
Thus, angle between C–C bond vectors and *bc* plane (ϕ_2) = 26.6°

Volume of parallelpiped defined by C1→C2, C1→C3 and C1→C6 =
Magnitude of scalar triple product (C1→C6).[(C1→C2)×(C1→C3)]
= V_{Me}**(1) = 128.8 Å^3**

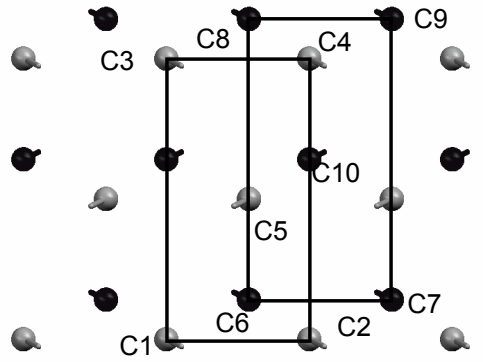
Volume of parallelpiped defined by C1A→C2A, C1A→C3A and C1A→C6A =
Magnitude of scalar triple product (C1A→C6A).[(C1A→C2A)×(C1A→C3A)]
= V_{Me}**(2) = 192.2 Å^3**

S10. Projection of the terminal C–C bond vectors onto the methyl group interface (the *bc* plane) (cont.)

Pentadecanoic acid (C_{15}):

	x / Å	*y* / Å	*z* / Å
C1	0	0	0
C2	0	4.9556	0
C3	0	0	9.720
C4	0	4.9556	9.720
C5	0	2.863	4.860
C6	-2.826	2.863	1.369
C7	-2.826	7.819	1.369
C8	-2.826	2.863	11.089
C9	-2.826	7.819	11.089
C10	-2.826	4.956	6.229
C1A	1.302	0.519	-0.250
C2A	1.302	5.474	-0.250
C3A	1.302	0.519	9.470
C4A	1.302	5.474	9.470
C5A	1.302	2.344	4.610
C6A	-4.128	2.344	1.619
C7A	-4.128	7.230	1.619
C8A	-4.128	2.344	11.339
C9A	-4.128	7.230	11.339
C10A	-4.128	5.475	6.479

[Fractional y coordinate = 0.578]



Origin shift in ångstroms in *bc* plane = C1→C6 = + 2.863 *y* + 1.369 *z*
bc cell = 4.9556 Å x 9.720 Å
Thus, origin shift in FRACTIONAL coordinates in the *bc* plane = (0.578, 0.141)

Magnitude of C1→C1A vector projected in *bc* plane = C1→C1A
= (+ 0.519 *y* – 0.250 *z*) = **0.576 Å**

C–C vectors projected in *bc* plane: C1→C1A = + 0.519 *y* – 0.250 *z*
C5→C5A = – 0.519 *y* – 0.250 *z*
Scalar product (C1→C1A).(C5→C5A) = –0.2069 = C1→C1A C5→C5A $\cos\phi_1$
Thus, angle between C–C bond vectors projected in *bc* plane (ϕ_1) = 128.6° = 51.4°

Scalar product (C1→C1A).$(C1\rightarrow C1A)_{proj}$ = 0.3319
= C1→C1A $(C1\rightarrow C1A)_{proj}$ $\cos\phi_2$
Thus, angle between C–C bond vectors and *bc* plane (ϕ_2) = 66.1°

Volume of parallelpiped defined by C1→C2, C1→C3 and C1→C6 =
Magnitude of scalar triple product (C1→C6).[(C1→C2)×(C1→C3)]
= V_{Me}**(1) = 136.1 Å^3**

Volume of parallelpiped defined by C1A→C2A, C1A→C3A and C1A→C6A =
Magnitude of scalar triple product (C1A→C6A).[(C1A→C2A)×(C1A→C3A)]
= V_{Me}**(2) = 261.5 Å^3**