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Crystal Structures and Melting Points of Saturated Triglycerides in the β-2 Phase*

BY SIJMEN DE JONG AND TON C. VAN SOEST†

Unilever Research Laboratory, Olivier van Noortlaan 120, *Vlaardingen, The Netherlands*

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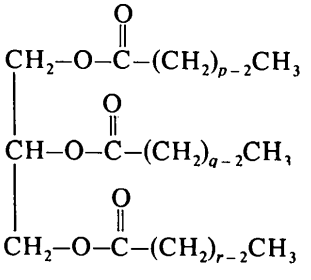
A comprehensive packing analysis of the crystal structures of nine homologous series of saturated triglycerides [$CH_2(OCOC_{p-1}H_{2p-1})CH(OCOC_{q-1}H_{2q-1})CH_2(OCOC_{r-1}H_{2r-1})$ or $p.q.r$] is presented. The model-building approach is based on the known molecular conformation of β-2 10.10.10 and on the $T_{\parallel}$ subcell packing mode of the hydrocarbon chains. The structure of the terrace-like arrangement of the terminal methyl groups then appears to be crucial to the solution of our crystal-packing problem. The analysis shows that there are two or three solutions for the crystal structure of each β-2 phase triglyceride. Comparison with experimental evidence (X-ray powder diffraction data and melting points) allows a definite assignment. The work enables a classification of all β-2 crystallizing triglycerides into a number of submodifications (β-2*A*, ..., β-2*E*), each with a characteristic methyl terrace, which is reflected in the angle of tilt (long spacings) and the melting points. Besides the structural influence of the methyl terraces on the melting points it is shown that the variation in the melting points of triglycerides is partly entropic in origin.

1. Introduction

Polymorphism is quite a general characteristic of long-chain aliphatic compounds. In view of their technological and biological importance, this aspect has been studied extensively. In particular, triglycerides or triacylglycerols (I), which are the constituents of edible fats, have received a great deal of attention, because the occurrence of different crystal modifications influences the processing and characteristics of edible-fat products. Much of the background work on the polymorphism of fats concerned investigations into pure triglycerides or suitably selected mixtures of well defined compositions. The techniques applied include: thermal analysis (DTA and DSC), X-ray diffraction (single-crystal or powder diffraction), dilatometry, infrared spectroscopy, nuclear magnetic resonance, dielectric measurements and microscopic observations (Chapman, 1962).



(I)

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† To whom correspondence should be addressed.

Attempts have been made to explain the observed physical properties in terms of the crystal structure of each phase. For this reason, X-ray diffraction investigations are of special importance. Unfortunately, it is very difficult to grow sufficiently large single crystals – without disorder or twinning – suitable for a complete structure analysis (see, however, Albon, 1976). Therefore, only a few structures have been solved and other means have to be sought for elucidating crystal structures, such as a systematic consideration of all conceivable packing modes satisfying specific requirements (intermolecular contacts, crystallographic and non-crystallographic symmetry, conformational restrictions *etc.*). Such a model-building approach even has a clear advantage over straightforward single-crystal structure analyses. If this approach proves to be successful, the crystal structures of a large number of triglycerides can be derived from a few major packing principles in a uniform way.

In this paper, we present a packing scheme for the β-2 phase of triglycerides with saturated acyl chains bearing an even number of C atoms. The proposed structures are checked against experimental X-ray diffraction and melting-point data. Some preliminary results of our work have been published (van Soest & de Jong, 1976).

2. State of affairs

Much of our present knowledge of the polymorphism of glycerides is based on the pioneer work of Malkin (1954), Lutton (1950) and Chapman (1962). It is now generally accepted that there are three major classes of triglyceride crystalline modifications (α, β′ and β) which

may be obtained under certain well defined conditions (temperature, type of solvent, purity of products). The main difference between these modifications is the lateral packing of the hydrocarbon chains. The various packing modes of long hydrocarbon chains are precisely described by subcells (Chapman, 1965). The presence of a large number of these subcells in the true crystallographic unit cell of a long-chain compound causes a small number of strong X-ray reflections characteristic of the subcell in question. The β modification, for instance, is associated with the triclinic subcell $T_{\parallel}$ (Vand & Bell, 1951). This modification (or subcell) can generally be identified by three strong reflections – the so-called short spacings ($d < 6$ Å) with d values close to 4·60, 3·85 and 3·70 Å.

The powder diffraction recordings also show strong reflections at higher (>6 Å) d values [the long spacings (LS, d_{00l})] which suggest that the molecules are stretched and packed in layers. The magnitudes of the long spacings, especially for homologous series, provide data on the angle of tilt (τ), and the length of the molecule and show whether the molecules are packed in the '2' or the '3' mode (Fig. 1).

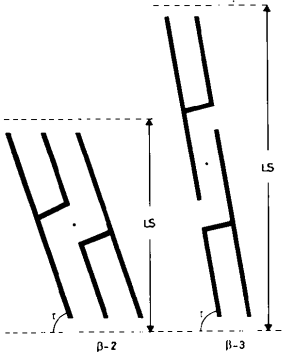

Fig. 1. Arrangement of triglyceride molecules in the β-2 and β-3 modifications.

More detailed information on the crystal structure of triglycerides crystallizing in the β-2 phase has been obtained from single-crystal X-ray analyses. Vand & Bell (1951) established the parallel packing of the hydrocarbon chains by a partial structural analysis of 12.12.12.* According to Chapman (1962), Vand later succeeded in solving the structure in projection. A great step forward was the work of Larsson (1964*c*), who studied the solid-state behaviour of several glycerides, mainly by X-ray single-crystal methods. As to the β-2 modification, he was the first to publish full details on a triglyceride crystal structure, namely that of 12.12.12 (Larsson, 1964*a*). Almost at the same time, Jensen & Mabis (1966) published their highly accurate analysis of the crystal structure of the homologous 10.10.10.

These studies revealed the molecular geometry (conformation at the glycerol group!) and the packing of the molecules in the crystal lattice. Table 1 gives the unit-cell dimensions of 10.10.10 and 12.12.12 and our own data on 18.18.18. The latter are slightly more accurate than our values published previously (Skoda, Hoekstra, van Soest, Bennema & van den Tempel, 1967). The unit-cell axes **a**, **b** and **c** have been chosen so as to obtain a close correspondence with the respective subcell axes $\mathbf{a}_s$, $\mathbf{b}_s$ and $\mathbf{c}_s$. Table 1 also includes the subcell dimensions of 10.10.10 and 12.12.12 derived from published fractional coordinates. The subcell dimensions of 18.18.18 have been derived in a different way, which will be explained at the end of § 3.5. The values in Table 1 very clearly show the structural resemblance of the unit cells of these homologous triglycerides (*p.p.p*), apart, of course,

* In the following, triglycerides will be denoted as *p.q.r* where *p*, *q* and *r* are the number of C atoms in each acyl chain, *e.g.* 14.16.18 [see formula (I)].

Table 1. *Unit-cell and subcell parameters of β-2 phase triglycerides*

Triglyceride	*a* (Å)	*b* (Å)	*c* (Å)	α(°)	β(°)	γ(°)	Transformation matrix*	Reference
p.p.p								
10.10.10	14·256 (30)	5·488 (10)	33·54 (7)	64·34 (15)	125·75 (15)	122·94 (15)	$\bar{1}\bar{1}0/100/211$	Jensen & Mabis (1966)
$T_{\parallel}$ subcell	4·396 (9)	5·488 (10)	2·539 (6)	70·8 (2)	110·0 (2)	121·6 (2)		
12.12.12	14·27 (8)	5·44 (4)	38·87 (10)	65·6 (5)	125·0 (5)	121·3 (5)	$1\bar{1}0/010/\bar{1}31$	Larsson (1964*a*)
$T_{\parallel}$ subcell	4·39 (3)	5·44 (4)	2·558 (6)	70·9 (5)	110·2 (5)	119·9 (5)		
18.18.18	14·13 (4)	5·45 (2)	53·75 (13)	68·0 (2)	123·2 (2)	122·5 (5)	–	This work
$T_{\parallel}$ subcell	4·36 (1)	5·45 (2)	2·543 (6)	72·0 (2)	109·7 (2)	121·4 (5)		
p.p + 2.*p*								
10.12′.10	14·04 (10)	5·51 (5)	30·3 (4)	75 (1)	108 (1)	119 (1)	$1\bar{1}0/010/021$	Doyne & Gordon (1968)
$T_{\parallel}$ subcell	4·37 (3)	5·51 (5)	2·47 (3)	75 (1)	107 (1)	118 (1)		

* Matrix for transforming the reported choice of axes: *e.g.* for 10.10.10, our *a*, *b* and *c* axes are related to those of Jensen & Mabis (1966) (*a*′, *b*′ and *c*′) by $\mathbf{a} = -\mathbf{a}' - \mathbf{b}'$, $\mathbf{b} = \mathbf{a}'$ and $\mathbf{c} = 2\mathbf{a}' + \mathbf{b}' + \mathbf{c}'$.

from the lengths of the *c* axes. Moreover, the subcells of 10.10.10, 12.12.12 and 18.18.18 are also very much alike. Fig. 2 shows a projection of the 10.10.10 molecules along **b***, including a few subcells.

Apparently in an attempt to grow a β′ single crystal, Doyne & Gordon (1968) obtained a single crystal of 2-ω-bromoundecanoyl-1,3-didecanoyl glycerol in the β-2 modification. Since an ω-bromoundecanoyl chain is structurally equivalent to a C12 acyl chain, we will consider this triglyceride derivative as a specimen of the homologous series $p.p+2.p$ denoted as 10.12′.10. The isomorphism of 12.12.12 and 12′.12′.12′ (Larsson, 1964*a*) indicates the correctness of this assumption. The crystal structure of 10.12′.10 is shown in Fig. 3; the unit-cell and subcell parameters are included in Table 1; these differ slightly from the others because of the effect of a Br atom on the structure, and the different arrangement of the terminal methyl groups (the so-called methyl terrace).

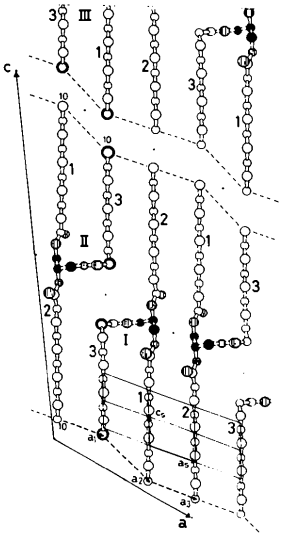

Fig. 2. Projection along **b*** of the crystal structure of 10.10.10 ($p.p.p$, $p=10$) in the β-2 phase (submodification *A*). ○ Chain carbon, ● glycerol carbon, ◍ oxygen. The ○ carbon atoms are used in the discussion of the *c*-axis packing (see § 3.5).

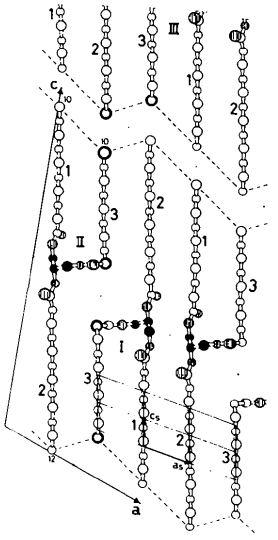

Fig. 3. Projection of the crystal structure of 10.12′.10 ($p.p+2.p$, $p=10$) in the β-2 phase (submodification *B*).

The latest significant contribution to the solution of the β-2 problem was provided by Lutton (1971) who, on the basis of the crystal structures of 10.10.10 and 10.12′.10, proposed packing schemes for 16.16.18, 16.18.18 and 18.16.18 using short-spacing data from powder diffraction diagrams to support his proposals. We extended his analysis systematically to homologous series of other triglycerides, employing also long-spacing and melting-point data to obtain additional evidence.

Table 2 summarizes the triglycerides crystallizing in the β-2 form together with their long spacings and melting points. Tables 3 and 4 include long-spacing data for *trans*-unsaturated triglycerides (Minor & Lutton, 1953) and glycerol ether esters (Lutton & Stewart, 1970) in the β-2 modification respectively. We interpret the crystal structures of these compounds as if they were normal saturated triglycerides, because replacement of a *trans* double bond (⁄CH=CH⁄) or an ether group (⁄O–CH_2⁄) by a single bond (⁄CH_2–CH_2⁄) and an ester group (⁄O–CO⁄) respectively, does not significantly affect the molecular structure.

This paper presents a general analysis of the packing of triglyceride molecules in the β-2 phase to explain the data in Tables 2–4. Attempts are made to explain, for instance, the difference between the long spacings of 14.18.18 (45 Å) and 16.16.18 (42 Å) although both have the same total number ($n \equiv p+q+r=50$) of acyl C atoms. We also deal with the factors determining melting points; for instance, the low melting point of 12.14.16 (about 49 °C, $n=42$) compared with that of 14.14.14 (about 58 °C, $n=42$).

3. General packing analysis

In this section, the possible crystal structures of triglycerides in the β-2 phase will be examined systematically, starting from the X-ray analysis data for 10.10.10 and 10.12′.10. We assume a $T_{\parallel}$ subcell packing of the hydrocarbon chains. The theoretical derivation of the crystal structures of β-2 triglycerides then proceeds in five steps.

3.1. *Molecular geometry*

The molecular geometry of any triglyceride $p.q.r$ is directly obtained from 10.10.10 (Jensen & Mabis,

1966) by simple extension or shortening of the acyl chains to the appropriate lengths, while maintaining the flat zigzag geometry (all-*trans* conformation). There is only one problem in this step, *viz* the distinction (or rather the lack thereof) between chains 1 and 3 for asymmetric triglycerides ($p \neq r$). One of the chains of 10.10.10 in the β-2 phase (Fig. 2), say chain 1, forms one long chain with chain 2, whereas chain 3 branches off at the glycerol group and packs alongside chain 1 by making a bend at the α-CH_2 group. This definition

Table 2. *Experimental long-spacing and melting-point data of β-2 phase triglycerides with even-numbered saturated acyl chains*

Triglyceride	*n*	Long spacing (Å)	Melting point (°C)
24.24.24	72	58·2[a]	86[a]
22.22.22	66	54·0[b]	82·5[b]
20.20.20	60	49·5[b]	78·1[b]
18.18.18	54	44·70[c], 52·9[g], 51·4[d], 49·8[g], 48·9[d] 40·7[f], 40·5[g], 39·6[d], 36·0[g], 35·0[d]	72·6[c], 73·5[b], 72·5[p]
16.16.16	48	40·6[h], 48·0[g], 45·6[g], 44·9[d], 35·9[d] 32·7[g], 31·7[d]	65·5[h], 66·4[n], 66·0[p]
14.14.14	42	35·8[h], 35·45[i], 42·9[g], 40·4[g], 32·0[g] 28·7[g]	57·0[h], 58·5[b]
12.12.12	36	31·40[j], 38·0[g], 34·6[e], 28·3[g], 25·1[g]	46·4[h,j], 46·5[b]
10.10.10	30	26·83[h,l]	31·9[k], 32·1[b], 31·5[h]
8.8.8	24	22·7[b]	9·9[b], 10·0[g]
6.6.6	18	17·8[f]	−25[f,l]
p.*p*.*p* + 2			
16.16.18	50	42·5[m], 42·1[n], 41·5[f], 41·3[o]	62·5[m,o], 62·7[n], 63·5[p]
14.14.16	44	37·7[m], 37·5[t]	54[m], 54·4[t]
12.12.14	38	33·0[m]	43·5[m], 42·8[v]
10.10.12	32	28·4[m]	30[m]
p.*p* + 2.*p* + 2			
16.18.18	52	46·5[m], 45·7[f], 44·7[n], 43·2[f]	65[m], 65·2[n], 66·2[p]
14.16.16	46	41·5[m], 40·7[f]	57[m]
12.14.14	40	36·5[m]	46·5[m], 48·5[q]
10.12.12	34	31·8[m]	35·5[m], 32·6[u]
p.*p* − 2.*p*			
18.16.18	52	44·2[r], 42·7[f], 43·1[n]	68[r], 68·5[n], 67·7[p]
16.14.16	46	39·0[r], 39·2[s], 38·5[f]	60[r], 60·3[s], 61[t]
14.12.14	40	34·7[r]	50[r]
12.10.12	34	30·0[r]	38·5[r], 38·8[u]
p.*p* + 2.*p*			
16.18.16	50	41·4[v]	65·5[v]
14.16.14	44	37·6[v]	–
10.12′.10	32	28·4[w]	–
p.*p* + 2.*p* + 4			
14.16.18	48	40·7[x], 40·6[f], 40·5[y]	59·0[x], 58·5[y]
12.14.16	42	35·7[x], 35·9[f]	48·8[x], 49·8[z]
p.*p* + 4.*p* + 4			
18.22.22	62	54·6[aa]	73·5[aa]
14.18.18	50	45·0[bb], 44·9[f]	62[bb], 62·5[cc]
12.16.16	44	39·8[bb,o]	54[bb], 55·4[o]
10.14.14	38	35·2[bb]	43·5[bb]
8.12.12	32	–	28·4[u]
p.*p* + 4.*p* + 2			
14.18.16	48	43·8[f]	–
p.*p*.*p* + 4			
18.18.22	58	48·1[dd]	65[dd]
14.14.18	46	39·5[dd]	46[dd]

(*a*) Simpson & Hagemann (1975). (*b*) Lutton & Fehl (1970). (*c*) Skoda *et al.* (1967). (*d*) Knoop & Samhammer (1961). (*e*) Buchheim (1970). (*f*) This work. (*g*) Frede & Precht (1977). (*h*) Clarkson & Malkin (1934). These are representative values. See also (*b*), (*d*), (*e*), (*g*), (*i*) and Trillat & Nowakowski (1931), Bailey, Jefferson, Kreeger & Bauer (1945), Filer, Sidhu, Daubert & Longenecker (1946), Seto, Asai & Mito (1956). (*i*) Lutton (1945). (*j*) Larsson (1964*a*). (*k*) Jensen & Mabis (1966). (*l*) Scheij (1899). (*m*) Carter & Malkin (1939*a*). (*n*) Lutton, Jackson & Quimby (1948). (*o*) Schlenk (1965). (*p*) Knoester, de Bruijne & van den Tempel (1972). (*q*) Averill, Roche & King (1929). (*r*) Malkin & Meara (1939). (*s*) Jackson & Lutton (1949). (*t*) Chapman (1958). (*u*) McElroy & King (1934). (*v*) Lutton & Hugenberg (1960). (*w*) Doyne & Gordon (1968). (*x*) Sidhu & Daubert (1947). (*y*) Filer, Sidhu, Chen & Daubert (1945). (*z*) Perry, Weber & Daubert (1949). (*aa*) Jackson & Lutton (1950). (*bb*) Carter & Malkin (1939*b*). (*cc*) Daubert & Clarke (1944). (*dd*) Lutton & Fehl (1972).

Table 3. *Long spacings of trans-unsaturated triglycerides*

Br = brassidoyl (C22:*t*13), E = elaidoyl (C18:*t*9), Pe = petroselaidoyl (C18:*t*6). The data are taken from Minor & Lutton (1953), unless otherwise indicated.

Triglyceride	*n*	Long spacing (Å)
p.p.p		
Br.Br.Br	66	53·6[a]
18.Pe.18	54	44·8
18.E.18	54	45·0, 44·9[b]
Pe.Pe.18	54	44·6
E.E.18	54	44·75
E.18.E	54	44·8
Pe.Pe.Pe	54	44·6
E.E.E	54	44·6, 44·1[a], 44·8[c]
p.p + 2.*p* + 2		
16.Pe.Pe	52	43·4
16.E.E	52	44·1
p.p − 2.*p*		
E.16.E	52	43·2
p.p + 2.*p*		
16.Pe.16	50	41·7
16.E.16	50	42·05

(*a*) Carter & Malkin (1947). (*b*) Malkin & Wilson (1949). (*c*) Filer *et al.* (1946).

Table 4. *Long spacings of glycerol ether esters (Lutton & Stewart, 1970)*

Py = palmityl (hexadecyl) and Sy = stearyl (octadecyl).

'Triglyceride'	*n*	Long spacing (Å)
p.p.p		
Sy.18.18	54	45·0
Py.16.16	48	40·4
p.p.p + 2		
16.16.Sy	50	38·5
p.p + 2.*p* + 2		
Py.18.18	52	46·4
Py.Sy.18	52	43·2

of chains 1 and 3 only refers to the rough, essentially two-dimensional conformation of the molecules. The numbering, for instance, does not change upon reflection or inversion and has, therefore, nothing to do with the stereospecific numbering of triglycerides (IUPAC–IUB Commission on Biochemical Nomenclature, 1968). In the following, the notation *p.q.r* will also comprise the conformation: the C_p acyl chain forming the back leg, C_q the back and C_r the front leg of a chair.

At this point it is perhaps worthwhile to comment upon the often used descriptions 'tuning fork' and 'chair' for triglyceride conformations (Lutton, 1948). Although these terms suggest particular shapes, they were only devised for distinguishing between a conformation with adjacent chains 1 and 3 and a conformation with adjacent chains 1 and 2. This designation is confusing because the conformation of 10.10.10 in the β-2 phase would then be a tuning fork and not a chair, whereas the molecular shape is clearly that of a chair. We therefore propose to use the notation 1,3 and 1,2 conformation without referring to the detailed geometry of the triglyceride molecule.

3.2. *Molecular pairs*

The next step is the formation of a pair of triglyceride molecules packed around a centre of symmetry (Fig. 2). The exact packing was taken from the crystal structure of 10.10.10 (Jensen & Mabis, 1966). At this early stage of 'crystal building', the $T_{\parallel}$ subcells already become apparent. The molecules lie approximately in the (010) plane of both the subcell and the ultimate unit cell. These molecular pairs constitute the basic units from which the crystal will be built up. We do not assume the presence of other elements of symmetry, so that the space group will be $P\bar{1}$, just as for 10.10.10, 12.12.12 and 10.12′.10. For asymmetric triglycerides ($p \neq r$), this choice of space group implies that the present packing analysis applies only to racemic triglycerides.

3.3. *a-Axis packing*

If such molecular pairs are placed side by side to form a two-dimensional array, the lateral packing obtained defines the unit-cell *a* axis. The number of packing modes of these molecular pairs is restricted because the packing has to accord with the $T_{\parallel}$ subcell packing of the hydrocarbon chains. This may be formulated by expressing **a** in terms of $\mathbf{a}_s$ and $\mathbf{c}_s$:

$$\mathbf{a} = 3\mathbf{a}_s + t\mathbf{c}_s \quad (t = 0, \pm 1, \pm 2, \ldots). \qquad (1)$$

This means that adjacent molecular pairs may be shifted along their long-chain axes in discrete multiples of the subcell c_s axis, *i.e.* in steps of 2·54 Å. Using the 10.10.10 crystal structure, we found that such shifts do not give rise to unacceptably short contacts (using small van der Waals radii of 1·65 Å for C and 1·35 Å for O). For the known structures of 10.10.10, 12.12.12 and 10.12′.10, $t = -1$, *i.e.* $\mathbf{a} = 3\mathbf{a}_s - \mathbf{c}_s$ (Figs. 2 and 3).

At this stage of the analysis it becomes clear that the methyl groups will generally not lie on a straight line but rather form a boundary with a particular structure. Since this methyl-group arrangement is an important feature of the whole crystal structure, it is useful to have a short notation for it. Fig. 2 shows that the unit-cell vector **a**, connecting, for instance, the methyl groups of chains 2 in adjacent unit cells, is a vectorial sum of three vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$, which consecutively connect the methyl groups of chain 2, chain 3, chain 1 and chain 2 of the next cell:

$$\mathbf{a} = \mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3. \qquad (2)$$

Because the lateral packing of the hydrocarbon chains

is determined by the subcell packing, we also have an expression such as equation (1) for $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$:

$$\mathbf{a}_i = \mathbf{a}_s + t_i\mathbf{c}_s$$
$$[t_i = 0, \pm 1, \pm 2, \ldots; (i = 1, 2, 3)]. \quad (3)$$

Combination of (1), (2) and (3) gives

$$t = t_1 + t_2 + t_3. \quad (4)$$

The detailed structure of the methyl boundary is then described by three indices (t_1,t_2,t_3), which may be called the *boundary indices*. For 10.10.10 and its homologues, these indices are (0,−1,0) and for 10.12′.10 (1,−1,−1) (Figs. 2 and 3).

Notice that only t_3 may be freely chosen at this stage of the packing analysis as t_1 and t_2 are fully determined by the lengths of the acyl chains of the triglyceride concerned. The following relationships are found between t_1 and t_2 and p, q and r:

$$t_1 = (q - r)/2$$
$$t_2 = (r - p - 2)/2. \quad (5)$$

Boundaries with $(t_1,t_2,t_3) = (i,j,k)$ or (j,k,i) or (k,i,j) cannot be distinguished because of the repetitive nature of the boundary: ...*ijkijkijkijkij*....

Since t_1 and t_2 (*i.e.* i and j, or j and k, or k and i) are related to the acyl chain lengths *via* equation (5), this implies that each particular methyl boundary may accommodate three different homologous series of triglycerides (except for the special case $t_1 = t_2 = t_3$; see § 3.5). For example, the methyl boundary structure as in Fig. 2 is not altered when chains 3 of 10.10.10 are lengthened by two CH_2 groups, giving 10.10.12 and a concomitant change of the boundary indices from (0,−1,0) to (−1,0,0). A subsequent lengthening of chains 2 transforms 10.10.12 into 10.12.12, again leaving the structure of the methyl-group arrangement intact, apart from a shift along $\mathbf{a}_s$ [indices are now: (0,0,−1)]. Finally, lengthening of chains 1 gives the crystal structure of 12.12.12, a homologue of the starting triglyceride 10.10.10.

3.4. *b-Axis packing*

The following step concerns the extension of the packing into the **b** direction. We examined all feasible packings conforming to the $T_{\parallel}$ subcell packing, *i.e.* $\mathbf{b} = u\mathbf{a}_s + \mathbf{b}_s + v\mathbf{c}_s$.

In all cases except $u = v = 0$, we found too short contacts always involving carbonyl O atoms. Therefore, we assume that the unit-cell b axis coincides with the b_s subcell axis:

$$\mathbf{b} = \mathbf{b}_s, \quad (6)$$

just as in 10.10.10 and 10.12′.10.

For long-chain compounds, the (001) plane of the unit cell is frequently designated by indices referring to the subcell. In our case, the plane index is $(t0\bar{3})_s$, where t has the same meaning and numerical value as that in equation (1) and the subscript s indicates that the index refers to the subcell. The structure of the methyl boundary may also be expressed in this way by indexing the three planes formed by the b axis and $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ respectively, giving $(t_10\bar{1})_s$, $(t_20\bar{1})_s$ and $(t_30\bar{1})_s$. Although this notation is somewhat more detailed, we will use the indices (t_1,t_2,t_3) for the characterization of the methyl boundary structure.

3.5. *c-Axis packing*

The foregoing steps resulted in a monomolecular layer extending in the **a** and **b** directions. The next and final step is stacking these layers such that an efficient packing results at the methyl boundaries. Evidently, close packing at the methyl end-groups is only achieved if the boundary of the upper side of a layer has exactly the same shape as that of the lower side of the layer above it. If the methyl boundary on the lower side has the indices (i,j,k), the order of the indices of the methyl boundary on the upper side will be reversed (k,j,i) since the boundaries of both sides are related by inversion centres. This means that for the most general case where i, j and k are different, the boundaries on the upper side do not pack closely with those on the lower side of the layers (*cf.* Fig. 8; $i = -2$, $j = 1$, $k = 0$). Boundaries related by a centre of symmetry have the same shape only if at least two of the three boundary indices are equal. Since t_1 and t_2 are determined by p, q and r [equations (5)] and t_3 could so far be freely chosen, there are now only two choices left for t_3: $t_3 = t_1$ or $t_3 = t_2$. There are, therefore, two packing possibilities for each triglyceride in the direction of the a axis. A special case presents itself if $t_1 = t_2$. Then t_3 may still be freely chosen. According to equations (5), this happens to be so when

$$p + q + 2 = 2r, \quad (7)$$

e.g. for 16.18.18, 18.16.18 and 12.18.16 and their homologues. The condition that two of the boundary indices must be equal can also be formulated as: the methyl groups form a terrace, *i.e.* a repetitive structure of three methyl groups forming one row followed by a step.

An even more special case arises if $t_1 = t_2 = t_3$. Then all methyl groups are in a flat plane and one may only formally speak of a terrace. Most long-chain compounds with simpler molecular structures, compared to triglycerides, have such a flat plane.

For a better understanding of the mode of packing of the layers, it is useful to consider the c axis as the vector connecting the methyl groups of chains 3. This vector can be seen as the sum of five vectorial contributions, consecutively connecting the atoms indicated by heavy circles in Figs. 2 and 3, *viz* the methyl C of chain 3 in

molecule (I), the α-C atom of this chain, the corresponding atom in molecule (II), the methyl group of chain 3 in molecule (II), the opposite methyl group and the methyl group of chain 3 in molecule (III). The first and the third contributions add to $(r-2)\mathbf{c}_s$. The combined second and fourth contributions constitute a vector $\mathbf{c}_o$ describing those parts of the crystal structure which are not packed according to the triclinic subcell (*i.e.* the glycerol groups and the methyl boundary).

From the published crystal structures of 10.10.10, 12.12.12 and 10.12′.10 we derived the following expression:

$$\mathbf{c}_o = 0{\cdot}43\mathbf{a}_s + 0{\cdot}51\mathbf{b}_s + 3{\cdot}40\mathbf{c}_s.$$

Probably, this $\mathbf{c}_o$ may not be used for other terraces because the use of a constant $\mathbf{c}_o$ leads to different packing densities for the various terraces, as the angle between $\mathbf{c}_o$ and the (001) plane varies with t. Since we assume that the weak van der Waals interactions across the methyl boundary will not appreciably affect the 'local' density, we impose the restriction that the volume of the non-subcell region must be equal for all kinds of terraces. An expression for $\mathbf{c}_o$ which satisfies this constraint is then

$$\mathbf{c}_o = 0{\cdot}43\mathbf{a}_s + 0{\cdot}51\mathbf{b}_s + (3{\cdot}54 + 0{\cdot}14t)\mathbf{c}_s. \qquad (8)$$

The fifth contribution to the c axis equals $-\mathbf{a}_2$ for 10.10.10 (Fig. 2) and $+\mathbf{a}_1$ for 10.12′.10 (Fig. 3). The former situation is generally applicable to $t_3 = t_1$ and the latter to $t_3 = t_2$. There is also a third and intermediate situation for $t_1 = t_2$. Then the above-mentioned fifth vectorial contribution to $\mathbf{c}$ vanishes since the methyl groups of chains 3 are already opposite each other.

Adding all five contributions and using equations (3) and (5) gives the following expressions for the c axis:

$$\mathbf{c} = \mathbf{c}_o + \mathbf{a}_s + \left(\frac{q+r-4}{2}\right)\mathbf{c}_s \quad \text{for } t_3 = t_2 \qquad (9.1)$$

$$\mathbf{c} = \mathbf{c}_o - \mathbf{a}_s + \left(\frac{p+r-2}{2}\right)\mathbf{c}_s \quad \text{for } t_3 = t_1 \qquad (9.2)$$

$$\mathbf{c} = \mathbf{c}_o + (r-2)\mathbf{c}_s \quad \text{for } t_2 = t_1. \qquad (9.3)$$

This completes, in principle, the general packing analysis of arbitrarily saturated triglycerides $p.q.r$ in the β-2 modification. For each triglyceride, we derived the matrix transforming the subcell axes $\{\mathbf{a}_s,\mathbf{b}_s,\mathbf{c}_s\}$ into the unit-cell axes $\{\mathbf{a},\mathbf{b},\mathbf{c}\}$ so that it is also possible to inversely derive the subcell dimensions from the unit-cell dimensions. The $T_{\parallel}$ subcell parameters for 18.18.18 (Table 1) were derived in this way.

3.6. *General conclusions*

The above analysis allows the following conclusions:

– the packing of the triglyceride molecules is determined by the hydrocarbon-chain subcell packing and by the architecture of the methyl terrace;

– there are as many β-2 (sub)modifications as there are different methyl terraces (including the flat planes);

– each terrace is associated with three (homologous series of) triglycerides;

– each triglyceride may pack in at least two different ways.

The last conclusion is especially important, because it implies that for each triglyceride crystallizing in a β-2 modification, two (sometimes three) crystal structures are possible. One may expect that, in practice, the more stable will generally be preferred. From their occurrence or not one may therefore draw conclusions about the relative stabilities associated with the different methyl terraces.

So far we have not made any restrictions as to the relative lengths of the three acyl chains. According to the above analysis, any triglyceride can pack in two β-2 modifications (even an extreme case, for instance 22.16.10). Table 2 shows that all β-2 phase triglycerides have chain lengths which differ by a maximum of four C atoms. We assume that this has to do with the steepness of the methyl terrace and therefore introduce the empirical restriction:

$$t_i = -1, 0 \text{ or } +1 \quad (i = 1, 2 \text{ or } 3). \qquad (10)$$

Combining this restriction with equation (5) gives $r = p$, $p+2$ or $p+4$ and $q = r-2$, r or $r+2$. The following limited list of potentially β-2 crystallizing triglycerides is then obtained: $p.p.p$, $p.p-2.p$, $p.p+2.p$, $p.p.p+2$, $p.p+2.p+2$, $p.p+4.p+2$, $p.p+2.p+4$, $p.p+4.p+4$ and $p.p+6.p+4$. Note that $r \geq p$, so that for asymmetric triglycerides the conformation has to be taken such that the longer of the two primary acyl chains occupies position 3 and the shorter position 1 (§ 3.1). The above triglycerides are given in Table 5 together with their possible terraces. This table also shows which triglycerides are associated with a common methyl terrace. For convenience, we characterized each terrace by a trivial alphabetic index.

3.7. *Long spacings*

We have written a special computer program (*BETA2*) for calculating the unit-cell dimensions and the fractional atomic coordinates of the β-2 structures of any triglyceride. We assumed the following dimensions for the $T_{\parallel}$ subcell: $a_s = 4{\cdot}38$, $b_s = 5{\cdot}46$, $c_s = 2{\cdot}545$ Å, $\alpha_s = 71$, $\beta_s = 110$ and $\gamma_s = 121°$ (*cf.* Table 1). Given these dimensions, the angles of tilt (τ) for each terrace (Table 5) can be calculated easily.

Our choice for $\mathbf{c}_o$ [equation (8)] leads to a very simple expression for the long spacing as a function of n and τ:

$$\mathrm{LS} = d_{001} = (n + 6{\cdot}62)\frac{2{\cdot}545}{3}\sin\tau. \qquad (11)$$

Table 5. *Possible methyl terraces* (t_1,t_2,t_3) *for potentially* β-2 *crystallizing triglycerides*

Triglyceride	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*
$p.p-2.p$		−1, −1, 1			−1, −1, 0				−1, −1, −1
$p.p.p$	0, −1, 0				0, −1, −1				
$p.p+2.p$		1, −1, −1				1, −1, 1			
$p.p.p+2$	−1, 0, 0				−1, 0, −1				
$p.p+2.p+2$	0, 0, −1		0, 0, 1	0, 0, 0					
$p.p+4.p+2$			1, 0, 0				1, 0, 1		
$p.p+2.p+4$		−1, 1, −1				−1, 1, 1			
$p.p+4.p+4$			0, 1, 0				0, 1, 1		
$p.p+6.p+4$						1, 1, −1	1, 1, 0	1, 1, 1	
t	−1	−1	1	0	−2	1	2	3	−3
(001)	$(103)_s$	$(103)_s$	$(\bar{1}03)_s$	$(001)_s$	$(203)_s$	$(\bar{1}03)_s$	$(\bar{2}03)_s$	$(\bar{1}01)_s$	$(101)_s$
$\tau(°)$	60·0	60·0	71·0	67·4	52·2	71·0	67·5	60·1	45·3

3.8. *Short spacings*

One would not normally expect much difference between the short spacings of the various triglycerides, since these are mainly determined by the subcell. In the foregoing analysis we assumed a triclinic subcell with fixed dimensions. There may, however, be slight variations in the subcell dimensions, depending on the chain lengths or the methyl terrace. Moreover, equation (8) for $\mathbf{c}_o$ might not be fully correct.

Therefore, differences between short spacings are expected to be quite small for triglycerides with a common methyl terrace, whereas those for triglyceride crystal structures with different methyl terraces may become perceptible.

3.9. *Melting points*

A similar behaviour may be expected for the melting temperatures: triglycerides crystallizing with the same methyl terrace may be considered to belong to an extended homologous series with solid-state properties characteristic of that series and different from those of other series. For example, in the case of $p.p.p$, $p.p.p+2$ and $p.p+2.p+2$ we speak of triglycerides crystallizing in the β-2*A* submodification (Table 5) with an *A*-type methyl terrace. Each submodification then has a certain thermodynamic stability, which is reflected in the melting points of the triglycerides. Of two submodifications, the more stable is associated with a higher melting point for a given n.

Within an extended homologous series of triglycerides connected with a particular submodification, a gradual increase in melting points may be expected accordingly as n increases. However, there is an essential difference between symmetric ($p = r$) and asymmetric ($p \neq r$) triglycerides, which requires special attention. In synthetic preparations and also in most natural fats asymmetric triglycerides are present as a racemic *mixture*, whereas symmetric triglycerides form a one-component system. Therefore, asymmetric triglycerides will have an additional entropy of mixing $R \ln 2$ in the liquid state. On the basis of the equation $T_m = \Delta H_m/\Delta S_m$, which relates the melting temperature T_m with the enthalpy and entropy of fusion (ΔH_m and ΔS_m respectively), a higher melting entropy results in a lower melting point. It is possible to estimate the magnitude of the effect of the $R \ln 2$ term on the melting point. For high-melting triglycerides, typical values for ΔH_m and T_m are 170 kJ mol^{-1} and 340 K, giving a value of 500 J mol^{-1} K^{-1} for ΔS_m (Knoester, de Bruijne & van den Tempel, 1972). The effect of $R \ln 2 = 5{\cdot}6$ J mol^{-1} K^{-1} is then more than one per cent, which also applies to the melting temperature (about 4 K). For short-chain triglycerides, this effect will be slightly larger. One should be well aware of this effect when demonstrating the structural equivalence of a series of crystalline triglycerides on the basis of their melting points.

4. Results

We will first discuss the long spacings for each homologous series using the data from Tables 2, 3 and

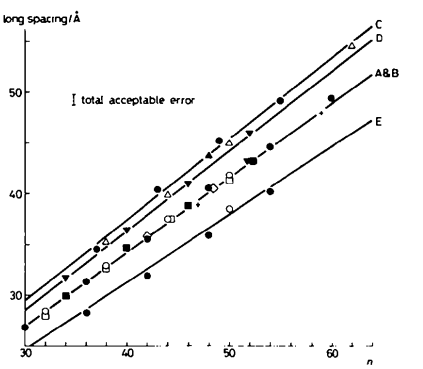

Fig. 4. Long spacings of β-2 phase triglycerides. Individual observations are taken from Tables 2, 3 and 4; the lines drawn correspond to equation (11) (● $p.p.p$, ○ $p.p.p+2$, ▼ $p.p+2.p+2$, ■ $p.p-2.p$, ◊ $p.p+2.p+4$, △ $p.p+4.p+4$, ▲ $p.p+4.p+2$, + $p.p.p+4$).

4 and then combine the triglycerides according to each submodification and discuss the short spacings and melting points. In Fig. 4 we have plotted the experimental long-spacing data from Tables 2, 3 and 4 against n. The lines are the theoretical long-spacing lines corresponding to the linear equation (11) for which the angles of tilt were taken from Table 5.

4.1. *Long spacings*

Measured long spacings are found to be accurate to within 0·5 Å. Our assumption that all triglycerides have a constant subcell and the uncertainty regarding $\mathbf{c}_o$ probably lead to an error of the same magnitude. We therefore consider a difference of less than 1 Å between observed and calculated long-spacing values as acceptable.

4.1.1. *The p.p.p series.* Theoretically, the monoacid triglycerides may belong to the A as well as to the E submodification (Table 5), but practically all measured long spacings point to the A submodification. Detailed crystal structures of 10.10.10 and 12.12.12 are known from single-crystal diffraction analyses; these structures are valid for the whole homologous series (Fig. 2).

The E submodification has a smaller angle of tilt ($\tau = 52°$) and consequently shorter long spacings. We observed additional long-spacing lines at 13·6 and 8·1 Å belonging to the β-2E submodification (LS 40·7 Å, calculated 40·6 Å) superimposed on a normal β-2A diffraction pattern of 18.18.18 crystallized from a slowly cooled melt.

Recently, Frede & Precht (1977) have extended the work of Knoop & Samhammer (1961) on additional weak long-spacing lines observed in the powder diffraction diagrams of some monoacid triglycerides. Like Knoop & Samhammer, they postulate the existence of five different β-2 modifications, which they termed $\beta_{\rm I}$, $\beta_{\rm II}$, $\beta_{\rm III}$, $\beta_{\rm IV}$ and $\beta_{\rm V}$ in order of decreasing angles of tilt. Their $\beta_{\rm III}$ form corresponds to the normal β-2 form (type A).

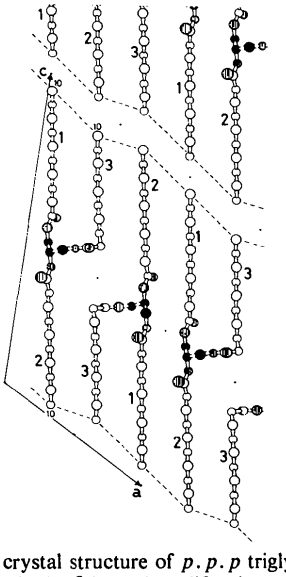

Fig. 5. Probable crystal structure of $p.p.p$ triglycerides ($p = 10$) in the β-2 E submodification.

The long spacings of their $\beta_{\rm IV}$ modification correspond, within 1 Å, to our β-2E long-spacing values. Frede & Precht, however, suggest a structure with a c-axis packing as in the β-2A submodification but with an a-axis packing as in the β-2E submodification. This leads to an impossibly short contact between the methyl groups of chains 2. For this reason, we prefer to assign the β-2E structure to their $\beta_{\rm IV}$ modification even though their calculated long spacings show a seemingly better agreement with their measured spacings (Fig. 5).

The remaining long-spacing values (Table 2) for $p.p.p$ triglycerides (p = 12–18) cannot be explained by our packing analysis. Should these long spacings belong to genuine β-2 modifications – as the short spacings suggest – then the corresponding crystal structures are probably not perfectly close-packed.

In our view, the Frede & Precht $\beta_{\rm II}$ long-spacing values can best be explained by assuming a C-type a axis [terrace (0,−1,2)] and a c axis according to equation (9.3), but with $r + 1$ instead of r to account for the loose packing ('void') between the methyl groups of chains 3. The correspondence between the calculated and measured long spacings is good (deviation 0·3–1·0 Å). Frede & Precht propose a different structure with a D-type a axis [terrace (0,−1,1)] but this leads to a larger discrepancy (0·6–2·0 Å) between their calculations and measurements. Buchheim (1970) has performed an electron diffraction analysis on a single crystal of $\beta_{\rm II}$ 12.12.12, the structure of which is in agreement with a D-type a axis and c axis according to equation (9.3) with $r \rightarrow r + 1$. The unit-cell dimensions agree, within three per cent, with our values computed for such a crystal structure. However, it is not clear from Buchheim's paper whether the dimensions of his unit cell were directly derived from his diffraction recordings or from packing concepts.

Frede & Precht's $\beta_{\rm I}$ and $\beta_{\rm V}$ long spacings are difficult to explain. The long spacings of their $\beta_{\rm I}$ modification are even larger than the α long spacings (Lutton & Fehl, 1970) which correspond to an angle of tilt of 90°! If we suppose that the $T_{\parallel}$ subcell is still appropriate for this modification, we may have to deal with a different molecular structure (1,2 conformation?) and, consequently, with a different lateral packing of the molecules. The structure proposed by Frede & Precht, which is based on the known molecular structure and the usual b-axis packing, then results in far too short (2·2–2·7 Å) long spacings.

Finally, their $\beta_{\rm V}$ long spacings correspond to an angle

of tilt of about 45° and point to an *I*-type *a* axis. Frede & Precht propose such a structure which, however, shows a very great overlap of the tails of chains 2. For this reason, we reject their model. The agreement between their calculated and measured long spacings must therefore be fortuitous. Admittedly, we are not yet able to give a satisfactory explanation for these extra very weak β_v long-spacing lines.

The triglycerides with *trans*-unsaturated acyl chains (Table 3) and the monoalkyl diacyl glycerols (Table 4), which resemble the monoacid triglycerides, all have a long spacing characteristic of the β-2*A* submodification.

4.1.2. *The* $p.p.p+2$ *series.* The $p.p.p+2$ triglycerides may also crystallize in the *A* and *E* submodifications. Just as with the monoacid triglycerides, all long-spacing values point to the *A* submodification. This crystal structure was proposed earlier (Fig. 5 of Lutton, 1971). However, the long spacing of the monoalkyl diacyl glycerol 16.16.Sy (38·5 Å) clearly indicates an *E*-type crystal structure (calculated LS 38·0 Å).

4.1.3. *The* $p.p+2.p+2$ *series.* According to Table 5, the $p.p+2.p+2$ triglycerides may occur in three β-2 submodifications: *A*, *C* or *D*. The long spacings of 16.18.18, 14.16.16, 12.14.14 and 10.12.12 can be explained by both the *C* and *D* submodifications (Fig. 4). Lutton has previously proposed a β-2*A* structure for these triglycerides (Fig. 4 of Lutton, 1971). There is indeed some evidence that this submodification may occur as well. We have obtained X-ray diagrams for 16.18.18 (crystallized from chloroform or acetone/chloroform) with a double set of long spacings: one corresponding to the value reported by Carter & Malkin (1939*a*) (46·5 Å) and the other (43·2 Å) to a β-2*A* structure (calculated LS 43·1 Å).

Also the long spacings of 16.Pe.Pe (43·4 Å, Minor & Lutton, 1953) and Py.Sy.18 (43·2 Å, Lutton & Stewart, 1970) and probably 16.E.E (44·1 Å, Minor & Lutton, 1953) are associated with the β-2*A* submodification, whereas Py.18.18 (46·4 Å, Lutton & Stewart, 1970) is either *C* or *D* type. Lutton's own value (44·7 Å; not included in Fig. 8) is difficult to account for (Lutton, Jackson & Quimby, 1948). We have never observed this long spacing, nor is there any other published evidence for such a value. The short spacings (§ 4.2) suggest that 16.18.18 and its homologues do not crystallize in the *C* form but give β-2*D* crystals instead. These can be obtained in pure form by crystallization from benzene at 5 °C.

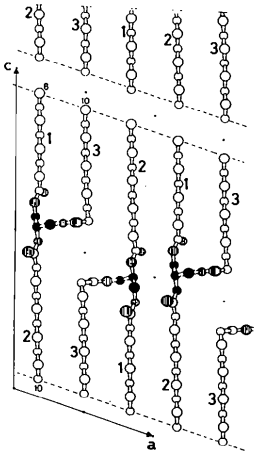

Fig. 6. Crystal structure for $p.p+2.p+2$ triglycerides ($p=8$) in the β-2 *D* submodification.

Fig. 6 presents the possible crystal structure for a triglyceride of this homologous series in the *D* submodification. As the stacking of the molecular layers is in this case (methyl groups in one plane) not determined by the presence of a 'real' methyl terrace, all three packing modes in the **c** direction [corresponding to equations (9.1), (9.2) and (9.3)] are possible. In this respect, one may also speculate on the possibility of a disordered packing of the layers. Due to the smoothness of the *D*-type terrace there is yet another possibility of layer packing with alternate directions of chain tilt [space group $P\bar{1} \rightarrow P2_1/a$; compare the β_1 and β_2 forms of racemic monoglycerides (Larsson, 1964*b*)].

4.1.4. *The* $p.p-2.p$ *series.* Just as the foregoing $p.p+2.p+2$ triglycerides, $p.p-2.p$ triglycerides satisfy equation (7) so that three submodifications are possible: *B*, *E* or *I* (Table 5). All long-spacing data point to the β-2*B* submodification. This structure conforms to Lutton's proposal (Fig. 2 of Lutton, 1971).

4.1.5. *The* $p.p+2.p$ *series.* The $p.p+2.p$ triglycerides normally crystallize in the β' phase. Under special conditions, β-2 phase crystals have been obtained (Lutton & Hugenberg, 1960). Two β-2 submodifications are theoretically possible: *B* and *F* (Table 5). All long spacings are only compatible with a β-2*B* submodification. The crystal structure of 10.12′.10, which has been solved completely, is representative of this series (Fig. 3).

4.1.6. *The* $p.p+2.p+4$ *series.* The $p.p+2.p+4$ triglycerides can also 'choose' between the *B* and the *F* submodifications. The long spacings of 14.16.18 and 12.14.16 are clearly indicative of the *B* submodification. The crystal structure is depicted in Fig. 5 of van Soest & de Jong (1976).

4.1.7. *The* $p.p+4.p+4$ *series.* Triglycerides of this $p.p+4.p+4$ series may be in the β-2*C* or the β-2*G* submodification. Apparently, these triglycerides crystallize in the β-2*C* submodification (Fig. 7).

4.1.8. *The* $p.p+4.p+2$ *series.* Triglycerides of this $p.p+4.p+2$ series are generally β' stable. A β-2 phase has never been reported. We have, however, obtained a β-2 diffraction pattern of a 1:1 mixture of 14.18.16 and 16.16.18 crystallized from acetone/chloroform (5:1). This pattern could only be interpreted as a superposition of a β-2*A* pattern of

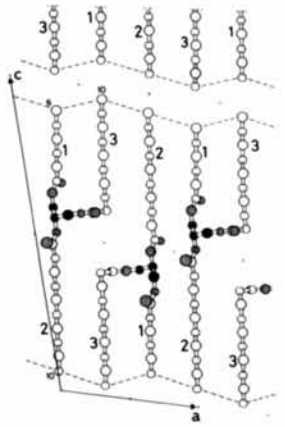

Fig. 7. Proposal for the crystal structure of $p.p+4.p+4$ triglycerides ($p=6$) with a *C*-type methyl terrace.

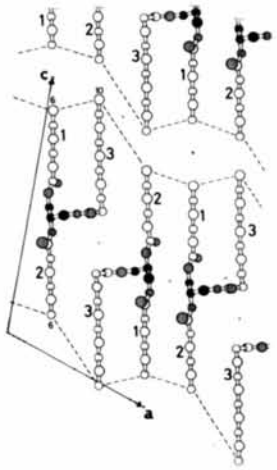

Fig. 8. Probable crystal structure for the $p.p.p+4$ homologous series ($p=6$). Loosely packed areas are indicated.

16.16.18 and a β-2*C* pattern of 14.18.16 with a long spacing of 43·8 Å, being close to the expected value of 43·1 Å for a *C*-type structure.

4.1.9. *The* $p.p+6.p+4$ *series.* The $p.p+6.p+4$ triglycerides may, in principle, crystallize in the *F*, *G* or *H* submodifications. So far, all our observations have demonstrated the absence of a β-2 phase for these triglycerides.

4.1.10. *The* $p.p.p+4$ *series.* The $p.p.p+4$ series is the only homologous series not included in Table 5. Leaving the restriction (10) aside, two methyl terraces are possible: (−2,1,−2) and (−2,1,1). The long spacings calculated for these structures are 39·0 and 50·6 Å for 18.18.22, and 31·7 and 41·2 Å for 14.14.18 and differ considerably from the measured values of 48·1 and 39·5 Å respectively (Lutton & Fehl, 1972). The observed long spacings conform to an angle of tilt $\tau = 58°$, being close to the value appropriate for a structure with $t=-1$. This gives the structure as shown in Fig. 8, which is not close-packed [methyl terrace (−2,1,0)].

Table 6. *Summary of possible β-2 submodifications for nine homologous series of triglycerides*

Symbols: + normally occurring β-2 form, □ alternative β-2 form with some evidence for its occurrence, − theoretically possible but (as yet) unobserved β-2 form; no symbol: combination theoretically impossible.

	Submodification								
Triglyceride	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*
$p.p-2.p$		+			−				−
$p.p.p$	+				□				
$p.p+2.p$		+				−			
$p.p.p+2$	+				□				
$p.p+2.p+2$	□		−	+					
$p.p+4.p+2$			+				−		
$p.p+2.p+4$		+				−			
$p.p+4.p+4$			+				−		
$p.p+6.p+4$						−	−	−	

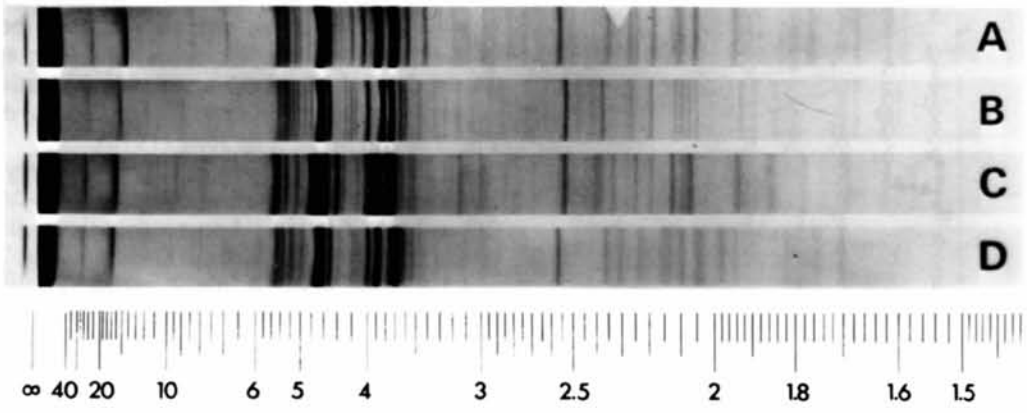

Fig. 9. Powder diffraction diagrams of (*A*) β-2*A* type 16.16.16, (*B*) β-2*B* type 14.16.18, (*C*) β-2*C* type 14.18.18 and (*D*) β-2*D* type 16.18.18.

The calculated long spacings [equation (11), $n = 59$ and 47!] of 48·2 and 39·4 Å respectively are now in very close agreement with the observed values.

Table 6 summarizes our findings showing the relation between the triglyceride molecular structure and the possible β-2 submodifications. It does not include the somewhat isolated $p.p.p + 4$ series.

4.2. *Short spacings*

The short-spacing patterns of triglycerides belonging to different submodifications show subtle differences. Within one submodification, the differences are much smaller. Therefore, we present the diffraction patterns of only one representative example for the *A*, *B*, *C* and *D* β-2 submodifications (Fig. 9).

It is not easy to characterize each pattern by a few outstanding features. It is rather the general appearances of these patterns which differ slightly due to small shifts of the spacings and minor variations in the intensities. Lutton (1971) has already pointed to the proximity of the two strong lines in the 3·6–3·9 Å region for the *B*-type triglycerides 18.16.18 and 16.18.16 compared to other triglycerides. However, it is generally the region of the weak 'super-short' spacings ($1{\cdot}5 < d < 3{\cdot}5$ Å) that shows the differences most clearly. For example, the *A* submodification has relatively prominent lines at 1·77 and 1·95 Å, which are lacking in the *B*-type pattern. The *C*-type pattern of 14.18.18 is distinct because of reflections at 1·85 and 3·13 Å; 16.18.18 has characteristic lines at 1·71, 1·99 and 2·05 Å and differs considerably from 14.18.18. We tentatively consider this as evidence that 16.18.18 crystallizes in a different submodification, the β-2*D* form. This form has all the terminal methyl groups at a layer boundary located in one plane, (001) – a situation formerly ruled out by Larsson (1972), apparently because he overlooked the possibility of other packing modes in the **a** direction. Our diffraction diagram of 18.18.18 with *A*- and *E*-type long spacings, shows a prominent line at 4·17 Å. Since the diffraction pattern of *E*-type 16.16.Sy (Lutton & Stewart, 1970) also shows a fairly strong line in this neighbourhood, we assume that such a line is symptomatic of a β-2*E* submodification.

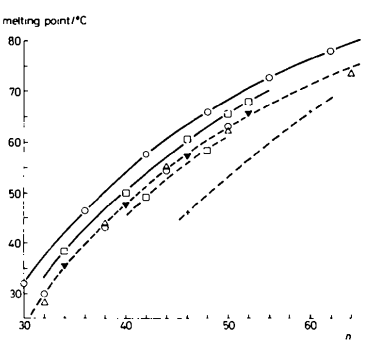

Fig. 10. Melting points of β-2 phase triglycerides (○ *A*-type, □ *B*-type, △ *C*-type, ▼ *D*-type, + $p.p.p + 4$; —— symmetric, – – – asymmetric).

4.3. *Melting points*

In Fig. 10, the melting points of Table 2 have been plotted as a function of *n*. When more than one melting point is given in Table 2 for a particular triglyceride, the average is taken. We assume that the 'true' melting points deviate from these values by 1 °C at most. The melting points are, therefore, a good indication of the close structural relationship between the three different homologous series of triglycerides which may belong to one common submodification. Fig. 10 shows that the melting points of *A*-, *C*- or *D*-type triglycerides are about 3 °C higher than those of the *B* type when comparing asymmetric with asymmetric and symmetric with symmetric triglycerides. Within a certain submodification, there is a difference of 3–6 °C between symmetric and asymmetric triglycerides.

5. Conclusions and discussion

A careful combination of the data obtained from the single-crystal X-ray analyses of 10.10.10, 12.12.12 and 10.12′.10, the powder diffraction data and melting points of many other triglycerides as well as the results of a theoretical packing analysis have enabled us to draw up a model-building scheme detailing the crystal structures and melting points of a large range of saturated triglycerides in the β-2 phase.

The main conclusion from our work is that there are several β-2 submodifications, namely *A*, *B*, *C*, *D* and *E*, which may be distinguished by their long spacings or angles of tilt (which decrease in the order $C \gtrsim D > A = B > E$), by their short-spacing patterns (Fig. 9) and by their melting points. Each submodification is associated with a maximum of three homologous triglyceride series. Each triglyceride may, in principle, crystallize in at least two submodifications; generally, only one submodification is observed. For instance, submodification *A* is generally preferred to *E*, *B* to *E* and *F*, *C* to *G* and probably *D* to *A* and *C*. The melting points are a more direct measure of the stability of each phase. They show the *B* submodification is less stable than the *A*, *C* and *D* submodifications, which are almost equally stable, so that we arrive at the following tentative order of decreasing stabilities: $D \gtrsim A \simeq C > B > E > F, G, H$ and *I*. The last four submodifications have not been observed. Of all potentially β-2 crystallizing triglycerides listed in Table 5, only 12.18.16 and its homologues have never been observed in a β-2 phase. We only obtained a β' modification of 12.18.16 with a melting point of 53–54 °C. Since 12.18.16 would have

to crystallize in the unstable *F*, *G* or *H* submodification, it may be expected that a further search for the β-2 phase 12.18.16 will not be successful.

The only triglycerides crystallizing in a β-2 modification, which were not expected to do so, are the homologous 14.14.18 and 18.18.22. To explain the observed long spacings we proposed a structure not closely packed. The loose packing is substantiated by the very low melting points (Fig. 10) of 14.14.18 and 18.18.22 (Lutton & Fehl, 1972) in this metastable phase. The only observations we cannot satisfactorily account for are the deviating long spacings of 12.12.12, 14.14.14, 16.16.16, 18.18.18 (Knoop & Samhammer, 1961; Frede & Precht, 1977) and 16.18.18 (Lutton, Jackson & Quimby, 1948). None of these long-spacing values has ever been mentioned or commented on in the literature and one may speculate whether these observations indeed concern genuine β-2 phases.

Attempts to derive the crystal structures of triglycerides on the basis of packing concepts have been made by, for instance, Knoop & Samhammer (1961), Paulicka & Hoerr (1963), Gunstone (1964), Ivanovszky (1966*a*,*b*), Lutton (1971) and more recently by Simpson & Hagemann (1975) and Frede & Precht (1977). To some extent, our work is an extension and generalization of Lutton's studies, who also deserves credit for drawing attention to the importance of the methyl-terrace structure.

The study of Simpson & Hagemann (1975) has some shortcomings. An important aspect of their work concerns the supposed lengthening of the *a* axis and shortening of the *b* axis with increasing chain lengths. However, from Table 1 it can be concluded that the *a* axis becomes shorter (this is also true of their choice of unit-cell axes) whereas the *b* axis will probably attain a constant value for 12.12.12 and higher homologues. Furthermore, they derive a unit cell for 24.24.24 by lengthening the unit-cell *c* axis of 12.12.12, which is not quite the same as lengthening the chain axes. Their subcell dimensions and also, therefore, their assignment for the short spacings are wrong.

In common with our approach, Frede & Precht (1977) have chosen the $T_{\parallel}$ subcell as the very logical basis for deriving the various packing modes of β-phase triglycerides. Their work is confined to monoacid triglycerides and they studied only different *a*-axis packings [*cf.* equation (1)] but no other layer stackings (*c*-axis packing).

Besides the design of a scheme giving the packing of triglyceride molecules in the β-2 phase, a major result of our work is a better understanding of the melting points, achieved by arranging these systematically, taking into account structural and thermodynamic considerations. To our knowledge, the effect of the entropy of mixing for the liquid state has never been mentioned in the extensive literature on the melting behaviour of triglycerides (*cf.* Bailey, 1950). The entropy effect will, of course, be present in other phases as well, as long as the crystalline phase discriminates between enantiomeric molecules. Although we feel that the crystal structures proposed here are essentially correct, we hope that X-ray single-crystal structure analyses will ultimately confirm this. Therefore, we intend to study certain aspects of triglyceride polymorphism by means of single-crystal electron diffraction, which does not require large single crystals.

The crystal structures presented in this paper certainly provide a good basis for more detailed analyses of β-2 triglyceride crystal structures. As to our work on the β-2 phase, we intend to extend and refine our packing analysis for the various submodifications, using van der Waals energy calculations. The purpose of this work is twofold: first, to correlate the observed stabilities with calculated lattice energies and, second, to obtain improved unit cells and subcells which may help in explaining the differences between the short-spacing patterns of the powder diffraction diagrams. A similar approach will be applied to other phases. A publication on the β-3 crystal modifications is in preparation (van Soest & de Jong, 1978). We are also investigating the structure of binary mixtures and the crystal structures of triglycerides with oleic acid chains, utilizing the new insights into the structures of the various β-2 submodifications.

6. General

The X-ray powder diffraction experiments have been carried out by means of Guinier–de Wolff and Guinier–Lenné (Simon) cameras. The cell dimensions of 18.18.18 were measured on the automatic Philips PW 1100 single-crystal diffractometer of the Twente University of Technology. High-purity triglycerides were synthesized in our laboratory according to recently published procedures (Mank, Ward & van Dorp, 1976).

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References

ALBON, N. (1976). *J. Cryst. Growth*, **35**, 105–109.
AVERILL, H. P., ROCHE, J. N. & KING, C. G. (1929). *J. Am. Chem. Soc.* **51**, 866–872.
BAILEY, A. E. (1950). *Melting and Solidification of Fats*, ch. III. New York: Interscience.
BAILEY, A. E., JEFFERSON, M. E., KREEGER, F. B. & BAUER, S. T. (1945). *Oil Soap (Chicago)*, **22**, 10–13.
BUCHHEIM, W. (1970). *Kiel. Milchwirtsch. Forschungsber.* **22**, 3–61.

CARTER, M. G. R. & MALKIN, T. (1939*a*). *J. Chem. Soc.* pp. 577–581.
CARTER, M. G. R. & MALKIN, T. (1939*b*). *J. Chem. Soc.* pp. 1518–1521.
CARTER, M. G. R. & MALKIN, T. (1947). *J. Chem. Soc.* pp. 554–558.
CHAPMAN, D. (1958). *J. Chem. Soc.* pp. 3186–3188.
CHAPMAN, D. (1962). *Chem. Rev.* **62**, 433–456.
CHAPMAN, D. (1965). *The Structure of Lipids*, pp. 260–291. London: Methuen.
CLARKSON, C. E. & MALKIN, T. (1934). *J. Chem. Soc.* pp. 666–671.
DAUBERT, B. F. & CLARKE, T. H. (1944). *J. Am. Chem. Soc.* **66**, 690–691.
DOYNE, T. H. & GORDON, J. T. (1968). *J. Am. Oil Chem. Soc.* **45**, 333–334.
FILER, L. J. JR, SIDHU, S. S., CHEN, C. & DAUBERT, B. F. (1945). *J. Am. Chem. Soc.* **67**, 2085–2089.
FILER, L. J. JR, SIDHU, S. S., DAUBERT, B. F. & LONGENECKER, H. E. (1946). *J. Am. Chem. Soc.* **68**, 167–171.
FREDE, E. & PRECHT, D. (1977). *Fette, Seifen, Anstrichm.* **79**, 69–75.
GUNSTONE, F. D. (1964). *Chem. Ind. (London)*, pp. 84–89.
IUPAC–IUB COMMISSION ON BIOCHEMICAL NOMENCLATURE (1968). *Chem. Phys. Lipids*, **2**, 156–167.
IVANOVSZKY, L. (1966*a*). *Seifen, Oele, Fette, Wachse*, **92**, 535–539.
IVANOVSZKY, L. (1966*b*). *Seifen, Oele, Fette, Wachse*, **92**, 565–567.
JACKSON, F. L. & LUTTON, E. S. (1949). *J. Am. Chem. Soc.* **71**, 1976–1980.
JACKSON, F. L. & LUTTON, E. S. (1950). *J. Am. Chem. Soc.* **72**, 4519–4521.
JENSEN, L. H. & MABIS, A. J. (1966). *Acta Cryst.* **21**, 770–781.
KNOESTER, M., DE BRUIJNE, P. & VAN DEN TEMPEL, M. (1972). *Chem. Phys. Lipids*, **9**, 309–319.
KNOOP, E. & SAMHAMMER, E. (1961). *Milchwissenschaft*, **16**, 201–209.
LARSSON, K. (1964*a*). *Ark. Kemi*, **23**, 1–15.
LARSSON, K. (1964*b*). *Ark. Kemi*, **23**, 29–34.
LARSSON, K. (1964*c*). *Ark. Kemi*, **23**, 35–56.
LARSSON, K. (1972). *Fette, Seifen, Anstrichm.* **74**, 136–142.
LUTTON, E. S. (1945). *J. Am. Chem. Soc.* **67**, 524–527.
LUTTON, E. S. (1948). *J. Am. Chem. Soc.* **70**, 248–254.
LUTTON, E. S. (1950). *J. Am. Oil Chem. Soc.* **27**, 276–281.
LUTTON, E. S. (1971). *J. M. Oil Chem. Soc.* **48**, 245–247.
LUTTON, E. S. & FEHL, A. J. (1970). *Lipids*, **5**, 90–99.
LUTTON, E. S. & FEHL, A. J. (1972). *J. Am. Oil Chem. Soc.* **49**, 336–337.
LUTTON, E. S. & HUGENBERG, F. R. (1960). *J. Chem. Eng. Data*, **5**, 489–490.
LUTTON, E. S., JACKSON, F. L. & QUIMBY, O. T. (1948). *J. Am. Chem. Soc.* **70**, 2441–2445.
LUTTON, E. S. & STEWART, C. B. (1970). *Lipids*, **5**, 545–553.
MCELROY, O. E. & KING, C. G. (1934). *J. Am. Chem. Soc.* **56**, 1191–1192.
MALKIN, T. (1954). *Prog. Chem. Fats Other Lipids*, **2**, 1–50.
MALKIN, T. & MEARA, M. L. (1939). *J. Chem. Soc.* pp. 103–108.
MALKIN, T. & WILSON, B. R. (1949). *J. Chem. Soc.* pp. 369–372.
MANK, A. P. J., WARD, J. P. & VAN DORP, D. A. (1976). *Chem. Phys. Lipids*, **16**, 107–114.
MINOR, J. E. & LUTTON, E. S. (1953). *J. Am. Chem. Soc.* **75**, 2685–2686.
PAULICKA, F. R. & HOERR, C. W. (1963). *Encyclopedia of X-rays and Gamma Rays*, edited by G. L. CLARK, pp. 1081–1087. New York: Reinhold.
PERRY, E. S., WEBER, W. H. & DAUBERT, B. F. (1949). *J. Am. Chem. Soc.* **71**, 3720–3726.
SCHEIJ, L. T. C. (1899). *Recl Trav. Chim. Pays-Bas*, **18**, 169–210.
SCHLENK, W. JR (1965). *J. Am. Oil Chem. Soc.* **42**, 945–957.
SETO, T., ASAI, K. & MITO, A. (1956). *Mem. Coll. Sci. Univ. Kyoto Ser. A*, **28**, 1–10.
SIDHU, S. S. & DAUBERT, B. F. (1947). *J. Am. Chem. Soc.* **69**, 1451–1453.
SIMPSON, T. D. & HAGEMANN, J. W. (1975). *J. Am. Oil Chem. Soc.* **52**, 303–306.
SKODA, W., HOEKSTRA, L. L., VAN SOEST, T. C., BENNEMA, P. & VAN DEN TEMPEL, M. (1967). *Kolloid Z. Z. Polym.* **219**, 149–156.
SOEST, T. C. VAN & DE JONG, S. (1976). *Recl Trav. Chim. Pays-Bas*, **95**, 162–165.
SOEST, T. C. VAN & DE JONG, S. (1978). In preparation.
TRILLAT, J. J. & NOWAKOWSKI, A. (1931). *Ann. Phys. (Paris)*, **15**, 462–485.
VAND, V. & BELL, I. P. (1951). *Acta Cryst.* **4**, 465–469.