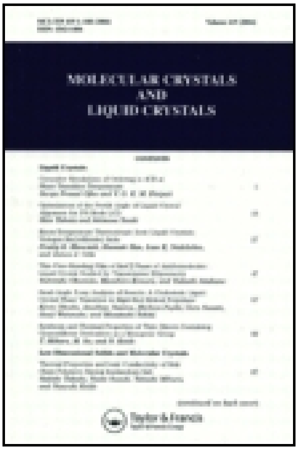

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# Conductivity in Liquid Crystals

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# Conductivity in Liquid Crystals‡

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**Abstract**—Dark and photoconductivities of nematic, smectic and cholesteric materials have been measured with particular attention to the changes in properties at phase transitions. Although a reasonably large photoresponse could be found in several liquid crystals at room temperature, only a very small photoresponse occurred in the liquid crystal state. At the transition point solid → liquid crystal the dark conductivity, $\sigma_D$ and the thermal activation energy, $E_a$ typically show large changes, while in the liquid crystal → liquid transition, $\sigma_D$ and $E_a$ change only slightly. Both transition temperatures can easily be identified in the plots of log $\sigma$ vs $1/T$, and agree well with microscopic and calorimetric observations. Cholesteric materials show a surprising *decrease* in dark conductivity at the solid → cholesteric transition during heating, in contrast with the behavior of nematic and smectic materials.

## Introduction

In recent years there have been a large number of investigations of the conductivity of molecular crystals,[1] and some of these investigations have dealt with anomalies associated with solid–liquid transitions.[2–4] For example, when naphthalene is melted, there is an extremely sharp increase in conductivity of about three orders of magnitude,[2] and similar increases have been noted for eight other hydrocarbons.[3] The mobility of charge carriers during such a transition is reported to decrease by three orders of magnitude in the case of pyrene,[4] going from mobilities of the order of one to mobilities of approximately $10^{-4}\,\mathrm{cm}^2\,\mathrm{v}^{-1}$

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$sec^{-1}$. Both because of its relevance to this problem, and because liquid crystals undergo orientation effects[5] and induced phase changes[6] in electric fields, a systematic study was conducted of changes in conductivity associated with phase transitions in liquid crystals.

One aspect of the problem is to find a liquid crystal system in which photoinjection experiments are possible so that drift mobility measurements, which have been so effective in elucidating the mechanism of charge transport in organic crystals,[7] could be performed. Results of a screening program in which representative liquid crystals containing aromatic moieties were tested for photoresponse are presented below.

The second aspect of the problem is to examine changes in dark conductivities and activation energies of conduction at the phase transitions. Although interpretation of absolute values of these parameters is fraught with difficulty, the relative values at phase transitions are both diagnostic and reproducible. Below are reported the electric behaviors of nematic, smectic and cholesteric materials at such transitions.

## Experimental

*Materials*: All of the compounds studied in detail were purified by successive recrystallizations until their melting ranges were reproducible, and in good agreement with literature values. Although in general zone refining was not efficient as a purification procedure, p-anisylidene-p′-biphenylamine was purified by 20 passes in a Fisher zone refiner.

*Measurements*: Sandwich cells were constructed from quartz plates with evaporated gold electrodes or tin oxide conducting glass plates. The liquid crystal was melted between these plates with a .005″ teflon spacer, and the edges sealed with an epoxy cement. Conductivity was measured using a Cary 401 Vibrating Reed Electrometer or a Keithley 610B Electrometer (conventional two electrode D.C. method). The applied voltage, from a Keithley 241 power supply, was negative on the illuminated side of the sample. Illumination was supplied by a 150 watt xenon lamp, whose beam was passed through a water filter to eliminate heating effects. The lamp was 25 cm from the sample, and the illumination was through the semi-transparent gold or tin oxide electrode. The samples were mounted in an evacuable, heated cell with a quartz window similar to that previously described.[8] Measurements were performed in vacuo.

## Results and Discussion

### PHOTORESPONSE OF LIQUID CRYSTALLINE MATERIALS AT ROOM TEMPERATURE

Table 1 lists three materials which show a large photo-current to dark current ratio at room temperature. Of the group of compounds screened, these are the only compounds which show a reasonably large steady state photoresponse. Variation from sample to sample is reflected in the range of the ratio reported. Of these 3 compounds, *p,p'*-dimethoxystilbene shows no evidence of actually being a liquid crystal when purified, although it is reported in the literature.[5]

Part B and C of Table 1 lists a group of compounds which show little or no photoresponse at room temperature and a few compounds showing a large transient photoresponse. For example, *p*-anisylideneaminocinnamic acid shows a transient photocurrent/dark current of 1150, and then a negative (!) steady state photocurrent. It must be remembered that not only can electrode effects be responsible for this kind of behavior, but photochemical reactions may be occurring in these compounds.

Unfortunately even those compounds showing a large photoresponse at room temperature show only a very small residual photo-response when heated to the liquid crystal region. This of course is partially anticipated from the typical increase in dark current in the solid having an activation energy of approximately 1 eV, whereas for *p*-anisylidene-*p'*-biphenylamine the photocurrent activation energy in the solid is approximately 0.3 eV. Diethyl *p,p′*-azoxydicinnamate does show a small photocurrent in the smectic region, complicated by a pronounced photovoltaic effect, which is being further investigated.

TABLE 1 Photoresponse of Some Liquid Crystals at Room Temperature ‡

| Compound | Type | Photocurrent/Dark current |
|---|---|---|
| *A. Compounds Showing Pronounced Photoresponse* | | |
| *p*-Anisylidene-*p′*-biphenylamine | Nematic | 200–800 |
| Diethyl *p,p′*-azoxydicinnamate | Smectic | 25–75 |
| *p,p′*-Dimethoxystilbene | Nematic(?) § | 145 |
| *B. Compounds Showing Little or No Photoresponse* | | |
| Diethyl *p,p′*-azoxydibenzoate | | |
| *p*-Acetoxycinnamic acid | | |
| *p*-Anisylideneaminophenyl acetate | | |
| *p*-Anisalazine | | |
| *N*-*p*-anisylidene-*p*-phenylazoaniline | | |
| *C. Compounds Showing a Transient Photoresponse* | | |
| *p,p′*-Azoxyanisole | | |
| *p,p′*-Azoxyphenetole | | |
| *p*-*p*-Anisylideneaminocinnamic acid | | |
| Cholesteryl 3, 5-dinitrobenzoate | | |

‡ 150 watt xenon lamp 25 cm from sample, water filter (50mW/cm$^2$).
§ Compound is probably not a liquid crystal.

## MEASUREMENTS OF DARK CONDUCTIVITY CHANGES AT THE PHASE TRANSITIONS

Table 2 lists the changes in conductivity of some typical liquid crystals at phase transitions for one smectic and three nematic materials. At the transition temperature of solid–liquid crystal one finds a marked increase in conductivity. At the liquid to liquid crystal transition there is essentially no change in the conductivity, although a slight inflection is observed in the conductivity temperature plot. One is able to recognize the existence of this latter phase transition but there is no dramatic change in the conductivity. Only one value in the table, that for conductivity ratio on cooling of p-anisylideneaminophenyl

Table 2 Changes in Conductivity of Liquid Crystals at Phase Transitions

| Compounds | Type | $\sigma$ liquid crystal/$\sigma$ solid Heating | $\sigma$ liquid crystal/$\sigma$ solid Cooling | $\sigma$ liquid/$\sigma$ liquid crystal Heating | $\sigma$ liquid/$\sigma$ liquid crystal Cooling |
|---|---|---|---|---|---|
| *p*-Anisylidenebiphenylamine | Nematic | 800 | 840 | 1 | 1 |
| *p*-Anisylideneaminophenylacetate | Nematic | 20‡ | 5700‡ | 1 | 1 |
| Diethyl *p,p'*-azoxydicinnamate | Smectic | 30 | 33 | — | — |
| *p*-*n*-Hexyloxybenzylideneaminotoluene | Nematic | 6 | — | 1.1 | — |

‡ These values are very different because of marked supercooling.

acetate, shows a disagreement between heating and cooling cycles, and this disagreement is due to the marked supercooling as one goes from the nematic phase to the solid phase for this material.

Table 3 shows the corresponding changes in the activation energies of conduction of liquid crystals at the phase transitions. There is a large change in the slope of the temperature dependence

Table 3 Changes in Activation Energy of Conduction of Liquid Crystals at Phase Transitions

| Compound | Type | E solid (eV) | E liquid crystal (eV) | E liquid (eV) |
|---|---|---|---|---|
| *p*-Anisylidenebiphenylamine | Nematic | 0.9 | 0.54 | 0.46 |
| *p*-Anisylideneaminophenyl acetate | Nematic | 1.8 | 0.56 | 0.41 |
| Diethyl *p,p'*-azoxydicinnamate | Smectic | 1.3 | 0.72 | — |
| *p*-*n*-Hexyloxybenzylideneaminotoluene | Nematic | 1.6 | 0.67 | 0.45 |
| Cholesteryl nonanoate | Smectic | 1.3 | 0.82 | 0.60 |
|  | Cholesteric |  | 0.81 |  |
| Cholesteryl propionate | Cholesteric | 1.1 | 0.89 | 0.81 |

as one goes from the solid to the liquid crystal region, and only a slight change associated with the liquid crystal–liquid transition. From these data it is possible to accurately determine the temperatures for both solid–liquid crystal and liquid crystal–liquid transitions. Table 4 compares the values from the conductivity-temperature curves with those determined by the more conventional melting studies or differential scanning calorimetry, and the agreement is extremely good. The most surprising aspect of these studies is the contrast in behavior of the nematic liquid crystals and the cholesteric liquid crystals in their conductivity behavior.

Figure 1 shows the temperature dependence of conductivity of *p*-anisylidene-*p*′-biphenylamine. One can see the transition from solid to liquid crystal phase as a marked increase in conductivity which is noticeable both upon heating and cooling cycles. This would be the kind of behavior that one would expect

TABLE 4 Phase Transition Temperatures Observed in Conductivity Studies

| | | Transition Temperatures | | | |
|---|---|---|---|---|---|
| | | Solid → Liquid Crystal | | Liquid Crystal → Liquid | |
| Compound | Type | Literature | Conductivity Studies | Literature | Conductivity Studies |
| *p*-Anisylidene-*p*-biphenylamine | Nematic | 161‡ | 162 | 177‡ | 178 |
| *p*-Anisylideneaminophenylacetate | Nematic | 81.5‡ | 80 | 108‡ | 104 |
| Diethyl *p*,*p*′-azoxydicinnamate | Smectic | 140‡ | 140 | 249‡ | — |
| *p*-*n*-Hexyloxybenzylideneaminotoluene | Nematic | 58§ | 58 | 73§ | 74 |
| Cholesteryl nonanoate | Smectic | 76.3‖ | | | |
| | Cholesteric | 80.6‖ | 78–80 | 92.1‖ | 93 |

‡ International Critical Tables.

§ Sample furnished by Dr G. H. Brown.

‖ R. Ennulat, 2nd International Liquid Crystal Conference, Lecture 7, Kent State University, Ohio (1968).

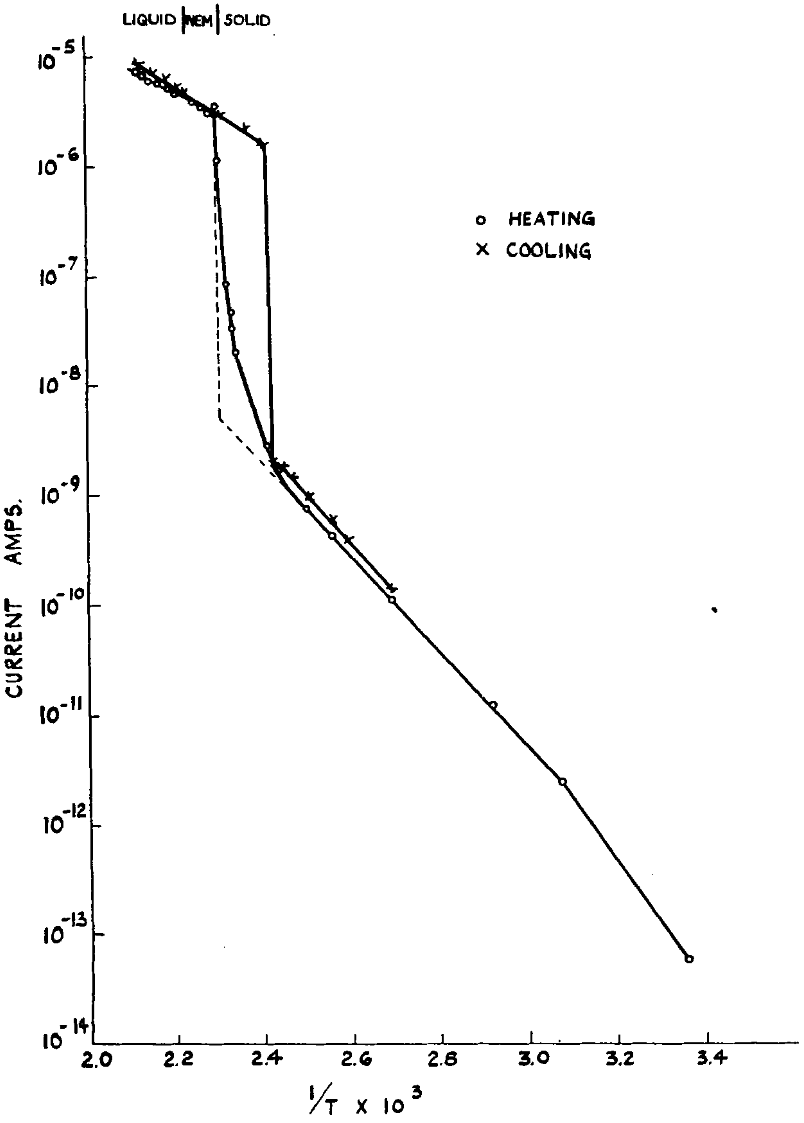

Figure 1. Temperature Dependence of Conductivity of *p*-Anisylidene-*p*′-biphenylamine. Field Strength 80 Vcm$^{-1}$.

to see in such a phase transition based upon other work on organic solids.

Figure 2 shows the result for cholesteryl nonanoate. Here as one heats the solid, a marked decrease in conductivity occurs at the solid-cholesteric transition. The conductivity increases in the cholesteric phase transition from cholesteric to isotropic liquid. In the cooling curve, one cannot distinguish the cholesteric and smectic phases precisely although there is some slight indication of perturbation in the conductivity in the region of the monotropic cholesteric-smectic transition. The major effect is supercooling to a temperature in the normal solid state in which a sudden increase of the conductivity occurs as one returns from the supercooled liquid crystal phase to the solid phase.

The temperature dependence of dark conductivity of cholesteryl propionate was also examined, and it behaves similarly to cholesteryl nonanoate; the decrease in conductivity at the solid-cholesteric phase is about one order of magnitude over a temperature range of about 5°. There is no smectic phase present preceding this transition. Thus the decrease in conductivity appears to be general for cholesteric compounds.

For cholesteryl nonanoate, the current–voltage characteristics were examined. Ohm's law is obeyed up to $1.5 \times 10^4\,\text{Vcm}^{-1}$ in solid, cholesteric, and liquid states. In the liquid crystal region superlinear behavior is observed above this voltage, and at approximately $10^5\,\text{Vcm}^{-1}$ breakdown occurs. It is slightly below this breakdown region than an electric field induced phase change has been reported in a cholesteric mixture.[6] An attempt was made to observe this induced phase change by going through the solid-smectic-cholesteric phase transitions at field strengths just below breakdown. However, fluctuation in the observed currents at these field strengths was too large to allow a determination of this behavior.

The unusual behavior of cholesteric compounds on melting is difficult to explain. As has already been stated, there are profound differences in aromatic crystals associated with the solid–liquid phase transitions where mobility decreases by several

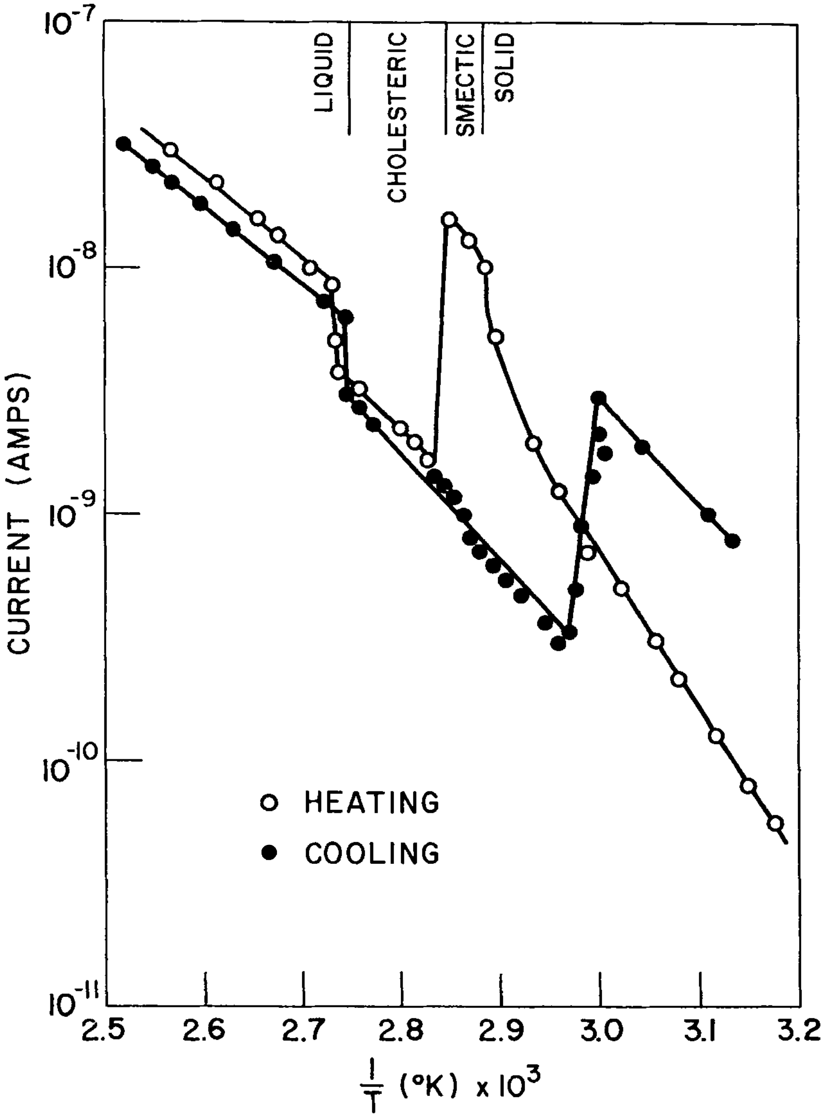

Figure 2. Temperature Dependence of Conductivity of Cholesteryl Nonanoate. Field Strength 8000 $Vcm^{-1}$.

orders of magnitude and conductivity increases by several orders of magnitude. Thus the transport mechanism in the solid and liquid appear to be fundamentally different. It is likely that carrier motion in the normal isotropic liquid cannot be treated by the same type of delocalized model as is the case for the solid. In the absence of independent information regarding either the nature and concentration of charge carriers or their mobility, it is impossible to draw conclusions about the observed conductivity differences at phase transitions for the nematic and cholesteric phases. One would argue in either of the following ways: If mobility decreases in the cholesteric phase, the charge carrier concentration need not increase as markedly as it does in the nematic phase. Alternatively, long range order may still prevail in the cholesteric phase and a delocalized model may be applicable. It is possible that mobility would *not* be changed so dramatically at the phase transition. The dominant effect might then be an increase in carrier trapping in the liquid crystal region effectively reducing carrier concentration. It is a possibility, therefore, that while nematic materials behave much more like an ordinary organic liquid, the cholesteric phase may have mobilities typical of organic crystals. At present these ideas are very speculative, and direct mobility information is certainly required. Efforts are continuing to find a suitable liquid crystal to evaluate mobilities.

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