

Structure of C_{15} -, C_{17} - and C_{19} -mono-acid β -triacylglycerols

Robert B. Helmholdt,* René Peschar and Henk Schenk

Laboratory for Crystallography, Institute of Molecular Chemistry (IMC), Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Correspondence e-mail: rbh@science.uva.nl

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The crystal structures of β -1,2,3-tris(pentadecanoyl)glycerol (β - $C_{15}C_{15}C_{15}$), β -1,2,3-tris(heptadecanoyl)glycerol (β - $C_{17}C_{17}C_{17}$) and β -1,2,3-tris(nonadecanoyl)glycerol (β - $C_{19}C_{19}C_{19}$) have been determined from high-resolution X-ray powder diffraction data. Grid search and Rietveld refinement have been used to determine and refine the structures, respectively. As in β -1,2,3-tris(tridecanoyl)glycerol (β - $C_{13}C_{13}C_{13}$) and the even-numbered mono-acid triacylglycerols, all three odd-numbered monoacid triacylglycerols crystallize in space group $P\bar{1}$ with $Z = 2$ in an asymmetric tuning-fork conformation and have a lateral acyl chain packing resulting in a layered structure.

1. Introduction

Differences in packing of long-chain hydrocarbon compounds, such as n -alkanes ($n > 10$), fatty acids and triacylglycerols (TAGs, see Fig. 1), as a function of temperature and temperature gradient may result in a variety of crystalline phases, phase transitions, and complex crystallization and melting properties. An example of the latter is melting-point alternation, characterized by relatively lower melting points of odd-numbered series members in comparison to the neighboring even-numbered ones.

Melting-point alternation theories have been reviewed by Larsson (1966) and Boese *et al.* (1999). Assuming identical molecular arrangement within the layers, but allowing for a different layer stacking for even- and odd-numbered members, Larsson explained melting-point alternation for all types of long-chain compounds by differences in packing densities at the layer interface and the methyl-end group structure.

Von Sydow (1956) correlated the melting-point alternation in fatty acids with differences in the estimated van der Waals interaction between the methyl contact planes. Boese *et al.* (1999) showed that this theory also holds for short-term

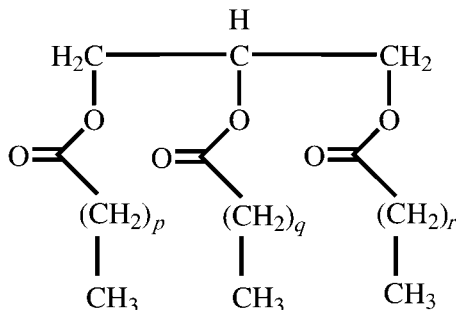


Figure 1

Chemical structure diagram of triacylglycerols. For example, the mono-acid triacylglycerol $C_{15}C_{15}C_{15}$ has $p = q = r = 13$.

Table 1

Unit-cell parameters.

(a) For the β phase of the triacylglycerols $C_{13}C_{13}C_{13}$, $C_{15}C_{15}C_{15}$, $C_{17}C_{17}C_{17}$ and $C_{19}C_{19}C_{19}$, as determined from the synchrotron XRPD data when the acyl chains are as parallel as possible with the longest axis.

Compound	$C_{13}C_{13}C_{13}^{(a)}$	$C_{15}C_{15}C_{15}$	$C_{17}C_{17}C_{17}$	$C_{19}C_{19}C_{19}$
a (Å)	11.9438 (6)	11.8998 (1)	11.8664 (2)	11.8680 (1)
b (Å)	41.342 (1)	46.3879 (4)	51.450 (1)	56.5143 (9)
c (Å)	5.4484 (3)	5.4400 (1)	5.4321 (1)	5.4280 (1)
α (°)	71.905 (4)	72.359 (1)	72.765 (2)	73.064 (1)
β (°)	100.291 (5)	100.211 (1)	100.095 (1)	100.020 (1)
γ (°)	121.824 (3)	121.125 (1)	120.577 (2)	120.084 (1)
Volume (Å ³)	2172.5 (1)	2448.9 (1)	2725.8 (1)	3011.8 (1)
D_{calc} (g cm ⁻³)	1.04	1.04	1.03	1.03

(b) For the β -triacylglycerides $C_{13}C_{13}C_{13}$, $C_{15}C_{15}C_{15}$, $C_{17}C_{17}C_{17}$ and $C_{19}C_{19}C_{19}$, as determined from the synchrotron XRPD data.

Compound	$C_{13}C_{13}C_{13}^{(a)}$	$C_{15}C_{15}C_{15}$	$C_{17}C_{17}C_{17}$	$C_{19}C_{19}C_{19}$
a (Å)	5.4484 (3)	5.4400 (1)	5.4321 (1)	5.4280 (1)
b (Å)	11.9438 (6)	11.8998 (1)	11.8664 (2)	11.8680 (1)
c (Å)	34.208 (2)	38.4863 (7)	42.956 (2)	47.566 (1)
α (°)	83.227 (8)	87.394 (1)	89.286 (3)	86.741 (1)
β (°)	86.105 (5)	88.450 (2)	89.708 (2)	88.221 (1)
γ (°)	79.709 (5)	79.789 (1)	79.905 (1)	79.980 (1)
Volume (Å ³)	2172.5 (1)	2448.9 (1)	2725.8 (1)	3011.8 (1)

References: (a) Van Langevelde (2000) and Van Langevelde *et al.* (2001a).

n -alkanes ($n < 9$). The odd-numbered n -alkanes have an optimal interaction at only one chain end, are less densely packed and, consequently, have a lower melting point than the even-numbered ones. Thus, intermolecular distances between the methyl-end groups appear to be responsible for the alternation in the packing densities, whereas the lateral packing does not play any role.

In the case of TAGs, melting-point alternation has only been observed for the β phase. The absence of melting-point alternation in the β' -stable TAG series has been attributed by Larsson to the orthorhombic subcell arrangement, having roughly the same packing density over the methyl gap for even- and odd-numbered series members.

On the basis of the crystal structure of β - $C_{13}C_{13}C_{13}$ (Van Langevelde *et al.*, 2001a) and the crystal structures of even-numbered ($n = 10$ –18) mono-acid series members (Gibon *et al.*, 1984; Jensen & Mabis, 1966; Van Langevelde *et al.*, 1999, 2001b; Van Langevelde, 2000), the alternation of melting points between even- and odd-numbered series members was explained by a weaker interaction between two adjacent molecular layers in the case of the latter. The larger intermolecular distances and a relatively larger occupiable volume in the case of odd-numbered series members are in agreement with the expected less dense packing for odd-numbered TAG series members (Lutton & Fehl, 1970).

Here we report the crystal structures of three other odd-numbered series members in the β -phase, β -1,2,3-tris(pentadecanoyl)glycerol (β - $C_{15}C_{15}C_{15}$), β -1,2,3-tris(heptadecanoyl)glycerol (β - $C_{17}C_{17}C_{17}$) and β -1,2,3-tris(nona-decanoyl)glycerol (β - $C_{19}C_{19}C_{19}$). The structures have been

determined from high-resolution synchrotron X-ray powder diffraction (XRPD) data, exploiting the assumed homology with β - $C_{13}C_{13}C_{13}$, β - $C_{16}C_{16}C_{16}$ and β - $C_{18}C_{18}C_{18}$.

2. Materials and methods

2.1. Samples, sample preparation and data collection

The compounds β - $C_{15}C_{15}C_{15}$, β - $C_{17}C_{17}C_{17}$ and β - $C_{19}C_{19}C_{19}$ were purchased as colorless crystalline powders from Sigma Chemical Co. (St Louis, MO) with a purity of approximately 99%.

The XRPD patterns of the compounds have been recorded at the high-resolution X-ray powder diffraction station at beamline BM16 (ESRF, Grenoble, France; Fitch, 1996) with a fixed wavelength of 0.85005 Å. A capillary with a diameter of 1.5 mm was filled with powder and rotated during exposure.

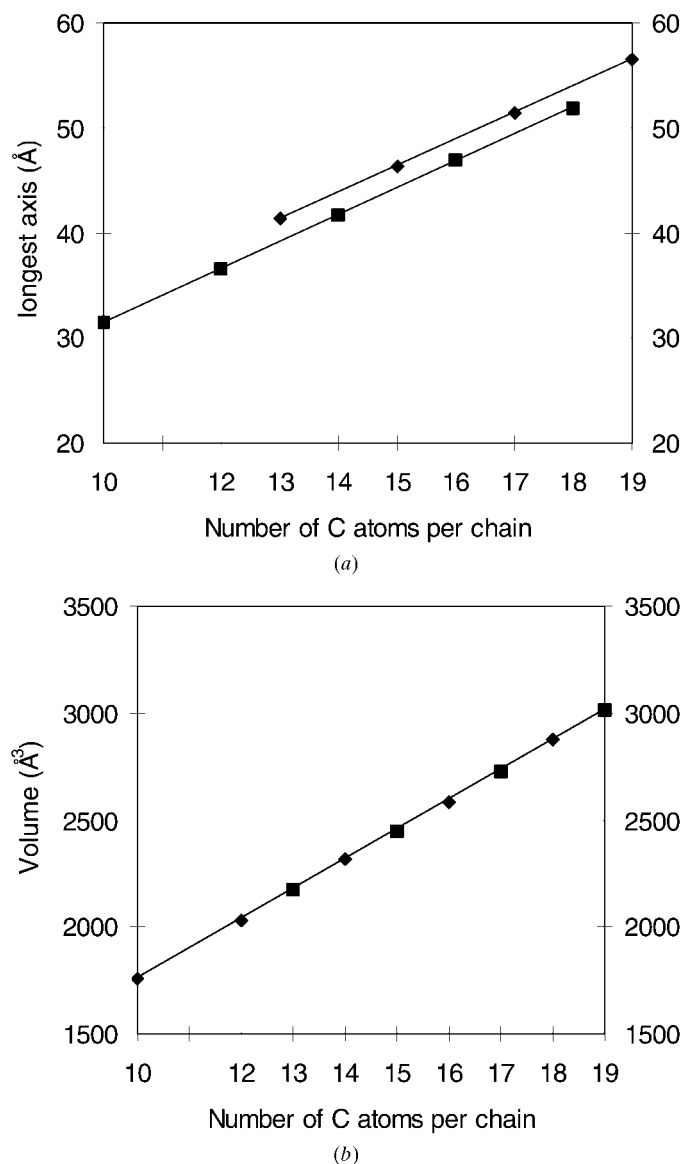


Figure 2
(a) Longest axis (b axis) versus number of C atoms (squares even-, diamonds odd-numbered TAGs) in an acyl chain. (b) Unit-cell volume versus number of C atoms in an acyl chain.

Table 2

Typical parameters of the full pattern decomposition (FPD), the grid search and the Rietveld refinement (RR) for the compounds $C_{13}C_{13}C_{13}$, $C_{15}C_{15}C_{15}$, $C_{17}C_{17}C_{17}$ and $C_{19}C_{19}C_{19}$.

Compound	$C_{13}C_{13}C_{13}^{(a)}$	$C_{15}C_{15}C_{15}$	$C_{17}C_{17}C_{17}$	$C_{19}C_{19}C_{19}$
<i>FPD</i>				
2θ range ($^{\circ}$)	2–28	1.5–18.5	1.5–18.5	1.5–18.5
R_p	0.087	0.079	0.065	0.070
R_{wp}	0.136	0.106	0.087	0.092
S	–	10.1	3.7	5.0
<i>Grid search</i>				
$R(F^2)$	–	0.265	0.349	0.248
<i>RR</i>				
2θ range ($^{\circ}$)	2–50	1.5–50	1.5–50	1.5–50
R_p	0.047	0.057	0.068	0.061
R_{wp}	0.053	0.080	0.089	0.080
S	–	6.0	3.0	3.4

Reference: (a) Van Langevelde *et al.* (2001a).

Continuous scans were made at $T = 243$ K from 0.0 to $50^{\circ} 2\theta$, with a $0.5^{\circ} 2\theta \text{ min}^{-1}$ and a sampling time of 50 ms, and eventually binned at $0.005^{\circ} 2\theta$.

2.2. Cell parameters

The lines obtained from the synchrotron powder patterns of β - $C_{15}C_{15}C_{15}$ and β - $C_{19}C_{19}C_{19}$ were indexed using a locally modified version of the cell-indexing program *ITO* (Visser, 1969). However, in the case of β - $C_{17}C_{17}C_{17}$ *ITO* was not able to find an acceptable solution and a systematic search procedure was used to determine the cell parameters. In this systematic search procedure all six cell parameters can be varied systematically in preset intervals, while the calculated peak positions are compared with the observed ones. On the basis of the assumed homology of the series (Table 1) an educated guess for the cell parameter intervals is possible, thus limiting the amount of computer time required considerably. Owing to the triclinic system, in which these fats crystallize, not only the reduced cells are given but also the sets of parameters for which the acyl chains are as parallel as possible with the longest cell axis. This is also the most convenient way to compare the structures of the odd-numbered TAGs with the even-numbered ones, for which a similar cell choice has been used. All the cell parameters have been refined using the program *MRIA* (Zlokazov & Chernyshev, 1992).

2.3. Grid search and refinement

Accurate reflection intensities have been obtained from the high-resolution synchrotron XRPD pattern using the full-pattern decomposition (FPD) module of the program *MRIA*. In the FPD a split-type pseudo-Voigt peak-profile function (Toraya, 1986) was used.

A starting model for β - $C_{15}C_{15}C_{15}$ was made from the crystal structure of β -1,2,3-tris(hexadecanoyl)glycerol (β - $C_{16}C_{16}C_{16}$ or β -PPP; Van Langevelde, 2000; Van Langevelde *et al.*, 1999) by replacing the terminating $-\text{CH}_3$ groups of the palmitic chains with H atoms using the program *Xtal* (Hall *et al.*, 1995). Starting models for β - $C_{17}C_{17}C_{17}$ and β - $C_{19}C_{19}C_{19}$ were made

from the crystal structure of β -1,2,3-tris(octodecanoyl)glycerol (β - $C_{18}C_{18}C_{18}$ or β -SSS; Van Langevelde, 2000; Van Langevelde *et al.*, 2001b) by either replacing the terminating $-\text{CH}_3$

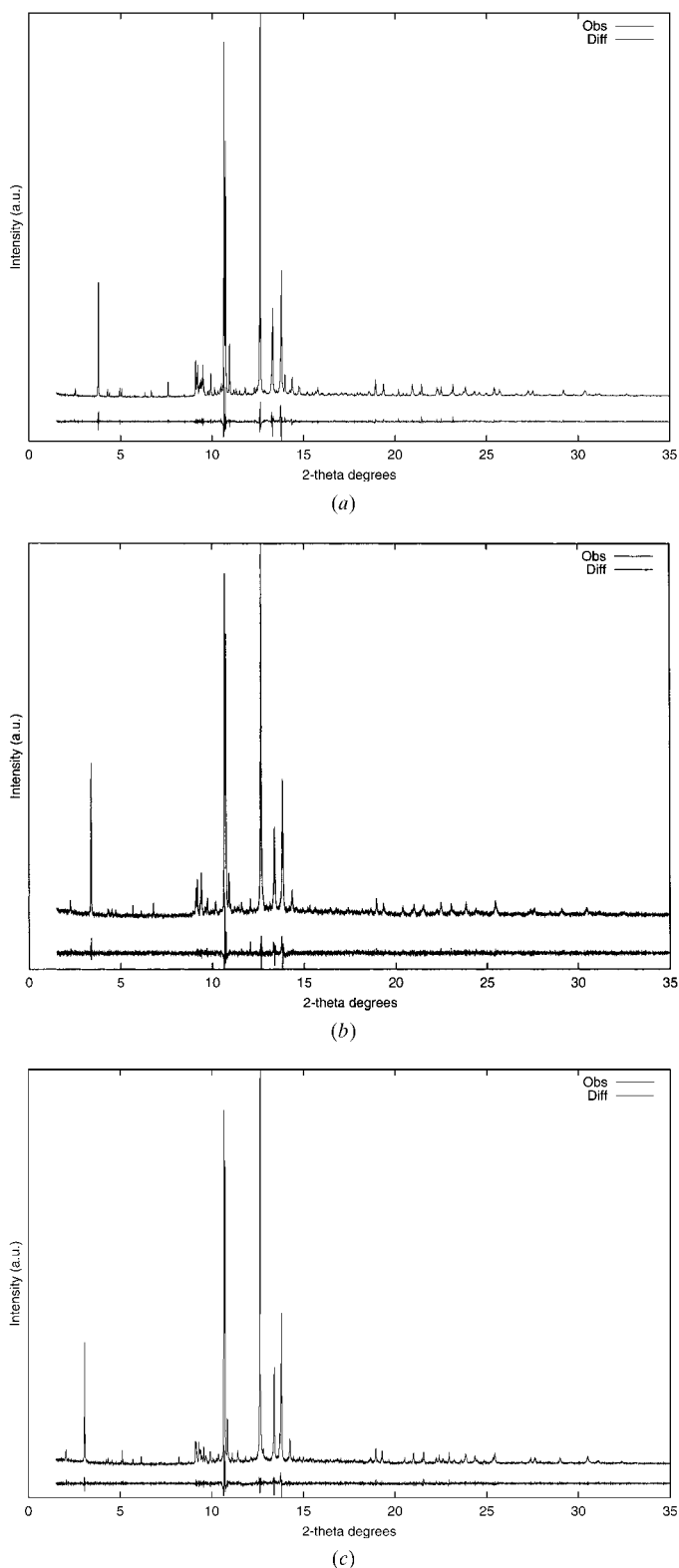


Figure 3 Synchrotron powder diffraction patterns ($\lambda = 0.85005 \text{ \AA}$) of (a) β - $C_{15}C_{15}C_{15}$, (b) β - $C_{17}C_{17}C_{17}$ and (c) β - $C_{19}C_{19}C_{19}$. The upper pattern is observed and the lower pattern the difference between the observed and calculated patterns.

Table 3
Value ranges for selected geometric parameters (\AA , $^\circ$).

	$C_{13}C_{13}C_{13}^{(a)}$	$C_{15}C_{15}C_{15}$	$C_{17}C_{17}C_{17}$	$C_{19}C_{19}C_{19}$
C=O	1.20–1.26	1.19–1.23	1.24–1.28	1.25–1.27
C–O	1.28–1.47	1.35–1.47	1.23–1.47	1.25–1.47
C–C	1.48–1.59	1.46–1.56	1.47–1.58	1.45–1.60
O–C–C	112–118	105–112	113–118	113–116
O=C–C	122–128	124–126	121–125	120–127
O=C–O	119–126	115–120	120–123	116–124
C–O–C	111–123	109–116	111–125	112–121
C–C–C	108–116	108–118	108–116	105–116

Reference: (a) Van Langevelde *et al.* (2001a).

Table 4
Overall r.m.s. differences (\AA) in position between corresponding atoms after matching of the crystal structures.

	$C_{13}C_{13}C_{13}$	$C_{15}C_{15}C_{15}$	$C_{17}C_{17}C_{17}$	$C_{19}C_{19}C_{19}$
$C_{13}C_{13}C_{13}$	0.000	–	–	–
$C_{15}C_{15}C_{15}$	0.147	0.000	–	–
$C_{17}C_{17}C_{17}$	0.090	0.155	0.000	–
$C_{19}C_{19}C_{19}$	0.130	0.152	0.137	0.000

groups of the stearic chains with H atoms in the case of β - $C_{17}C_{17}C_{17}$ or by extending these chains by replacing one H atom with a $-\text{CH}_3$ group using the program *Xtal*.

To locate these possible models in the asymmetric unit a grid-search procedure (Chernyshev & Schenk, 1998) was applied to the 250 low-order X_{obs} values (for the definition of X_{obs} values see Chernyshev & Schenk, 1998) obtained by the FPD procedure. The obtained translational and rotational parameters were refined, followed by a full-pattern Rietveld refinement (*RR*). Soft restraints were applied to the atomic distances (σ is $\sim 1\%$ of the ideal bond lengths) during *RR*. Under these conditions the coordinates of all atoms (O, C and H) were refined as well as the coupled isotropic atomic displacement parameters (U_{iso}) of the C atoms and the O atoms. The U_{iso} values for H atoms were fixed at 0.05 \AA^2 . The preferred orientation was refined using the first 14 coefficients of the symmetrized harmonics-expansion method (Ahte *et al.*, 1989; Järvinen, 1993).

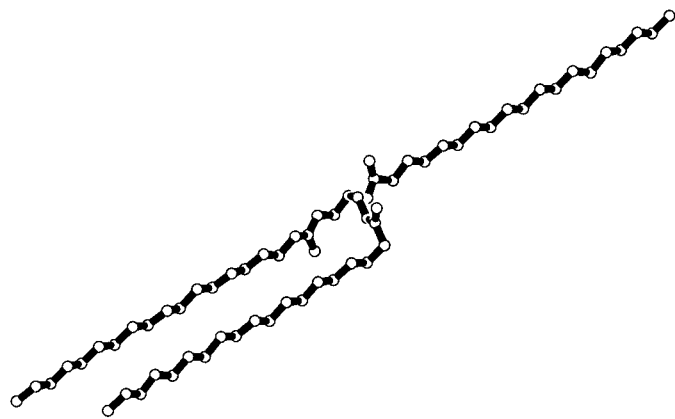


Figure 4
PLATON (Spek, 2001) representation of the crystal structure of β - $C_nC_nC_n$, $n = 19$.

Table 5
Angles ($^\circ$) between the acyl chains, and between the acyl chains and the longest cell axis for the compounds $C_{13}C_{13}C_{13}$, $C_{15}C_{15}C_{15}$, $C_{17}C_{17}C_{17}$ and $C_{19}C_{19}C_{19}$.

Compound	$C_{13}C_{13}C_{13}^{(a)}$	$C_{15}C_{15}C_{15}$	$C_{17}C_{17}C_{17}$	$C_{19}C_{19}C_{19}$
a chain \wedge b chain	0.8	0.8	0.3	0.6
b chain \wedge c chain	3.4	3.1	0.8	1.2
c chain \wedge a chain	2.6	2.8	0.5	0.8
a chain \wedge b axis	6.1	5.6	4.7	3.9
b chain \wedge b axis	6.0	4.9	4.7	4.2
c chain \wedge b axis	6.7	5.7	4.6	4.4

Reference: (a) Van Langevelde *et al.* (2001a).

On the basis of the crystal structure of β - $C_{13}C_{13}C_{13}$ and the even-numbered series members an explanation for the melting point alternation in the β - $C_nC_nC_n$ -type TAG series has been proposed (Van Langevelde *et al.*, 2001a). In order to assess the correctness of this explanation some geometric (distance) analyses have been carried out. Structures were matched by minimizing the distance between corresponding C and O atoms, resulting in an overall root-mean-square (r.m.s.) expressing the quality of the fit. Matched crystal structures were visually analyzed using the program *PLUVA* v3.0 (Driessen *et al.*, 1988). Distances between chain-terminating C atoms of two adjacent chain layers were calculated for the known structures of $C_nC_nC_n$ -type TAG series using the program *BONDLA* (Hall *et al.*, 1995). Occupiable volumes (unit-cell volume not occupied by atoms but large enough to fit in atomic probes with a certain radius) were calculated using the program *Cerius²* (Molecular Simulations Inc., 1995), employing a probe with 1.6 \AA radius and atomic van der Waals radii.

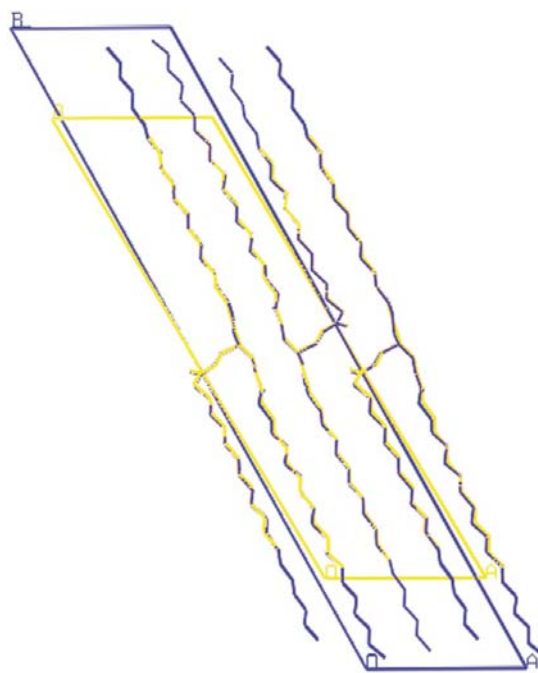


Figure 5
The crystal packing of the odd-numbered TAGs β - $C_{13}C_{13}C_{13}$ and β - $C_{19}C_{19}C_{19}$ showing the matching of these molecules. The c axis is perpendicular to the plane of the paper.

Table 6

Shortest distances (< 4.4 Å) between methyl-end atoms of adjacent chain layers for β -TAGs.

CCC = 1,2,3-tridecanoylglycerol; LLL = 1,2,3-tridodecanoylglycerol; MMM = 1,2,3-tritetradecanoylglycerol; PPP = 1,2,3-trihexadecanoylglycerol; SSS = 1,2,3-trioctadecanoylglycerol.

	Atom number x	$C_{xa}-C_{xc}$ (Å)	$C_{xb}-C_{xb}$ (Å)	$C_{xa}-C_{xa}$ (Å)
CCC ^(a)	10	3.73	4.09	3.66
LLL ^(b)	12	3.70	4.08	3.65
C ₁₃ C ₁₃ C ₁₃ ^(c)	13	3.79	>4.4	3.73
MMM ^(d)	14	3.55	4.05	3.54
C ₁₅ C ₁₅ C ₁₅	15	3.81		3.79
PPP ^(e)	16	3.67	4.01	3.65
C ₁₇ C ₁₇ C ₁₇	17	3.84		3.80
SSS ^(d)	18	3.65	4.02	3.66
C ₁₉ C ₁₉ C ₁₉	19	3.84		3.70

References: (a) Jensen & Mabis (1966); (b) Gibon *et al.* (1984); (c) Van Langevelde *et al.* (2001a); (d) Van Langevelde *et al.* (2001b); (e) Van Langevelde *et al.* (1999).

3. Results and discussion

The unit-cell parameters of the compounds were refined on the synchrotron XRPD pattern and are given in Table 1(a), while the cell parameters of the reduced cells are given in Table 1(b). Table 1(a) shows that only the b axis changes significantly as a function of the chain length, the increment to the next member of the series being 5.057 Å. This is in good agreement with the expected chain lengthening of 5.0 Å, based on an average Csp^3-Csp^3 bond length of 1.524 Å and a $Csp^3-Csp^3-Csp^3$ angle of 109.3°. The same effect has been found for the series of even TAGs with $n = 10, 12, 14, 16$ and 18, for which the average increment is 5.1 Å (Gibon *et al.*, 1984; Jensen & Mabis, 1966; Van Langevelde *et al.*, 1999, 2001b; Van Langevelde, 2000). This change, as well as the change in cell volume (280 Å³ on average) between two subsequent members of the series, is linear for this part of the series (Fig. 2). The space group of all these TAGs is $P\bar{1}$ with $Z = 2$. The FPD procedure was applied to the 1.5–18.5° 2θ range of the synchrotron XRPD pattern and resulted in the R_p , R_{wp} and S values given in Table 2. The RR procedure was applied to the 2θ range 1.5–50.0°, resulting in a final fit between the observed and calculated XRPD pattern with R_p , R_{wp} and S values, as given in Table 2, while the observed and difference patterns are given in Fig. 3. The fractional atomic coordinates for the three structures have been deposited¹ and the value ranges of selected geometric parameters are listed in Table 3.

Like the even-numbered series members, the odd-numbered series members are crystallized in an asymmetric tuning-fork conformation (Fig. 4). The zigzag planes of the acyl chains are parallel packed, which is common to the crystal packing of the β phase, forming layers of laterally packed acyl chains bordered by either a methyl-end group plane or glycerol moieties. The conformations of the odd-numbered β -

¹Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV0044). Services for accessing these data are described at the back of the journal.

Table 7

Occupiable volume per unit cell for β -triacylglycerides.

	Unit-cell volume (Å ³)	Occupiable volume (Å ³ per unit cell)	% occupiable volume per unit-cell volume
CCC†	1761.3	55.5	3.15
LLL	2029.9	65.3	3.22
C ₁₃ C ₁₃ C ₁₃	2172.5	72.3	3.33
MMM	2314.7	76.5	3.30
C ₁₅ C ₁₅ C ₁₅	2448.9	83.8	3.39
PPP	2581.1	86.8	3.36
C ₁₇ C ₁₇ C ₁₇	2725.8	94.7	3.43
SSS	2879.6	98.7	3.43
C ₁₉ C ₁₉ C ₁₉	3011.8	105.5	3.48

† See notes under Table 6.

triacylglycerol molecules are almost identical, besides the difference in chain length, as expressed by the low overall r.m.s. values (Table 4) obtained by matching these molecules. The packing of the molecules within one layer, constituting two chain layers linked by glycerol moieties, is almost identical (Fig. 5), as also shown from the angles between the chains and the unit-cell axes, and between the chains mutually (Table 5), in which case a chain is defined as the least-squares line through the C atoms constituting the chain.

Two adjacent layers of odd-numbered β -C _{n} C _{n} C _{n} ($n = 15, 17, 19$) are arranged in the same way as for β -C₁₃C₁₃C₁₃ (Van Langevelde *et al.*, 2001a; Table 6) which has its hydrocarbon chain ends positioned in an in-line manner. However, the methyl end-group interaction of the odd-numbered β -C _{n} C _{n} C _{n} is not identical to the methyl end interaction of the even-numbered ones, which is shown by the different distances between the terminating C atom of adjacent molecular layers (Table 6). The distances between the terminating C atoms of the a and c chains, and the b chains in two adjacent layers are larger than the corresponding distances of the even-numbered series members. Furthermore, between two adjacent molecular layers of the odd-numbered triacylglycerides a larger

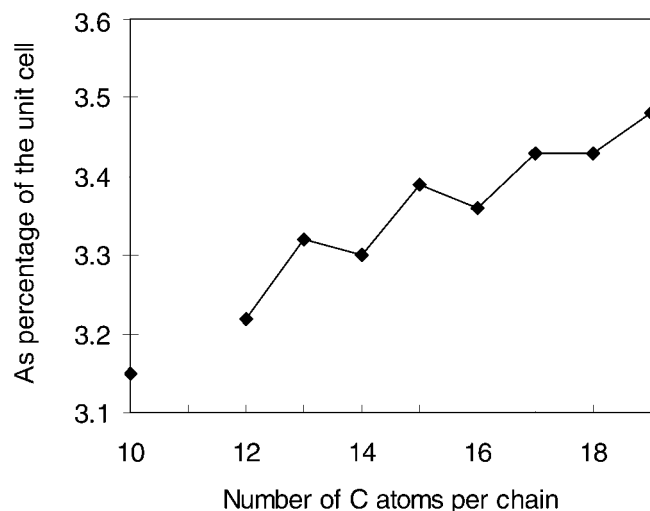


Figure 6

% occupiable volume per unit-cell volume versus number of C atoms in an acyl chain.

occupiable volume is present than for the even-numbered series members (Table 7 and Fig. 6), so the interaction between the molecular layers in the odd-numbered members is weaker than in the even-numbered ones, resulting in a lower melting point for an odd-numbered member compared with neighbouring even-numbered ones. As put forward in Van Langevelde *et al.* (2001a), the lattice energy of these triacylglycerides can be considered to consist of two parts:

(i) the lattice energy of the crystal packing within a molecular layer and

(ii) the lattice energy between two adjacent molecular layers.

The influence of the lattice energy of the crystal packing within a molecular layer for the total lattice energy will become larger with increasing chain length, resulting in a decreasing difference in melting between two successive odd- and even-numbered triacylglycerols. This effect indeed seems to be present, as judged from Fig. 6, because the % occupiable volume between two adjacent even-odd members decreases gradually from 0.11 ($C_{13}C_{13}C_{13}$ – LLL) to 0.05 ($C_{19}C_{19}C_{19}$ – SSS).

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References

- Ahtee, M., Nurmela, M., Suortti, P. & Järvinen, M. (1989). *J. Appl. Cryst.* **22**, 261–268.
- Boese, R., Weiss, H.-C. & Bläser, D. (1999). *Angew. Chem. Int. Ed.* **38**, 988–992.
- Chernyshev, V. V. & Schenk, H. (1998). *Z. Kristallogr.* **213**, 1–3.
- Driessen, R. A. J., Loopstra, B. O., De Bruijn, D. P., Kuipers, H. P. C. E. & Schenk, H. (1988). *J. Comput.-Aided Mol. Des.* **2**, 225–233.
- Fitch, A. N. (1996). *Materials Science Forum*, edited by R. J. Cernik, R. Delhez & E. J. Mittemeijer, Vol. 228, pp. 219–222. Aedermannsdorf: Trans Tech Publications.
- Gibon, V., Blanpain, P., Norberg, B. & Durant, F. (1984). *Bull. Soc. Chim. Belg.* **93**, 27–34.
- Hall, S. R., King, G. S. D. & Stewart, J. M. (1995). *Xtal*, Version 3.4. Universities of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.
- Järvinen, M. (1993). *J. Appl. Cryst.* **26**, 525–531.
- Jensen, L. H. & Mabis, A. J. (1966). *Acta Cryst.* **21**, 770–781.
- Larsson, K. (1966). *J. Am. Oil Chem. Soc.* **43**, 559–562.
- Lutton, E. S. & Fehl, A. J. (1970). *Lipids*, **5**, 90–99.
- Molecular Simulations Inc. (1995). *Cerius²*, Release 2.0. Biosym Molecular Simulations Inc., San Diego, USA.
- Spek, A. L. (2001). *PLATON*. Utrecht University, The Netherlands.
- Toraya, H. (1986). *J. Appl. Cryst.* **19**, 440–447.
- Van Langevelde, A. J. (2000). PhD Thesis. University of Amsterdam, The Netherlands.
- Van Langevelde, A., Peschar, R. & Schenk, H. (2001a). *Chem. Mater.* **13**, 1089–1094.
- Van Langevelde, A., Peschar, R. & Schenk, H. (2001b). *Acta Cryst.* **B57**, 372–377.
- Van Langevelde, A., Van Malssen, K., Hollander, F., Peschar, R. & Schenk, H. (1999). *Acta Cryst.* **B55**, 114–122.
- Visser, J. W. (1969). *J. Appl. Cryst.* **2**, 89–95.
- Von Sydow, E. (1956). *Arkiv Kemi*, **9**, 231–254.
- Zlokazov, V. B. & Chernyshev, V. V. (1992). *J. Appl. Cryst.* **25**, 447–451.