Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Correlation between Electrical Properties and Optical Behaviour of Nematic Liquid Crystals

Hans Gruler [a] & Gerhard Meier [a]

[a] Institut für Angewandte Festkörperphysik der Fraunhofer-Gesellschaft, 78 Freiburg, Germany

To cite this article: Hans Gruler & Gerhard Meier (1971): Correlation between Electrical Properties and Optical Behaviour of Nematic Liquid Crystals, Molecular Crystals and Liquid Crystals, 12:4, 289-298

To link to this article: http://dx.doi.org/10.1080/15421407108082782

Molecular Crystals and Liquid Crystals. 1971. Vol. 12, pp. 289–298

Correlation between Electrical Properties and Optical Behaviour of Nematic Liquid Crystals†

HANS GRULER and GERHARD MEIER

Institut für Angewandte Festkörperphysik
der Fraunhofer-Gesellschaft, 78 Freiburg, Germany

Received October 12, 1970; *in revised form November* 30, 1970

Abstract—The results of simultaneous electrical and optical investigations in *p*-azoxyanisole and di-*n*-heptoxy-azobenzene are presented. The role of fluid flows is discussed in connection with their importance for domain formation. The mechanism of domain formation and turbulence occurrence is found to be different for d.c. and very low frequencies than it is for higher frequencies. For strong electric fields the behaviour of azoxyanisole is very different from that of the azo compound, a fact attributed to the different sign of the dielectric anisotropy.

We performed investigations on the behaviour of nematic liquid crystals in electric fields. The compounds were *p*, *p*′-dimethoxy-azoxybenzene (*p*-azoxyanisole, PAA) and *p*, *p*′-di-*n*-heptoxy-azobenzene which have a negative respectively a positive dielectric anisotropy. The layers were oriented parallel by wall effects. The electrical conductivity was of the order of 10^{-8}–10^{-10} Ω^{-1} cm^{-1} for the azoxy compound and 10^{-10}–10^{-12} Ω^{-1} cm^{-1} for the azo compound. The current voltage characteristics were measured both under d.c. and a.c. conditions. The optical behaviour in electric fields was simultaneously observed with a polarizing microscope. The reflected or transmitted light was measured by a photomultiplier.

The basic experimental setup is shown in Fig. 1. The sample was placed between SnO_2-coated glass plates. SnO_2 was chosen because of its excellent chemical stability. The temperature was controlled to within ± 0.2 °C by a Mettler heating stage. Generally, the characteristics depend on the rate at which the measurements are made.

---

† Presented at the Third International Liquid Crystal Conference in Berlin, August 24–28, 1970.

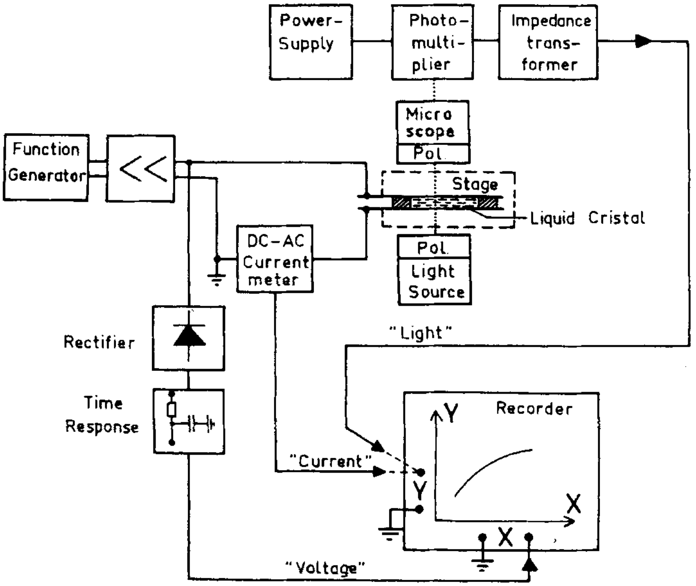

Figure 1. Experimental setup for the measurements.

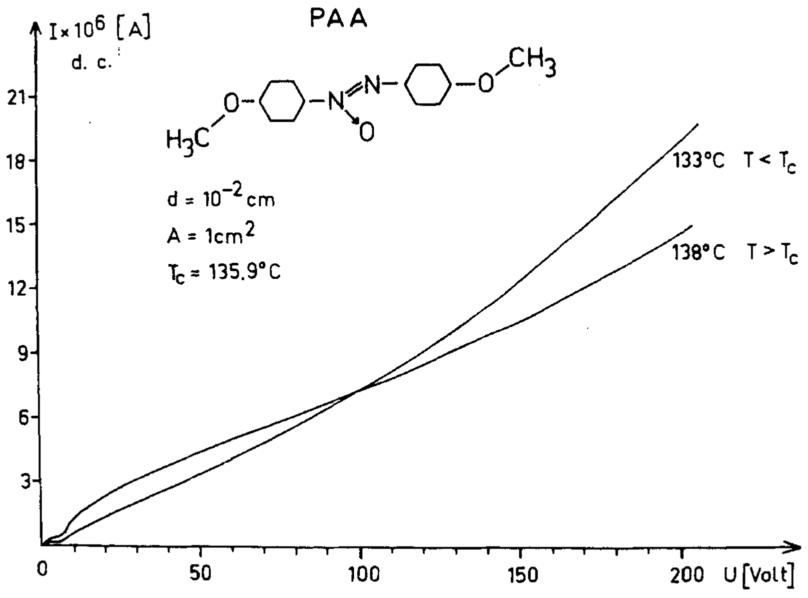

Figure 2. Typical d.c. current-voltage curves for PAA.

Our curves were measured in most cases at a rate of 1 V/min. At this rate no difference between measurements with increasing and decreasing voltage were observed. When the rate is chosen too fast a hysteresis arises in going up and down. Moreover, polarization effects are always present. In order to have clearly defined conditions the polarity was not changed and the measurements were not started before the polarization voltage, which is of the order of magnitude of 1 V, had been established.

Figure 2 shows the d.c. characteristic taken for PAA. Other materials, such as heptoxy-azobenzene, show essentially the same behaviour. The two curves were recorded just below and just above the clearing point. We noticed two basic facts:

(1) At an applied voltage of the order of several volts the d.c. curve shows a strong change in conductivity not only for the nematic phase but also for the isotropic phase. In the nematic state the change of the conductivity is connected with the formation of domains.

(2) For higher voltages the current increase is stronger for the nematic phase than for the isotropic phase.

Figure 3 shows a set of current-voltage curves in the low voltage range with the temperature as a parameter. Note that there is an increase in conductivity in the nematic phase as well as in the isotropic phase. The relative change in the conductivity is slightly larger in the nematic phase than in the isotropic phase. The characteristics for the nematic and the isotropic phases are slightly different. The lower graph shows the transmitted light intensity, which is small when domains are present in the specimen. It is noticed that the threshold voltage for domain formation is strictly connected to the kink in the current voltage curve.

The kink in the d.c. current-voltage curve cannot be explained by the anisotropy of the electrical conductivity in the nematic liquid crystal. In the isotropic phase this explanation would not be possible anyway.

In the region of the increased conductivity regular fluid flows were made visible by small particles introduced into the liquid.(1–3) These fluid flows were observed in the nematic phase as well as in the isotropic phase. There appears to be a direct connection between the fluid flows and the change in conductivity.

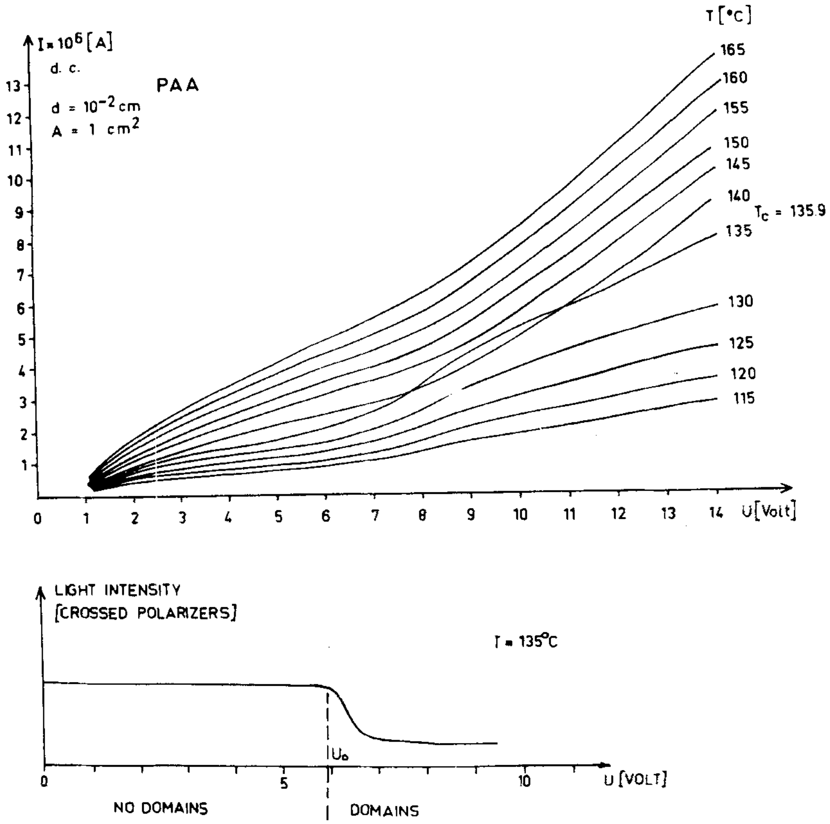

Figure 3. D.c. current and correlated light intensity as a function of the applied voltage in PAA.

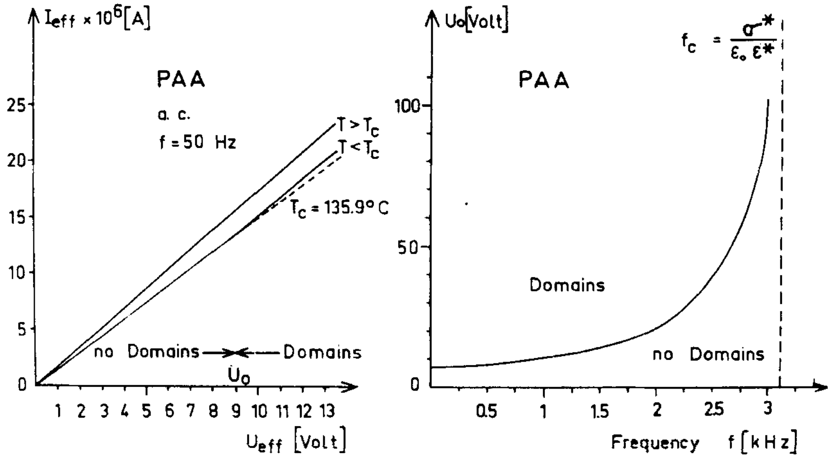

Figure 4. Left: Typical a.c. current-voltage curves. Right: Frequency dependence of the threshold voltage in PAA.

A.c. current-voltage measurements on PAA are shown in the left part of Fig. 4. In the nematic phase only a small change in the a.c. characteristic was observed above the threshold voltage for domain formation. Above approximately 15 Hz we observed that in the isotropic phase the fluid flow vanished and in the nematic phase the fluid flow became weaker than under d.c. conditions. On the right part of Fig. 4 the threshold voltage for domain formation is plotted as a function of the frequency.(1) The threshold voltage increases with frequency. There is a cutoff frequency above which domains cannot be obtained. The cutoff frequency is equal to the dielectric (space charge limited) relaxation frequency given by $\sigma/(\epsilon_0 \cdot \epsilon)$.(4) The measurements are not precise enough to determine which conductivity and which dielectric constant should be taken. In the figure we used the measured a.c. conductivity. In the case of the dielectric constant the anisotropy amounts only to a few percent and therefore the question is of little numerical importance. The value used was that of Maier and Meier(5) measured at a frequency of 100 kHz. The agreement of the cutoff frequency with the dielectric relaxation frequency is good. This was established for conductivities between 10^{-8} and $10^{-10}\ \Omega^{-1}\ \mathrm{cm}^{-1}$.

The value of the dielectric relaxation frequency is obtained by assuming that the formation of domains is connected to space charges. At the same time the cut off frequency is the limit for the formation of domains as well as of fluid flows. This gives a strong hint that a close correlation exists between domains and space charges.

The d.c. characteristic of the azo compound is not very different from that of PAA. Again a fluid flow was observed but of a smaller order of magnitude Also the kink in the d.c. curve is less pronounced for heptoxy-azobenzene than for PAA. Figure 5 shows the threshold voltage for domain formation as a function of the frequency. In contrast to PAA there was no upper frequency limit for the threshold voltage. The threshold voltage in this material exhibited a maximum value. In the region of low frequency and d.c. the layer remained oriented parallel below the threshold voltage. Above the threshold voltage we found domains. When domains existed we observed a slight fluid flow. At higher voltages the domains changed into inversion walls, and the fluid flow vanished.

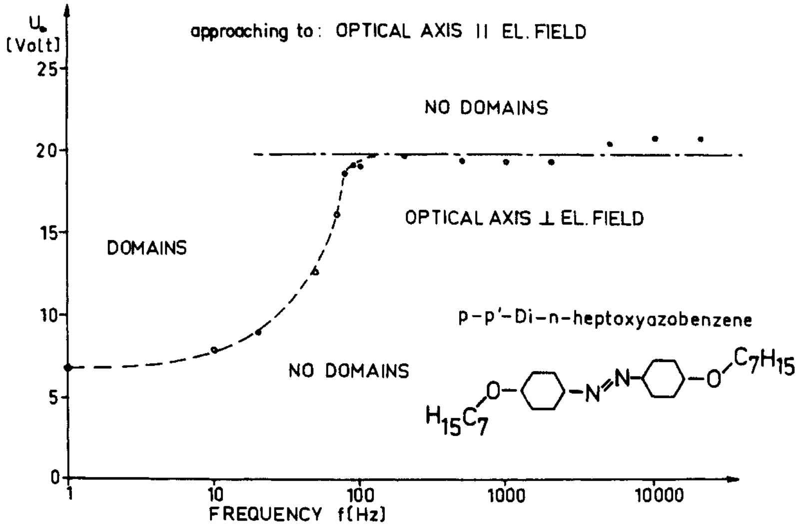

Figure 5. Frequency dependence of the threshold voltage in heptoxy-azobenzene ($\sigma \sim 10^{-10}\ \Omega^{-1}\,\text{cm}^{-1}$).

At high frequencies no domains existed. Above the threshold voltage the oriented layer gradually lined up with the applied electric field. In the high frequency region the effect of the electric field was similar to that of the magnetic field. Also at d.c. or very low frequencies the layer lined up with the electric field when the field strength was high enough. These effects result from the positive dielectric anisotropy.

PAA, however, exhibited under similar conditions a heavy turbulence connected with strong scattering of light. Heilmeier *et al.*(6) investigated this effect in anisylidene-*p*-aminophenylacetate (APA PA) and called it " dynamic scattering ". They observed, however, no or little dynamic scattering in *p*-*n*-ethoxybenzylidene-*p*'-aminobenzonitrile (PEBAB). In order to explain these experimental observations they proposed a model from which it follows that compounds with molecules having a dipole moment perpendicular to the long axis should exhibit the dynamic scattering effect whereas those with molecules whose dipole moment lies along the long axis should exhibit essentially no effect. This model proves right in most cases but does not hold true for our azo compound which behaves like

PEBAB, even though the molecular dipole moment is practically perpendicular to the long molecular axis.

Thus, the position of the molecular dipole moment alone cannot decide the behaviour in the electric field. The anisotropy of the molecular polarizability has to be taken into account, too. In fact, we consider the sign of the dielectric anisotropy to be the decisive quantity.

This sign is always positive when the dipole moment is parallel to the long molecular axis. A dipole moment perpendicular to the long molecular axis on the other hand, may lead to a positive or negative dielectric anisotropy depending on the value of the dipole moment relative to the anisotropy of the polarizability. Our azo compound, for instance, has a large positive anisotropy of the polarizability and a comparatively small dipole moment perpendicular to the long molecular axis. Thus, the resulting dielectric anisotropy is positive.

We like to point out that domains existed in PAA as well as in heptoxyazobenzene. The domains were always connected with a fluid flow. The fluid flow existed at d.c. or low frequencies in the nematic as well as in the isotropic state. Therefore we suggest that the domain formation at d.c. or low frequencies is caused essentially by a fluid flow and not by the Helfrich mechanism.(7) True, the Helfrich model does imply a fluid flow but only in the nematic phase. Thus, it cannot describe the d.c. or low frequency case.

At high frequencies, however, there are several observations which indicate that the predominant cause of domain formation is probably the mechanism proposed by Helfrich: 1. The fluid flow exists only in the nematic phase. 2. The cutoff frequency for domain formation is equal to the dielectric relaxation frequency, which is in agreement with Helfrich's model. 3. The observed and calculated threshold voltages are of the same order of magnitude. (For a detailed discussion of these questions see also Ref. (8)).

Figure 2 shows that in the low voltage region the current in the nematic state is smaller than the current in the isotropic state. This has already been observed by Svedberg(9,10) who made measurements only for weak electric fields. He explained this effect in terms of the anisotropic electrical conductivity. In the high voltage region the current is larger in the nematic state than in the isotropic state. We see this effect better in Fig. 6. The current ratio of the nematic phase to the isotropic phase is plotted as a function of the applied field. The values of the currents were obtained by extrapolation to the clearing point. In the upper curve we see how strong this effect can be.

The observed effect must be strongly related to the mechanism of charge carrier generation. Several possible mechanisms were discussed by Heilmeier *et al.*(6,11) The Schottky effect and the field-assisted dissociation lead to the relation

$$\log j \propto \left(\frac{E}{\epsilon}\right)^{1/2}.$$

A crude estimate shows that our measurements do not fit this formula and thus other effects must be considered, too. In a recent paper, Heilmeier *et al.*(11) pointed out that the presence of water promotes electron injection by lowering the potential barrier between the electrode and the liquid crystal. A lowering of the effective work function of the electrode material can arise from the existence of double layers between the electrode and the liquid crystal (a detailed discussion for dielectric liquids is given in Ref. (12)). The smaller the work function, the larger the influence of the double layers on the current. In fact, this seems to be a possible explanation of our observations, if we assume that the double layers are different in the nematic and in the isotropic state.

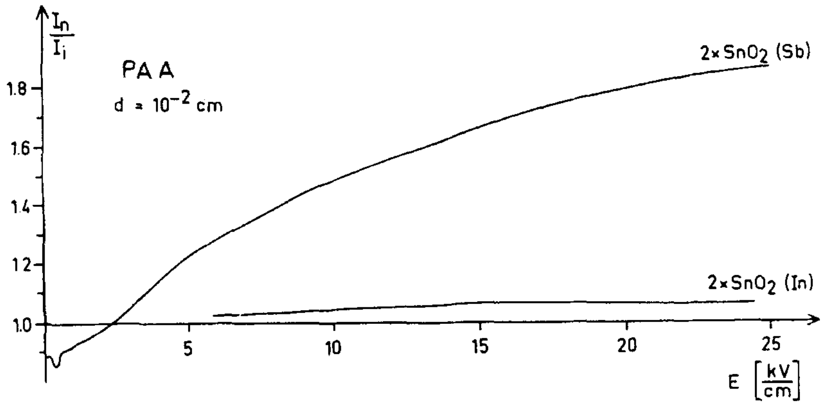

Figure 6. Ratio of the currents in the nematic and in the isotropic state as a function of the applied electric field.

Figure 6 shows measurements with different electrode materials. Both electrodes were SnO_2 doped with Sb (Antimony) for the upper curve, whereas for the lower curve the electrodes were In (Indium) doped. We got values similar to the lower curve when we took metal electrodes such as Al or Cr. We presume that the large difference o the two curves arises from a change of the work function.(13)

There is a connection between the curves of Fig. 6 and the hysteresis loops measured by Williams and Heilmeier,(14) and Vistin and Kapustin(15) at frequencies of 30 to 1000 Hz and higher. We found a hysteresis loop not only in the nematic but also in the isotropic state if the electrodes are Sb doped SnO_2. When we took In doped SnO_2 or metals, we could see a hysteresis loop only in the nematic state but not in the isotropic state. This seems to be the key to understanding the discrepancy between the results of the RCA group and that of the Russian group.

A surprising effect was seen in PAA in the region of high voltage. With increasing voltage the overall turbulence vanished giving way

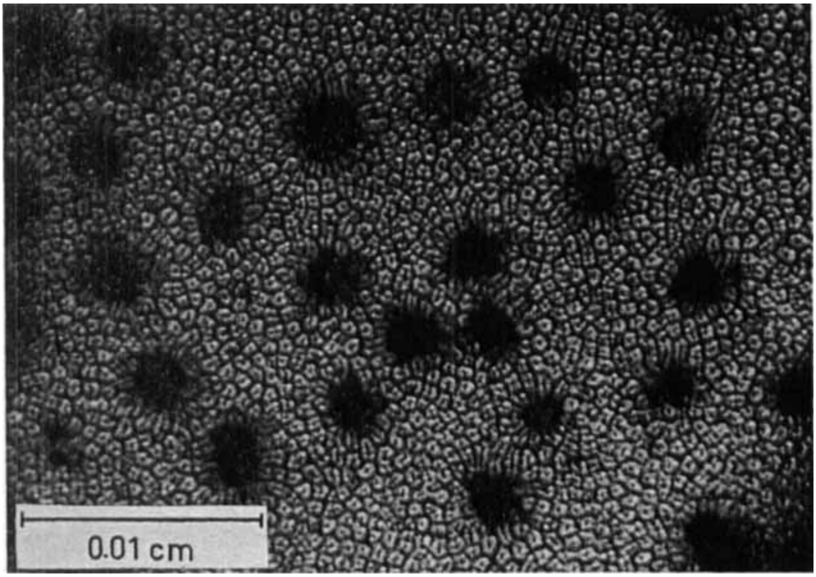

Figure 7. Optical transmission pattern of PAA in an intense electric field. Temperature 135.0 °C (clearing point 135.9 °C), voltage 62.5 Volt (d.c.), thickness 10^{-2} cm, exposure time 1/15 sec.

to a certain regularity (Fig. 7). At the dark spots a strong turbulence was observed. These spots were surrounded by a pattern, which we attribute to a certain regularity in the fluid flow. At still higher fields the pattern turned turbulent again.

REFERENCES

1. Kassubek, P., Diplomarbeit Freiburg 1966, unpublished.
2. Durand, G., Veyssié, M., Rondelez, F. and Léger, L., *C.R. Acad. Sc. Paris* **270B,** 97 (1970).
3. Koelmans, H. and van Boxtel, A. M., *Phys. Letters* **32A,** 32 (1970).
4. Spenke, E., " Electronic Semiconductors," McGraw-Hill Book Company, Inc., New York, Toronto, London (1958), p. 116.
5. Maier, W. and Meier, G., *Z. Elektrochem., Ber. Bunsenges. physik. chem.* **65,** 556 (1961).
6. Heilmeier, G. H., Zanoni, L. A. and Barton, L. A., *Proc. IEEE* **56,** 1162 (1968).
7. Helfrich, W., *J. Chem. Phys.* **51,** 4092 (1969).
8. Orsay Liquid Crystal Group, IIIrd International Liquid Crystal Conference, Berlin 1970.
9. Svedberg, T., *Arkiv f. Matematik, Astronomi o. Fysik* **9** (9), 11 (1913).
10. Svedberg, T., *Ann. Physik* **44,** 1121 (1914).
11. Heilmeier, G. H. *et al.*, *IEEE Trans. Electron Devices* **ED-17,** 22 (1970).
12. Progress in Dielectrics, Vol. I, Heywood & Comp. Ltd., London 1959, p. 97, T. J. Lewis: The Electric Strength and High-Field Conductivity of Dielectric Liquids.
13. The influence of a Sb doping on the electrical properties of SnO_2 was investigated by A. Fischer: *Z. Naturforschg.* **9a,** 508 (1954).
14. Williams, R. and Heilmeier, G. H., *J. Chem. Phys.* **44,** 638 (1966).
15. Kapustin, A. P. and Vistin, L. K., *Kristallografiya* **10,** 118 (1965).