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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: 21 Mar 2007.

To cite this article: T. E. Kubaska , C. E. Tarr & T. B. Tripp (1974): Influence of Magnetic and D. C. Electric Fields on the Molecular Alignment of a Nematic Liquid Crystal, Molecular Crystals and Liquid Crystals, 29:1, 155-163

To link to this article: http://dx.doi.org/10.1080/15421407408083196

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Mol. Cryst. Liq. Cryst., 1974, Vol. 29, pp. 155–163
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Influence of Magnetic and D.C. Electric Fields on the Molecular Alignment of a Nematic Liquid Crystal†

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(*Received August 22, 1974*)

The molecular alignment of *p*-ethoxy-d_5-*p'*-acetoxy-d_3-azobenzene (EAAB-d_8) was observed using N.M.R. techniques. Absorption line shapes were recorded as a function of d.c. electric field from 0 to 12 kV/cm with the electric field perpendicular to a 7 kG magnetic field. The results are interpreted in terms of a simple model of flow cells and these results are used to predict the shape of the dielectric loss curve.

INTRODUCTION

A number of studies have been made to determine the influence of magnetic and electric fields on the molecular alignment in nematic liquid crystals.[1] Many of these studies have been concerned with "anomalous alignment" in which the molecular alignment is dominated by the conductivity rather than by the dielectric properties of the materials. In such cases, the conductivity and dielectric anisotropies are of opposite sign, and it is observed

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that the conductivity determines the direction of molecular alignment in electric fields below some critical frequency, while the dielectric anisotropy dominates at higher frequencies.[1,2] In the present work d.c. electric fields were applied to a sample contained in a cell whose geometry is very similar to those used by Carr and his co-workers.[1]

The situation is further complicated by hydrodynamic flow of the nematic material, which, coupled with anomalous alignment, gives rise to the formation of well defined domains in thin samples. Similar effects have been observed in thick samples in optical and dielectric studies.[3] The optical studies show evidence of a flow mechanism similar to that observed in thin samples, but which may not be identical to that responsible for domain formation. To avoid ambiguity, we shall refer to the field/flow structures in thick samples as "flow cells."

The present study made use of pulsed N.M.R. techniques in an attempt to obtain more quantitative information about molecular alignment in thick samples than is possible from optical or dielectric measurements. These N.M.R. data were analyzed in the context of a simple model for flow cells, and the results were used to predict the shape of the plot of the dielectric loss vs. electric field.

EXPERIMENT

The molecular orientation of *p*-ethoxy-d_5-*p*′-acetoxy-d_3-azobenzene (EAAB) was monitored by observing the N.M.R. absorption line shape. Using the compound with deuterated end groups simplifies the line shape.

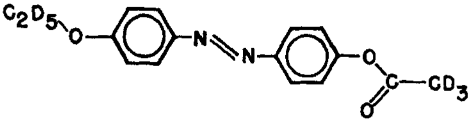

FIGURE 1 Structure of *p*-ethoxy-d_5-*p*′-acetoxy-d_3-azobenzene.

Sample preparation

P-nitrophenyl ethyl-d_5 ether was prepared by refluxing for two hours 0.1 mole C_2D_5Br (Bio-Rad 99 atom % D) with 24 gm *p*-nitrophenol sodium salt in a mixture of 70 cc water and 120 cc ethanol. The mixture was cooled by the addition of 200 gm crushed ice, filtered and washed with cold water. The crude ether was reduced to the corresponding amine with tin and hydrochloric acid,[4] and the free amine was steam distilled from an alkaline solution. The procedure for preparing EAAB from the amine has been

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described elsewhere.[5] In the present case, acetic anhydride-d_6 (Bio-Rad 99 atom % D) was used. The EAAB-d_8 was purified by four recrystalizations from 2-propanol, chromatography on silica gel (Fisher 20–40 mesh, grade 28) with chloroform, and one recrystalization from 2-propanol. The solid to nematic transition temperature was 117°C.

N.M.R. techniques

The magnetic susceptibility χ is proportional to the Fourier transform of the free induction decay (FID) observed in a pulsed N.M.R. experiment.[6] In particular, the absorption line shape is χ'' the imaginary part of χ and is proportional to the Fourier cosine transform of the FID, while the real (dispersion) part of χ, χ', is proportional to the Fourier sine transform. By using phase sensitive detection in the pulsed N.M.R. apparatus, it is possible to distinguish between χ' and χ''.

The Fourier transforms were performed using the method described by Clark[7] in which the phase detected FID undergoes boxcar integration. The output of the boxcar is given by:

$$V(H) \alpha \int_0^{\infty} S(t)(\cos(1/\gamma(H - H_0)t)\cos\phi + \sin(1/\gamma(H - H_0)t)\sin\phi)\,dt$$

where $S(t)$ is the FID, H the magnetic field at which the integral is performed, H_0 the resonant magnetic field, γ the gyromagnetic ratio of the resonant nucleus, and ϕ is the phase difference between the reference and nuclear signals in the phase sensitive detector. Note that the upper limit of the integral (boxcar gate duration) may be finite as the FID goes to zero in a finite time, on the order of one millisecond. Thus, by setting $\phi = 0$ and sweeping H in a time long compared to the repetition rate of the FID, we obtain $V(H)$ which is proportional to $\chi''(H)$.

All measurements were made at $H_0 \sim 7$ kG ($\omega_0 = 30$ MHz) using pulsed N.M.R. apparatus that has been described elsewhere.[8,9] The output of the boxcar was digitized to 9 bit accuracy using a Nicolet Instruments Model 1074 signal averaging computer whose memory addressing was proportional to the swept magnetic field ($H - H_0$). The contents of signal averager memory were recorded by a digital magnetic tape recorder for computer analysis.

Sample cell

The sample was carefully degassed and sealed under vacuum in a 1 cm square pyrex tube. The sample cell contained 9, 0.13 mm (0.005 inch) platinum plates supported in slotted teflon guides. This geometry provided a plate spacing of 1.074 mm, which yields an electric field $E \approx 0.93U$, where E is in kV/cm and the applied electric potential, U, is in kV.

The sample temperature was maintained ~ 2°C above the sample's solid-nematic phase transition temperature using an electronically controlled air-flow heating system. The temperature stability was better than ± 0.5°C, and temperature gradients over the sample volume were less than 0.5°C.

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DATA ANALYSIS

Model of flow cells

In the following analysis we assume that the flow cells have a particularly simple form. Let us suppose that if the applied magnetic and electric fields are perpendicular, then the flow cells are approximately rectangular with their sides parallel to the applied fields. Further, assume that a fraction of the molecules are parallel to or make a small angle with the flow directions forming the cell boundaries. Very little is known about the structure of these flow cells, especially the details of the molecular arrangement. The experimental results appear to be adequately described by assuming that the remaining molecules are randomly oriented with respect to the applied fields, and this assumption is used in the analysis that follows.

Analysis of N.M.R. spectra

The proton absorption spectra are split by the dipolar interaction of the ring protons. An analysis of the molecular structure shows that the dipolar splitting is primarily due to the ortho interactions of protons on these sites. Other interactions produce further splittings of the resonance line, but, in the resolution of the experiment, these are observed only as a broadening of the line. We note that the para-axis of the molecule (and hence the internuclear vector connecting the ortho protons) makes a fixed angle ψ with the molecular axis, and that the dipolar splitting is a function of the angle α between the internuclear vector and the magnetic field. The dipolar splitting ΔH may then be written as:[10]

$$\Delta H \alpha |3 \cos^2 \alpha - 1| = \tfrac{1}{2}|3 \cos^2 \theta - 1|(3 \cos^2 \psi - 1),$$

so that:

$$\Delta H \alpha |3 \cos^2 \theta - 1|.$$

Thus, a measurement of the dipolar splittings yields information about the molecular orientation.

The absorption spectra are assumed to be due to molecules of three

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different classes: those oriented parallel to the magnetic field, those oriented parallel to the electric field (perpendicular to the magnetic field), and those having a random orientation. Since the area under each dipolar split absorption peak is proportional to the number of molecules in the orientation producing that splitting, the percentage of molecules in each class can be determined by decomposing the absorption spectra into its constituent peaks and calculating the contribution of each to the total area.

Several different line shapes, including Gaussian, Lorenzian, and hybrid, were tried to determine which best fit the experimental spectra. In all cases Gaussian line shapes were found to most accurately represent the data.

The half-widths and positions of the spectra due to molecules oriented parallel to and perpendicular to the magnetic field were determined in the limiting cases of zero and maximum electric field where peak overlap is minimal. Measurements of the splitting and line width were also made as a function of angle, and it was noted that the line width narrowed slightly as the angle θ was increased from zero to $\pi/2$. Also, by measuring the linewidth as a function of electric field with the electric and magnetic fields parallel, some motional narrowing was observed for electric fields above ~ 3 kV/cm.

The contributions to the line shape from the randomly oriented molecules were taken into account by making an integral average of contributions from a uniform angular distribution of molecules. In this integration the motionally narrowed values of the half-width were used, and a linear interpolation was incorporated to account for its slight angular dependence. The integral yields a broad spectrum which may itself be adequately described by decomposition into two pairs of lines located near the positions corresponding to parallel and perpendicular orientations. The half-widths of these two pairs of lines are significantly broader than those of the well-aligned molecules.

The experimental spectra also contained a small peak at the center of the resonance. Since this peak was observed to be independent of molecular orientation, it was attributed to a small number of undeuterated sites on the alkyl end groups.

A sum of Gaussian line shapes was least squares fit to the data. The sum consisted of a single peak at the center of the resonance as described above, a pair of dipolar split peaks due to molecules oriented parallel to the magnetic field, a pair of peaks corresponding to molecules aligned parallel to the electric field, and, finally two pairs of peaks due to randomly oriented molecules. The positions and half-widths of all the peaks were those determined as described above, and the amplitudes were the fit parameters, subject to the constraint that the amplitudes of the peaks contributed by the randomly oriented molecules are not linearly independent.

RESULTS

Representative data and corresponding least square fits are shown in Figures 2–4. Figures 2 and 3 show the limiting cases of zero and maximum electric field. The maximum electric field of 12.1 kV/cm was not exceeded to prevent excessive heating and possible decomposition. Figure 4 shows the results for an intermediate value of electric field in which the randomly oriented

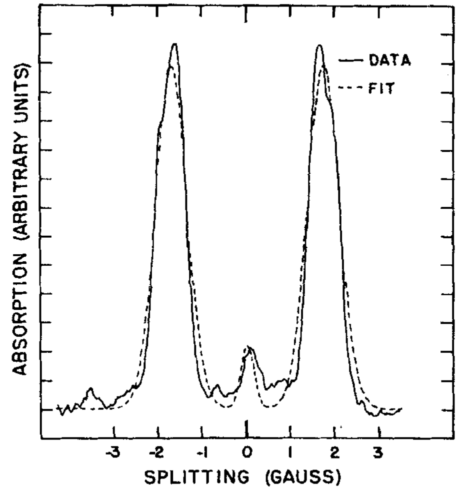

FIGURE 2 Proton N.M.R. absorption spectrum of EAAB-d_8 in a 7 kG magnetic field and fit of Gaussian lines.

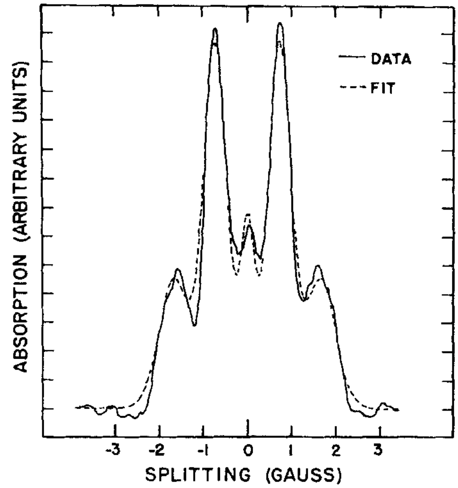

FIGURE 3 Proton N.M.R. absorption spectrum of EAAB-d_8 in a d.c. electric field of 12.1 kV/cm perpendicular to a 7 kG magnetic field.

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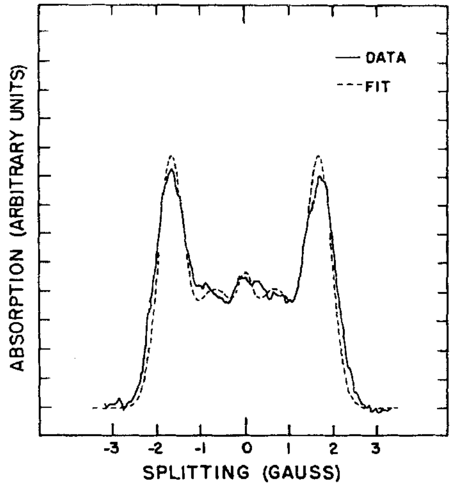

FIGURE 4 Proton N.M.R. absorption spectrum of EAAB-d_8 in a d.c. electric field of 2.78 kV/cm perpendicular to a 7 kG magnetic field.

molecules make a significant contribution to the broad central part of the spectrum.

Figure 5 shows the fractions attributed to each of the three classes of molecules as a function of electric field. The total fraction of molecules excludes the single peak at the center of the spectrum, whose area was constant within experimental error. It is interesting to note that, while the fractions of well-aligned molecules parallel to the magnetic and electric

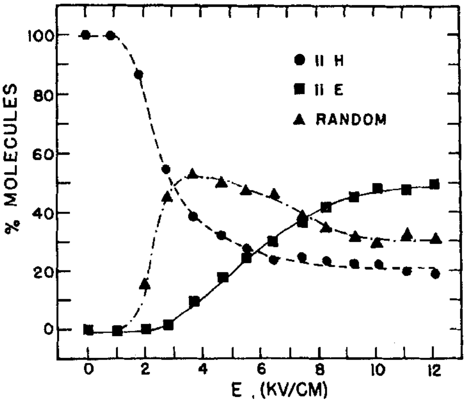

FIGURE 5 Fraction of molecules alligned parallel to, perpendicular to, and randomly with respect to the magnetic field as a function of a d.c. electric field applied perpendicular to the magnetic field.

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fields change monotonically, the fraction associated with randomly oriented molecules has a maximum near 4 kV/cm. Further, it is seen that there is a threshold for reorientation at about 2 kV/cm, and the various fractions appear to tend toward limiting values at high fields.

Dielectric loss

The measurement of dielectric loss is a primary technique in studies of molecular orientation in liquid crystals (see, for example, Refs. 1 and 3). It should, therefore, be particularly interesting to compare the present results with the dielectric loss measurements.

The dielectric loss ε'' can be represented as:

$$\varepsilon'' = N(\theta)(\varepsilon''_{\parallel} \cos^2 \theta + \varepsilon''_{\perp} \sin^2 \theta),$$

where $N(\theta)$ is the fraction of molecules making an angle θ with a reference axis (in our case the external magnetic field), and $\varepsilon''_{\parallel}$ and $\varepsilon''_{\perp}$ are the values of ε'' parallel and perpendicular to the reference axis, respectively. Averaging over all angles, under the assumptions of our simple model for the flow cells, one obtains:

$$\varepsilon'' = N_{\parallel}\varepsilon''_{\parallel} + N_{\perp}\varepsilon''_{\perp} + \tfrac{1}{2}N_R(\varepsilon''_{\parallel} + \varepsilon''_{\perp}),$$

where $N_{\parallel}$ is the fraction of molecules oriented parallel to the reference axis, $N_{\perp}$ is the fraction oriented perpendicular to the reference axis, and N_R is the fraction randomly oriented.

Figure 6 shows the dielectric loss as a function of electric field predicted on the basis of the N.M.R. results summarized in Figure 5. It should be stressed that this is a prediction of the dielectric loss curve, and not the result

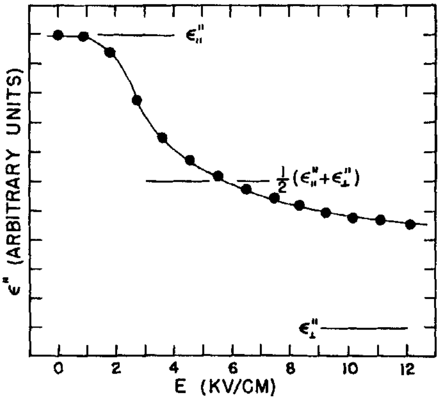

FIGURE 6 Dielectric loss as a function of applied d.c. electric field computed from the data shown in Figure 5.

of direct measurement. Further, it should be noted that the shape of the dielectric loss curve predicted for the present case of d.c. electric fields is not identical to those obtained for low frequency a.c. electric fields in other nematic liquid crystals.

CONCLUSION

The results of least squares fits of simple Gaussian line shapes are in good agreement with the experimental proton absorption spectra. These results are used to predict dielectric loss as a function of electric field. In summary, the N.M.R. technique described here appears to be useful in extracting information about the molecular orientation.

Acknowledgements

It is a pleasure to thank Profs. E. F. Carr and J. H. Parker, Jr. for several stimulating discussions related to this work. We are also indebted to Mr. M. E. Field for his technical assistance.

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