# Unit Cell Dimensions of Some Long Chain Fatty Acid Polymorphs

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## ABSTRACT

Unit cell dimensions and space group assignments for several polymorphic fatty acids have been determined by using single-crystal X-ray precession photography. This technique is useful to distinguish the closely similar B- and E-forms of stearic acid which have nearly identical crystal long spacings but significantly different unit cell dimensions and monoclinic angles. Other samples studied were the B-form of arachidic and behenic acids and the unsaturated acids, *trans*-9-octadecenoic and *trans*-5-eicosenoic.

## INTRODUCTION

Crystallographic analyses of the normal long chain fatty acids have been reported often over the years. In each instance, the justification for the analysis has been based upon claims that samples have been more highly purified and that new procedures ensured the identity and singularity of the polymorph. The data, however, are still incomplete and in disagreement, especially with regard to the various polymorphic modifications of each acid. von Sydow (1) has investigated polymorph formation of a series of homologous long chain fatty acids with respect to solvent and temperature effects, and conditions were determined for obtaining specific polymorphic forms. However, many polymorphs will undergo phase changes while standing at room temperature or during X-ray analyses, and it is, therefore, necessary to reestablish the authenticity of the specimen just prior to its analysis. In recent publications (2,3), methods that use IR and NMR spectral analyses have been presented for the characterization of long chain fatty acids and their various polymorphic modifications. In the present report, analyses of single crystals of two closely similar polymorphs of stearic acid are reported and compared with that of some closely related saturated and unsaturated fatty acids.

## EXPERIMENTAL PROCEDURES

The fatty acids used were recrystallized materials obtained by fractional distillation of the methyl esters. The mp, obtained by the thermostatic sealed tube method (4), agreed closely with published values. The desired polymorphic modifications were obtained by solvent crystallization at the appropriate concentration and temperature (2,3). Final identification of the specific polymorph was based upon IR spectral analyses just prior to obtaining X-ray photographs.

Suitable crystals were selected from samples viewed under a polarizing microscope. The selected specimen was mounted on the end of a fine wire with household cement. The crystal was aligned in the X-ray beam by use of a microscope and light-reflection equipment. A Phillips Electronics X-ray unit equipped with a copper target and nickel filter was operated at 35 kvp and 15 ma. Line-up photographic shots were taken with a Polaroid cassette mounted on a Charles supper precession camera. Final photographs were taken at room temperature (ca. 23 C) using Kodak no-screen medical X-ray film with appropriate combinations of precession angle, layer-line screen, and screen setting to obtain zero, first, and second level photographs. Lattice angles were measured with a protractor and spacings with a glass rule with a dial indicator. Space groups were determined on the basis of systematic absences.

## RESULTS AND DISCUSSION

The unit cell dimensions are presented in Table I. To compare differences, the interrelationship between the cell constants, the long spacing, and the length of the carbon chain must be considered carefully.

The approximate length of a fatty acid chain can be calibrated using well established molecular parameters: $C_1^{C_2}\cdots C_3$, 2.52 Å; $C_1=C_2$, 1.33 Å; C=O, 1.22 Å; C-OH, 1.29 Å; van der Waal contact C···C, 3.5-4.0 Å; and hydrogen bonding contact O···O, 2.5-2.8 Å.

It is interesting to know whether the fatty acid chain axis is parallel or tilted with respect to the *a-b* or 001 plane and the *c* axis of the unti cell. If the monoclinic angle is equal to 90°, then the long spacing and *c* axis become identical in magnitude and direction.

The angle of tilt of the long chain axis with respect to the a-b plane may be determined from a plot of the number of carbon atoms in the chain vs the long spacings for a homologous series of fatty acids. A linear plot is indicative of a single polymorphic modification, the slope of the line representing the change in long spacing/carbon atom. For the saturated fatty acid dimer, $\Delta$L.S. equals 2.52 Å when

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TABLE I

Unit Cell Characterizations

| Fatty acid | Stearic acid | | Arachidic | Behenic | Elaidic | Eicosenoic |
|---|---|---|---|---|---|---|
| Polymorphic modification | B-Form | E-Form | B-Form | B-Form | Low form | – |
| *a* axis | 5.79 | 5.65 | 5.49 | 5.62 | 5.03 | 5.00 |
| *b* axis | 7.38 | 7.42 | 7.40 | 7.40 | 7.36 | 7.43 |
| *c* axis | 50.14 | 48.51 | 48.55 | 52.93 | 50.55 | 55.67 |
| $\beta$-Angle | 119° | 115° | 90° | 93° | 90° | 91° |
| Volume Å$^3$ | 1872 | 1834 | 1972 | 2034 | 1871 | 2010 |
| Crystal | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | --- | $P_{21}/^a$ | --- | --- | $P_{21}/^m$ | --- |
| Long spacing | 43.85 | 43.95 | 48.55 | 52.86 | 50.55 | 55.67 |

the long chain axis is perpendicular to the a-b plane. The angle of the tilt ($\tau$) is determined by the relationship $\sin \tau = \Delta L.S./252$.

The long chain axis may or may not be parallel to the *c* axis regardless of the angle of tilt (as previously defined), unless the monoclinic angle ($\beta$) is equal to 90°. Because of minor variations in the van der Waal contact distance between terminal methyl groups as well as O···O distance involving hydrogen bonding, an accurate value for the angle between the chain axis and the *c* axis could be obtained only from a complete x-ray diffraction analyses of the representative compounds. However, an approximate value is provided by the well documented results from previous x-ray analyses of fatty acids.

For the B-form of the saturated fatty acids investigated herein, a value of $\Delta L.S.$ equal to 2.19 Å was obtained from the linear relationship between measured long spacing and number of carbon atoms in each hydrocarbon chain. The corresponding angle of tilt ($\tau$) is 60.3°. Both the $C_{20}$ and $C_{22}$ acids exhibited $\beta$-angles (monoclinic angles) of 90 and 93°, with their long spacings equal to their *c* axis lengths. The calculated carbon chains lengths and *c* axis lengths, however, are not equal; and, therefore, the carbon chain axis and *c* axis are not parallel. The differences, 6 and 7 Å, respectively, are too great to be accounted for by variations in interchain contact distances. The calculated length of the $C_{18}$ dimer approximates the length of the *c* axis, indicating that the chain axis and *c* axis are parallel. The $\beta$-angle, however, is not equal to 90°, and the long spacing and *c* axis are not equal in length. It is interesting to note that for the three saturated acids investigated herein, the angles of tilt are equal, yet all three have different monoclinic angles.

The cell parameters for the two polymorphic modifications of stearic acid (B- and E-forms) are markedly different. The E-form has smaller *a* and *c* axes lengths and a smaller $\beta$-angle than the B-form. The calculated angle of 14° between the *c* axis and the chain axis for the E-form is significantly different from that found for the B-form. This indicates a closer chain packing and a larger angle of tilt for the E-form.

The monounsaturated fatty acids (elaidic and 5-eicosenoic) exhibited $\beta$-angles of 90 and 91° with *c* axes equal in length to the long spacings. In addition, the $\Delta L.S.$ for the two acids calculates to be 2.56 Å, which is in close agreement with the value of 2.52 Å indicative of an angle of tilt of near 90°. Also, the calculated chain length of *c* axis length indicates that the *c* axis and the chain axis are parallel.

## REFERENCES

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