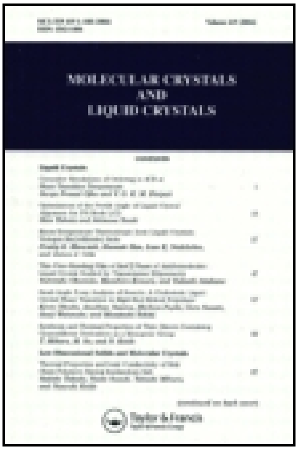


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# Low Frequency Electrical Properties of Nematic p,p′ Azoxyanisolet

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# Low Frequency Electrical Properties of Nematic *p,p′* Azoxyanisole‡

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**Abstract**—The dependence of the electrical characteristics of *p, p′* azoxyanisole on time, voltage and history was measured in order to determine whether this substance is ferroelectric in the nematic state. The results imply that the observed remanent polarization (hysteresis) and the nonlinearity of the low-frequency impedance are due to electrochemical processes rather than to ferroelectricity.

## Introduction

Nematic liquid crystals in field-free thermal equilibrium exhibit a long range order direction which changes significantly over distances of the order of microns. This structure, considered in conjunction with the relatively high molecular mobility, suggests that domain-inducing electric fields may occur—in analogy with ferroelectric solids.

At low frequencies several nematic liquid crystals exhibit nonlinear impedance and hysteresis.[1,2,3] Because these effects resemble the behavior of ferroelectrics, it has been suggested[1,2] that the investigated nematic substances may also be ferroelectric.§ On the other hand, the Saupe–Maier theory,[4] which successfully explains many aspects of liquid crystal structure, predicts the absence of polar ordering.[4,5]

Evidently, the question of whether or not nematic liquids are

‡ Work supported by a NASA Institutional Grant.

§ The " ferroelectricity " envisioned here is of course not one of the standard varieties discussed in the case of solids.

ferroelectric is of central importance to the theory of the phase. The present experiments were chiefly intended to answer this question. The applicable portion of our experimental results qualitatively agrees with previous work. However, additional information indicates that the non-linearities and hysteresis are due to the motion and accumulation of charge carriers.

The effect of a magnetic field applied parallel to the electric field was also investigated. It was found that a 6000 G magnetic field, sufficiently strong to align the phase,[6] altered the conductivity by less than 10% and did not affect the remanent polarization in a consistent way. Since the possibility of antiparallel domain alignment rules this method out as a strong test, it will not be mentioned again.

## Experimental Method

A circular parallel plate capacitor with 10 cm$^2$ polished copper electrodes, separated by one or more 0.01 cm thick Teflon spacers, was used. The cell was cleaned with benzene and acetone before each new sample was introduced. The temperature was controlled by circulating oil. All measurements were performed between 120° and 127° C. The maximum temperature drift for any particular set of measurements was 2° C; in most cases the variation was less than 1° C. Distillation Products or Aldrich *p,p'* azoxyanisole was employed; there were no significant differences between the two materials. The resistivity was typically of the order of $10^9$ ohm cm, which suggests an impurity content comparable to values reported in the earlier work.[2]

The principal measuring circuit is indicated in Fig. 1. As in references 2 and 3, an electrometer-matched Sawyer-Tower circuit was also used to obtain Lissajous figures and hysteresis loops. After we had ascertained that our sample behaved in the manner previously reported, the Sawyer–Tower method was abandoned in favor of the similar, but more easily interpretable circuit of Fig. 1. Low frequency phenomena were taken through several cycles to establish dynamic equilibrium.

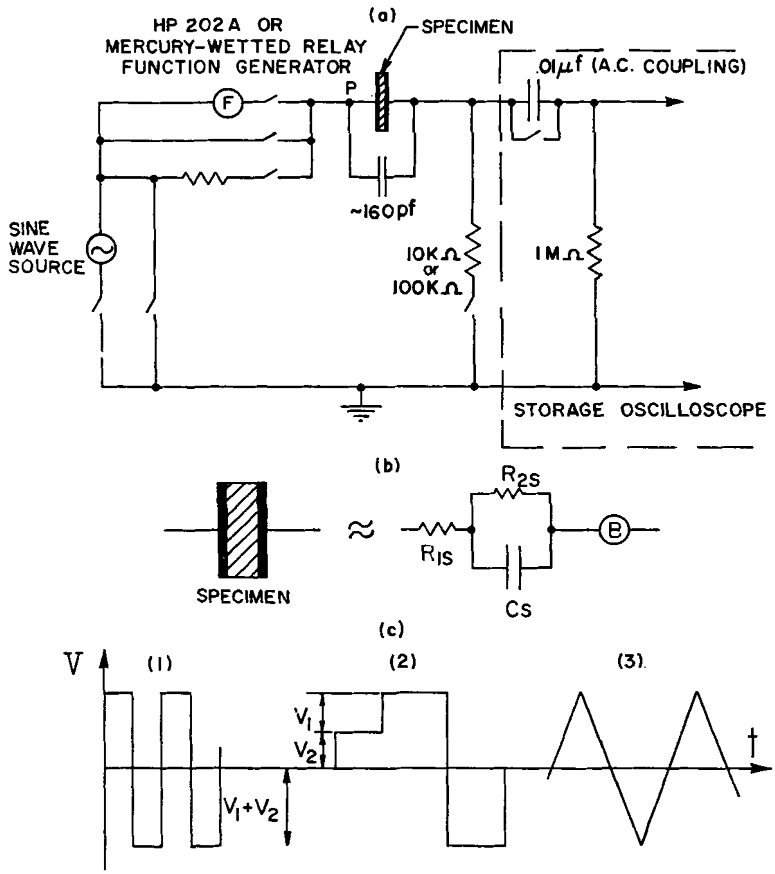


Figure 1. (a) Measurement circuit. The switches choose between various input impedances and exciting signals. The oscilloscope horizontal amplifier is connected to point $P$ for obtaining I–V plots. The oscilloscope was sometimes replaced by an electrometer-matched strip-chart recorder.

(b) Specimen equivalent circuit. $B$ is a history-dependent voltage source. $R_{2s} \simeq 1M\Omega$ and $R_{1s}$ is probably much less than $R_{2s}$. Both $R$'s depend on total voltage applied and history.

(c) Function generator wave forms. The frequencies in (1) and (3), the step durations in (2) and the voltage amplitudes are variable.

## Experimental Results

### I. I–V Curves

The circuit of Fig. 1, with triangular ramp excitation, Fig. 1 (c3), was used to inspect the frequency dependence of hysteresis loops and nonlinearities. The circuit yields I–V plots since the voltage drop across the 10 or 100 kΩ load resistor was negligible compared to that across the specimen. The resulting I–V loops (Fig. 2) are seen to be dominated by a resistive component which becomes progressively more nonlinear as the frequency drops below 1 cps. A depolarization or discharge current at zero applied electric field is also observed. This current is not just a normal capacitive discharge since its duration is $\gg RC$, where $C$ is the specimen plus lead-wire capacity, and $R$ is the specimen resistance plus other resistances in series with it. Thus it is apparent that nonlinear and hysteretic behavior of the specimens occurs for cycling periods longer than about one second.

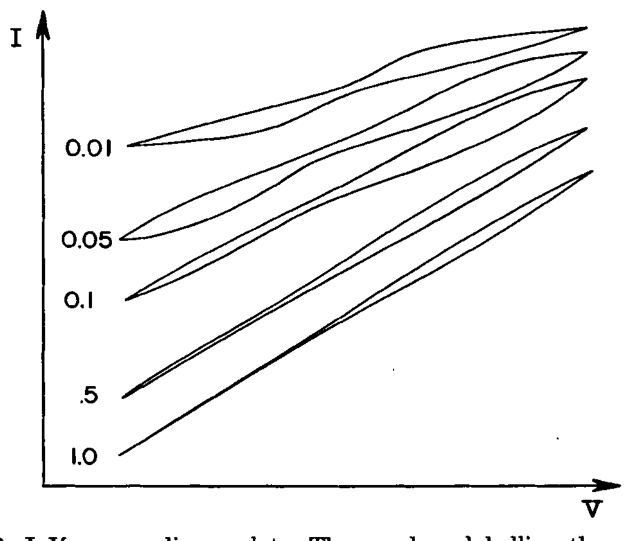


Figure 2. I–V curves, linear plot. The numbers labelling the curves are frequencies, in cycles per second. Successive curves are displaced for better visibility.

## II. Current Transients

In order to find the cause of the above-described hysteresis and nonlinearity, transient and AC plus transient measurements were performed. The circuit of Fig. 1, utilizing exciting wave form (c2) was employed to obtain the transients shown on Fig. 3(b). The exciting wave form is also given on Fig. 3(a). Because of the wide variations in amplitude and time scale of the observed effects, Fig. 3(b) is somewhat schematic. Figure 3(c) shows the actual shape of the peak near $t_3$; it is typical also of opposite polarity peaks, as near $t_4$. The initial $RC$ spike is shown schematically on Fig. 3(c), since its time scale is again much smaller than that of the main effect. The indicated time $\tau$ is defined as the interval between voltage reversal and the peak in the current transient. Figure 3(b) also schematically depicts $I_r$, a "depolarization," or " discharge," current of small amplitude which continues to flow long after the exciting voltage is removed. The time dependence of $I_r$ is not exponential. The initial decay to approximately half amplitude requires times of the order of minutes. The process can be hastened by shorting the specimen. The observed effect is similar to that described by Hart and Mungall.[7]

If $I(t_i + \Delta t)$ is the total current at time $t_i + \Delta t$, the voltage $V_i$ having been applied at $t_i$, and if $I_i$ is the asymptotic value of $I(t_i + \Delta t)$, then

$$I(t_1 + \Delta t) - I_1 \gg I(t_2 + \Delta t) - I_2,$$

where $t_2 > t_1$, and $V_2 = 2V_1$. I.e., the first transient is much larger than subsequent transients. The currents $I_i$ varied approximately linearly with $V_i$ as did $I(t_1 + 0) - I_1$. There were several unexplained, but probably history dependent, deviations from this behavior. The charge integrals

$$q = \int_0^{t_f} \{I(t_1 + \Delta t) - I_1\} \, d(\Delta t)$$

were also approximately linear in the applied voltage $V_1$. The

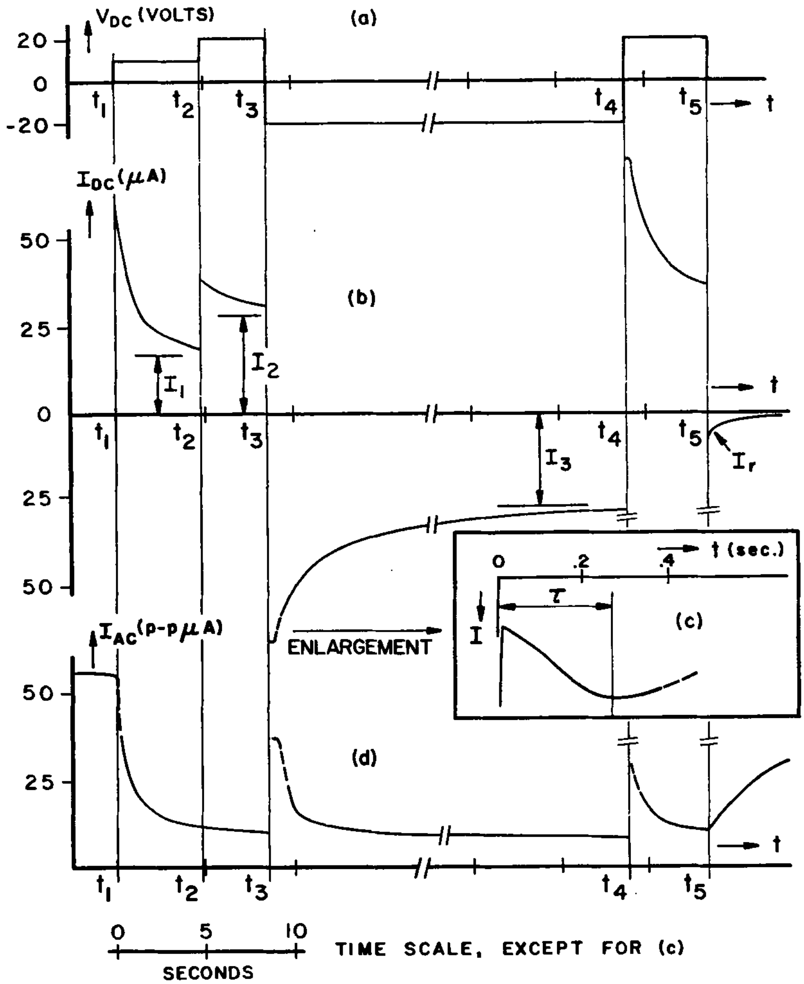


Figure 3. Voltage and current *vs.* time. Plot (a) shows the stepped exciting voltage which produces the DC transient response shown in (b). The discharge current $I_r$ is indicated schematically. The insert, plot (c), is an expanded time-scale view of the current reversal peak located near $t_3$ on plot (b). The initial spike on plot (c) is schematic. Plot (d) gives the amplitude of the sinusoidal current superposed on the DC transients shown on (b), when a constant amplitude 50 cps, 5.4 V $p$–$p$ signal is superposed on the stepped exciting voltage. The times $t_i$ locate voltage steps.

cut-off time $t_f$ was of the order of minutes; beyond that time the integrand became negligibly small. Graphical integration was used.

The initial and reverse polarity transient charge integrals $q$ were each approximately $10^{-3}$ coulombs, for an applied field of 2000 V/cm. As the integrands were not simple exponentials, several transient processes may contribute to them.

On Fig. 3(b) the current $I_r$ begins at $t_5$, after the exciting voltage $V_2$ is removed from the specimen cell. The integral $q_r$ of this discharge current $I_r$ was approximately $10^{-4}$ coulombs, for a previously applied field of 2000 V/cm. The integral $q_r$ was again approximately linear in the field. However, the accuracy of $q_r$ is doubtful due to background currents.

The delay time $\tau$, defined above, was found to vary approximately as $1/V$, where $V$ is the reverse polarity voltage step. A typical value for $\tau$ was 0.25 sec, for $V = 20$ V and cell spacing $d = 0.01$ cm.

Symmetric square wave excitation, Fig. 1 (c1), with frequencies $<0.5$ cps produced current wave forms of the type seen in Fig. 3(b), between times $t_3$ and $t_5$. A sudden increase of the frequency at constant exciting voltage amplitude produced an asymmetric current wave which reverted, after a time of several seconds, to a symmetric wave with larger amplitude than at the lower frequency. At frequencies above 10 cps a conventional RC element wave form was observed.

## III. Superposition of AC and DC

The current flowing in the specimen in response to sinusoidal excitation of frequency $>10$ cps was found to be typical of an ordinary *RC* element. However, the AC conductance was strongly modified by the superposition of a DC bias. In these experiments the specimen was excited by wave form (c2) of Fig. 1, superposed on a 50 cps sinusoidal voltage of amplitude less than $V_1$. The frequency was set at the relatively low value of 50 cps to avoid shunting of the specimen resistance by the specimen and lead-wire capacity. There was no appreciable frequency dependence of the

AC conductance. The results are shown in Fig. 4, and more schematically in Fig. 3(d). The amplitude of the AC component of the current was measured either by blocking the DC component at the oscilloscope, or by measuring the trace width on an oscilloscope picture of the total current. Neither measurement was accurate near the DC switching point.

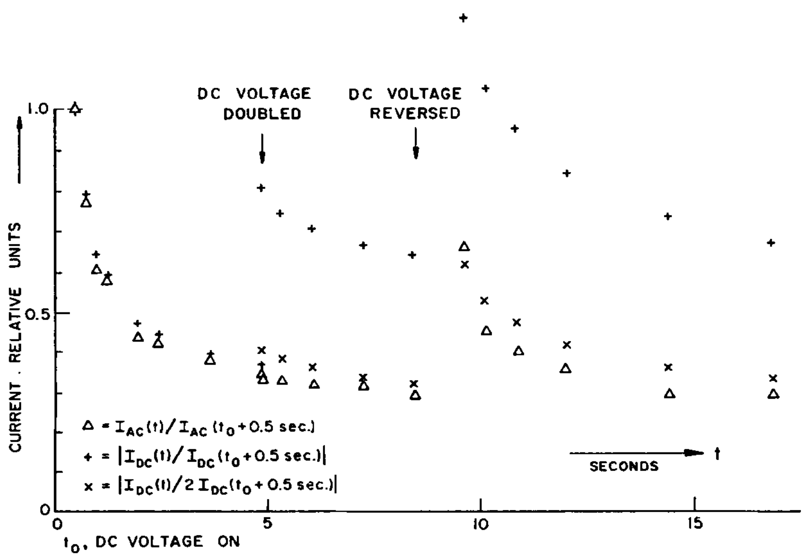


Figure 4. AC and DC conductance for simultaneous excitation with constant amplitude 50 cps sinusoidal voltage and D3 steps, as indicated on graph. This plot is an alternate representation of the data in Fig. 3(b) and 3(d).

The sinusoidal current component was much larger in the absence of *DC* bias ($t < t_1$, $t > t_5$, on Fig. 3(d)) than in its presence. The return of the AC to its pre-DC bias level, for $t > t_5$, was faster than the decay of the discharge current $I_r$. Whereas the first DC bias step switched on produced a marked decrease in the AC, doubling the amplitude of the bias produced essentially no effect ($t_3 > t \geqslant t_2$ on Fig. 3(d); vicinity of $t = 5$ sec on Fig. 4). The AC conductance was generally 10–30 percent larger than the DC, but normalized time plots yielded essentially identical curves (Fig. 4).

**Discussion and Summary**

The main experimental results may be summarized as follows:

(1) The electrical currents which flow in response to DC-step excitation, or in response to cyclic excitation with periods greater than one second, exhibit transient asymmetry, hysteresis, and non-linearity (Fig. 2 and Figs. 3(b), (c)). Upon removal of the exciting voltage a transient discharge current $I_r$ appears. The current which flows in response to a polarity reversal step exhibits a peak, displaced from the time of polarity reversal by a time $\tau$ which is inversely proportional to the voltage.

(2) The AC conductance measured by cyclic excitation with periods less than 0.1 second is typical of a conventional RC circuit element.

(3) The alternating current flowing in response to cyclic excitation with periods less than 0.1 second, superposed on a steady or stepped biasing potential, exhibits essentially the same behavior as the DC component (Fig. 3(d) and Fig. 4). The AC conductance is greatly reduced by the application of DC bias, whereas the application of additional DC bias has little effect on the AC. Upon removal of the DC bias the AC conductance returns slowly to its non-bias magnitude.

The DC and low frequency effects summarized in (1) permit, but do not require, an interpretation in terms of "ferroelectricity." An interpretation involving a superposition of charge carrier transport and storage effects is also possible. The higher frequency zero-bias AC conductance results (2) provide neither support nor contradictions to either interpretation. They do imply that bulk polarization or charge carrier transient effects which may occur are restricted to the low frequency domain. The conclusions derived from the pure AC experiments, together with the observed behavior of the AC conductance in the presence of DC bias (3), rule out "ferroelectricity" and imply that the DC bias modulates the conductance, both AC and DC. This modulation can occur through current-carrier sweep-out and spatially non-uniform storage.

The types of measurement performed in this experiment and the lack of knowledge about the specific impurity content and the nature of the electrode contact do not permit more than speculation concerning the actual charge transport mechanisms. There is evidently at least one steady and one transient conductance component. There also exists at least one storage mechanism which provides for the discharge current $I_r$. If the current reversal transient peak delay-time $\tau$ is assumed to measure a transit time (electric field drift) of stored charge from the vicinity of one electrode to the other, mobilities in the range 0.2–0.5 $\times 10^{-4}$ $cm^2$/V-sec are obtained. This number is low, but not unreasonably so.[8]

Future experiments on purer material and with better characterization of the contacts may yield a more specific explanation of the phenomena which occur.[7] In spite of the uncertainty as to what actually does take place, we believe that we have shown that the curious electrical behavior of *p,p'* azoxyanisole should be explained in electrochemical terms rather than on the basis of ferroelectricity. The fact that the material is liquid crystalline does not seem to be relevant. This interpretation is supported by the fact[9] that the low frequency electrical response anomalies persist, essentially unmodified, into the isotropic phase.

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