The Thermal Expansion of the Crystalline B- and C-Forms of Stearic Acid

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The changes with temperature of the cell dimensions and the density of the B- and C-forms of stearic acid have been determined. The influence on the c-axis is very slight. The effect on the subcell axes is similar to the disturbing effect of branching groups, *i. e.* the a_s-axis, ~ 4.95 Å, is almost unchanged but the b_s-axis, ~ 7.40 Å, is appreciably increased.

In connection with studies on polymorphism of normal fatty acids and transitions between the different polymorphs [1-3] it was found necessary to determine the variation of the cell dimensions of two polymorphs of an acid for temperatures between 0°C and the transition and melting points, respectively. The B- and C-forms of stearic acid were chosen. The structure of the B-form of stearic acid has been described by von Sydow [4]. The C-form of stearic acid has a structure analogous with the C-form of lauric acid, which has been described by Vand *et al.*[5] The cell dimensions of the C-forms of the whole homologous series have been determined by Abrahamsson and von Sydow [6] at one temperature (+ 23°C). Some of these data are given in Table 1.

Table 1. Dimensions of the B- and C-form of stearic acid and the orthorhombic subcell (O ⊥) at room temperature (+23°C) [3,4,6].

	a Å	b Å	β	Space group	a_s, $a \sin \beta$ and b, respectively	b_s, b and $a \sin \beta$, respectively
O ⊥	4.95	7.40	90°	$P\ b\ n\ m$	4.95	7.40
B-form	5.59	7.40	117°22′	$P2_1/a$	4.96	7.40
C-form	9.36	4.96	128°14′	$P2_1/a$	4.96	7.35

These crystal forms have both the same chain packing: the common orthorhombic type [3] with every second chain plane perpendicular to the others (O⊥). The main difference between the structures is that in the case of the B-form the structure is tilted over the long subcell axis (7.40 Å) giving an increase in the short axis (4.95 Å to 5.59 Å) while in the case of the C-form the structure is tilted over the short subcell axis (4.95 Å) increasing the long axis from 7.40 Å to 9.36 Å (Table 1). These tilts are necessary to give space for the carboxylic groups, which are held together two and two by hydrogen bonds.

The B-form, which is obtained by crystallization from various solvents [2], is the stable form at room temperature but it is irreversibly transformed into the C-form by raising the temperature above + 46°C[1]. The C-form is stable up to the melting point + 69°.7C [1]. Solid phase in equilibrium with melt is always of the C-form.

By X-ray diffraction spectrometry the variations with temperature of the cell-dimensions and the densities of the B- and C-forms of stearic acid have been determined by measuring the variations with temperature of the diffraction angles of four reflexions of each crystal form.

TECHNIQUE

The X-ray spectrometer equipped with a scintillation counter and the heating arrangement used are constructed by Prof. G. Hägg. A shallow teflon beaker was used as specimen holder for the finely chopped crystal specimens.

The determination of the diffraction angle for a reflexion at a particular temperature was carried out in the following manner. After stabilising the specimen at the correct temperature for half an hour, the diffraction peak was located within ± 5′. The peak was scanned back and forth 4 times and exactly for each ½′ an artificial extra pulse was given to the rate meter. In this way the peak could be located within 0.1′, the standard deviation for the eight measurements generally being 0.07—0.09′. During these manipulations the temperature was recorded five times. The mean temperature is correct within ± 0.4°C.

Owing to serious orientation effects and comparatively low intensities, the best position of the specimen holder for registration of one particular reflexion

Table 2. The cell dimensions and the calculated density of the B-form of stearic acid at temperatures between 0°C and its transition point.

Temp. °C	a Å	b Å	c Å	β	ϱ_{calc} gcm^{-3}
0	5.591	7.368	49.439	117° 15′.2	1.0444
10	5.592	7.381	49.412	117° 18′.8	1.0432
20	5.594	7.400	49.388	117° 21′.9	1.0414
30	5.595	7.420	49.365	117° . 24′.5	1.0391
40	5.595	7.443	49.343	117° 25′.3	1.0365
45	5.595	7.457	49.337	117° 26′.4	1.0349

was found empirically. This, of course, implies that no absolutely correct diffraction angles were obtained, but the changes with temperature were very accurately determined. The curves Θ vs. temperature for every reflexion were therefore put on an absolute scale by comparison with the data from the previous structure investigations [4,6], which were of course, also used for indexing.

The following reflexions were used:

B-form (005), (020), (201) and (2, 1, $\overline{19}$)
C-form (005), (110), (200) and (2, 1, $\overline{20}$)

The cell dimensions and the density were calculated for each 10°C in both cases.

It was not possible to measure (2, 1, $\overline{20}$) at temperatures over 50°C with any accuracy, owing to the lowering of intensity and broadening of the peak. Thus some of the data above this temperature are obtained by extrapolation.

RESULTS AND DISCUSSION

The cell dimensions and densities of the crystalline B- and C-forms of stearic acid at different temperatures are given in Tables 2 and 3. The accuracy is the same as in the earlier papers [4,6], but as regards changes in dimensions and densities, which are given in Figs. 1 and 2, the accuracy is much higher (< 0.001 Å for a- and b-axes, < 0.005 Å for c-axes, < 0.1 for β and < 0.0002 gcm^{-3} for ϱ_{calc}).

As can be seen the changes in the c-dimensions are comparatively very small. As the molecules are very nearly parallel to the c-axis [3-5], this means that the length of the molecule of stearic acid is almost independent of temperature in the interval investigated. Of the other axes, the shortest in both cases are hardly at all influenced by temperature changes, but the medium ones are very sensitive. As the changes in β are very small, these conclusions are directly transferable to the subcell-dimensions, i.e. the shortest subcell

Table 3. The cell dimensions and the calculated density of the C-form of stearic acid at temperatures between 0°C and the melting point.

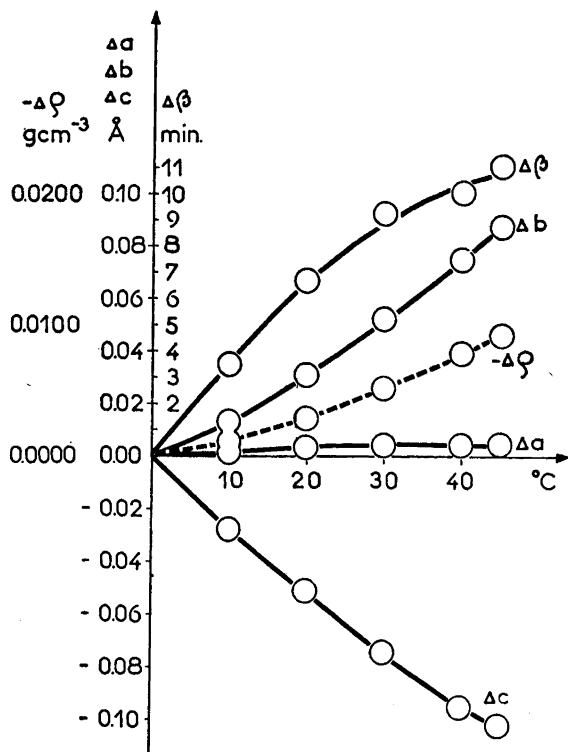| Temp. °C	a Å	b Å	c Å	β		ϱ calc gcm^{-3}
0	9.268	4.961	50.747	128°	7'.4	1.0293
10	9.312	4.960	50.762	128°	13'.8	1.0259
20	9.351	4.958	50.750	128°	16'.3	1.0226
30	9.399	4.955	50.761	128°	17'.1	1.0183
40	9.452	4.950	50.753	128°	16'.2	1.0135
50	9.508	4.942	50.721	128°	12'.1	1.0087
60	9.562 *	4.935	50.69 *	128°	7' *	1.0040
70	9.617 *	4.923	50.66 *	128°	0' *	0.9995

* extrapolated

Fig. 1. The changes of the cell dimensions and the calculated density of the B-form of stearic acid.

dimension ($\sim$ 4.95 Å) is almost unchanged but the largest one ($\sim$ 7.40 Å) If very variable with temperature. This is also observed for n-hydrocarbons [7]. is the packing of the hydrocarbon chains is disturbed in other ways, *e.g.* by branching groups, the effect on the subcell dimensions is the same. In the case of 14-heptacosanol [8] the dimensions are 4.95 and 7.8 Å, respectively, and for *trans*-DL-9,10-methyleneoctadecanoic acid [9] they are 4.98 and 8.12 Å. As that of branching [9] the effect of temperature is certainly a trend to achieve a hexagonal closepacking of cylindrical rods (*e.g.* rotating hydrocarbon chains) which happens when the b_s-axis is increased from 7.40 Å to 8.6 Å.

The decrease in the density of the C-form is larger than for the B-form, which indicates that the C-structure is more flexible than the B-structure. It might have been expected that the density curve of the B-form would intersect the curve of the C-form at the transition temperature (B → C, 46°C) but this is not the case (Tables 2 and 3). This calls for caution in discussing molecular interactions and its connection with density. It is obvious from this investigation that not only chain packing and end group packing [3], but also the arrangement of the carboxylic groups are important factors in this connection.
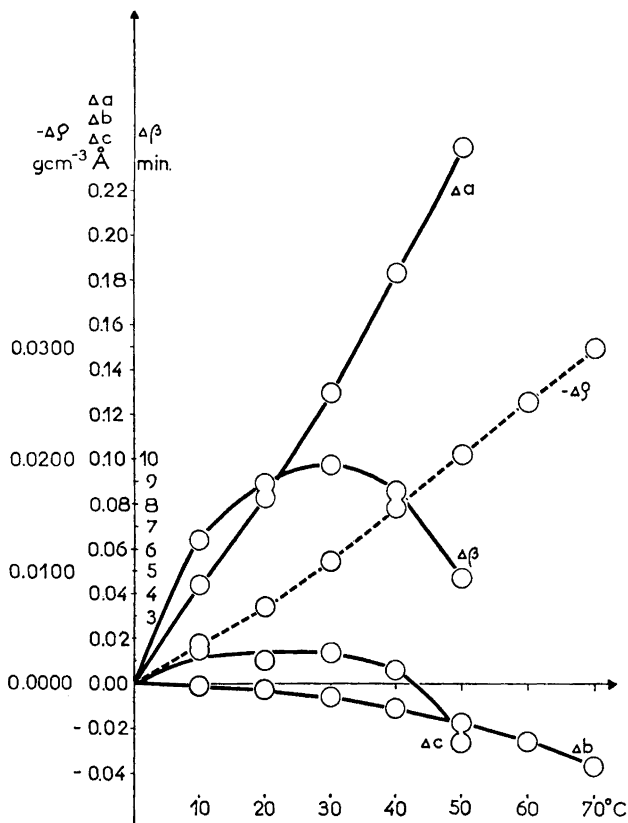
Fig. 2. The changes of the cell dimensions and the calculated density of the C-form of stearic acid.

REFERENCES

1. Stenhagen, E. and von Sydow, E. *Arkiv Kemi* **6** (1953) 309.
2. von Sydow, E. *Acta Chem. Scand.* **9** (1955) 1685.
3. von Sydow, E. *Arkiv Kemi* **9** (1956) 231.
4. von Sydow, E. *Acta Cryst.* **8** (1955) 557.
5. Vand, V., Morley, W. M. and Lomer, T. R. *Acta Cryst.* **4** (1951) 324.
6. Abrahamsson, S. and von Sydow, E. *Acta Cryst.* **7** (1954) 591.
7. Müller, A. *Proc. Roy. Soc. London.* **A 138** (1932) 514.
8. Welsh, H. K. *Acta Cryst.* **9** (1956) 89.
9. Brotherton, T., Craven, B. and Jeffrey, G. A. *Acta Cryst.* **11** (1958) 546.