Crystal Packing of a Homologous Series β′-Stable Triacylglycerols

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ABSTRACT: From a homologous series of $C_nC_{n+2}C_n$ (n = even) triacylglycerols which are β′-stable, Guinier X-ray powder diffraction photographs were used to determine cell parameters and space groups. The powder diffraction patterns are consistent with a pseudo-orthorhombic unit cell with space group *Ic*2*a*. Only one axis is changing as a function of chain lengthening. The experimental results were used to propose a β′-crystal packing for triacylglycerols. In contrast to earlier proposed β′-crystal structures, the acyl chains of this structure are not tilted with respect to the methyl-end group plane. Furthermore, with only one molecule in the asymmetric unit, overall orthogonal chain packing is obtained when the intramolecular acyl zigzag planes are parallel.

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Polymorphism of fats and triacylglycerols (TAG) is a permanent subject of research because it may have important implications for the manufacturing of many different food products such as chocolate and margarine. Pure TAG crystallize in the different polymorphic phases α, β, and/or β′ and sometimes even several different β′- and/or β-polymorphs exist (1,2). The different polymorphic phases and their variants can be distinguished by X-ray diffraction through typical reflections in the fingerprint region of the X-ray powder diagram (d-spacings from 3.0 to 6.0 Å) (3,4). Table 1 shows the characteristics of the X-ray patterns of the different phases.

Depending on the TAG type the most stable phase is either β′ or β. De Jong and Van Soest (5) showed that TAG of the type $C_nC_{n+2}C_n$ and $C_nC_{n+4}C_{n+2}$ (n = even) are normally β′-stable. Most other types are generally β-stable. TAG mixtures also show differences in phase stability. For example, milk fat is β′-stable (6) while cocoa butter has β as the most stable phase (7,8).

TABLE 1
Characteristics of Triacylglycerol (TAG) Polymorphs (3,4)

Polymorph	d-Spacing (Å)	Subcell lattice	Acyl chain orientation	Symbol
α	4.15	Hexagonal	Random	H
β′	3.80, 4.20	Orthorhombic	Orthogonal	$O_\perp$
β	3.65, 3.85, 4.57	Triclinic	Parallel	$T_{/\!/}$

The phase behavior of pure TAG as well as TAG mixtures is very complex. Their phase transitions are generally irreversible and depend on experimental circumstances such as temperature and time, and their thermal history as is demonstrated by memory effects (9). Knowledge of this behavior, particularly the β′ → β phase transition is very important, especially for the chocolate industry, since unwanted phase transitions of cocoa butter may cause fat bloom, a white appearance of fat crystals on the surface. Therefore, control of these transitions determine to a large extent the quality of chocolate products.

Crystal structure information of the different phases is indispensable to understand the mechanism of these transitions. Unfortunately, so far only crystal structures of β-polymorphs of pure TAG have been reported (10–15), all [β-1,2,3-tridecanoyl-glycerol, or tricaprin, or $C_{10}C_{10}C_{10}$(β-CCC); β-1,2,3-tridodecanoyl-glycerol, or trilaurin, or $C_{12}C_{12}C_{12}$ (β-LLL); β-1,2,3-trihexadecanoyl-glycerol, or tripalmitin, or $C_{16}C_{16}C_{16}$ (β-PPP); and β-2-11-bromoundecanoyl-1,3-didecanoyl-glycerol, or $C_{10}C_{11}$ Br C_{10} (β-$CL^{Br}C$)] crystallizing in space group $P\bar{1}$. The molecules are in a so-called asymmetric "tuning-fork" conformation (Fig. 1), in which the two outer acyl chains (I and III) point in one direction and the middle acyl chain (II) in the opposite direction. They are packed like stacked chairs and the zigzag planes of the chains are parallel. Van Langevelde *et al.* (15) showed the correspondence between the structures in this $C_nC_nC_n$ (n = even) series. $CL^{Br}C$ is a heavy-atom analog of 1,3-didecanoyl-2-dodecanoyl-glycerol, or $C_{10}C_{12}C_{10}$ (CLC) and therefore expected to be β′-stable; however, the crystal structure shows clearly a β-polymorph.

Efforts made to determine the crystal structure of TAG in the β′-phase were not successful, and difficulties with growing reasonable single crystals played an important role in all trials. Nevertheless, it appeared to be possible to determine unit-cell parameters and space group of a few β′-polymorphs. Larsson (16) determined unit-cell parameters and orthorhombic space group $P2_12_12_1$ of β′-LLL and suggested on the basis of packing arguments the acyl chains of β′-LLL being tilted with respect to the methyl end-group plane. The direction of this tilt then alternates between successive chain layers. For β′-1,3-dihexadecanoyl-2-octadecanoyl-glycerol, or $C_{16}C_{18}C_{16}$ (β′-PSP) he suggested that the alternating tilt of chains will be realized

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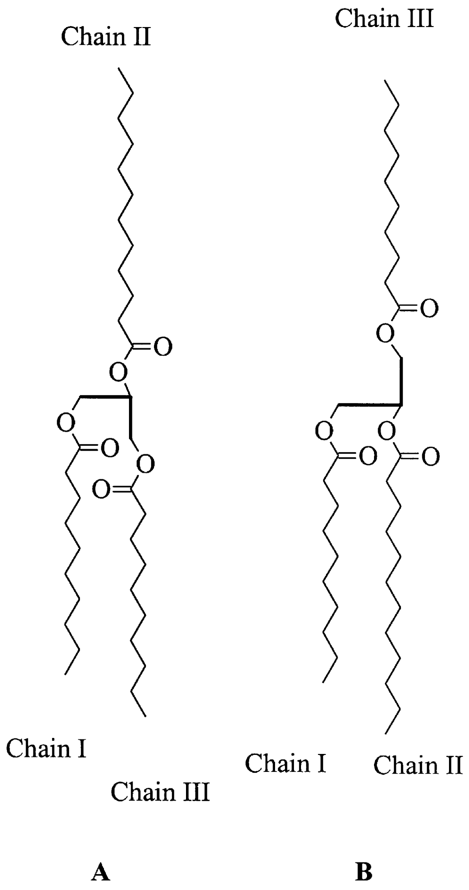

FIG. 1 (A) Schematic representation of a tuning-fork conformation. (B) Schematic representation of a chair conformation. In both A, and B, the orientation of carbonyl and the zigzag planes are randomly chosen.

at the glycerol moiety. Hernqvist and Larsson (17) determined the unit-cell parameters and space group of β′-1,2,3-triundecanoyl-glycerol, or triundecanoin (β′-$C_{11}C_{11}C_{11}$) and postulated a similar alternating chain-tilt angle (τ) and the necessity of two molecules in the asymmetric unit (17,18).

Birker *et al.* (19) revealed from a single-crystal analysis the unit-cell parameters and space group of β′-1,3-didodecanoyl-2-tetradecanoyl-glycerol, or $C_{12}H_{14}C_{12}$ (β′-LML) and concluded LML to be monoclinic with space group *C*2, but exhibiting pseudo-orthorhombic symmetry. Based on this space group they assumed alternating tilts again and, moreover, the impossibility of straight LML molecules in the cell. Attempts to solve the crystal structure of β′-LML through single-crystal X-ray diffraction failed because of twinning (De Graaff, R.A.G., personal communication, 1997).

Structural evidence and theories of β′-crystal packing developed so far are not comprehensive. To contribute to the understanding of the packing we investigated a series of the β′-stable $C_nC_{n+2}C_n$ TAG. Their unit cells and space groups were determined from X-ray powder diffraction data and used to propose a β′-crystal packing. In contrast to earlier proposed β′-crystal packings our results imply that with a straight TAG molecule no chain tilt is present in the β′-phase of the $C_nC_{n+2}C_n$ (n = even) series. Also on the basis of the results the difference in crystallization behavior between these β′-stable and β-stable TAG will be discussed.

MATERIALS AND METHODS

Samples, sample preparation, and measurements. A series of $C_nC_{n+2}C_n$ TAG [CLC, LML, 1,3-ditetradecanoyl-2-hexadecanoyl-glycerol, or $C_{14}C_{16}C_{14}$ (MPM), and PSP] was obtained from Unilever Research Laboratorium (Vlaardingen, The Netherlands). From these samples X-ray powder diffraction photographs were made with Cu$K\alpha_1$ radiation (λ = 1.54060 Å) at room temperature, with an Enraf-Nonius FR 552 Guinier Johannson camera (Enraf-Nonius, Delft, The Netherlands) equipped with a Johannson monochromator. Samples were prepared by pressing a thin layer of powder on a mylar foil. To improve particle statistics the sample holder was either spin or translated during exposure. The Guinier photographs were read out by means of an optical instrument in order to collect the accurate positions of as many lines as possible. The subsequent indexing of the diagrams was carried out with the indexing program ITO (20).

Model building and manipulation. For displaying and manipulating the structure model the program Cerius$^{2\text{TM}}$ (21) was used. A starting model for CLC was created from the crystal structure of β-LLL [Refcode: BTRILA05, CSD (22)] by replacing the terminating ethyl groups of the outer acyl chains with a hydrogen atom. For this model structure atomic charges were calculated with the Charge Equilibration method (21). By using this model with the unit cell and space group as determined from the Guinier photograph a plausible crystal-packing model was proposed. During manipulation the cell parameters were kept fixed and the CLC molecules were allowed to translate and rotate as rigid units only.

RESULTS AND DISCUSSION

Determination of cell parameters and space group. Reflections corresponding with d-spacings of 3.8 and 4.2 Å were present in all X-ray powder diagrams (Fig. 2) confirming the samples to be β′-polymorphs. From the diffractograms cell parameters of CLC, LML, MPM, and PSP have been determined (Table 2). The patterns of these TAG show identical extinction conditions hkl: $h + k + l = 2n + 1$, $0kl$: $l = 2n + 1$ and $hk0$: $h = 2n + 1$, corresponding with an *I*-centered orthorhombic cell having a *c*-glide perpendicular to the *a*-axis and an *a*-glide perpendicular to the *c*-axis implying one of the space groups *Ic*2*a* or *Icma* (45 or 72, respectively, in non-standard setting).

After evaluating the Guinier photographs of CLC and MPM in more detail, an anisotropic peak broadening was noticed. The $h00$- and $00l$-reflections are sharp, but most other reflections are broadened, some of them being 2–3 times broader than the sharp ones. This could have a physical origin such as strong anistropy in the size of the crystallites or bent crystals; however, it may also be caused by a lower sym-

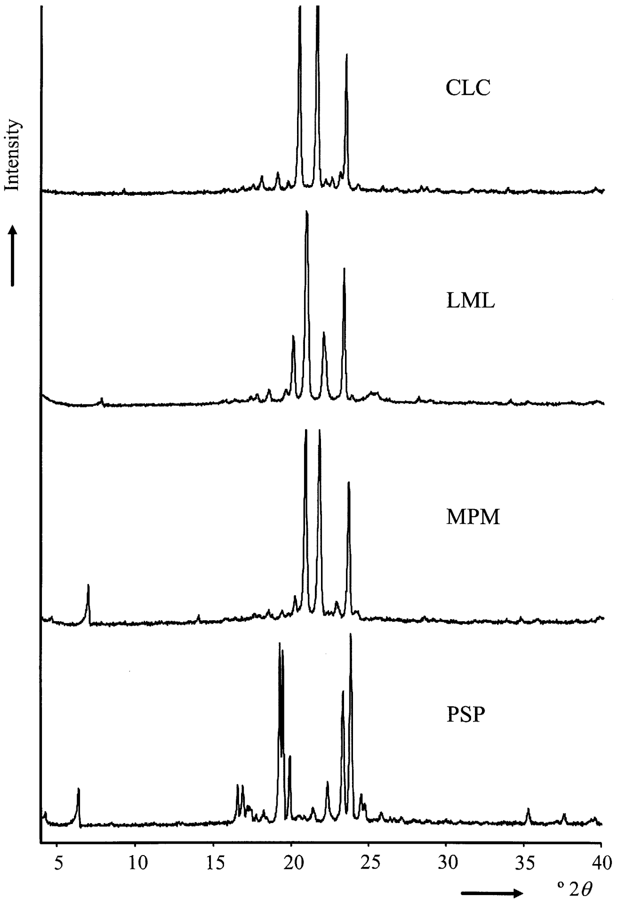

FIG. 2. Digitized Guinier X-ray powder diagrams of CLC, LML, MPM and PSP (λ = 1.54060 Å). CLC, 1,3-didecanoyl-2-dodecanoyl-glycerol, or $C_{10}H_{12}O_{10}$; LML, 1,3-didodecanoyl-2-tetradecanoyl-glycerol, or $C_{12}H_{14}O_{12}$; MPM, 1,3-ditetradecanoyl-2-hexadecanoyl-glycerol, or $C_{14}H_{16}O_{14}$; PSP, 1,3-dihexadecanoyl-2-octadecanoyl-glycerol, or $C_{16}H_{18}O_{16}$.

metry with a small angle deviation from 90°. To test the latter, the 2θ–values of the reflection positions of CLC were calculated with $\beta = 90.3°$ which caused all reflections *hkl* and $hk\bar{l}$ to occur at slightly different angles (see Table 3). Comparing this list with the Guinier photograph there is a striking correlation between the 2θ-difference ($\Delta 2\theta$) of *hkl* and $hk\bar{l}$, and the half-width of the corresponding peak. None of the observed broadened peaks shows a tendency of splitting, suggesting that the deviation from the orthorhombic symmetry is very small. Therefore, it is appropriate to state that the cell is pseudo-orthorhombic with the space group being pseudo-*Ic*2*a* or pseudo-*Icma*. The same is true for MPM, which shows a similar peak broadening.

For LML and PSP a small peak splitting is observed. However, the same pseudo-space group that was derived for CLC and MPM—*Ic*2*a* or *Icma*—is consistent with the extinctions in the diagrams of LML and PSP.

The two possible space groups for the compounds can be reduced to *Ic*2*a* only, since *Icma* would have a mirror plane perpendicular to the *b*-axis, and with eight molecules per unit cell this implies completely symmetric molecules in the mirror plane. This is not in agreement with the proposed orthogonal packing of the acyl zigzag planes for β′-TAG. The alternative, with molecules at both sides of that mirror plane, would result in 16 molecules in the cell and an improbable density of ~2 g/cm^3. Consequently, the space group of these TAG is *Ic*2*a*.

Birker *et al.* (19) also reported cell parameters of β′-LML comparable to the parameters as determined in this study (Table 1). They also observed the *Ic*2*a* pseudosymmetry but concluded finally that the space group was *C*2.

Structural relationship. The molecular structure of this series of β′-stable TAG differs only by lengthening the acyl chains with an additional -CH_2-CH_2-. Their melting points lie on a smooth curve [Fig. 3; (19)]. Moreover, a comparison of the determined unit-cell parameters reveals that the lengths

TABLE 2
Cell Parameters of β′-Polymorphs of TAG

Cell parameter	$C_{11}C_{11}C_{11}$[a]	LLL[b]	LML[c]	CLC	LML	MPM	PSP
a (Å)	23.6	23.6	22.9	22.78(4)	22.84(3)	22.60(4)	23.17(4)
b (Å)	5.69	5.69	5.7	5.70(1)	5.72(1)	5.66 (1)	5.72(1)
c (Å)	58.5	58.8	66.8	57.67(12)	67.39(15)	75.93(12)	83.79(19)
α (°)	90.0	90	90	90.0	90.0	90.0	90.0
β (°)	90 ± 0.5	90	91	90.0[d]	90.84(12)	90.0[d]	90.94(13)
γ (°)	90.0	90	90	90.0	90.0	90.0	90.0
Space group	$P2_1/c$	$P2_12_12_1$	*C*2	p-*Ic*2*a*	p-*Ic*2*a*	p-*Ic*2*a*	p-*Ic*2*a*
Volume (Å^3)	7856	7896	8718	7487(43)	8803(57)	9713(51)	11103(79)
Z	8	4	8	8	8	8	8
Density (g/cm^3)	0.96	0.510	1.02	1.03	1.01	1.03	1.00
Observed lines				51	57	59	59
Indexed lines				50	57	61	59
Range (°2θ)				5–35	2.5–40	4–40	4–35

[a] Ref. 17.
[b] Ref. 16.
[c] Ref. 19.
[d] Small deviation from 90.0° is possible.

Abbreviations: $C_{11}C_{11}C_{11}$, 1,2,3-triundecanoyl-glycerol or triundecanoin; CLC, 1,3-didecanoyl-2-dodecanoyl-glycerol or $C_{10}C_{12}C_{10}$; LLL, 1,2,3-tridodecanoyl-glycerol or trilaurin or $C_{12}C_{12}C_{12}$; LML, 1,3-didodecanoyl-2-tetradecanoyl-glycerol or $C_{12}C_{14}C_{12}$; MPM, 1,3-ditetradecanoyl-2-hexadecanoyl-glycerol or $C_{14}C_{16}C_{14}$; PSP, 1,3-dihexadecanoyl-2-octadecanoyl-glycerol or $C_{16}C_{18}C_{16}$.

TABLE 3
Calculated Reflections of a Cell Slightly Deviating from Orthorhombic Symmetry (*a* = 22.78 Å, *b* = 5.70 Å, *c* = 57.67 Å, and β = 90.3°) Compared with Observed Peak Broadening

h	*k*	*l*	$2\theta^a$	d	$\Delta 2\theta^b$	$2\theta^c$	Character
0	0	2	3.062	28.8336	—	3.06	Sharp
1	0	−1	4.159	21.2273	15	N.O.	—
1	0	1	4.174	21.1514			
1	0	−3	5.995	14.7298	31	6.01	Broad
1	0	3	6.026	14.6540			
0	0	4	6.125	14.4168	—	N.O.	—
2	0	0	7.754	11.3915	—	7.76	Sharp
2	0	−2	8.323	10.6136	30	8.30	Broad
2	0	2	8.353	10.5757			
1	0	−5	8.567	10.3118	37	8.58	Broad
1	0	5	8.604	10.2684			
0	0	6	9.193	9.6112	—	9.21	Sharp
2	0	−4	9.862	8.9609	51	9.89	Broad
2	0	4	9.913	8.9154			
1	0	−7	11.393	7.7603	38	11.38	Broad
1	0	7	11.431	7.7343			
3	0	−1	11.735	7.5344	16	N.O.	—
3	0	1	11.751	7.5242			
2	0	−6	12.006	7.3649	63	12.03	Broad
2	0	6	12.069	7.3270			
0	0	8	12.268	7.2084	—	12.28	Sharp
3	0	−3	12.499	7.0758	45	12.53	Broad
3	0	3	12.544	7.0505			
3	0	−5	13.916	6.3581	68	13.94	Broad
3	0	5	13.984	6.3276			
1	0	−9	14.327	6.1766	40	N.O.	—
1	0	9	14.367	6.1598			
2	0	−8	14.495	6.1058	69	14.50	Very broad
2	0	8	14.564	6.0769			
0	0	10	15.352	5.7667	—	N.O.	—
4	0	0	15.544	5.6957	—	15.55	Sharp
3	0	−7	15.816	5.5984			
4	0	−2	15.831	5.5933	83	15.85	Broad
4	0	2	15.862	5.5822			
3	0	7	15.899	5.5692			
1	1	−2	16.308	5.4307	8	16.30	Sharp
1	1	2	16.316	5.4281			
4	0	−4	16.691	5.3068	60	16.71	Broad
4	0	4	16.751	5.2879			
1	1	−4	17.156	5.1640	15	17.16	Rather sharp
1	1	4	17.171	5.1596			
2	0	−10	17.183	5.1559	74	N.O.	—
2	0	10	17.257	5.1342			
1	0	−11	17.322	5.1148	40	N.O.	—
1	0	11	17.362	5.1031			
2	1	−1	17.450	5.0777	7	17.45	Rather sharp
2	1	1	17.457	5.0756			
2	1	−3	17.980	4.9291	21	17.99	Somewhat broadened
2	1	3	18.001	4.9234			
4	0	−6	18.046	4.9112		N.O.	—
3	0	−9	18.051	4.9099	99	N.O.	—
4	0	6	18.130	4.8887			
3	0	9	18.145	4.8847			
0	0	12	18.446	4.8056	—	N.O.	—
1	1	−6	18.489	4.7947	20	18.49	Rather sharp
1	1	6	18.509	4.7895			
2	1	−5	19.005	4.6657	33	19.02	Somewhat broadened
2	1	5	19.038	4.6576			
5	0	−1	19.517	4.5443	16	N.O.	—
5	0	1	19.533	4.5406			
3	1	−2	19.692	4.5043	19	19.70	Somewhat broadened
3	1	2	19.711	4.5000			
4	0	−8	19.798	4.4804	102	N.O.	—
4	0	8	19.900	4.4577			
5	0	−3	19.985	4.4390		N.O.	—
2	0	−12	19.998	4.4361	89	N.O.	—
5	0	3	20.033	4.4285			
2	0	12	20.074	4.4195			
1	1	−8	20.213	4.3894	25	N.O.	—
1	1	8	20.238	4.3841			
1	0	—13	20.358	4.3585			
3	1	−4	20.398	4.3499	78	20.39	Broadness cannot be determined
1	0	13	20.399	4.3499			
3	1	4	20.436	4.3421			
2	1	−7	20.452	4.3387	43	N.O.	—
2	1	7	20.495	4.3296			
3	0	−11	20.518	4.3249	101	N.O.	—
3	0	11	20.619	4.3038			
5	0	−5	20.906	4.2455	76	N.O.	—
5	0	5	20.982	4.2303			
3	1	−6	21.532	4.1234	53	21.54	Broadness cannot be determined
0	0	14	21.555	4.1191			
3	1	6	21.585	4.1134			
4	0	−10	21.856	4.0630	116	N.O.	—
4	0	10	21.972	4.0418			
4	1	−1	22.094	4.0198	12	22.11	
4	1	1	22.106	4.0177			

[a] Calculated.

[b] 10^{-3} °2θ.

[c] Observed. Abbreviation: N.O., not observed.

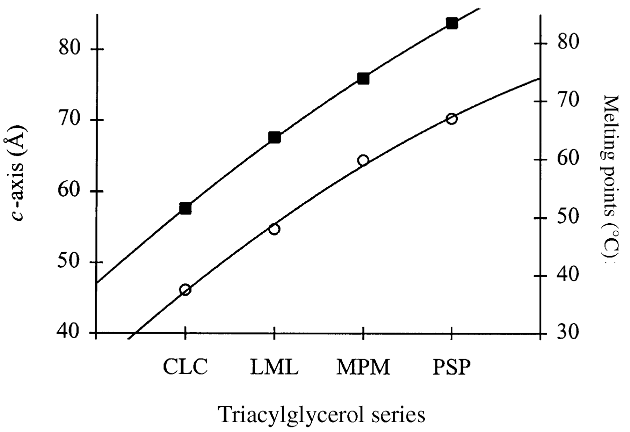

FIG. 3. The length of the *c*-axis (black squares) and the melting points (open circles) (23) of four $C_nC_{n+2}C_n$ triacylglycerols. For abbreviations see Figure 2.

of the two shorter axes *a* and *b* are approximately the same throughout the series and that the length of the long axis *c* increases with the length of the acyl chains.

The slight variation in the length of the *a*- and *b*-axes may be caused by variation in the acyl chain flexibility. Upon lengthening of the acyl chains, the ratio between cell space occupied by the chains, the methyl-end group region, and the glycerol moiety changes. This will finally lead to increasing domination of the acyl chains in the crystal packing, which will allow variation in the length of the *a*- and *b*-axes.

Since this is a homologous series it is appropriate to consider CLC, which is used for model building and manipulation, as representative for LML, MPM, and PSP as well.

Molecular orientation. The molecular structure of CLC is based on the crystal structure of β-LLL, known as the asymmetric "tuning-fork" conformation (Fig. 1A). This rigid CLC model was positioned in the orthorhombic unit cell as determined from the Guinier pattern, whereas the other seven molecules follow from the *Ic*2*a* space-group symmetry. Consequently, the crystal-packing model is controlled by three positional and three orientational parameters.

In contrast to earlier proposed crystal packings for the β′-polymorph, no chain tilt ($\tau = 90°$) is found for this series using this straight TAG molecule. We first calculated two molecules to fit the diagonal of the *I*-centered unit cell resulting in a τ of *ca.* 68° for the CLC molecules. However, upon lengthening of the acyl chains tilted chains would cause either a change of the *a*- and/or *b*-axes as well, or a varying τ upon chain lengthening. A varying τ is unlikely for this series and no relevant change of these axes could be observed. But even more important, when the TAG molecules are positioned with their chains tilted to the *ab*-plane, the symmetry imposed by the *Ic*2*a* space group causes an unreasonable packing. Facing the *ac*- and/or the *bc*-plane the molecules then are crossed and have too close contacts. Only when the acyl chains are parallel to the *c*-axis, and thus perpendicular to the *ab*-plane, can acceptable lateral packing be obtained. This can be seen in Figure 4A and 4B, which face the *ac*- and *bc*-plane, respectively.

Lateral chain packing. Since the molecular structure for CLC is based on the crystal structure of β-LLL, the zigzag planes of its three acyl chains are parallel. Rotation and translation of this rigid model in the unit cell while keeping the acyl chains parallel to the *c*-axis resulted in overall orthogonal lateral packing of the acyl chains. The angle between the zigzag planes of the acyl chains and the *ac*-plane of the unit cell is ~45° (Fig. 4C) resulting in a crystal packing for β′-CLC in which the zigzag planes within one molecule are parallel, but in which the chains of adjacent molecules are orthogonally packed. Having the acyl chains parallel to the *c*-axis and ~45° to the *ac*-plane, overall orthogonal chain packing is obtained not only with intramolecular parallel zigzag planes but also with intramolecular orthogonal zigzag planes.

Methyl end-group region. The *ac*-plane of the unit-cell model (Fig. 4A) shows no methyl end-group planes or terraces, and the acyl chain ends of adjacent layers do not overlap. From other projections it can be seen that the acyl chain ends penetrate in the adjacent layers, but no atomic overlap or close contact can be observed. As a consequence of the acyl chains being perpendicular to the *ab*-plane, more overlap is expected upon chain lengthening. Addition of $-CH_2-CH_2-$ to an acyl chain should result in a lengthening of 2.49 Å, based on an average C_{sp3}-C_{sp3} bond length of 1.524 Å and C_{sp3}-C_{sp3}-C_{sp3} angle of 109.3°. Going from one compound to the next in this series would give a *c*-axis lengthening of 4 times 2.49 Å, or 9.96 Å. However, the *c*-axis of the determined unit cells is not increasing linearly. From CLC to LML the *c*-axis increases 9.7 Å, implicating equal penetration for these compounds. From LML to MPM and from MPM to PSP the *c*-axis increase is less, 8.5 and 7.9 Å respectively.

Tuning fork vs. chair conformation. The model we built for β′-CLC is the only one we can get at the moment, since only crystal structures of asymmetric tuning-fork conformations are available for long-chain TAGs and attempts to build a plausible model for β′-CLC in the chair conformation, with acyl chain II in one direction together with I or III and the remaining acyl chain in the opposite direction or in a bent conformation, were not successful. In the chair conformation the difference between the length of the neighboring chains (I and II or II and III) is expected to be less, but equal for β′-stable TAG types $C_nC_{n+2}C_n$ and $C_nC_{n+4}C_{n+2}$ respectively. The plane of the methyl-end groups may be more smooth. Therefore, a chair conformation could also be a plausible model for the β′-polymorph of $C_nC_{n+2}C_n$ type TAG.

Suggesting a chair conformation for β′-stable TAG makes it possible to understand the absence of a β-phase for β′-stable TAG, since in the solid state it is impossible to transform a chair conformation into a tuning-fork.

The difference between tuning fork and chair crystallization can also explain the unexpected β-phase for $CL^{Br}C$, the heavy-atom analog of CLC. The bromine atom and a methylene fragment have a comparable size but a different mass. Therefore it is likely that the other chains (I and III) become neighbors, which results in a tuning-fork conformation that is β-stable as well.

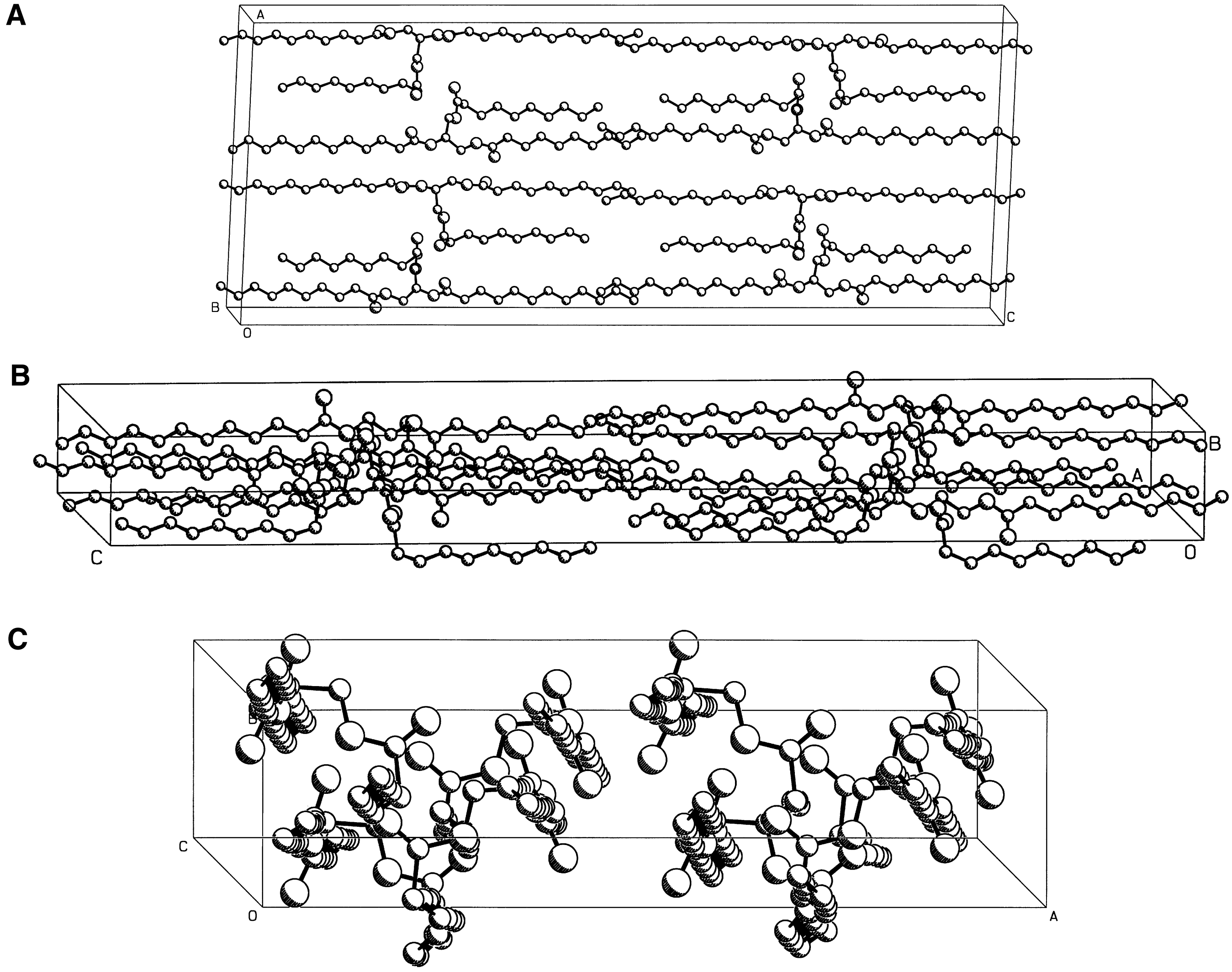

FIG. 4. Projections of the CLC unit-cell model. The CLC molecules are related *via Ic2a* symmetry resulting in eight molecules in the cell. (A) The *b*-axis is approximately perpendicular to the plane of the paper. The acyl chains of CLC are parallel to the *c*-axis. No methyl end-group planes or -terraces are observed but overlap of acyl chain ends. (B) The *a*-axis is approximately perpendicular to the plane of the paper. The acyl chains of CLC are perpendicular to the *ab*-plane and therefore parallel to the *c*-axis. (C) The *c*-axis is approximately perpendicular to the plane of the paper. The zigzag planes of the acyl chains within one molecule are parallel, but between molecules orthogonal. The angle between the zigzag planes and the *ac*-plane of the unit cell is ~45°. For abbreviation see Figure 2.

It should be noted that the conclusions are only valid for this specific type of TAG. Other β′-stable TAG or β′-polymorphs of β-stable TAG or TAG mixtures may very well have tilted or bent acyl chains and/or nonparallel intramolecular acyl chain zigzag planes. Unit-cell parameters of β′-polymorphs of $C_{11}C_{11}C_{11}$ and LLL (Table 2) fit very well in the series described in this paper. Clearly single-crystal structure determination only can point out the correctness of the presented model.

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