Wide-Line NMR Spectra of Some Saturated and Unsaturated Long Chain Fatty Acids[1]

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ABSTRACT

Wide-line NMR spectra were obtained on a series of homologous normal long chain fatty acids: decanoic, lauric, myristic, palmitic, stearic and behenic as well as three isostructural unsaturated acids: elaidic, *trans*-5-eicosenoic and brassidic. Also included are NMR spectra of metastable forms of both the saturated and unsaturated acids. NMR parameters are correlated with carbon chain length, crystal long spacing and density. Polymorphic forms are distinguished on the basis of line width and second moment differences.

INTRODUCTION

The crystal structures of the long chain fatty acids have been investigated extensively during the past 50 years. These investigations have centered around the ability of the long chain carboxylic acids to exist in more than one crystalline state, i.e., their polymorphic behavior. The normal saturated and unsaturated fatty acids exist in two and sometimes three different polymorphic modifications. Because the fatty acid polymorphs are but solid phases of the same chemical composition differing in crystalline form, wide-line proton magnetic resonance would seem particularly well suited to the characterization of these materials. Wide-line proton magnetic resonance has already been applied to the study of crystal structure of high polymers (1).

In a recent investigation, Chapman et al. (2) have reported line width and second moment differences for various polymorphic modifications of fatty acid mono-, di- and triglycerides. Except for the work of Grant and Dunnell (3) on proton magnetic resonance absorption of the C-form of stearic acid, the long chain fatty acids have received little attention.

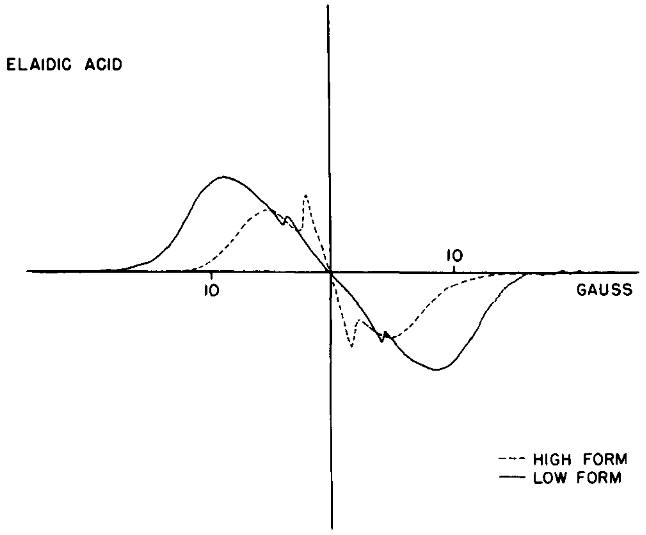

FIG. 1. Wide-line NMR spectra for the high and low melting polymorphic forms of elaidic acid.

EXPERIMENTAL PROCEDURES

The fatty acids used in this investigation were recrystallized materials prepared from fractionally distilled methyl esters. The melting points, determined by the thermostatic sealed tube method (4), are in good agreement with the best literature values. The "stable form," C-form of the saturated acids, was obtained by allowing the acids to crystallize from the melt at room temperature (about 23 C) (5). The B-forms of stearic and behenic acids were obtained by crystallization from benzene at room temperature. Two forms of elaidic acid were obtained using the procedure of Harris et al. (6). Those samples not specifically mentioned were crystallized from acetone at room temperature. Crystal long spacings were determined on each of the acids and their polymorphic modifications from their x-ray diffraction patterns. A General Electric diffractometer, model XRD-5 equipped with a copper target was used. NMR spectra were obtained on a Varian VF 16 F spectrometer at ambient temperatures (ca. 23 C). Pertinent instrumental parameters were: RF frequency, 16 MHz; sweep width, 50 gauss; sweep rate, 5 gauss/min; modulation sweep width, 2.6 gauss. All of the spectral data obtained represent replicate analyses.

RESULTS AND DISCUSSION

Proton magnetic resonance spectra were obtained on a series of homologous saturated fatty acids: decanoic, lauric, myristic, palmitic, stearic and behenic. Spectra were also obtained on the B-forms of stearic and behenic acids. Additionally, proton magnetic resonance spectra were obtained on a number of isostructural unsaturated fatty acids: elaidic, *trans*-5-eicosenoic and brassidic which were crystallized from solvent and from the melt.

Illustrated in Figure 1 are typical wide-line NMR spectra. The spectra are obtained as the first derivative of the absorption curve. Line width is a measure of the separation

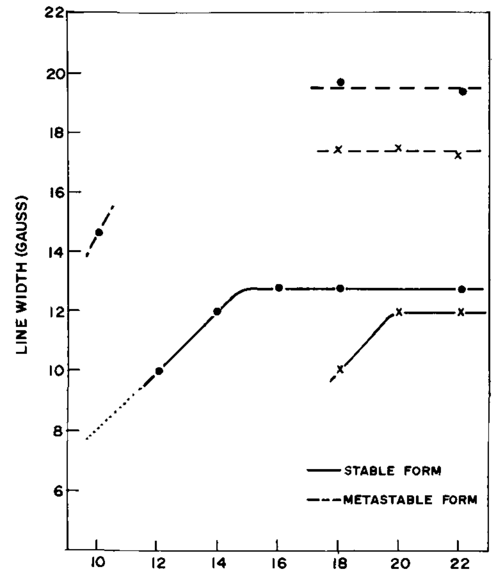

FIG. 2. Line width as a function of the total number of carbon atoms in the molecule. Closed circles represent the saturated acids and the crosses represent the unsaturated acids.

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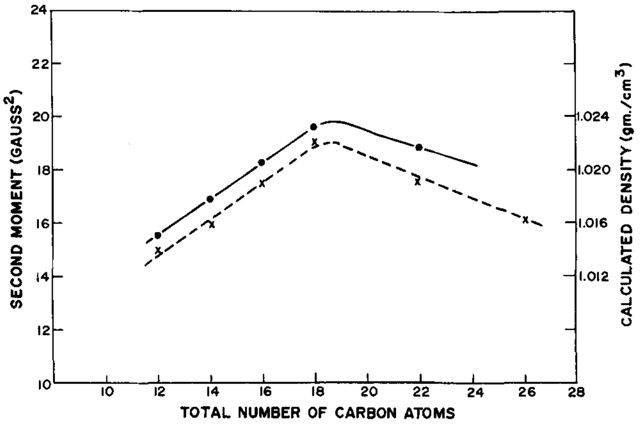

FIG. 3. Second moment of saturated acids as a function of the total number of carbon atoms in the molecule represented by closed circles. Density as a function of total number of carbon atoms in the molecule represented by crosses.

between the maximum and minimum points of the first derivative curve in gauss. Second moment is calculated directly from the normalized first derivative curve in gauss^2. The measured line widths and second moment values are considered accurate to ± 0.2 gauss and ±0.5 gauss^2, respectively.

Line Width

Figure 2 illustrates line width variation with carbon chain length of both the satable and metastable polymorphs of the saturated and unsaturated acids. The line width of the unsaturated acid (crosses) is significantly smaller than that of its saturated counterpart (closed circles) with limiting values of each of 12.0 and 12.8 gauss, respectively. This difference can only be attributed to increased proton mobility as a result of the ethylenic group in the chain. The rather sharp decrease in line width with decreasing chain length in each series is ascribed to the onset of motional processes which allow greater mobility of the protons along the carbon chain. The terminal methyl protons being free to rotate about their triad axes do not contribute significantly to the line width of the acids (3). As illustrated in Figure 1 the B-form of the saturated acids, stearic and behenic, have significantly larger line width values, suggesting hindered reorientational motion about their chain axes. Similarly, the "metastable forms" of the unsaturated acids have increased line width values. It should be mentioned that, of the three unsaturated acids investigated, only elaidic acid is reported to exist in two polymorphic forms, as characterized by both x-ray diffraction pattern and melting point. The other two acids, eicosenoic and brassidic, differ only in their method of preparation, crystallization from solvent and from the melt. The line width values indicate crystalline structures similar to those of the two forms of elaidic acid and are herein referred to as metastable (solvent) and stable (melt) forms. While the line widths of the metastable forms of both the saturated and unsaturated acids are larger than the corresponding stable forms, the relative line widths would indicate that the same factors which result in differences between the stable forms are also factors in the line widths of the metastable forms. It would seem that the CH-groups in the unsaturated acids are less hindered than the CH_2-groups and thus make a smaller contribution to the overall line width of the acid. It would be pointed out that the line width values of the decanoic acid sample is larger than would have been expected by extrapolation of the curve (dotted segment) for the saturated acid stable forms. The magnitude of the difference would further suggest that it is the metastable form which is obtained by crystallization from the melt. Although the crystal long spacing is identical with the single value reported by Slagle and Ott (7), these results would indicate that it is not the long spacing of the C-form but probably that of the B-form.

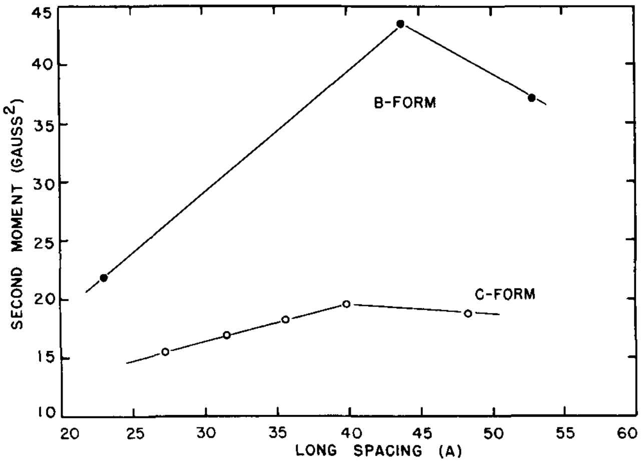

FIG. 4. Second moment variation of saturated acids with crystal long spacing. Closed circles represent metastable polymorphic modification. Open circles represent stable polymorphic modification.

Second Moment

Second moment is a measure of the chain lattice rigidity and interproton distances and would seem to provide the most useful information. If the protons are free to rotate, the second moment will be small. If the interproton distances are small and the chain lattice rigid, the second moment will be large. The second moment values for the saturated acids are presented in Figure 3 as they vary with the total number of carbon atoms in the molecule. Since the physical properties which affect the value of the second moment are also properties which influence density, a comparative plot of density versus total carbon number is included. The density values were calculated from the unit cell dimension using the data of Abrahamsson and von Sydow (8). As the carbon chain length increases, the second moment increases linearly from a low of 15.6 gauss^2 for lauric acid to a maximum of 19.6 gauss^2 for stearic decreasing to 18.8 gauss^2 for behenic acid. This same maximum in the density curve was attributed by von Sydow as being a result of the monotone increase in the low density CH_2-groups opposed by parallelization of the carbon chain resulting in closer packing of the molecules due to greater van der Waals interaction. The second moment values of the B-forms of decanoic, 21.8; stearic, 43.3; and behenic, 35.8 gauss^2, indicate that the metastable B-form is more dense than the stable C-form of the acid.

Fatty acids crystallize in double layers as dimers oriented with their carboxyl groups in juxtaposition. The distance between the terminal methyl groups of the dimer is the crystal long spacing. Polymorphism in long chain fatty acids is caused by the different possible angles of tilt of the parallel carbon chains to the terminal planes formed by the methyl groups. Therefore for each crystal form of the acid there is a linear function of the total number of carbon atoms in the chain. The relationship between crystal long spacing and second moment for the saturated acids is illustrated in Figure 4. The second moment maximum is still evident in the plot for the stable form. The second moment values for the metastable B-forms would appear also to go through a maximum. The shapes of the two curves would indicate that there is little variation in interproton distance whereas the magnitude of the values would suggest the metastable form is a more highly orientated structure.

Of the unsaturated acids investigated, the two forms of elaidic acid exhibited the largest differences, in second moment: 15.5 (stable) and 31.8 gauss^2 (metastable). The second moment differences between the two forms of eicosenoic and brassidic acids were less pronounced, 28.6 and 34.4 gauss^2 and 27.6 and 35.2 gauss^2, for the stable and metastable forms respectively.

ACKNOWLEDGMENT

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