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## Triclinic Lattice Constants of Saturated Mono-Acid Triglycerides

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### Abstract

Different triclinic crystal modifications of saturated, mono-acid triglycerides [ $C_{3n+3}H_{2(3n+1)}O_6$ ], especially of trilaurin, were investigated. Calculated results show good correspondence with the measured diffraction data. Besides the known stable  $\beta$  modification (space group  $P\bar{1}$ ), at least four further triclinic crystal forms are theoretically possible, and their existence is supported by evidence from the present experiments. Unit cells, subcells, chain distances, angles of chain tilts of the molecules and densities were determined for all crystal structures.

### 1. Introduction

On the basis of electron and X-ray diffractometric studies, it has been known for some time that triglycerides may exist in three major modifications: the  $\alpha$ ,  $\beta'$  and the  $\beta$  forms. This so-called polymorphism is characteristic of the crystallization of fats. It means that they can exist in different energetically favourable molecular arrangements with the same chemical composition.

The molecular form of triglycerides is more complicated than that of normal paraffins or fatty acids. While the latter consist primarily of unbranched chains, the triglyceride molecule contains a glycerol group linked with three fatty-acid chains. This conjugated structure is why relatively little is known about the

crystal structure of a number of modifications of triglycerides.

The  $\alpha$ ,  $\beta'$  and  $\beta$  forms have hexagonal ( $H$ ), orthorhombic ( $O\perp$ ) and triclinic ( $T\parallel$ ) chain packings. The studies on single crystals by Larsson (1964), Jensen & Mabis (1963, 1966), as well as Buchheim & Knoop (1969) and Buchheim (1970), on the  $\beta$  and  $\beta'$  forms, led to the exact atomic arrangement of the triclinic modification as well as the unit-cell parameters of the orthorhombic modification.

In an earlier report (Frede & Precht, 1977), we pointed out that the  $\beta$  modification of saturated mono-acid triglycerides can occur in at least five different chain packings (space group  $P\bar{1}$ ). These crystal forms have more or less the same  $T\parallel$  subcell packings. They differ primarily in the angle of tilt of the molecules.

We started from the proposition that – as is the case in the well known stable  $\beta$  structure (*cf.* Larsson, 1964; Jensen & Mabis, 1966), which we designated as the  $\beta_{III}$  form – the molecules are arranged head-to-head with the two equivalent fatty-acid chains in the so-called 2 position. A report by de Jong & van Soest (1978) further includes in a model relative shifts of mono-molecular layers. In our investigations of binary triglyceride mixtures (Precht & Greiff, 1978), we were able to establish the existence of larger quantities of the  $\beta_{IV}$  form.

The results of de Jong & van Soest (1978), as well as the occurrence of  $\beta_{IV}$  reflections of relatively high intensity in our X-ray diffraction patterns, has induced us to undertake a study on the various arrangements existing for the  $\beta_n$  modifications of triglycerides.

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## 2. Experimental

To obtain X-ray diffraction patterns from polycrystalline samples, we used a Geiger-Müller counter X-ray diffractometer, manufactured by Philips. Debye-Scherrer patterns were obtained of the substances trilaurin, trimyristin, tripalmitin, and tristearin with a tube current of 40 kV using Ni-filtered Cu radiation ( $\lambda = 1.5418 \text{ \AA}$ ),  $\frac{1}{4}^\circ$  X-ray divergence and receiving slits, and an angular velocity of  $\frac{1}{8}^\circ \text{ min}^{-1}$ .

For the electron diffraction patterns, we used the Philips electron microscope EM 301. Tripalmitin single crystals were produced by atomizing small quantities of a saturated petroleum ether solution with an ultrasonic atomizer at 3 MHz, and by positioning 400-mesh nets into this atomized mist. Carbon-damped Formvar material was used as a carrier film.

## 3. Chain-packing analysis

We assume that the known triclinic molecular arrangement of the  $\beta_{III}$  form represents a state of minimal free energy. This energetic state of the triglyceride crystal is primarily caused by the lateral arrangement of the fatty-acid chains. It can be described unequivocally by a triclinic subcell, *i.e.* the smallest recurrent unit of the  $\text{CH}_2$  groups, which are arranged in a zigzag pattern in the fatty-acid chains. It can therefore be concluded that a minimum of free energy and thereby an energetically favourable chain packing is provided by keeping the approximate dimensions of the subcell. However, slight changes of the subcell parameters may occur, particularly for triglycerides with chains of different lengths.

We assume that the molecular form is identical for  $\beta_n$  modifications and that two molecules situated on the same plane, with the glycerol groups facing each other form a fixed unit in all possible triclinic forms. The first hypothesis is supported by our X-ray diffraction patterns. In the patterns the position and intensity of the diffraction reflections of the various  $\beta_n$  forms are practically stable in the short-spacing range ( $18^\circ \leq 2\theta \leq 25^\circ$ ), while a change in the distance of the glycerol groups from each other would result in an increase of free energy (second hypothesis).

We further hypothesize that shifts of double molecules along the chains, *i.e.* along the subcell axis  $c_s$ , are possible and, furthermore, that monomolecular layers can be shifted by the vector  $ua_s + vc_s$ ,  $u$  and  $v$  representing integral numbers (de Jong & van Soest, 1978).

In Fig. 1 a number of triglyceride molecules in the triclinic crystal lattice of the  $\beta_{III}$  form are schematically represented.  $P_1 \equiv (0,0,1)$  and  $P_2 \equiv (x_1, x_2, 0)$  are the relative coordinates of the points of intersection of the straight elongations of the fatty-acid chains of a triglyceride molecule in the 2 and 1 positions with the

upper and lower  $ab$  plane of the unit cell. The distance  $A = \overline{P_1 P_2}$  is expressed by the equation:

$$A = Nc_s + d$$

with  $d$  representing the difference between the distance  $\overline{P_1 P_2}$  and twice the length of the chains of the fatty-acid branches  $Nc_s$ .  $N$  gives the number of the C atoms and characterizes the type of substance (*e.g.*  $N = 18$  is tristearin). Therefore,  $d$  is a measure of the distance of adjacent molecule layers. The parameter of the unit cell  $a$  is represented by the equation (*cf.* Fig. 1a):

$$a = 3a_s + b - c_s.$$

New molecular arrangements are caused by shifting two neighbouring molecules forming a unit by  $(3 - n)c_s$  along the chain. In Fig. 1(b), for instance,  $n = 2$ , *i.e.* a change is effected by a shift in  $c_s$ . Presupposing that  $b_n = b_s$  in approximately all  $\beta_n$  modifications, the following general equations result:

$$a_n = 3a_s + b_s - (n - 2)c_s \quad (1)$$

and

$$A_n(N) = [N + (1 - x_1)(3 - n) + d/c_s] c_s.$$

Furthermore, the following correlations can be deduced from Fig. 1:

$$c_n(N) = x_1 a_n + x_2 b_n + A_n(N). \quad (2)$$

Considering the shift of monomolecular layers by the vector  $ua_s + vc_s$ , equations (1) and (2) yield the following results:

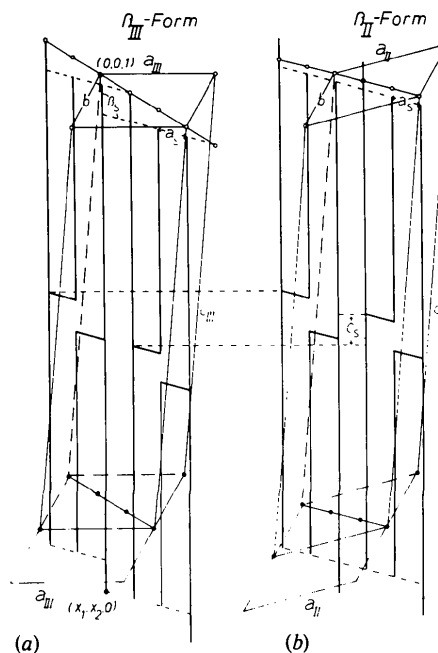


Fig. 1. Arrangement of the triglyceride molecules in transition from the  $\beta_{III}$  to the  $\beta_{II}$  modification. Circles signify the points of intersection with the chains of the molecules drawn in on the  $ab$  plane. Filled circles are the points of intersection of a lower molecule layer.

$$\mathbf{c}_{n,u,v}(N) = (3x_1 + u)\mathbf{a}_s + (x_1 + x_2)\mathbf{b}_s + (3 + N - n - x_1 + v + d/c_s)\mathbf{c}_s, \quad (3)$$

$$\alpha_{n,u,v}(N) = \arccos[\mathbf{b}_n \cdot \mathbf{c}_{n,u,v}(N) / b_n c_{n,u,v}(N)], \quad (4)$$

$$\beta_{n,u,v}(N) = \arccos[\mathbf{a}_n \cdot \mathbf{c}_{n,u,v}(N) / a_n c_{n,u,v}(N)] \quad (5)$$

and

$$\gamma_n = \arccos(\mathbf{a}_n \cdot \mathbf{b}_n) / a_n b_n. \quad (6)$$

It is now also possible to calculate the following correlation for the thickness of the crystal layers  $K_{n,u,v}(N)$  ( $d_{001}$  values) and the angles of tilt of the molecules  $\tau_n(N)$  of the five  $\beta_n$  modifications for the triglycerides trilaurin ( $C_{12}$ ) up to tristearin ( $C_{18}$ ):

$$K_{n,u,v}(N) = [N + d/c_s + v + (1 - x_1)(3 - n) + u(n - 2)/3] c_s \sin \tau_n. \quad (7)$$

de Jong & van Soest assume in their model that, as in the energetically particularly favourable  $\beta_{III}$  form, no lattice holes may occur, and that the distance of the atoms may not be too small. We are primarily interested in establishing a theoretical framework for the diffraction reflections that we arrived at experimentally. So far (Frede & Precht, 1977) we had not totally excluded single and double compressions ( $S_1$  and  $S_2$ ). It becomes apparent from our calculations that, on the basis of our hypotheses, the experimentally established diffraction lines can only be interpreted as resulting at least from single and double lattice holes ( $L_1$  and  $L_2$ ). But we intend also to discuss triple holes ( $L_3$ ) and single compressions ( $S_1$ ).

To determine unit cells or the thicknesses of crystal layers, the values  $x_1$  and  $x_2$  of the chain intersection point  $P_2$  and  $d$  have to be computed. As we were trying to compare our results with the data on single crystals of the  $\beta_{III}$  form of trilaurin, which were experimentally established by Buchheim (1970), we took as the starting point for our calculations Larsson's (1964) atomic coordinates of the  $\beta_{III}$  form of trilaurin. Fig. 2(a) shows an X-ray diffraction pattern that, recorded from these data, has been worked out with a computer by employing a Lorentz, polarization and temperature factor.

A comparison with the experimentally recorded diffraction pattern of Fig. 2(c) shows that the 302 and  $2\bar{1}4$  reflections,\* which are clearly separated here, appear as one line in the diagram computed on the basis of Larsson's data. As a line splitting of these two reflections occurred during all our measurements, and since the literature speaks of two separated peaks, a slight modification of Larsson's unit cell seems unavoidable. For this purpose, diffraction patterns were recorded at the smallest possible angle velocity of our X-ray goniometer ( $\frac{1}{8}^\circ \text{ min}^{-1}$ ). From these findings the

following optimal unit cell was calculated using a specially compiled computer program, which can also correct the minimal line displacements caused by mutual superimposition:  $a = 12.15$  (5),  $b = 5.48$  (3),  $c = 31.76$  (15) Å,  $\alpha = 94.9$  (5),  $\beta = 96.2$  (5),  $\gamma = 100.4$  (5)°. The equivalent values found by Larsson are:  $a = 12.35$  (8),  $b = 5.44$  (4),  $c = 31.75$  (10) Å,  $\alpha = 94.0$  (5),  $\beta = 96.7$  (5),  $\gamma = 99.2$  (5)°. The new parameters of the unit cell can be regarded as somewhat more precise than earlier values published by us (Precht, 1977).

By using Larsson's relative atomic coordinates and the new unit cell, it becomes apparent (*cf.* Fig. 2b) that the new computer-based diffraction pattern and the experimental findings coincide to a very large extent. The line splitting between reflections 302 and  $2\bar{1}4$  is primarily caused by the slightly changed  $a$  and  $\gamma$  values, respectively.

The computation of the  $x_1$  and  $x_2$  values shows that particularly the first ten C atoms – computed from the methyl group – of the fatty acids in the 1 and 2 positions are situated approximately on a straight line. The distance  $A$  of points  $P_1$  and  $P_2$  is given in the equation:

$$\mathbf{A} = -x_1 \mathbf{a} - x_2 \mathbf{b} + \mathbf{c}$$

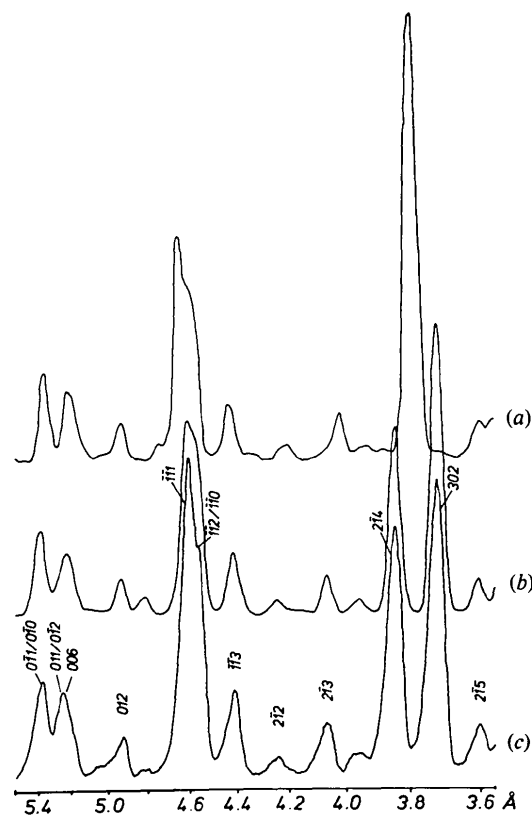


Fig. 2. Diffraction pattern of the  $\beta_{III}$  form of trilaurin, (a) calculated after Larsson's (1964) results, (b) after the modified unit cell, (c) experimentally obtained diffraction pattern.

\* On the indexing of the reflections, *cf.* Precht (1977).

with

$$A = [N + (1 - x_1)(3 - n)]c_s + d,$$

$$x_1 = 0.75 \quad \text{and} \quad x_2 = -2.23.$$

Further computation shows that  $d = 5.03 \text{ \AA}$ . If these values are used in the equation system (1-6) for the unit cell described above, the subcell can be calculated by solving the equation system for  $a_s, \dots, \gamma_s$ :

$$a_s = 4.39, \quad b_s = 5.48, \quad c_s = 2.56 \text{ \AA},$$

$$\alpha_s = 71.8, \quad \beta_s = 108.4, \quad \gamma_s = 121.4^\circ.$$

These subcell parameters differ from Larsson's data, particularly in the values for  $b_s$ ,  $\alpha_s$  and  $\gamma_s$  ( $5.40 \text{ \AA}$ ,  $74.8^\circ$  and  $120.5^\circ$ ). It has to be pointed out that these differences are not only caused by using the new unit cell, but, in particular, by employing the system of equations (1-6), which provides a closely approximated relation between the parameters of the unit cell and the subcell. The values  $x_1$  and  $x_2$ , the subcell and  $d$  have been calculated in such a way that the resulting parameters of the unit cell, which are of particular interest here, are quite precise. These new data are to be preferred over the data that we published earlier (Frede & Precht, 1977).

The three most pronounced X-ray diffraction lines in the short-spacing range result from the subcell reflections 100, 010 and 110. By using the subcell, the following interplanar spacings can be established:  $d_{100} = 3.68$ ,  $d_{010} = 4.60$  and  $d_{110} = 3.90 \text{ \AA}$ . According to Fig. 3, the three shortest spacings of neighbouring hydrocarbon chains can be computed. The angles  $\angle(\mathbf{b}_s, \mathbf{c}_s) = \alpha_s$ ,  $\angle(\mathbf{a}_s, \mathbf{c}_s) = \beta_s$  and  $\angle(\mathbf{a}_s, \mathbf{b}_s) = \gamma_s$  yield the equations:

$$d_1 = a_s \sin \beta_s;$$

$$d_2 = b_s \sin \alpha_s$$

and

$$d_3 = x \{ 1 - (a_s \cos \beta_s + b_s \cos \alpha_s)/x \}^{1/2}$$

with

$$x = (a_s^2 + b_s^2 + 2a_s b_s \cos \gamma_s)^{1/2}.$$

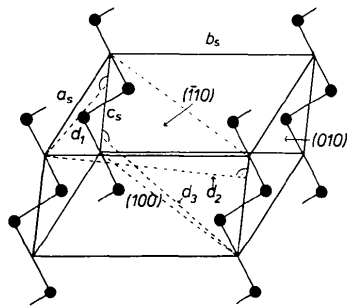


Fig. 3. On the derivation of the shortest distances  $d_1$ ,  $d_2$  and  $d_3$  between neighbouring hydrocarbon chains in the triclinic subcell.

The distances  $d_1 = 4.7$ ,  $d_2 = 5.21$  and  $d_3 = 4.76 \text{ \AA}$  can thus be computed.

In a deposited table\* all theoretically possible unit cells have been compiled using trilaurin as an example. Our further computations of a change in the chain packing in the  $\mathbf{b}$  direction result in too small atomic spacings between neighbouring molecules. We shall, therefore, omit these calculations here.

#### 4. Discussion of the molecular arrangement

##### 4.1. The $\beta_1$ modification

Three different crystal structures with the following periodicities in the area of terminal groups of the fatty-acid chains can apply for the  $\beta_1(n,u,v)$  modification:

$$(1) \beta_1(1,-1,1): \dots NL_3 L_3 \dots, 1:1$$

$$(2) \beta_1(1,0,0): \dots NNL_2 \dots, 2:2$$

$$(3) \beta_1(1,1,0): \dots NL_1 N \dots, 3:3.$$

$N$  means normal (no lattice defects),  $L_1 =$  single,  $L_2 =$  double,  $L_3 =$  triple holes. The positions of comparable chains relative to one another [Larsson ( $\beta_{111}$ )  $\equiv$  2:2 position] are also given.

Our experimentally established reflections on the  $\beta_1$  form are the most difficult to interpret. The high long-spacing value of  $37.97 (15) \text{ \AA}$  for trilaurin does not show a close correspondence with the value of  $K_{1,0,0} = 35.2 \text{ \AA}$  from equation (7). On the other hand, a theoretical layer thickness of  $38.4 \text{ \AA}$  for the  $\beta(1,-1,1)$  structure can be established, which is comparable to the experimental findings.

In Fig. 4 the molecular arrangements of the  $\beta(1,-1,1)$  and  $\beta(1,0,0)$  modifications are given projected along the  $b$  axis. The dashed circles signify gaps in the crystal lattice. According to Fig. 4(a), it would hardly seem probable that a molecular configuration with lattice gaps of such magnitude ( $L_3$  holes) could occur.

Our computations of the  $\beta(1,0,0)$  structure show that changes of  $a_s$ ,  $b_s$ ,  $\beta_s$  and  $\gamma_s$  cause only slight changes in the thickness of the crystal layer  $K_{1,0,0}$ . The experimental  $d_{001}$  value can be generated primarily through slightly changed  $\alpha_s$  and  $x_1$  parameters.

From our test results on the thickness of the crystal layer of the  $\beta_1$  form, the general equation

$$K = 2.496N + 8.020$$

\* Tables of the theoretical structure data of trilaurin and of the subcells and angles of tilt of the chains have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38310 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

can be computed. Taking an approximately constant  $c_s$  value of 2.56 Å for all  $\beta_1$  modifications of the various substances, according to equation (7) with  $d = 5.03$  Å,  $\tau$  and  $x_1$  can be found:

$$\tau = \arcsin 2.496/2.56 = 77.2^\circ$$

and

$$x_1 = 1 - (8.02/\sin \tau - 5.03)/2 \times 2.56 = 0.38.$$

With  $\alpha_s = 77.3^\circ$  and the value  $x_1 = 0.38$ , we obtain  $K_{1,0,0} = 38.0$  Å for the  $\beta_1(1,0,0)$  structure of trilaurin.

We consider a molecular arrangement, as shown in Fig. 4(a), to be highly improbable. Although there are also large lattice holes in Fig. 4(b), this seems to be the only possibility corresponding to the measured spacings based on our initial hypotheses (chain periodicity: ...  $NNL_2$  ...).

From numerous single-crystal patterns of tripalmitin, which were obtained with the help of electron diffraction (selected-area diffraction), a subcell pattern could be attributed to the  $\beta_1$  modification. A comparison with diffraction patterns of the  $\beta_{III}$  form showed that the  $d_{100}$  value of the  $\beta_1$  form of the interplanar spacings of the three subcell reflections with the highest intensity 100, 010,  $\bar{1}10$ , was 0.08 Å larger than that of the  $\beta_{III}$  form. The interplanar spacings  $d_{010}$  and  $d_{\bar{1}10}$ , however, showed the same values for both forms. We assume that comparable differences exist between the two triclinic modifications of trilaurin.

The mentioned widening of the angle  $\alpha_s$  from  $71.8$  to  $77.3^\circ$  results in a pronounced increase of  $d_{010}$  and a decrease of  $d_{100}$ .  $b_s$  has to become smaller in order to produce a decrease of  $d_{010}$ . We assume the following dimensions for the subcell:  $a_s = 4.44$ ,  $b_s = 5.29$ ,  $c_s = 2.56$  Å,  $\alpha_s = 77.3$ ,  $\beta_s = 108.3$  and  $\gamma_s = 119.3^\circ$ . With  $x_1 = 0.38$ ,  $x_2 = -2.23$  and  $d = 5.03$  Å, the following crystal-lattice parameters for the  $\beta_1$  modification of trilaurin are obtained:  $a = 11.29$ ,  $b = 5.29$ ,  $c = 38.25$  Å,  $\alpha = 95.2$ ,  $\beta = 84.9$  and  $\gamma = 93.4^\circ$ ,  $K_{1,0,0} = 38.0$  Å,  $\tau = 77.2^\circ$  and  $D = 0.937$  g cm $^{-3}$ . For the subcell spacings the following values are obtained:  $d_{100} = 3.76$ ,  $d_{010} = 4.60$  and  $d_{\bar{1}10} = 3.90$  Å. The three shortest distances of neighbouring hydrocarbon chains are:  $d_1 = 4.22$ ,  $d_2 = 5.16$  and  $d_3 = 5.09$  Å. These values correlate with the experimental findings. The crystal layers have the same thicknesses;  $d_{100}$  is 0.08 Å larger than with the initial subcell,  $d_{010}$  and  $d_{\bar{1}10}$  remain the same.

These calculations are intended to show that with relatively few small changes in the crystal lattice, one can obtain the existing experimental findings. However, it is difficult to understand why the molecular arrangement in Fig. 4(b) with lattice holes of such magnitude is stable over a long period of time. We are trying to obtain further data on the crystal structure with the help of electron diffraction on single crystals of the  $\beta_1$  form of tripalmitin.

#### 4.2. The $\beta_{II}$ modification

Four different crystal structures with the following periodicities in the area of terminal groups of the fatty-acid chains can apply for the  $\beta(n,u,v)_{II}$  modification:

- (1)  $\beta(1,1,0)$ : ...  $NL_1 NNL_1 N$  ..., 3:3
- (2)  $\beta(1,0,0)$ : ...  $NNL_2 NNL_2$  ..., 2:2
- (3)  $\beta(2,0,0)$ : ...  $NNL_1 NNL_1$  ..., 2:2
- (4)  $\beta(2,1,0)$ : ...  $NL_1 NNL_1 N$  ..., 3:3.

We further assume that the molecular arrangement with  $n = 1$  and  $u = v = 0$  corresponds to the  $\beta_1$  form, and shall confine our discussion to the other structures.

A comparison with Buchheim's (1970)  $\beta_{II}$  unit cell, which was obtained without model calculations solely from single-crystal data by electron diffraction ( $a = 11.60$ ,  $b = 5.30$ ,  $c = 34.7$  Å,  $\alpha = 89$ ,  $\beta = 85$  and  $\gamma = 96^\circ$ ), shows that these values correspond well to a  $\beta(2,0,0)$  arrangement.

By slightly changing the subcell and the value  $x_2$ , we arrive exactly at Buchheim's data. By solving the equation system (1-6) for the subcell parameters, we obtain, with  $x_1 = 0.75$ ,  $x_2 = -1.6$ ,  $d = 5.02$  Å and the above given unit cell, the values:  $a_s = 4.42$ ,  $b_s = 5.3$ ,  $c_s = 2.56$  Å,  $\alpha_s = 74.1$ ,  $\beta_s = 105.5$ ,  $\gamma_s = 119.4$  and  $\tau =$

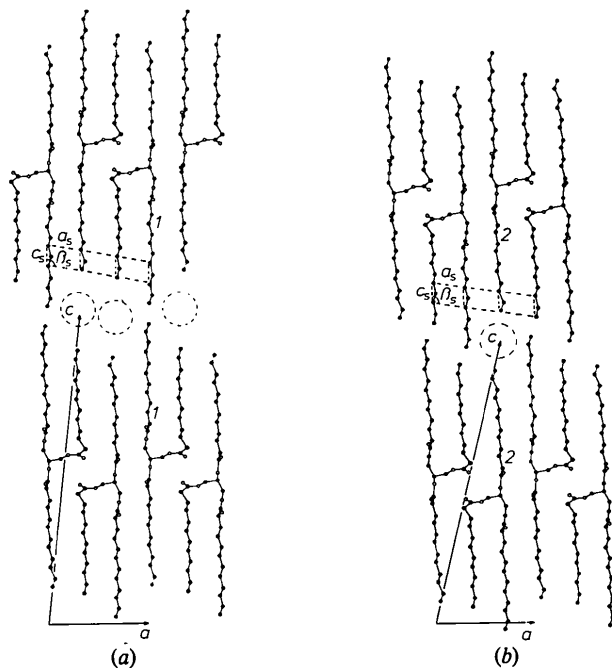


Fig. 4. Possible molecular arrangements of the  $\beta_1$  modification of trilaurin projected along the  $b$  axis.

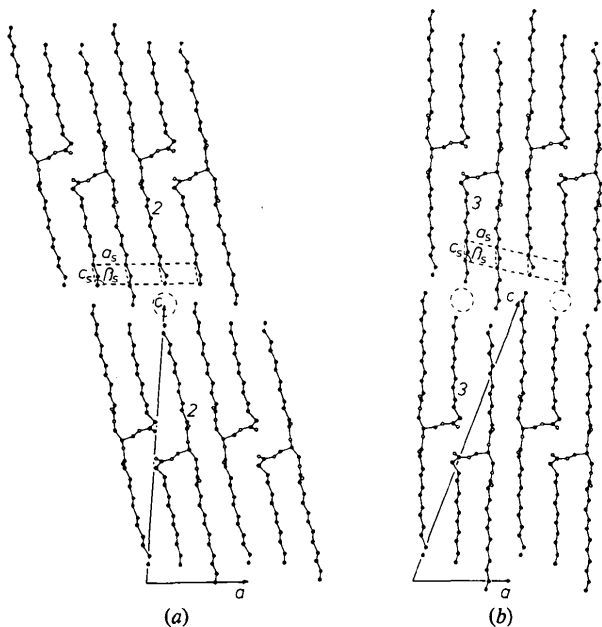


Fig. 5. Possible molecular arrangements of the  $\beta_{II}$  modification of trilaurin projected along the  $b$  axis.

$71.7^\circ$ . Furthermore, the following subcell interplanar spacings can be calculated:  $d_{100} = 3.80$ ,  $d_{110} = 3.91$  and  $d_{010} = 4.55 \text{ \AA}$ .

We were unable to show experimentally any  $\beta_{II}$  long spacing with trilaurin. From the general equation for the thickness of the crystal layers it follows that  $K = 2.369N + 7.354$ .  $K$  could be obtained from the measured data for  $C_{14}$ ,  $C_{16}$  and  $C_{18}$ . From this an extrapolated value of  $35.8 \text{ \AA}$  can be computed for  $C_{12}$ . This value is  $1.3 \text{ \AA}$  larger than the  $d_{001}$  interplanar spacing found by Buchheim. If we start from the assumption that the modification, which we have so far designated as  $\beta_{II}$ , assigns to a second crystal structure, apart from a molecular arrangement with  $n = 2$ ,  $u = v = 0$  the experimental data best correlate with the assumption  $n = 1$ ,  $u = 1$  and  $v = 0$ .

Fig. 5(b) shows that the modification of Larsson's molecular arrangements consists, apart from a shift of double molecules along the chain by  $c_s$ , in a shift of monomolecular layers by the vector  $a_s$ . If our initial cell is slightly changed to  $\alpha_s = 71.2^\circ$ , and if the base point is shifted to  $x_1 = 0.43$ , a crystal-layer thickness of  $35.8 \text{ \AA}$  results for the  $\beta(1,1,0)$  structure. Furthermore, the following values are obtained:  $a = 11.07$ ,  $b = 5.48$ ,  $c = 37.12 \text{ \AA}$ ,  $\alpha = 93.5$ ,  $\beta = 74.8$ ,  $\gamma = 92.9^\circ$  and  $D = 0.978 \text{ g cm}^{-3}$ . The chain's angle of tilt is  $\tau = 71.1^\circ$ .

#### 4.3. The $\beta_{III}$ modification

Starting from the known stable  $\beta_{III}$  structure, it is not possible by shifting monomolecular layers to obtain a crystal-layer thickness that has been found experi-

mentally up to now. A shift along  $a$ , gives an arrangement with the lowest possible number of lattice holes. For the periodicity in the area of terminal groups of the fatty-acid chains, we obtain:

$$\dots NL_1 NNL_1 N \dots$$

The resulting  $d_{001}$  interplanar spacing of  $32.1 \text{ \AA}$  for  $C_{12}$  has so far not been proved.

A comparison of the theoretical values from equations (1-6) with Jensen's & Mabis's (1966) experimental results yield a close correlation. The authors give the following unit cell for tricaprin:  $a = 5.488 (10)$ ,  $b = 12.176 (30)$ ,  $c = 26.93 (7) \text{ \AA}$ ,  $\alpha = 85.35 (15)$ ,  $\beta = 87.27 (15)$  and  $\gamma = 79.28 (15)^\circ$ . To be able to compare these data with our theoretical values, the following transformation matrix must be used:

$$\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ -1 & 0 & 1 \end{pmatrix}$$

This yields:  $a = 12.176$ ,  $b = 5.488$ ,  $c = 27.23 \text{ \AA}$ ,  $\alpha = 98.89$ ,  $\beta = 92.45$  and  $\gamma = 100.72^\circ$ . Our theoretical values for tricaprin are:  $a = 12.14$ ,  $b = 5.48$ ,  $c = 27.32 \text{ \AA}$ ,  $\alpha = 99.0$ ,  $\beta = 92.8$  and  $\gamma = 100.4^\circ$ .

#### 4.4. The $\beta_{IV}$ modification

We showed in an earlier publication (Precht & Greiff, 1978) that trimyristin has relatively large amounts of the  $\beta_{IV}$  modification. Gas chromatographic analyses showed small amounts of free  $C_{14}$  fatty acids (approximately 3%). Closer investigations proved that the reflections of the  $\beta_{IV}$  form of triglycerides cannot be attributed to the known  $C$  form of fatty acids (Vand, Morley & Lomer, 1951) although the long spacings of both forms hardly differ from one another. Up to now we had assumed (Frede & Precht) a molecular arrangement with  $n = 4$  and  $u = v = 0$  for the  $\beta_{IV}$  form. This would result in the following periodicities in the region of the fatty-acid chains:

$$\dots NNS_1 NNS_1 \dots$$

*i.e.* single compressions ( $S_1$ ) would be present.

Possibly the few data known until now on the crystal structure of the  $\beta_n$  modifications (with  $n \neq III$ ) can be explained by slight impurities caused by free fatty acids. In comparison with the triglycerides examined, in the case of the  $\beta_{IV}$  form, fatty acids with extremely short chains might occupy places on the crystal lattice, so that compressions can be partly avoided. The remaining  $S_1$  defects can then possibly be explained by the existence of  $2g1$  kinks (Pechhold, Blasenbrey & Woerner, 1962). No kink effects have been established, however, in the very densely packed triclinic chain arrangements. Previous discussions of such lattice defects referred exclusively to the less dense

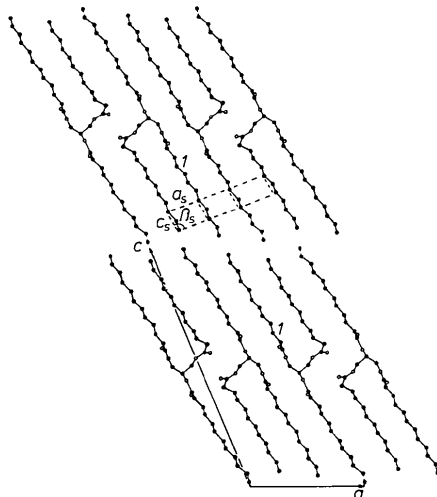


Fig. 6. Molecular arrangement of the  $\beta_{IV}$  modification of trilaurin projected along the  $b$  axis.

chain packings of the orthorhombic modifications of paraffins (Blasenbrey & Pechhold, 1967), polyethylene (Pechhold, 1968), triglycerides (Precht, Frede & Greiff, 1978), or to the system tetradecylammonium beidellite/tetradecanol (Lagaly, Fitz & Weiss, 1975).

In all possible configurations  $\beta(4,1,0)$  and  $\beta(4,-1,1)$  structures with periodicities in the area of terminal groups of fatty acids  $\dots NL_1 N \dots$  and  $\dots NNN \dots$  and relative chain positions 3:3 and 1:1 would provide a satisfactory interpretation of the measured long spacings. Under energy considerations, a crystal lattice with  $n = 4$ ,  $u = -1$  and  $v = 1$  is to be preferred, as it has no lattice defects. de Jong & van Soest also point to this arrangement. With tristearin, the authors found  $\beta_{IV}$  long spacings of the  $\beta$ -2E modification, using their nomenclature. Although our experimental  $d_{001}$  value (28.3 Å) correlates better with the  $\beta(4,0,0)$  structure (28.2 Å), we assume along with the Dutch authors that the molecules in the  $\beta_{IV}$  form are arranged as in Fig. 6 ( $n = 4$ ,  $u = -1$ ,  $v = 1$ ). According to our calculations, a slight change of our initial subcell ( $\beta_s = 110.2^\circ$ ) results in a crystal layer thickness of 28.3 Å. Fig. 6 shows that in comparison to the most stable  $\beta$  modifications, we have here a shift of triglyceride pairs

along  $-c_s$  and a shift of monomolecular layers by the vector  $-\mathbf{a}_s + \mathbf{c}_s$ .

It is surprising that in a seemingly stable lattice arrangement (cf. Fig. 6) the  $\beta_I$  and  $\beta_{II}$  structures usually occur more frequently with saturated triglycerides.

#### 4.5. The $\beta_V$ modifications

Two arrangements are possible:

$$\beta_V(5,0,0): \dots NNS_2 \dots, 2:2$$

and

$$\beta_V(5,1,0): \dots NL_1 N \dots, 3:3.$$

Disregarding the molecular arrangement that we have considered thus far, in which the  $\beta_{IV}$  form showed double compressions ( $S_2$ ), only one crystal structure is applicable.

Fig. 7 shows that triglyceride pairs are shifted by  $-2c_s$  along the chain, in comparison to Larsson's molecular arrangement. Furthermore, the monomolecular layers have been shifted by  $a_s$ . The theoretical (26.8 Å) and experimental thicknesses of crystal layers differ by 1.65 Å. Our calculations show that with a subcell change ( $c_s = 2.53$  Å and  $\beta_s = 113^\circ$ ), a correlation between experimental and theoretical value of 25.1 Å can be achieved.

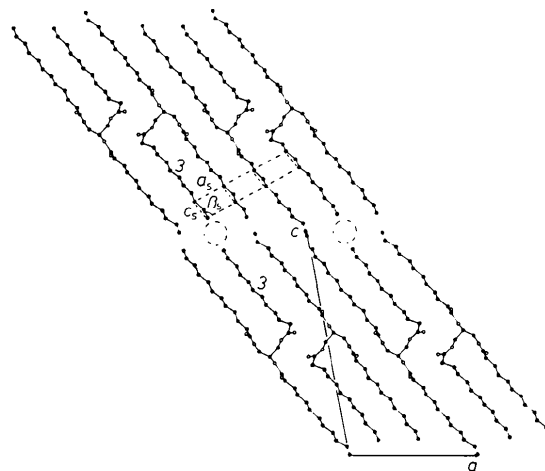


Fig. 7. Molecular arrangement of the  $\beta_V$  modification of trilaurin projected along the  $b$  axis.

Table 1. Comparison of experimental and theoretical monomolecular crystal layers

Triglyceride	$\beta_I(1,0,0)$ Å		$\beta_{II}(1,1,0)$ Å		$\beta_{III}(3,0,0)$ Å		$\beta_{IV}(4,-1,1)$ Å		$\beta_V(5,1,0)$ Å	
	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.
C <sub>12</sub>	37.97	38.0	35.8*	35.8	31.36	31.4	28.3	28.3	25.1	25.1
C <sub>14</sub>	42.94	42.9	40.36	40.5	36.14	35.9	32.0	32.4	28.7	28.8
C <sub>16</sub>	48.00	47.9	45.56	45.3	40.36	40.4	35.9†	36.6	32.7	32.5
C <sub>18</sub>	52.92	52.9	49.83	50.0	45.20	44.9	40.5	40.7	36.0	36.3
							40.8‡			

\* Obtained through linear extrapolation from the other values in the column.

† Knoop's & Samhammer's (1961) values.

‡ de Jong's & van Soest's (1978) values.

### 5. Supplemented structure parameters and relations

Starting from the assumption that the subcell values which have been calculated for the various  $\beta_n$  modifications of trilaurin coincide approximately for all triglycerides from trilaurin to tristearin the theoretical [cf. equation (7)] and experimental values of crystal layer thicknesses can be compared in Table 1.

Furthermore, equation (7) allows theoretical equations for the crystal-layer thicknesses to be derived taking into account the computed subcell parameters of trilaurin. In Table 2 these equations are juxtaposed to the experimentally obtained relations.

Thanks are due to Deutsche Forschungsgemeinschaft for making available the equipment required

Table 2. Relations for the crystal-layer thicknesses from trilaurin ( $N = 12$ ) to tristearin ( $N = 18$ ); comparison of experimental and theoretical results

Modification	$K(N)_{\text{exp.}} (\text{\AA})$	$K(N)_{\text{theor.}} (\text{\AA})$
$\beta_1(1,0,0)$	$2.496 N + 8.020$	$2.496 N + 8.001$
$\beta_{11}(2,0,0)$	—	$2.431 N + 5.383$
$\beta_{11}(1,1,0)$	$2.369 N + 7.354$	$2.369 N + 7.354$
$\beta_{111}(3,0,0)$	$2.255 N + 4.400$	$2.248 N + 4.418$
$\beta_{111}(4,-1,1)$	$2.047 N + 3.567$	$2.064 N + 3.540$
$\beta_V(5,1,0)$	$1.890 N + 3.247$	$1.861 N + 2.770$

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## Neutron Diffraction at 15 and 120 K and *ab initio* Molecular-Orbital Studies of the Molecular Structure of 1,2,4-Triazole

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### Abstract

The crystal structure of 1,2,4-triazole,  $C_2H_3N_3$ , has been refined using single-crystal neutron diffraction data [ $\lambda = 1.0470(1) \text{\AA}$ ] measured at 15 and 120 K. The crystal data at 15 K [120 K] are  $M_r = 69.07$ ;  $Pbca$ ;  $Z = 8$ ;  $a = 9.748(2)$  [9.760(2)],  $b = 9.331(2)$  [9.345(2)],  $c = 6.927(2)$  [6.989(2)]  $\text{\AA}$ ;  $D_n = 1.456$  [1.439]  $\text{g cm}^{-3}$ . The final agreement factors are  $R(F) = 0.039$  [0.055],  $wR(F^2) = 0.050$  [0.054],  $S = 1.309$  [1.114] for 1249 [1258] observations. The molecule is very close to planar, with the ring atoms deviating from their least-squares plane by less than 0.0015 (6)  $\text{\AA}$ . The

(X-ray diffractometer and electron microscope) in the experimental studies.

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H atoms deviate from this plane by less than 0.061(2)  $\text{\AA}$ . Thermal-motion corrections based on rigid-body and segmented-body analyses resulted in differences of less than 0.005  $\text{\AA}$  in the corrected bond lengths from the two refinements. *Ab initio* molecular-orbital calculations were carried out at the Hartree-Fock (HF) 3-21G level, using GAUSSIAN83 to optimize the geometry of the isolated molecule for minimum energy. There are differences between the thermally corrected experimental and calculated bond lengths for the ring bonds of between 0.010 and 0.030  $\text{\AA}$ . These differences are largely accounted for by estimations of corrections for approximation in the