Electric and Magnetic Field Effects in p-Methoxy Benzylidene p′-n-Butylaniline

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Molecular alignment in the nematic phase of p-methoxy benzylidene p′-n-butylaniline (MBBA) in the presence of electric and magnetic fields is investigated. The relative effectiveness of electric and magentic fields on the nematic liquid crystal MBBA is discussed. In the dielectric regime it is found that the threshold fields for chevron formation are considerably different from the threshold fields for inducing changes in the dielectric constant.

Introduction

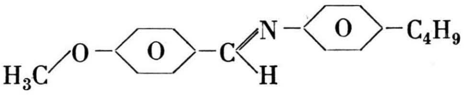
The effectiveness of electric and magnetic fields on the molecular alignment of nematic materials exhibiting negative dielectric anisotropy and positive conductivity anisotropy has been studied extensively [1–4]. A magnetic field aligns the molecular long axis into its direction, while in the presence of electric fields the molecular alignment is frequency dependent. In samples with resistivities of the order of 10^9 ohm·cm, the long molecular axes usually prefer a direction perpendicular to an electric field for frequencies of the order of kHz and parallel to the field for dc and very low audio frequencies [5–7]. It is established now that this effect is associated with the counteracting influences of the dielectric and conductive anisotropies and the relaxation time of the space-charge which results from the conductivity anisotropy. The dc and low frequency electric fields produce Williams-domains [8] in the sample and this has been satisfactorily explained theoretically [9, 10].

For frequencies above a critical frequency, the effectiveness of the electric field for producing molecular alignment is found to depend only on the dielectric anisotropy. The high frequency electric field tries to produce an ordering with the long axes perpendicular to the electric field while the magnetic field aligns the long axes along its direction, and therefore the relative effectiveness of the two fields can be examined, for a "parallel" configuration of the fields. This can be done by comparing the field strengths at a value of the dielectric constant corresponding to a "random orientation" of the molecules [6]. For this value of $\varepsilon_{\text{random}}$ the following relation

$$\frac{E}{H} = \frac{1}{300} \left[\frac{\mu_{\parallel} - \mu_{\perp}}{\varepsilon_{\perp} - \varepsilon_{\parallel}} \right]^{1/2} \tag{1}$$

is satisfied, where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are the low frequency dielectric constant parallel and perpendicular to the long axes respectively, $\mu_{\parallel}$ and $\mu_{\perp}$ are the magnetic permeabilities parallel and perpendicular to the long axes, E = electric field in volts/cm and H = magnetic field in oersteds.

The present work deals with a detailed investigation of electric field effects and relative effectiveness of E and H on the nematic liquid crystal p-methoxy benzylidene p′-n-butylaniline (MBBA),



which is known from dielectric measurements at 1 MHz to have negative dielectric anisotropy. The relative effectiveness of electric and magnetic fields on ε for random orientation is investigated.

Experimental

The commercial MBBA sample obtained from Vari-Light Co. (USA) was purified through fractional distillation under reduced pressure. The dielectric cell was similar in design to the one reported earlier [11]. The glass plates were separated by a 310 μm stainless steel wire. Electric fields of the order of 30 kV/cm were employed. The sample shows positive conductivity anisotropy with a conductivity ratio $\sigma_{\parallel}/\sigma_{\perp} = 1.25$ measured at 50 Hz. The domains and chevrons were observed optically with the help of a long focal length travelling microscope. The work was mainly carried out at room temperature.

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Results and Discussion

Since a magnetic field can align the long axes of the molecules, the dielectric constant along the long axes, $\varepsilon_{\parallel}$, can be obtained when the magnetic field is parallel to the r.f. field, while $\varepsilon_{\perp}$ the dielectric constant perpendicular to the long axes, can be obtained when the magnetic field is perpendicular to the r.f. field. The dielectric constant variation from parallel to perpendicular orientation can be interpreted in terms of molecular alignment.

A) Electric Field Dependence of the Dielectric Constant

For a negative dielectric anisotropic material an external electric field parallel to the r.f. measuring field is expected to turn the director, i.e. the long axes of the molecules perpendicular to the electric field direction E, such that the measured ε is higher. But the application of a static electric field parallel to the r.f. electric field causes anomalous dielectric behaviour, i.e. a decrease in the dielectric constant. The change in ε is dependent upon the frequency of the applied electric field, its strength, and magnetic field. The behaviour of ε as a function of E, the electric field strength, at different frequencies is shown in Figure 1. The variation of ε in the absence of a magnetic field is qualitatively in good agreement with the ε variation in the presence of a magnetic field perpendicular to the electric field. The only difference is that higher threshold voltages are necessary to cause a decrease in ε. When the frequency is increased, the threshold voltages for the anomalous alignment also increase; but the nematic director never reaches a parallel orientation as is caused by dc fields. At higher fields below the cutoff frequency the slight increase in ε may be due to thermal effects[4]. As the frequency is increased beyond the cutoff frequency, the nematic director attains perpendicular orientation with respect to the electric field.

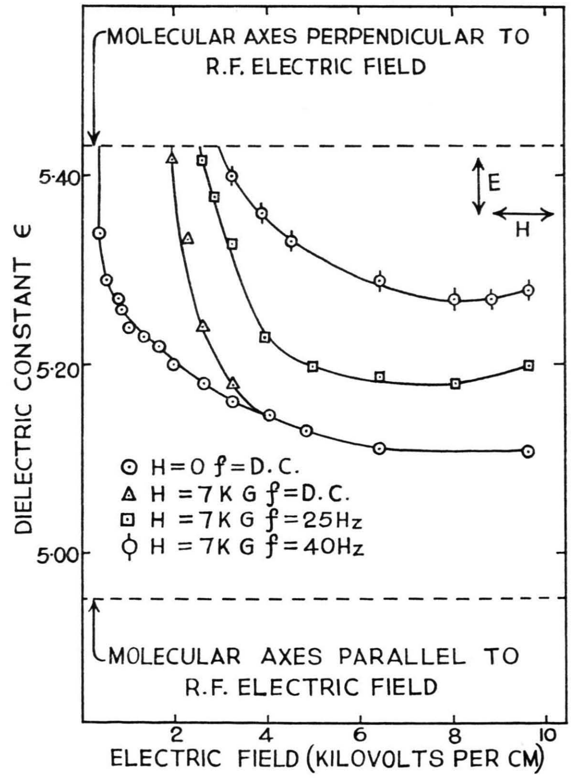

Fig. 1. Dielectric constant ε of MBBA at 1 MHz as a function of externally applied electric fields of various frequencies. A static magnetic field of 7000 G was applied perpendicular to the external electric field, which was parallel to the r. f. electric field. The temperature was 32 °C.

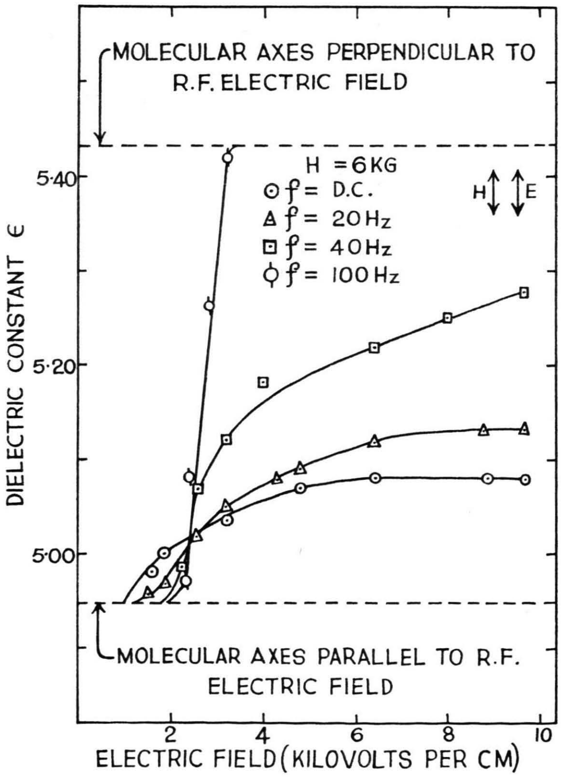

Fig. 2. Dielectric constant ε of MBBA at 1 MHz as a function of externally applied electric fields of various frequencies. A static magnetic field of 6000 G was applied parallel to the external electric field, which was parallel to the r. f. field. The temperature was 32 °C.

The dielectric constant variation with an external electric field in the presence of a parallel magnetic field is shown in Figure 2. For the lower dotted line, corresponding to a value of $\varepsilon = 4.95$, the nematic director is parallel to the r.f. field. At low frequencies, the increase of ε with E indicates that the nematic director is slowly turning away from the parallel orientation with respect to the r.f. field. When the frequency is increased just above the critical frequency, f_c, the nematic director suddenly changes from the parallel to a perpendicular orientation. The field range required to cause such a change in orientation is very small and is independent of the frequency above the critical frequency. The sharp increase in ε in the high frequency regime indicates that the conductivity anisotropy is no more playing any part in aligning the nematic director. The gradual increase of ε with the frequency as a function of the electric field evidences the decreasing influence of the conductivity anisotropy in changing molecular ordering.

B) Molecular Alignment in a 200 Hz Electric Field

The relative effectiveness of electric and magnetic fields in producing molecular alignment has been studied in a 200 Hz electric field for various magnetic field strengths. Figure 3 shows the variation of the dielectric constant, ε, with the external electric field parallel to the r.f. electric field and the magnetic field. The results show that a change in dielectric constant from $\varepsilon_{\parallel} = 4.95$ (lower dotted line) to $\varepsilon_{\perp} = 5.43$ (upper dotted line) corresponds to a 90° reorientation of the molecular axes. The relative effectiveness of the electric and magnetic fields was compared for a random orientation of molecules in the plane of E and H. The validity of Eq. (1) has been examined at the random value of the dielectric constant, $\varepsilon_{\text{random}} = \frac{1}{2}(\varepsilon_{\parallel} + \varepsilon_{\perp}) = 5.19$. It can be seen from Table 1 that the E/H ratio, for various magnetic field strengths is fairly a constant, indicating the absence of any effect other than that due to the dielectric anisotropy.

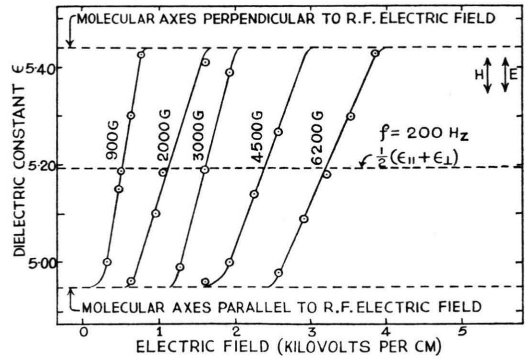

Fig. 3. Dielectric constant ε of MBBA at 1 MHz as a function of an externally applied 200 Hz electric field. The individual curves are for various values of a static magnetic field applied parallel to the external electric field and r. f. measuring field. $T = 32$ °C.

Table 1. Ratios of Electric Field to Magnetic Field corresponding to a Random Orientation of the Molecules Employing a 200 Hz Electric Field.

$H \parallel E$	$f = 200$ Hz
H (Gauss)	$\frac{E}{H}$ $\frac{\text{Volts}}{\text{cm Gauss}}$
900	0.535
2000	0.532
3000	0.535
4500	0.522
6200	0.525

Taking the values of $\Delta\varepsilon$ and $\Delta\mu$ from the literature[12, 13], the ratio E/H comes out to be 0.53 Volt/cm·Gauss. The above E/H values are in fair agreement with the value 0.500 obtained by Parker[14] and the calculated value from the literature[12, 13].

The E/H ratios for low frequencies in a crossed field configuration are found to be lower than the E/H ratios above f_c in a parallel field configuration. Since the ratio E/H is the relative effectiveness of fields on molecular alignment, the lower values of E/H for low frequencies is in good agreement with theory. On the other hand, the increase in the E/H ratio with the frequency below f_c suggests that the relative effectiveness of fields is also dependent upon the frequency.

Figure 4 shows the changes in the ordering of the molecules in the presence of magnetic fields of different strengths applied perpendicular to a 25 Hz electric field. The results are similar to those given in Figure 1. As in the case of the parallel field configuration of Fig. 3, the change in molecular ordering is less abrupt at higher magnetic field strengths and the threshold voltages for dielectric changes increased with increasing magnetic field strength. The dielectric constant does not reach down to the value of 4.95 at high electric fields, even if the magnetic field is switched off, suggesting that the magnetic field is superior to a low frequency electric field in ordering the molecules. This can be clearly seen from the curves in Fig. 1 also.

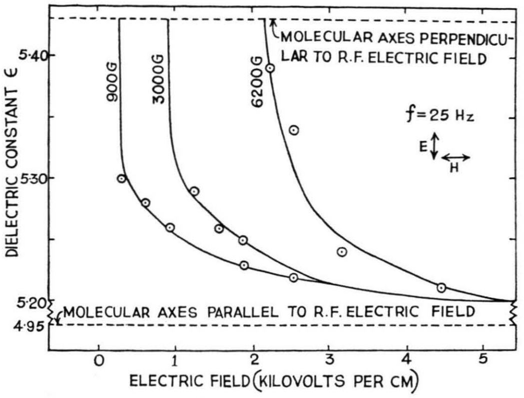

Fig. 4. Dielectric constant ε of MBBA at 1 MHz as a function of an externally applied 25 Hz electric field. The individual curves are for various values of a static magnetic field applied perpendicular to the external electric field which was parallel to the r. f. field. The temperature was 32 °C.

C) Frequency Dependence of Threshold Voltages and Fields

The threshold electric fields for the domain formation, chevron formation and the dielectric change in the dielectric regime are shown in Figure. 5. E_{th} is frequency dependent and its variation is found to be in good agreement with the theory[9], according to which the frequency dependence of the threshold voltage in the conduction regime is given by

$$V_{\text{th}}^2 = V_{\text{H}}^2 [1 + (\zeta^2 - 1)\,(f/f_c)^2]/[1 - (f/f_c)^2] \quad (2)$$

where $V_{\text{H}} = V_0/(\zeta^2 - 1)^{1/2}$ is the dc Helfrich voltage and f_c is the cutoff frequency given by $f_c = (\zeta^2 - 1)/2\pi\tau$, where τ is the space-charge relaxation time given by $\tau^{-1} = 4\pi\,\sigma_{||}/\varepsilon_{||}$. ζ^2 is the Helfrich parameter characteristic of the material and is defined by

$$\zeta^2 = \left(1 - \frac{\varepsilon_{||}}{\varepsilon_a}\,\frac{1}{1 + \eta_0/\nu_1}\right)\left(1 - \frac{\sigma_\perp}{\sigma_{||}}\,\frac{\varepsilon_{||}}{\varepsilon_\perp}\right);$$

$$\varepsilon_a = \varepsilon_{||} - \varepsilon_\perp, \quad \eta_0 = \frac{\eta_1 + \eta_2 - \nu_1}{2}.$$

η_1, η_2 are Miescowicz viscosity coefficients and ν_1 is the twist viscosity. The parameter ζ^2 involves many unknowns and cannot be calculated. Instead, the value of $\zeta^2 = 4.3$ is first obtained using the experimental data at 40 Hz, $f_c = 89$ Hz and $V_{\text{H}} = 10$ V as obtained from observation. This value is nearer to the value obtained by Parker et al.[4]. Using the value of $\zeta^2 = 4.3$ in Eq. (2) the threshold voltages were calculated at other frequencies.

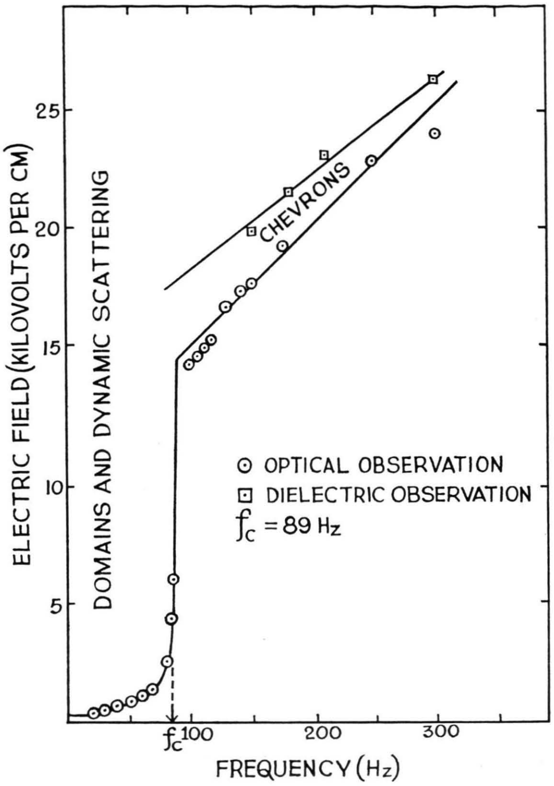

Fig. 5. Threshold electric field for domain formation, chevron formation and dielectric constant change in MBBA as a function of the frequency of the field. The temperature was 32 °C.

The calculated threshold voltages are in fair agreement with the experimentally observed ones and the value of ζ^2 being 4.3 is in good agreement with the theory.

Beyond f_c, at high field excitation the second instability (the dielectric regime) occurs for a field threshold E_{th}. When f is much larger than f_c, E_{th} is given by

$$\langle E_{\text{th}}^2 \rangle = A f. \quad (3)$$

where

$$A_{\text{CGS esu}} = 8\pi^2/|\varepsilon_a| \cdot C(\zeta^2) \cdot U.$$

From Ref.[10] $c(\zeta^2) \approx 1$, and $U = 1/\gamma_1 + 1/\eta_0$ is in the range of 4 ± 0.5 CGS units.

The calculated values of A in Eq. (3) are presented in Table 2.

The solid curve above the cutoff frequency is given by $E_{\text{th}}^2 = 2.4 \times 10^6 f$ at $f = 120$ Hz, $f_c = 89$ Hz and $E = 17.1$ kV/cm. The value obtained in the present work is in fair agreement with the values reported by Parker et al.[4] ($E^2 = 4.0 \times 10^5 f$ at $f = 300$ Hz, $f_c = 300$ Hz and $E = 11$ kV/cm), the Orsay

Table 2. Calculated values of 'A' in the dielectric regime.

f (Hz)	130	140	150	160	200	250	300
$A=E_{\text{th}}^2/f$ (C G S, e s u)	26.8	26.8	25.9	24.7	25.2	25.3	23.4

group[10] ($E^2=6.2\times10^6 f$ at $f=100$ Hz, $f_c=89$ Hz and $E=25$ kV/cm) and Wright et al.[15] ($E^2=3.2\times10^6 f$ at $f=250$ Hz, $f_c=230$ Hz and $E=28.3$ kV/cm).

Conclusions

The relative effectiveness of electric and magnetic fields on molecular alignment is found to be frequency dependent. In the low frequency regime the conductivity anisotropy plays a dominant role on the molecular alignment, while in the dielectric regime the dependence of molecular alignment is limited to the dielectric and permeability anisotropies. The consistent E/H ratio for various magnetic field strengths in the high frequency regime suggests that the molecular alignment is field dependent in that regime.

The optically observed threshold voltages for domain formation are the voltages at which anomalous alignment starts. The threshold fields for the chevron formation are considerably lower than the threshold fields for dielectric change. The cutoff frequency of the sample immediately after fractional distillation was 52 Hz, while after 24 hrs. it was 96 Hz. This rapid change in cutoff frequency suggests that the sample is very susceptible to the atmosphere. Even after repeated distillations under reduced pressure the cutoff frequency never fell below 50 Hz suggesting that distillation under reduced pressure is as good as zone-refining.

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[1] W. Helfrich, J. Chem. Phys. **51,** 4092 [1969].

[2] P. G. de Gennes, The Physics of Liquid Crystals, Oxford Press 1974.

[3] G. Durand and J. D. Litster, Ann. Rev. Mater. Sci. **3,** 269 [1973].

[4] J. H. Parker and E. F. Carr, J. Chem. Phys. **55,** 1846 [1971].

[5] E. F. Carr and L. S. Chou, J. Appl. Phys. **1973,** 3365.

[6] E. F. Carr, Mol. Cryst. Liq. Cryst. **7,** 253 [1969].

[7] R. P. Twitchell and E. F. Carr, J. Chem. Phys. **46,** 2765 [1967].

[8] R. J. Williams, J. Chem. Phys. **39,** 384 [1963].

[9] E. Dubois-Violette, P. G. de Gennes, and O. Parodi, J. Phys. **32,** 305 [1971].

[10] Orsay Liquid Crystal group, Mol. Cryst. Liq. Cryst. **12,** 251 [1971].

[11] M. N. Avadhanlu and C. R. K. Murty, Pramana Suppl. **1,** 289 [1975].

[12] F. Rondelez, D. Diguet, and G. Durand, Mol. Cryst. Liq. Cryst. **15,** 183 [1971].

[13] P. I. Rose, Mol. Cryst. Liq. Cryst. **26,** 75 [1974].

[14] J. H. Parker, Ph. d. Thesis submitted to University of Maine 1971.

[15] J. J. Wright and J. F. Dawson, Phys. Lett. **43 A** (2), 145 [1975].