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

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Version of record first published: 28 Mar 2007.

To cite this article: E. F. Carr & C. R. K. Murty (1972): Angular Dependent Studies in Liquid Crystals Involving Permeability and Dielectric Anisotropies, Molecular Crystals and Liquid Crystals, 18:3-4, 369-374

To link to this article: http://dx.doi.org/10.1080/15421407208083608

Molecular Crystals and Liquid Crystals. 1972. Vol. 18, pp. 369–374

Angular Dependent Studies in Liquid Crystals Involving Permeability and Dielectric Anisotropies†

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Received December 27, 1971

Abstract—This work shows that angular dependent studies are possible in liquid crystals of the nematic type when good measurements of the magnetic susceptibility and dielectric anisotropies or ratios of these quantities are available. It also attempts to help clear up some of the uncertainties in the literature regarding magnetic susceptibility and dielectric constant measurements.

1. Introduction

Molecules in the nematic mesophase can be aligned by either electric or magnetic fields. In the presence of static magnetic fields the long axes of the molecules prefer a direction parallel to the field, but in electric fields the preferred direction is often found to depend on the frequency of the applied field.[1] Experimental evidence has indicated[2] that the anomalous alignment, which is often observed in dc and very low ac electric fields, is associated with the conductivity, and this has been recently supported by many other workers.[3] For frequencies above a critical frequency region, which depends on the conductivity, the effectiveness of an electric field for producing molecular alignment should depend only on the dielectric anisotropy. All the work reported here involving electric fields is for frequencies above the critical region.

Measurements of the dielectric loss[4,5] at microwave frequencies

† Supported in part by the U.S. Army Research Office—Durham, Grant No. DA-ARO-D-31-124-71-G135.

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have been used to compare the relative effectiveness of magnetic and electric fields for producing molecular alignment. The microwave beam is polarized, so the power transmitted through a sample of liquid crystal depends on the orientation of the molecules. Since the transmitted power depends on the orientation of the molecules, information concerning the degree of ordering can be obtained from measurements of this power.

Anisal-*p*-aminoazobenzene is an example of a nematic liquid crystal which exhibits a positive low frequency dielectric anisotropy. This implies that in the presence of an electric field the molecules should prefer an orientation with their long axes parallel to the field, and this is what has been observed.[4] Dielectric loss measurements at a microwave frequency have been made in anisal-*p*-aminoazobenzene[4] in the presence of external magnetic and low frequency ac electric fields applied perpendicular to each other. Since the electric field tries to produce an ordering with the long molecular axes perpendicular to that preferred by the magnetic field, the relative effectiveness of the two fields can be obtained. This is accomplished by comparing them at a value of the dielectric loss corresponding to a random orientation of the molecules (or clusters of molecules). For this value of the dielectric loss the following relation is satisfied.

$$H_0 = \frac{\sqrt{\epsilon_\parallel' - \epsilon_\perp'}}{\sqrt{\mu_\parallel - \mu_\perp}} (300 E_0) \tag{1}$$

$\epsilon_\parallel'$ and $\epsilon_\perp'$ are the low frequency dielectric constants parallel and perpendicular to the axis of symmetry in the nematic phase of an ordered sample. $\mu_\parallel$ and $\mu_\perp$ are the permeabilities parallel and perpendicular to the symmetry axis. E_0 is the externally applied electric field in V/cm and H_0 is the magnetic field in oersteds (or gauss since μ is approximately one).

2. Results and Discussion

In NMR studies involving liquid crystals the magnetic field, which is necessary for obtaining the NMR spectra, normally determines the orientation of the molecules. This paper reports measurements involving wide-line NMR techniques employing conducting plates inside the sample cell for applying electric fields. If the electric

field is perpendicular to the magnetic field and the sample is anisal-*p*-aminoazobenzene, the molecules will prefer a direction parallel to whichever field is most effective. If the electric field makes an angle α with respect to the magnetic field, the following relation is satisfied

$$\cot(2\theta) = \frac{\dfrac{H^2(\mu_\parallel - \mu_\perp)}{9 \times 10^4 E^2(\epsilon_\parallel' - \epsilon_\perp')} + \cos(2\alpha)}{\sin(2\alpha)} \tag{2}$$

where θ is the angle between the symmetry axis of the sample (direction preferred by the long axes of the molecules) and the magnetic field. $(\mu_\parallel - \mu_\perp)$ and $(\epsilon_\parallel' - \epsilon_\perp')$ are as defined for Eq. (1). H is the external magnetic field in oersteds (or gauss since μ is approximately one) and E is the externally applied electric field in V/cm. This relation assumes that the only processes which are producing molecular alignment are those associated with the dielectric and permeability anisotropy.

The wide-line NMR spectrum of anisal-*p*-aminoazobenzene shows a triplet structure similar to that reported by Jain, Lee and Spence[6] for *p*-azoxyanisole. The side peaks resulting from the dipole–dipole splittings of the orthoaromatic protons should be separated as indicated below.

$$\Delta H = 1.8(3\cos^2\theta - 1). \tag{3}$$

ΔH is the separation of the side peaks measured in gauss and θ is the angle between the symmetry axis of the sample and the magnetic field. A plot of Eq. (3) shows good agreement with the measured values[7] of ΔH. The frequency of the externally applied electric field was 15 kHz and the strength of the external magnetic field was 1500 gauss. These results imply that only measurements of the dielectric and permeability anisotropy are necessary for this NMR experiment.

When this experiment was performed measurements of the dielectric anisotropy for anisal-*p*-aminoazobenzene were not available, so the ratio $(\mu_\parallel - \mu_\perp)/(\epsilon_\parallel' - \epsilon_\perp')$ in Eq. (2) was obtained from Eq. (1). The ratio E_0/H_0 in Eq. (1) was taken from the work employing microwave techniques.[4]

We have also investigated the possibility of angular dependent studies in *p*-methoxy-benzylidene, *p*-*n*-butyl-aniline (MBBA) which

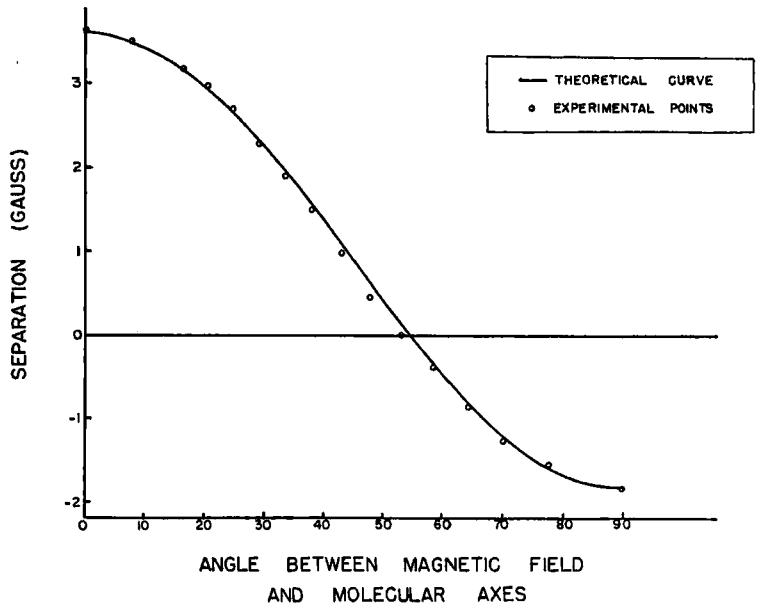

Figure 1. Separation of side peaks resulting from dipole–dipole splittings of the orthoaromatic protons in anisal-*p*-aminoazobenzene as a function of the angle formed by the magnetic field and the axis of symmetry. The experimental method involves wide-line NMR techniques.

exhibits a negative dielectric anisotropy. Since MBBA exhibits a wide-line NMR spectrum similar to that of anisal-*p*-aminoazobenzene, we were able to show that Eqs. (2) and (3) were satisfied by employing the NMR techniques described previously. The external magnetic field was 3000 gauss and the frequency of the externally applied electric field was 20,000 Hz. It is important to be well above the cutoff[8] frequency for these measurements. The experimental results were in good agreement with the theoretical predictions. In the presence of magnetic and electric fields acting simultaneously nematic materials with positive dielectric anisotropy align with their long molecular axes in a plane formed by the fields, but materials with a negative dielectric anisotropy tend not to be restricted to this plane as θ (angle between the symmetry axis and magnetic field) approaches 90°. One can permit θ to approach closer to 90° by increasing the magnitudes of the applied fields when investigating materials with a negative dielectric anisotropy.

There has been some uncertainty in the literature regarding dielectric and permeability anisotropy, but recent results by Gasparoux, Regaya and Prost[9] appear to have cleared up much of the difficulty. Microwave techniques[4] and the magnetic susceptibility measurements by Zwetkoff and Sosnovsky[10] give $(\epsilon_{\parallel}' - \epsilon_{\perp}') = 1.09$ for anisal-*p*-aminoazobenzene at $T = 155\,^{\circ}\mathrm{C}$. We have recently measured this difference at one megacycle employing a Franklin Oscillator-Wave Meter Combination[11] and found a value of 1.3. Although there is some error associated with each of these measurements we do not believe that the error can account for all this difference. Earlier work[4] indicated that there is not a dispersion region below 1 MHz. A study by Gasparoux, Regaya and Prost[9] has indicated that the method employed by Zwetkoff and Sosnovsky[10] yielded low results for the diamagnetic anisotropy of liquid crystals, and this could account for the difference.

Carr[4] calculated $(\epsilon_{\perp}' - \epsilon_{\parallel}')$ for *p*-azoxyanisole at $T = 132\,^{\circ}\mathrm{C}$ from E_0/H_0 ratios obtained from microwave measurements, and the susceptibility measurements of Zwetkoff and Sosnovsky.[10] The result was approximately 10% lower than that obtained by Maier and Meier.[12] From the results by Gasparoux, Regaya and Prost[9] we obtained a value of $(\epsilon_{\perp}' - \epsilon_{\parallel}') = 0.12$ which agrees with Maier and Meier.[12] We have obtained an E_0/H_0 ratio for *p*-azoxyanisole at $T = 120\,^{\circ}\mathrm{C}$ employing microwave techniques and found $(\epsilon_{\perp}' - \epsilon_{\parallel}') = 0.21$ using the results by Gasparoux, Regaya and Prost.[9] Maier and Meier[10] give $(\epsilon_{\perp}' - \epsilon_{\parallel}') = 0.21$ for $T = 120\,^{\circ}\mathrm{C}$.

Our measurements for the dielectric anisotropy for MBBA employing the Franklin Oscillator-Wave Meter Combination[11] were a little smaller than those reported by Diguet, Rondelez and Durand[13] but this could be due to impurity in our samples. The agreement between the work of Diguet, Rondelez and Durand,[13] the magnetic susceptibility measurements of Gasparoux, Regaya and Prost, and our measurements employing microwave techniques are within the limits of experimental error.

We have shown that angular dependent studies are possible in nematic materials employing magnetic and electric fields if good measurements of the diamagnetic susceptibility and dielectric constant are available. One has to be careful with materials where the anisotropy can depend on impurities. The dielectric anisotropy

is probably not as dependent on the dielectric properties of the impurity as it is on the effect of the impurity on the degree of ordering. We have noticed from our studies employing microwave techniques that the ratio $(\mu_{\parallel} - \mu_{\perp})/(\epsilon_{\perp}' - \epsilon_{\parallel}')$ appears to be independent of temperature for MBBA and anisal-*p*-aminoazobenzene, but not for *p*-azoxyanisole. This may imply that there are changes due to temperature in the processes which are responsible for the dielectric constant in some materials. This aspect of the work needs further consideration.

Acknowledgement

The authors wish to thank Mr. D. P. McLemore for his help with some of the measurements.

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