Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

Determination of the Degree of Orientation in Thin Films of Nematic Liquid Crystals from Infrared Dichroic Measurements in a Homogeneous Electric Field

V. D. Neff [a], L. W. Gulrich [a] & G. H. Brown [a]

[a] Department of Chemistry, Kent State University, Kent, Ohio

To cite this article: V. D. Neff, L. W. Gulrich & G. H. Brown (1966): Determination of the Degree of Orientation in Thin Films of Nematic Liquid Crystals from Infrared Dichroic Measurements in a Homogeneous Electric Field, Molecular Crystals, 1:2, 225-239

To link to this article: http://dx.doi.org/10.1080/15421406608083271

Molecular Crystals. 1966. Vol. 1, pp. 225–239

Printed in Great Britain

Determination of the Degree of Orientation in Thin Films of Nematic Liquid Crystals from Infrared Dichroic Measurements in a Homogeneous Electric Field†

V. D. NEFF, L. W. GULRICH and G. H. BROWN
Department of Chemistry, Kent State University, Kent, Ohio

Received December 13, 1965

Abstract—Two methods are described for the determination of the degree of orientation in thin films of nematic liquid crystals. Both methods are based on the measurement of infrared absorption intensities in the presence of a homogeneous d.c. electric field. In the first method the infrared dichroic ratio is determined by applying the electric field perpendicular to the direction of propagation of the polarized radiation. In the second method the electric field is applied parallel to the direction of propagation and does not require polarized radiation. An expression is derived for the dependence of the dichroic ratio on the magnitude of the applied field using a simple model of a domain acting as a rigid dipole.

These methods were applied to the liquid crystal *p*-methoxybenzylidene-*p'*-cyanoaniline. The degree of orientation was determined over the temperature range of the liquid crystal. The maximum degree of orientation was found to be 0.33 at 106° C.

Introduction

Various methods have been introduced in the past for the study of the degree of molecular orientation in nematic liquid crystals influenced by external electric or magnetic fields. These include the determination of dielectric and diamagnetic anisotropy[1,2] and the determination the second moments of n.m.r. bands.[3,4] In this paper we propose a method which involves the measurement of infrared dichroic ratios in a homogeneous d.c. electric field. Dichroic

---

† Work supported in part by N.I.H. Grant GM 10789-05 and Army Contract DA-44-009-AMC-1074(T).

measurements on nematic liquid crystals have been reported before[5] where orientation was attained by rubbing the surface of a sodium chloride crystal. In this procedure one has no control over the extent of orientation of domains. Also one would expect that the strong forces due to the charge induced on the surface of the sodium chloride would have a complicated effect on the degree of orientation.

Theory

In considering a theory of the relationship between the dichroic ratio and the electric field strength we adopt the view that a thin film of a nematic liquid crystal is made up of clusters of molecules or domains. The tendency toward parallel ordering of the molecules in the nematic phase leads one to associate a macroscopic dipole moment $\vec{P}$ with each domain. The existence of domains in thin films has been demonstrated most recently by Williams[6] and Kapustin.[7] We will assume that the domain responds to an applied field by exerting a torque on $\vec{P}$. The domain is assumed to respond to the torque by rotating as a rigid unit. This model is due originally to Kast[8] and its limitations were pointed out long ago by Frenkel.[9] Most of Frenkel's objections refer however to transient conditions with a.c. fields where the response of the system is limited by viscous forces.

A measure of the degree of orientation which characterizes the nematic structure is concerned with the tendency of the molecules to align along a preferred axis within a given domain. Hence we will introduce two orientation angles as shown in Fig. 1. The angle θ will describe the direction of the $\vec{P}$ axis with respect to the applied field. The angle α will designate the angle between the vibrational transition moment $\vec{M}$ of the molecule and $\vec{P}$. The latter serves as a structure parameter with which to characterize the degree of order in the nematic phase. The general theory of the relation between dichroic measurements and molecular order in non-crystalline materials has been treated in detail by Fraser.[10, 11, 12] We shall consider only the case in which the vibrational transition moment lies along the long axis of the molecule. Hence $\vec{M}_i$ also describes the direction of the long axis. The angles ϕ and ϕ' are taken about the $\vec{E}$ and $\vec{P}$ axes, respectively. We shall assume a uniform distribution of domain and molecular orientation about these axes. The dichroic ratio, R, is defined as

$$R = \frac{\epsilon_\pi}{\epsilon_\sigma} \tag{1}$$

where ϵ_π is the absorption coefficient measured with the electric vector of the polarized radiation directed along $\vec{E}_\pi$ as shown in Fig. 1. Similarly ϵ_σ is measured along $\vec{E}_\sigma$. The absorption coefficient in turn is proportional to the square of the scalar product of the electric vector and the transition moment summed over all molecules within a given domain and over all domains. That is

$$\epsilon_\pi \propto \sum_j \sum_i (\vec{M}_{ji}.\vec{E}_\pi)^2 \tag{2}$$

We now replace the sum by an integral over the angular coordinates obtaining

$$R = \frac{\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi} F(\alpha,\theta)[\cos^2\alpha\cos^2\theta + \sin^2\alpha\sin^2\theta\sin^2\phi] \times \sin\alpha\sin\theta\, d\alpha\, d\theta\, d\phi\, d\phi'}{\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi} F(\alpha,\theta)[\cos^2\alpha\sin^2\theta\sin^2\phi + \sin^2\alpha(\cos\phi + \sin\phi\cos\theta)^2 \times \sin\alpha\sin\theta\, d\alpha\, d\theta\, d\phi\, d\phi'} \tag{3}$$

where $F(\alpha, \theta)$ is an angular distribution function

$$F(\alpha,\theta) = \frac{f(\alpha,\theta)}{\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi} f(\alpha,\theta)\sin\alpha\sin\theta\, d\alpha\, d\theta\, d\phi\, d\phi'} \tag{4}$$

We further assume that the distribution in α is independent of that in θ and write

$$f(\alpha,\theta) = g(\alpha)f(\theta) \tag{5}$$

This amounts to the assumption that the orientation of the domains is affected only by the applied electric field whereas the orientation of molecules within a domain is affected only by intermolecular forces within the domain. The distribution is a direct measure of the molecular order. Since the physical data will not lead to the determination of a unique $g(\alpha)$ we are reduced to assuming a certain distribution and to calculating R as a function of the orientation parameter. In order to conform to the usual orientation parameter used for nematic liquid crystals we define

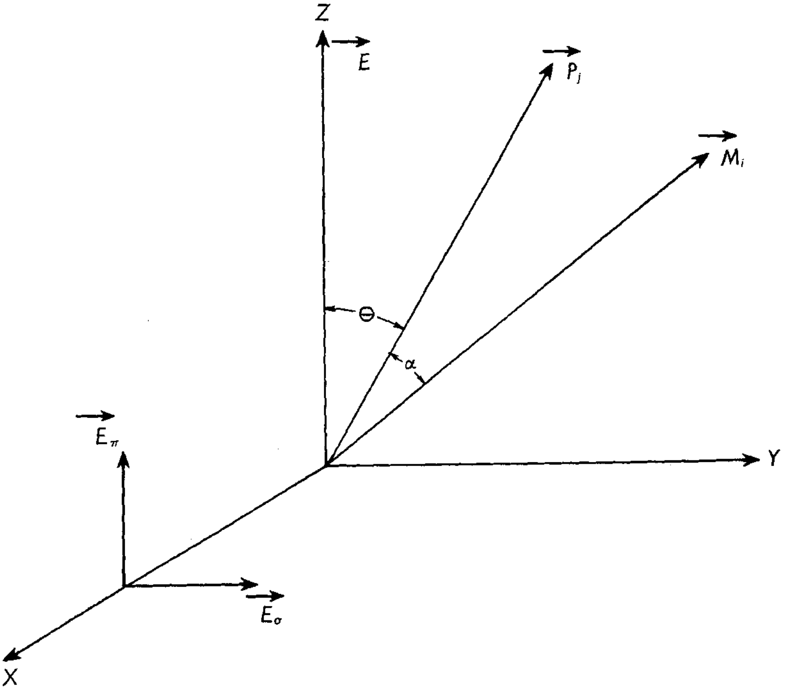

Figure 1. Coordinate system showing the direction of the dipole moment $\vec{P}_j$ of the jth domain and the vibrational transition moment $\vec{M}_i$ of the ith molecule.

$$g(\alpha) = \delta(\bar{\alpha} - \alpha) \tag{6}$$

where the delta function in $\bar{\alpha}$ defines the average angle between the long axis of the molecule and the domain axis. With this assumption the expression for R reduces to

$$R(\bar{\alpha},\theta) = \frac{\cos^2\bar{\alpha}\langle\cos^2\theta\rangle+\frac{1}{2}\sin^2\bar{\alpha}\langle\sin^2\theta\rangle}{\frac{1}{2}\cos^2\bar{\alpha}\langle\sin^2\theta\rangle+\frac{1}{4}\sin^2\bar{\alpha}\langle 1+\cos^2\theta\rangle} \tag{7}$$

where $\langle\sin^2\theta\rangle = \dfrac{\int_0^\pi f(\theta)\sin^3\theta\,d\theta}{\int_0^\pi f(\theta)\sin\theta\,d\theta}$ and $\langle\cos^2\theta\rangle = \dfrac{\int_0^\pi f(\theta)\cos^2\theta\sin\theta\,d\theta}{\int_0^\pi f(\theta)\sin\theta\,d\theta}$

It is instructive to consider some limiting forms of Eq. (7) in the absence of any specific assumptions about $f(\theta)$. As $\langle\sin^2\theta\rangle$ approaches zero corresponding to perfect orientation of domains along $\vec{E}$, R reduces to

$$R = 2\cot^2\bar{\alpha}$$

The degree of orientation S is defined by

$$S = (1-\tfrac{3}{2}\sin^2\bar{\alpha})$$

When $\sin^2\bar{\alpha}$ is equal to two-thirds corresponding to $S=0$, Eq. (7) reduces to

$$R(\alpha,\theta) = 1 \text{ (for all } \theta).$$

We also wish to consider a second method for determining the degree of orientation which does not require the use of polarized radiation. This method involves application of the electric field parallel to the direction of propagation of the incoming radiation. The coordinate system is shown in Fig. 2. Again the z axis is chosen as the direction of the applied field. $\vec{E}_x$ and $\vec{E}_y$ represent the electric vectors of unpolarized radiation propagating along the z axis. We define a "dichroic ratio" $R'(\bar{\alpha},\theta)$ as follows:

$$R' = \epsilon/\epsilon' \tag{8}$$

where ϵ is the absorption coefficient measured before and ϵ' that measured after switching on the electric field. Geometrical considerations similar to those shown previously lead to the following expression for R'

$$R'(\bar{\alpha}, \theta) = \frac{\cos^2\bar{\alpha}\langle\sin^2\theta\rangle + \frac{1}{2}\sin^2\bar{\alpha}\langle 1+\cos^2\theta\rangle}{\cos^2\bar{\alpha}\langle\sin^2\theta\rangle' + \frac{1}{2}\sin^2\bar{\alpha}\langle 1+\cos^2\theta\rangle'} \tag{9}$$

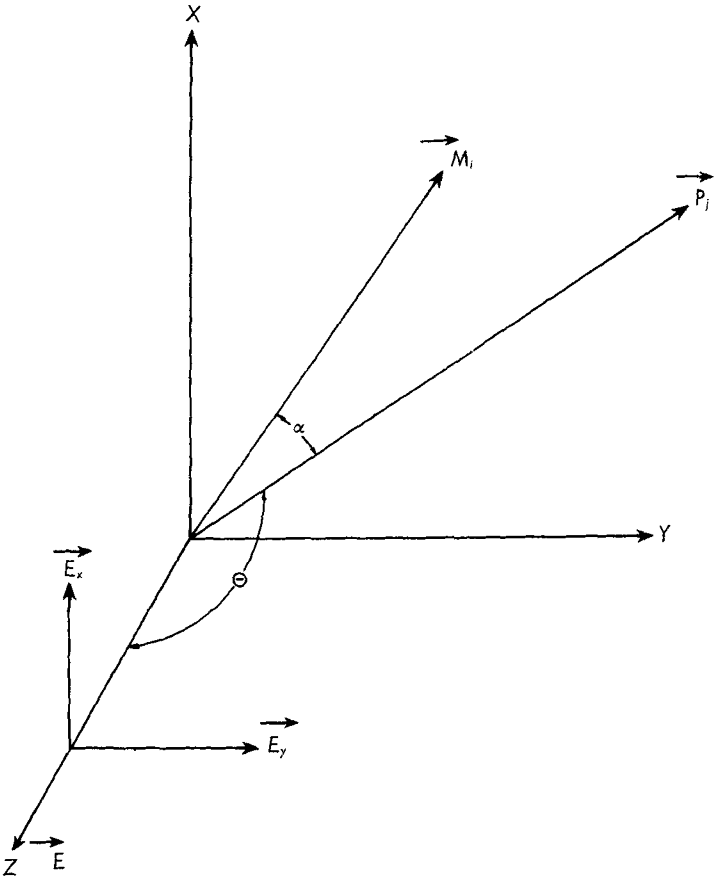

Figure 2. Coordinate system showing the direction of the applied field E parallel to the direction of propagation of the infrared radiation.

where the prime in the denominator indicates the values obtained after the field is switched on.

Two factors determine the orientation of the domains. The first is the effect of the container which tends to align the domain axis parallel to the wall in the absence of the applied field.[6, 7] The second is the applied field which, in Method B, exerts a torque tending to orient the domain axis perpendicular to the wall. The distribution function $f(\theta)$ should contain parameters describing both of these effects. We assume a very simple model from which to calculate $f(\theta)$ in terms of parameters describing the interaction with the field and the container wall. This is shown in Fig. 3. The z axis is the direction of the applied field and is perpendicular to the surface of the container (y axis). The potential energy of the domain in the presence of the field is assumed to have the form

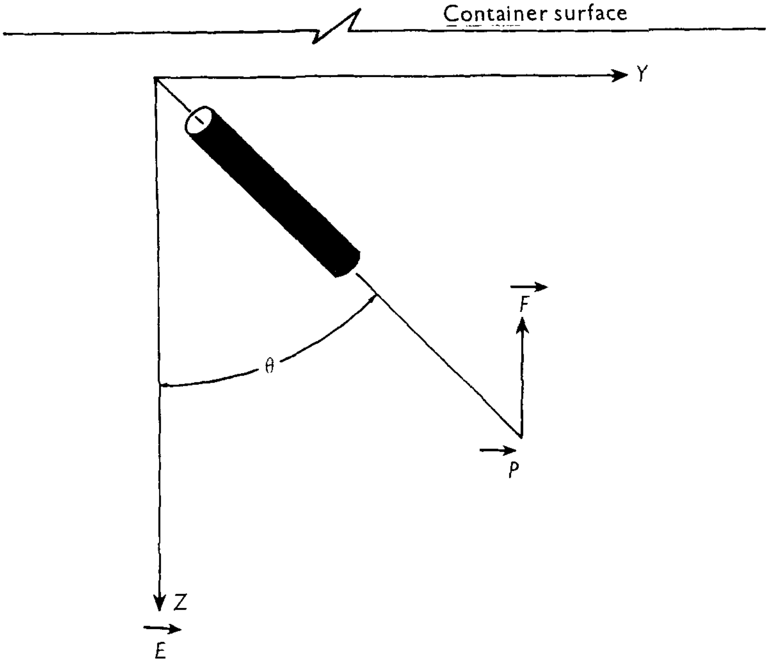

Figure 3. Force, F, which tends to orient a rod-shaped domain parallel to the surface of the container.

$$U = -PE\cos\theta + \mu\cos^2\theta \tag{10}$$

The first term is the usual electrostatic energy of a dipole in a uniform field, where P is the magnitude of the dipole moment and E the field strength. The second term is the energy of a restoring torque tending to orient the domains parallel to the surface. The empirical restoring force has a direction perpendicular to the wall and a magnitude given by

$$F = b\cos\theta \tag{11}$$

where b is a force constant in dynes and $\mu = ab/2$, where a is the length of a rod-shaped domain. A thermal distribution of domains then leads to

$$f(\theta) = \exp\left[\frac{PE\cos\theta}{kT} - \frac{\mu\cos^2\theta}{kT}\right] \tag{12}$$

The above expression is to be used in conjunction with Eq. (9) to obtain R' as a function of E and T. When S is zero, R' reduces to unity for all values of θ. Also if S is unity, corresponding to perfect alignment of molecules, R' reduces to

$$R' = \langle\sin^2\theta\rangle / \langle\sin^2\theta\rangle'$$

Experimental

The liquid crystalline compound chosen for these studies was *p*-methoxybenzylidene-*p*'-cyanoaniline hereafter referred to as MBC. The compound was prepared by the method of Gray[13] and purified by several recrystallizations. The measured resistivity of the MBC in the liquid crystalline state was found to be approximately 10^8 Ω-cm. This compound was chosen because the direction of the transition moment of the CN stretching vibration is well defined and is directed along the long axis of the molecule.

The dichroic ratios, R and R', were determined on a Perkin-Elmer Model 21 spectrophotometer employing a standard polarizer consisting of six AgCl plates mounted parallel at Brewster's angle.

Two different cells were employed for measurements with polarized (Method A) and ordinary (Method B) radiation. Cell A was constructed of two IRtran II plates with stainless steel electrodes fastened at the ends with epoxy cement. The separation of the electrodes was approximately 2 cm. This large separation of electrodes required a high voltage output to create the necessary field strength. This was accomplished with the rectified and filtered output from an r.f. H.V. oscillator with a maximum output of 15 kV. Cell B was constructed from two 0.500 in. *p*-type silicon wafers with a resistivity of 5 Ω-cm. In this case the cell windows themselves served as the electrodes. External electrical contact was made with stainless steel rings pressed against the wafer surfaces. In this study the electrode separation varied from 10 to 120 microns. The low output voltage required for the silicon cell was supplied by conventional half-wave rectified 60 cycle current with an LC-Π type filter. Mylar spacers were used for both cells. Both cells were placed in a rotatable heating furnace designed to fit in the light path of the spectrophotometer. The furnace was heated by resistance coils imbedded in alundum, cast to fit the outline of the cell.

Results and Discussion

The region of interest in the infrared spectrum of MBC is shown in Fig. 4. The CN stretching band is shown at 4.45 μ. A second weak band occurring at 4.92 μ was shown experimentally to have approximately the same dichroic ratio as the CN band. This band has been assigned as the first overtone of the asymmetric stretching vibration of the methoxy group. The transition moment for this vibration would be expected also to be directed along the long axis of the molecule providing the methoxy group is allowed to assume any position about this axis. The dotted line in Fig. 4 represents the spectrum obtained with the field off and the solid line with the field on (Method B). For thick films, where the intensity of the CN band was too great for accurate intensity measurements, we used the 4.92 μ band.

The dichroic ratio was determined as a function of the applied field strength by both Methods A and B described previously. In both cases the dichroic ratio increased with increasing field up to a saturation value. We will consider, however, only the somewhat more accurate results obtained by Method B since in this case we did not need to use a polarizer and we were able to control the low voltages more accurately.

As mentioned previously R' approaches a limiting value for high fields of the order of 5 kV/cm. This may be seen in Fig. 5 where R' approaches 1.72 for a 120 μ film at 106° C. We assume that this

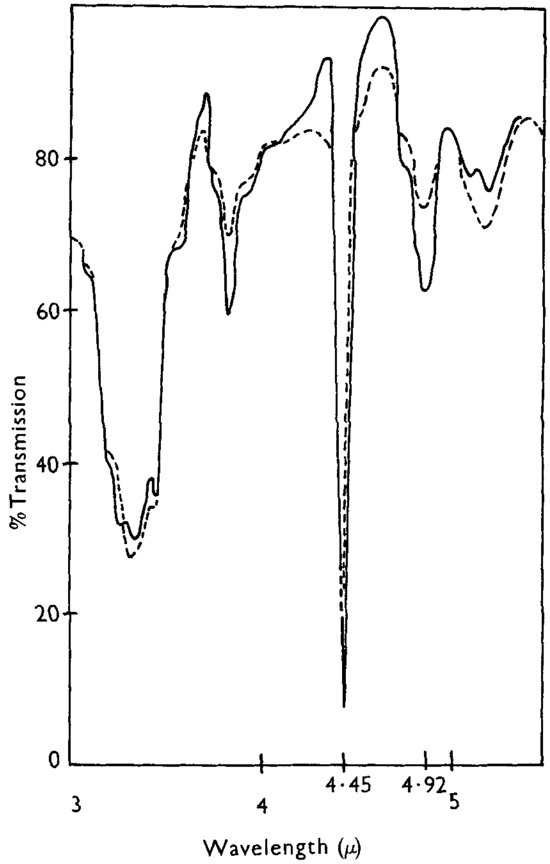

Figure 4. Infrared spectrum of a 120 μ film of MBC from 3 to 6 μ. The dotted line represents the spectrum obtained after switching on the field.

limiting value corresponds to essentially complete orientation of the domains along the z axis. Under these conditions $\langle \sin^2 \theta \rangle$ approaches zero. In order to compare the experimental values of R' with those predicted from Eq. (9) it is necessary to compute the

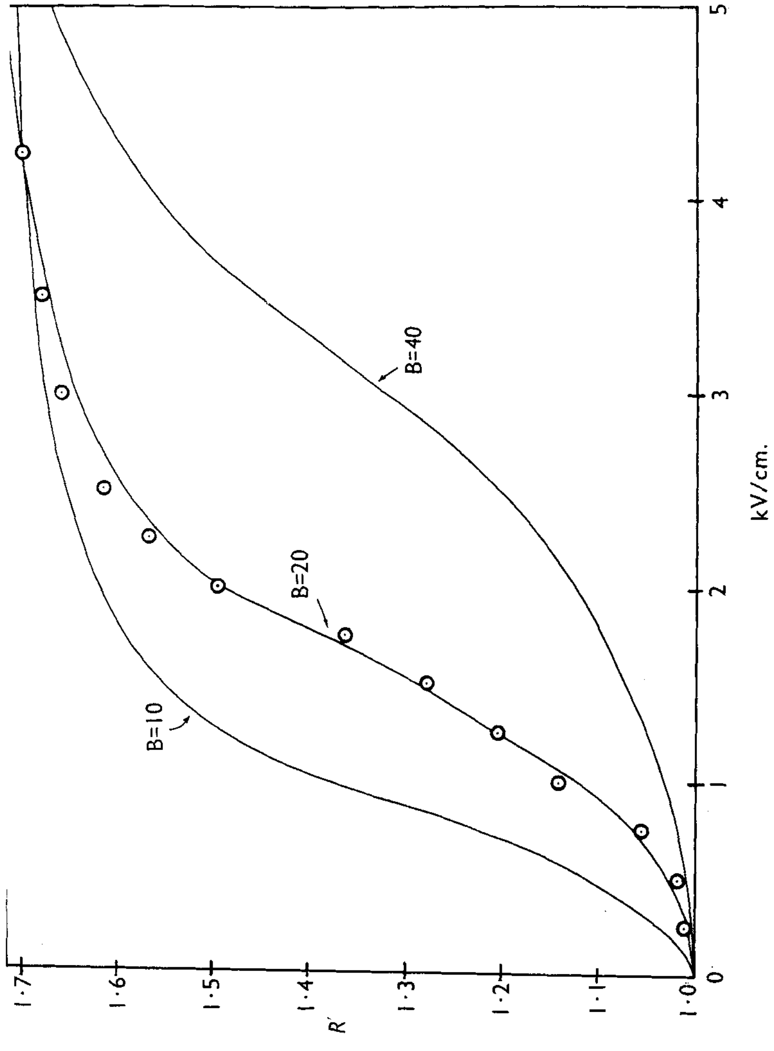

Figure 5. The points in the figure represent the values of R' obtained experimentally up to 6 kV/cm. These were obtained from a 120 μ film at 106°C. The solid lines were calculated from Eq. (9) for different values of $B = \mu/kT$.

integral $\langle \sin^2\theta \rangle$ as a function of $A = PE/kT$ and $B = \mu/kT$. This was done by numerical integration on an IBM 1620 computer. Figure 6 shows the variation of $\langle \sin^2\theta \rangle$ over a range of values of A from zero to 100 and B from 0 to 20. Since $\langle \sin^2\theta \rangle$ approaches zero for $A = 100$ we have assumed that $PE/kT = 100$ at a field strength of 5 kV/cm and temperature of 106° C. Under these conditions P is found to be $3.14 \times 10^5 D$. The value of B was obtained by determining the best fit of Eq. (9) to the experimental points in Fig. 5. The best fit was obtained for $B = 20$. Curves are also shown for $B = 10$ and 40 in the same figure. Under these conditions μ is found to be 1.43×10^{-12} ergs. For $B = 20$, $\langle \sin^2\theta \rangle$ approaches 0.95 when E approaches zero. This corresponds to almost complete orientation of the domains parallel to the surface in the absence of an applied field. The limiting value of R' in Fig. 5 yields $S = 0.33$ at 106° C. The S value determined by Method A under the same conditions was 0.30.

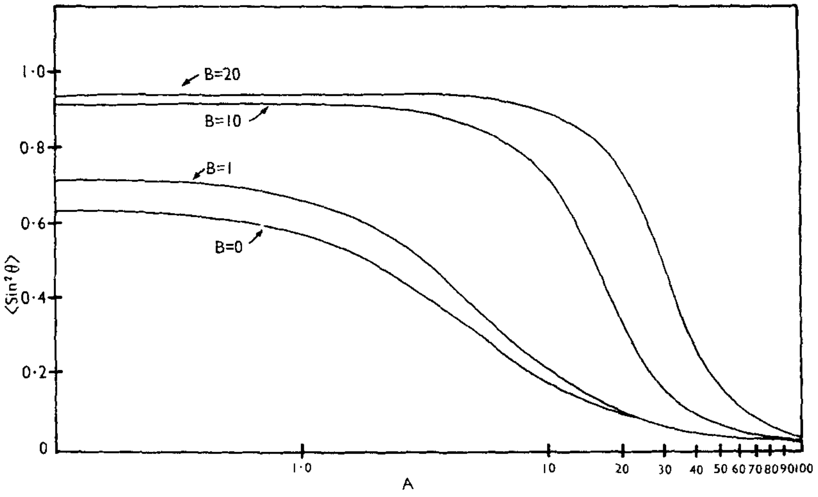

Figure 6. The relation between $\langle \sin^2\theta \rangle$ and $A = PE/kT$ for several values of B.

The degree of orientation obtained by Method B is shown as a function of temperature over the liquid crystal range of MBC in

Fig. 7. Approximately the same S values were obtained for films varying in thickness from 20 to 120 μ.

One further observation concerning Method B is of note. It was found that the infrared radiation was scattered appreciably by the

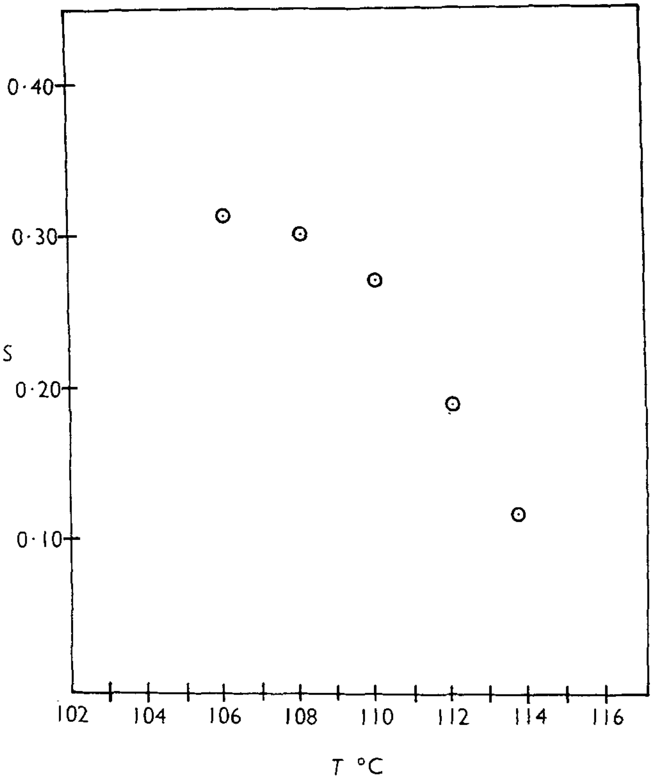

Figure 7. The degree of orientation (S) of MBC over the temperature range of the liquid crystal.

sample when the field was turned on. The phenomenon was confirmed as a scattering effect by the fact that it occurred at all wavelengths and the magnitude decreased approximately as $(1/\lambda^4)$. This effect is shown in Fig. 8. The scattering increases up to approximately 1.5 kV/cm and then begins to decrease. This observation is in accord with the optical effects observed on thin films of para-azoxyanisol by Williams[6] and is consistent with the assumption of domain formation in these films.

The degree of orientation obtained for MBC is somewhat lower than that obtained by others on para-azoxyanisol by different methods.[3] We have no good explanation for the lower degree of orientation of this liquid crystal. Any theory of order in the nematic structure must consider in detail the nature of the intermolecular forces. It should be borne in mind, however, that most of the experimental work on orientation deals with thin films and no theory of liquid crystal structure has adequately taken account of the very important effect of the surface of the container on molecular orientation in these films.

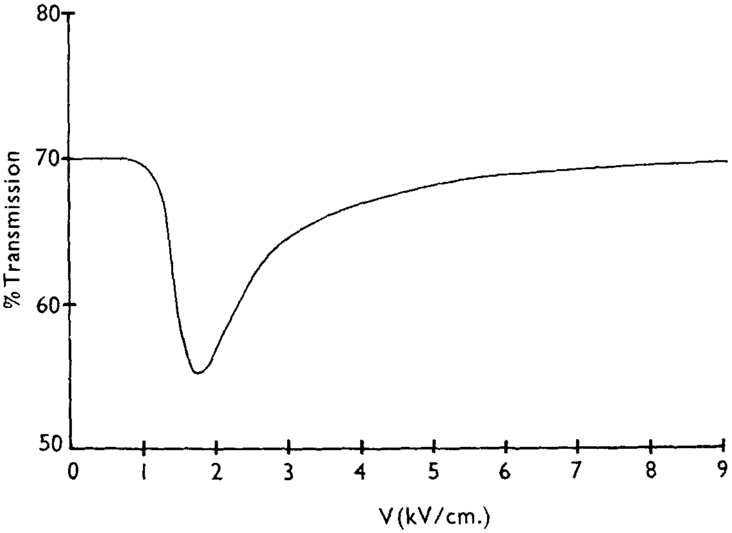

Figure 8. Change in background intensity due to scattering measured at 2.7 μ.

REFERENCES

1. Chatelain, P., *Bull. Soc. Franc. Mineral. Crist.* **78**, 262 (1955).
2. Zwetkoff, V., *Acta Physicochim. URSS* **16**, 132 (1942).
3. Weber, K. H., *Discuss. Faraday Soc.* **25**, 74 (1958).

4. Lippman, H., *Ann. Physik.* **7**, 287 (1958).
5. Meier, W. and Englert, G., *Z. Elektrochem.* **64**, 689 (1960).
6. Williams, R., *J. Chem. Phys.* **39**, 384 (1963).
7. Kapustin, A. P. and Vistin, L. K., *Soviet Phys. Cryst.* **10**, 95 (1965).
8. Kast, W., *Z. Physik.* **71**, 39 (1931).
9. Frenkel, J., *Kinetic Theory of Liquids*, Dover Publications, Inc. (1955), p. 304.
10. Fraser, R. D. B., *J. Chem. Phys.* **21**, 1511 (1953).
11. Fraser, R. D. B., ibid. **24**, 89 (1956).
12. Fraser, R. D. B., ibid. **28**, 1113 (1958).
13. Gray, G. W. *et al.*, *J. Chem. Soc.* 4359 (1955).