THE PROTON RESONANCE ABSORPTION IN LIQUID CRYSTALS

Thesis for Degree of Master of Science

MICHIGAN STATE COLLEGE

HERBERT A. MOSES

1953

This is to certify that the

thesis entitled

Proton Resonance Absorption
in Liquid Crystals

presented by

Herbert A Moss

has been accepted towards fulfillment
of the requirements for

M. S. degree in Physics

R. D. Spence
Major professor

Date July 10, 1953

THE PROTON RESONANCE ABSORPTION IN LIQUID CRYSTALS

By

HERBERT A. MOSES

A THESIS

Submitted to the School of Graduate Studies of Michigan State College of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE

Department of Physics

1953

Acknowledgement

I wish to express my utmost gratitude to Professor Robert D. Spence for his patience and sound guidance in the respective phases of this problem, and for his undying enthusiasm which has been a constant source of inspiration.

Harold A. Moss

CONTENTS

INTRODUCTION

Recently it has been shown that the proton resonance of the liquid crystal, parazoxyanisole, exhibits an anamalous structure.[1] This thesis reports additional work on liquid crystals suggested by the initial discovery. Prior to the work presented here, study has been made solely on the nematic, thread-like liquid crystals and it is the purpose of this thesis to report the absorption line characteristics of other types of mesomorphic (liquid crystalline) substances.

It is believed that the liquid crystalline state consists of an ordered arrangement of groups. (The word "crystalline" has been assigned to indicate the property of anisotropy, characteristic of this phase.) Three types of liquid crystals exist: nematic, smectic, and cholesteric. The nematic liquid crystals possess long molecules which maintain some definite orientation in the intermediate state. In the smectic and cholesteric compounds we have a slightly different situation. The molecules of these substances are in the shape of planes which lend to the overall nature of a planal mesomorphic state. The main difference between a smectic and cholesteric structure is that the former consists of planes whose thickness is the order of one molecule, while

1. R.D. Spence, H.A. Moses, P.L. Jain, "The Proton Magnetic Resonance in Liquid Crystals," Journal of Chemical Physics, February, 1953, p. 208.

the latter consists of planes from 500 to 5000 molecules in thickness.[2]

EXPERIMENTAL APPARATUS

The apparatus used consists of an electro-magnet[3] operated at 7300 gauss, a "twin-T" radiofrequency bridge, oscillator, preamplifier, receiver, and cathode-ray-oscilloscope. This apparatus is essentially the same as that discussed by Villaire[4] in his thesis. The only new component added to the above is a thirty cycle generator which is described in detail in the appendix.

The linewidth variations were measured by means of a timing signal and using the relationship $\Delta H = dt\,\omega H_m$ in which H_m = the maximum value of the modulating field, and dt = the time duration corresponding to the linewidth. It is believed that the measurements taken contain no more than $\pm$ 10 % experimental uncertainty, the limitations on linewidth measurement being 0.1 gauss.

2. Glasstone, Textbook of Physical Chemistry, pgs. 504 to 508.

3. Luck, Jerome Arthur, Design and Construction of a Laboratory Electromagnet, Thesis, Michigan State College, 1950.

4. Villaire, Alfred Edmond, The Radiofrequency Bridge Method of Detecting Nuclear Resonance Signals, Thesis, Michigan State College, 1952.

RESULTS

SODIUM STEARATE

$$[CH_3-(CH_2)_{16}-\overset{O}{\overset{\|}{C}}-O-Na]$$

Sodium Stearate has been used as a typical smectic liquid crystal and the resonance absorption line observed. Above 260°C. this sample of sodium stearate is in the liquid state. The linewidth measurements indicate a width of approximately 1.10 gauss with a slight broadening at the lower limit of the state to 1.15 gauss. When the transition point to the liquid crystal state is reached (260°C.), the linewidth increases to 1.33 gauss and remains constant until 200°C.. As the substance cools below this solid transition point, a marked increase in linewidth occurs. The average width of the line in the solid state is 2.8 gauss. The most important observation made is the fact that a single line exists in all states with only the loss of wiggles (going from liquid to liquid crystal state) and broadening, giving indication of a change taking place in the substance.[5]

5. No evidence of an unidimensional melt taking place at 70°C. has been observed in the form of a linewidth change.

SODIUM OLEATE

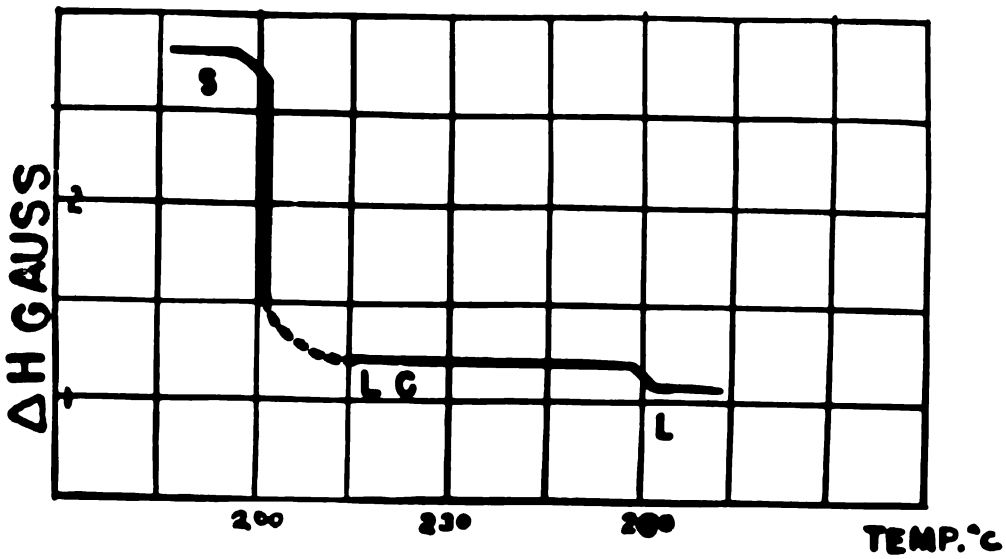
$$\left[CH_3-(CH_2)_7-CH=CH-(CH_2)_7-\overset{O}{\overset{\|}{C}}-O-Na\right]$$

Sodium oleate behaves much the same as sodium stearate. Sodium oleate is also a smectic type liquid crystal with an upper transition point of 235°C. (liquid to liquid crystal phase) and a lower transition point of 135°C. (liquid crystal to solid state). Throughout the liquid state a steady linewidth of 0.69 gauss is maintained and finally broadens to 1.17 gauss at the transition point 235°C. . (The linewidth change is more distinct than that of the stearate.) At 135°C. another sharp transition occurs as the liquid crystal solidifies. In the solid state the linewidth becomes 1.37 gauss. Here again, as in sodium stearate, one line exists in all these states.

It is believed that a disruption of the polar bonds occur in these smectic substances on heating from the solid state, to give rise to this liquid crystal state.[6]

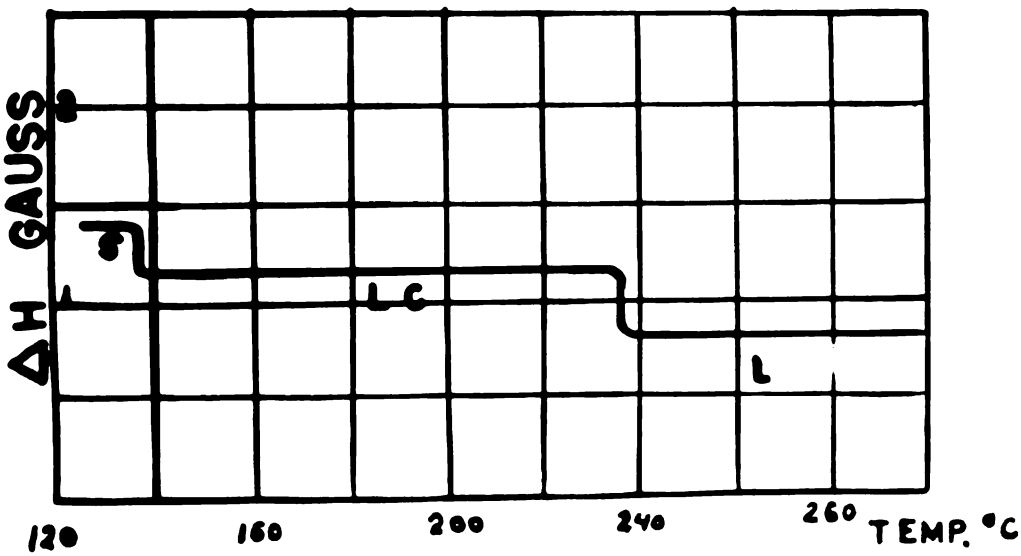
(See graphs of ΔH vs. temperature)

6. Gallay, Willard & Puddington, "Physical States of Anhydrous Sodium Salts," Canadian Journal of Research, 1943, p. 202.

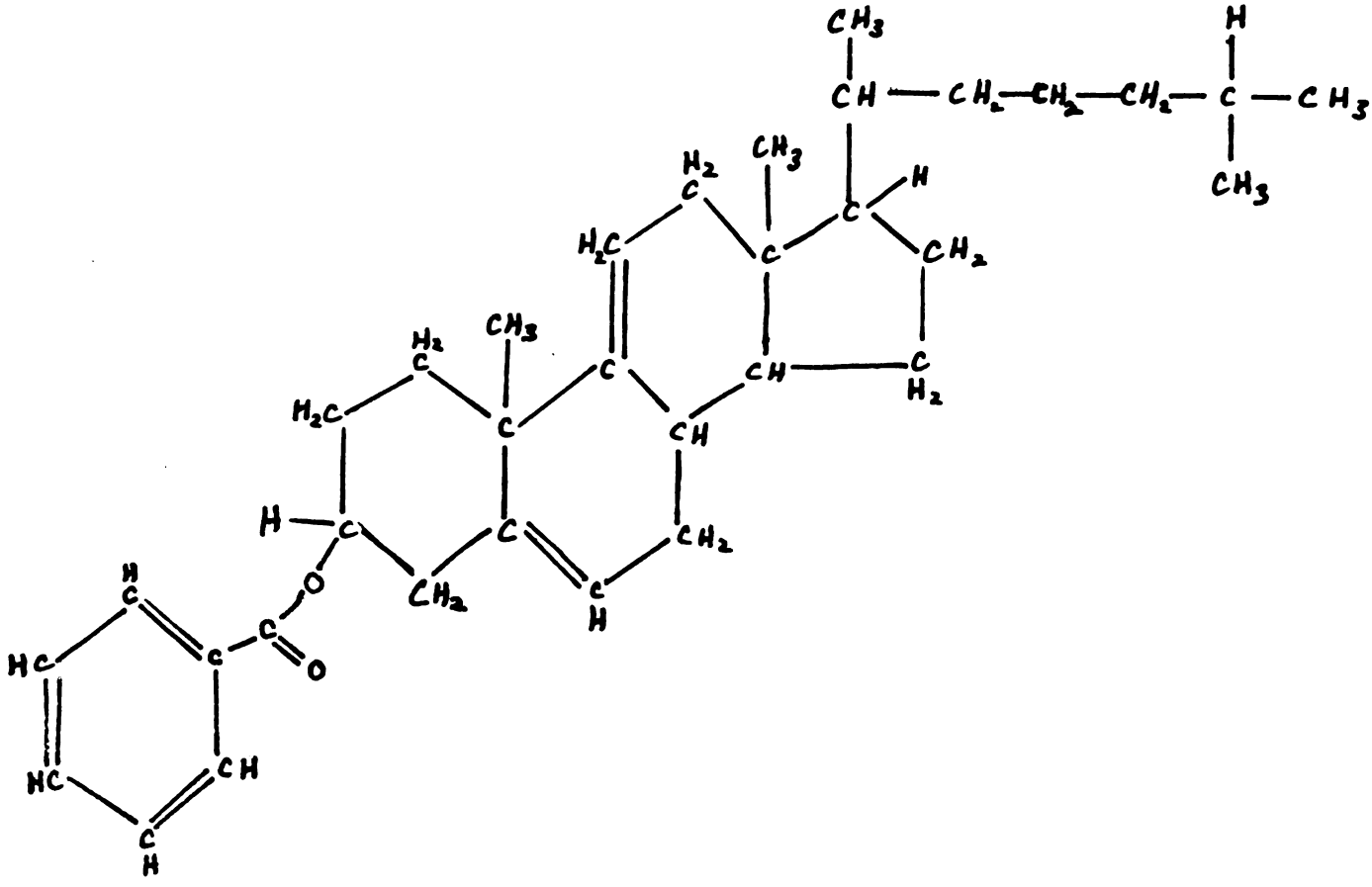


SODIUM STEARATE

L = LIQUID STATE
LC = LIQUID CRYSTAL STATE
S = SOLID STATE

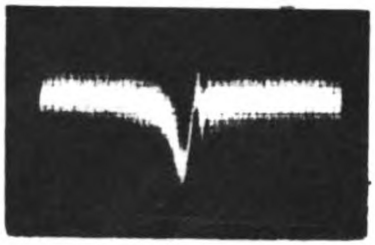


SODIUM OLEATE



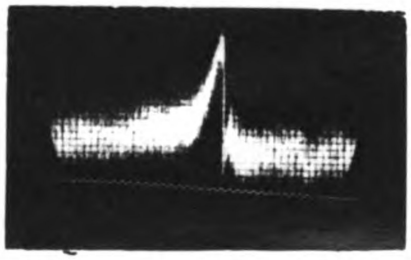
The cholesteric compound, cholesteryl benzoate, like the nematic compounds described above, also exhibits one resonance line throughout the liquid, liquid crystal, and solid states. In the liquid state the line is 0.76 gauss. As we approach the transition point to the liquid crystal state (178.5°C.), the line widens to 0.87 gauss and then quickly

SODIUM STEARATE
LIQUID STATE
MODULATING FIELD = 31 v.
TIME SIGNAL 4800/sec.

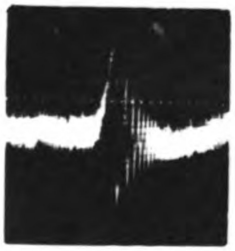


SODIUM STEARATE
TRANSITION POINT FROM LIQ.
TO LIQ.CRYSTAL STATE

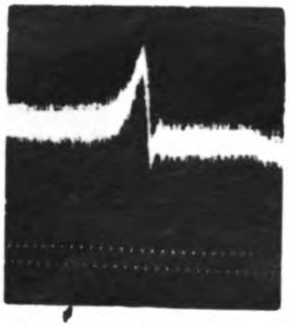
SODIUM STEARATE
LIQUID CRYSTAL STATE
MODULATING FIELD=30v.
TIME SIGNAL 4800/sec.



SODIUM STEARATE
SOLID STATE
MODULATING FIELD=64 v.
TIME SIGNAL 4800/sec.



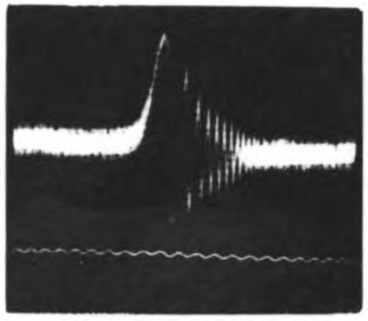
SODIUM OLEATE
LIQUID STATE



MODULATING FIELD=30v.
TIME SIGNAL 4800/sec.

SODIUM OLEATE
LIQUID CRYSTAL STATE

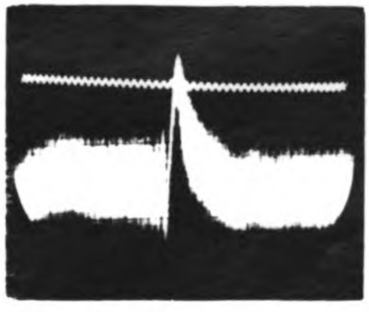
SODIUM OLEATE
SOLID STATE
MODULATING FIELD = 45v
TIME SIGNAL 4800/sec.



CHOLESTERYL BENZOATE
LIQUID STATE
MODULATING FIELD = 30v
TIME SIGNAL 4800/sec.

CHOLESTERYL BENZOATE
TRANSITION POINT FROM
LIQ. TO LIQ. CRYSTAL STATE

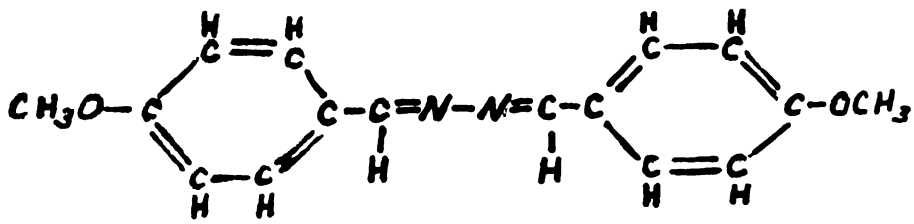
CHOLESTERYL BENZOATE
LIQUID CRYSTAL STATE
MODULATING FIELD = 30v.
TIME SIGNAL 4800/sec.



CHOLESTERYL BENZOATE SOLID STATE
MODULATING FIELD = 30v TIME SIGNAL 4800/sec.

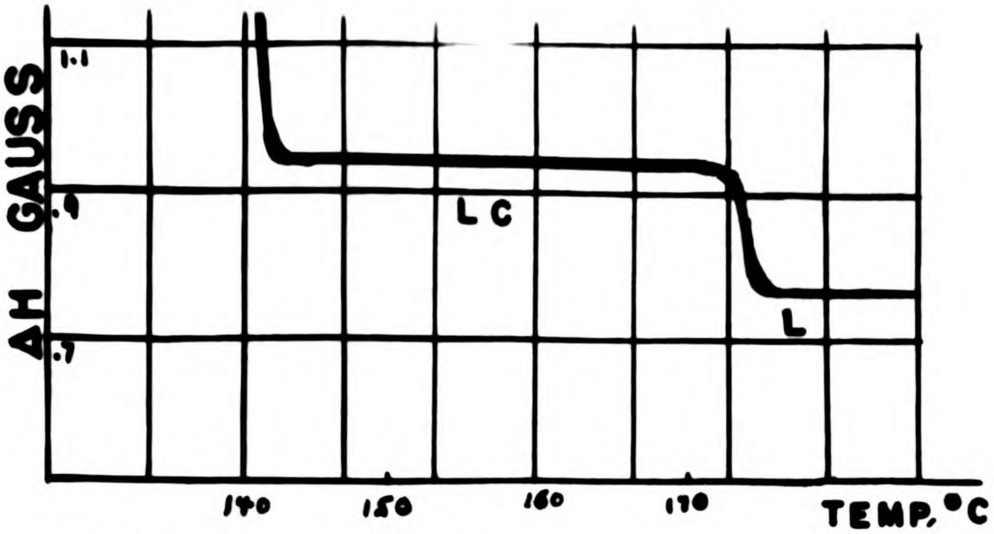
assumes the value of 0.95 gauss as the substance passes into the liquid crystalline state. This value remains quite constant throughout the mesomorphic state until the lower transition point (139.1°C.) is reached. In the solid state the average linewidth is 1.29 gauss.

ANISALDAZINE



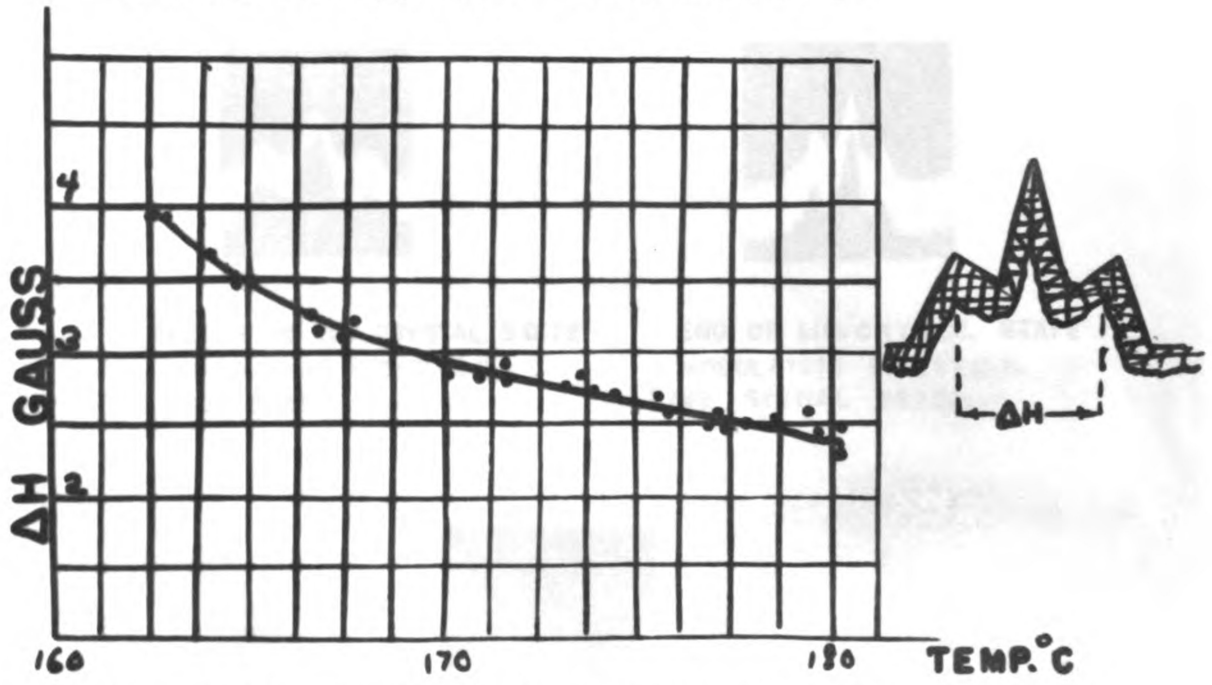
The most exciting compound of those investigated is anisaldazine, a nematic type liquid crystal. In the liquid state the linewidth is 0.72 gauss from 207°C. to 177°C. . At this point the line begins to widen until we reach 0.95 gauss, an increment above the transition point to the liquid crystal state (180.7°C.).

As the substance goes into the mesomorphic state, the line splits into three lines, the center of which is the greatest amplitude. The peak to peak distance of the outer satellites was noted carefully as the substance cooled to the solid state, and a variation of this distance plotted against temperature. This variation is not linear, but very nearly so. The total



LIQ. LIQ.CRYSTAL & SOLID STATES OF

CHOLESTERYL BENZOATE



SATELLITE PEAK VARIATION IN THE
LIQUID CRYSTAL STATE OF

ANISALDAZINE

ANISALDAZINE LINES

LIQUID STATE
MODULATING FIELD = 25v
TIME SIGNAL 10,000/sec.

BEGINNING OF LIQUID CRYSTAL STATE
MODULATING FIELD=25v
TIME SIGNAL 10,000/sec.

MIDDLE OF LIQ. CRYSTAL STATE
MODULATING FIELD=20v
TIME SIGNAL 10000/sec.

END OF LIQ. CRYSTAL STATE
MODULATING FIELD=18.3v
TIME SIGNAL 9625/sec.

SOLID STATE
MODULATING FIELD=64.5 v.
TIME SIGNAL /965 sec.

range comprises 1.36 gauss, the maximum value being 3.76 gauss at 180.7°C. and the minimum value being 2.40 gauss at 162.1°C. . The line observed from the solid state of anisaldazine is slightly greater than 3.8 gauss.

A measurement was made of the relative amplitudes of the main and satellite peaks, the average of forty readings giving a ratio of

$$\frac{\text{center peak amplitude}}{\text{satellite peak amplitude}} \quad \frac{2.14}{1}$$

This is in good agreement with theoretical predictions (see theory).[7]

ROTATION EXPERIMENT

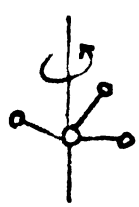
Under the assumption that the three component line of the liquid crystal state may be annihilated or its shape transformed by breaking the group structure, the sample was rotated, and a "cork-screw" object was rotated in the sample of anisaldazine. For this purpose a small air turbine motor

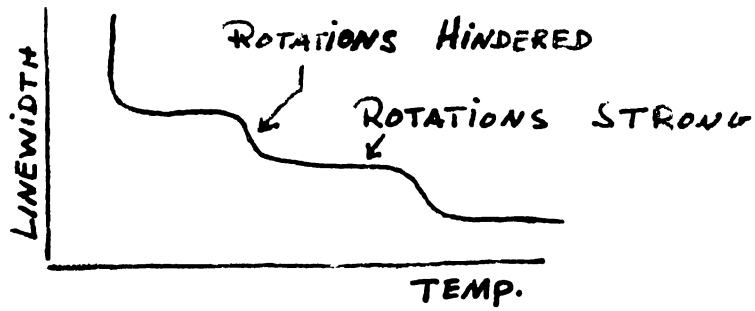
7. This portion of the thesis has been presented at the Rochester, New York meeting of the American Physical Society, June 18, 1953.

was used with a variable speed control. A negative result was obtained in all cases, the three line structure persisting throughout rotation.

THEORY

It is believed that the broadening of the absorption line, such as that observed in the smectic and cholesteric liquid crystals upon a decrease in temperature, is due to a hindered rotation of the molecules. Representing this schematically we might picture it as follows:



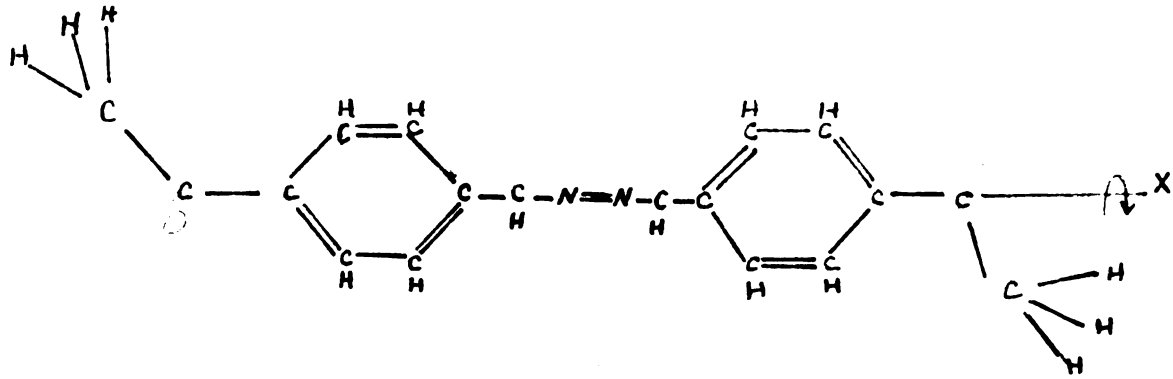


For the case of anisaldazine we have a different situation. The three lines arise from the basic configuration of the molecule and its rotation about an axis parallel to the

8. H.S. Gutowsky, G.E. Pake, "Structural Investigations by Means of Nuclear Magnetism, Hindered Rotation in Solids," Journal of Chemical Physics, vol. 18, February, 1950, pgs. 162-170.

applied magnetic field..

In order to understand this phenomenon it is necessary to redraw the anisaldazine molecule, taking into account the angle the C-O bond makes with the center structure.



Let us analyze the molecule from the end group to the N of N=N.

It can be seen from the diagram that the vector distance between the end group protons will be continually changing as the molecule rotates about the X axis, since the angles of these hydrogen atoms change.. Due to this variation, an averaging out process takes place and one single line results from all three (when applied to the whole molecule, six) protons.

The same type of reasoning does not apply to the H's in the benzene ring. Here the proton distances are fixed and the symetry of rotation leads us to a consideration of each proton individually. The interaction of protons on opposite sides of the benzene ring may be neglected, since the distances between

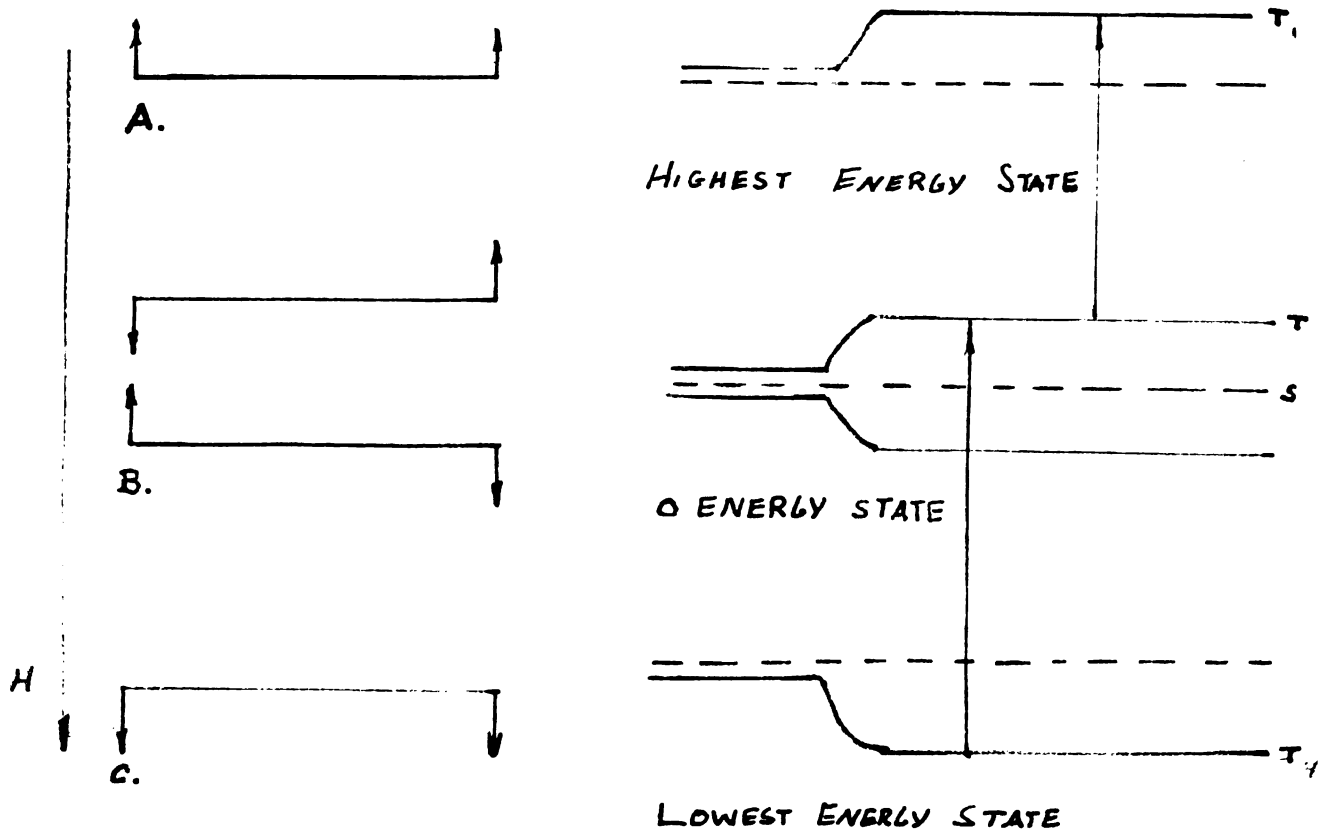
these are too large.[9] However, the two adjacent protons on each side of the ring act as a dipole and give rise to the two satellite peaks. Each set of two protons contribute to one-half of the amplitude of these peaks. Since there are three protons in the end group, plus one proton in the center group (for half the molecule) which give rise to the single line, and effectively two protons in the benzine ring giving rise to the satellite peaks, the ratio of amplitudes should be 4:2 or 2:1. This number is verified quite well by the data cited above.[10]

A quantum mechanical argument applied to the above two H's in the benzene ring leads to an elementary explanation of why we might expect two lines to arise from a dipole in an applied magnetic field.

The dipole may be orientated in three different ways with respect to the applied field, both parallel, both anti-parellel, or one parallel and the other anti-parallel to the field. This is shown in the drawing below.

9. The field due to a dipole of magnetic moment μ, at a distance r from the dipole = μ/r^3.

10. The area measured under the major and satellite peaks will bear the same ratio. The above measurement is made on the assumption that the three linewidths are equal. This is very nearly so.



Zeeman Energy States

In "A" above, the protons are such as to require a maximum amount of energy to maintain this orientation and thus belong to the state of highest energy. The minimum state is that of "C" since here the protons are aligned with the applied field. On the center diagram above, "B", we have a neutral orientation giving rise to the O energy state.

Considering the dipole alone and the individual fields of each proton, we get an additive effect in case "A". The field of proton "1" tends to superimpose on that of "2" and likewise,

the field of proton "2" tends to reinforce that of "1". The total effect is one of an even larger energy required to maintain the fixed orientation. This raises the energy level to T_1 in the diagram. We can use a similar argument to explain the lowering of the energy level to T_4 in case "C", however, now considering a partial annulment of fields. We must apply a quantum argument for the splitting of the O state into two separate energy levels, but this will not be described here.

Whereas equal transition existed between the three initial energy states, now only unequal transitions may occur between the triplet energy states (labeled T in the diagram). This gives rise to two transition frequencies possible for the hydrogen atoms. Thus the absorption line splits.[11]

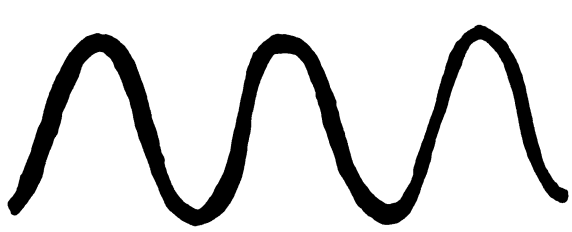
11. R.D. Spence, Colloquium, Michigan State College, April 8, 1953, and H.S. Gutowsky, a private letter to R.D. Spence upon publication of the article on para-zoxyanisole.

APPENDIX

The only new component added to the circuit described by Villaire[12] is a thirty cycle generator. A diagram and detailed explanation of various stages of this circuit is shown on the following pages.

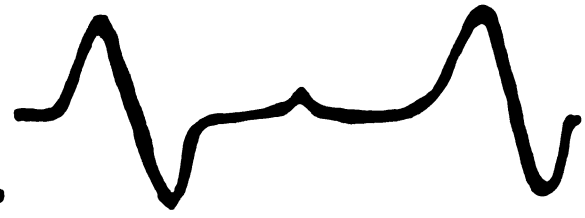
Essentially, a sixty cycle, 115 volt signal is impressed on a 6SN7 phase inverter and choke in the first stage. Due to the inductance, di/dt drops to 0 and gives rise to the wave shape shown in figure C. This resultant wave form is sent through the multivibrator and a thirty cycle pulse fed back at point D in the diagram. Smoothing out of the general thirty cycle signal pictured in figure D and clipping off of the pip occur in the final filter stage of the generator.

12. Villaire, op. cit.



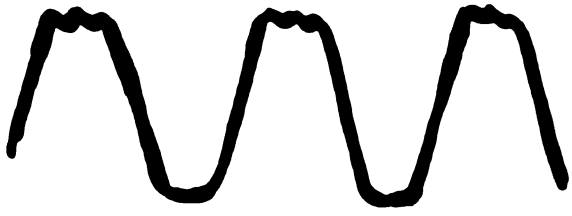
A.

INPUT SIGNAL
60 ~



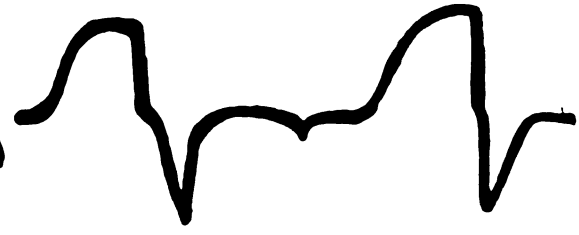
D.

SIGNAL ON CATHODE OF
VT_2 (6SN7)
30 ~



B.

SIGNAL FROM PLATE OF
VT_1 (6SN7)

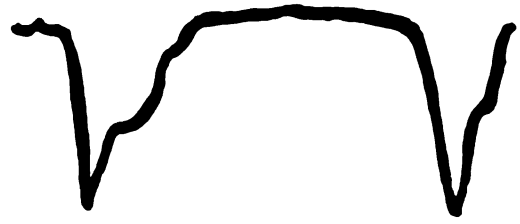


E.

SIGNAL ON PLATE OF
VT_3 (6SL7)

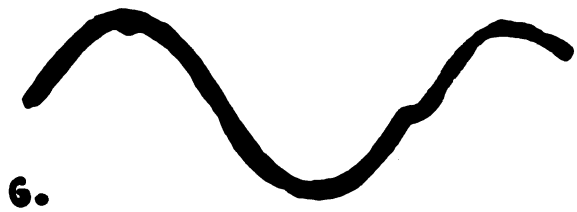
C.

SIGNAL ON GRID OF
VT_2 (6SN7)



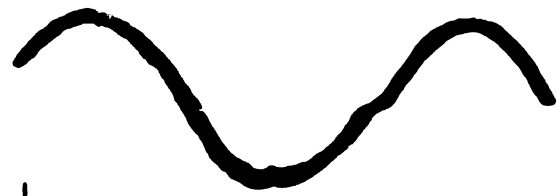
F.

SIGNAL ON GRID OF
VT_3 (6SL7)



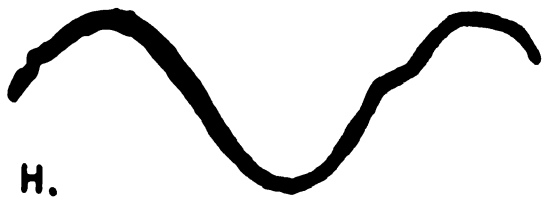
6.

SIGNAL ON CONTROL GRID OF VT_4 (6SJ7)



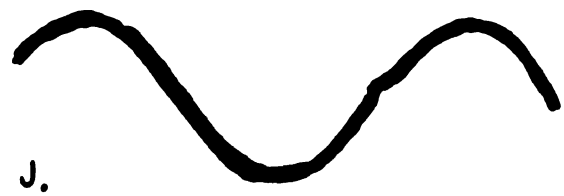
I.

SIGNAL ON GRID VT_5 (6SN7)



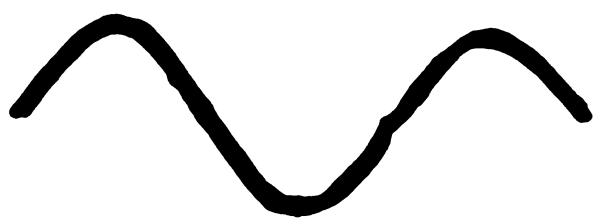
H.

SIGNAL ON PLATE OF VT_4 (6SJ7)



J.

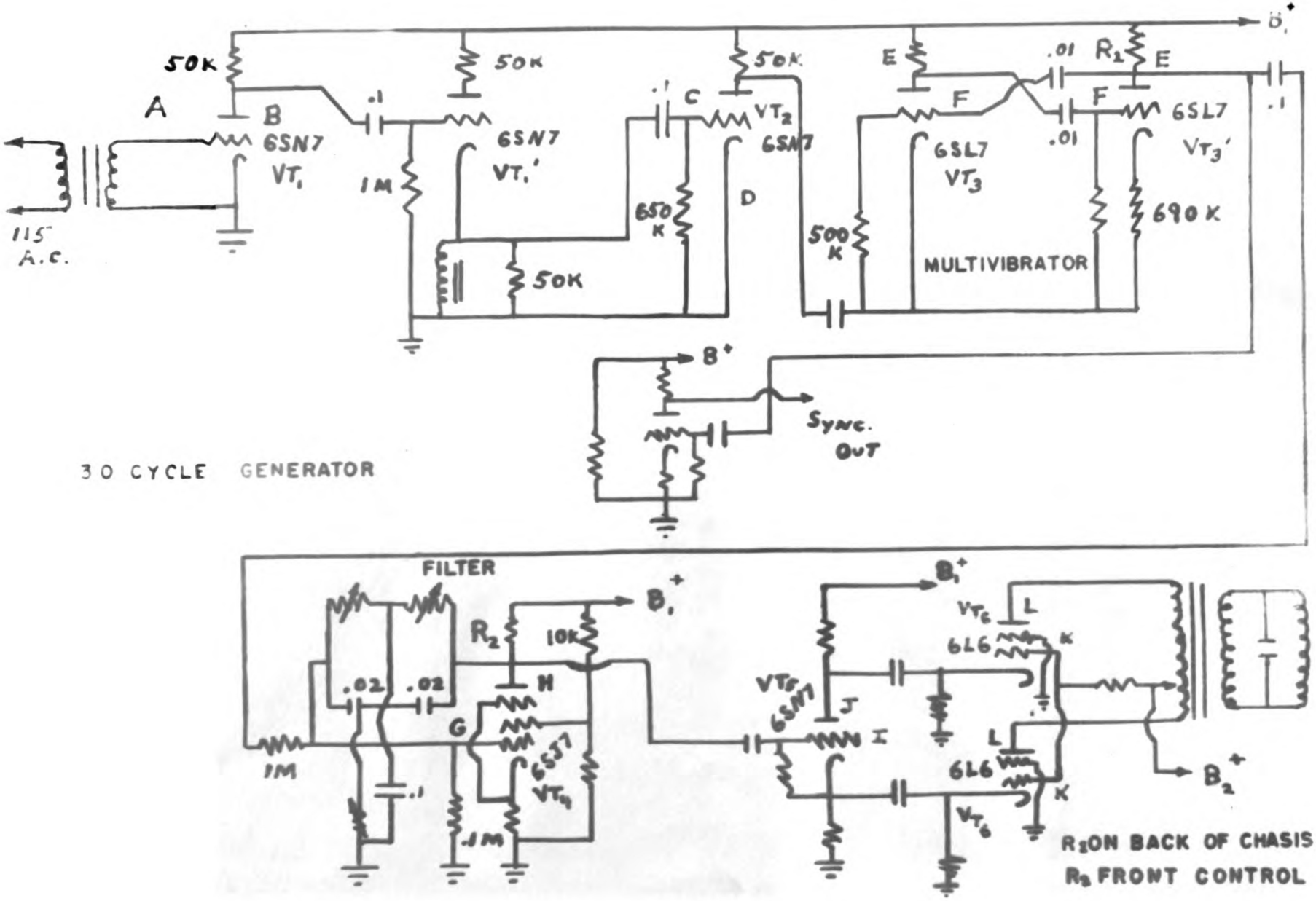
SIGNAL ON PLATE OF VT_5 (6SN7)



K. & L.

SIGNAL ON GRID & PLATE OF 6L6'S (VT_6 VT_6')

OUTPUT SIGNAL


50K
A
B
6SN7
VT1
115
A.C.
.1
1M
50K
6SN7
VT1'
50K
.1
C
VT2
6SN7
650
K
D
50K
E
.01
R1
E
F
F
6SL7
VT3
.01
6SL7
VT3'
500
K
690 K
MULTIVIBRATOR
.1
B+
Sync.
Out
30 CYCLE GENERATOR
FILTER
B1+
R2
10K
.02
.02
H
G
1M
6SJ7
VT4
.1
.1M
B1+
VT5
6SN7
J
I
VT6
L
6L6
K
L
6L6
K
B2+
R1 ON BACK OF CHASIS
R2 FRONT CONTROL

BIBLIOGRAPHY

1. R.D. Spence, H.A. Moses, P.L. Jain, "The Proton Magnetic Resonance in Liquid Crystals," Journal of Chemical Physics, vol. 21, February, (1950), pg. 208.

2. Glasstone, Textbook of Physical Chemistry, D. Van Nostrand & Co. N.Y., Sixth printing (1940), pgs. 504-508.

3. A. Luck, Design and Construction of a Laboratory Electromagnet, Masters Thesis, Michigan State College, (1950).

4. A.E. Villaire, The Radiofrequency Bridge Method of Detecting Nuclear Resonance Signals, Masters Thesis, Michigan State College, (1952).

5. W. Gallay & Puddington, "Physical States of Anhydrous Sodium Salts," Canadian Journal of Research, (1943), pg. 202.

6. H.S. Gutowsky, G.E. Pake, "Structural Investigation by Means of Nuclear Magnetism, Hindered Rotations in Solids," Journal of Chemical Physics, vol. 18, February, (1950), pgs. 162-170.