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Preliminary Work on Orientation of Nematic Liquid-Crystalline Molecule by Electronic Spectra

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Absorption spectra of a nematic liquid-crystalline molecule (4-butyl-4′-ethoxyazobenzene) were measured in sandwich-type cells with very thin gaps which ranged from 0.2 to 1.0 μm when the cells were empty. The intensity ratio of the first (354 nm) to second (240 nm) band in the liquid state (86 °C) decreases as the state changes into liquid-crystalline (LC) states (70 and 48 °C). According to results of dichroism analysis and MO calculation, the 354 nm and 240 nm bands are due to π-π^* transitions polarized along the molecular long and short axes, respectively (with an angle of about 66°to each other). This finding coupled with an assumption that the molecular orientation of the liquid state is isotropic, allows a qualitative discussion on the orientation of molecule in the LC state, leading to a conclusion that the molecular long axis against the cell surface takes two kinds of orientation with respective tendencies to be parallel in the interface region and perpendicular in the bulk region.

Descriptions[1] have been given for a problem concerning the orientation of liquid-crystalline (LC) molecules, *i.e.*, the problem of the orientational order parameter.[2] Many approaches to this problem seem to be limited to optical phenomena associated with the refractive index or, indirectly, to dichroic and anisotropic magnetic properties of guest dye molecules, which are induced by orientation of host LC molecules. No direct approaches by means of analyzing anisotropic absorption spectra of oriented LC molecules from the viewpoint of electronic structure, have been attempted except few cases,[3,4] where linear dichroisms of LC molecules oriented by rubbing were measured but no interpretation of spectra was given.[4]

Since the electronic transition moment of a molecule has to be correlated closely with the molecular structure if the absolute transition direction of LC molecule itself is known or determined beforehand, knowledge of the molecular orientation of LC state should be obtained *via* analysis of anisotropic electronic spectra. Thus, for instance, the relative intensity of two absorption bands of a molecule in the isotropic (liquid) state, whose transition moment vectors cross each other, must change depending on its orientation in the LC state.

With a view to investigating the molecular orientation in the LC state from the viewpoint of molecular structure, we conducted an experiment as the first step to make sure the above consideration. As a result, we observed the fact that the relative intensity of the first and second bands of an LC molecule which is considered to take the nematic phase[5] changes with transition from the liquid (isotropic) to LC state. The present communication will report the cause for anisotropic absorption spectra and results obtained through qualitative discussion on the state of molecular orientation induced by that cause.

Experimental

Commercially available 4-butyl-4′-ethoxyazobenzen (BEAB) was purified by repeated recrystallization from aqueous ethanol. Polarized absorption spectrum of BEAB in a stretched poly(vinyl alcohol) (PVA) film was measured with a Shimadzu UV-360 spectrophotometer equipped with a rotatable Rochon-type polarizer. The polarization of electronic absorption bands of BEAB was determined by the stretched PVA film method.[6,7]

The sandwich-type cell used comprised two polished quartz glass plates of 3×23×23 mm size. We did not apply intentionally to the glass plates any surface treatments such as rubbing or coating. The two glass plates were held tight with adhesive except the cell entrance of appropriate size through which melted BEAB was introduced. The gaps of the empty cells were estimated to be in the range 0.2—1.0 μm from interference spectra recorded on the UV-360. In a vacuum vessel, the sample was melted and was introduced into the cell through the entrance by being sucked up under atmospheric pressure.

The cell was set in a cell holder which was specially designed to fit the sample compartment of UV-360. The temperature in the cell holder could be controlled within about ±1 °C with a handmade temperature controller. In the liquid-crystalline (nematic) state, however, all sample cells prepared as above exhibited a slight positive dichroism such that the direction of sucking up provides an optical axis, though the liquid (isotropic) state did not show any dichroism. The dichroism reappeared whenever the sample cell was cooled to the LC state after it had been heated to the isotropic state.

Results

The absorption spectrum of BEAB in ethanol indicates that the absorbance of the first band (A_1) is larger than that of the second (A_2) (see Table 1). The intensity ratio $R_{12}^{?}=A_1/A_2$ is about 1.71, which is considered as the value when BEAB is free from the molecular interaction.

Figure 1 shows the polarized absorption spectra of BEAB in a stretched PVA film, where $A_\parallel$ and $A_\perp$ are the absorbances for the polarized lights whose electric vectors are parallel to and perpendicular to the stretching direction of the film, respectively. R_d is the ratio of the absorbances (optical densities), $R_d=A_\parallel/A_\perp$.

It is known that a long molecule in a polymer film under uniaxial stretching inclines its long axis preferentially to the stretching direction of film. Thus it

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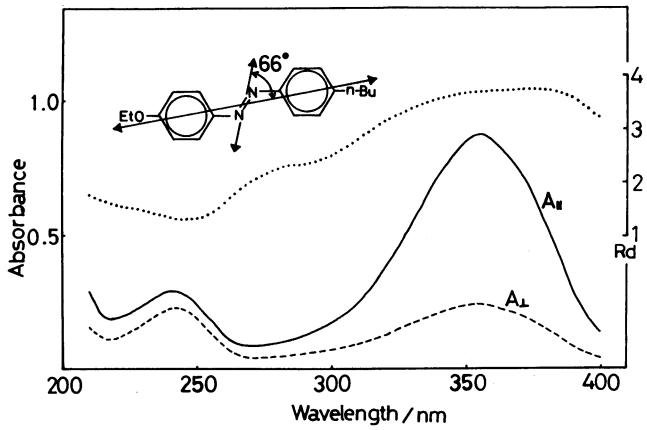

Fig. 1. Polarized absorption spectra of BEAB in a stretched PVA film. R_s=3.86 is the stretch ratio of the film (Ref. 6). The angle between the transition moments of the first (354 nm) and second (240 nm) bands is obtained from the values of R_d and R_s by the dichroism analysis (Ref. 7).

TABLE 1. EXPERIMENTAL AND CALCULATED RESULTS FOR THE ABSORPTION SPECTRUM OF BEAB

Band	λ_{max} /nm[a,d]	$\varepsilon[f]$[a,d]	Polarization[b]	Angle[c,d]
1	345[362]	21400[1.24]	17.5° (log axis)	66°[76°]
2	237[235]	13100[0.33]	48.5° (short axis)	

a) Observed in ethanol. ε is the extinction coefficient and f is the oscillator strength. b) The angle of the transition moment to the orientation axis of molecule (Ref. 7). c) The angle between the two transition moments as determined by the dichroism analysis (Ref. 7). d) [ ]: Results calculated by the semiempirical MO (PPP) method.

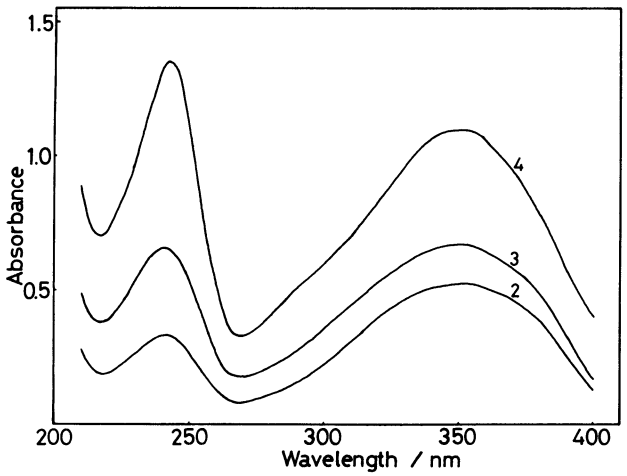

Fig. 2. Absorption spectra of BEAB in the LC state at the lower temperature (48°C). The number indicated along the curve is the measurement number in Table 2.

follows that the R_d value for a long axis-polarized band is high, whereas for a short axis-polarized band is low. According to Fig. 1, the R_d value is high for the first band (354 nm) and is low for the second (240 nm), implying that the first and second bands are polarized along the long and short molecular axes, respectively. The transition moments corresponding to the two bands cross each other, as shown in Fig. 1, with an angle of about 66° as determined from the R_d values by the dichroism analysis.[7]

In Table 1, the observed results for the absorption spectra of BEAB are compared with the results calculated by the semiempirical MO (PPP) method.[8] The calculated results reproduce the observed ones fairly well.

Absorption spectra of BEAB in sandwich-type cells with various gaps have been measured with natural light for the liquid state (at 86°C) and for the LC states at higher (70°C) and lower (48°C) temperatures. The spectra at the lower temperature are shown in Fig. 2 as an example. Spectra observed with different cells having different gaps, *i.e.*, different optical path lengths in the range 0.2—1.0 μm, indicate that the absorption intensity for the isotropic state is directly proportional to the path length, whereas for the LC state, as is evident from Fig. 2, the relative intensity of A_1 and A_2 changes with path length (compare the R_{12} values in Table 2).

Discussion

The intensity ratios R_{12} ($=A_1/A_2$) for different path lengths estimated for the isotropic state are almost constant as given by $R_{12}=1.69\pm0.04$ (see R_{12} of Liq. (86°C) in Table 2), which can be compared with $R_{12}^0=1.71$ for the free BEAB molecule. The former is nearly equal to the latter. Let us assume, therefore, that the molecular structure of BEAB in the isotropic state is similar to that in ethanol solution, and that the angle between the transition moments of A_1 and A_2 of the molecule itself is kept constant even in the LC state.

The fact that the R_{12} values for the isotropic state are almost constant irrespective of the cell gap, refers to two useful facts: First, Lambert's law is regarded as being realized. Therefore, the absorbance can be substituted for the optical path length of cell of which the absolute value is difficult to be determined, in such a concrete way that different cell gaps for the LC state can be graduated by referring to the absorbances for the corresponding cells in the isotropic state. Second, the R_{12} value of 1.69 is considered as the value of isotropic distribution of the BEAB molecules. The extent of anisotropy of the LC state, therefore, can be determined from the deviation of R_{12} from $R_{12}=1.69$.

The absorption spectrum of BEAB changes as follows: As the condition goes from the isotropic to LC state at the higher temperature and then to the lower temperature, the absorbance of the first band decreases considerably, while the second band increases slightly. This means that the dimension of the projection of the molecular long axis onto the plane of cell becomes smaller with the change from the liquid to LC state. In other words, the BEAB molecule tends to incline its long axis to the direction of light propagation, *i.e.*, to the direction perpendicular to the plane of the cell.

Now, let us examine the relation between R_{12} of LC state and the cell gap. The data of R_{12} are summarized in Table 2, where, in place of cell gaps, the absorbances

TABLE 2. ABSORPTION DATA FOR NATURAL LIGHT OF BEAB IN VARIOUS CELL GAPS

Cell No.	Meas. No.	Cell gap[a] (Abs.)	Intensity ratio R_{12} Liq.(86°C)	LC(70°C)	LC(48°C)
I[b]	1	0.40	1.69	1.75	1.67
	2	0.51	1.68	1.68	1.58
II	3	0.96	1.67	1.24	1.02
III[b]	4	1.93	1.71	1.07	0.808
	5	2.37	1.73	1.01	0.765
IV	6	2.92	1.68	0.987	0.723

a) The absorbance (Abs.) of the first band in the isotropic state is used instead of cell gap. b) The data of the two measurements of cell Nos. I and III are those obtained for different spots of the same cells.

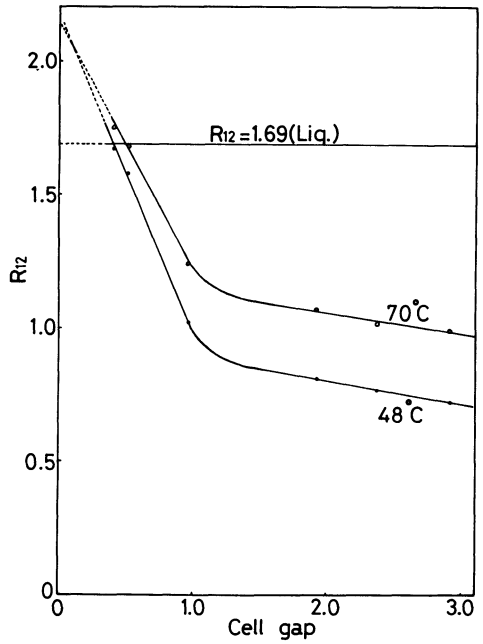

Fig. 3. The R_{12}-cell gap relations for BEAB in the isotropic state (86°C) and in the LC states at higher (70°C) and lower (48°C) temperatures. R_{12} is the absorbance ratio of the first and second bands. The cell gap is graduated by the absorbance for the first band in the isotropic state.

of the first band measured in the liquid state are used. From the data in Table 2, the relationship between R_{12} and cell gap (in absorbance scale) is obtained as shown in Fig. 3. According to the figure, the R_{12} values for the LC state are smaller than 1.69 for the liquid state except for very small cell gaps.

Figure 3 shows that the R_{12} value decreases steeply in the range of smaller cell gaps and slowly in that of larger cell gaps. Figure 3 shows also that the two slopes of R_{12} at the lower (48°C) and the higher temperature (70°C) are nearly equal to each other in the range of cell gaps larger than 1.0, and moreover that the difference of R_{12} in this range is larger than that in the smaller range of cell gaps.

The above-mentioned facts about the behavior of R_{12} indicate that the thinner the cell gap, the greater the emphasis of the characteristic of R_{12} in the interface region and that the thicker the greater that of R_{12} in the bulk region. In order to discuss the above characteristics, we have considered that the molecular orientation in a cell can be divided into two kinds of orientation states with respective characteristics in the interface and bulk regions.

Taking into account that the two interfaces are common to all cells, the difference between the thick and thin cells is attributable to the part of bulk. For this reason, we can get absorption spectra for the bulk itself from difference spectra for various cell thicknesses. In this way, difference spectra have been obtained for the LC state at the higher and lower temperatures. The difference spectra at the lower temperature are shown in Fig. 4 as an example. As is evident from this figure, all of the difference spectra in the respective temperatures are quite similar in shape to one another. This indicates that the oriented state in the bulk region is kept constant independently of the thickness. Moreover, the relative intensity of the first band is apparently larger for the higher temperature than for the lower. This implies that the inclination of the molecular long axis is prevented and is caused to shift to an isotropic state by elevation of temperature. Incidentally, though not observed apparently in the difference spectra at the higher temperature, a new band appears

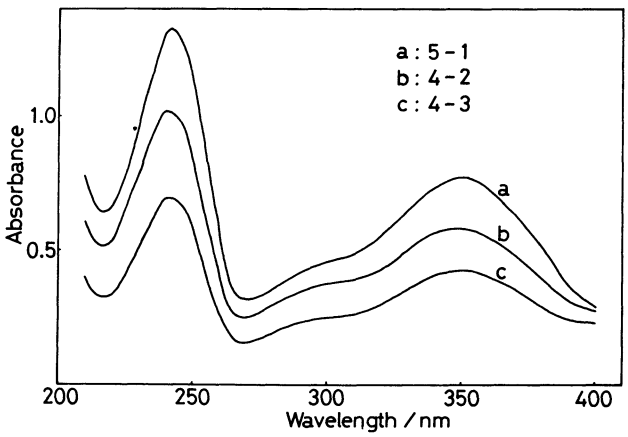

Fig. 4. The difference spectra of BEAB in the LC state at the lower temperature (48°C). The numbers given for a, b, and c are the measurement numbers (Table 2) used for subtruction.

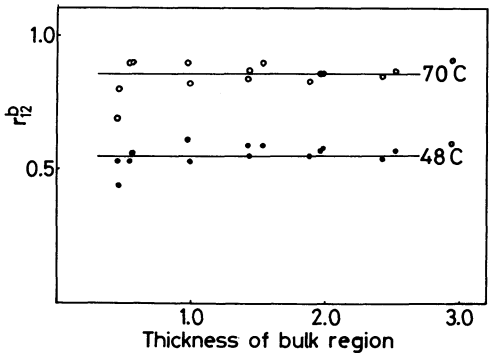

Fig. 5. The relation of r_{12}^b and thickness of bulk region in the LC state. The r_{12}^b value is the ratio of the first and second bands of difference spectrum. The thickness is graduated by absorbance of the first band in the isotropic state.

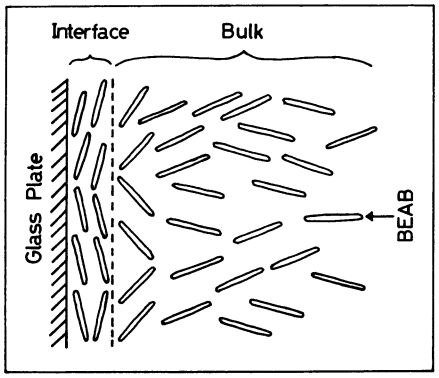

Fig. 6. A model for the molecular orientation of BEAB in the LC state in a thin glass cell.

at around 290 nm in Fig. 4, but at present its cause remains unexplained.

Defining r_{12}^{b} for difference spectra in the same sense as R_{12} and plotting r_{12}^{b} against the thickness of bulk, we obtain Fig. 5. For each temperature, r_{12}^{b} is regarded as nearly constant, the average values being about 0.6 (48 °C) and 0.9 (70 °C). These values are smaller than those corresponding to R_{12} (Fig. 3), which suggests that the intensity ratio (r_{12}^{f}) of the first and second bands for the interface region is larger than $R_{12}=1.69$. In fact, the R_{12} value larger than 1.69 is observed for the thinnest cell in the LC state (see Table 2 and Fig. 3).

If this is true, it is concluded that the LC state consists of two kinds of orientation states such that the molecular long axis inclines to the direction parallel to the cell plane in the interface region or perpendicular to the cell plane in the bulk region. Figure 6 shows schematically a model for the orientation of BEAB molecules in the cell. This model gives explanations for the findings already pointed out in Fig. 3 as follows: According to the model in Fig. 6, the following expression for R_{12} is obtained:

$$R_{12}=\frac{A_1}{A_2}=\frac{\varepsilon_1^{f}p^{f}+\varepsilon_1^{b}p^{b}}{\varepsilon_2^{f}p^{f}+\varepsilon_2^{b}p^{b}},$$

where ε and p are the molecular extinction coefficient and path length (cell gap), respectively, the superscripts f and b indicate the interface and bulk regions, respectively, and the subscripts 1 and 2 stand for the first and second bands, respectively. In the above expression, only p^{b} is a variable, which increases with increasing cell gap. R_{12} is, therefore, a hyperbolic function of p^{b}. $R_{12}\simeq\varepsilon_1^{b}/\varepsilon_2^{b}=r_{12}^{b}$ for $p^{b}\gg p^{f}$, and $R_{12}=\varepsilon_1^{f}/\varepsilon_2^{f}=r_{12}^{f}$ for $p^{b}=0$. Since $r_{12}^{b}<r_{12}^{f}$, the first derivative of R_{12} with respect to p^{b} is negative. Thus, the R_{12} value decreases along the hyperbolic curve with increasing cell gap (p^{b}), *i.e.*, the R_{12} value decreases steeply in the range of smaller cell gaps and gradually in that of larger cell gaps, which tendency is responsible for approximately two straight lines of different slopes to have been observed as shown in Fig. 3. When the temperature (T) is raised in the LC state, the molecular orientations in the interface and bulk regions approach each other through thermal motion, resulting in the same orientation ($r_{12}^{f}=r_{12}^{b}=1.69$) in the isotropic state. In other words, if $T<T'$, $r_{12}^{f}(T)>r_{12}^{f}(T')>1.69$ and $r_{12}^{b}(T)<r_{12}^{b}(T')<1.69$. The model predicts, therefore, that the two curves for the higher and lower temperatures in Fig. 3 must cross each other, which seems indeed to have been realized as the dotted lines at the small cell gaps. Strictly speaking, the model does not, however, explain the finding that the slopes of the two lines for 70 and 48 °C in Fig. 3 are nearly equal for larger cell gaps, because the model claims that the slopes of the two hyperbolic curves for different temperatures are the same only when they are both zero (horizontal). Therefore, the model in Fig. 6 is applicable fairly well to smaller cell gaps, but finds some difficulty in being applied to larger cell gaps.

To tell the truth, we expected at first that the orientation state in LC is only one kind. But actually, as shown in Fig. 6, it has become clear that the two kinds of orientation states exist in a cell. The orientation state in the bulk region, in this case, is thought to be the orientation in the LC state itself. (The reason why the molecules in the bulk region are arranged altogether perpendicularly to the cell plane is not clear.) If so, what makes the orientation in the interface induced? As pointed out in the Experimental section, the dichroism always reappears in the LC state even after it has disappeared in the isotropic state. This means that the orientation in the interface does not originate from the so-called flow alignment.[9] Therefore, the motive force for the orientation in the interface must remain on the cell wall. As the motive force concerned, a kind of rubbing effect in the interface region is considered which is generated by the friction when the melted sample is sucked up into the cell.

Knowledge of the rubbing effect on the cell wall *via* the fluid just mentioned may be obtained, provided that an absorption spectrum for the interface region has been determined and then, from analysis of the spectrum, details of the molecular arrangement relative to the cell wall have been clarified.

In principle, an absorption spectrum may be determined for the interface region as well as for the bulk region and accordingly the molecular orientations in both the regions may be analyzed in a three dimensional space. However, in this preliminary work, we could not do so because of the involvement of considerably large experimental errors as manifested in Fig. 5. But qualitatively, the above-mentioned conclusions concerning the orientation of BEAB molecules in the cell can be derived.

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