A STUDY OF MULTI-PHASE LIQUID CRYSTAL BY MEANS OF NUCLEAR MAGNETIC RESONANCE

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A STUDY OF MULTI-PHASE LIQUID CRYSTAL BY MEANS OF NUCLEAR MAGNETIC RESONANCE

BY

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Richard D. Ewing

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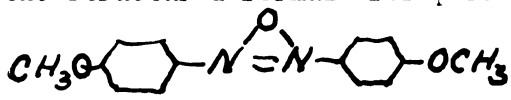
Introduction

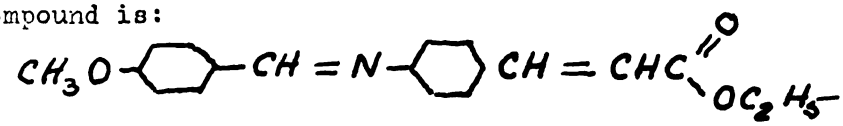
Previous proton magnetic resonance work with compounds of a single liquid phase[7] has shown that it is often possible to obtain a unique line shape for the singal of this phase as apposed to those of solid crystalline and liquid phases. Each of these signals consists of a single line - a weak, wide line for the solid crystalline phase while that for the liquid phase is an extremely strong, narrow line. On the other hand, the signal from the liquid crystal phase in a compound such as para-azoxynisol which has just one liquid crystal phase consists of three lines - a relatively strong, narrow line flanked by two satellite lines. A qualitative explanation for this line shape is best seen from the structural formula for para-azoxyanisol:



The protons in the methyl groups on each end of the molecule contribute a triplet shape to the signal, but on this is superimposed a doublet from the protons on the benzens rings along the axis of the molecule.

However not all compounds which contribute crystal phases also exhibit unique line shapes for the signals of these phases[4], but seemingly only those which have ethyl, or methyl groups, or both, on the ends of the molecules. In the cases of compounds with ethyl groups on the ends, the expected signal shape would be one of five peaks - a high, center peak flanked by two pairs of satellite peaks.

However, this thesis is not so much concerned with distinguishing the liquid crystal phase as much, but rather with an attempt to distinguish by nuclear magnetic resonance the various liquid crystal phases in compounds which are known to contain several liquid crystal phases, each of these seperate phases by nuclear resonance methods. Specifically, the compound ethylanisal <u>para</u>-aminocinnate which has three liquid crystal phases[2] was examined in order to determine whether each phase could be distinguished by means of the proton magnetic resonance signal of that particular phase. Chemically, this compound is:



From what was mentioned previously, the expected shape for the signal from the liquid crystal phase in general would be a signal of five peaks from the ethyl group[3], superimposed upon a triplet from the methyl group, then these in turn are superimposed upon a doublet from the protons in the benzene rings, and finally the protons along the axis of the molecule will contribute to the center peak. This generally signaled what was found with one qualification which will be explained later.

Dipole - Dipole Interaction

The classical Hamiltonian for the interaction of two magnetic dipoles in a magnetic field $\underline{H}$ is:

$$\mathcal{H}' = \frac{\underline{\mu}_1 \cdot \underline{\mu}_2}{r^3} - 3\,\frac{(\underline{\mu}_1 \cdot \underline{r})(\underline{r} \cdot \underline{\mu}_2)}{r^5}$$

where; $\underline{\mu}$ = magnetic moment of the protons

$\underline{r}$ = distance between protons of a pair.

Then expanding $\underline{\mu}_1, \underline{\mu}_2, \underline{r}$ in rectangular coordinates with the following relations

$$\underline{\mu}_i = \gamma \hbar \underline{I}_i = \gamma \hbar (\underline{i} I_{xi} + \underline{j} I_{yi} + \underline{k} I_{zi})$$

$$\underline{r} = \underline{i} x + \underline{j} y + \underline{k} z$$

where: γ = magnetogyric ratio

$\hbar$ = $\frac{\text{Planck's constant}}{2\pi}$

$\underline{I}$ = spin of the protons

After substitution of these quantites and some juggline, one finds; in terms of the direction cosines, a_1, a_2, a_3.

$$\mathcal{H}' = \frac{\gamma \hbar^2}{r^3}\Big[I_{x1} I_{x2}(1-3a_1^2) + I_{y1} I_{y2}(1-3a_2^2)$$

$$+ I_{z1} I_{z2}(1-3a_3^2) - 3(I_{x1} I_{y2} + I_{y1} I_{x2}) a_1 a_2$$

$$- 3(I_{x1} I_{z2} + I_{z1} I_{x2}) a_1 a_2$$

$$- 3(I_{y1} I_{z2} + I_{z1} I_{y2}) a_2 a_3\Big]$$

Then, introducing the polar and azimuthal angles θ & φ and then discarding all terms which contribute to the transitions $\Delta m = \pm 1, \pm 2$ one finds,[2,8]

$$\mathcal{H}' = -I_{z1} I_{z2} (3\cos^2\theta - 1) + \frac{1}{4}\left[(I_{x1} - i I_{y1})(I_{x2} + i I_{y2}) + (I_{x1} + i I_{y1})(I_{x2} - i I_{y2})\right](3\cos^2\theta - 1)$$

Consider two non-interacting protons in a magnetic field H_z Then for the Hamiltonian :

$$\mathcal{H}_0 = \mu H_z = \gamma H_z (I_{z1} + I_{z2})$$

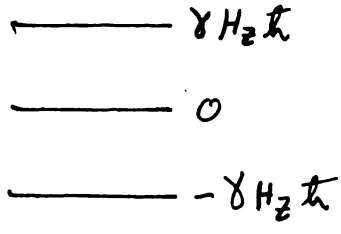
Then using the Hamiltonian asan operator in the matrix form and operating on two eigen functions:

$$\psi^+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \psi^- = \begin{pmatrix} 0 \\ -1 \end{pmatrix}$$

One can write.

$$\mathcal{H}_0 \psi_i = E_i^0 \psi_i$$

where the elements of this diagonalized matrix give directly the energy levels, E_i^0



However, now consider the same two dipoles only interacting in H_z . Then it becomes necessary to add the interaction term found previously to H. Thus, for the total Hamiltonian,

$$H = H_0 + H'$$

The result of this interaction term is to produce a shift in the energy levels just given.

Let: E_i^o = Unperturbed energy levels

E_i' = Perturbed energy levels

ϵ_i' = Shift from unperturbed to perturbed energy

Similar, let:

φ_i = wave function for perturbed energy levels

ψ_i = wave function for unperturbed energy levels

ϵ_i = wave function for shift in energy levels.

Then by direct substitution:

$$(\mathcal{H}_o + \mathcal{H}')(\psi_i + \chi_i) = (E_i^o + \epsilon_i)(\psi_i + \chi_i)$$

Assume $\psi_i >> \chi_i$ so that χ_i can be neglected, and, since already know: $\mathcal{H}_o \psi_i = E_i^o \psi_i$

then: $\mathcal{H}' \psi_i \cong \epsilon_i \psi_i$

Thus, the problem now becomes one of finding H in diagonal form, so that elements of the diagonal are the shifts of energy levels, ϵ_i.

Adjoint Matrices

if, $A = \begin{pmatrix} a & b \\ c & d \end{pmatrix}$ $\longrightarrow A_j^{\dagger} A_i = \delta_{ij}$

then $A^{\dagger} = \begin{pmatrix} a^* & c^* \\ b^* & d^* \end{pmatrix}$ where: $\delta_{ij} = 0$ if $i \neq j$, $= 1$ if $i = j$

Since, $\mathcal{H}' \psi_i \cong \epsilon_i \psi_i$

then, $\psi_i^{\dagger} \mathcal{H}' \psi_j \cong \epsilon_i \delta_{ij}$ where: $\delta_{ij} = 0$ if $i \neq j$, $= 1$ if $j = i$

Theorem: If we have linear operations such that each operates in only its own eigen function then:

$$\sum \mathcal{H}_i (\pi_i \varphi_i) = \sum E_i (\pi_i \varphi_i)$$

then, for non-interacting protons:

$$\mathcal{H}_0 = \mu H_z = \gamma H_z (I_{z1} + I_{z2})$$

$$\psi^+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\psi^- = \begin{pmatrix} 0 \\ -1 \end{pmatrix}$$

for protons:

then, $\Psi_1 = \psi_1^+ \psi_2^+ \longrightarrow$ orientation $\uparrow\uparrow$

$\Psi_2 = \psi_1^+ \psi_2^- \longrightarrow$ " " " $\uparrow\downarrow$

$\Psi_3 = \psi_1^- \psi_2^+ \longrightarrow$ " " " $\downarrow\uparrow$

$\Psi_4 = \psi_1^- \psi_2^- \longrightarrow$ " " " $\downarrow\downarrow$

However, to insure that H is diagonalized it is better to use:

$$\Phi_1 = \Psi_1$$

$$\Phi_2 = \frac{1}{\sqrt{2}}(\Psi_2 + \Psi_3)$$

$$\Phi_3 = \frac{1}{\sqrt{2}}(\Psi_2 - \Psi_3)$$

$$\Phi_4 = \frac{\#}{\sqrt{2}} = \Psi_4$$

Now have:

$$\Phi_j^\dagger \mathcal{H}' \Phi_i = \epsilon_i$$

$$\mathcal{H}' = \frac{\gamma^2\hbar^2}{r^3}(I_{z1}I_{z2})(3\cos^2\theta - 1)$$

$$- \frac{\gamma^2\hbar^2}{4r^3}\left[(I_{x1} - iI_{y1})(I_{x2} + iI_{y2}) + (I_{x1} + iI_{y1})(I_{x2} - iI_{y2})\right](3\cos^2\theta - 1)$$

where:

$$(m \mid I_x + iI_y \mid m-1) = \sqrt{(I+m)(I-m+1)}$$

$$(m \mid I_x - iI_y \mid m+1) = \sqrt{(I-m)(I+m+1)}$$

$$(m \mid I_z \mid m) = m$$

Consider: $\Phi_i^\dagger \mathcal{H}' \Phi_i = \epsilon_i$

1. $\Phi_i^\dagger (I_{z1} I_{z2}) \Phi_i = \epsilon_i$

(a) $\Phi_1^\dagger (I_{z1} I_{z2}) \Phi_1 = \psi_1^\dagger \psi_2^\dagger (I_{z1} I_{z2}) \psi_1^+ \psi_2^+ = \frac{1}{4}$

$$\epsilon_1' = -\frac{\gamma^2 \hbar^2}{4 r^3}(3\cos^2\theta - 1)$$

(b) $\Phi_4^\dagger (I_{z1} I_{z2}) \Phi_4 = \frac{1}{4}$

$$\epsilon_4' = -\frac{\gamma^2 \hbar^2}{4 r^3}(3\cos^2\theta - 1)$$

(c) $\Phi_2^\dagger (I_{z1} I_{z2}) \Phi_2 = -\frac{1}{4}$

$$\epsilon_2' = +\frac{\gamma^2 \hbar^2}{4 r^3}(3\cos^2\theta - 1)$$

(d) $\Phi_3^\dagger (I_{z1} I_{z2}) \Phi_3 = -\frac{1}{4}$

$$\epsilon_3' = +\frac{\gamma^2 \hbar^2}{4 r^3}(3\cos^2\theta - 1)$$

2. $\Phi_i^\dagger [(I_{x1} - i I_{y1})(I_{x2} + i I_{y2})] \Phi_i$

(a) $\Phi_1^\dagger [(I_{x1} - i I_{y1})(I_{x2} + i I_{y2})] = 0 = \epsilon_1''$

(b) $\Phi_4^\dagger [(I_{x1} - i I_{y1})(I_{x2} + i I_{y2})] = 0 = \epsilon_4''$

(c) $\Phi_2^\dagger [(I_{x1} - i I_{y1})(I_{x2} + i I_{y2})] = \frac{1}{2}$

$$\epsilon_2'' = \frac{\gamma^2 \hbar^2}{8 r^3}(3\cos^2\theta - 1)$$

(d) $\Phi_3^\dagger [(I_{x1} - i I_{y1})(I_{x2} + i I_{y2})] = -\frac{1}{2}$

$$\epsilon_3'' = \frac{\gamma^2 \hbar^2}{8 r^3}(3\cos^2\theta - 1)$$

3. $\Phi_i^\dagger [(I_{x1} + i I_{y1})(I_{x2} - i I_{y2})] \Phi_i$

(a) $\Phi_1^\dagger [(I_{x1} + i I_{y1})(I_{x2} - i I_{y2})] \Phi_1 = 0 = \epsilon_1'''$

(b) $\Phi_4^\dagger [(I_{x1} + i I_{y1})(I_{x2} - i I_{y2})] \Phi_4 = 0 = \epsilon_4'''$

(c) $\Phi_2^\dagger [(I_{x1} + i I_{y1})(I_{x2} - i I_{y2})] \Phi_2 = \frac{1}{2}$

$$\epsilon_2''' = \frac{\gamma^2 \hbar^2}{8 r^3} (3\cos^2\theta - 1)$$

(d) $\Phi_3^\dagger [(I_{x1} + i I_{y1})(I_{x2} - i I_{y2})] \Phi_3 = -\frac{1}{2}$

$$\epsilon_3''' = -\frac{\gamma^2 \hbar^2}{8 r^3} (3\cos^2\theta - 1)$$

Thus, for the shifts to the perturbed energy levels,

$$\epsilon_1 = \epsilon_1' + \epsilon_1'' + \epsilon_1''' = -\frac{\gamma^2\hbar^2}{4r^3}(3\cos^2\theta - 1) = -\mu^2 r^{-3}(3\cos^2\theta - 1)$$

$$\epsilon_2 = \epsilon_2' + \epsilon_2'' + \epsilon_2''' = +\frac{\gamma^2\hbar^2}{2r^3}(3\cos^2\theta - 1) = +2\mu^2 r^{-3}(3\cos^2\theta - 1)$$

$$\epsilon_4 = \epsilon_4' + \epsilon_4'' + \epsilon_4''' = -\frac{\gamma^2\hbar^2}{4r^3}(3\cos^2\theta - 1) = -\mu r^{-3}(3\cos^2\theta - 1) \; ; \; \epsilon_3 = 0$$

Resonance absorption then occur for the perturbed system when[5]

$m = +1 \rightarrow m = 0$ $\quad h\nu = 2\mu H_z + 3\mu^2 r^{-3}(3\cos^2\theta - 1)$

$m = 0 \rightarrow m = -1$ $\quad h\nu = 2\mu H_z - 3\mu^2 r^{-3}(3\cos^2\theta - 1)$

Substitute:

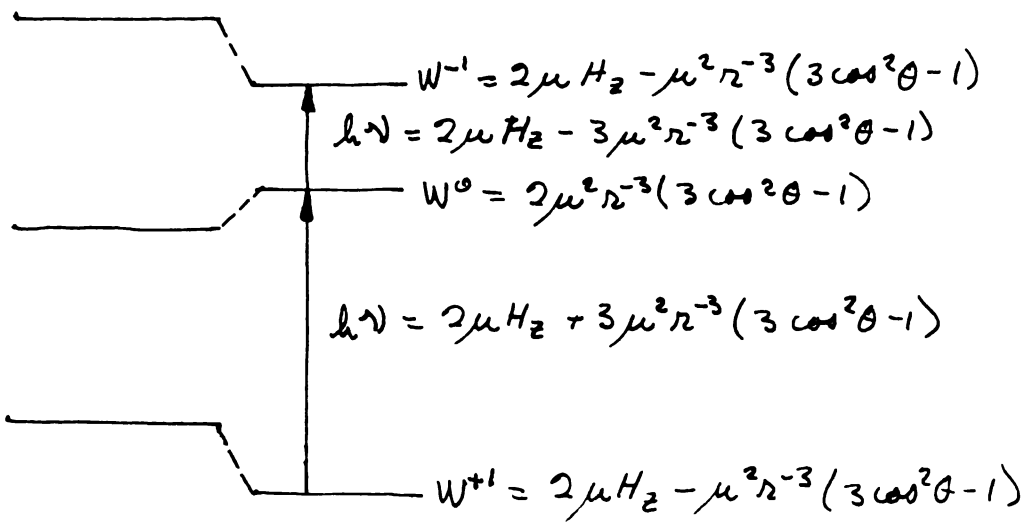
$$h\nu = 2\mu H^*$$

where H^* is the resonance field value

$$H^* = H_z \pm \alpha(3\cos^2\theta - 1)$$

where $\alpha = \frac{3}{2}\mu r^{-3}$

Thus, the energy level diagram showing the effect of the perturbing dipole - dipole interaction on the unperturbed levels.

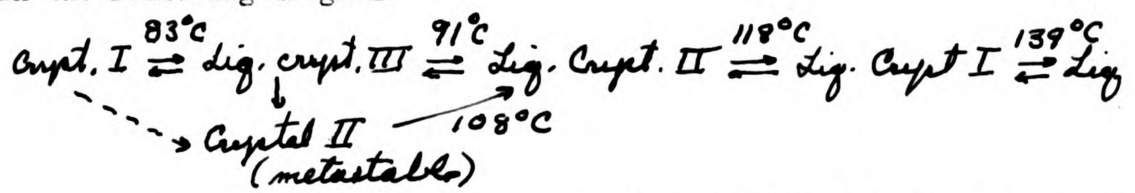


Apparatus

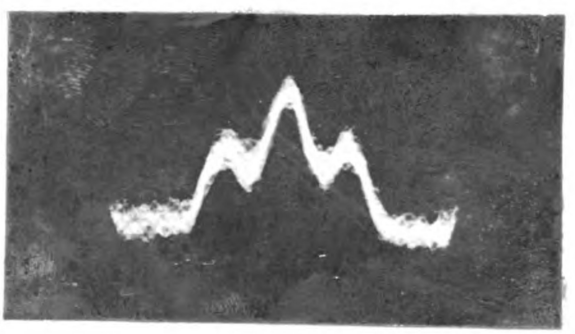
In the detection of the signal, the apparatus used is essentially the same as the radio-frequency bridge method discussed by Villaire[9]. The line widths are then measured with the same method and accuracy as was done by Moses[4].

Discussion

In the attempt to dectect liquid crystal phases, the compound ethyl anisal para- aminocinnamate was used. According to the optical observations of Bernal and Crowfoot[1] this compound possesses three liquid crystal phases, with the transition temperatures as indicated in the following diagram.



As was stated before, the expected signal from the liquid crystal phases would consist of five peaks. However, the actual signal found for all the liquid crystal phases was of the form shown in figure I



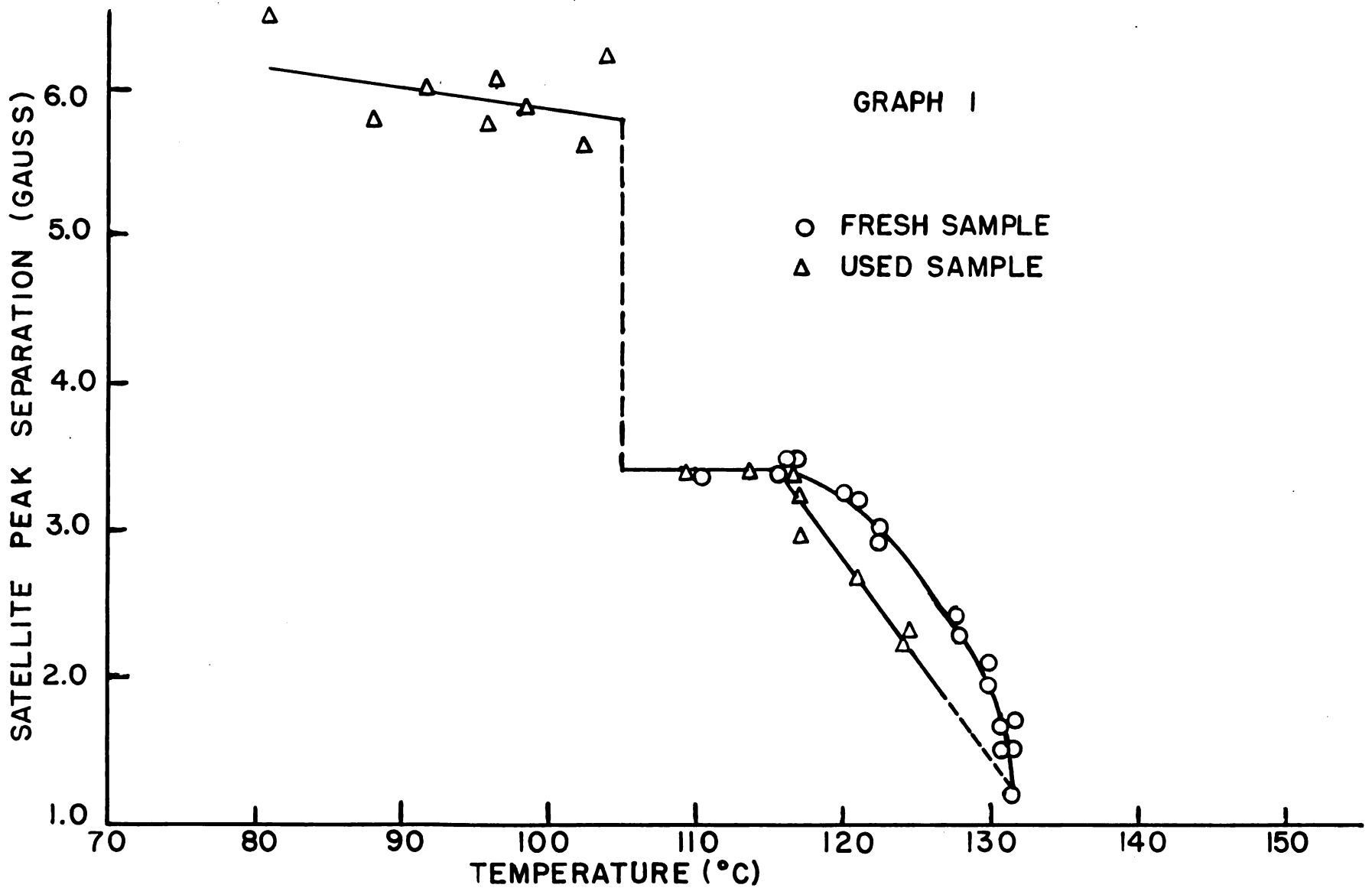
The apparent absence of two satellite peaks here is in accord with previous experimental results which have shown that molecules with a methyl group on one end and an ethyl group on the other two of the satellites are masked so that the overall picture is simply a triplet.

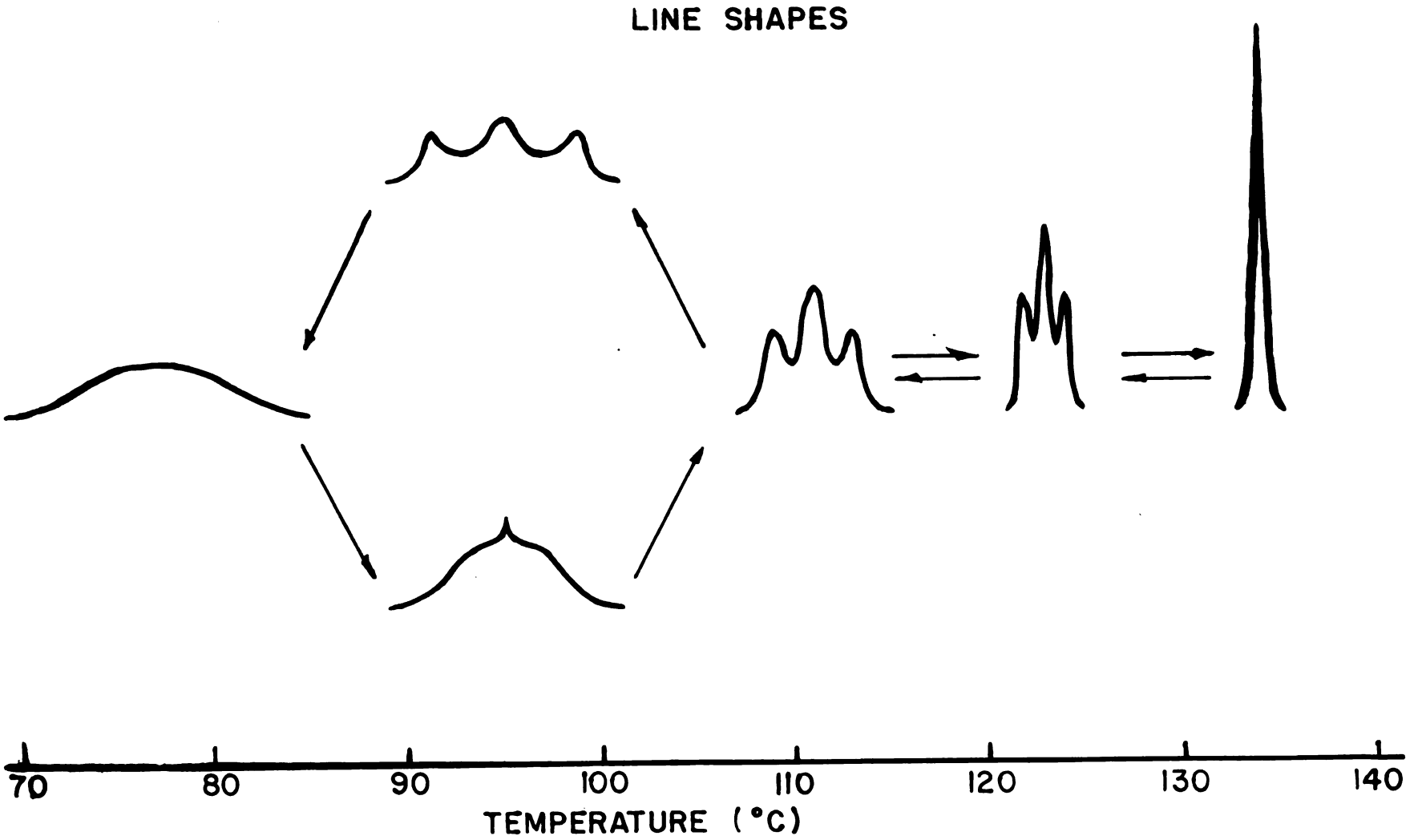
Before continuing, it should be pointed out that the compound used appeared to be impure. This was derermined by merely visually observing the various phase transitions for a small sample in a temperature bath. It was found that each transition occurred about $1\text{-}4^{0}$ c lower than the respective transitions indicated by Bernal and Crowfoot.[1]

However, it seemed to exhibit enough line structure and be sufficiently pure to warrant going ahead with the work.

In order to detect these various liquid crystal phases, the satellite peak separation of a signal was measured as a function of temperature. These peak separations were then plotted versus temperature, and graph #1 was obtained. Here the peak separation is measured in guass and the temperature in degrees centrigrade.

In this graph there appears to be three very distinct portions which are taken to be the magnitude of the satellite peak separation in each of the three liquid crystal phases. The portion of the curve at the right which slopes rapidly up from the liquid phases is taken to be the first liquid crystal phase. The satellite peak separations here vary from 1.2 guass at 131.2^{0}c, which is close to the clear point, up to the 3.4 guass at 117^{0}c.


GRAPH I
FRESH SAMPLE
USED SAMPLE
SATELLITE PEAK SEPARATION (GAUSS)
6.0
5.0
4.0
3.0
2.0
1.0
70
80
90
100
110
120
130
140
150
TEMPERATURE (°C)


LINE SHAPES
70
80
90
100
110
120
130
140
TEMPERATURE (°C)

The two lines of this section seem to indicate some decomposition in the compound upon successive heatings. The line drawn through the circles represents a sample of which the data was obtained upon the first heating, while the line through the triangles represents the same sample after it has been heated previously. And while the results shown here are not sufficient to positively state that a trend is established as shown, that is, successive heatings decompose the compound in such a manner as to produce lower satellite peak separations in the first liquid crystal phase, still it is the opinion of the author that this is so, especially since it was found by visual observations that the clear point was lowered by as much as 15^{0}c. upon many heatings.

The exact cause of this decomposition is not known.

The second section of the curve from 117^{0}c. down to 108^{0} represents the second liquid crystal phase and here the satellite peak separation remains constant at 3.4 guass. It should be noted here that the transition from the first to the second liquid crystal phase is represented as merely the change in slope of the curve. This is in qualitative agreement with the observations of Bernal and Crowfoot[1], who state that there is but a small difference in the optical behavior of these two phases, then at 105^{0}c. a sharp discontinuty occurs and there is a sudden increase in peak separation. This third portion of the curve then is taken to represent the third liquid crystal phase and here the peak separations vary from 5.8 guass at 105^{0}c to 6.8 guass at 80^{0}c. Thus, these transitions appear to agree with those of

Bernal and Crowfoot as well as could be expected considering the purity of the sample.

The next graph shows the change in shape of the signal with temperature. Each of the three peaked signals represents the three liquid crystal phases, while the single peak at the extreme right is the signal of the liquid phase. An interesting feature of this compound is that while it is heated it appears to go from a solid crystalline phase with its characteristic broad line into a second metastable solid crystalline phase with the same type signal only with a spike on top. From here it passes into the second liquid crystal phase and then into the first and after that into the liquidphase.

On cooling, however, it traces back along through the first and second liquid crystal phases, b t then it jumps into the third liquid phase at 105^{0}c. But it is not at all positive that here the compound is all in the third liquid crystal phase, but rather it is possible that, as Bernal and Crowfoot indicate there is a coexistance of both this liquid crystalphase and the metastable crystalline phase.

We point at which the compound passes from the third liquid crystal phase into the solid crystalline phase was not determined due to the difficultyy in obtaining a workable signal past80^{0}c.

Thus, from these results it appears to have been possible to detect all the general features of the various phase transitions which were found by Bernal and Crowfoot by optical observations.

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