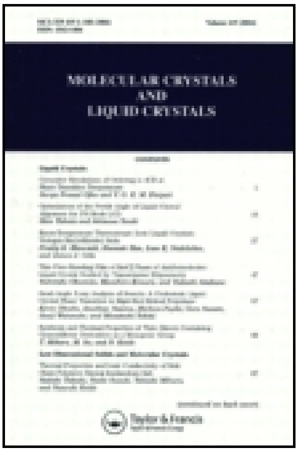

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Spontaneous Orientation of Alkyl and Alkoxy Cyanobiphenyl Liquid Crystals on the Metallic Substrate

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Spontaneous Orientation of Alkyl and Alkoxy Cyanobiphenyl Liquid Crystals on the Metallic Substrate

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Infrared reflection absorption spectroscopy (IR-RAS) was applied to analyze the spontaneous orientation behavior of alkyl and alkoxy cyanobiphenyl liquid crystals on the metallic substrate. The long axis of the liquid crystal molecules was shown to orient perpendicular to the substrate plane. The orientation function was evaluated from the relative intensity of the CN stretching vibration and the out-of-plane deformation of the biphenyl ring. The temperature dependence of orientation functions was studied using a heating and cooling apparatus. The orientation functions gradually decreased with the rise in temperature in the liquid crystal phase and fell off to the range of 0.1–0.2 above liquid crystal – isotropic transition. The orientation function of the terminal methyl group was evaluated from the relative intensity of the symmetric and asymmetric stretching vibrations of the methyl group. The orientation of the methyl group was discussed in relation to the conformation of the methylene sequence.

Keywords: Liquid crystal, alkyl cyanobiphenyl, alkoxy cyanobiphenyl, molecular orientation, IR/RAS, phase transition

INTRODUCTION

Alkyl and alkoxycyanobiphenyls are the popular liquid crystals which are suitable for the use in electro-optic devices. The orientation behavior of liquid crystals has been a subject of considerable attention,[1–5] because the molecular orientation controls the electro-optical properties. The anisotropic dielectric constants of alkylcyanobiphenyls were measured in the presence of external electric and magnetic fields.[1] The orientational order parameter of liquid crystals has been measured by polarized infrared (IR) spectroscopy,[2] polarized Raman spectroscopy,[3] and birefringence.[4] The order parameter was studied in the liquid crystal phase as a function of temperature.[2–4] The molecular orientation of liquid crystal was investigated in the presence of the external electric field with the use of polarized attenuated total reflection (ATR) IR spectroscopy.[5,6]

On the other hand, infrared reflection absorption (IR-RAS) has been extensively studied for the purpose of analyzing the structure of thin films on metallic substrates.[7–14] According to the theoretical work by Greenler,[6] the absorption intensity of the IR-RAS spectrum is dominated by the surface selection rule, in which the molecular vibrations with a transition moment perpendicular to the substrate are strongly observed in the spectrum, but the vibrations with a parallel transition moment do not absorb IR radiation. The IR-RAS spectroscopy was applied to characterize the Langmuir-Blodgett monolayer assemblies.[8-10,14] The molecular orientation in organic thin films was also studied by the IR-RAS spectroscopy.[11-13,15]

In this work, the spontaneous orientation of alkoxy and alkyl-cyanobiphenyl liquid crystals on the metallic substrate was examined by analyzing the relative band intensities in the IR-RAS spectra. Attention was focused on the effects of temperature and alkyl groups on the orientation behavior of liquid crystals.

EXPERIMENTAL

The samples studied in this work are alkyl and alkoxy cyanobiphenyls obtained from Aldrich Co. Ltd. The liquid crystal samples were purified by vacuum distillation. The transition temperatures of the liquid crystals were determined by differential scanning calorimetry and the results are summarized in Table I. The liquid crystals were dissolved in petroleum ether. The 200μl of the solution was spread over the aluminum substrate with a 20 × 30 mm dimension and the solvent was allowed to evaporate. The thickness of the liquid crystal film was calculated from the concentration of the solution and the area of the substrate.

The IR-RAS spectra were measured with a 83° angle of incidence using a Perkin Elmer model 1800 Fourier transform infrared spectrometer equipped with a variable-angle specular reflection accesory (Harrick scientific Inc.,) and a liquid-nitrogen-cooled MCT detector. Incident IR radiation was polarized parallel to the plane of incidence by a KRS-5 wire-grid polarizer. The sufficient signal-to-noise ratio was achieved by averaging 1000 scans of 4 cm^{-1} resolution. The reference spectrum was obtained with an aluminum mirror without samples.

The apparatus for the temperature dependence of IR-RAS is shown in Figure 1. The temperature dependence of IR-RAS was examined using an environmental chamber, a heating plate, a cold air generator, and a liquid-nitrogen container (10 × 10 × 40 mm). The IR-RAS spectra above room temperature were measured by fixing the heating

TABLE I

Transition temperature of liquid crystals

Compound	T_{cn}^{*1} (°C)	T_{ns}^{*2} (°C)	$T_{ni}(T_{si}^{*3})$(°C)
4-Pentyloxy-4′-cyanobiphenyl (5OCB)	47.0		66.8
4-Penty-4′-cyanobiphenyl (5CB)	(20)*4		34.8
4-Hexyl-4′-cyanobiphenyl (6CB)	14.2		29.3
4-Heptyl-4′-cyanobiphenyl (7CB)	15.2 (29)*4		41.3
4-Octyl-4′-cyanobiphenyl (8CB)	21.0	35.0	47.0

*1 T_{cn}: Crystal – nematic transition temperature
*2 T_{ns}: Nematic – smectic transition temperature
*3 T_{ni}: Nematic – isotropic transition temperature
T_{si}: Smectic – isotropic transition temperature
*4 From ref. 2. The transition temperature is sensitive to the cooling condition.

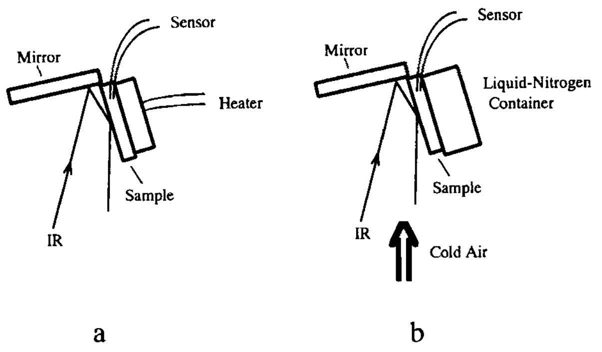

FIGURE 1 The apparatus for the temperature dependence experiment of IR-RAS.

plate to the aluminum substrate (Fig. 1a). The temperature was controlled to an accuracy of 1 °C by a sensor which was attached directly to the aluminum substrate. The spectra at lower temperatures (5–25 °C) were obtained by introducing cold air into the environmental chamber (Fig 1b). The liquid crystals were crystallized on the substrate by fixing the liquid nitrogen container to the aluminum substrate (Figure 1b), and the IR-RAS spectra of the crystallized samples were measured at lower temperatures.

RESULTS AND DISCUSSION

The thickness dependence of the IR-RAS spectra of 4-pentyloxy-4′-cyanobiphenyl (5OCB) is shown in Figure 2. The absorption intensity of the spectra increases almost linearly with increasing the thickness of the 5OCB films in the thickness range of 0.3–2.5 $\mu g/cm^2$. If the density of the sample is assumed to be 1.0, the thickness of the sample corresponds to 3–25 nm. The absorption intensities of IR-RAS are proportional to the thickness of the samples in this thickness range.

The IR-RAS spectrum of 4-heptyl-4′-cyanobiphenyl (7CB) is shown in Figure 3 together with the transmission spectrum and the spectrum in solution. The transmission spectrum of the 7CB film was measured on the KBr plate. The spectrum in the isotropic state was measured in n-heptane solution (500–1200 cm^{-1}) and in carbon-tetrachloride solution (900–4000 cm^{-1}). The relative intensity of the absorption bands is quite different between reflection and transmission spectra. The absorption bands at 2230 cm^{-1} (CN stretching), 1609 cm^{-1} (CC stretching of biphenyl ring), and 1493 cm^{-1} (CC stretching of biphenyl ring) are observed more strongly in the RAS spectrum than in the transmission spectrum, while the absorption band at 812 cm^{-1} (out-of-plane bending of biphenyl ring) appears more strongly in the transmission spectrum than in the reflection spectrum. The change in the relative absorption intensity suggests that the liquid crystal molecules are oriented perpendicular to the substrate both in the metallic substrate and in the KBr plate. The transition moments of the absorption bands at 2230 cm^{-1}, 1609 cm^{-1}, and 1493 cm^{-1} are parallel to the long-axis of the biphenyl ring whereas the absorption band at 812 cm^{-1} polarized perpendicular to the biphenyl ring.

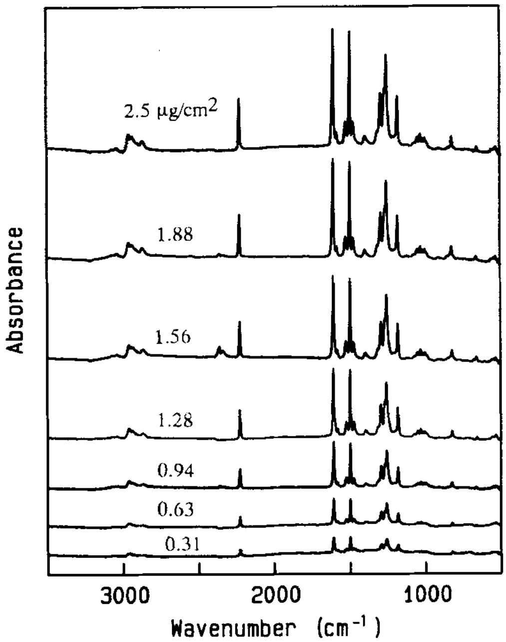

FIGURE 2 The thickness dependence of IR-RAS spectra of 4-pentyloxy-4′-cyanobiphenyl (5OCB).

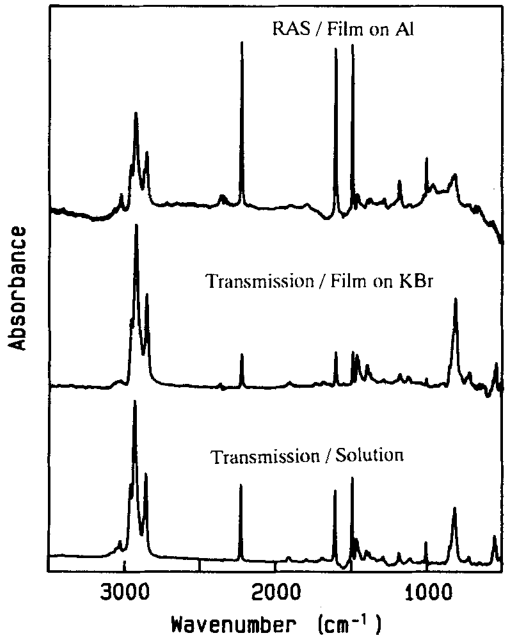

FIGURE 3 The IR-RAS spectrum (upper), the transmission spectrum (middle), and the solution spectrum (lower) of 4-heptyl-4′-cyanobiphenyl (7CB).

In the IR-RAS experiments, IR radiation polarized parallel to the plane of incidence is intensified at the surface of the substrate, whereas the radiation with perpendicular polarization has a node at the surface. As a result, the molecular vibrations having the components of the transition moment normal to the metallic substrate are expected to appear with enhanced intensity, while the component of transition moment parallel to the substrate does not interact with the electric field of the IR radiation. The long-axis of the biphenyl unit is shown to orient perpendicular to the metallic substrate, because the molecular vibrations with the transition moments parallel to the long-axis of the biphenyl unit are enhanced in the IR-RAS experiment.

Matsui *et al* have recently reported the orientation behavior of 8CB and 5CB on two kinds of alignment layers.[15] One was the SiO obliquely evaporated alignment layer and another was the rubbed polyimide film. They reported that the long molecular axis was aligned with a slant away from the alignment direction. On the other hand, the substrate used in this work is the evaporated aluminum layer without alignment treatment. The molecular orientation on the metallic substrate should have the cylindrical symmetry with respect to the normal of the substrate. The long axis of the liquid crystal molecules tends to orient normal to the substrate. Thus the orientation behavior of the liquid crystal depends upon the substrate.

In the transmission spectrum, the electric field vector of radiation is parallel to the KBr plate, and the vibrations with the transition moments parallel to the substrate plate are observed strongly. The enhancement of out-of plane deformation vibration (812 cm^{-1}) in the transmission spectrum suggests that the long-axis of the biphenyl ring is oriented perpendicular to the KBr Plate, as found for the sample on the metallic substrate.

The temperature dependence of IR-RAS spectra of 5OCB is shown in Figure 4. The CN stretching vibration and the skeletal stretching vibration of the biphenyl ring strongly appear and the out-of plane deformation of the biphenyl ring is weakly observed in the spectrum at room temperature. The IR-RAS spectra do not change with the rise in temperature in the solid state (25.3 °C–47.5 °C). The result suggests that the long-axis of the biphenyl unit is oriented perpendicular to the substrate plane in the solid state. The intensity of the CN stretching vibration decreases and that of the out-of-plane deformation increases with the rise in temperature from 47.5 °C to 64 °C. The orientation of the molecules is gradually relaxed as the temperature rises in the liquid crystal phase.

Figure 5 shows the temperature dependence of IR-RAS spectra of 4-octyl-4′-cyanobiphenyl (8CB) in the liquid crystal phase. The relative intensity of the CN stretching vibration and the out-of-plane deformation vibration changes with the rise in temperature, and the orientation of 8CB molecules is relaxed as temperature rises in the liquid crystal phase. The change in orientation during crystal – liquid crystal transition is shown in Figure 6. The sample was crystallized at the liquid-nitrogen temperature, and subsequently warmed up to 12°C. The out-of-plane deformation vibration appears strongly in the solid state (12 °C–20 °C). The biphenyl units are randomly oriented on the metallic substrate, or otherwise the long-axis of the biphenyl unit is tilted by 56° from the normal of the substrate. The absorption intensity of the out-of plane deformation vibration markedly decreases with the rise in temperature from 20 °C–21.2 °C. The perpendicular orientation of

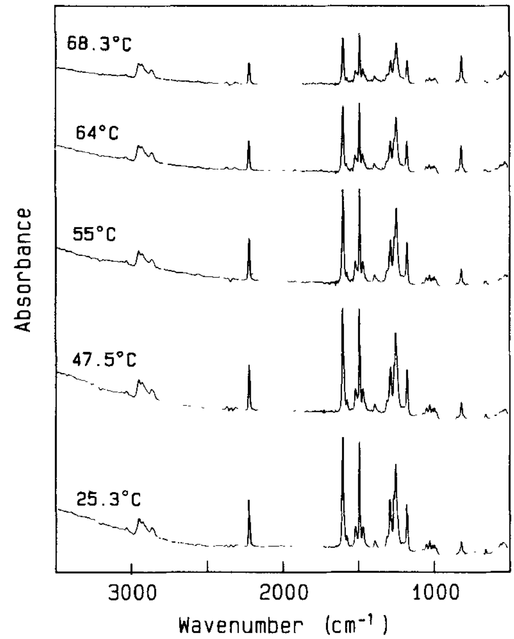

FIGURE 4 The temperature dependence of IR-RAS spectra of 5OCB. The film thickness is 2.5μg/cm^2.

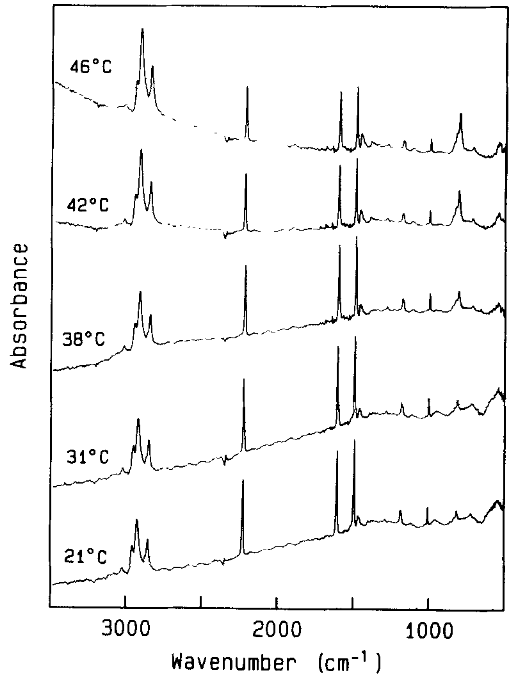

FIGURE 5 The temperature dependence of IR-RAS spectra of 4-octyl-4′-cyanobiphenyl (8CB) in the liquid crystal phase. The film thickness is 2.5μg/cm^2.

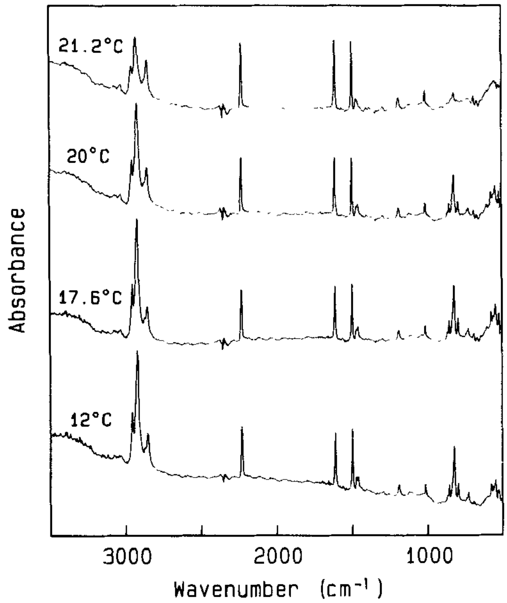

FIGURE 6 The change of IR-RAS spectra of 8CB during crystal – liquid crystal transition. The film thickness is $2.5 \mu g/cm^2$.

the biphenyl unit is induced by the transition from the crystal phase to the liquid crystal phase.

The orientation function of the biphenyl unit can be calculated from the relative intensity of the CN stretching vibration and the out-of-plane deformation vibration. It is assumed that the transition moment of the CN stretching vibration is parallel to the long-axis of the biphenyl unit and that the transition moment of the out-of-plane deformation is perpendicular to it. The assumption holds if one can neglect the coupling of the vibrations of the methylene sequence with the vibrations of the biphenyl unit. The coordinate system for the analysis is shown in Figure 7. The angle θ is measured between the normal of the substrate (Z-axis) and the long-axis of biphenyl

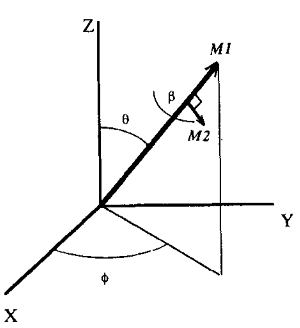

FIGURE 7 The coordinate system for the analysis.

unit, and ϕ is the rotational angle of the projection of the molecular axis to the substrate plane. The orientation function, f, of the molecular axis is expressed as

$$f = (3\langle\cos^2\theta\rangle - 1)/2 \tag{1}$$

If the molecular axis of the biphenyl unit is perfectly oriented perpendicular to the substrate plane, $f = 1$. The parallel orientation of the biphenyl unit in the substrate plane corresponds to $f = -0.5$. The unit vector ***M1*** stands for the direction of transition moment that is parallel to the biphenyl unit, and ***M2*** represents the unit vector of the transition moment polarized perpendicular to the biphenyl unit. The unit vectors are given by

$$\begin{aligned} \boldsymbol{M1} &= \sin\theta\cos\phi\,\boldsymbol{i} + \sin\theta\sin\phi\,\boldsymbol{j} + \cos\theta\,\boldsymbol{k} \\ \boldsymbol{M2} &= (\cos\beta\cos\theta\cos\phi + \sin\beta\sin\phi)\boldsymbol{i} \\ &\quad + (\cos\beta\cos\theta\sin\phi - \sin\beta\cos\phi)\boldsymbol{j} \\ &\quad + \cos\beta\sin\theta\,\boldsymbol{k} \end{aligned} \tag{2}$$

where $\boldsymbol{i}$, $\boldsymbol{j}$, and $\boldsymbol{k}$ are the unit vectors along the X-, Y-, and Z-axes respectively. The angle β represents the angle of rotation of ***M2*** around the molecular axis. The absorption intensity of the vibration with parallel polarization, A_1 is calculated by averaging over angles β, ϕ, and θ.

$$\begin{aligned} A_1 &= 3A_1(\text{iso})\langle(\boldsymbol{k}\cdot\boldsymbol{M1})^2\rangle \\ &= 3A_1(\text{iso})\langle\cos^2\theta\rangle \end{aligned} \tag{3}$$

The absorption intensity for the vibration with perpendicular polarization, A_2 is obtained in an analogous way.

$$\begin{aligned} A_2 &= 3A_2(\text{iso})\langle(\boldsymbol{k}\cdot\boldsymbol{M2})^2\rangle \\ &= 3A_2(\text{iso})\langle\sin^2\theta\rangle/2 \end{aligned} \tag{4}$$

A_1(iso) and A_2(iso), are the absorption intensities of the isotropic sample for the corresponding vibrations. The orientation function, f, of the biphenyl unit is calculated from Equations 3 and 4.

$$f = (D - 1)/(D + 2) \tag{5}$$

$$\begin{aligned} D &= (A_1 A_2(\text{iso}))/(A_1(\text{iso})\,A_2) \\ &= 2\langle\cos^2\theta\rangle/\langle\sin^2\theta\rangle \end{aligned} \tag{6}$$

As a result, the orientation function of the biphenyl unit can be calculated from the relative band intensity of two vibrations with opposite directions of transition moments. In this work, the orientation function was calculated from the relative band intensity of the 2230 cm^{-1} band and the 812 cm^{-1} band.

The orientation functions of the biphenyl units are plotted against temperature, and the results are shown in Figures 8–10. The circles represent the results of the tempera-

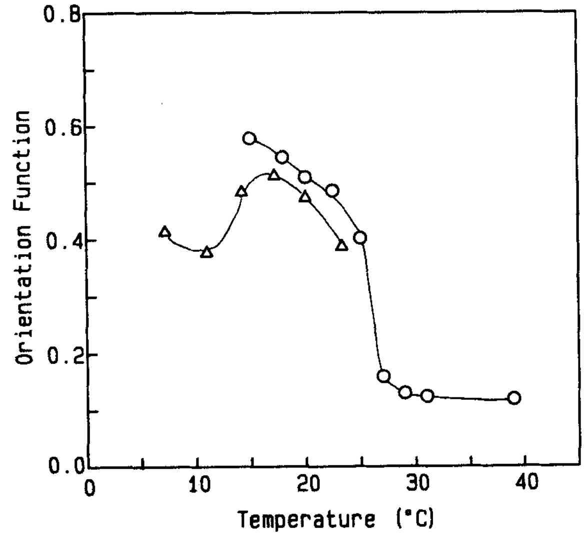

FIGURE 8 The temperature dependence of orientation functions of the biphenyl units of 4-hexyl-4′-cyanobiphenyl (6CB).

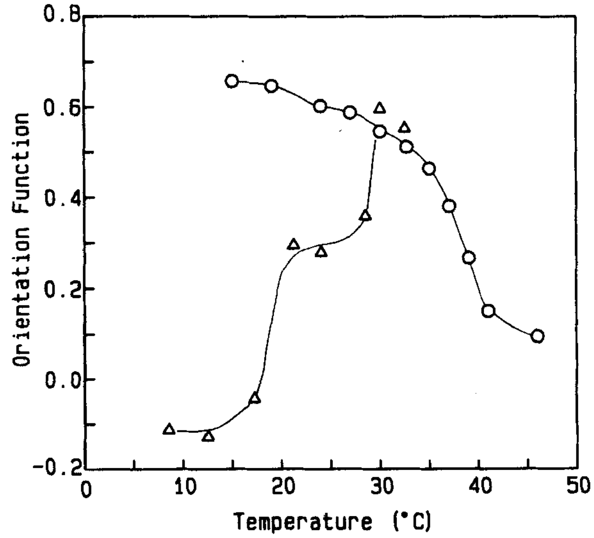

FIGURE 9 The temperature dependence of orientation functions of the biphenyl units of 7CB.

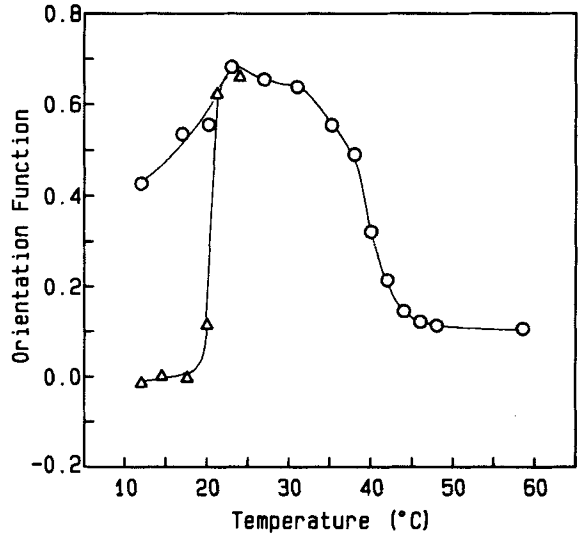

FIGURE 10 The temperature dependence of orientation functions of the biphenyl units of 8CB.

ture dependence experiment in which the temperature is lowered from room temperature to 10 °C, and then is gradually raised. The triangles express the temperature dependence of the orientation function for the samples sufficiently crystallized at the liquid-nitrogen temperature. The temperature dependence of the IR-RAS was measured during heating. The orientation function gradually decreases with the rise in temperature in the liquid crystal state, and the orientation of the biphenyl unit is sharply randomized with the rise in temperature in the range of the liquid crystal – isotropic transition. The molecular axes of the liquid crystals are slightly oriented perpendicular to the substrate, even in the isotropic phase.

The orientation function of the sample crystallized at the liquid-nitrogen temperature is much lower than that in the liquid crystal phase. The biphenyl units are either randomly oriented, or inclined from the normal of the substrate. The orientation function sharply increases with the rise in temperature in the temperature range of the crystal – liquid crystal transition. The orientation function below the crystal – liquid crystal transition depends upon the thermal history of the samples. As alkylcyanobiphenyls are highly super-cooling, they are hardly crystallized in the temperature range of 10–25°C. If the temperature is lowered from room temperature to 10 °C, the high degree of perpendicular orientation is preserved even below the crystal – liquid crystal transition. The super-cooling nature of 4-heptyl-4′-cyanobiphenyl (7CB) is marked among the alkylcyanobiphenyls studied in this work.

Figure 11 shows the IR spectrum of 7CB in the wavenumber region of 2700–3100 cm^{-1}. The orientation function of the terminal methyl group can be evaluated from the relative intensity of the CH_3 symmetric stretching vibration (2870 cm^{-1}) and the CH_3 asymmetric stretching vibration (2956 cm^{-1}). The symmetric stretching vibration appears strongly in the IR-RAS spectrum whereas its absorption intensity is reduced in the transmission spectrum. The transition moment of the symmetric

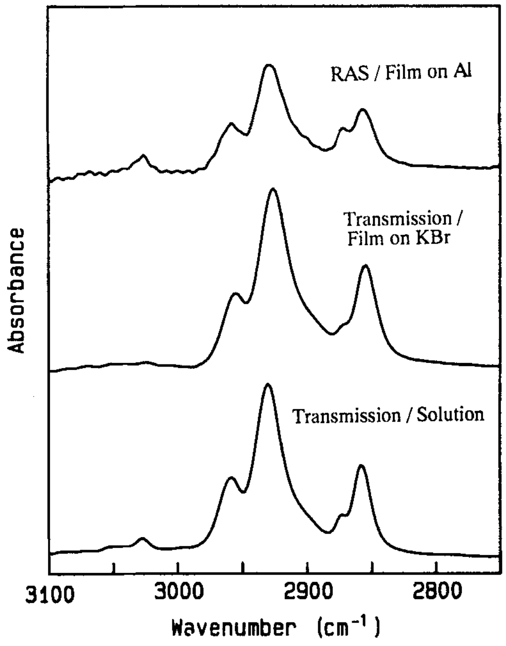

FIGURE 11 The IR-RAS spectrum (upper), the transmission spectrum (middle), and the solution spectrum (lower) of 7CB in the wavenumber region of 2700–3100 cm^{-1}.

stretching vibration is parallel to the axis of the terminal methyl group and that of the asymmetric stretching vibration is perpendicular to it. The terminal methyl group is shown to orient normally to the metallic substrate. The overlapping absorption bands were resolved by the least-square curve fitting procedure, and the absorption intensities of the CH_3 stretching vibrations were evaluated. The orientation function of the methyl group was determined by use of Equations 5 and 6. The orientation functions of the methyl group and the biphenyl unit are summarized in Table II. If the methyl group is distributed around the highly oriented biphenyl ring, the orientation function of methyl group, f_m, is related to the orientation function of the biphenyl ring, f_b,[16]

$$f_m = f_b / f_\gamma \tag{7}$$

$$f_\gamma = (3\langle\cos^2\gamma\rangle - 1)/2 \tag{8}$$

TABLE II

Orientation functions

Compound	f_b	f_m	$\langle\cos^2\gamma\rangle$
5CB	0.521	0.238	0.638
6CB	0.488	0.005	0.337
7CB	0.550	0.250	0.636
8CB	0.686	−0.011	0.322

where γ is the angle between the long-axis of the biphenyl unit and the axis of the terminal methyl group.

The angle γ depends upon the conformation of the methylene sequence. If the methylene sequence has an all-trans zig-zag conformation, the axis of the methyl group in 5CB and 7CB is parallel to the long axis of the biphenyl unit ($\langle\cos^2\gamma\rangle = 1.0$), and the value of $\langle\cos^2\gamma\rangle$ is 0.11 for 6CB and 8CB. The results in Table II suggest that the methylene sequence contains gauche conformations.

The value of $\langle\cos^2\gamma\rangle$ was calculated as a function of the gauche fraction, by averaging over the possible conformation of the methylene sequence.[17]

$$\langle\cos^2\gamma\rangle = \Sigma w_i \cos^2\gamma_i / \Sigma w_i \tag{9}$$

The angle, γ_i, is spun between the long-axis of the biphenyl unit and the axis of the terminal methyl group of the i-th conformation. The statistical weight fraction, w_i, of the i-th conformation is expressed as,

$$w_i = (1.0 - w_g)^{n_i}(w_g/2)^{m_i} \tag{10}$$

where w_g is the fraction of gauche (G) and gauche′ (G′) conformations in a CH_2—CH_2 bond, n_i is the number of trans conformation in the i-th sequence, and m_i is the number of gauche and gauche′ conformations. The extremely high-energy conformation, the -GG′-sequence, was excluded from the sum of Equation 9.

The calculated results are shown in Figure 12 as a function of the gauche fraction. The values of $\langle\cos^2\gamma\rangle$ of 5CB and 7CB decrease with increasing the gauche fraction, whereas those for 6CB and 8CB increase with the gauche fraction. The experimental values of $\langle\cos^2\gamma\rangle$ of 5CB and 7CB are in agreement with the theoretical results for

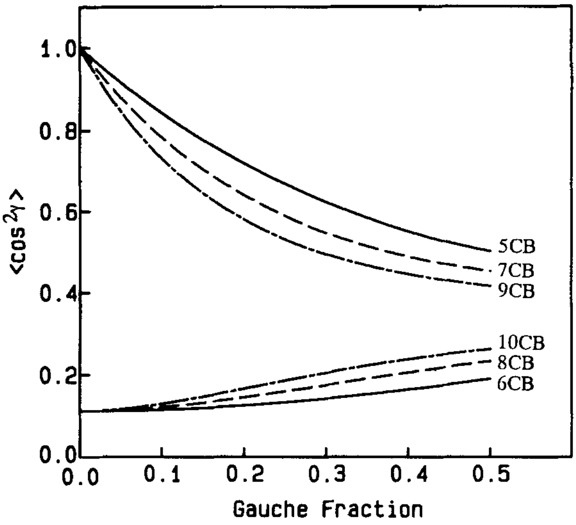

FIGURE 12 The calculated values of $\langle\cos^2\gamma\rangle$ as a functions of the gauche fraction.

$w_g = 0.2$–0.3. The experimental values of γ for 6CB and 8CB tend to be larger than the predicted values. One of the possible reasons for the difference is that the intermolecular interaction has some effects on the conformation of the methylene sequence. In conclusion, the methylene sequence of alkylcyanobiphenyls contains the gauche conformations in the liquid crystal phase.

CONCLUSION

The spontaneous orientation behavior of alkyl and alkoxy cyanobiphenyl liquid crystal on the metallic substrate was studied with the use of IR-RAS spectroscopy. The orientation functions were evaluated from the relative intensity of the two vibrations whose transition moments were perpendicular to each other. The long axis of the liquid crystal is shown to orient perpendicular to the metallic substrate in the liquid crystal phase. The orientation function of liquid crystal molecules gradually relaxes as temperature rises in the liquid crystal phase, and sharply randomizes in the range of liquid crystal – isotropic transition. On the other hand, in the solid state, the biphenyl units are either randomly oriented or inclined from the normal of the substrate. The perpendicular orientation of the liquid crystals sharply develops as temperature rises in the range of crystal – liquid crystal transition.

The orientation of the terminal methyl group was discussed in relation to the conformation of the methylene sequence. The averaged angle between the axis of the methyl group and that of the biphenyl unit was obtained from the orientation functions of the two groups. It is suggested that the methylene sequence contains the gauche conformations in the liquid crystal state.

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