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Faraday Rotation in Nematic Liquids

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Abstract—The magnetic rotation of MBBA has been determined in the nematic and isotropic phase at a fixed wavelength (546 nm). The rotation is difficult to measure in the nematic phase because of birefringence effects due to incomplete alignment. The effects of birefringence were minimized by averaging rotations measured in forward and reverse magnetic fields. The Verdet constant increases with increasing temperature in the nematic phase up to the clearing point where it rises abruptly to a constant value in the isotropic phase.

The Verdet constants of seven alkyl homologs of MBBA have been determined at a fixed temperature in the isotropic phase.

1. Introduction

Many mechanical and optical measurements have been made on nematic liquids in the isotropic and anisotropic (nematic) phase.(1) One optical property which has, as yet, not been studied is the magnetic or Faraday rotation. In this paper we report on measurements of the Faraday rotation in MBBA (4-methoxybenzylidene-4′-*n*-butylaniline) at a fixed wavelength.

The optical effect of a uniform magnetic field in an isotropic medium can be measured in terms of a complex rotation

$$\Phi = \phi - i\theta \tag{1}$$

where

$$\phi = \frac{2\pi}{c}(n_- - n_+), \qquad \theta = \frac{2\pi}{c}(k_- - k_+)$$

The angle ϕ, the rotation of the plane of polarization, is determined by the difference of the refractive indices (n_+ and n_-) for right and left circularly polarized waves. The angle θ, a measure of the

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magnetic circular dichroism, is determined by the corresponding difference in absorption coefficients (k_+ and k_-). We shall be concerned with measurements in regions free of absorption bands.

In an anisotropic medium the situation is complicated by the occurrence of double refraction. It is well known that the magnetic rotation can only be properly defined in a birefringent medium if the measurement is made along an optic axis.⁽²⁾ In order to measure Faraday rotation in a uniaxial nematic liquid there must be complete alignment of the optic axis in a direction parallel to the magnetic field vector. The birefringence resulting from even slight misalignment can complicate the interpretation of experimental measurements.

2. Experimental

The experimental conditions required that measurements be made on fairly thin films (0.01–0.04 cm) and, since Faraday rotations are normally weak, it is necessary to use a polarimeter capable of resolving the very small angles of rotation. We used the Bendix ETL–NPL electronically controlled, self balancing polarimeter. This instrument operates on the principle of the Faraday effect by rotating a modulated light signal of 546.1 nm to a null position. The sensitivity is 10^{-4} degree of arc. We modified the instrument so that an electromagnet with hollow tapered pole faces and a thermally insulated sample compartment could be accommodated between the polarizer and analyzer sections. Rotation and sample temperature were recorded simultaneously on a Texas Instruments multi-channel recorder. The temperature in the sample compartment was controlled to within 0.05 °C and was measured by a thermistor bridge. Sample cells were made from microscope slides. The clearing point of the MBBA used was 46 °C. Fresh samples were used for the measurements at different temperatures.

The field gradient produced in the plane of the liquid crystal film by the tapered pole faces of the electromagnet is a sourse of error in the measurement. We determined the magnitude of this error indirectly by comparing the measured rotation of water (1 cm path length) with the best recorded value.⁽³⁾ Our results agreed to within 1% of the reported value.

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3. Results and Discussion

The rotation measurements in the nematic phase proved difficult due to the effects of non-uniform orientation. In fact, apparent rotation due to birefringence was noticeable even when extreme care was taken to achieve uniform orientation by carefully cleaning the cell surfaces and coating them with lecithin. Anomalous rotation due to birefringence was apparent even when samples examined by conoscopic observation in a polarizing microscope showed the dark cross typical of observation along the optic axis. Birefringence was confirmed by the fact that the rotation did not change sign upon reversal of the magnetic field.

The alignment problem proved to be so critical that we suspected the possibility of domain formation in the liquid crystal due to an applied magnetic field parallel to the direction of the optic axis (i.e., the director). Optical rotation due to domain formation in a magnetic field perpendicular to the optic axis has been reported previously by Williams.⁽⁴⁾ We tested this possibility by constructing a Bitter⁽⁵⁾ magnet which would allow the observation of the liquid crystal in a uniform magnetic field (~3000 G) parallel to the direction of orientation in an optical microscope. The optical geometry employed is shown in Fig. 1. We found no evidence of domain formation under these conditions.

We are forced to the conclusion that, due to the strong birefringence of the nematic phase, even the slightest misalignment of the liquid crystal will lead to an apparent rotation. Furthermore, we are convinced that alignment of an MBBA sample in a magnetic field is a relative term. Complete alignment is probably rarely achieved, especially in low magnetic fields.

It was possible to determine the Verdet constant of MBBA in the nematic phase by subtracting the effects of birefringence. We define the Verdet constant (v) as follows

$$v = \phi / Hd \tag{2}$$

where ϕ is the rotation in minutes, H is the magnetic field strength in Gauss and d is the path length in cm. Rotation measurements were made by varying the magnetic field at a fixed temperature. The rotation as a function of the applied field at 22 °C is shown in

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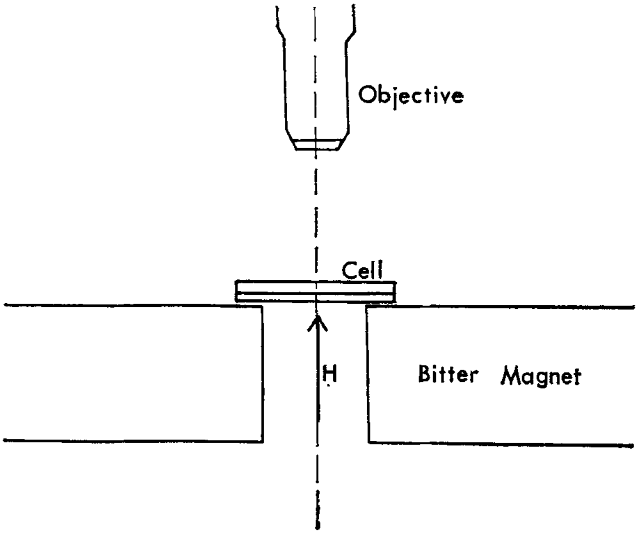

Figure 1. Schematic diagram for observation of domain formation.

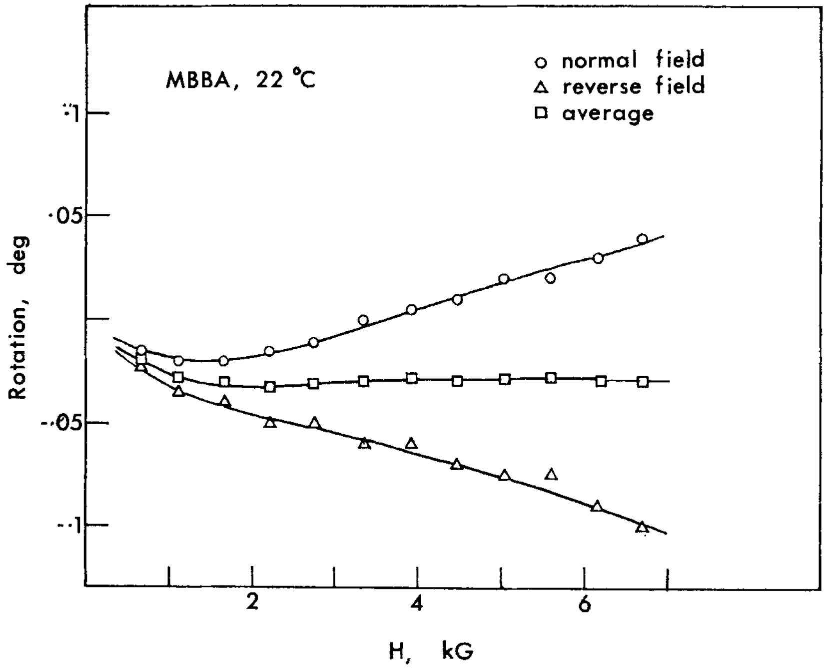

Figure 2. Apparent rotation of MBBA at 22 °C as a function of magnetic field strength. ○ normal field, △ reverse field, □ average of normal and reverse fields. ($\lambda = 546.1$ nm.)

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Fig. 2. The data are shown for the magnetic field in the forward and reverse directions. Since the apparent rotation due to birefringence is invariant under reversal of the field vector we can eliminate the birefringence by averaging the two curves and subtracting the resultant from the original data. This is shown in Fig. 3. The expected linear variation of magnetic rotation with field strength is obtained from the data. The Verdet constants obtained in this way are shown in Fig. 4. The Verdet constant, which increased slightly with temperature in the nematic phase and rose abruptly at the transition temperature, could be reproduced to within only about 6% in the nematic phase due to the alignment problem. Reproducibility was particularly poor in the region beginning approximately 5 °C below the temperature of the nematic–isotropic phase transition. In this region the alignment of the liquid crystal is critically sensitive to thermal inhomogeneities and to the history of sample preparation, even in strong (~5000 G) magnetic fields.

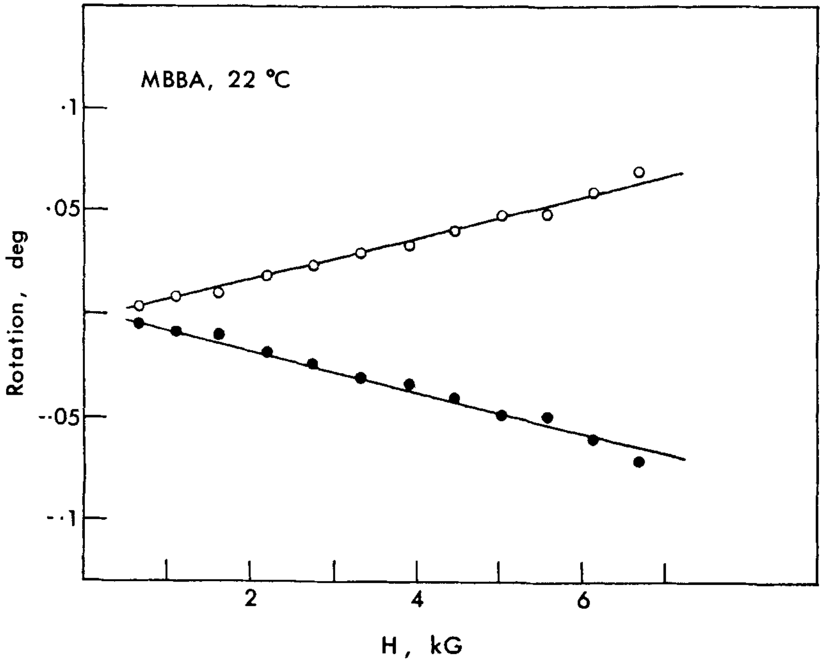

Figure 3. Magnetic rotation of MBBA at 22 °C as a function of magnetic strength. ○ normal field, ● reverse field.

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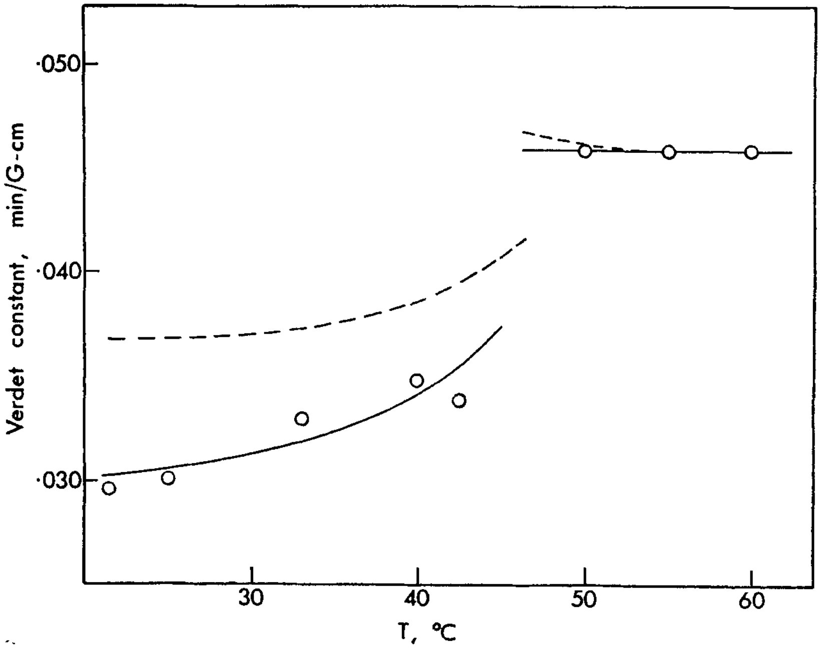

Figure 4. Verdet constant of MBBA as a function of temperature. ——— experimental, – – – calculated.

The Verdet constant could be measured quite accurately in the isotropic phase (0.1%).

We do not attempt to interpret the rotation data in terms of any detailed theory including the effects of intermolecular forces. Aside from the fact that the theory of magnetic rotation is quite complicated for large molecules involving accurate expressions for wave functions of excited electronic states,(6) the uncertainty in the data in the nematic phase precludes any detailed comparison with theory. Instead we compare the Faraday rotation with the known refractive index of MBBA.(7) The lowest frequency electronic absorption band for MBBA occurs at 320 nm as shown in Fig. 5. We assume that this band is sufficiently remote so that a simple phenomenological equation of the Becquerel type(8) can be used to relate the Verdet constant to the ordinary refractive index. That is, we assume

$$v = K(n^2 - 1)^2/n \tag{3}$$

where the constant K depends on wavelength and, in a complicated

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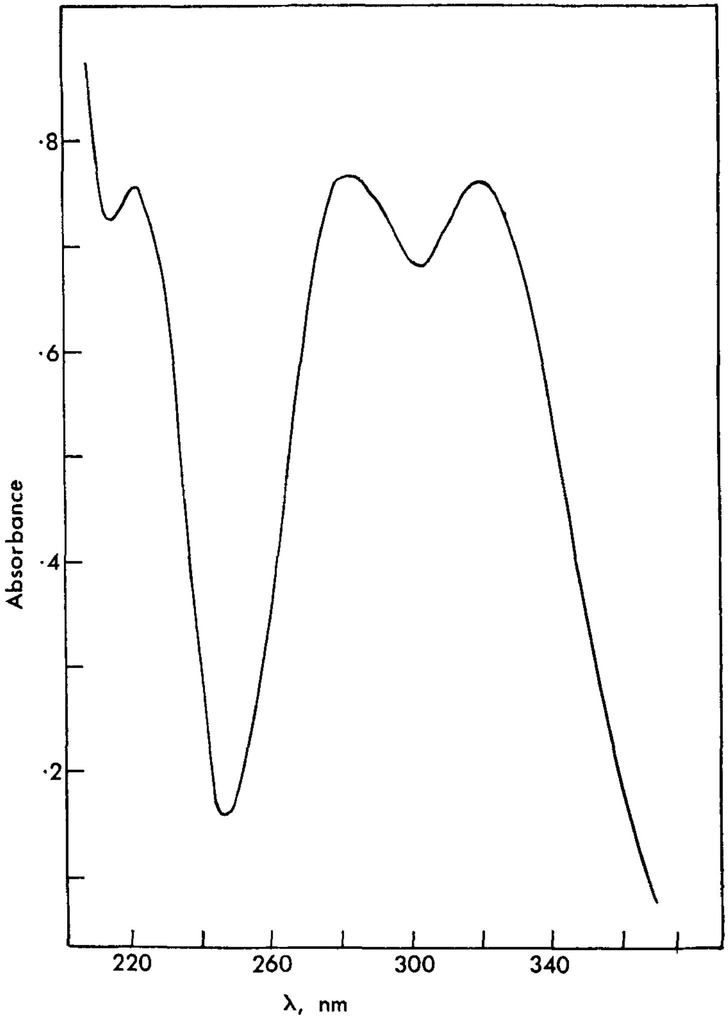

Figure 5. Absorbance (of MBBA in Ethanol) as a function of wavelength. $c = 4.07 \times 10^{-5}$ M, cell length = 1 cm.

way, on molecular parameters which are asumed to be approximately the same in the nematic and isotropic phase, and n is the refractive index of the ordinary wave. The major factor in the variation of the refractive index (and thereby the Verdet constant) in the nematic as compared to the isotropic phase is the effect of molecular orientation. The factor $(n^2 - 1)^2/n$ for MBBA is shown as the dotted line

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in Fig. 4. The constant K was determined from the experimental Verdet constant in the isotropic phase. The reported values of the refractive index(7) were adjusted for the wavelength of our experiment using the Drude equation. We see that the measured Verdet constant roughly follows the empirical relation with the refractive index, thus showing the effect of parallel molecular orientation in the nematic phase.

We have also determined the magnetic rotation of several homologs of MBBA: the methoxybenzylidene-*n*-alkylanilines. The Verdet constants were determined in the isotropic phase at 70 °C. These are shown in Fig. 6 where the number of alkyl carbon atoms varies from three to nine. The solid curve was calculated from Eq. (3) using the refractive indices determined at 70 °C. The constant K was determined, quite arbitrarily, from the Verdet constant of the pentyl compound. Although the measured Verdet constants again follow roughly the trend of the empirical relation with refractive

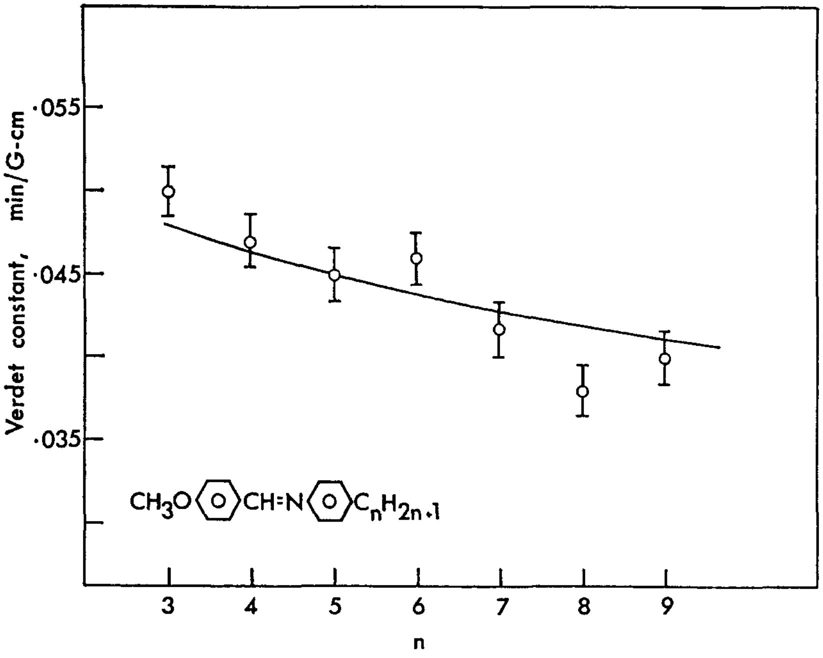

Figure 6. Verdet constants for a series of methoxybenzylidene-*n*-alkylanilines as a function of *n*, the number of carbon atoms in the alkyl chain. Calculated line is scaled to C_5 homolog.

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index, we see there are positive and negative deviations from the curve. The deviations do not alternate regularly between odd and even alkyl chains although a regular alternation has been reported for the clearing points of this series.(9)

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