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THE INFLUENCE OF A MAGNETIC FIELD ON THE WICKOWAVE DIELECTRIC CONSTANT OF A LIQUID CRYSTAL

Ву

Edward F. Carr

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

DOCTOR OF PHILOSOPHY

Department of Physics
1954

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THE INFLUENCE OF A MAGNETIC FIELD ON THE MICROWAVE DIELECTRIC CONSTANT OF A LIQUID CRYSTAL

Εу

Edward F. Carr

AN ABSTRACT

Submitted to the School of Graduate Studies of Michigan State College of Agriculture and Applied Science in partial fulfillment of the requirements for the segree of

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Department of Physics
Year 1954

Approved	$\mathcal{R}.D.$	Spince	

The real and imaginary parts of the complex dielectric constant of the liquid crystal and normal liquid phases of pazoxyanisole and pazoxyphenetole have been measured at a frequency of 15300 Mc. The measurements were made in the absence and presence of a static magnetic field which was applied parallel and perpendicular to the microwave electric field for pazoxyanisole and parallel to the microwave electric field for pazoxyanisole and parallel to the microwave electric field for pazoxyphenetole, and at various temperatures in the liquid crystal and normal liquid phases.

The values of the complex dielectric constant were obtained by measuring the power reflected from a cell containing the sample whose length was changed by a movable short-circuiting plunger. The results for the imaginary part of the dielectric constant of p-azoxyanisole were further checked by measuring the transmission through a section of sample. This was accomplished by replacing the plunger with a matched detector.

This experiment showed that a magnetic field was capable of producing large changes in the observed values of the complex dielectric constant of compounds in the liquid crystal phase. A reorientation phenomena was observed which required a length of time varying from a fraction of a minute to a few minutes to take place after the magnetic field was turned off. By using this phenomena it was shown that

the magnetic moment responsible for the alignment in the liquid crystal phase was induced and not permanent.

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INTRODUCTION

The compounds para-azoxyanisole and para-azoxyphenetole are simple examples of substances which exhibit a liquid crystal phase. As is the case with several other of the compounds which possess such a phase, their liquid crystal phases are characterized by the fact that they flow like ordinary liquids but in the presence of an electric or magnetic field they show the anisotropy commonly associated with the crystalline phase. The temperature range of the liquid crystal phase in p-azoxyanisole is 118-135.8° C and for para-azoxyphenetol 138-168° C.

The liquid crystal phase was first observed by Reinitzer¹ in 1888. He noticed that cholesteryl benzoate melts sharply to form a turbid liquid and at a higher temperature it changes sharply to a normal liquid. Lehmann² studied these phenomena in 1889, and discovered the fact that the turbid liquid is doubly refracting and gives interference patterns in polarized light. During the past sixty-five years many observers have studied substances which possess a liquid crystal phase in the solid, liquid crystal, and normal liquid phases. These substances are usually called liquid crystals. The liquid crystal phase has been studied in the absence and in the presence of external forces such as those arising from static electric and magnetic fields

and the walls of the container in which the compound is placed. Experiments have been carried out on dielectric constants. X-ray studies. electric and magnetic susceptibility, viscosity, specific heat, and double refraction. As a result of a variety of experiments, many observers have attempted to construct a theory of the liquid crystal state. The most popular theory to date is the swarm theory, which is however not accepted by all workers in the field. Even among those scientists who accepted the swarm theory there appears to be no detailed agreement about the structure of a swarm; however, they agree that a swarm is a group of molecules that are somehow held together as a separate unit, and the number of molecules in a swarm may be the order of a million. According to the swarm theory. which was discussed by Ornstein and Kast3, the liquid crystal phase is made up of such swarms.

In the remainder of this introduction, experiments on dielectric measurements will be discussed, which are closely allied to the work reported in this thesis. The complex dielectric constant will be denoted by

$$\epsilon = \epsilon' - i \epsilon''$$

$$\epsilon' = \frac{C^2}{C^2}$$

where c is the velocity of light and v is the velocity of electromagnetic wave in the medium to be studied and ϵ'' represents the power absorbed.

Low Frequency Dielectric Constant C

The low frequency dielectric constant of these compounds has been studied by several investigators. In 1899 Abegg and Seitz measured ϵ' in p-azoxyanisole and found that it varied from 4 to 4.3, corresponding to a temperature change of 150° C down to the solid state, in the solid state it decreased rapidly to about 2.3. In 1904 Eichwald reported values of approximately 6 for ϵ' in both para-azoxyanisole and para-azoxyphenetole. Buhmer repeated the measurements on both compounds, using the same method as Eichwald, and reported 4.8 for the normal liquid state and 4.9 for the liquid crystal state for both compounds.

In the year of 1924 Jezewski⁷ and Kast⁸, independently, investigated the effect of an external magnetic field on the low frequency dielectric constant. Jezewski used the resonance method which consists of two oscillating circuits coupled together. In the primary circuit, which consisted of an inductance, and a condenser, oscillations are excited. This circuit was coupled to a secondary circuit, which consisted of two inductances and a variable condenser. At resonance

$$n = \frac{1}{2\pi \sqrt{LC}}$$

where n is the frequency of the oscillations. Resonance is obtained by varying the capacity in that part of the

circuit, which includes the condenser that is filled with the liquid to be studied. The external magnetic field was applied both parallel and perpendicular to the plates of the liquid-filled condenser. A magnetic field of 4000 gauss parallel to the condenser plates produced no noticeable change in the dielectric constant. A magnetic field perpendicular to the condenser plates (parallel to the oscillating electric field) produced a decrease in the dielectric constant with increasing field, and the change decreased with increasing temperature. The measurements were carried out at a wave length of 720 meters (.42 Mc). The results as given by Jezewski are shown in Table I where $\Delta \epsilon$ represents the decrease in the dielectric constant. Although the values of $\boldsymbol{\xi}'$ for para-azoxyanisole and paraazoxyphenetole are not in complete agreement with other results, the variation which takes place with increasing field should be significant.

Kast measurements were at a wave length of 200 meters, and his results were similar to Jezewski's in that they showed a decrease in the dielectric constant with increasing field, and also this effect decreased with increasing temperature.

Ornstein⁹ published a theoretical discussion of the anistropy of liquid crystals. His theory gave expressions for the dielectric constant of a liquid crystal in a magnetic field based on (1) molecular theory, (2) a crystal

TABLE I

THE VARIATION IN THE DIELECTRIC CONSTAIT & AS A PENCIFOR OF THE APPLIED MAGNETIC FIELD (The results were taken from a paper by Jezewski.)

Pa	ra -a zoxyan	isole (€' = 6.9)			
T = 122°	C	T = 135° C			
Field (Gauss)	$\Delta \epsilon' \epsilon'$	Field (Gauss)	$\Delta \epsilon' \epsilon'$		
300	•0r#	500	.000		
500	.020	2000	.002		
1000	.022	4000	.002		
2000	.027	7350	.003		
4000	.030				
7300	.027				
Pa	ra-azoxyph	enetole ($\epsilon' = 6.3$)			
T = 143° C		T = 154°	T = 154° C		
Field (Gauss)	$\Delta \epsilon / \epsilon'$	Field (Gauss)	$\Delta \xi' \xi'$		
150	.004.	150	.000		
300	.011	500	.022		
500	•030	1000	.040		
1000	. 948	4,000	.048		
2000	.050	7350	•049		
4000	.054				
7350	•057				

aggregation theory. The results thus obtained were compared to Kast⁸, and complete agreement was found for the crystal theory mentioned above under (2). Ornstein assumed the presence of a permanent magnetic moment in the liquid crystal which is now believed to be incorrect.

Jezewski¹⁰, in 1927, extended his studies of the effect of an external magnetic field on the dielectric constant using a wave length of 250 meters (1.2 Mc). Figure 1 taken from Jezewski's paper shows the effect of an external magnetic field, which is parallel to the oscillating electric field, on the dielectric constant for para-azoxyanisole and para-azoxyphenetole. The dielectric constant is shown as a function of temperature in the presence of a field of 5000 gauss, and also in the absence of any externally applied field. Figure 2 plotted from Jezewski's data shows the angular dependence for a magnetic field of 5000 gauss at two temperatures for each of the liquid crystals, para-azoxyanisole and para-azoxyphenetole. The dielectric constant is plotted as a function of angle, between the external magnetic field and the oscillating electric field. The results are in agreement with the relation

where ϵ_0 represents the dielectric constant for the magnetic field parallel to the electric field and ϵ_{90}

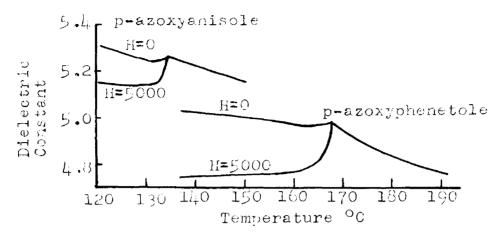


Fig. 1

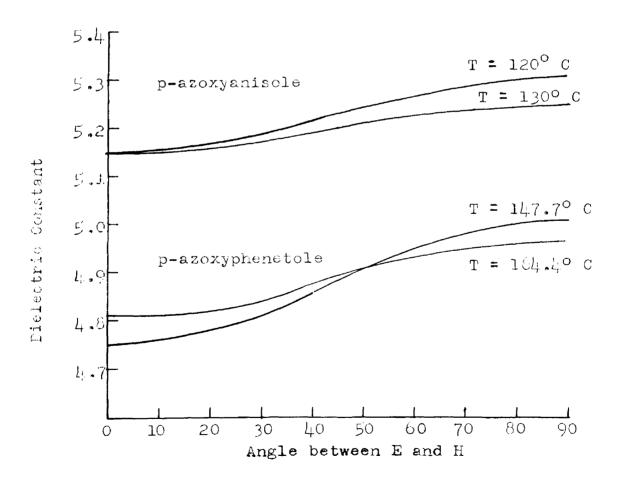


Fig. 2

for the case where the magnetic field is perpendicular to the electric field.

Kast¹¹ has, independently, studied the effect of a magnetic field at an angle with the electric field and obtained results which are in agreement with the previously mentioned results of Jezewski. Jezewski¹² has shown that small discrepancies which appeared in the previously mentioned work could be due to the orienting effect of the walls and the capacity of the condenser.

Jezewski¹³ has studied the effect of an external static electric field on the low frequency dielectric constant. He used the resonance method which is shown in Figure 3. The batteries which are indicated by B in the diagram supplied the external electric field, which was parallel to the oscillating electric field. The condenser C_{3} contained the liquid to be measured, and C_1 is a variable condenser which was used to obtain resonance. Some of his measurements for different temperatures are shown in Figures 4 and 5. The behavior of the dielectric constant ϵ' was similar to that of an external magnetic field applied parallel to the oscillating electric field, in that it decreased with increasing electric field. In the normal liquid phase, p-azoxyanisole showed a very small effect, but p-azoxyphenetole shows practically no effect due to the external static field.

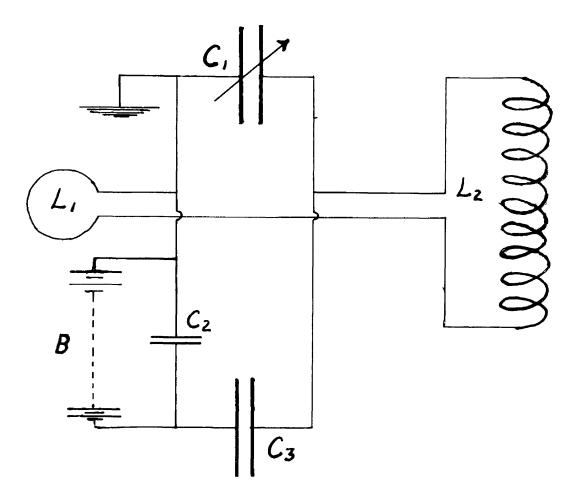


Fig. 3. Experimental set-up used by Jezewski to study the effect of a static electric field on the low frequency dielectric constant. The condenser C_3 contains the liquid to be measured, and C_1 is a variable condenser with a range of 100 - 300 MMF. The static electric field is supplied by batteries, indicated by B in the diagram, connected in series. L_2 is a coil with 20 turns and L_1 is a loop with a diameter of 21 cm.

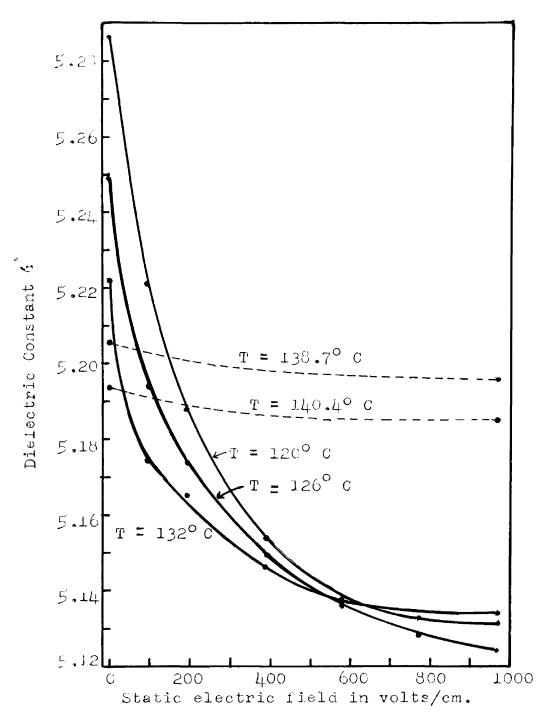


Fig. 4. The effect of a static electric field on the dielectric constant for p-azoxyanisole. Data for the plot was taken from Jezewski's data.

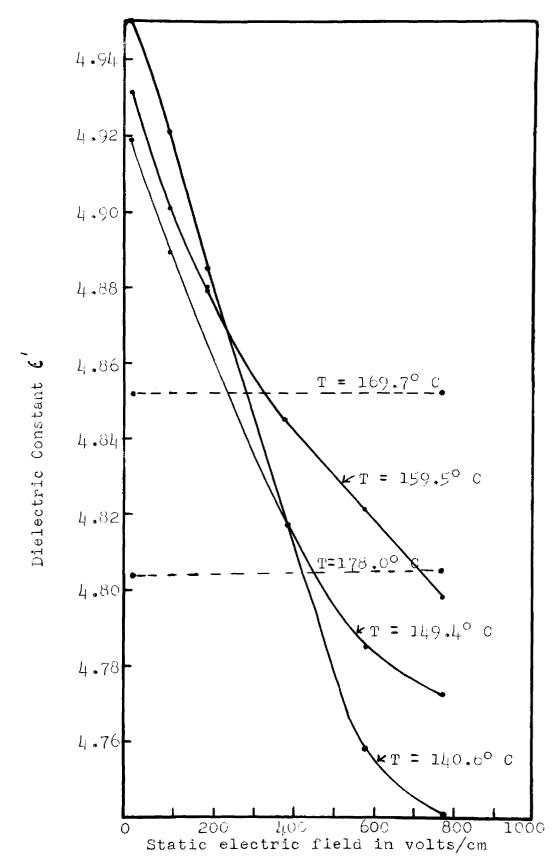


Fig. 5. The effect of static electric field on the dielectric constant for p-azoxyphenetole. Data for the plot was taken from Jezewski's data.

Jezewski¹⁴ has measured the dielectric constant in the presence of both an external static electric field and magnetic field. The magnetic field was maintained at 4000 gauss and the static electric field was varied in a manner similar to the previously mentioned experiment. Some of his results are shown in Figures 6 and 7 for the magnetic field applied parallel and perpendicular to the oscillating electric field, and for H = 0. Since the change in the dielectric constant is proportional to the capacitance change $\Delta \mathcal{C}$, the ordinate represents a change in the dielectric constant which decreases and thus $\Delta \mathcal{C}$ is indicated by negative numbers. Figures 6a, 6b, and 6c represent the same measurements on para-azoxy-anisole except they are at three different temperatures.

Maier 15 has studied the dielectric constant in the absence of an externally applied magnetic or electric field. His results, which are shown in Figure 8, show an increase in the dielectric constant corresponding to an increase in voltage for the liquid crystal state, but do not indicate any change for the normal liquid state. The results show a decrease in the dielectric constant for an increase in temperature, which agrees with the results of Jezewski 10 in the absence of any applied field. Maier discusses his results on the basis of a theory given by Freedericksz and Repiewa 16. In applying this theory it is assumed that the substance is made up of

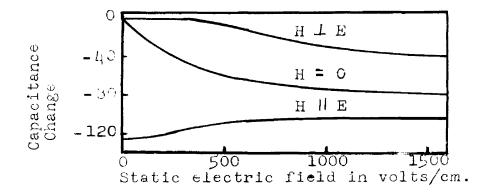


Fig. 6a. P-azoxyanisole (T = 118.6 °C, H = 4000 gauss)

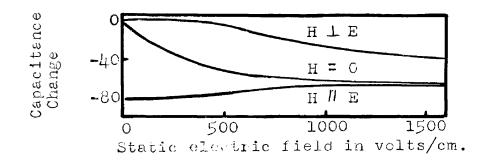


Fig. 6b. P-azoxyanisole (T = 125 °C, H = 4000 gauss)

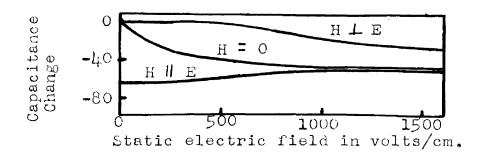


Fig. 6c. P-azoxyanisole $(T = 129.5 \text{ }^{\circ}\text{C}, H = 4000 \text{ gauss})$

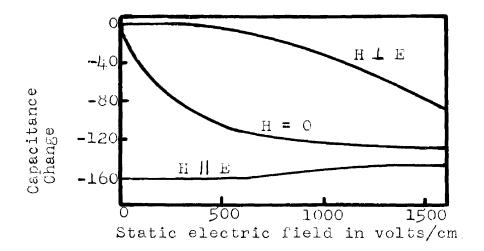


Fig. 7a. P-azoxyphenetole (T = 140.6 $^{\circ}$ C, H = 4000 gauss)

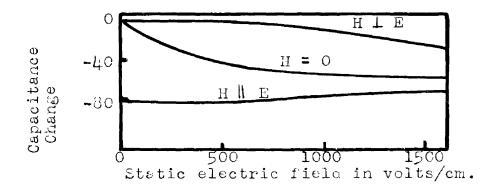


Fig. 7b. P-azoxyphenetole $(T = 165.3 \circ C, H = 4000 \text{ gauss})$

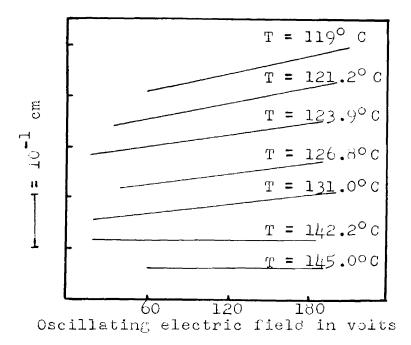


Fig. 8. The low frequency dielectric constant of pazoxyanisole as a function of the voltage of the oscillating electric field (*\mathbb{T} = .615 Mc). The electric field was varied from 22 volts to 198 volts which corresponded to a variation of 37 volts/cm to 330 volts/cm. The ordinate represents a measure of the capacity for the liquid-filled condenser which is proportional to the dielectric constant. The results in this Figure were taken from Maier.

Fig. 9. P-azoxyanisole molecule. Dipole moment.

rotationally symmetric particles of volume v, which possess the dielectric constant ϵ , in the direction of the axis of rotation and a larger dielectric constant ϵ_2 in each of the perpendicular directions. The particles are assumed to execute independent Brownian motion in the absence of any field.

Maier 17 has investigated the dielectric constant anisotropy in compounds similar to p-azoxyanisole and p-azoxyphenetole and has related the sign of the anisotropy to the dipole moments of the various groups found in the compounds. The dipole moment of the free pazoxyanisole molecule has a magnitude of M = 2.3 Debye units 18 , and the contributions to this dipole moment are indicated by the arrows in Figure 9. These contributions to the dipole moment are valid only for the free molecule. In molecular association the relative motions of different portions of the molecule with respect to each other must be taken into account. Kreutzer 19 has measured the endothermic heat of transition from the nematic to the normal liquid, and the resultant discontinuous increase in the specific heat from which he concludes that the assumed rotation of the O-CH, groups begins at the transition from the liquid crystal to the normal liquid phase and not in the liquid crystal phase.

Low Frequency Dielectric Loss &

Buhner⁶ in his measurements of the dielectric constant also mentioned something about the loss. In pazoxyanisole he reported a strong absorption for both the liquid crystal and normal liquid states, but none for the solid state. In pazoxyphenetole he reported strong absorption for the liquid crystal state, somewhat less for the normal liquid state, and none for the solid state.

From X-ray studies of p-azoxyanisole in an oscillating electric field ${\rm Kast}^{20}$ predicted a relaxation frequency of about 10^5 cycles per second. A more detailed study of this relaxation frequency was reported by Ornstein and ${\rm Kast}^{13}$ by measuring the dielectric loss in a condenser filled with p-azoxyanisole over a frequency range 5000 to 3,000,000 cycles per second. Figure 10 shows the dielectric loss as a function of frequency for two different temperatures. The results show a strong temperature dependence, since a relaxation frequency is clearly shown for T = 122° C, but does appear over the frequencies covered for T = 124° C.

$$Tan S = \frac{1}{\omega RC}$$

where ω is the angular frequency, R is the resistance of the circuit and C is the capacitance of the condenser. Figure 11 shows the critical frequency (relaxation frequency)

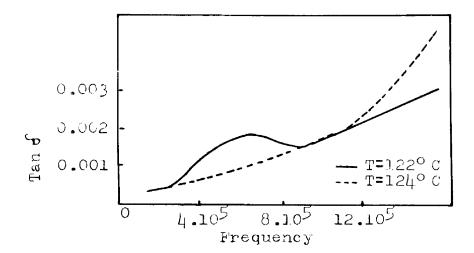


Fig. 10. Dielectric loss of p-azoxyanisole as a function of frequency. The results were taken from a paper by Ornstein and Kast.

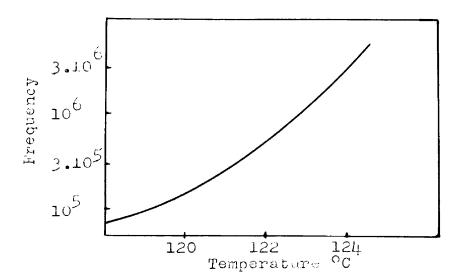


Fig. 11. Critical frequencies as a function of temperature for p-azoxyanisole. The results were taken from a paper by Ornstein and Kast.

as a function of temperature, and confirms the strong temperature dependence which is indicated in Figure 10. To obtain more accurate results from Figure 10, the increase in Tan f with increasing frequency with the condenser empty should be subtracted from the results shown. Kast and Ornstein extended these measurements down into the solid state and another loss-maximum appeared just before the crystallization occurred, which was nearly at the same temperature for all frequencies used.

Optical Studies

Double refraction in liquid crystals has been studied by many observers starting with the investigations of Lehmann² and continuing at the present time. Pellet and Chatelain²¹ have measured the index of refraction in p-azoxyanisole and p-azoxyphenetole to an accuracy of one part in fifteen hundred by using the method of prisms. Some of their results are shown in Figures 12 and 13 for two different wave lengths. They measured the index of refraction for both the ordinary and extraordinary rays over a temperature range covering the liquid crystal and normal liquid states. All measurements in the normal liquid showed no double refraction. In the liquid crystal state where some type of molecular alignment is present. the optic axis is along the axis of the molecule (long axis of the molecule) for both p-azoxyanisole and p-azoxyphenetole.

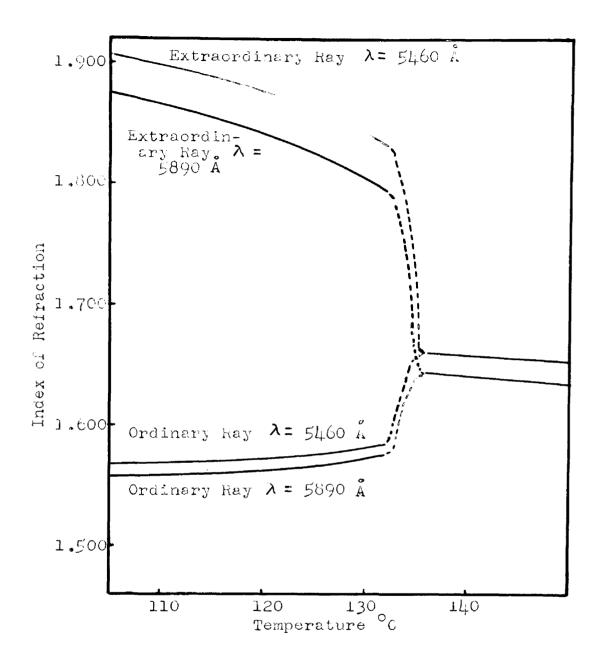


Fig. 12. Index of refraction as a function of temperature for p-azoxyanisole. This data was taken from Pelette and Chatelain's paper.

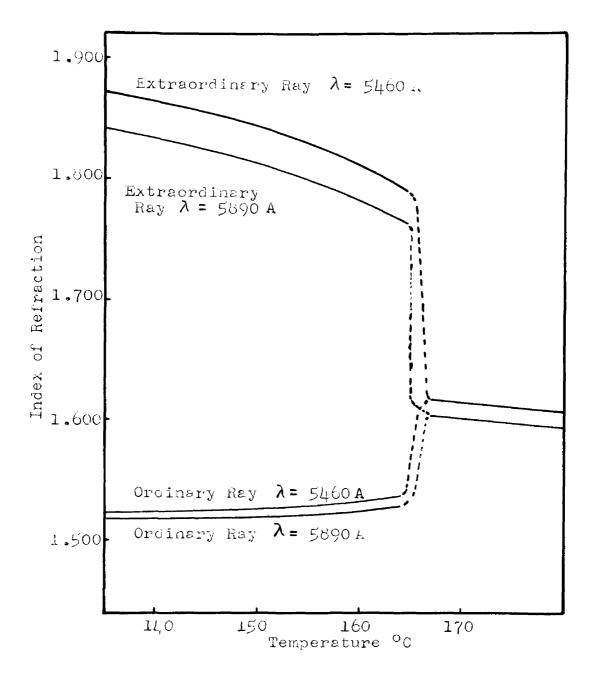


Fig. 13. Index of retraction as a function of temperature for p-azoxyphonetole. This data was taken from Pelette and Chatelain's paper.

Repiewa, Zolina and Freedericksz²² have measured the dielectric constant in the presence of a magnetic field. In their experiments it was necessary to use very thin layers, and therefore they also had the orientation effect of the walls. Much of their work consisted of studying the alignment of molecules due to a magnetic field and a wall.

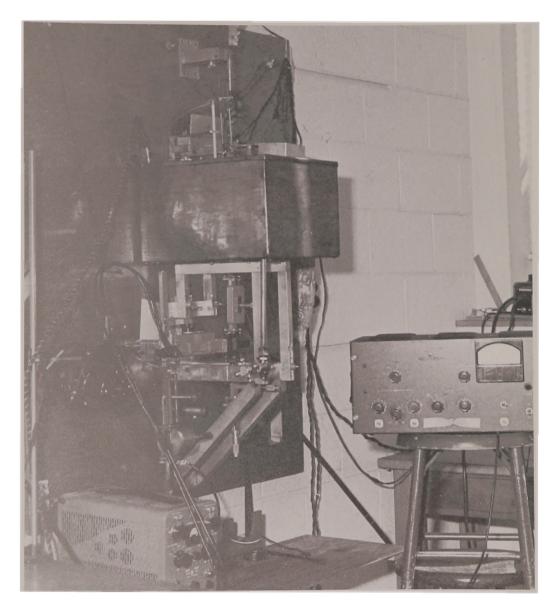
Many observers have studied the loss in the optical region, but due to another probable absorption frequency in the infra red region and the scattering of light in the liquid crystal state, the results do not seem to be very significant as far as interpreting any of the original work reported in this thesis. Some work will be mentioned briefly. Bjornstahl²³ measured the extinction coefficient for p-azoxyanisole and p-azoxyphenetole for different wave lengths and found a strong wave length dependence in the optical region. In the liquid crystal state the extinction coefficient increases with increasing temperature and decreasing wave length. The extinction coefficient in the normal liquid is much less than in the liquid crystal state. The effect of a magnetic field3 on the absorption of light has also been reported. Because of the strong orientating forces due to the walls of the container, it is difficult to get any good quantitive results with the thin layers of liquid crystal which one must use. More recent work on the effect of a magnetic 

Fig. 14. Photograph of experimental set-up

EXPERIMENTAL

Reflection Method

Figure 15 shows a block diagram of the experimental set-up. The klystron was a Varian X-12 which has a range from 12,400 Mc to 17,500 Mc. All the measurements reported in this thesis were made at 15,300 Mc. The tube was modulated by a 1000 cycle square wave from a Hewlett-Oackerd Power Supply. The microwave power was transmitted through the attenuator to the second directional coupler where most of the power was absorbed. A portion of the power was coupled into the cell containing the liquid crystal. By using a directional coupler in conjunction with the attenuator, the klystron was well isolated from the cell. The cell was a section of coin silver wave guide with a thin mica window at the bottom. fitted with a movable short circuiting plunger. Power reflected from the cell was measured by a crystal detector connected to a recorder or tuned amplifier.

The real part of the dielectric constant was obtained by moving the short circuiting plunger with a micrometer screw, and thus determining the wave length inside the cell. The imaginary part of the dielectric constant was obtained from the amplitude of the reflection maxima.

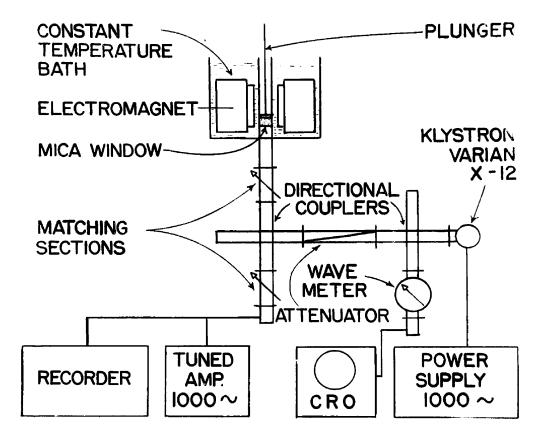
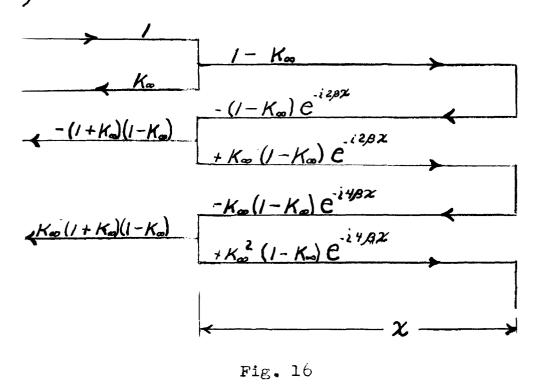


Fig. 15. Block diagram of experimental Set-up

7

The theory for computing the dielectric constant from these measurements will be presented by using the concept of multiple reflections. Figure 16 shows the relative amplitude of the various reflected and transmitted waves at the air-dielectric interface. In this figure, x represents the length of dielectric in the cell, K_{∞} the electric reflection coefficient for $x = \infty$, and β the propagation constant.



The amplitude of the incident wave is taken to be one and is indicated by the number 1 in the upper left hand corner of the diagram. The amplitude of the first reflected wave is K_{∞} , because it is what would be reflected if x was infinite, and the transmitted wave is (1 - K_{∞}). The reflection coefficient ($K_{\rm E}$) at the plunger is taken

to be -1, because we assume total reflection at the surface of the plunger, therefore the first wave which is reflected from the plunger will arrive at the air-dielectric interface with an amplitude of $-(I-K_{\infty})e^{-i2.62}$. The amplitudes of various other transmitted and reflected waves are indicated on the diagram for consecutive traversals of the cell. The amplitude of the wave to be measured will be the sum of all amplitudes for waves leaving the cell plus the first reflected wave at the air-dielectric interface, and can be written as follows

$$K_E = K_{\infty} - \sum_{n=1}^{\infty} K_{\infty}^{n-1} (1 - K_{\infty}^2) e^{-2in/3x}$$

where n represents the number of wave which is reflected from the plunger. This equation may be written as

$$\frac{K_{E}}{K_{\infty}} = 1 - \frac{1 - K_{\infty}^{2}}{K_{\infty}^{2}} \sum_{n=1}^{\infty} \left(K_{\infty} e^{-2i \beta x} \right)^{n}$$

Since this is a geometrical series, the sum may easily be evaluated and the square of the absolute value can be expressed as follows

$$\frac{\left|K_{\mathcal{L}}\right|^{2}}{\left|K_{\infty}\right|^{2}} = \frac{\left|1 - \frac{1}{K_{\infty}} e^{-2\beta''\chi} e^{-i(2\beta'\chi + \phi)}\right|^{2}}{\left|1 - K_{\infty} e^{-2\beta''\chi} e^{i(2\beta'\chi - \phi)}\right|^{2}}$$

where $\beta = \beta' - i\beta''$ and ϕ is the phase angle of $h \approx 1$.
Introducing the following notations,

$$\beta_{o} = \frac{2\pi}{\lambda_{o}}$$

$$b' = \frac{\beta'}{\beta_{o}}$$

$$b'' = \frac{\beta''}{\beta_{o}}$$

where λ_{δ} is the guide wave length in air, we have that

(1)
$$|K_E|^2 = \frac{|K_{\infty}|^2 + e^{-4b''F} - 2|K_{\infty}|e^{-2b''F}}{1 + |K_{\infty}|^2 e^{-4b''F} - 2|K_{\infty}|e^{-2b''F}|e^{-2b''F}} \cos(2b'F + \phi)$$

Since the amplitude of the observed wave is proportional to K_E , the observed power is proportional to K_E because of the square law characteristics of the crystal detector. K_E can be represented as shown in the following diagram

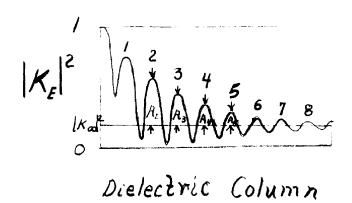


Fig. 17

where the numbers 1 - 6 indicate the points for the values of x corresponding to the first six maxima. Table II gives the values of $\left|\mathbf{K}_{\mathrm{E}}\right|^{2}$ at the different maxima for various values of the complex dielectric constant, and for two different frequencies which are in the best operating range for this set-up. In general these values could not be used to interpret results on other liquids, but they could be an aid in analyzing other results in this region.

In order to carry out the computations shown in Table II, it is necessary to obtain relations for K 00 and • . We consider the following illustration



where Zo represents the impedance in the empty wave guide and Z the impedance in the liquid dielectric. Since we have a polarized wave, the boundary conditions at the air-dielectric interface can be expressed as follows

$$E_i + E_r = E_t$$

$$H_i + H_r = H_t$$

MAXIMA FOR KENLLCTED MAVES

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MAXIMA FOR ABPLECTED WAVES

Guide N	Juide Width 1.5120 cm.	120 cm.		•	KE Tor t	the First Six Maxima	t Six Ma	xima		
Freq. ir Mc	-9	6.	0	1	2	m	4	٦	· Ş	2 00 1
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where E_{ℓ} , E_{r} , and E_{ℓ} represent the electric field for the incident, reflected and transmitted waves respectively, and H_{ℓ} , H_{r} and H_{ℓ} represent the magnetic field for the incident, reflected, and transmitted waves respectively. Using the following relations

$$Z_o = \frac{E_i}{H_i} = -\frac{E_r}{H_r}$$

$$Z_o' = \frac{E_i}{H_s}$$

we have that

$$\frac{E_{t}}{H_{t}} = \frac{E_{i} + E_{r}}{H_{c} + H_{r}} = Z_{o} \frac{E_{i} + E_{r}}{E_{i} - E_{r}}$$

$$Z_{o}^{'} = Z_{o} \frac{1 + E_{i}/E_{r}}{1 - E_{i}/E_{r}} = Z_{o} \frac{1 + K_{\infty}}{1 - K_{\infty}}$$

$$K_{\infty} = \frac{Z_{o}^{'} - Z_{o}}{Z_{o} + Z_{o}}$$

For a TE-mode the wave impedance 25 is given by

$$Z_o = \frac{\omega \mu}{\beta_o}$$

for the air filled guide and

$$Z_o' = \frac{\omega \mu}{\beta' - i \beta''}$$

for the dielectric filled guide. The relations for K_{∞} and the phase angle can be expressed as follows

$$K_{\infty} = \frac{\beta_{o} - \beta' + i\beta''}{\beta_{o} + \beta' - i\beta''}$$

$$K_{\infty} = \sqrt{\frac{1 + b'^{2} + b''^{2} - 2b'}{1 + b'^{2} + 2b'}}$$

$$\phi = Tan^{-1} \frac{b''}{1 - b'} + Tan^{-1} \frac{b''}{1 + b'}$$

In order to derive an expression for $\boldsymbol{\mathcal{E}}'$, we start with the wave equation for the axial component of the magnetic field for the TE_{Ol} mode,

$$\nabla^2 H_z - \frac{1}{v^2} \frac{\partial^2 H_z}{\partial t^2} = 0$$

where v is the velocity in the medium. The solution of this equation is

(2)
$$H_z = f(xy) e^{i(\beta z - \omega t)}$$

$$\beta^{2} = \frac{\omega^{2}}{V^{2}} - \frac{(2\pi)^{2}}{(2h)^{2}}$$

where b is the width of the wave guide. If we take M to be equal to one for a dielectric and use the following relation for the velocity in the medium

$$V = \frac{c}{\sqrt{\epsilon \mu}}$$

we have that

$$\beta^2 = \frac{\omega^2}{c^2} \epsilon - \frac{\pi^2}{b^2}$$

We next make the following substitutions and equate the real and imaginary parts.

$$\beta = \beta' - i\beta''$$

$$\epsilon = \epsilon' - i\epsilon''$$

$$(3) \quad \epsilon' = \frac{c^2}{\omega^2} \left(\beta' + \beta''^2 - \frac{\beta^2}{b^2}\right)$$

$$(4) \quad \epsilon'' = \frac{2c^2}{\omega^2} \beta'\beta''$$

where $\beta'=2\pi/\lambda_0$ and λ_0 is the guide wave-length in the dielectric. We can write equation (1) as follows

$$\frac{|K_{E}|^{2}}{|K_{\infty}|^{2}} = \frac{1 + \frac{1}{|K_{\infty}|^{2}} e^{-\frac{4}{3}i^{*}\xi}}{1 + |K_{\infty}|^{2} e^{-\frac{4}{3}i^{*}\xi}} - \frac{2}{|K_{\infty}|} e^{-\frac{2}{3}b^{*}\xi} e^{-\frac{2}{3}b^{*}\xi} + \phi}$$

and for } large we make the following approximation

$$\frac{|K_{E}|^{2}}{|K_{\infty}|^{2}} = 1 - \frac{2}{|K_{\infty}|} e^{-2b^{"\xi}} \cos(2b'\xi + \phi)$$

which may be written

$$|K_E|^2 - |K_\infty|^2 = -2K_\infty e^{-2b^*\xi}$$
 $|K_E|^2 - |K_\infty|^2 = -2K_\infty e^{-2b^*\xi}$

where the left side of this equation represents the $\mathcal{A}s$ indicated in Figure 17. From this equation we obtain the relation that

$$\beta'' = \frac{1}{\lambda_d} \ln \left(\frac{A_n}{A_{n+1}} \right)$$

We now substitute for β' and β'' in equations (3) and (4) $\epsilon' = \left(\frac{\lambda}{\lambda_{\theta}}\right)^{2} \left(1 - \left[\frac{1}{2\pi} \ln \frac{R_{n}}{A_{n+1}}\right]^{2}\right) + \left(\frac{\lambda}{2b}\right)^{2}$ (6) $\epsilon'' = \frac{1}{2\pi} \left(\frac{\lambda}{\lambda_{\theta}}\right)^{2} \ln \left(\frac{R_{n}}{R_{n+1}}\right)^{2}$

The accuracy for ϵ' was checked for ϵ' = 4 and ϵ'' = .4 and the error was found to be much less than .1 percent. The error increases by increasing ϵ'' . Equation (6) was a good approximation for ϵ'' , but was not accurate enough for the final results. The final results were

obtained by using the computed values shown in Table II. Maxima for intermediate values of $\boldsymbol{\epsilon}'$ and $\boldsymbol{\epsilon}''$ were approximated from the values given in the table.

Transmission Method

The results for the imaginary part of the dielectric constant for p-azoxyanisole were further checked by measuring the transmission through a section of sample. The experimental set-up was the same as shown in Figure 15, except the plunger was removed, and a matched detector was placed at the end of the cell. The relative power was measured for various temperatures and values of the magnetic field and for different orientations of the magnetic field relative to the electric field. Since the power measured in an electromagnetic wave is proportional to the amplitude squared, it will be proportional to the square of the right side of the equation (2) which gives the relative values of \$\mathcal{\beta}\$". If we use the following relation

$$\epsilon'' = \frac{\lambda^2}{\pi \lambda_d} \beta''$$

where λ is the wave length in air, the values of ϵ'' can be obtained.

Microwave Components

One of the directional couplers was purchased from Sperry Gyroscope Company, and the other was copied from it. The Sperry Coupler is a cross guide coupler with a

range of 12.4 - 17.0 Kmc, and its coupling is approximately 20 db. The directivity is greater than 25 db at 15.2 Kmc and 15 db at either end of its range.

The matching sections were slide screw tuners. One was purchased from Hewlett Packerd Company and the other constructed similar to it.

The variable attenuator was obtained from the Hewlett Packard Company and had a range of 0 - 20 db.

Figure 18 shows a side view of the wave meter. The cavity of the wave meter was made of brass. The top and bottom were fastened to the cylinder of the wave meter by means of four screws in each. The cavity was coupled to the wave guide by means of two small holes as indicated in the diagram. The section of wave guide shown in the diagram was an integral part of the wave meter. The screw which moved the plunger was taken from a micrometer.

In order to calibrate the wave meter, use was made of the relation

$$\frac{1}{\lambda^2} = \frac{1}{\lambda_c^2} + \frac{1}{(2d)^2}$$

where λ represents the wave length to be measured, d the effective distance from the bottom of the wave meter, and λ_{C} is the cut off wave length. For the TE_{cl} mode in a cylindrical cavity

$$\lambda_c = 1.2197(2a)$$

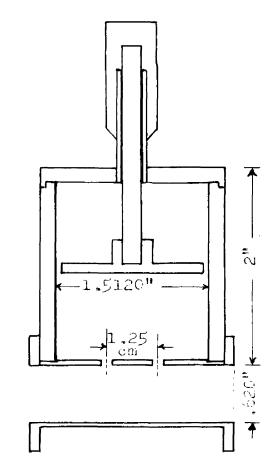


Fig. 18. Wave meter

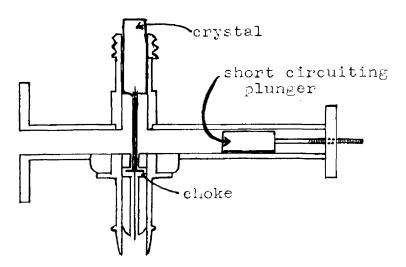


Fig. 19. Detector mount

TABLE III
WAVE METER CALIBRATION

Frequency (Mc)		TE ₀₁₂	TE ₀₁₁
14000	2.1414	.6814	.1064
14100	2.1262	.6664	•0989
14200	2.1112	.6518	•0916
14300	2.0964	.6376	.0845
14400	2.0819	. 6240	•0777
14500	2.0675	.6106	.0710
14600	2.0534	•5979	.0647
14700	2.0394	•5853	.0583
14800	2.0256	•5731	.0522
14900	2.0120	. 56 1 2	.0463
15000	1.9986	•5497	.0406
15100	1.9854	•5385	•0350
15200	1.9723	•5275	.0295
15300	1.9594	. 5169	.0242
15400	1.9467	. 5065	.0190
15500	1.9341	•4964	.0139
15600	1.9217	.l ₄ 865	•0090
15700	1.9095	•4769	.0042
15800	1.8974	.4675	0005
15900	1.8855	•4583	0051
16000	1.8737	•4492	0097
16100	1.8621	.4406	0140
16200	1.8506	.4319	0183
16300	1.8392	.4235	0225
16400	1.8280	.4153	0266
16500	1.8169	.4073	0307

where a is the radius of the cavity. The effective distance d for a certain reading on the micrometer screw was obtained by taking readings on the TE_{012} and TE_{011} modes then subtracting. This was repeated for a number of readings. It was found that the effective distance d for zero reading over the range covered was very consistant. The frequencies corresponding to the micrometer readings for the TE_{011} and TE_{012} modes are given in Table III. The fifth digit is uncertain.

The detector mount was constructed as shown in Figure 3. The type of crystals used were 1N26 and 1N31.

Temperature Bath

The dimensions of the temperature bath were 14" by 14" by 9", and it was constructed by soldering copper sides to a quarter-inch brass plate. The temperature bath contained two stirrers which were run by small electric motors, an electromagnet which was capable of producing fields up to 2000 gauss, a 500 watt immersion heater, and an external heater. The external heater was a piece of half-inch copper tubing coming out of the bottom and into the side of the bath. Part of the tube was wrapped with wet asbestos, then enough nicrome wire was wrapped around it to draw a current of 10 amperes at 115 volts. The nicrome wire was then covered with a thick layer of wet asbestos and dried.

The thermometer was placed near the bottom of the cell. The smallest division on the thermometer was 1/2 degree, and an attempt was made to calibrate it to .1 of a degree by comparison with a precision thermometer. However as a result of the open ends at the top and bottom of the cell the error in measuring the temperature was estimated to be +.5 °C.

One of the difficulties in carrying out the experiment was obtaining a suitable liquid for the bath which had the desired properties of high flash point, low viscosity, and low vapor pressure. Crisco was used first but turned rancid after being used a few times and the odor was very unpleasant. It also had the disadvantage of not being a liquid at room temperature. Gulf Crown E oil was tried next, but it was found to be much too viscous to provide the uniformity of temperature desired. Peanut oil was finally tried and proved to be very suitable in all respects.

Cell and Micrometer Screw

The cell was a continuation of the wave guide passing through the middle of the bath and about two inches from the bottom. A problem which gave considerable difficulty here was the construction of a flange joint at the bottom of the bath which would prevent hot oil from leaking in and which would at the same time minimize the microwave reflections. Rubber gaskets of various types were used

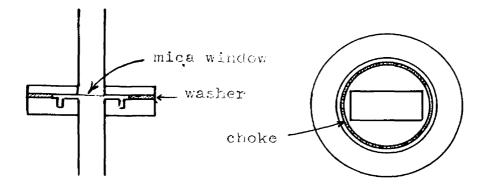


Fig. 20. Flange joint in temperature bath.

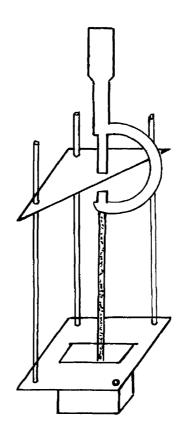


Fig. 21. Micrometer set-up.

but only silicon rubber would stand the heat. The silicon rubber available at the time was too thick for the joint. Cork gaskets were tried but they dissolved in the hot oil. The final method which proved to be satisfactory is shown in Figure 20. The flanges were soldered to the silver wave guide with pure lead using an acid flux. The flanges were held together by small screws then covered with a coat of gyptal and baked for a few hours with a heat lamp. Usually three or four coats were added in this manner to avoid a leak. Gyptal softens at high temperatures, but since it did not have to support any force, it acted like a thick glue and prevented oil from leaking in. A teflon plug one-half wave length long was tried in place of the mica window, but it softened at high temperatures and came loose.

Figure 21 shows the micrometer set-up for moving the plunger. The plunger was made of brass and was about three inches long with grooves milled in the sides for the liquid dielectric to move around the plunger.

Preparation of P-azoxyanisole and P-azoxyphenetole

The p-azoxyanisole was prepared by Mr. Caswell of
the chemistry department of Michigan State College, and
the following is his description of the method of preparation.

4, 4'-dimethoxyazoxybenzene (p-azoxyanisole) was prepared by a modification of the method of Gattermann and Ritschke. 26, 27 A solution of sodium methoxide in methanol was prepared by dissolving 60 g. of sodium metal in 600 ml of commercial C. P. grade methanol in a two-liter roundbottom flask fitted with a reflux condenser topped with a calcium chloride tube. When all of the metal had dissolved. and the solution had cooled to 35-40°C. 100 g. (0.65 mole) of p-nitroanisole (Eastman C. P. grade) was added to the solution, and the resulting mixture was allowed to stand, with occasional shaking, until a lemon-yellow color was attained. The mixture was then warmed slowly on a Glas-Col mantle until it began to boil gently. (Rapid heating resulted in a violent and uncontrollable reaction.) As the boiling point was reached, the color of the mixture became a deep red; and after 5-10 minutes of gentle boiling, a vigorous ebullition subsided gradually, accompanied by the deposition of a yellow, dense, crystalling precipitate. The mixture was then gently refluxed for an additional six hours to ensure completion of the reaction.

The reaction mixture was allowed to cool to room temperature, and was poured into a three-liter Erlenmeyer flask and diluted with 1800 ml of distilled water to complete the precipitation of the product. The resulting mixture was chilled in an ice bath and the product was recovered by filtration with suction.

The crude product was recrystallized from about 3.5 liters of methanol to which had been added approximately 20 ml of concentrated hydrochloric acid to promote crystallization 28 and to remove basic byproducts. A yield of 77.2 g (92 percent) of a yellow, crystalline powder was obtained, m.p. 120.4-120.7°C (corrected); transition point, 135.2-135.6°C (corrected).

The p-azoxyphenetole was prepared by Mr. R. V. Patel of the chemical engineering department of Michigan State College, and the following is his description of the method of preparation.

ester."²⁹, ³⁰ One mole of alkyl ester was put in a three-necked flask and 1.5 moles of a 25 percent solution of NaOH was added while stirring. The temperature was raised to 80°C and 1.5 moles of glucose was added slowly while maintaining the temperature at 80°C for 45 minutes. The mixture was filtered and washed with water. The precipitates were distilled to remove impurities, such as unreacted nitrophenyl alkyl ester or any side products. The product was purified further by recrystallization from alcohol and benzene.

RESULTS AND DISCUSSION

Dielectric Constant - E'

Figures 22 and 23 show the temperature dependence of the real part of the complex dielectric constant for paraazoxyanisole and para-azoxyphenetole in zero magnetic field and in a field of 2000 gauss parallel to the microwave electric field. Table IV gives the computed values which are plotted in Figures 22 and 23. The fourth digits are uncertain. The estimated error is about 0.1 percent for the H11 case and 0.2 percent for the other two cases. In paraazoxyanisole the results for a field of 2000 gauss perpendicular to the electric field were about 0.2 percent lower than those obtained in a zero field. Thus in this case the dielectric constant in a parallel magnetic field exceeds that in a perpendicular field. This situation is exactly opposite that found by Jezewski 10 in his measurements of the static dielectric constant. Maier 17 has interpreted Jezewski's results as indicating that the contribution to the static dielectric constant from the permanent electric dipole moment, which is perpendicular to the axis of the molecule, is greater than the contribution from the induced polarization along the axis of the molecule. Evidently at microwave frequencies the induced polarization yields the predominant effect.

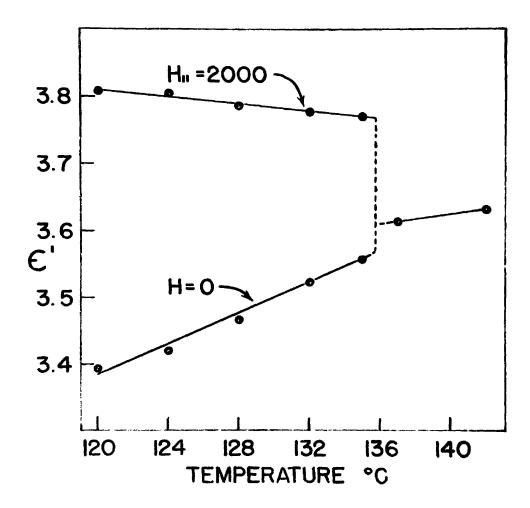


FIG. 22. Temperature dependence of the real part of the complex dielectric constant in a magnetic field of 2000 gauss parallel to the microwave electric field and in zero field for para-azoxy-anisole. Results for with a magnetic field of 2000 gauss perpendicular to the microwave electric field were found to be almost the same as for zero field. The liquid crystal range is 118 - 135.8°C.

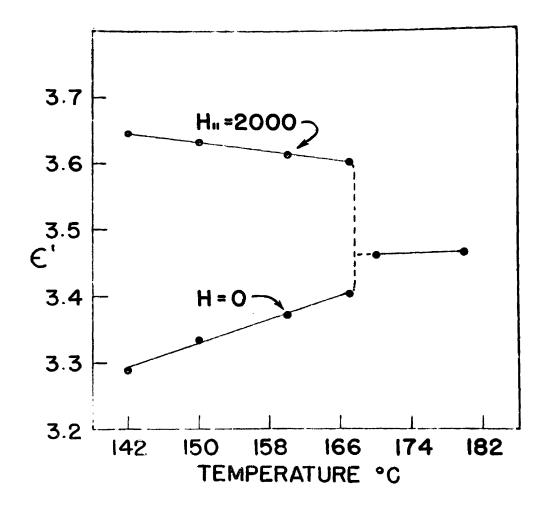


FIG. 23. Temperature dependence of the real part of the complex dielectric constant in a magnetic field of 2000 gauss parallel to the microwave electric field and in zero field for para-azoxy-phenetole. The liquid crystal range is 138 -168°C.

TABLE IV

MICROVAVE DIBINOTALO CONSTANT (7 = 15.3 hmc)

		P-azozyanisole	
Temperature in OC	H = 0	H ₁ = 2000 Gauss	N ₁₁ ≈ 200 Gauss
120	3.394		3.304
124	3.420	about 0.2	J.805
128	3.466	percent lower	3 . 786
132	3.524	-	3.779
135	3.559	than for H = 0	3.772
1.37	3.614	36.14	3.614
142	3.633	3(-33	3.633

P-azoxyphenetole

Temperature in OC	H = 0	H _{ll} = 2000 Gauss
142	3.289	3.645
150	3.334	3.631
160	3.372	3.613
167	3.404	3.602
170	3.462	3.462
130	3 . 467	3.467

At present there appears to be no satisfactory theory for dealing with the dynamic dielectric constant of an anisotropic liquid such as we are considering here. By borrowing from the theory of the complex dielectric constant of conventional liquids we may write down the following tentative expressions for the parallel and perpendicular cases.

$$(1) \epsilon_{n} = \epsilon^{i} + \epsilon_{n}^{d} - \Delta \epsilon_{n} \left\{ \frac{(\omega \Upsilon_{n})^{2}}{1 + (\omega \Upsilon_{n})^{2}} + i \frac{\omega \Upsilon_{n}}{1 + (\omega \Upsilon_{n})^{2}} \right\}$$

$$(2) \epsilon_{1} = \epsilon_{1}^{d} - \Delta \epsilon_{1} \left\{ \frac{(\omega \gamma_{1})^{2}}{1 + (\omega \gamma_{1})^{2}} + i \frac{\omega \gamma_{1}}{1 + (\omega \gamma_{1})^{2}} \right\}$$

These expressions consist of separate dipolar terms for the parallel and perpendicular cases with ϵ^i added to the parallel case to represent the contribution from the induced moment. For the dipolar terms the \mathcal{T} 's, and $\Delta \epsilon$'s denote the relaxation time and the change in the dipolar contribution to the real part of the dielectric constant in passing from $\omega \gamma \ll 1$ to $\omega \gamma \gg 1$. The ϵ^d 's represent the dipolar contributions for $\omega \gamma \ll 1$. To these equations we must add the assumptions that for this frequency of observation $(\omega \gamma_{ii})^2 \gg 1$, and that ϵ^i decreases rather markedly with temperature. The plausibility of the last assumption follows from the disorienting effect of thermal motions.

As in most liquids we should expect the "s to decrease with increasing temperature. This supposition will be further justified in the next section. Therefore, for the perpendicular

case the real part of the dielectric constant should increase with increasing temperature. For the parallel case the contribution to the real part from the dipolar term is small and its temperature dependence is unimportant compared to the decreasing contribution from $\boldsymbol{\epsilon}^2$ as the temperature increases.

Dielectric Loss - 6"

As is shown in Figure 24, the dielectric loss of the liquid crystal phase of para-azoxyanisole decreases in a static magnetic field parallel to the microwave electric field and increases if the magnetic field is perpendicular to the electric field. A similar situation prevails for the liquid crystal phase of para-azoxyphenetole. Figure 25 shows the decrease in loss in a parallel magnetic field for this Table V gives the computed values which are plotted in Figures 24 and 25. The estimated error is about two percent in the measurement of 6" except in p-azoxyphenetole for the case where H = 0 where it is about five percent. From Figures 24 and 25 it is clear that regardless of the magnitude or orientation of the applied magnetic field. increases as the temperature of the liquid crystal phase increases. The total increase throughout the liquid crystal phase is approximately the same for corresponding values and orientations of the magnetic field for the two compounds. In the case H = 0 the values of ξ'' fluctuate in time and the results plotted for this case represent

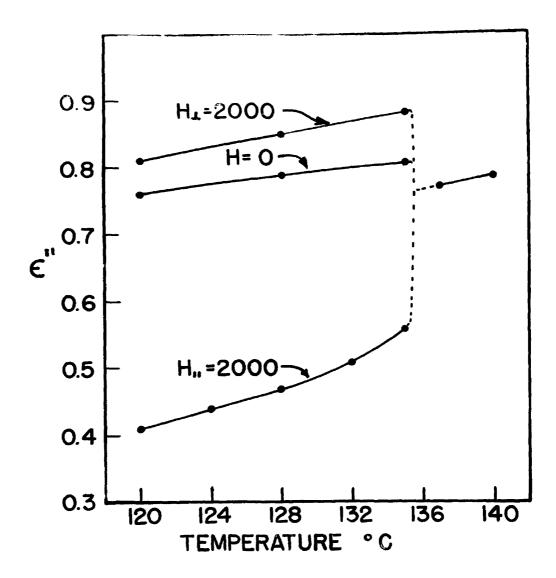


FIG. 24. The temperature dependence of the imaginary part of the complex dielectric constant in a magnetic field of 2000 gauss parallel and perpendicular to the microwave electric field, and in zero field, for para-azoxyanisole.

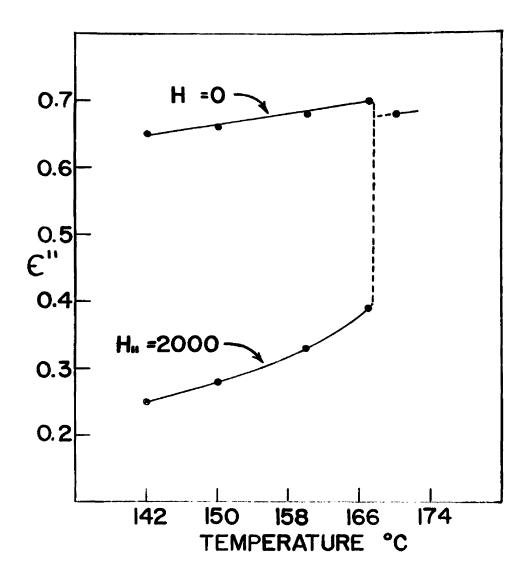


FIG. 25. The temperature dependence of the imaginary part of the complex dielectric constant in a magnetic field of 2000 gauss parallel to the microwave electric field and in zero field for para-azoxyphenetole.

(7 = 15.3 kmc)

P-azonyanisole

Temperatire in OC	11 = C	H ₄ = 2000 Ganas	II _t ∗ °C Bεulo
120	.76	.31	.41
124			· L. L.
128	•79	•ô5	· 47
132			.51
135	.31	.69	.56
137	. 78	•73	.78
•L, 2	.30	.00	.80

P-azcxypnenetole

n = 0	H _{ll} = 2000 Geouse
.65	.25
.66	, 28
• U.J	•33
.70	•39
.68	.63
	.65 .66 .63

a time average of such values. This fluctuation will be referred to again later in this thesis.

Since this frequency of 15,300 Mc was 15,000 times that at which Kast²⁰ reported finding an absorption maxima in para-azoxyanisole, it seems unlikely that the microwave absorption which was observed can be regarded as merely a high frequency manifestation of the absorption which he found. It appears that these compounds possess another relaxation frequency higher than that reported by Kast. We have previously assumed that our frequency of observation is considerably greater than 1/4 where T is the relaxation of the postulated absorption. In the simple Debye theory the relaxation time should be proportional to η/T where η is the viscosity and $\mathcal T$ is the absolute temperature. Since in equations 1 and 2, we have assumed the absorption due to the induced moment to be negligible, ϵ'' is proportional to 1/T or T/η for $\omega > 7/T$. The viscosities of paraazoxyanisole and para-azoxyphenetole in the presence of a static magnetic field have been measured by Miesowicz31 by observing the decrement of the vertical oscillations of a thin glass plate dipping into the liquid. From such observations he obtained the viscosity for various temperatures, for various values of the magnetic field intensity and for different orientations of the magnetic field in respect to the measuring plate. Before we can apply his data to this problem we must form some picture of the relation between

the molecular motion induced by dipping the plate at a given angle with respect to the magnetic field, and that produced by the microwave electric field applied at a given angle with respect to the magnetic field. Since the long axis of paraazoxyanisole and para-azoxyphenetole molecules is the axis of lease diamagnetic susceptibility, they tend to orient themselves with this axis parallel to the magnetic field. has shown that the permanent electric dipole moment for liquid crystals with a central azoxy group is transverse to the long axis of the molecule, and therefore the application of a microwave electric field parallel to the magnetic field tends to produce a rotation about an axis perpendicular to the plane of the permanent electric dipole moment and the magnetic field. The appropriate viscosity for the case in which the electric field is applied parallel to the magnetic field is that observed when the dipping plate is perpendicular to the magnetic field and therefore to the long axis of the molecules. this case the motion induced in the molecules by the motion of the plate is also about an axis perpendicular to the magnetic field. Figure 26 shows the plotted values of for para-azosyanisole calculated from Miesowicz's data as a function of temperature in zero field and in a field of 3800 gauss perpendicular to the dipping plate. Althoug a detailed comparison of Figures 24 and 26 reveals certain numerical discrepancies, there is sufficient agreement in the general form of the two plots to suggest that our simple model is

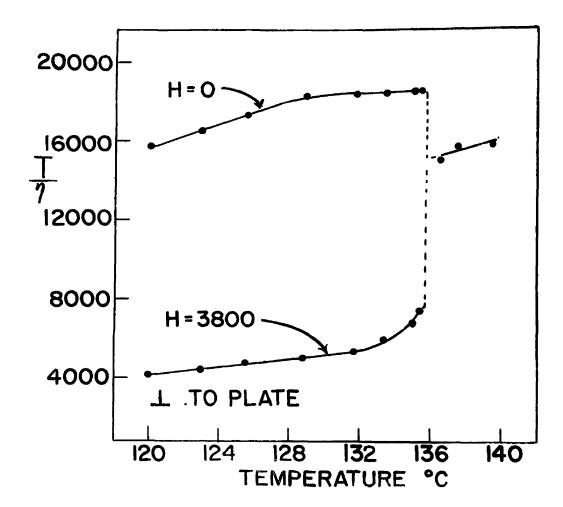


FIG. 26. Temperature dependence of the quantity 7/7 where T is the absolute temperature and 7 is the viscosity from Miesowicz's data.

essentially correct. Such differences as do appear may possibly be explained by

- a) the fact that the measured viscosity is a macroscopic rather than a microscopic viscosity implied by the Debye theory,
- b) the constants of proportionality between τ and η/τ are different for the case H = O and H parallel to the electric field,
- c) a small temperature and field dependence of the quantities $\Delta \epsilon$ and ϵ^d .

The order of magnitude of **\(\)** in the liquid crystal phase is the same as for the normal liquid, and this indicates that the loss is primarily due to a rotation of the molecules rather than a rotation of swarms.

Figure 27 shows the field dependence of the imaginary part of the complex dielectric constant for para-azoxyanisole at a temperature of 124°C. In para-azoxyphenetole the results of the field dependence were quite similar to those of para-azoxyanisole. The general shape of this curve is very much like that observed by Miesowicz, for the field dependence of the viscosity. Miesowicz's results show the region of saturation to be at a higher field than shown by our results, but this could be expected on the basis of the orientation phenomena to be discussed next.

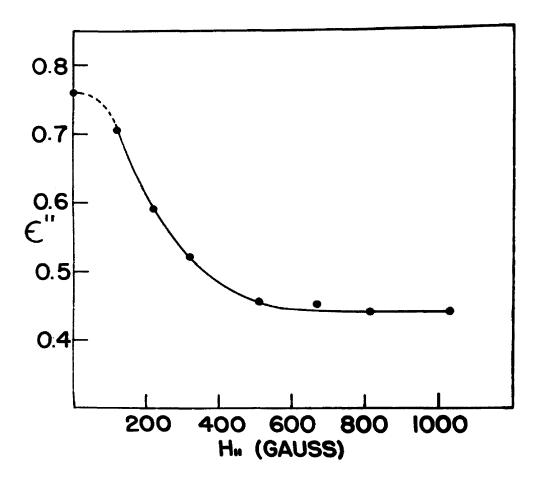


FIG.27. Field dependence of the imaginary part of the complex dielectric constant for para-azoxyanisole at a temperature of 124°C.

Reorientation Phonomena

It was shown earlier that the microwave dielectric loss in the liquid crystal phase of para-azoxyanisole and para-azoxyphenetole is decreased by the application of a magnetic field parallel to the microwave electric field. If the magnetic field, which produces the anisotropy of the liquid crystal phase, is suddenly turned off, a length of time varying from a fraction of a minute to a few minutes is required for the liquid crystal to return to the zero field distribution. This can be shown by measuring the change of the dielectric loss after the external magnetic field is turned off. The time required to return to the zero field distribution is dependent upon the temperature, and decreases as the temperature is increased. For any given temperature there is some variation in the "orientation" time. This variation appears to be related to the fluctuations observed in the measurements of & in zero field. These may have their source in thermal currents in the liquid crystal phase.

By suddenly reversing an externally applied magnetic field of about 200 gauss, it can be shown that the aligning effect of the magnetic field is entirely due to the diamagnetic nature of these compounds. At the field and temperature, at which the observations were made, about one minute was necessary to produce the alignment in the liquid crystal, when the field was turned on. If the alignment were due to a permanent magnetic moment the molecules or swarms would

have turned over when the field was reversed and while turning over they would pass through a state of random orientation. Due to the long time required for the alignment to take place, this random distribution would have caused a change in the dielectric loss as the magnetic field was reversed. Reversing the magnetic field showed that there was no turning over of the particles which implies that the magnetic moment in para-azoxyanisole is induced.

It is interesting to consider the effect of this reorientation relaxation process on other measurements. For
example one might question whether viscosities measured
by an oscillating plate such as used by Miesowicz can actually be considered as the true viscosities if the period of
oscillation is much less than the time for the disturbed liquid to return to its original orientation.

BIBLIOGRAPHY

- 1. Reinitzer, F. Beiträge zur Kenntnis des Cholesterins. Monatshefte für Chemie (Wien) 9:421 (1888).
- 2. Lemman, C. Oper fliessende Krystalle. Z. 1. phys. Chem., L3:129 (1889).
- 3. Ornstein, L. and Kast, W. New Arguments for the Swarm Theory of Liquid Crystals. Faraday Soc. Trans., 29: 931-944 (1933).
- 4. Abegg, A. and Seitz, W. Über das dielektrische Verhalten einer kristallinischen Flüssigkeit. 2. f. phys. Chem., 29:491 (1899).
- 5. Eichwald, E. Neue Untersuchungen über die kristallinischen Flüssigkeiten. Inauguraldissertation. Marburg (1904).
- 6. Schenck. Kristallinische Flüssigkeiten. Leipzig (1905). 157 pp.
- 7. Jezewski, M. Dielectric Constant of Liquid Crystals in a Magnetic Field. J. de Physique et le hadium. 6:59-64 (1924).
- 8. Kast, W. Dielektrische und Leitungsanisotiopie der flüssigen Kristalle. Ann. d. Physik, 73:145-160 (1924).
- 9. Ornstein, L. S. Die Theorie flüssiger kristalle mit besonderer Berücksichtigung der Øielekbrizitätskonstanten und der elektrischen Leitfähigkeiten. 4. f. krist., 79: 30-121 (1931).
- 10. Jezewski, M. Über elektrische Anisotropie der kristallinischen Flüssigkeiten. Z. Physik, 40:153-160 (1927).
- 11. Kast, W. Dielektrische Untersuchungen an dem anisotropen Zustand des para-Azozyanisols. Ann. d. Physik, 83, 3: 351-417 (1927).
- 12. Jezewski, M. Über dielektrische Anisotropie der nematischen Flüssigkeiten im magnetischen Feld. Z. Physik, 52: 268-274 (1928).
- Jezowski, M. Über den Einfluss des elektrostatischen Feldes auf die Dielektrizitätskonstante der Körper in nematischer Phase (flüssige Kristalle). Z. Physik, 51:159-164 (1928).

- 14. Jezewski, M. Über die dielektrischen Eigenschaften der nematischen Flüssigkeiten im gleichzeitigen magneto-und elektrostatischen Folge. Z. Physik, 52:878 (1928).
- 15. Maier, W. Die Felcstärkeabhängigkeit der Dielektrizitätskonstante des p-Azoxyanisols. Ann a. Physik, 33: 210-225 (1938).
- 16. Fréedericksz, V., and Remiewa, A. Theoretisches und Experimentalles zur Frage nach der Natur anisotropen Flüssigkeiten.. 2.1. rnysik, 42. (:532-540 (1927).
- 17. Maier, W. Zur Frage der molekularen Struktur kristalliner Flüssigkeiten: II Die dielektrische Anisotropie geordneter kristalliner Flüssigkeiten vom Typ des p.p'-Azoxyanisols. 2. Naturforsch., 2a:458-465 (1947).
- 18. Errera, J. Elektrisches Moment des p-Azoxyanisols. Phys. Zeits. 29:426-429 (1928).
- 19. Kreutzer, C. Kalorimetrische Messungen beim Übergang von der anisotropen zur isotropen flüssigen Phase.
 Ann. d. Physik, 33:192-209 (1938).
- 20. Kast, W. Anisotrope Flüssigkeiten (Flüssige kristalle) im elektrischen Felde. Z. Physik, 71:39 (1931).
- 21. Pellet and Chatelain. Sur les indices des cristaux liquides mesure par la methode du prisme et étude theorique. Bull. soc. franc. mineral, 73:154-172. (1950).
- 22. Fréedericksz, V., and Zonlina, V. Forces Causing the Orientation of an Anisotropic Liquid. Faraday Soc. Trans. 29:919-930 (1933).
- 23. Bjornstahl, Y. Untersuchungen über anisotrope Flüssigkeiten. Ann. G. Physik, 56:161-207 (1918).
- 24. Zwetkoff. Streuung des Lichtes durch anisotrope Flussigkeiten Parts I and II. Acta physicochimica. 9.1:111-140 (1938).
- 25. Ramo and Whinnery: Fields and Waves in Modern Radio, John Wiley and Sons. (1944).
- 26. Gattermann and Ritschke, Berichte, 23, 1739 (1890).
- 27. Vorlander, Lerichte, 1423 (1907).
- 28. Blatt, A. H. "Organic Syntheses," Coll. Vol. II, Pp. 57-58. John Wiley and Sons., Inc., (1943).

- 29. Gaudry, N., and Reirstead, N. F. Chloronitropenzones by Dextrose and by Sodium Arsenite. Can. J. Research, 278:8906 (1949).
- 30. Galbraith, H. w., Degering, E. F. and Hitch, E. F. J. Am. Chem. Soc., 73:1323 (1951).
- 31. Miesowicz, M. Der Einfluss des magnetischen Peldes auf die Viskosität der Flüssigkeiten in der nematischen Phase. Bull. Acad. polon d. Sciences et Letues (Serie A):223-247 (1936).