研 究 速 報

UDC 543.422-145.4 : 547.551.2-144
547.832.1.03

NEMATIC LIQUID CRYSTAL AS AN ANISOTROPIC SOLVENT IN SPECTROSCOPIC MEASUREMENTS

分光学的測定における異方性溶媒としてのネマティック液晶

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1. Introduction

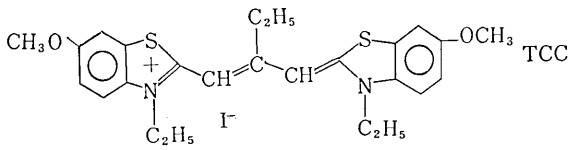
Nematic liquid crystals can easily be oriented by the surface treatment of the substrate, as well as by dc electric fields or magnetic fields[1]. The liquid crystal thus oriented can be used as an anisotropic solvent where the rotational movement of the solute molecules is restricted. Sackmann[2),3)] and Ceasar and Gray[4)] have reported that absorption measurement of molecules dissolved in ordered liquid crystals is useful to gain information on the absolute direction of transition moments in molecules.

In this paper we report the results of polarized light-absorption experiments on a thiacarbocyanine dye, which is of importance in photographic science, dissolved in oriented p-methoxybenzylidene-p-n-butylaniline (MBBA), and some informations derived therefrom.

2. Experimental

MBBA distilled three times was used as the liquid crystal solvent. This compound shows the nematic state in the temperature range of 20–41°C, and the measurements were carried out at 22°C. The absorption edge of MBBA is situated around 420 nm, and is therefore suited for absorption experiments on a colored thiacarbocyanine dye which absorbs light in the wavelength range of 500–650 nm.

As the solute compound, 3, 3′, 9-triethyl-6, 6′-dimethoxy-thiacarbocyanine iodide (abbreviated as TCC hereafter), supplied from Japan Research Institute for Photosensitizing Dyes Co., was employed.



TCC

Flat glass cells with the optical path of 50 μ were prepared. The inner sides of the windows of the cell were treated with a polyester resin so as to orient the liquid crystal molecules parallel to the windows. The direction of the optical axis could easily be determined by means of a polarizing microscope.

Surface treatment of the inner sides of the windows with lecithin and subsequent addition of a small amount of a benzoic acid derivative could bring about another orientation where the long axes of the solvent and the solute molecules are ordered perpendicular to the windows.

The absorption spectra were measured with the Shimadzu Spectrophotometer Model MPS-50. A linearly polarizing filter was placed between sample and the light source of the spectrophotometer in order to control the direction of the electric vector of the incident light.

3. Results and Discussion

3.1 Absorption Spectra of the Dye

In Fig. 1, absorption spectra of TCC in oriented MBBA are shown as a function of the angle between the directions of the preferred orientation and the electric vector of the incident light.

It would be reasonable to assume that this rather long molecule orients with its long molecular axis parallel to the long axis of the solvent molecule. It is seen from Fig. 1 that the absorption

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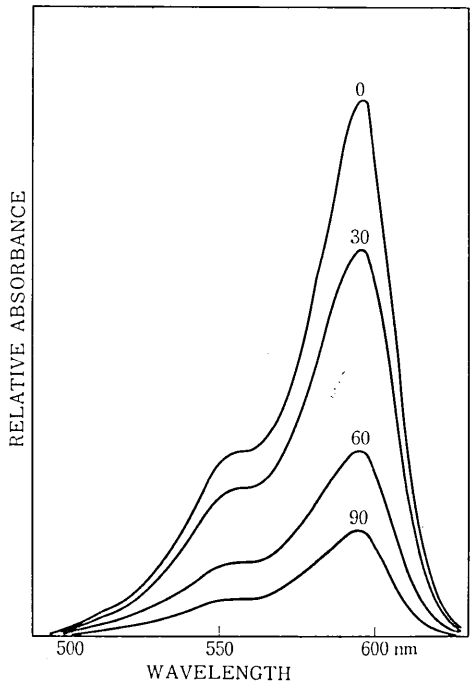

Fig. 1 Absorption spectra of TCC saturated in ordered MBBA at 22℃. Numbers on the curves indicate the angles between the directions of the electric vector of the incident light and of the preferred orientation.

is significantly more intense when the incident electric vector is parallel to the direction of orientation, leading to the conclusion that the transition moment of TCC lies along the long molecular axis.

Compared with the absorption spectrum of the ethanol solution of this dye, a slight shift of the absorption peak to the longer wavelengths was observed, which presumably was caused by the difference in the dielectric constant. Any aggregate band, which often appears in aqueous solution or on the silver halide grains, was not detectable. This suggests that TCC exists mainly as isolated molecules in oriented MBBA.

When the solvent and solute molecules were oriented perpendicular to the windows of the cell, the absorption intensity became much smaller, and was independent of the electric vector direction of the incident light.

3.2 Estimation of the Orientational Order Parameter

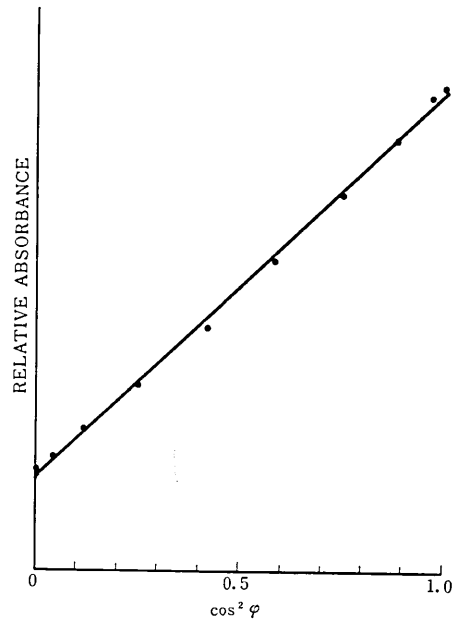

Fig. 2 Plot of D_φ vs $\cos^2\varphi$ (see text) on the basis of the measurements for TCC.

According to Maier and Saupe[5], the orientational order parameter S of the nematic liquid crystal phase is defined as

$$S=\frac{3\langle\cos^2\theta\rangle-1}{2} \qquad (1)$$

where θ is the angle between the preferred orientational direction and the long molecular axis of a liquid crystal molecule. The arrangement of the solvent molecules and therefore also of the solute molecules is rotationally symmetric with respect to the preferred orientational direction. The total absorption intensity D_φ, where the electric vector of the incident light makes the angle φ to the preferred orientational direction, is the sum of the apparent oscillator strengths of all molecules in this direction. When the transition moment lies along the long molecular axis of the solute molecule, D_φ can be written as

$$D_\varphi=D_0\left(S\cos^2\varphi+\frac{1-S}{3}\right) \qquad (2)$$

where D_0 is a constant.

In Fig. 2, values of D_φ are plotted against $\cos^2\varphi$, on the basis of the absorption measurements of TCC illustrated in Fig. 1. As can be seen, a linear relationship is established, from which the

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orientational order parameter S is calculated to be around 0.577. This value agrees fairly well with those measured by means of other techniques.[1] Thus the method of polarized light-absorption of a dye is found to be a convenient one for the determination of the order parameter of a liquid crystal phase.

(Manuscript received, March 23, 1974)

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次 号 予 告 (6月号)