

Structure of mono-acid even-numbered β -triacylglycerols

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Abstract

The crystal structure of the β polymorph of tripalmitin (1,2,3-trihexadecanoylglycerol, β -PPP) has been determined by single-crystal X-ray diffraction. The molecules crystallize in space group $P\bar{1}$ in an asymmetric tuning-fork conformation. This structure and the already-known crystal structures of β -tricaprin (β -CCC) and β -trilaurin (β -LLL) could be matched in an overlap model. Apart from a difference in chain length, the three structures are almost identical. The overlap model can be used to predict the crystal structure of the other members of the $C_nC_nC_n$ -type ($n = \text{even}$) TAG series reasonably accurately. This is demonstrated by predicting the crystal structure for β -trimyristin (β -MMM) and successively comparing the experimental and calculated X-ray powder diagrams.

1. Introduction

Polymorphic behaviour is often shown by long-chain compounds such as triacylglycerols (TAGs, see also Table 1). In general, TAGs as well as TAG mixtures, such as milk fat and cocoa butter, crystallize in two or three different phases, α and β' or α , β' and β , respectively. In general practice DSC (differential scanning calorimetry) is used to investigate these phases, although X-ray powder diffraction is a much more suitable technique for identification since each polymorph has its own distinctive diffraction pattern. Table 2 shows the characteristic reflections in the fingerprint region (d spacings from 3.0 to 6.0 Å) for the different phases.

The phase transformations of TAGs and their mixtures ($\alpha \rightarrow \beta'$, $\alpha \rightarrow \beta' \rightarrow \beta$, or $\alpha \rightarrow \beta$) are monotropic (Hagemann, 1988), implicating only one stable phase. For mono-acid even-numbered TAGs ($C_nC_nC_n$, $n = \text{even}$) the most stable phase is β , whereas for $C_nC_{n+2}C_n$ and $C_nC_{n+4}C_{n+2}$ ($n = \text{even}$) the β' -phase is the most stable (De Jong & Van Soest, 1978). For TAG mixtures a difference in relative phase stability exists as well: milk fat is β' -stable and cocoa butter is β -stable (Timms, 1984). The phase and phase transitions depend on several factors, such as temperature and time.

Since TAGs are used in many consumer products it is important to understand the complex behaviour of these compounds. Therefore, the crystal structures of TAGs in different polymorphic phases are necessary. Until now only three crystal structures of long-chain TAGs have been published; all are β polymorphs. Jensen & Mabis (1963) were the first to present a full single-crystal structure determination (Table 3). They determined the structure of β -CCC from an incomplete three-dimensional data set, obtained through equi-inclination Weissenberg photographs collected with Fe $K\alpha$ radiation. This structure has an asymmetric 'tuning-fork' conformation, characterized by the two outer capryloyl chains (I) and (III) pointing in one direction and the middle one (II) in the opposite direction. The space group is $P\bar{1}$, which results in a packing of the molecules like stacked chairs. The zigzag planes of all the acyl chains are parallel. This crystal structure refined poorly ($R = 0.179$), but later a further refinement based on photometric data resulted in a final R value of 0.051 (Jensen & Mabis, 1966).

Long before the work of Jensen & Mabis (1963, 1966), Vand & Bell (1951) succeeded in determining the hydrocarbon chains of a TAG using the method of Vand (1951) to determine the signs of the structure factors of long-chain compounds. This method is based on describing the periodic regions of electron-density distribution within one unit cell as subcells. Using this method it was possible to determine the alkyl chains of β -LLL. This result gave the first experimental evidence for the typical chain packing of the β polymorphs. Later, Larsson (1965) presented the crystal structure of β -LLL, refined to an R value of 0.20. $L^{Br}L^{Br}L^{Br}$, an isomorphously crystallizing heavy-atom analogue of LLL, was used to derive an initial model, preceding the final structure refinement. The space group of β -LLL is $P\bar{1}$ and its structure is also in the tuning-fork conformation. Gibon *et al.* (1984) further refined the structure of β -LLL to a final R value of 0.06.

Skoda *et al.* (1967) determined unit-cell parameters of β -SSS from single-crystal Weissenberg photographs. They found a difference between this experimental cell and the cell which they had predicted from β -LLL. Based on this observation they concluded that β -LLL

Table 1. List of abbreviations

Abbreviation	Systematic name	Trivial name	Chemical code
AAA	1,2,3-Trieicosanoylglycerol	Triarachidin	C ₂₀ C ₂₀ C ₂₀
BBB	1,2,3-Tridocosanoylglycerol	Tribehenin	C ₂₂ C ₂₂ C ₂₂
CCC	1,2,3-Tridecanoylglycerol	Tricaprin	C ₁₀ C ₁₀ C ₁₀
CL ^{Br} C	2-(11-Bromoundecanoyl)-1,3-didecanoylglycerol		C ₁₀ C ₁₁ BrC ₁₀
CLC	1,3-Didecanoyl-2-dodecanoylglycerol		C ₁₀ C ₁₂ C ₁₀
L ^{Br} L ^{Br} L ^{Br}	1,2,3-Tri(11-bromoundecanoyl)glycerol		C ₁₁ BrC ₁₁ BrC ₁₁ Br
LLL	1,2,3-Tridodecanoylglycerol	Trilaurin	C ₁₂ C ₁₂ C ₁₂
MMM	1,2,3-Tritetradecanoylglycerol	Trimyristin	C ₁₄ C ₁₄ C ₁₄
PPP	1,2,3-Trihexadecanoylglycerol	Tripalmitin	C ₁₆ C ₁₆ C ₁₆
SSS	1,2,3-Trioctadecanoylglycerol	Tristearin	C ₁₈ C ₁₈ C ₁₈
TAG(s)	Triacylglycerol(s)		
TTT	1,2,3-Tritetracosanoylglycerol	Trilignocerin	C ₂₄ C ₂₄ C ₂₄

Table 2. Characteristics of TAG polymorphs (Abrahamsson et al., 1978; Hoerr & Paulicka, 1968)

Polymorph	<i>d</i> spacing (Å)	Subcell lattice	Acyl chain orientation	Symbol
α	4.15	Hexagonal	Random	H
β'	3.80, 4.20	Orthorhombic	Orthogonal	O _⊥
β	3.65, 3.85, 4.57	Triclinic	Parallel	T

and β -SSS are not completely 'homologously isomorphous'. De Jong & Van Soest (1978) presented a somewhat different unit cell for β -SSS, but no experimental details concerning this determination have been published.

A crystal structure of a β -TAG having much longer chains ($n = 24$) has been predicted by Simpson & Hagemann (1975). They determined the unit-cell parameters of TTT by X-ray powder diffraction and computer calculations. Indexing programs were not able to solve the problem. Therefore, they systematically varied the cell axes and subsequently calculated X-ray diffraction patterns to match the experimental one. This determination does not seem very accurate, since the standard uncertainties of the cell parameters are much larger than those achieved from single-crystal data of related TAGs.

The first crystal structure determination of a TAG with unequal fatty-acid chain lengths was published by Doyne & Gordon (1968). They determined the crystal structure of CL^{Br}C, a heavy-atom analogue of CLC, which is a C_{*n*}C_{*n*} + 2C_{*n*}-type ($n = \text{even}$) TAG. Therefore, CL^{Br}C was expected to be β' -stable, but the $P\bar{1}$ crystal structure shows tuning-fork molecules in the β phase.

To complete the most relevant part of the β -C_{*n*}C_{*n*}C_{*n*} ($n = \text{even}$) series, we have determined the crystal structure of β -PPP by single-crystal X-ray diffraction and refined it to a final *R* value of 0.078. The structure is compared with the known crystal structures of β -CCC and β -LLL and the (dis)similarities are pointed out. These crystal structures were used to build an average

model for this series of TAGs from which currently unknown crystal structures of the remaining members may be predicted. Powder diffraction intensities have been used to verify the correctness of the prediction.

2. Materials and methods

2.1. Samples, sample preparation and measurements

PPP was obtained from the Unilever Research Laboratory (Vlaardingen, The Netherlands). Single crystals were grown from a solution of PPP in *n*-dodecane over 6 d at 303.83 K. The initial dimensionless supersaturation was 0.46. The solution with grown crystals was kept at room temperature for a few months. The crystals were removed from the solution by filtering over a Büchner funnel and subsequent washing with acetone. See Table 4 for full experimental details.

MMM was purchased as a whitish powder from Sigma Chemical Co. (St Louis, USA) with a purity of approximately 99%. An X-ray powder diffraction photograph of this sample was taken using an Enraf-Nonius FR 552 Guinier Johannson camera equipped with a Johannson monochromator (Cu $K\alpha_1$ radiation, $\lambda = 1.54060$ Å). The sample was prepared by pressing a thin layer of powder gently on Mylar foil. During exposure the sample holder was spun in order to improve particle statistics. The Guinier photograph was read out in order to collect the accurate positions of as many lines as possible.

The X-ray powder diffraction pattern of MMM has been recorded with a Philips 1710 diffractometer (Philips, Almelo, The Netherlands) having Bragg-Brentano geometry with a divergence slit of 0.5°, an anti-scatter slit of 1° and a receiving slit of 0.05 mm. A step scan with $2\theta = 2$ –100° and a 0.02° step size, Cu $K\alpha$ radiation and a step time of 6 s was used.

2.2. Crystal structure determination and indexing

Unit-cell parameters of PPP were refined by a least-squares fitting procedure using 23 reflections with $78 \leq 2\theta \leq 83^\circ$. Corrections for Lorentz and polarization

Table 3. Cell parameters of β -TAGs from the literature

	β -CCC ^(a)	β -CCC ^(b)	β -CL ^{Brc} ^(c)	β -LLL ^(d)	β -LLL ^(e)	β -SSS ^(f)	β -SSS ^(g)	β -TTT ^(h)
<i>a</i> (Å)	5.50	5.488 (1)	12.35 (10)	12.35 (8)	12.08 (2)	11.97 (4)	14.13 (4)	13.1 (1)
<i>b</i> (Å)	12.10	12.18 (3)	5.51 (5)	5.44 (4)	31.62 (3)	5.45 (2)	5.45 (2)	5.30 (1)
<i>c</i> (Å)	27.03	26.93 (7)	29.3 (4)	31.75 (10)	5.47 (1)	45.88 (13)	53.75 (13)	58.9 (3)
α (°)	85.25	85.35 (15)	96 (1)	94.0 (5)	94.82 (1)	87.2 (2)	68.0 (2)	94 (1)
β (°)	87.30	87.27 (15)	102 (1)	96.7 (5)	100.45 (2)	103.0 (2)	123.2 (2)	98 (2)
γ (°)	79.64	79.28 (15)	96 (1)	99.2 (5)	96.41 (1)	101.0 (5)	122.5 (5)	99 (2)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
<i>V</i> (Å ³)	1762.5	1761.3	1923.2	2082.8	2029.9	2862.7	2902.1	3982.2
<i>Z</i>	2	2	2	2	2	2	2	2
<i>D</i> _{calc} (g cm ⁻³)	1.03	1.04	1.11	1.01	1.04	1.03	1.01	0.95
<i>R</i> value	0.179	0.051	0.19	0.20	0.06	—	—	—
No. of reflections	600	2220	365	682	1850	—	—	—

(a) Jensen & Mabis (1963); (b) Jensen & Mabis (1966); (c) Doyne & Gordon (1968); (d) Larsson (1965); (e) Gibon *et al.* (1984); (f) Skoda *et al.* (1967); (g) De Jong & Van Soest (1978); (h) Simpson & Hagemann (1975).

effects were applied. The structure was solved using the program package *CRUNCH* (de Gelder *et al.*, 1993) and H atoms were calculated. The structure was refined with *Xtal* (Hall *et al.*, 1995) using a full-matrix least-squares refinement on *F*. The refinement began with strong restraints at the non-H atoms, which were loosened at each step until they were not restrained at all. The H atoms were restrained at 0.96 Å from their carrier atom. Anisotropic atomic displacement parameters for the non-H atoms and isotropic for the H atoms were used.†

The crystal structures of β -CCC and β -LLL were taken from the Cambridge Structural Database (CSD; Allen & Kennard, 1993), with refcodes TCAPIN10 and BTRILA05, respectively. The coordinates of CL^{Brc} were taken from Doyne & Gordon (1968).

Cell parameters for MMM were determined by indexing the Guinier diffraction pattern, which was carried out using the program *ITO* (Visser, 1969).

2.3. Structure comparison, model building and structure prediction

Since the molecular structure of the C_{*n*}C_{*n*}C_{*n*}-type (*n* = even) TAGs differ by the addition of a —CH₂—CH₂— fragment to the acyl chains only, and since the melting points of their β polymorphs lie on a smooth curve (Lutton & Fehl, 1970), this series can be considered as homologous (De Jong & Van Soest, 1978). The cell parameters and space groups of these TAGs as found in the literature are listed in Table 3.

The structures of β -CCC, β -CL^{Brc}, β -LLL and β -PPP have been compared in order to find a model which expresses their structural resemblance. Matching was performed by minimizing the distance between corresponding C and O atoms, resulting in an overall r.m.s. (root mean square) value expressing the quality of the fit. For visualization and structural comparison of these

structures version 2.5c of the program *PLUVA* (Driessen *et al.*, 1988) was used.

With the structures of β -CCC, β -LLL and β -PPP an overlap model was built. The structures were fitted and their unit cells were transformed to obtain unambiguously comparable unit cells for the whole series.

A crystal structure model for β -MMM was built using the determined cell parameters and the Cartesian coordinates of PPP. An X-ray powder diffraction pattern was calculated with the program *Cerius²* (Molecular Simulations Inc., 1995) and compared with the experimental pattern. Minimization of the difference pattern was performed using *DBWS*, which is incorporated in *Cerius²* (Molecular Simulations Inc., 1995). Since an asymmetric profile function such as a split-Pearson VII is not available in this version of *DBWS*, the pseudo-Voigt function with an additional asymmetry parameter was used to fit the powder pattern instead.

Crystal structure models for β -SSS, β -TTT, β -AAA and β -BBB were also predicted. For the latter two no experimental data are available.

3. Results and discussion

3.1. Determination of cell parameters and space group

The cell parameters of PPP and space group are as given in Table 4. Since one direction of the crystals is larger than the diameter of the beam it was not possible to keep the whole crystal in the X-ray beam during measurement. This may have contributed to the relatively large *R* value. However, crystals of PPP, like crystals of most TAGs, are so soft that cutting them to the desired dimensions without drastically affecting the crystal quality is extremely difficult.

The chemical structure diagram and an *ORTEP* representation of the crystal structure of β -PPP are shown in Fig. 1. The fractional coordinates and atomic displacement parameters are listed in Table 5.

Under the experimental conditions given in §2.1 PPP crystallizes in an asymmetric tuning-fork conformation:

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0087). Services for accessing these data are described at the back of the journal.

Table 4. *Experimental details for β -PPP*

Crystal data		Frequency of standard reflections	Every 60 min
Chemical formula	$C_{51}H_{98}O_6$	Intensity decay (%)	15
Chemical formula weight	807.33	Total collection time (h)	625
Cell setting	Triclinic	Refinement	
Space group	$P\bar{1}$	Refinement on	F
a (Å)	5.4514 (8)	R	0.078
b (Å)	11.945 (1)	wR	0.071
c (Å)	40.482 (3)	S	0.803
α (°)	84.662 (7)	No. of reflections used in refinement	4491
β (°)	86.97 (1)	No. of parameters used	909
γ (°)	79.77 (1)	H-atom treatment	x, y, z, U refined, restrained at 0.96 Å
V (Å ³)	2581.1 (5)	Weighting scheme	$w = 1/[10 + 0.01(\sigma F_o)^2 + 0.001/(\sigma F_o)]$
Z	2	$(\Delta/\sigma)_{\max}$	0.012
D_x (Mg m ⁻³)	1.039	$\Delta\rho_{\max}$ (e Å ⁻³)	0.409
Radiation type	Cu $K\alpha$	$\Delta\rho_{\min}$ (e Å ⁻³)	-0.462
Wavelength (Å)	1.5418	Extinction method	None
No. of reflections for cell parameters	23	Source of atomic scattering factors	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV, Tables 2.2B and 2.3.1); Cromer & Mann (1968)
θ range (°)	39–41.5	Computer programs	
μ (mm ⁻¹)	0.5	Data collection	<i>CAD-4 Software</i> (Enraf–Nonius, 1989)
Temperature (K)	243	Cell refinement	<i>CELCON</i> (local program)
Crystal form	Plank shaped	Data reduction	<i>Xtal ADDREF</i> (Hall <i>et al.</i> , 1995)
Crystal size (mm)	0.9 × 0.18 × 0.08 and 0.75 × 0.23 × 0.05	Structure solution	<i>CRUNCH</i> (de Gelder <i>et al.</i> , 1993)
Crystal colour	White	Structure refinement	<i>Xtal CRYLSQ</i> (Hall <i>et al.</i> , 1995)
Data collection		Preparation of material for publication	<i>Xtal BONDLA CIFIO</i> (Hall <i>et al.</i> , 1995)
Diffractometer	Enraf–Nonius CAD-4		
Data collection method	$\omega/2\theta$ scans		
Absorption correction	None		
No. of measured reflections	10 591		
No. of independent reflections	10 591		
No. of observed reflections	4491		
Criterion for observed reflections	$I_{\text{net}} > 2.5\sigma(I_{\text{net}})$		
θ_{\max} (°)	74.92		
Range of h, k, l	-6 → h → 4 -14 → k → 14 -50 → l → 50		
Standard reflections	10 $\bar{2}$ and 1 $\bar{1}\bar{2}$		

palmitic chains (I) and (III) are pointing in one direction and chain (II) in the opposite direction, being an elongation of chain (I). As a result, in projection just two chains connected by a glycerol can be observed when the molecule is positioned with the chains perpendicular

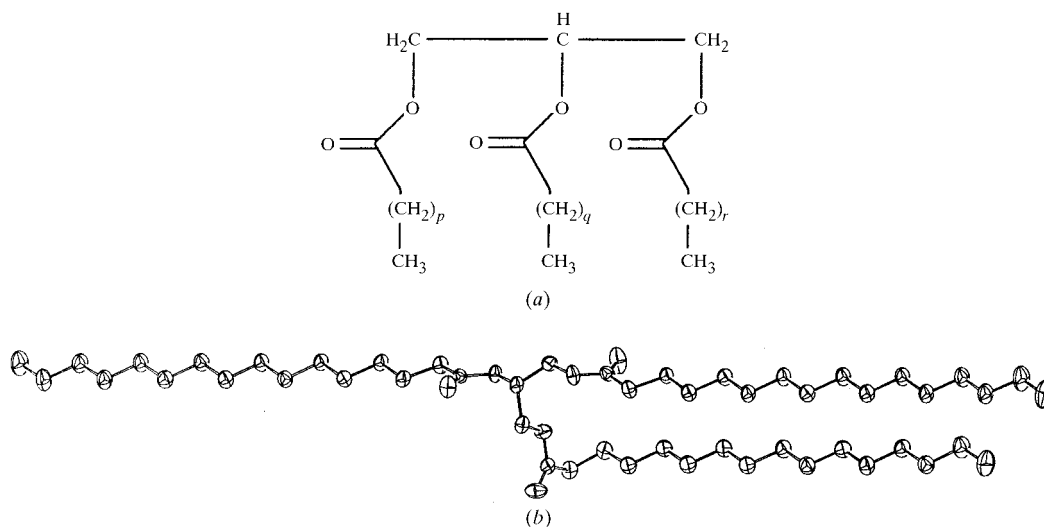
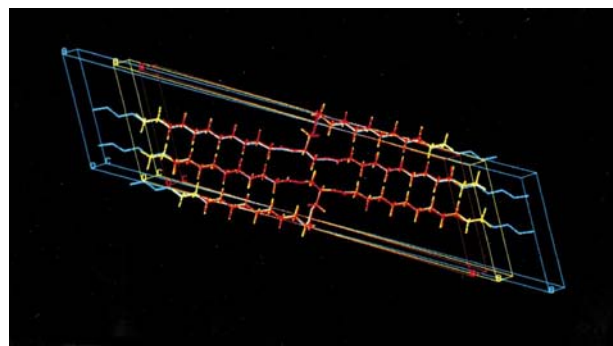


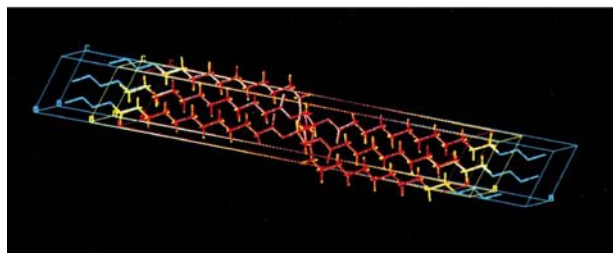
Fig. 1. (a) Chemical structural diagram of PPP ($p = q = r = 14$). (b) ORTEP representation of the crystal structure of β -PPP.

to the screen or paper. Bond lengths and angles are listed in Table 6.

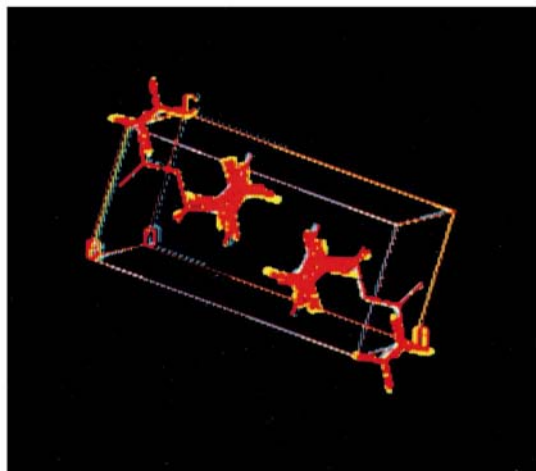
The PPP molecules are packed like stacked chairs forming layers of laterally packed acyl chains interrupted by a glycerol region. At the boundaries of these layers methyl end-group planes can be observed. The acyl chains are tilted with respect to these planes. The zigzag planes of all acyl chains are parallel, which is common to the crystal packing of β -TAGs.



(a)



(b)



(c)

Fig. 2. Crystal structure model of matching β -TAGs. The cell and structure of β -CCC are red, for β -LLL they are yellow and for β -PPP blue. (a) The c axes are approximately perpendicular to the plane of the paper. (b) The a axes are approximately perpendicular to the plane of the paper. (c) The acyl chains are perpendicular to the plane of the paper.

Table 5. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for β -PPP

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
C1	0.3061 (11)	0.4096 (5)	0.98145 (16)	0.037 (4)
C2	0.4352 (10)	0.3173 (5)	1.00549 (14)	0.033 (4)
C3	0.5551 (10)	0.2092 (5)	0.98965 (14)	0.035 (4)
O1a	0.4871 (7)	0.4338 (3)	0.95602 (10)	0.038 (3)
C1a	0.4069 (10)	0.4690 (5)	0.92541 (15)	0.034 (4)
O2a	0.1876 (7)	0.4891 (4)	0.92015 (11)	0.063 (4)
C2a	0.6137 (11)	0.4812 (6)	0.90063 (17)	0.039 (4)
C3a	0.5318 (11)	0.5633 (6)	0.87052 (15)	0.035 (4)
C4a	0.7422 (11)	0.5716 (6)	0.84474 (17)	0.039 (5)
C5a	0.6671 (12)	0.6600 (6)	0.81605 (17)	0.040 (5)
C6a	0.8705 (12)	0.6706 (6)	0.78952 (16)	0.039 (4)
C7a	0.7941 (11)	0.7610 (6)	0.76141 (16)	0.041 (5)
C8a	0.9929 (12)	0.7715 (6)	0.73459 (17)	0.041 (5)
C9a	0.9174 (12)	0.8628 (6)	0.70649 (17)	0.043 (5)
C10a	1.1160 (12)	0.8726 (6)	0.67930 (17)	0.043 (5)
C11a	1.0402 (12)	0.9628 (6)	0.65132 (17)	0.044 (5)
C12a	1.2390 (12)	0.9721 (6)	0.62394 (17)	0.044 (5)
C13a	1.1600 (13)	1.0608 (7)	0.59556 (18)	0.049 (5)
C14a	1.3620 (13)	1.0706 (7)	0.56885 (18)	0.049 (5)
C15a	1.2852 (17)	1.1569 (9)	0.5401 (2)	0.072 (7)
C16a	1.490 (2)	1.1688 (11)	0.5141 (2)	0.082 (9)
O1b	0.2413 (6)	0.2916 (3)	1.02907 (9)	0.034 (3)
C1b	0.3136 (10)	0.2504 (4)	1.06000 (13)	0.030 (4)
O2b	0.5276 (6)	0.2365 (4)	1.06743 (10)	0.046 (3)
C2b	0.1009 (11)	0.2246 (6)	1.08184 (16)	0.038 (4)
C3b	0.1762 (11)	0.1417 (6)	1.11169 (15)	0.035 (4)
C4b	-0.0359 (11)	0.1299 (6)	1.13698 (15)	0.036 (4)
C5b	0.0389 (11)	0.0403 (6)	1.16551 (16)	0.038 (4)
C6b	-0.1658 (12)	0.0295 (6)	1.19207 (16)	0.039 (5)
C7b	-0.0892 (12)	-0.0614 (6)	1.22014 (16)	0.040 (5)
C8b	-0.2886 (12)	-0.0717 (6)	1.24701 (16)	0.041 (5)
C9b	-0.2114 (12)	-0.1620 (6)	1.27501 (17)	0.042 (5)
C10b	-0.4102 (12)	-0.1717 (6)	1.30226 (17)	0.042 (5)
C11b	-0.3320 (12)	-0.2621 (6)	1.33050 (17)	0.044 (5)
C12b	-0.5295 (12)	-0.2725 (6)	1.35746 (17)	0.045 (5)
C13b	-0.4493 (13)	-0.3627 (6)	1.38546 (17)	0.046 (5)
C14b	-0.6465 (13)	-0.3746 (7)	1.41265 (17)	0.047 (5)
C15b	-0.5659 (15)	-0.4641 (7)	1.44061 (19)	0.057 (6)
C16b	-0.7661 (18)	-0.4745 (9)	1.4676 (2)	0.069 (7)
O1c	0.3667 (7)	0.1792 (3)	0.96935 (10)	0.042 (3)
C1c	0.4272 (10)	0.0787 (5)	0.95592 (14)	0.034 (4)
O2c	0.6228 (7)	0.0151 (4)	0.95909 (11)	0.050 (3)
C2c	0.2141 (10)	0.0561 (6)	0.93600 (16)	0.039 (4)
C3c	0.1296 (11)	0.1529 (6)	0.90963 (17)	0.041 (5)
C4c	0.3290 (12)	0.1690 (6)	0.88321 (17)	0.042 (5)
C5c	0.2475 (12)	0.2598 (6)	0.85524 (17)	0.042 (5)
C6c	0.4468 (12)	0.2721 (6)	0.82840 (17)	0.044 (5)
C7c	0.3709 (12)	0.3606 (6)	0.79987 (17)	0.043 (5)
C8c	0.5707 (12)	0.3698 (6)	0.77302 (17)	0.043 (5)
C9c	0.4951 (12)	0.4590 (6)	0.74445 (17)	0.043 (5)
C10c	0.6933 (13)	0.4689 (6)	0.71748 (17)	0.045 (5)
C11c	0.6192 (12)	0.5591 (6)	0.68925 (17)	0.044 (5)
C12c	0.8152 (12)	0.5696 (7)	0.66218 (18)	0.046 (5)
C13c	0.7376 (12)	0.6612 (6)	0.63434 (17)	0.045 (5)
C14c	0.9330 (13)	0.6718 (6)	0.60709 (18)	0.047 (5)
C15c	0.8544 (14)	0.7639 (7)	0.5796 (2)	0.058 (6)
C16c	1.0492 (19)	0.7754 (10)	0.5521 (2)	0.074 (8)

3.2. Crystal structure comparison and model building

The overall r.m.s. values resulting from crystal structure matching between β -CCC, β -LLL and β -PPP are

Table 6. Selected geometric parameters (\AA , $^\circ$) for β -PPP

C1—O1a	1.433 (7)	C5b—C6b	1.522 (9)
C1—C2	1.502 (8)	C6b—C7b	1.518 (9)
C2—O1b	1.441 (7)	C7b—C8b	1.509 (9)
C2—C3	1.522 (8)	C8b—C9b	1.512 (9)
C3—O1c	1.460 (7)	C9b—C10b	1.516 (9)
O1a—C1a	1.341 (7)	C10b—C11b	1.521 (9)
C1a—O2a	1.203 (7)	C11b—C12b	1.504 (9)
C1a—C2a	1.487 (8)	C12b—C13b	1.514 (10)
C2a—C3a	1.525 (9)	C13b—C14b	1.513 (10)
C3a—C4a	1.520 (9)	C14b—C15b	1.510 (10)
C4a—C5a	1.516 (9)	C15b—C16b	1.515 (12)
C5a—C6a	1.516 (9)	O1c—C1c	1.345 (7)
C6a—C7a	1.515 (9)	C1c—O2c	1.199 (6)
C7a—C8a	1.506 (9)	C1c—C2c	1.524 (9)
C8a—C9a	1.521 (9)	C2c—C3c	1.524 (9)
C9a—C10a	1.514 (9)	C3c—C4c	1.509 (9)
C10a—C11a	1.510 (9)	C4c—C5c	1.520 (9)
C11a—C12a	1.519 (9)	C5c—C6c	1.511 (9)
C12a—C13a	1.514 (10)	C6c—C7c	1.513 (9)
C13a—C14a	1.514 (10)	C7c—C8c	1.508 (9)
C14a—C15a	1.505 (11)	C8c—C9c	1.520 (9)
C15a—C16a	1.511 (14)	C9c—C10c	1.507 (10)
O1b—C1b	1.354 (6)	C10c—C11c	1.515 (9)
C1b—O2b	1.200 (6)	C11c—C12c	1.502 (10)
C1b—C2b	1.480 (8)	C12c—C13c	1.518 (10)
C2b—C3b	1.515 (9)	C13c—C14c	1.505 (10)
C3b—C4b	1.520 (8)	C14c—C15c	1.513 (10)
C4b—C5b	1.520 (9)	C15c—C16c	1.509 (12)
O1a—C1—C2	107.2 (4)	C5b—C4b—C3b	113.1 (5)
O1b—C2—C1	104.7 (4)	C4b—C5b—C6b	114.6 (5)
O1b—C2—C3	109.4 (5)	C7b—C6b—C5b	113.9 (5)
C1—C2—C3	114.0 (5)	C8b—C7b—C6b	114.5 (5)
O1c—C3—C2	106.7 (4)	C7b—C8b—C9b	114.4 (5)
C1a—O1a—C1	118.0 (4)	C8b—C9b—C10b	114.6 (5)
O2a—C1a—O1a	120.8 (5)	C9b—C10b—C11b	114.6 (5)
O2a—C1a—C2a	126.2 (6)	C12b—C11b—C10b	114.7 (5)
O1a—C1a—C2a	113.0 (5)	C11b—C12b—C13b	114.2 (5)
C1a—C2a—C3a	113.1 (5)	C14b—C13b—C12b	114.8 (5)
C4a—C3a—C2a	112.7 (5)	C15b—C14b—C13b	114.7 (6)
C5a—C4a—C3a	112.8 (5)	C14b—C15b—C16b	113.9 (7)
C4a—C5a—C6a	114.7 (5)	C1c—O1c—C3	116.0 (4)
C7a—C6a—C5a	114.0 (5)	O2c—C1c—O1c	124.6 (6)
C8a—C7a—C6a	114.7 (5)	O2c—C1c—C2c	124.3 (6)
C7a—C8a—C9a	114.8 (5)	O1c—C1c—C2c	111.0 (4)
C10a—C9a—C8a	114.9 (5)	C3c—C2c—C1c	112.6 (6)
C11a—C10a—C9a	114.9 (5)	C4c—C3c—C2c	113.1 (5)
C10a—C11a—C12a	114.8 (5)	C3c—C4c—C5c	114.8 (5)
C13a—C12a—C11a	114.6 (5)	C6c—C5c—C4c	114.1 (5)
C14a—C13a—C12a	113.9 (6)	C5c—C6c—C7c	115.6 (5)
C15a—C14a—C13a	114.6 (6)	C8c—C7c—C6c	114.8 (5)
C14a—C15a—C16a	114.3 (7)	C7c—C8c—C9c	114.8 (5)
C1b—O1b—C2	116.5 (4)	C10c—C9c—C8c	115.2 (5)
O2b—C1b—O1b	121.8 (5)	C9c—C10c—C11c	115.2 (5)
O2b—C1b—C2b	126.3 (5)	C12c—C11c—C10c	115.7 (5)
O1b—C1b—C2b	111.9 (5)	C11c—C12c—C13c	114.7 (5)
C1b—C2b—C3b	113.9 (5)	C14c—C13c—C12c	114.9 (5)
C2b—C3b—C4b	113.9 (5)	C13c—C14c—C15c	114.5 (6)
		C16c—C15c—C14c	115.0 (7)

very small (Table 7), the common part of them being almost identical. The atoms of the glycerol moiety and the chain atoms correspond very well, even at the end of the chains. There is no indication of chain-end swaying, neither from the coordinates of the chain-end atoms nor from their atomic displacement parameters.

Table 7. Overall r.m.s. values after matching of the β -TAG crystal structures

	β -CCC ^(a)	β -LLL ^(b)	β -PPP ^(c)	β -CL ^{Br} C ^(d)
β -CCC ^(a)	0.000	—	—	—
β -LLL ^(b)	0.033	0.000	—	—
β -PPP ^(c)	0.070	0.059	0.000	—
β -CL ^{Br} C ^(d)	0.238	0.247	0.251	0.000

(a) Jensen & Mabis (1966); (b) Gibon *et al.* (1984); (c) this work; (d) Doyne & Gordon (1968).

Matching β -CL^{Br}C to these structures resulted in much larger overall r.m.s. values around 0.25. Therefore, this structure is not taken into account in the further considerations.

To facilitate the comparison of the homologous series of molecules, which differ in chain length only and thus are expected to have similar cells, the experimental cells of β -CCC, β -LLL and β -PPP (Table 3) were transformed so that the longest cell axis is parallel to the acyl chains (Table 8). After these transformations only the *b* axis changes significantly as a function of the chain length (Fig. 2), the increment to the next member of the series being 5.1 \AA . This is in good agreement with the expected chain lengthening of 5.0 \AA , based on an average Csp^3-Csp^3 bond length of 1.524 \AA and Csp^3-Csp^3 angle of 109.3 $^\circ$. This change, as well as the change of the cell volume, is linear for this part of the series (Fig. 3), which provides a good basis for crystal structure prediction of the unknown members of this series.

The positions of the molecules in the transformed unit cell with regard to the origin are the same for all the members of this series, so all have identical interactions at the glycerol and methyl end-group region, and identical lateral chain packing. Having this model of matching β -TAG structures positioned with the acyl chains perpendicular to the screen or paper (Fig. 2c), full overlap of structures and unit cells is observed. Calculating the lattice-plane distances for the lattice planes (nearly) parallel to the acyl chains (Fig. 4, Table 9)

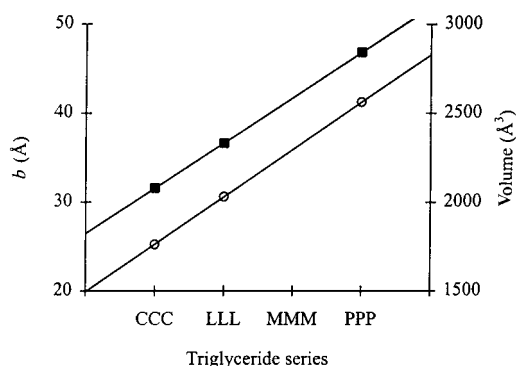


Fig. 3. The length of the *b* axis (black squares) and the unit-cell volume (open circles) of β -CCC, β -LLL and β -PPP (Table 8).

Table 8. Cell parameters of the β -TAG crystal structures after transformation to the setting used in the model

Cell parameter	β -CCC ^(a)	β -LLL ^(b)	β -PPP ^(c)	β -CL ^{BrC} ^(d)
a (Å)	12.18	12.08	11.95	12.35
b (Å)	31.56	36.61	46.84	35.27
c (Å)	5.49	5.47	5.45	5.51
α (°)	73.4	73.4	73.8	74.8
β (°)	100.7	100.5	100.2	96.0
γ (°)	119.2	118.7	118.1	123.7
V (Å ³)	1761.3	2029.2	2581.1	1923.2
D (g cm ⁻³)	1.04	1.04	1.04	1.11
Transformation matrix	0 1 0	1 0 0	0 -1 0	-1 0 0
	-1 -1 -1	-1 1 2	2 2 -1	1 -2 -1
	-1 0 0	0 0 1	1 0 0	0 -1 0

(a) Jensen & Mabis (1966); (b) Gibon *et al.* (1984); (c) this work; (d) Doyne & Gordon (1968).

Table 9. Characteristic d spacings (Å) for the β -TAGs of the overlap model

See Table 8 for cell parameters. These lattice planes are (almost) parallel to the acyl chains. $d(1\bar{1}1)$ is somewhat tilted with respect to the acyl chains.

	$d(001)$	$d(101)$	$d(1\bar{1}1)$	$d(20\bar{1})$	$d(3\bar{1}0)$
β -CCC ^(a)	5.25	4.61	4.54	3.84	3.74
β -LLL ^(b)	5.23	4.60	4.54	3.82	3.70
β -PPP ^(c)	5.23	4.58	4.55	3.82	3.64

(a) Jensen & Mabis (1966); (2) Gibon *et al.* (1984); (c) this work.

Table 10. Predicted and experimental cell parameters of β -TAGs

Values in the first column for each of MMM, SSS, AAA, BBB and TTT are predicted from the model.

Cell parameter	MMM	MMM ^(a)	SSS	SSS ^(b)	SSS ^(c)	AAA	BBB	TTT	TTT ^(d)
a (Å)	12.07	12.11	12.07	11.97	12.11	12.07	12.07	12.07	13.10
b (Å)	41.72	41.53	51.95	52.08	53.83	57.06	62.17	67.30	70.95
c (Å)	5.47	5.48	5.47	5.45	5.45	5.47	5.47	5.47	5.30
α (°)	73.6	74.6	73.6	72.8	73.1	73.6	73.6	73.6	72.6
β (°)	100.5	100.4	100.5	101.0	100.2	100.5	100.5	100.5	99.0
γ (°)	118.7	118.0	118.7	117.9	121.3	118.7	118.7	118.7	122.1
V (Å ³)	2314.2	2341.7	2881.7	2862.7	2902.1	3165.1	3448.6	3733.1	3982.2
Transformation matrix		1 0 0		-1 0 0	1 1 0				-1 0 0
		-1 1 2		1 -2 -1	-4 1 -1				2 -4 -1
		0 0 1		0 -1 0	0 1 0				0 -1 0

(a) Determined from Guinier data; (b) Skoda *et al.* (1967); (c) De Jong & Van Soest (1978); (d) Simpson & Hagemann (1975).

results in identical values for each member of the series. Since many scatterers are at these planes, strong reflections can be expected and these reflections are indeed responsible for the characteristic β diffraction pattern.

3.3. Crystal structure prediction

The uniform unit cell provides linear lengthening of the b axis and a linear increase of cell volume (Fig. 3; Table 8) upon chain lengthening. Combined with the common orientation and position of the molecules, crystal structures of the unknown members of the series can be predicted.

For β -MMM unit-cell parameters and the crystal structure were calculated (Tables 10 and 11). The

calculated cell parameters deviate only slightly from those determined from the Guinier X-ray powder photograph (Table 10). The calculated X-ray powder diagram of β -MMM agrees with the measured pattern (Fig. 5). Background coefficients, scale factor, isotropic displacement parameters, zero-point shift and cell parameters were refined. The width parameters of the profile function, U , V and W , could not be refined since there was too much peak overlap. During minimization all atomic coordinates were fixed. The remaining differences in peak shape, *e.g.* asymmetry and intensity, are due to instrumental line broadening, particle size distribution, lattice imperfections and preferred orientation.

In this way, cell parameters and crystal structure models can also be predicted for β -SSS, β -AAA, β -BBB

and β -TTT (Table 10). Since these TAGs lie outside the range studied, the resulting extrapolated parameters should be used with some care. Nevertheless, the calculated cell parameters of β -SSS deviate only slightly from those determined by Skoda *et al.* (1967).

In contrast, the cell parameters predicted for β -TTT differ appreciably from those given by Simpson & Hagemann (1975). Moreover, the measured density of β -LLL (Vand & Bell, 1951) as well as the calculated densities (Table 3) deviate largely from the density of β -TTT measured by Simpson & Hagemann (1975). As already mentioned, the cell parameters for β -TTT as determined by Simpson & Hagemann (1975) are less reliable, in view of their much larger standard uncertainties and, in particular, since they imposed the measured β -TTT density as an additional constraint to their cell-parameter determination.

De Jong (1980) also showed correspondence between the unit cells of these β -TAGs. He transformed the unit cells of β -CCC, β -LLL, β -MMM and β -PPP. With his cell choice the a and c axes, and α and β , change upon chain variation. A quantitative crystal structure prediction originating from that series has not been published.

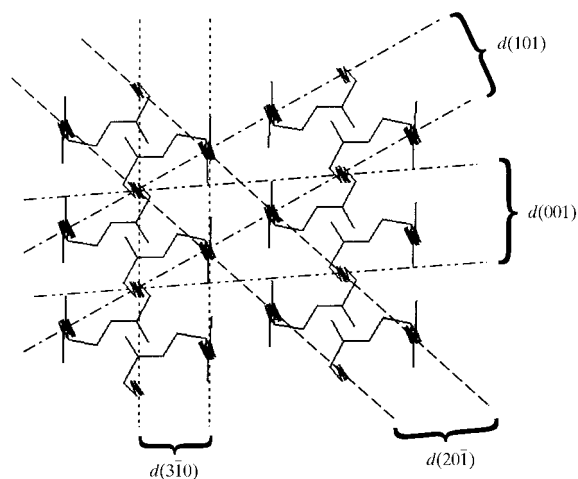


Fig. 4. Crystal structure of β -PPP, with the acyl chains perpendicular to the plane of the paper. The lattice planes responsible for the characteristic d spacings are indicated (Table 9).

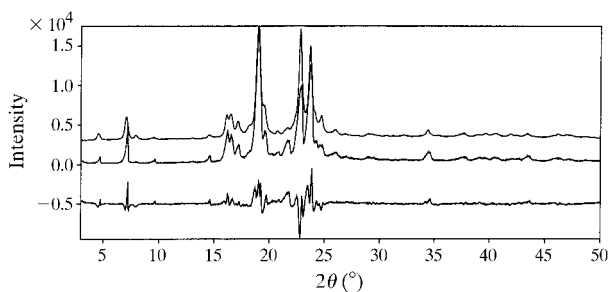


Fig. 5. Calculated (upper) versus experimental (middle) X-ray powder diagram of β -MMM and the difference (below).

Table 11. Fractional coordinates of the crystal structure model of β -MMM

Cell parameters of β -MMM: $a = 12.11$, $b = 41.53$, $c = 5.48$ Å, $\alpha = 74.6$, $\beta = 100.4$ and $\gamma = 118.0^\circ$. The volume is 2341.7 Å³ and the space group is $P\bar{1}$, with $Z = 2$ resulting in a density of 1.02 g cm⁻³.

Atom	x	y	z
C1	0.36043	0.47869	-0.25544
C2	0.31679	0.50574	-0.42934
C3	0.17892	0.48801	-0.51994
O1a	0.33407	0.45012	-0.38794
C1a	0.30848	0.41573	-0.25086
O2a	0.31795	0.40983	-0.02278
C2a	0.27162	0.38790	-0.41034
C3a	0.29314	0.35405	-0.27214
C4a	0.25052	0.32508	-0.43327
C5a	0.28114	0.29284	-0.30449
C6a	0.23922	0.26303	-0.45732
C7a	0.27296	0.23142	-0.32824
C8a	0.23035	0.20130	-0.47596
C9a	0.26500	0.16970	-0.34782
C10a	0.22102	0.13916	-0.49460
C11a	0.25486	0.10770	-0.36646
C12a	0.20994	0.07695	-0.51315
C13a	0.24149	0.04503	-0.38103
C14a	0.19850	0.01504	-0.53207
O1b	0.33797	0.53224	-0.28058
C1b	0.35831	0.56698	-0.41041
O2b	0.35929	0.57534	-0.63734
C2b	0.37592	0.59152	-0.23972
C3b	0.35306	0.62508	-0.37090
C4b	0.39132	0.65350	-0.20714
C5b	0.35922	0.68556	-0.33538
C6b	0.40092	0.71540	-0.18130
C7b	0.36668	0.74696	-0.31050
C8b	0.40954	0.77714	-0.16225
C9b	0.37574	0.80864	-0.29191
C10b	0.41986	0.83924	-0.14499
C11b	0.38642	0.87100	-0.27605
C12b	0.42932	0.90127	-0.12995
C13b	0.39564	0.93276	-0.26255
C14b	0.43752	0.96330	-0.11708
O1c	0.10934	0.46523	-0.29491
C1c	-0.01629	0.45020	-0.33072
O2c	-0.07269	0.45379	-0.53167
C2c	-0.07785	0.42784	-0.08185
C3c	-0.03444	0.39818	0.05206
C4c	-0.07061	0.36850	-0.09696
C5c	-0.03622	0.33705	0.03694
C6c	-0.07710	0.30690	-0.11118
C7c	-0.04608	0.27482	0.01812
C8c	-0.08997	0.24467	-0.13051
C9c	-0.05829	0.21254	-0.00141
C10c	-0.10171	0.18225	-0.14829
C11c	-0.06848	0.15050	-0.02134
C12c	-0.11153	0.12010	-0.16578
C13c	-0.07606	0.08879	-0.03596
C14c	-0.11943	0.05819	-0.17952

4. Conclusions

The crystal structures of the β - $C_nC_nC_n$ ($n = \text{even}$) series TAGs are very similar, as can be concluded from the overlap model. From the two known structures of β -CCC and β -LLL alone, it was difficult to predict accurate cell parameters and crystal structures for the

whole $C_nC_nC_n$ series. However, the determination of the PPP crystal structure made it possible to determine the structural relationships in the series.

As long as this series exhibits linear behaviour, accurate crystal structure models can be predicted easily by extrapolation of the cell parameters and copying of the atomic coordinates. It is expected that the series deviates from linearity when the acyl chains become very short and lateral-chain packing is no longer dominant.

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