A PROTON MAGNETIC RESONANCE INVESTIGATION OF
MOLECULAR MOTION IN OLEIC ACID AND ELAIDIC ACID

by

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ABSTRACT

A study of the n.m.r. absorption of oleic acid has been carried out between 77°K. and 287°K. A sharp increase in line width and second moment is observed below 100°K. indicative of an increase in the intramolecular interactions. A narrow line, indicative of liquid-like motion, is observed at temperatures above 208°K. The second moment and line width decrease rapidly as the melting point is approached, dropping to liquid-like values at 287°K.

The experimental data are compared with the theoretical data obtained from the known crystal structure. From this comparison, a crystal transition is proposed to take place below 100°K., and heteronuclear premelting is proposed to take place above 208°K.

It is likely that end methyl group rotation takes place at all temperatures but there is no extensive torsional oscillation or vibration below 260°K. and there is little apparent change in the cell dimensions between 260°K. and 100°K.

Elaidic acid has been studied between 77°K. and 315°K. The line width and second moment increase slightly below 170°K. and a narrow component is observed above 225°K.
The line width and second moment fall sharply only at
the melting point, decreasing to a liquid-like line.

As no crystal structure is available for elaidic
acid, the experimental data are compared with experimental
and theoretical data for oleic acid and stearic acid.
Some form of molecular vibration or hindered rotation is
proposed to account for the transition at 170°K., and
heteronuclear premelting is proposed to take place above
225°K. The difference in the behaviour of oleic acid
and elaidic acid near the melting point is explained in
terms of the molecular shape.
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Chapter 1</td>
<td>THEORY</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Theoretical Second Moment</td>
<td>3</td>
</tr>
<tr>
<td>Chapter 2</td>
<td>APPARATUS</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Broad-line NMR Spectrometer</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Principle of Operation</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Construction and Assembly</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>Variable Temperature Apparatus</td>
<td>17</td>
</tr>
<tr>
<td>Chapter 3</td>
<td>METHOD</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>Preparation of Samples</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>Calibration of Spectrometer</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>Running of Spectra</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>Analysis of Spectra</td>
<td>24</td>
</tr>
<tr>
<td>Chapter 4</td>
<td>OLEIC ACID</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>Description of Spectra</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>Pure Oleic Acid</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>Impure Oleic Acid</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>Recrystallized Oleic Acid</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>Theoretical Second Moment</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>Discussion</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>Proton Parameters</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>Crystal Structure</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>Crystal Transition</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>Molecular Motion</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>Summary</td>
<td>43</td>
</tr>
<tr>
<td>Chapter 5</td>
<td>ELAIDIC ACID</td>
<td>Page Number</td>
</tr>
<tr>
<td>-----------</td>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td></td>
<td>Description of Spectra</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Crystal Structure</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>Theoretical Second Moment</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>Discussion</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>Molecular Motion</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>BIBLIOGRAPHY</td>
<td>50</td>
</tr>
<tr>
<td>APPENDIX I</td>
<td>Extrapolation of Inter-molecular Second Moments</td>
<td>54</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

To Follow Page

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1</td>
<td>Block Diagram of 30mcs Broad-line Spectrometer</td>
<td>17</td>
</tr>
<tr>
<td>Figure 2</td>
<td>Nuclear Magnetic Resonance Variable Temperature Dewar</td>
<td>19</td>
</tr>
<tr>
<td>Figure 3</td>
<td>Line Width Versus Temperature Plot for Oleic Acid</td>
<td>28</td>
</tr>
<tr>
<td>Figure 4</td>
<td>Second Moment Versus Temperature Plot for Oleic Acid</td>
<td>28</td>
</tr>
<tr>
<td>Figure 5</td>
<td>Line Width Versus Temperature Plot for Elaidic Acid</td>
<td>46</td>
</tr>
<tr>
<td>Figure 6</td>
<td>Second Moment Versus Temperature Plot for Elaidic Acid</td>
<td>46</td>
</tr>
</tbody>
</table>
INTRODUCTION

Pioneer work on the use of nuclear magnetic resonance to observe molecular motion was done by Alpert (1,2). Later Gutowsky and Pake (3) made a more quantitative treatment of the field, basing their work on the work of Van Vleck (4). Several papers have been published which treat various aspects of molecular motion from a theoretical standpoint (5,6,7,8,9).

If the crystal structure of the sample being studied is known, it is possible to calculate a spectral parameter, the second moment (4), and this may then be compared with the second moment found experimentally. Using the formulae for theoretical changes in the second moment due to specific types of motion (6,7,9), some estimate of molecular motion may be attempted.

The study of molecular motion in fatty acids and their salts has been the object of several investigations in this laboratory (10,11,12,13,14). In these studies it was possible to see not only the onset of simple types of motion in the sample, but also extensive motion, (pre-melting), and crystal phase transitions. Most salts of fatty acids exhibit a large number of phase transitions below their melting point (15,16,17), however, most of these do not represent a significant change in the crystal
structure or in the molecular motion and are therefore not distinguishable by nuclear magnetic resonance.

As a departure from the studies of fatty acids mentioned above, which were all normal straight-chain acids, this present work deals with the cis and trans isomers of \( \Delta^{9,10} \) octadecenoic acid, (oleic and elaidic acid, resp.), in which molecular motion would be expected to be somewhat more complex due to the steric effects of a bent chain. The crystal structure is available for oleic acid and it is therefore possible to compare theoretical and experimental parameters. For elaidic acid, no crystal data are available and one must settle for a comparison with the spectra obtained for oleic acid and for normal paraffin acids.

Three samples of oleic acid were studied, one pure, one impure, and one recrystallized from acetone. The first two were studied between 77°K. and 287°K. and the latter between 77°K. and 250°K. The elaidic acid studied was pure and was observed between 77°K. and 315°K.
Chapter I

THEORY

There are available many excellent books and reviews on the theory of nuclear magnetic resonance (18,19,20,21, 22,23,24). It is felt that it is sufficient to refer to these books and reviews and refrain from reproducing here a condensed version of general n.m.r. theory. The book by Andrew (18) also contains an excellent bibliography of the early literature on the subject. For the sake of completeness, however, the equations regarding theoretical second moments and molecular motion will be discussed briefly in the following paragraphs since they will be referred to extensively in the discussion of results.

Theoretical Second Moment

In a rigid solid, the magnetic nuclei will react with each other as well as with an applied field, and the magnitude of this interaction is determined by the inter-nuclear distances and by the orientation of the inter-nuclear vectors with respect to the applied magnetic field. The result of these interactions is to broaden the spectral line due to the nuclear resonance absorption of energy. The extent of this broadening may be expressed as the line width $\Delta H$, which is defined as the distance in gauss
between the line envelope at the points of maximum slope, or as the second moment $\Delta H_2^2$, which is expressed by the Van Vleck formula (4):

$$\Delta H_2^2 = \frac{3I(I+1)}{5N} g^2 \beta^2 \sum_{i>k} r_{ik}^{-6}$$

$$+ \frac{4\beta^2}{15N} \sum_{i \neq f} g_f^2 r_{if}^{-6}$$

where $\Delta H_2^2$ is the rigid lattice second moment for a powdered sample, $r_{ik}$ is the distance between the $j$th and $k$th nuclei which have a spin $I$ and a nuclear g-factor $g$. $r_{if}$ is the distance between nucleus $j$, of the species under investigation, and nucleus $k$, of spin $I_f$ and nuclear g-factor $g_f$, and $N$ is the total number of nuclei at resonance in the unit cell considered.

If the molecule undergoes some form of motion, the internuclear distances and the internuclear vectors with respect to the magnetic field must be time averaged and if the motion has a frequency of the order of the line width, the line width and second moment will decrease. For simple types of motion calculations have been made of this decrease in second moment (3,9). For a powdered sample containing nuclei rotating about a single axis,
\[ \Delta H^2_{2,\text{rot}} = F(\gamma_k) \frac{3(I+1)}{5N} g^2 \beta^2 \sum_{j>k} r_{jk}^{-6} \]

\[ + F(\gamma_{if}) \frac{4\beta^2}{15N} \sum_{i,f} I_f(I_f+1)g^2 r_{if}^{-6} \]

where \( F(\gamma_k) = \frac{1}{4} (3\cos^2\gamma_k - 1) \) and \( \gamma_k \) is the angle between the axis of rotation of \( r_{jk} \) and \( r_{ik} \) itself (3).

It was suggested by Anderson (24) and shown theoretically and experimentally by Andrew et al. (25,26,27,28) that the second moment should remain invariant, as the motion should result in sidebands to the central peak. In practice, however, the motion is of such widely varied frequency that the sidebands are diffuse and unobservably weak.

We might note that vibrations will also affect the second moment and line width of the spectrum (29,30,31,32) and this point will be dealt with at greater length in the discussion.

If, at some temperature, the sample being observed undergoes a change in crystal structure which causes a significant change in \( \sum_{j>k} r_{jk}^{-6} \), we would expect to observe this in the plot of \( \Delta H^2_2 \) versus temperature.
Similarly, if all or some molecules in the sample start to rotate freely or in a hindered manner, we would again expect the resultant decrease in second moment to show up in the experimental curves.
APPARATUS

The experimental observations on the samples in this work were performed on two spectrometers operating at several frequencies. The early work on oleic acid was done on a Varian 4200/4300 dual purpose spectrometer at 40mcs. Later a 60/56.4mcs unit was obtained and the bulk of the work on oleic acid was done at these frequencies. Finally, a broad-line spectrometer operating at 30mcs was constructed and the work on elaidic acid and re-crystallized oleic acid was carried out on this spectrometer. As the assembly and adjustment of the latter spectrometer occupied a considerable portion of the time spent on this work, the details of construction and operation will be covered in some depth.

Broad-line NMR Spectrometer.

Principle of Operation

To carry out a nuclear magnetic resonance experiment one needs basically a steady magnetic field $H_0$, and

The author presupposes that the reader is familiar both with basic nuclear magnetic resonance theory and with simple electromagnetics and electronics (18,33).
an oscillating magnetic field $H_i$. If the $H_i$ field is oscillating at right angles to $H_o$, nuclei precessing about $H_o$ will feel a torque due to $H_i$ and, if the frequency of precession is equal in magnitude to the frequency of $H_i$, energy will be absorbed into the nuclear system. With a simple set-up like the above the observer is unaware that any absorption is taking place, there being in general no visible change in the physical properties of the sample due to absorption.

To understand how one is able to 'observe' the nuclear magnetic resonance absorption of energy, we must investigate the macroscopic effects on the sample due to the fields $H_o$ and $H_i$, and investigate the changes in these effects due to resonance absorption.

If one passes an oscillating current through a coil, two linearly oscillating magnetic fields will be generated parallel to the axis of the coil. These fields will oscillate in opposite directions and will be $90^\circ$ out of phase. The net field will be given by:

$$ H = 2H_i \cos \omega t $$

where $H_i$ is the magnitude of the component fields and $\omega$ is the angular frequency of oscillation. These fields will in turn induce in the sample two oscillating fields
whose strength will be proportional to the susceptibility of the sample. These two fields are given by:

\[ m' = 2H_i \chi' \cos \omega t \]
\[ m'' = 2H_i \chi'' \cos \omega t \]

where \( \chi' \) and \( \chi'' \) are the real and imaginary components respectively of the susceptibility and can be related to the nuclear system. The absorption and dispersion of energy are the mean values of \( H \frac{dm'}{dt} \) and \( H \frac{dm''}{dt} \) respectively (18). We see then that as the nuclear system changes due to resonance absorption of energy and due to nuclear interactions, the fields \( m' \) and \( m'' \) will vary. It remains to measure these macroscopic effects.

The fields \( m' \) and \( m'' \) are oscillating at a frequency \( \omega \) and if we encircle them with a coil they will induce a voltage in it which is proportional to their strength and hence proportional to the strength of absorption and dispersion. We need only amplify this voltage to obtain the desired nuclear magnetic resonance signal.

If the receiver coil is mounted orthogonal to the transmitter coil, the only voltage induced in it will be that due to \( m' \) and \( m'' \). This voltage, however, will be the vector sum of the voltages due to these magnetic
fields and as we want only the voltage due to $m''$, we must enhance it. This is accomplished by introducing 'leakage', i.e., by introducing a voltage in phase with that due to $m''$. The resultant total voltage will now be primarily proportional to the absorption signal.

![Diagram](attachment:image.png)

The above description is the basis of the Bloch system of nuclear magnetic induction. The spectrometers used in this work were based upon this system.

The actual broad-line n.m.r. experiment is somewhat more involved than is indicated in the foregoing description. Basically, we want to vary $H_0$ while holding $\omega$ constant and detect the change in voltage in the receiver coil. However, after detection the signal we have will be DC and if $X''$ is small as is the case with most samples, the DC signal will likewise be small. In order to amplify this signal it is desirable that it be an AC signal and we achieve this by sweeping the steady field $H_0$ through a small portion of the signal line-width. This sweeping is
usually done at audio frequencies and is accomplished by using a pair of helmholtz coils mounted with their axes parallel to the $H_0$ field. In this way the signal after detection in the receiver is an amplitude modulated audio signal which may be further amplified and detected with an audio detector or in our case with a phase-sensitive or 'lock-in' amplifier. The trace of this final signal as a function of $H_0$ will be the derivative of the trace of $\chi'$ or $\chi''$ as a function of $H_0$.

To accomplish the above tasks, we need a magnet capable of being scanned over a wide field range (10-50 gauss), an audio oscillator and amplifier to drive the sweep coils and to drive the phase sensitive detector, a transmitter-receiver, an output audio amplifier and phase sensitive detector, a recording voltmeter, an oscilloscope, and stabilized power supplies for the above. The transmitter, receiver and modulation coils are usually mounted in a probe constructed to hold them rigid and mutually orthogonal. The probe will also contain electrical or mechanical devices to 'balance' the probe, i.e., to deflect the magnetic flux lines in such a manner as to achieve better orthogonality than would be possible from mechanical movement of the coils. Leakage is then introduced with these same devices.
Construction and Assembly (34)

Probe

Varian V-4331 wide-line probe. This probe, unlike the V-4331 used in the dual purpose spectrometer, had a permanent receiver coil mounted inside a 20mm glass tube extending the entire length of the probe. 'Paddles' made of brass discs and graphite rings were used to balance the probe.

Transmitter

Varian V-4310C 30 mcs. The transmitter used a 10mcs crystal to drive a two-stage oscillator, the first stage being at 10mcs and the second being at 30 mcs. The oscillator was used to drive a radio-frequency amplifier and the output of this amplifier was transformer coupled to a tuned plate circuit. Attenuation was achieved at the amplifier by varying the bias on the screen grid, and at the output by means of resistors.

The transmitter was modified from the manufactured specifications in two ways;

1. The output was increased by removing the resistor used to feed the output attenuator.
2. The modulation input, used in calibrations, was revised to remove undesirable parasitic oscillations
and to improve the modulated wave form. The modulation voltage was originally fed across the grid-bias resistor of the first oscillator stage. This has the effect at high modulation levels of disturbing the oscillator balance by lowering the grid voltage below that necessary to maintain oscillation. This set-up also provided a feed-back loop which allowed the oscillator to modulate itself at the feed-back frequency. To remove these undesirable effects, the modulation voltage was fed across the control grid biasing resistor of the rf amplifier. In this way, nearly 100% amplitude modulation was achieved with no distortion of wave form. Possibly due to the Miller effect (33), this method of modulation input also produced frequency modulation which was desirable for calibration purposes.

Receiver

The receiver, incorporated in the same unit as the transmitter, employed an untuned preamplifier and three tuned radio-frequency amplifiers, all capacitor coupled. A tuned plate, tuned grid oscillator supplied the 25mcs heterodyne frequency to the mixer, the output of which was transformer coupled to the IF amplifier. Further transformer coupling to a diode provided detection and the resultant audio signal was coupled to the output with a
cathode follower, using a tuned grid for a frequency response control. Receiver gain was controlled by varying the cathode bias on the second and third rf amplifiers.

Output Control Unit

Varian V-4270B. The audio signal from the receiver was fed via an attenuator to a bridged-T tuned amplifier. The low gain of the amplifier except at the tuned frequency resulted in an improved signal-to-noise ratio. The output of this amplifier was capacitor coupled to the primary of an audio transformer. The secondary of the transformer was coupled, through a driven DPDT switch and an RC filter, to the grid of a differential amplifier. The differential amplifier output was fed to a DC millivolt recorder.

The DPDT switch was driven at the sweep modulation frequency in such a manner as to keep the voltage at the grid of the differential amplifier of constant sign, ie:

![Diagram of DPDT switch](before DPDT after)

The mean voltage at the output was then proportional to the amplitude of the input signal. Response was varied by means of RC circuits on the grids of the differential amplifier.
Sweep Unit and Sweep Amplifier

Varian V-4250B and V-4240 respectively. The sweep unit consisted of an audio oscillator followed by a capacitor coupled audio amplifier and a cathode follower. The output was fed via an attenuator to the grid of a second amplifier and a cathode follower. The final output was fed to the sweep amplifier. Voltage for the syncroverter amplifier was taken from the first cathode follower while voltage for the x-axis drive of the oscilloscope was taken from across a section of the attenuator and was fed to a cathode follower.

The sweep amplifier was a one stage push-pull amplifier transformer coupled to the output, which was fed via an attenuator to the sweep coils.

The syncroverter amplifier consisted of a two stage triode amplifier followed by a cathode follower which fed a push-pull amplifier transformer coupled to the output. Syncroverter phasing was achieved by bridging the plate and cathode of the second triode amplifier with a capacitor and a variable resistor. The phase of the voltage at the output was related to the total reactance of the RC bridge.
Electromagnet and Power Supply

The magnet was a Varian V-4007 six-inch water cooled electromagnet with a one and one-half inch gap.

The magnet power supply was a V-2200A. It consisted of a full-wave rectifier feeding voltage to the plates of four triodes in parallel, (gate tubes). The output voltage at the cathodes was controlled by adjusting the grid voltage. A high-gain DC chopper-amplifier was coupled across a set of reference resistors which were in series with the gate tubes and the magnet coils. Any change in the voltage drop across the resistors was amplified and an appropriate voltage was applied to the grids of the gate tubes to adjust the voltage drop to the desired value. By varying the size of the resistors, more or less bias was applied to the grids and a variation in magnet current resulted.

The chopper-amplifier referenced itself with a set of standard cells, and if their voltage was changed, the current to the magnet was changed. Hence, we could scan through a region of field strength by applying a small voltage to the reference batteries.

Precession Field Scanning Unit

Varian V-4280. This unit consisted of a standard 1.34 volt cell, a set of resistors and a motor driven
helipot. The helipot was wired in parallel with a voltage divider in such a way that at its mid point the output voltage was zero and went positive and negative in each direction from the middle. In this way we were able to scan the field, at various rates, up to thirty gauss on either side of $H_0$.

**Power Supply Units**

Varian V-426OB and V-4360C. These units supplied the highly filtered B+ to the above units. They also supplied the 12.6 volt DC filaments in the transmitter-receiver and the 6.3 volt AC filaments in the other units. The B+ was obtained from a full-wave tube rectifier and the output was stabilized with a glow discharge tube. The DC filament supply came from a diode bridge rectifier and was filtered, but only stabilized to the extent that the input was stabilized with a sola transformer.

The above units were mounted in a pair of relay racks which were enclosed in a wooden cabinet. A block diagram of the spectrometer appears in Figure 1.

**Variable Temperature Apparatus**

The variable temperature apparatus used in this work had to hold a sample for periods of from one to eight hours at a constant temperature between 77°K. and 315°K.
FIGURE 1  BLOCK DIAGRAM OF 30 mc. BROAD LINE SPECTROMETER
The apparatus had to contain the sample tube and had to fit inside the receiver coil of the spectrometer. For liquid nitrogen temperature runs, we needed only a simple dewar with an enlarged top to contain sufficient liquid nitrogen so that refilling was necessary only once per spectrum, (approx. 1 hour).

For temperatures between 77°K and room temperature, the usual cryoscopic baths were not adequate as very few of them use non-hydrocarbon solvents. Cooled or heated gas was thus used and the apparatus had to carry the gas past the sample and exhaust it to the room outside the magnet gap. Provision had to be made also for thermocouples to monitor the temperature of the sample. The original apparatus (35) was designed to fit into the probe of the V-4200/4300 spectrometer. This arrangement of dewars had the disadvantage of requiring three pieces of glass around the sample tube, two for the dewar and one for the lead. It was possible to use only one thermocouple, in the exhaust stream well removed from the sample, thus making temperature measurements uncertain. The second arrangement (35), still requiring three pieces of glass inside the receiver coils, does allow for two thermocouples, one in the inlet and one in the exhaust streams. An added advantage is the simplicity of the leads, which in some cases were not dewared, styrofoam and asbestos lagging
being sufficient.

In the broad-line spectrometer the probe was open at the top and bottom and had an enlarged receiver coil, allowing the use of the improved dewar shown in Figure 2, which did not require the glass lead. This improved the filling factor of the receiver, a greater volume of sample being inside the receiver coil. With this arrangement we again have thermocouples in the inlet and exhaust streams, simple inlet and exhaust leads and the added advantage of being able to change samples without having to warm the apparatus in order to open it.

The gas used to cool the samples was, in the earlier work, obtained by boiling liquid nitrogen from a large dewar and passing the gas through the dewars and over the sample. Boiling the nitrogen at a more rapid rate resulted in a cooler temperature. The disadvantage of this method was that heat had to be supplied to boil the nitrogen, partially defeating the purpose of the method. Also, large quantities of liquid nitrogen were consumed during an experiment and recharging the tank required that the apparatus be partially disassembled. An improved method, allowing cooler temperatures to be reached, was to pass tank nitrogen through copper coils immersed in liquid nitrogen. By increasing the flow, lower temperatures were
FIGURE 2  VARIABLE TEMPERATURE DEWAR
obtained. The big disadvantage here was that for relatively warm temperatures a very slow flow rate was used, resulting in a large thermal gradient over the sample, (hence the need for two thermocouples). For temperatures above about 200⁰K. a dry-ice acetone bath was used to cool the coils, thus allowing a more rapid flow.

The samples were heated by passing dry air through a manifold and over a heating element inside a brass cyclinder. The temperature was varied by means of a variac, the flow being kept high to reduce thermal gradients.
Chapter 3

METHOD

Preparation of Samples

The sample of pure oleic acid was prepared from 99\% pure oleic acid obtained from the Hormel Institute. The liquid acid was poured into a previously cleaned and dried tube which had been thinned out at the bottom to increase the volume of sample in the receiver coil. The sample tube was heated under vacuum at 383°K. for 24 hours and then sealed. The impure acid was Fischer "purified grade" oleic acid and was prepared as above. The re-crystallized acid was Fischer "purified grade" oleic acid and was crystallized from acetone at 262°K., pulverized, dried under vacuum at 262°K. and then sealed in a sample tube.

The sample of elaidic acid was prepared from Hormel 99 +\% pure elaidic acid. The acid was melted and poured into a sample tube which was then evacuated and the sample warmed to remove trapped gases and moisture. The tube was sealed under vacuum.

Calibration of the Spectrometer

As we were interested in the shape of the nuclear
magnetic resonance absorption curve as a function of $H_0$, it was necessary to calibrate the field scan of the magnet as a function of distance along the axis of the recorder chart. This was done by frequency modulating the transmitter and recording the spectrum of a water sample. The transmitter output current was composed of the following frequencies:

$$\nu \pm n \nu_m \quad n = 1 \rightarrow \infty$$

where $\nu_o$ is the principal frequency, $\nu_m$ is the modulation frequency and $n$ is any integer. As $H_0$ is varied, the nuclei will absorb energy at each of the above frequencies. The resultant spectrum will be a series of lines on the recorder all equally spaced and of separation $2 \pi \nu_m$. Using the gyromagnetic ratio for the proton, the recorder chart could be calibrated in gauss per centimeter.

As the modulation field used in the spectrometer caused a broadening of the resonance line (36), it was necessary to calibrate this field in order to apply a correction. This was done by scanning through the signal from a sample of water, (a theoretically very narrow line), and measuring the line width. This width was taken to be $H_m$, the sweep amplitude in gauss.
As a normalization term was applied when analysing the spectra, it was not necessary to calibrate the transmitter power, the receiver gain or the output amplifier gain.

Running of Spectra

To obtain spectra, it was first necessary to locate the resonance position $H_0$ for the frequency used. This was done by placing a water sample in the receiver coil and scanning the magnetic field by means of the reference resistors in the Magnet Power Supply until a signal was obtained. As the samples used produced spectra which were symmetrical about $H_0$, 'resonance' was found with the helipot of the Precession Field Scanning Unit at the mid point. In this way, the entire spectrum could be covered by the range of the helipot. After resonance was found, the sample being studied was placed in the dewar and the apparatus brought to the desired temperature. The magnet was moved well off resonance and the probe was balanced and leakage was introduced. The radio-frequency power and the modulation amplitude were adjusted to the maximum value possible without causing signal distortion. The receiver gain and the output amplifier gain were adjusted to give a near full scale deflection on the recorder at the maximum signal position. The time constant of the
output unit was set to give the least 'hash' without causing signal distortion and the spectrum was run. The spectrometer was generally stable enough so that no adjustments were necessary during the running of a spectrum, (about 1 hour), and it was usually not necessary to adjust the magnet to relocate \( H_0 \) during a series of runs, (up to 24 hours).

The temperature was monitored throughout a series of runs with thermocouples connected to a Speedomax recorder. Several times during each spectrum the voltage of each thermocouple was read with a Rubicon potentiometer and recorded.

**Analysis of Spectra**

The line width, \( \Delta H \), is defined as the width of the resonance absorption curve at maximum slope. This corresponds to the positive and negative peaks of the derivative curve. This distance was measured for each spectrum and recorded in units of gauss.

The second moment, \( \Delta H^2 \), of the resonance absorption line as taken from the derivative curve is given by (37):

\[
\Delta H^2 = \frac{1}{3} \frac{\int_0^\infty f(H) (H-H_0)^3 dH}{\int_0^\infty f(H) (H-H_0) dH}
\]

\[3.1\]
where $f'(H)$ is the intensity of the derivative curve in arbitrary units. The spectra were integrated numerically according to the following formula:

$$
\Delta H_2^2 = \frac{\text{SCALE}^2}{3} \frac{\sum n^3 y_n}{\sum n y_n} \quad 3.2
$$

where $y_n$ is the value of $f'(H)$, $n$ is units along the axis from the centre of the line and scale is the width of a unit in gauss.

The small broadening due to $H_m$ was corrected for using the formula (36):

$$
\Delta H_2^{\text{TRUE}} = \Delta H_2^{\text{OBS}} - \frac{1}{4} \Delta H_m^2 \quad 3.3
$$

As SPS computer program was written by Mr. W. R. Janzen to calculate the second moment using Formulae 3.2 and 3.3, and was used throughout this work.
Chapter 4

OLEIC ACID

Description of Spectra

Pure Oleic Acid

The spectra of pure oleic acid may be divided into four groups covering four temperature ranges: 77°K.-100°K.; 100°K.-207°K.; 207°K.-260°K.; 260°K.-289°K.

77°K.-100°K.

The spectra at 77°K. showed a broad line with a broad flat top. There was a slight peak in the middle of the broad top at 77°K. Although the spectrum at 91°K. was much narrower than at 77°K., there was still evidence of a broad top. At 98°K., however, the spectrum had narrowed considerably and the broad top had disappeared completely. The spectra throughout this region had broad tails.

100°K.-207°K.

At the low end of this region the spectra were, like those below 100°K., broad and with long tails. The tops were not quite as broad and showed evidence of a slight shoulder, i.e., the spectra came to a peak in two steps, similar to a broad line superimposed upon a broader one.

As the temperature was raised the shoulder became less and less distinct until the spectra became quite smooth and rounded on top. Throughout this region the spectra changed little in width or in second moment.

207°K.-260°K.

In this region a very narrow line appeared. The intensity of this line with respect to the broad line increased with increasing temperature. The width and second moment of the broad component did not change appreciably in this region although its intensity fell quite sharply as the narrow component became more intense. At the first sign of the narrow component, the broad line had a sharp smooth peak but as the narrow component became more intense the broad line became lower and flatter in the middle.

260°K.-289°K.

In this region the narrow line became rapidly more intense and the broad line became narrower. The second moment decreased rapidly.

Impure Oleic Acid

The spectra of impure oleic acid were quite similar to those of the pure acid. The narrow line appeared at
approximately the same temperature as in the pure acid but its intensity rose more rapidly. The line widths and second moments at temperatures above $150^\circ K$. were lower than those for the pure acid, with the second moments decreasing rapidly at temperatures above $200^\circ K$. The shoulder on the spectra noticeable at low temperatures remained in evidence almost to the melting point, giving the spectra the appearance of three superimposed lines.

**Recrystallized Oleic Acid**

This sample produced spectra which were similar in appearance to those of the previous two samples. The line widths and second moments at temperatures above $150^\circ K$. were lower than those of the pure acid but did not show the rapid decrease at higher temperatures which was seen in the impure sample. The narrow component appeared at about $210^\circ K$. as was the case in the previous samples and it had the same intensity with respect to the broad component as did the impure sample above.

Plots of line width and second moment as a function of temperature for the three samples appear in Figures 3 and 4. These plots show the rapid decrease in line width and second moment between $77^\circ K.$ and $100^\circ K.$ and the long plateau between $100^\circ K.$ and $260^\circ K.$ for the pure acid.
OLEIC ACID $\text{HC}_{18}^{\text{(cis)}}$

![Graph showing line width versus temperature for pure, impure, and recrystallized OLEIC ACID.](image)

**Figure 3**

**Temperature (degrees K)**

**Line Width (gauss)**

- **PURE**
- **IMPURE**
- **RECRYST.**

To follow page 28
Crystal Structure

Oleic acid exists in two phases, one melting at 13.3°C. and the other melting at 16.2°C. (38). Although these two phases had been reported as long ago as 1912 by Kirschner (39), Lutton (38) was the first to investigate them with any degree of thoroughness.

Lutton prepared the low melting phase by chilling a sample of oleic acid to 223°C. and then warming it to 283°C. and holding it there. The high melting form was obtained by holding a sample at 283°C. for several weeks. Abrahamsson and Ryderstedt-Nähringbauer (40) prepared single crystals of the low melting form by recrystallizing oleic acid from acetone at 259°C.

Lutton reports the following short and long spacings for the two forms of oleic acid investigated:

<table>
<thead>
<tr>
<th>mp. 13.3°C.</th>
<th>mp. 16.2°C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.19 (\AA), 40.5 (\AA)</td>
<td>4.65 (\AA), 3.67 (\AA), 84.4 (\AA) (42.2 (\AA))</td>
</tr>
</tbody>
</table>

From intensities and spacing he feels that the low melting form has a typical fatty acid crystal structure. However, he feels that the high melting form is unique in its crystal structure.
Abrahamsson et al. give the cell parameters for the low melting oleic acid as:

\[ a = 9.51 \, \text{Å} \quad b = 4.74 \, \text{Å} \quad c = 40.6 \, \text{Å} \]

for a pseudoorthorhombic cell.

The crystal structure as reported by Abrahamsson et al. resembles that of most long-chain fatty acids. The molecules appear in the crystal as dimers and are placed in rows radiating on both sides of the hydrogen bond-carboxyl linkage. This system gives a "ribbon" of molecules with a polar framework joining carbon chains. A series of these ribbons is laid down in a plane to form a "sheet" with the methyl end groups of one ribbon approaching those of another ribbon. Finally, these sheets are stacked in layers to form the complete crystal. Since the chains of oleic acid are bent at the position of the double bond, \((C_9-C_{10})\), the crystal has a rather poor packing factor.

Abrahamsson et al. report obtaining a second crystal from which they were able to obtain only the cell parameters, these being:

\[ a = 9.51 \, \text{Å} \quad b = 41.75 \, \text{Å} \quad c = 5.39 \, \text{Å} \quad \beta = 122^\circ \]

From the intensity data they were able to obtain, they
conclude that the crystal structure along the a-axis is similar for both crystals.

From powder photographs at different temperatures they obtained a melting point of 286°K. for the pseudo-orthorhombic crystal with no evidence, after melting, of lines due to the high melting form reported by Lutton.

Theoretical Second Moment

The theoretical second moment for the crystal structure reported by Abrahamsson et al. was calculated using Formula 1.1. The calculations were carried out on an IBM 1620 computer using a Fortran programme written by Mr. W. R. Janzen.

Two sets of proton coordinates were used in the calculations. The coordinates taken from the difference maps would necessarily be open to large errors and to check this a second set of coordinates were taken from a model of oleic acid constructed using the carbon skeleton of Abrahamsson et al. and the following parameters:

<table>
<thead>
<tr>
<th>Bond Length (Å)</th>
<th>Bond Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-C= 1.070</td>
<td>C-C-H 110°05'</td>
</tr>
<tr>
<td>H-C- 1.116</td>
<td>H-C-H 103°35'</td>
</tr>
<tr>
<td></td>
<td>C=C-H 120°00'</td>
</tr>
</tbody>
</table>

These parameters were averaged values taken from electron
diffraction work on long-chain hydrocarbons \[^{41,42,43,44}\] and on propylene \[^{45}\].

For simplicity the contributions to the second moment may be divided into two parts; intra-molecular interactions, i.e., interactions between the protons within a given molecule; and inter-molecular interactions, i.e., interactions between the protons on one molecule and the protons on all neighbouring molecules. As the interactions are inversely proportional to the sixth power of the internuclear distance, all computer calculations were terminated after a 5 Å internuclear distance. The contribution to the second moment for interactions beyond 5 Å was obtained using the following equation derived from Formula 1.1.

\[
\Delta H^2 = 14.32 \pi \rho \int_5^{\infty} r^{-4} dr
\]

where \(\rho\) is the average proton density in the sample. The results of these calculations are given in Table I.

**Discussion**

The most striking feature of the experimental plot of second moment as a function of temperature for pure oleic acid, (Figure 4), is the high value of the second moment at 77°K. We see that it is some 7.7 gauss\(^2\) higher than the theoretical value calculated from the parameters.
<table>
<thead>
<tr>
<th>Component of Second Moment</th>
<th>Parameters Used</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X-ray (^a)</td>
</tr>
<tr>
<td>Intra-molecular</td>
<td>15.85 gauss(^2)</td>
</tr>
<tr>
<td>Inter-molecular</td>
<td>5.72 &quot;</td>
</tr>
<tr>
<td>Integrated (^2)53°K.</td>
<td>0.89 &quot;</td>
</tr>
<tr>
<td>Total at 253°K.</td>
<td>22.46 gauss(^2)</td>
</tr>
<tr>
<td>Inter-molecular (^c)77°K.</td>
<td>8.60 gauss(^2)</td>
</tr>
<tr>
<td>Integrated</td>
<td>0.95 &quot;</td>
</tr>
<tr>
<td>Total at 77°K.</td>
<td>25.40 gauss(^2)</td>
</tr>
<tr>
<td>Internal methyl, rigid</td>
<td>1.69 gauss(^2)</td>
</tr>
<tr>
<td>External methyl, rigid</td>
<td>1.45 &quot;</td>
</tr>
<tr>
<td>Internal methyl, rotating</td>
<td>0.42 gauss(^2)</td>
</tr>
<tr>
<td>External methyl, rotating</td>
<td>0.88 &quot;</td>
</tr>
<tr>
<td>Total at 253°K. with end methyl rotation</td>
<td>20.64 gauss(^2)</td>
</tr>
<tr>
<td>Experimental at 253°K.</td>
<td>20.3 gauss(^2)</td>
</tr>
</tbody>
</table>


(b), (c), (d) See text.
of Abrahamsson et al. The experimental second moment at 253°K, the temperature at which the x-ray study was done, is however slightly lower than the theoretical value. As the theoretical second moment is for a rigid lattice, a situation which is more probable at 77°K than at 253°K, we are faced with the problem of explaining why the second moment is higher than the rigid value when little or no motion is likely and why it is lower when motion is probable. There are three possibilities which we may consider: (a), the proton parameters are in error resulting in a low value for the theoretical second moment; (b), the crystal structure of our sample of pure oleic acid was different from that used by Abrahamsson et al.; and (c), the increase in line width and second moment at 100°K. is due to a crystal transition, the crystal structure at 253°K. being the same as that of Abrahamsson et al., and the structure at 77°K. being different.

(a) Proton Parameters

As proton parameters obtained from x-ray studies are open to considerable error, it is reasonable to suppose that those given by Abrahamsson et al. are at least somewhat in doubt. To check this, we calculated the rigid lattice second moment for a model of oleic acid derived from the carbon skeleton of Abrahamsson et al. and using
average values for the hydrogen-carbon parameters obtained by electron diffraction. The intra-molecular second moment for this model was much higher than that calculated from the x-ray data but the inter-molecular second moment was proportionally smaller, resulting in a total second moment which was not significantly different. We must conclude then that although the second moment is a function of the sixth power of the inter-proton distances, for a crystal made up of molecules containing a large number of protons, any reasonable error in the proton parameters will not give a significant change in the total second moment. This conclusion is supported by the calculations of Janzen (14,35).

In using the proton parameters above, we have not taken into consideration the contraction of the cell lattice between 253°K. and 77°K. Singleton and Ward (46) have done a dilatometric study of oleic acid between 289°K. and 233°K., and extrapolating their results to 77°K. we arrive at a specific volume of 0.91 ml./gm. compared with 0.976 ml./gm. at 253°K. We must now consider whether the unit cell contracts isotropically or whether there is a preferential decrease along one or two axes. Lomer, in his x-ray study of potassium soaps (17), showed that the unit cell contracted along one axis only, that axis being the axis normal to the plane of the hydrocarbon chain, the a-axis in oleic acid. He felt that this uniaxial contraction
was due to the low moment of inertia of the chain about the axis along the chain direction. He felt that this low moment of inertia would allow a large vibrational amplitude in the direction normal to the plane of the chain. Assuming this to be the case for oleic acid, we may proceed to calculate the increase in the inter-molecular second moment due to the above contraction. We are assuming that the intra-molecular second moment remains reasonably static.

Several methods have been used to estimate the increase in inter-molecular second moment due to cell contraction and an analysis of these methods is attempted in Appendix I. The most accurate method is of course to reconstruct the unit cell with the appropriate axis reduced in length. This length was found by dividing the extrapolated volume at 77°K. by the product of the b and c axes. The calculation was carried out on the computer and the result of this calculation is given in Table I.

We see from these calculations that the theoretical second moment is still a long way removed from the experimental value and we are forced to conclude that the second moment discrepancy is not due simply to inaccurate proton parameters.
(b) Crystal Structure

It has been pointed out (47) that crystals of fatty acids obtained in different manners have different crystal structures. Our spectra for the sample of pure oleic acid were taken with the sample frozen from the melt, whereas Abrahamsson et al. grew their crystals from acetone. Lutton has pointed out, however, that when oleic acid is chilled and then warmed to below its melting point it exists in the low melting form. These are the approximate conditions used by us and our sample melted near 286°C so we are most likely working with the same crystal. To check this point a sample was prepared from impure oleic acid crystallized from acetone at 262°C. The second moment versus temperature plot is given in Figure 4. We see by this plot that the second moment at 253°C is somewhat lower than was the case with the pure acid but it is similar to that of the impure acid frozen from the melt. We see that the second moment at 77°C is again higher and that the overall plot of second moment versus temperature is not unlike those of the other acids. We are thus able to confirm our expectation that we are working at 253°C with the same crystal structure as that of Abrahamsson et al.
If the sample of pure oleic acid has the same crystal structure at 253°K. as that of Abrahamsson et al. as is indicated above, and if we assume that the change in proton coordinates due to cell contraction is insufficient to account for the increase in second moment at 100°K., then we might explain this increase by assuming a change in the crystal structure at 100°K. The crystal structure below 100°K. would have to have a high inter-molecular second moment, it being unlikely that the intra-molecular second moment would change appreciably due to changes in the arrangement of the molecules in the unit cell.

If we assume that the protons on one chain cannot come closer than 2.4 Å from the protons on another chain, (the van der Waals diameter (49)), and if we assume that only nearest neighbours interact, then we will require seven such interactions with an interaction distance of 2.4 Å to account for an inter-molecular second moment of 16 gauss². It is difficult to picture how fatty acid molecules could pack themselves to give such an arrangement, however. There are 689 inter-molecular interactions up to 5 Å for the crystal structure of Abrahamsson et al. Allowing seven nearest neighbour interactions per proton, there are then fourteen additional interactions per proton
up to $5 \, \text{Å}$. If we allow some of the protons to take up positions less than $2.4 \, \text{Å}$ from protons on opposing chains then the second moment will increase rapidly, allowing a less strict requirement as the number of nearest neighbours.

From the foregoing discussion, it would seem evident that the last of the three possibilities of explaining the observed behaviour of the second moment with temperature is the most probable. In order to confirm this conclusion it would be necessary to do an x-ray structural determination at $77^\circ\text{K.}$, or at least attempt a powder diffraction study, although it may be necessary to determine more than one axis in order to reach any conclusions.

**Molecular Motion**

Having concluded above that the pure oleic acid sample at $253^\circ\text{K.}$ was of the same crystal structure as that of Abrahamsson et al. we must account for the fact that the experimental second moment of the broad component at $253^\circ\text{K.}$ is lower than the theoretical value by 2.2 gauss$^2$. Previous n.m.r. evidence has shown that end methyl group rotation takes place in fatty acids and their salts even at $77^\circ\text{K.}$ (14,35,50). Using Formula 1.2, we may calculate the reduction in the second moment due to the interaction of the three rotating methyl protons amongst themselves.
As the axis of rotation is orthogonal to the interaction vectors, the second moment will fall to one-quarter of its rigid value. For the interactions between the methyl protons and the rest of the cell protons, averaging over the rotation is not so straightforward as both the distances and angles of interaction are changing. Andrew (5) has estimated, for a series of long-chain hydrocarbons, that the inter-molecular second moment will decrease by approximately the same ratio as the intra-molecular decrease. The results of the above calculation and estimate are given in Table I. We see that the resultant total second moment is in good agreement with the experimental second moment. It should be emphasized that although we can successfully explain the reduction in second moment by postulating end methyl group rotation only, we are not saying that other rotations and vibrations do not take place, in fact they probably do, but their rotational or vibrational frequencies are not high enough to cause a reduction in the second moment.

Not knowing the crystal structure at $77^\circ$K, we cannot of course say anything definite about the amount of motion. End methyl group rotation is likely in view of previous work but other extensive motion is not likely due to the necessarily dense packing.
The presence of a liquid-like line at temperatures above 207°K. must be considered in the light of the known crystal structure. In a crystal composed of normal hydrocarbon chains, rotation may be pictured as a system of intermeshing gears (5). In this picture it is necessary that not all of the chains in a given region rotate. In oleic acid, however, the rotating chain sweeps out a wide area due to the bent configuration (52). Thus, any rotation which takes place will create havoc with the neighbouring chains. The unit cell would have to expand greatly in order to allow the system of intermeshing gears proposed by Andrew to operate. In Andrew's system the rotation did not lead to a narrow line but just reduced the second moment of the broad line seen before rotation set in. In our system the rotation leads to a narrow line whose intensity is proportional to the number of molecules undergoing rotation, and a broad line, indicative of little motion in some regions of the sample. It would then appear that rather than having controlled rotation throughout the entire sample, we have chaotic motion in limited regions of the sample.

It has been suggested by Grant and Dunell (50), and by Clifford (51) that the narrow line appearing in fatty acid spectra below the melting point is due to heterophase premelting, i.e., the onset of motion around
impurity sites. Around these sites the crystal lattice will be deformed, giving sufficient expansion to the unit cell to facilitate the rotation of one or more chains. In the case of oleic acid, the initial motion spreads to a significant area of the sample. We have observed that the intensity of the narrow line in the impure sample is greater at a given temperature than in the pure sample. Also in the impure sample general rotation throughout the entire sample, indicated by a decrease in the second moment of the broad component, sets in at a lower temperature than is the case in the pure sample, again most likely due to impurity caused lattice distortion.

A consequence of the lattice expansion in the areas undergoing rotation will be the steep dilatometric curve observed by Singleton and Ward (46). We previously suggested that this volume change was due to a general lattice expansion, but if this were the case then we would not expect the plateau seen for the second moment between 170°K. and 260°K., (Figure 4).

One possible reason why no extensive motion takes place below 260°K. is the density of packing along the a-axis. It is along this axis that Lomer predicts the bulk of the vibration will take place. In oleic acid the potential energy barrier to such vibration is probably
very high. Indeed, Singleton and Ward report a small but sharp volume change at 268°K. and it may be that the molecules reorient about the double bond at this temperature so that they may more readily vibrate.

**Molecular Vibrations**

In the foregoing discussion we have not taken into account the vibrations which the protons on the chain undergo. It is difficult to make an accurate calculation of what effect this will have on the second moment of a complicated molecule. Grant and Dunell (50), using the formulae of Ibers and Stevenson (29), calculated that this vibrational motion would reduce the second moment by 5%. In their calculations they assumed that the carbon skeleton was stationary, giving them a low value for the moment of inertia of the vibrational modes. In view of this, they feel that their estimate of 5% is probably high. We find, for oleic acid, that a 2% reduction is sufficient to bring our theoretical value at 253°K. into line with the experimental value.

**Summary**

We have seen from the discussion that the second moment versus temperature plot for oleic acid, (Figure 4), may best be interpreted as follows. The crystal structure
of the sample in the region above 100°K. is the same as that of Abrahamsson et al. (40), while below 100°K. the sample takes up another crystal structure which is characterized by a very dense inter-molecular packing. For temperature below 260°K. the bulk of the molecules in the sample undergo no extensive motion beyond end methyl group rotation and vibration of the chain protons. It is possible that the molecules reorient after the onset of general motion to facilitate vibrations. It would appear that the premelting phenomenon characterized by the narrow line originates at impurity sites and causes extensive motion only in isolated areas of the sample, these areas growing rapidly in size only near the melting point. The volume change in these areas accounts for the coefficient of expansion observed in dilatometric studies.
Chapter 5

ELAIDIC ACID

Description of Spectra

The spectra of elaidic acid may be divided into three groups covering three temperature ranges: 77°K.-170°K., 170°K.-225°K., 225°K.-315°K.

77°K.-170°K.

In this region the spectra were broad although rounded on top and had broad tails. There was no evidence of shoulders on the curves.

170°K.-225°K.

In this region the spectra had much the same shape as in the lower region but had slightly shorter tails, resulting in a small decrease in second moment.

225°K.-315°K.

In this region a narrow line appeared which grew in intensity as the temperature was raised. The narrow line grew much more slowly than was the case in oleic acid, and even just below the melting point it was only a small fraction of the total intensity. Throughout this region the line width and second moment changed only slightly,
dropping sharply only within a few degrees of the melting point.

Plots of line width and second moment as a function of temperature appear in Figures 5 and 6, respectively.

Crystal Structure

The complete crystal structure of elaidic acid is not known and there is some disagreement in the literature as to the unit cell parameters. The early work of Volarovich et al. (53) reports that the unit cell is similar to that of stearic acid, i.e., monoclinic with orthorhombic packing (54). However, Lutton and Kolb (55) report, in a study of a series of trans octadecenoic acids, that the crystal structure is not similar to that of stearic acid. Their work is supported by the work of Swern et al. (56), who report a long spacing of 49.0 Å. Wilman (57) reports elaidic acid to be tetragonal with axes; a = 26.5 Å, c = 10.3 Å. Workers studying binary systems of cis and trans octadecenoic acids with normal paraffin chain acids (52,58) report that the trans acid packs with the straight chain acid without expansion of the crystal lattice, whereas cis causes expansion. Their conclusion was that the trans acids crystallize in a reasonably straight chain configuration, unlike the cis acids which have a marked bend at the position of the double bond. We might therefore expect the packing factor of elaidic acid to be
ELAIDIC ACID $\text{HC}_{18}^{\text{trans}}$

**Figure 5**

Temperature (degrees K) vs. Line Width (gauss)
ELAIDIC ACID $\text{HC}_{18}^\text{trans}$

**Figure 6**

**SECOND MOMENT (gauss$^2$)**

**TEMPERATURE (degrees K)**

To follow page 46
greater than that of oleic acid and to approximate that of stearic acid. This is born out by the dilatometric work of Singleton and Ward (46).

**Theoretical Second Moment**

As there are no detailed crystal data available it is not possible to calculate a theoretical second moment. One can, however, make a rough estimate of the second moment from the known values for oleic acid and stearic acid.

Grant and Dunell (50) calculate a second moment of 24.4 gauss$^2$ for stearic acid in the C-form. Their calculation was done from a model, not from the actual x-ray parameters, only the cell parameters being known. However, we have shown earlier that the total second moment is not likely to be much affected by any reasonable error in this method of attack. This value is higher than our calculated value of 22.5 gauss$^2$ for oleic acid and it is probable that elaidic acid lies somewhere in between these values if not somewhat higher.

**Discussion**

We see from the plot of second moment versus temperature, (Figure 6), that the second moment at 77°K. is 23.6 gauss$^2$ and falls to 20.5 gauss$^2$ in the region between
150°K. and 220°K. It is unlikely that this drop is due to the onset of methyl end group rotation. The decrease is almost double that calculated for oleic acid, (Table I), and previous work has shown that the end methyl group in fatty acids and their salts is probably rotating even at 77°K. Assuming that only methyl group rotation is lowering the second moment at 77°K., and assuming that this lowering is approximately that found in oleic acid, we calculate a rigid lattice second moment for elaidic acid at 77°K. of 25.4 gauss^2, (ie. experimental + end methyl reduction). This is somewhat higher than that calculated for stearic acid and is probably not far removed from the actual value.

**Molecular Motion**

The drop in second moment between 150°K. and 220°K. is probably due to the onset of a small amount of torsional oscillation. It may be that a small percentage of the molecules are rotating freely in the manner described by Andrew (5) or that all of the molecules are twisting through a small angle. The latter possibility seems more likely in view of the slight bend in the molecule and the close packing of the unit cell as reflected in its rigid lattice second moment.
The appearance of the narrow line at 225\(^o\)K. is undoubtedly the same phenomenon that was seen in oleic acid. The intensity of the line does not increase as rapidly as in oleic acid and this is probably due to the shape of the molecule. The more nearly linear molecule on rotating would not create as much havoc with its neighbours.

As in the case of oleic acid, there is a long plateau in the second moment versus temperature plot, ending just below the melting point. Although it is likely that there is some vibration or torsional oscillation in elaidic acid in this region, there would appear to be some barrier to more general motion until a very few degrees below the melting point. In normal hydrocarbons there is a continual decrease in second moment as the temperature is raised (5), this decrease becoming steeper near the melting point. In stearic acid, however, the line width and second moment remain quite steady until just below the melting point (50). It may be that the polar interactions in the fatty acids prevent the onset of large amounts of rotational motion and when these interactions finally do break, the crystal melts.
BIBLIOGRAPHY


34. Varian Associates, "Maintenance Instruction Sheets", #87-100-068.


38. Lutton, E. S., Oil and Soap, 23, 265 (1946).


Extrapolation of Inter-Molecular Second Moments

As the second moment increases as the inverse sixth power of the inter-proton distance decrease, and as the inter-proton distance decreases directly as the decrease in unit cell volume for a uniaxial contraction, the following ratio could be used to find the increase in the second moment on contraction to 77°C.

\[ \Delta H_{2\text{INTER}}' = \frac{\Delta H_{2\text{INT},V^6}}{V^5} \]  \hspace{1cm} A

A second possible formula which might be tried in an effort to find the increase in the inter-molecular second moment is the following:

\[ \Delta H_{2\text{INTER}}' = \frac{\Delta H_{2\text{INT},6\Delta V}}{V} \]  \hspace{1cm} B

This formula is derived from that used by Dunell et al. (48) to find the coefficient of linear expansion for an isotropic expansion. For a uniaxial expansion we have substituted volume for distance.

One should note, however, that as the intra-proton distances along the axis of contraction are fixed, the
inter-proton distances will increase at a rate which is higher than the rate of cell contraction. The total volume of the cell may be divided into $V_{\text{intra}}$, the volume of the molecular chain, and $V_{\text{inter}}$, the volume between the chains. If we approximate the volume of the hydrocarbon chains to a rectangular solid, with the protons forming the edges of the solid, we may estimate the ratio of $V_{\text{intra}}$ to $V_{\text{inter}}$. As only the $a$-axis dimension is critical in this calculation, we have:

$$\Delta H^{2'}_{\text{INTER}} = \frac{\Delta H^{2}_{\text{INT.}}(a - \frac{a}{n})}{(a'' - \frac{a}{n})}$$

$$a'' = \frac{V'}{b \times c}$$

where $n$ is the fraction of the cell volume occupied by $V_{\text{intra}}$, and $a$, $b$, and $c$ are the unit cell dimensions of oleic acid.

The results of the above calculations and the computer result found earlier are listed in Table II.
Table II  Extrapolated Inter-Molecular Second Moments

<table>
<thead>
<tr>
<th>Method of Extrapolation</th>
<th>Result (gauss$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Computer</td>
<td>8.60</td>
</tr>
<tr>
<td>Formula A</td>
<td>9.09</td>
</tr>
<tr>
<td>Formula B</td>
<td>7.90</td>
</tr>
<tr>
<td>Formula C</td>
<td>11.06</td>
</tr>
</tbody>
</table>

The first method, (Formula A), gives a value which is slightly higher than the computer value, whereas the second method, (Formula B), gives a lower value. The third method, (Formula C), gives a very high value. As the second method is only exact for an infinitesimal volume change, we might expect that it would give a low value if the volume change was appreciable. Formulae B and C, however, should not be so affected.

Uniaxial contraction of a unit cell whose component molecules are arranged in an orthorhombic array will only increase those interactions which have a component of their interaction vector lying along the axis contracted. All other interactions will be unaffected. We see then that none of the formulae used were in fact measuring the amount of increased interaction. They were giving a high result because interactions not affected by the contraction were added into the value of
the inter-molecular second moment used in the formulae. If we take 74% of the inter-molecular second moment at 253°K. and use it in Formula 0, the most accurate formula, we will obtain the computer value. This would indicate that, to a first approximation, about 74% of the intermolecular interactions in the crystal take place along the a-axis. In view of this we are probably not justified in assuming uniaxial contraction along the a-axis, the packing along this axis being too high. For contraction along the b-axis or for biaxial contraction, the extrapolated total second moment would be lower so this does not affect our conclusion about the second moment discrepancy.