Application of Infrared ATR Spectroscopy to Liquid Crystals. II.[1) Surface-induced Orientation of Nematic MBBA and Reorientation in Electric Fields

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A polarized infrared ATR technique was used to demonstrate the orientation of a nematic liquid crystal, *N*-(*p*-methoxybenzylidene)-*p*-butylaniline (MBBA), due to the walls of the electrode and an externally applied DC electric field. Polarized ATR spectra were obtained as a function of the field strength on liquid films 15 μm thick between a silicon ATR prism and a brass plate serving as electrodes. The observed infrared dichroism revealed the average orientation of molecules in boundary layers about 1 μm thick on the Si electrode surface. The ordering or packing of molecules before application of the field affects the response of molecules to the electric field in a striking manner. Molecular orientations on the Si electrode are discussed in some detail.

In recent years, dramatic developments were seen in the application of liquid crystals to electro-optical display devices.2) For example, a dynamic scattering effect3) has now proven to be most valuable in the application of nematic liquid crystals. Another important effect of electric field on liquid crystals is the change in orientation due to the anisotropy of the dielectric constants of the liquid crystal molecule.4)

Heilmeier and Zanoni5) have successfully obtained color switching using a nematic liquid crystal containing dissolved pleochroic dye molecules. This method is based on the guest-host interaction6,7) by which the orientation of the guest dye is controlled by the orientation of its nematic host in an applied electric field. For practical applications of this effect, however, a high response to the electric field is essential to the liquid crystal. However, it has been pointed out that the interaction between liquid crystal molecules and electrode surfaces may often lower the response of the liquid crystal. Despite this limitation, the field-induced orientation is very interesting for several aspects of application.2)

On the other hand, infrared spectroscopy is a powerful tool for obtaining information about the orientational behavior of liquid crystals. In this regard, therefore, it seems interesting to observe field-induced orientation using infrared techniques. Indeed, the molecular orientation of nematic *N*-(*p*-methoxybenzylidene)-*p*-cyanoaniline in DC electric fields has been investigated by Neff, Gulrich, and Brown8) using a transmission method. However, no other infrared study of field-induced orientation has yet appeared. This is probably due to the fact that extremely thin films are required for obtaining accurate intensity data because of the high absorption of liquid crystals, as is generally the case. This difficulty is removed when the ATR method9) is used, because the observed intensities are determined by the electric-field penetration of infrared radiation a few microns into the sample and are independent of the sample thickness.10) The most significant advantage of using the ATR method is that electric fields of electromagnetic radiation exist in all three spatial directions at the reflecting interface. Therefore, this technique can be used to obtain information about any orientation of the liquid crystal.

For the above reasons, the infrared ATR technique was first applied to the study of the orientation of MBBA liquid crystals, and quantitative data which enabled the determination of the orientation pattern and its degree of order were obtained.1) The present report describes the infrared ATR spectra of MBBA under the application of DC electric fields.

Experimental

The liquid crystal cell used for the ATR measurements has already been described in a previous paper.1) In brief, the liquid crystal was sandwiched between a silicon ATR prism and a conducting plate, which were held apart by a polyester spacer. The Si prism and the substrate plate served as electrodes; a DC electric field was applied normal to the liquid layer 15 μm thick. The Si prism served as the positive electrode. The liquid crystal was maintained at a constant temperature by an electric heater placed in a brass box in contact with the substrate plate.

The ATR spectra were measured by placing the liquid crystal cell in the sample beam of a double-beam ATR attachment, at an angle of incidence of 40 °. In order to account for the absorption of the sample prism itself, a similar Si prism was placed in the reference beam. The infrared radiation was polarized using a AgCl polarizer.

A brass plate polished to a high degree of flatness was used as an electrode opposite the Si prism. The electrode plate and Si prism were subjected to ultrasonic cleaning for 30 min in ethyl alcohol followed by rinsing in acetone. Guaranteed-grade MBBA reagent from a commercial source was used without further purification.

Results and Discussion

Infrared Dichroism from Polarized ATR Spectra. A detailed description has already been given of an approximate method of determining the orientation pattern of a liquid crystal from measured amounts of the dichroic ratio.1) Therefore, little will be given here concerning the method itself.

An ATR spectrum is essentially the reflection loss due to the interaction of an evanescent wave with an absorbing medium. According to Flournoy and Schaffers,11) the reflectivities of radiation having the electric vector polarized perpendicular and parallel to the plane of incidence are given respectively by

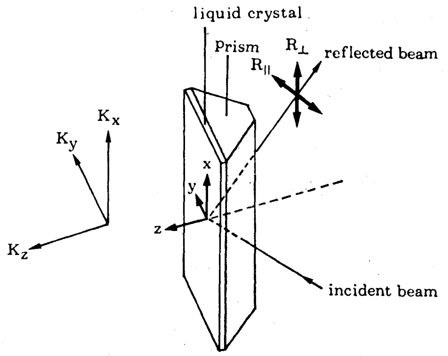

Fig. 1. Coordinate system showing the attenuated total reflection (ATR) from anisotropic absorbing liquid crystal. K_x, K_y, and K_z are the components of the absorption coefficient along the prism-fixed axes. $R_\parallel$ and $R_\perp$ indicate the reflectivities of the radiation polarized parallel and perpendicular to the plane of incidence, respectively.

$$\ln R_\perp = -pK_x$$

and

$$\ln R_\parallel = -qK_y - rK_z, \tag{1}$$

where p, q, and r are functions of the refractive indices of the absorbing medium and of the internal reflection prism, and the angle of incidence. Furthermore, K_x, K_y, and K_z are the components of the absorption coefficient along the prism-fixed axes shown in Fig. 1. In Fig. 1, the sample of the liquid crystal is assumed to be much thicker than the effective penetration depth of the evanescent wave.[10] The dichroic ratio D for a given vibration band can be written as

$$D = \frac{\log (R_\parallel^\circ/R_\parallel)}{\log (R_\perp^\circ/R_\perp)} = \frac{q}{p}\left(\frac{K_y}{K_x}\right) + \frac{r}{p}\left(\frac{K_z}{K_x}\right), \tag{2}$$

where $R_\parallel^\circ$ and $R_\perp^\circ$ are the background reflectivities measured with the radiation polarized parallel and perpendicular to the plane of incidence, respectively.

In order to calculate coefficients p, q, and r, it is desirable to know accurately the birefringence, $\Delta n = n_e - n_o$, in the infrared region for MBBA, where the extraordinary index n_e and ordinary index n_o correspond to the directions parallel and perpendicular to the optical axis of the director, respectively. In Eq. 2, the n_o contribution to the coefficients, q/p and r/p, is much smaller than the Δn contribution.[11] Therefore, n_o is conveniently assumed to be 1.54 in accordance with the value observed in the visible region,[12] as before.[1] On the other hand, the Δn for well oriented MBBA has been suggested to be 0.05—0.1 in the infrared region,[1] which is much less than 0.22 in the visible region.[12] Such a small birefringence change would, however, require a highly accurate measurement on the same system. Hence, the contribution from the birefringence was omitted in Eq. 2. Since birefringence is obviously related to the degree of order, its omission may result in an overestimation of the degree of order by about 10% for a sample of high structural order (if $\Delta n = 0.1$ in the infrared). For a less ordered sample, however, the error caused by the omission is negligibly small. Using the isotropic index of 1.54 assumed for MBBA and 3.42 for Si,[13] the coefficients were calculated for an incident angle of 40° and for one reflection at the Si-MBBA interface. The results are $p = 1.700$, $q = 1.215$, and $r = 2.384$. Upon substituting these values into Eq. 2, the observed dichroic ratio can be used to estimate the degree of anisotropy of the absorption coefficients.

This procedure can be simplified by assuming uniaxial symmetry for the nematic liquid crystals as follows. For example, if molecules in the liquid film are oriented normal to the Si prism surface (homeotropic), one finds $K_x = K_y$ from Fig. 1 and then Eq. 2 reduces to

$$D = 0.72 + 1.40\left(\frac{K_z}{K_x}\right). \tag{3}$$

If the molecules are oriented parallel, for instance, to the x axis which is perpendicular to the plane of incidence (uniformly homogeneous), one obtains

$$D = 2.12\left(\frac{K_z}{K_x}\right). \tag{4}$$

In particular, if the molecules are randomly oriented, *i.e.*, if $K_x = K_y = K_z$, the dichroic ratio becomes 2.12, regardless of the vibration type.

On the other hand, the degree of orientation order, S, is conveniently defined with respect to the orientation of the long axis of the molecule relative to the optical axis of the liquid crystal.[14] In this case the degree of order is given by

$$S = \frac{1}{2}(3\cos^2\alpha - 1) = \frac{(d-1)}{S_\beta(d+2)}, \tag{5}$$

with

$$S_\beta = \frac{1}{2}(3\cos^2\beta - 1),$$

where α is the angle between the long axis of the molecule and the optical axis of the uniaxial liquid crystal, and β is the angle between the long axis and the direction of the vibrational transition moment, as is shown in Fig. 2. In Eq. 5, $d = K_\parallel/K_\perp$, where $K_\parallel$ and $K_\perp$ are the absorption coefficients parallel and perpendicular to the optical axis, respectively, as is shown in Fig. 2. Accordingly, d is given by K_z/K_x for the homeotropic case, whereas it is given by K_x/K_z for the uniformly homogeneous case (if the preferred axis is x). Hence, the magnitude of K_z/K_x in the above examples acts as the measure for evaluating the orientation type and its

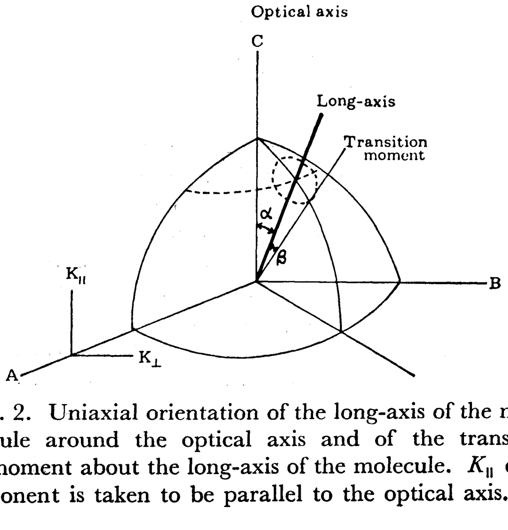

Fig. 2. Uniaxial orientation of the long-axis of the molecule around the optical axis and of the transition moment about the long-axis of the molecule. $K_\parallel$ component is taken to be parallel to the optical axis.

degree of order.

In terms of the d defined above, the degree of order S changes from 0 to 1, corresponding to a change from isotropic orientation or perfect orientation with $\alpha = 54°44'$ to perfect orientation with $\alpha = 0°$. It should, however, be mentioned that Eq. 5 is valid only when the molecules are packed as if they are allowed to rotate freely about their own long axes.

Based on Eq. 5, the β values of several important vibrations of MBBA were determined to within an accuracy of $\pm 10\%$ for highly-ordered homeotropic and uniformly-homogeneous liquids.[1] This fact demonstrates that Eq. 5 is a good approximation to the degree of order in terms of the orientation of the long axis of the molecule.

Orientation of Molecules at Electrode Surfaces. When a static electric field of rather low strength is applied to the liquid crystal, the primary effect of the field is the interaction with the dielectric tensor of the liquid so that the molecules tend to be oriented with their axes of maximum dielectric constant parallel to the field.[15] The reorientation is, however, often restrained by the surface orientation of the molecules at electrodes.[2] On the other hand, if the DC field is sufficiently high to produce hydrodynamic scattering, a greatly disordered texture is expected to be observed. In order to elucidate the electric-field effect on liquid crystals, it is necessary to know the original orientation produced by the electrode surfaces.

Because in the present work the Si ATR prism also served as an electrode, it is necessary to discuss the orientation of the MBBA molecules present on the Si prism surface. For this purpose, polarized ATR spectra were obtained for a thin liquid film of MBBA having an estimated thickness of 0.2 μm. The vaporized sample was deposited onto the reflection surface of the Si prism for nine internal reflections.

The observed ATR spectra are shown in Fig. 3. The absorption band assignments[1,16] and the observed D values are listed in Table 1, together with the β values[1] corresponding to these vibrations. On the other hand, when polarized infrared light was passed through the plane of the sample film at normal incidence, the spectrum was identical irrespective of the orientation of the electric field of the incident radiation. This demonstrates that the transition moments of the molecule are randomly oriented about the direction normal to the Si surface; the equality of K_x and K_y holds in the present case. Therefore, the dichroism observed from ATR spectra should be interpreted in terms of the uniaxial orientation of molecules about the z axis, which is perpendicular to the Si surface. On the basis of the assumption that the long axes of the molecules are uniaxially aligned with respect to the z axis, S values were calculated from the observed dichroic ratios[18] and the β values. The resulting S values are given in Table 1.

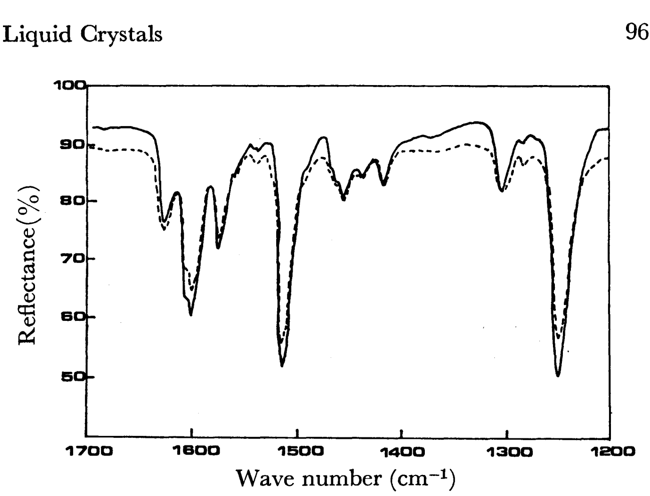

Fig. 3. Infrared polarized ATR spectra of thin MBBA liquid film (0.2 μm) at 25 °C deposited from vapor. Solid and broken lines refer to the orientation of the electric vectors of radiation parallel and perpendicular to the plane of incidence, respectively.

Thus, on the Si surface, MBBA molecules tend to be oriented with their long axes parallel to that surface in agreement with results based on other methods.[19] Nevertheless, the resulting S value for the 1630 cm⁻¹ band is much larger than that for other vibration bands. This fact suggests anomalous structure of the thin film such that the molecules may not have complete freedom of rotation about the long axes of the molecules in the film. Assuming uniaxial alignment of the long axes with respect to the z axis, as mentioned above, and no molecular rotation about the long axes, the distribution of the transition moments can be calculated using the simple relation,

$$2 \tan^2 \gamma = \frac{K_z}{K_x}, \tag{6}$$

where γ is the angle that the transition moment makes with the surface plane. The γ values thus obtained are also given in Table 1.

TABLE 1. FUNDAMENTAL DATA[18] OBTAINED FROM POLARIZED INFRARED ATR SPECTRA FOR A THIN LIQUID FILM OF MBBA AT 25 °C
(Thickness-0.2 μm)

Wave number (cm⁻¹)	Assignment	β[17] (degrees)	D	K_z/K_x	S	γ (degrees)
1630	C=N str.	32.1	1.21	0.27	0.82	20
1600	phenyl-ring str.	21.5	1.37	0.41	0.40	24
1578	phenyl-ring str.	10.5	1.26	0.32	0.44	22
1520	phenyl-ring str.	20.3	1.28	0.33	0.49	22
1250	C–O–C asym. str.	20.8	1.33	0.38	0.43	24
1160	phenyl C–H in-plane def.	15.9	—	—	—	—
1030	CH_3–O str. (C–O–C sym. str.)	43.0	—	—	—	—

While the film treated above is too thick for the determination of the orientation of the molecules adsorbed on or present near the Si surface, a "quasi-fixed" orientation may be supposed, because the orientation mechanism in thin films primarily involves the epitaxy.[20)] In this connection, it appears important to examine the existence of "quasi-fixed" orientation in thick films. For this reason, we now consider the case where a voluminous sample of MBBA comes in contact with the Si surface.

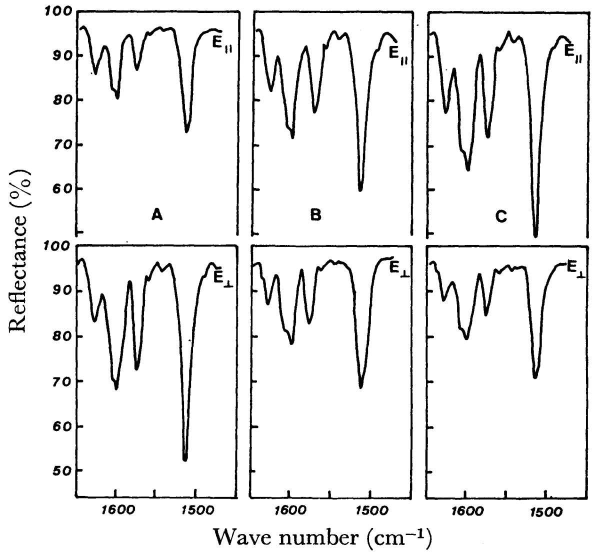

Fig. 4. Infrared polarized ATR spectra of MBBA (thickness: 2 mm).
$E_\parallel$ and $E_\perp$ refer to the polarized radiation used. A: original spectra (nematic; T=25 °C), B: spectra recorded 72 h later (nematic; T=25 °C), C: spectra of isotropic state (T=50 °C).

Figure 4 shows the polarized ATR spectra of MBBA liquid having a thickness of 2 mm. It must be mentioned here that each spectrum (A—C) appeared with the liguid layer about 1 μm thick at the Si-MBBA interface, depending upon experimental conditions. Accordingly, the three orientations that can be deduced from these spectra occur with the liquid having this thickness.

A brass plate was used as an opposite substrate. Since the substrate is very far from the Si prism surface, any possible orientation due to the substrate probably gives no contribution to the molecular orientation near the Si surface. Spectra (A) of Fig. 4 exhibit strong perpendicular dichroism, indicating that the preferred direction of the long molecular axes is parallel to the x axis, which is perpendicular to the plane of incidence, *viz.*, uniformly homogeneous orientation (see Fig. 1). This orientation almost disappears at an isotropic temperature of 50 °C, as is seen from spectra (C), but reappears upon lowering the temperature to the nematic temperature of 25 °C. The dichroic ratios taken from spectra (A) and (C) are given in Table 2.

The D values for spectra (C) are close to the value expected for isotropic orientation, but a difference of about 10% on the average is noticed between them. Since this discrepancy is greater than the limits of experimental error, the isotropic liquid may be influenced by the Si surface in contact with it.

Based on the dichroic ratios from spectra (A) and with the β values, the values of S were determined using Eqs. 3 and 5. The resulting S values are given in Table 2. As is seen in Table 2, the S values are indicative of a highly-ordered uniformly homogeneous orientation. The mechanism of the uniformly-homogeneous texture is, however, not understood in detail, but it is quite likely that the orientation is due to material flow[21)] along the Si wall surface. Spectra (A) remained almost unchanged generally for as long as 24 h, but changed into spectra (B) after 72 h. The dichroic ratios taken from spectra (B) are given in Table 2.

The magnitude of the dichroic ratios is well explained by assuming a randomly-homogeneous orientation with poor order, as is shown in Table 2. Thus, the orientation pattern arising from the flow orientation is regarded as about the same as that for a liquid 0.2 μm thick, as mentioned above. In the present case, however, the "quasi-fixed" structure is greatly quenched. This fact shows that the "quasi-fixed" structure is confined to the vicinity of the Si surface and that its degree of order decreases with increasing film thickness.

Orientation Behavior of Molecules in an Electric Field. In what follows we shall deal with a relatively thin liquid layer (15 μm) contained between a Si prism and a conducting substrate plate.

Since the liquid-crystal orientation near the surface extends into the bulk, the above mentioned "asymmetric-electrode" cell would give rise to an orientation distortion at the interface of different orientations from the electrodes. However, if the opposite electrode material interacts much more strongly with the molecules than does the Si electrode, a predominant orientation probably develops over large areas and, consequently, it would overcome the flow orientation or weakly-bound

TABLE 2. POLARIZED INFRARED ATR DATA FOR LIQUID MBBA (for a thickness of 2 mm)
A-flow orientation (25 °C), B-randomly homogeneous orientation (25 °C), and C-isotropic orientation (50 °C).

Wave number	A			B			C		
	D	K_z/K_x	S	D	K_z/K_x	S	D	K_z/K_x	$S^{a)}$
1630	0.82	0.39	0.59	1.53	0.58	0.34	2.01	0.92	0.05
1600	0.53	0.25	0.63	1.49	0.55	0.27	1.90	0.84	0.07
1578	0.43	0.20	0.60	1.47	0.54	0.23	1.91	0.85	0.06
1520	0.48	0.23	0.64	1.49	0.55	0.26	1.88	0.83	0.08

a) Calculated assuming that $K_x = K_y$.

orientation at the Si surface mentioned above. In fact, this is always the case provided the opposite electrode surface is specially treated to give a birefringent texture.[1] In other words, this means that the "quasi-fixed" orientation at the Si surface cannot exert any important role on the type of birefringent orientation.

To examine the DC electric-field effect on the orientation of MBBA, a brass plate was used as the opposite electrode. The surface of the brass electrode was coated with a very thin film of lecithin in order to obtain a uniform homeotropic texture in the absence of any field. Because MBBA has a negative dielectric anisotropy,[22] the molecules should be aligned perpendicular to the electric-field direction.

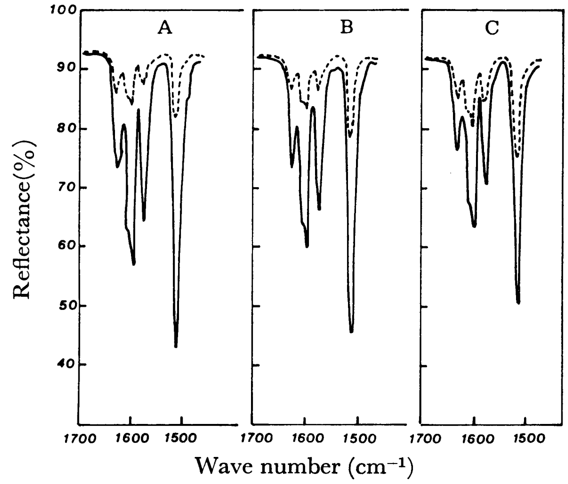

Fig. 5. Polarized infrared ATR spectra of nematic MBBA (25 °C); the opposite electrode: lecithin coated brass plate; thickness: 15 μm. Solid and broken lines refer to the electric vectors of radiation polarized parallel and perpendicular to the plane of incidence, respectively. The three sets of spectra correspond to different applied voltage; A: 0 V; B: 15 V rms; C: 30 V rms.

The polarized ATR spectra from a liquid 15 μm thick at 25 °C for different applied voltages are shown in Fig. 5. The dichroism of the vibration bands in the absence of any field indicates good homeotropic orientation of the sample. The average value of S deduced was 0.54. The dichroism of the vibration bands decreased with step increases in the voltage, indicating deformation of the homeotropic orientation. The S value can serve as an indicator of the extent of deformation.

The S value, which was obtained by averaging S over all vibration bands measured, is plotted as a function of the applied field in Fig. 6. As is shown in Fig. 6, the S value slightly decreased with increasing voltage up to 10 kV/cm and decreased more rapidly with subsequent increases in the electric field. Upon the removal of the field, the original arrangement was restored. The S value increased by 0.03, probably due to relaxation to a more stable form. Because dielectric reorientation always precedes dynamic scattering, the initial decrease in S probably arises from dielectric reorientation, whereas the second decrease in S is attributed to dynamic scattering. It is, however, significant that voltages applied above the threshold for dielectric orientation[15] produce no appreciable deformation of the homeotropic structure.

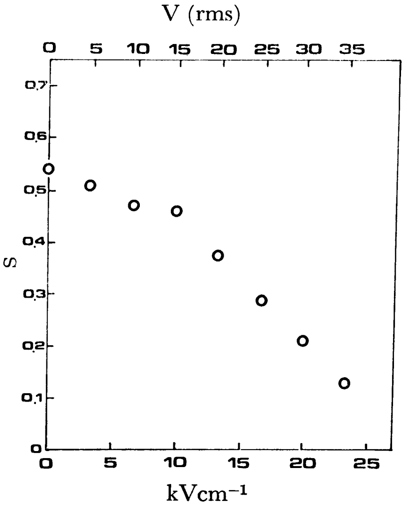

Fig. 6. The degree of order (S) of homeotropic orientation as a function of applied DC voltage.

In this connection, it has generally been assumed that molecules near the electrodes are maintained in place by the boundaries in an electric field.[23] This idea is probably based on the interaction between the liquid-crystal molecules and the electrode surfaces. However, since the same result was obtained when the Si-prism surface was coated with lecithin, the above limited electric-field response is, probably, ascribed to the strong aligning force of the lecithin which aligns the molecules perpendicular to the surface. In Fig. 6, the S value decreases as the applied voltage is increased, which indicates that dynamic scattering becomes more pronounced with increasing voltage. However, it is important to note that homeotropy of the liquid is still present even at high voltages.

In the light of these results, subsequent experiments were carried out using a new brass plate as the opposite electrode. The original texture observed was a flow orientation. The polarized ATR spectra recorded are depicted in Fig. 7(A). The S value obtained for that alignment was 0.59 on the average. The flow orientation remained for long periods of time. To attain sample stabilization, the liquid cell was permitted to stand for 15 hours and was maintained at 25 °C. The results of the ATR measurements are shown in Fig. 7(B). The parallel dichroism of the spectra is indicative of the tendency for the molecules to orient themselves perpendicular to the electrodes.

Based on the foregoing discussion, it is thought that the spontaneous homeotropy arises from the brass electrode surface. The values of K_z/K_x and of S calculated from the experimental D values are given in Table 3. The generally low S value is an indication of the rather weak aligning force of the brass electrode. However, a marked difference in S is seen between the 1630 and 1030 cm^{-1} bands, suggesting poor nematic-type packing of the molecules. To establish the average initial orientation, the values of γ were calculated from the K_z/K_x values using Eq. 6. The results of γ are given in Table 3 and the molecular orientation deduced is

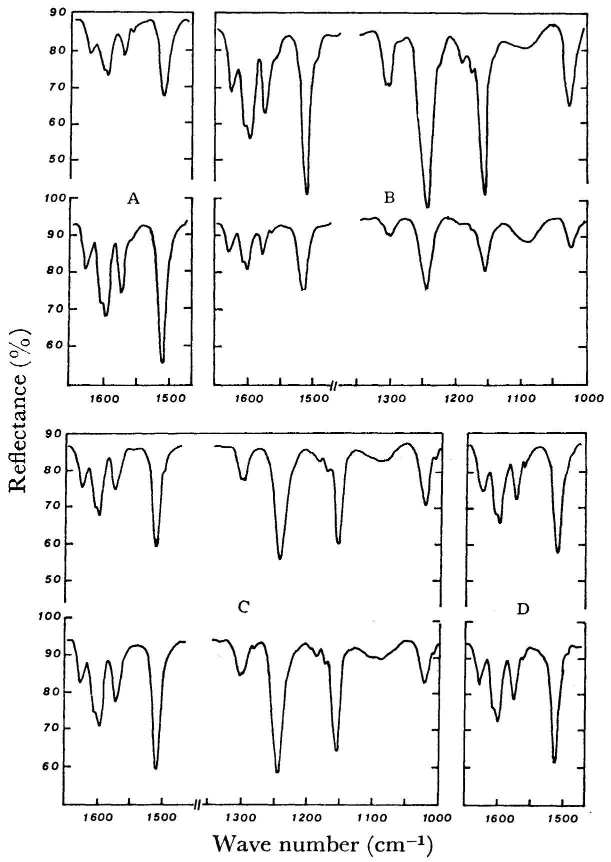

Fig. 7. Polarized infrared ATR spectra of nematic MBBA (25 °C) depending upon applied DC voltage. Upper and lower spectra were measured with the radiation polarized parallel and perpendicular to the plane of incidence, respectively. A: Initial flow orientation; B: homeotropic orientation appeared 15 h later in field-off; C: DC 5 V applied on B; D: DC 9 V applied on B.

depicted in Fig. 9(a).

A sharp change in dichroism was observed when a DC electric field was applied to this texture. In order to follow the sequence of spectral change in detail, measurements were carried out for driving voltages from 0 to 9 volts. For comparison, the polarized ATR spectra recorded at field strengths of 5 and 9 volts are reproduced in Figs. 7(C) and (D), respectively.

The dichroic ratios of the observed ATR spectra are plotted *versus* the external DC field in Fig. 8. As is

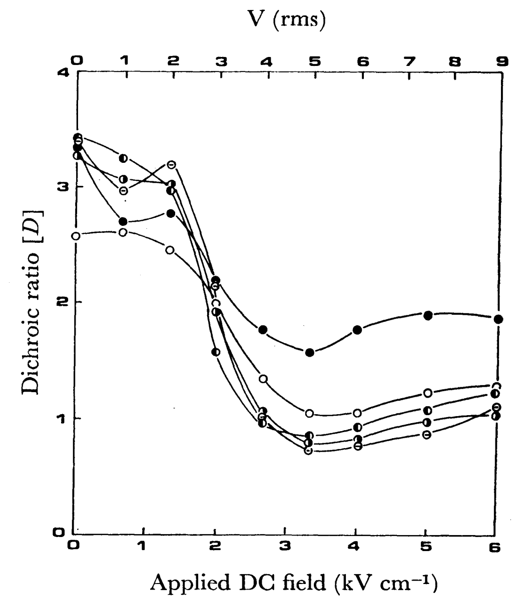

Fig. 8. Dichroic ratio (D) of various vibration bands as a function of applied DC voltage. ○: 1630 cm^{-1}; ⊖: 1578 cm^{-1}; ◑: 1520 cm^{-1}; ◐: 1250 cm^{-1}; ●: 1030 cm^{-1} band. The vibration assignments for these bands are presented in Table 1.

shown in the figure, reorientation begins at about 2 V and saturates at 5 V. Since the applied voltage exceeds 5 V, the dichroic ratios gradually decrease, probably due to domain formation[15] and the subsequent dynamic scattering, both of which interfere with the alignment.

The reorientation behavior mentioned above is in accord with that of the dielectric permittivity observed for relatively thick liquid MBBA by Ikeno *et al.*[24] Assuming the orientation at 5 V to be randomly homogeneous, the S values shown in Table 3 are obtained. The scattered values of S given in the table suggest that the molecules are packed in such a way that the rotation of the molecules about their own long axes is limited. Therefore, the γ values were calculated assuming uniaxial orientation of the long axis of the molecule, as before. The resulting values of γ are given in Table 3. Generally the change in γ with applied DC field appears to depend upon β. For example, the maximum change is found for the 1578 cm^{-1} band, whereas the minimum change is for the 1030 cm^{-1} band. Such behavior is understandable as a consequence of the negative

TABLE 3. POLARIZED INFRARED ATR DATA FOR LIQUID MBBA (for thickness of 15 μm) AT 25 °C
A-homeotropic orientation and B-randomly homogeneous orientation at a DC potential of 5 V.

Wave number	A				B			
	D	K_z/K_x	S	γ (degrees)	D	K_z/K_x	S	γ (degrees)
1630	2.59	1.33	0.17	39	1.06	0.24	0.88	19
1600	3.22	1.78	0.26	43	0.84	0.09	0.96	12
1578	3.43	1.93	0.25	45	0.79	0.05	0.90	9
1520	3.27	1.83	0.26	44	0.82	0.07	1.00	11
1250	3.41	1.92	0.29	44	0.93	0.15	0.80	15
1160	4.08	2.39	0.36	48	0.99	0.19	0.66	17
1030	3.34	1.88	0.75	44	1.78	0.75	0.33	32

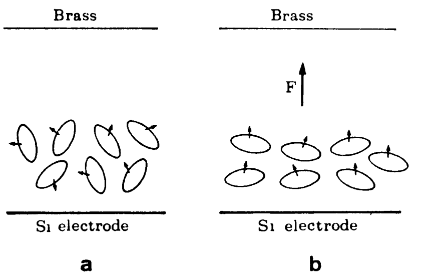

Fig. 9. Schematic representation of the molecular orientation of nematic MBBA before (a) and after (b) the application of DC electric field. Arrows indicate the dipole moments.

anisotropy of the molecule.

The molecular orientation in the DC electric field is drawn schematically in Fig. 9(b).

On the other hand, when the voltage was switched off, the sample exhibited a greatly improved homeotropy. An S value of 0.50, on the average, was obtained for this texture. This change is considered to be caused by the disturbance due to the applied field up to 9 V, as mentioned above.

When the 5 V DC voltage was subsequently applied, no appreciable dielectric distortion was observed: an average S value of 0.40 was obtained. Failure to produce a molecular reorientation comparable to that previously produced at the same voltage is consistent with the increased ordering or denser packing of the molecules before field application. Thus, the structure of the liquid film affects the response of molecules to the external electric field in a striking manner.

In conclusion, this ATR method affords three-dimensional information about the static and dynamic orientation behavior of liquid crystals in thin films. However, it must be emphasized that the surface influences of the electrodes are always important for interpreting observed results. This study will be extended to *N*-(*p*-ethoxybenzylidene)-*p*-cyanoaniline. The results for this compound will be published in the near future.

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