Fluorescence Anisotropy and Rotational Diffusion of Two Kinds of 4-*n*-alkyl-4'-cyanobiphenyls in Glycerol

Hideyo Matsuzawa*, Kentaro Watanabe and Makio Iwahashi

Department of Chemistry, School of Science, Kitasato University (1-15-1 Kitasato, Sagami-hara, Kanagawa-ken, 228-8555, JAPAN)

Abstract: Absorption and fluorescence spectra, fluorescence lifetimes, and steady-state and time-resolved fluorescence anisotropies were measured for 4-methyl-4'-cyanobiphenyl (1CB) and 4-hexyl-4'-cyanobiphenyl (6CB) in glycerol at various temperatures. The energies and intensities of the absorption and emission spectra for 1CB and 6CB were almost equally observed, and the fluorescence lifetimes around 1.0 ns were also almost equally obtained and did not depend on temperature. However, the time-resolved fluorescence anisotropies measured in glycerol solution indicated that the molecules of 1CB rotate more rapidly than those of 6CB: the rigid-sphere radii for 1CB and 6CB obtained by using the pulsed exciting light were evaluated as 1.3×10^{-10} m (1CB) and 1.8×10^{-10} m (6CB) in the low temperature region (2–10°C), whereas those evaluated in the high temperature regions (20–60°C for 1CB and 30–60 for 6CB) were 2.7×10^{-10} m (1CB) and 3.6×10^{-10} m (6CB). These radii evaluated in the high temperature region were in good agreement with those obtained by using steady-state exciting light, 2.9×10^{-10} m (1CB) and 3.4×10^{-10} m (6CB). It is noted that the increase of radius was observed across an intermediate temperature region (10–30°C for 1CB or 10–40°C for 6CB), and was more remarkable for 6CB than for 1CB. This implies that the movements of hexyl-chain are much more enhanced at high temperature, and are effectively reflected to the increase in radius of rotational diffusion. The changing phenomenon of movements of peripheral alkyl-chain in liquid-crystal molecules is important for the phase transition between liquid crystal and isotropic liquid phases: the changing to less vigorous movements of the alkyl-chain in 6CB is thought enough to contribute to the liquid-crystal formation of 6CB molecule.

Key words: liquid crystal, 4-*n*-alkyl-4'-cyanobiphenyl, 4-methyl-4'-cyanobiphenyl, 4-hexyl-4'-cyanobiphenyl, fluorescence anisotropy, fluorescence decay time

1 INTRODUCTION

4-*n*-Alkyl-4'-cyanobiphenyls (*n*CB, *n* is the carbon number in an alkyl chain) are known to make thermotropic liquid crystals and broadly used as display materials. Lydon and Coakley¹⁾ reported that 8CB in its smectic liquid crystal phase has a lamellar structure and that the thickness of the lamellar layer is $29.2 \pm 0.3 \times 10^{-10}$ m; 8CB molecules in the lamellar layer are thought to interpenetrate one another. Consequently, there would be interactions between alkyl chains and/or a stacking of biphenyl groups. 7CB in its liquid and/or nematic liquid crystal phase has a similar structure to that of 8CB²⁾. NMR and IR results^{3,5)} in the phase transition temperature regions suggest that the

cyanobiphenyl and alkyl parts differently contribute to the formation of liquid crystal: relatively rigid biphenyl part in 4-*n*-alkyl-4'-cyanobiphenyl molecule largely contributes to the formation of liquid crystal phase, while flexible alkyl part also contributes to the formation of liquid crystal phase and to the determination of the type of the liquid crystal phases.

However, the real dynamical molecular structures of the 4-*n*-alkyl-4'-cyanobiphenyls in their liquid and also in their liquid-crystal phases are still under a dark screen, although the molecules of the 4-*n*-alkyl-4'-cyanobiphenyls are thought to move vigorously in their liquid and even in their liquid-crystal phase.

*Correspondence to: Hideyo Matsuzawa, Department of Chemistry, School of Science, Kitasato University, 1-15-1 Kitasato, Sagami-hara, Kanagawa-ken 228-8555, JAPAN
E-mail: matsu@sci.kitasato-u.ac.jp

Accepted July 23, 2007 (received for review June 11, 2007)

Journal of Oleo Science ISSN 1345-8957 print / ISSN 1347-3352 online
<http://jos.jstage.jst.go.jp/en/>

The assembly structure of the molecules is important for the formation of the liquid crystal phase. Furthermore, for understanding the assembly structure of the liquid crystal, it is also essential to know the contributions of the alkyl and cyanobiphenyl parts to the movements of cyanobiphenyl molecule.

The situation of the π -electrons in the cyanobiphenyl part is thought to be unaffected by the alkyl part in the very dilute solution, where the n CB molecules do not approach each other in its excitation lifetime. In a concentrated condition, however, even in an isolated molecular situation, cyanobiphenyl part would be influenced by alkyl parts.

In general, the fluorescence emitted from molecules which are dispersed in viscous medium is partially polarized. This is customarily expressed in terms of molecular anisotropy, $\bar{r}$, which is measured at right angle to a polarized excitation beam.

In the present study, in order to know the contribution of the alkyl group to the formation of the liquid crystal phase, we studied the dynamical properties such as rotational diffusion (rotational movement) and dynamical molecular volume for 1CB and 6CB in dilute glycerol solution through the measurements of fluorescence lifetimes, and steady-state and time-resolved fluorescence anisotropies. In this study, we chose 6CB, as a typical 4- n -alkyl-4'-cyanobiphenyl, which forms a nematic liquid crystal, and 1CB which does not form liquid crystal.

2 EXPERIMENTAL

2.1 Materials

Sample of 1CB (Merck, 99.6% pure) was purified by twice-recrystallization from hexane. Samples of 6CB (Merck, 99.6%) and glycerol (Kanto Kagaku Co. Ltd, analytical grade sample for fluorescence measurements), which is used as a viscosity changeable solvent, were used without further purification. All the samples for fluorescence measurements, and also for the fluorescence decay-time measurements, were prepared after de-oxygen by bubbling with N_2 gas. Typical concentrations of sample for the measurements were dilute ($\sim 5 \times 10^{-5}$ mol dm $^{-3}$) enough to avoid the formation of association of n CB molecules in the ground and the excited states.

2.2 Optical measurements (method and apparatus)

Absorption spectra were measured on a Hitachi U-3210 spectrophotometer. Fluorescence spectra and steady-state fluorescence anisotropy, $\bar{r}$, were measured at right angle relative to the exciting beam with a Hitachi 850 spectrofluorometer. To prevent the scattering light interfering the fluorescence measurements, sharp-cut filters (UV29, 31) equipped in the instrument were used. All the optical mea-

surements were carried out under the temperature condition regulated within $\pm 0.1^\circ\text{C}$ using a water-circulating temperature controller (CTE-32, Yamato Science Instruments Co. Ltd.). Non-fluorescence-four-faced quartz cells having 1 cm light-path length were used for all fluorescence measurements.

2.3 Steady-state fluorescence anisotropy, $\bar{r}$

When a vertical (horizontal) polarizer is installed in the excitation part of the instrument, the steady-state fluorescence anisotropy, $\bar{r}$, is defined as:

$$\bar{r} = \frac{I_{VV} - I_{VH}}{I_{VV} + 2I_{VH}} \quad (1)$$

where I_{VV} and I_{VH} are the fluorescence intensities observed through a polarizer oriented perpendicular and parallel to the plane of polarization of the excitation beam. The first and the second sub-symbols of I mean the directions of the polarizing planes of the excitation part and of the emission part, respectively. Since the polarizers used in the instrument have a characteristic property in the polarization, we should consider the instrument constant for getting exact results. Thus, equation 1 becomes as follows:

$$\bar{r} = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}} \quad (2)$$

In this equation, G is a correction factor for detection system, which is expressed as the ratio of sensitivities of the detection system for vertically and horizontally polarized light; G is obtained by

$$G = \frac{I_{HV}}{I_{HH}} \quad (3)$$

where I_{HV} and I_{HH} are the fluorescence intensities polarized perpendicular and parallel components when the excitation beam is horizontally polarized. From equations 2 and 3, we obtain the following Azumi-McGlynn equation⁶⁾:

$$\bar{r} = \frac{I_{VV}I_{HH} - I_{VH}I_{HV}}{I_{VV}I_{HH} + 2I_{VH}I_{HV}} \quad (4)$$

We used a Hitachi polarizer unit (650-142) as the polarizers for determining the intensities of I_{VV} , I_{HH} , I_{VH} and I_{HV} .

2.4 Fluorescence decay time

Fluorescence decay time was measured on a Horiba NAES-700 time-resolution photoluminescence fluorometer, using a pulsed light source composed of high pressure hydrogen lamp. A band-pass filter (Hoya U-340) and a solution filter (0.500 kg dm $^{-3}$ NiSO $_4$) were used for the selection of the exciting light beam and a sharp-cut filter (Hoya L-40)

was used for preventing scattering light which interfere the fluorescence measurements. The temperature during the measurements was controlled within $\pm 0.1^\circ\text{C}$ with a low temperature controller (LCH-111 Labothermo Cool, Advantec Co. Ltd.).

2.5 Time-resolved fluorescence anisotropy, $r(t)$

The time-resolved fluorescence anisotropy, $r(t)$, to be measured is given by

$$r(t) = \frac{I_{VV}(t) - I_{VH}(t)G}{I_{VV}(t) + 2I_{VH}(t)G} \quad (5)$$

and

$$G = \frac{\int_0^t I_{HV}(t)dt}{\int_0^t I_{HH}(t)dt} \quad (6)$$

where $I_{VV}(t)$ and $I_{VH}(t)$ denote the fluorescence intensities of the sample measured with a polarization analyzer perpendicular and parallel, respectively, with respect to the electrical vector of the exciting light which is vertically polarized; G is the correction factor owing to the difference of the sensitivities of the detector to the vertically polarized and horizontally polarized lights.

3 RESULTS AND DISCUSSION

3.1 Absorption and fluorescence spectra

Figure 1 shows absorption and fluorescence spectra for 1CB and 6CB in glycerol at 20.3°C . 1CB and 6CB exhibit absorption bands having a peak at $35 \times 10^3 \text{ cm}^{-1}$, which is

Fig. 1 Absorption and Emission Spectra for 1CB and 6CB in Glycerol at 20.3°C . Solid line expresses 1CB and dashed line 6CB, respectively.

assigned to (π, π^*) transition of π -electron system of their cyanobiphenyl groups; they also emit fluorescence around $29 \times 10^3 \text{ cm}^{-1}$. The peak positions and the profiles of the absorption and fluorescence bands for 6CB are almost the same as those for 1CB. This indicates that the absorption and emission processes for the cyanobiphenyls are not influenced by the length of the alkyl chain attached to the cyanobiphenyl group.

3.2 Fluorescence decay time (Excited-state lifetime)

Figure 2 shows the convoluted fluorescence decay curve for 1CB in glycerol at 10.1°C . For comparison, the decay profile of hydrogen lamp source is also presented with a dashed and pointed line. Beyond the peak top of the fluorescence decay curve, decreasing curve is seen in the semi-log plot of intensity against time. The fluorescence lifetime can be obtained by the application of following equation to the observed decay curve:

$$\ln I(t) = \ln A_1 - \frac{1}{\tau} t \quad (7)$$

where $I(t)$ is the intensity of fluorescence at an arbitrary time t , A_1 is the initial fluorescence intensity and τ is the fluorescence lifetime for the sample. Actually, the decay profile of the lamp source influences the sample decay, and hence, the corrected lifetimes were calculated by the deconvolution method using least-squares fitting for the observed decay curves. Thus we obtained 998 ps (standard deviation, S.D. = 24.5 ps ; $\chi^2 = 1.25$) as the lifetime of 1CB at 10.1°C . Similarly, the values of τ for the 1CB and 6CB at

Fig. 2 Fluorescence Decay Curve (solid line) for 1CB in Glycerol at 10.1°C . Dashed and pointed line denotes light source. The lifetime was calculated as 998 ps (S.D. = 24.5 ps, $\chi^2 = 1.25$). The upper part of figure shows the residuals of the observed and the calculated values.

Table 1 Fluorescence Lifetimes, τ , of 1CB and 6CB in Glycerol at Various Temperatures. (S.D.: standard deviation)

1CB		6CB	
Temperature/°C	τ /ns (S.D.)	Temperature/°C	τ /ns (S. D.)
3.4	1.03 (0.026)	1.5	1.03 (0.026)
10.1	0.99 (0.025)	10.1	0.99 (0.025)
20.3	1.03 (0.022)	20.3	1.03 (0.012)
30.4	1.06 (0.012)	30.2	1.06 (0.012)
40.7	1.02 (0.012)	40.9	1.02 (0.012)
50.6	1.00 (0.016)	50.7	1.00 (0.016)
60.8	0.98 (0.013)

Fig. 3 Emission and Excitation Spectra for 1CB and 6CB in Glycerol at 11.0°C, and Their Fluorescence Anisotropies at Various Temperatures.

Solid line denotes 1CB and dotted line, 6CB.

various temperatures were determined and are listed in Table 1. It is worth noting that the fluorescence lifetimes are about 1 ns for both 1CB and 6CB and are independent of temperature.

3.3 Steady-state fluorescence anisotropy, $\bar{r}$

Figure 3 shows the fluorescence excitation and emission spectra for 1CB and 6CB in glycerol. The fluorescence spectra of *n*CB were measured by using the excitation light having 285 nm wavelength ($35.0 \times 10^3 \text{ cm}^{-1}$). As the viscosity of the glycerol decreases exponentially with increasing temperature⁹, it is possible to change the viscosity condition for *n*-cyanobiphenyls by using glycerol as a solvent for the observation of the steady-state fluorescence anisotropy, $\bar{r}$. Thus, we observed the $\bar{r}$ values for 1CB and 6CB in glycerol at various temperatures.

First of all, in order to determine the relative directions of the transition moments of absorption and fluorescence

Table 2 Steady-state Fluorescence Anisotropy, $\bar{r}$, for 1CB and 6CB in Glycerol at Various Temperatures.

Temperature/°C	$\bar{r}$ for 1CB	$\bar{r}$ for 6CB
11.0	0.318	0.315
20.3	0.313	0.309
29.7	0.299	0.296
39.1	0.301	0.294
48.4	0.242	0.267
57.8	0.224	0.242

oscillators in the lowest excited states of the cyanobiphenyl parts for 1CB and 6CB, steady-state fluorescence anisotropy, $\bar{r}$, was determined in high viscous glycerol at 11°C (its viscosity is $\sim 4 \text{ Pa s}$), where the rotational movements for the molecules of 1CB and 6CB are thought to be sufficiently low.

In the upper left in Fig. 3, $\bar{r}$ values for 1CB at various temperatures are represented by solid lines and those for 6CB by dashed lines, respectively. The $\bar{r}$ value for 1CB is 0.318 and that for 6CB is 0.315 at 11°C. These values are much higher than 0.1 and close to 0.4. In general, in the viscous medium where the molecules do not move within the fluorescence lifetime, $\bar{r}$ value takes the region of $-0.2 < \bar{r} < 0.4$. Namely, when the directions of the linear oscillators for the absorption and the emission are parallel to each other, $\bar{r}$ is 0.4; when those are perpendicular to each other, $\bar{r}$ is -0.2 ; and when the two planar oscillators for the absorption and the emission are parallel, $\bar{r}$ is $0.1^{7,8}$. This criterion leads to the conclusion that the emission oscillators of the cyanobiphenyl molecules are parallel to the oscillator of absorption. In addition, it has been clarified on the basis of molecular orbital calculations (Matsuzawa, H., unpublished data) that the lowest intense absorption band around $35.0 \times 10^3 \text{ cm}^{-1}$ observed in cyanobi-

phenyl molecules is assigned to 1A_1 state (in C_{2v} symmetry) and its transition moment is directed along the long axis of the cyanobiphenyl molecule.

If the *n*-cyanobiphenyl molecules rotate perpendicularly against the long axis of the molecules during the fluorescence lifetime, the change in $\bar{r}$ should be observed. Table 2 shows the $\bar{r}$ values in glycerol at various temperatures. Increase in temperature decreases $\bar{r}$ values for both 1CB and 6CB. Namely, the rotational movements of the molecules of 1CB and 6CB simply increase with increasing temperature upto 39°C; in the higher temperature region, 1CB having small methyl group rotates in glycerol more vigorously than 6CB having a long alkyl chain.

The steady-state fluorescence anisotropy measurements, however, can not indicate the detail for the difference between the rates of rotations of the 1CB and 6CB molecules. Thus, the rates of rotations of the 1CB and 6CB molecules will be discussed in the section of time-resolved fluorescence anisotropy. Before mentioning the time-resolved fluorescence anisotropy, we now discuss the effective molar volumes for 1CB and 6CB, which can be obtained from the $\bar{r}$ values and viscosities of glycerol at various temperatures.

3.4 Effective molar volume

By assuming that the molecules of 1CB and 6CB are rigid spheres, the following equation is applicable to the relation between the effective molar volume, v , and steady-state fluorescence anisotropy, $\bar{r}^2$:

$$\frac{1}{\bar{r}} = \frac{1}{\bar{r}_0} \left(1 + \frac{k_B T \tau}{v \eta} \right) \quad (8)$$

where $\bar{r}_0$ is steady-state fluorescence anisotropy under the condition that the viscosity, η , is infinity; k_B is the Boltzmann constant. If the $\frac{1}{\bar{r}}$ versus $\frac{T}{\eta}$ plot (the Perrin-Weber plot) gives a straight line, the v value should be obtained from the slope of the line and the fluorescence lifetime, τ .

Figure 4 shows the Perrin-Weber plot for 1CB and 6CB. Relatively good straight lines are obtained for both cyanobiphenyls. From the intercepts on $\frac{1}{\bar{r}}$ axis and slopes of the straight lines, we obtained $\bar{r}_0$ and v values for 1CB and 6CB, respectively. The values are 0.321 for 1CB and 0.315 for 6CB; the v values are $1.06 \times 10^{-28} \text{ m}^3$ for 1CB and $1.61 \times 10^{-28} \text{ m}^3$ for 6CB. Assuming rigid spheres for both 1CB and 6CB molecules, we obtained $2.94 \times 10^{-10} \text{ m}$ for the molecular radius of 1CB and $3.37 \times 10^{-10} \text{ m}$ for that of 6CB, respectively; the rotating 6CB molecule is larger than the rotating 1CB molecule.

Fig. 4 Perrin-Weber Plots for 1CB and 6CB in Glycerol. Open circles denote 1CB and closed circles, 6CB, respectively.

3.5 Time-resolved fluorescence anisotropy, $r^*(t)$

$I_{VV}(t)$, $I_{VH}(t)$, $I_{HV}(t)$ and $I_{HH}(t)$ in equation 5 were measured for 1CB and 6CB in glycerol at various temperatures. For the determination of the real fluorescence intensities of the samples, however, the convoluted waves, $I_D(t)$ and $I_T(t)$, are necessary instead of the difference in fluorescent intensities ($I_{VV}(t) - I_{VH}(t)G$) and the overall fluorescence intensity ($I_{VV}(t) + 2I_{VH}(t)G$) in equation 5. This is because the intensities of $I_{VV}(t)$ and $I_{VH}(t)$ include the effect of spreading of the light source. Thus, first of all, we assume that $I_D(t)$ and $I_T(t)$ are expressed as the following exponential functions.

$$I_D(t) = A_D \exp\left(-\frac{t}{\tau_D}\right) \quad (9)$$

$$I_T(t) = A_T \exp\left(-\frac{t}{\tau_T}\right) \quad (10)$$

$I_D(t)$ and $I_T(t)$ calculated using the convoluted $I_{VV}(t)$, $I_{VH}(t)$, $I_{HV}(t)$ and $I_{HH}(t)$ values for 1CB and 6CB in glycerol were plotted in the semi-log scale against time, t .

For example, Fig. 5 and 6 show the decay curves of $I_D(t)$ and $I_T(t)$ at 50.6°C obtained for 1CB and 6CB, respectively, which are relatively linear beyond their peak tops. Thus, the assumption that the $I_D(t)$ and $I_T(t)$ are expressed as the exponential functions of time, t , seems to be reasonable. Strictly speaking, the curves are composed of two components. However, the ratio of one component, having a short lifetime, to total curve is about 90%, while the ratio of second component, having a long lifetime, to the total curve is less than 10%. Thus the analysis was carried out only for the former component. The fluorescence anisotropy, $r^*(t)$, which suffers no effect from the spreading of the light source, is expressed as Eq. 11.

$$r^*(t) = \frac{I_D(t)}{I_T(t)} = r_0^* \exp\left(-\frac{t}{\theta^*}\right) \quad (11)$$

Fig. 5 Time Dependence of Overall Fluorescence Intensity ($I_T(t) = I_{VV}(t) + 2I_{VH}(t)$), Difference in Fluorescence Intensity between Vertically and Horizontally Polarized Emitted Light ($I_D(t) = I_{VV}(t) - I_{VH}(t)$) and Time Resolved Fluorescence Anisotropy, $r^*(t)$, for 1CB in Glycerol at 50.6°C.

where $r_0^* = \frac{A_D}{A_T}$. This equation was used for the estimation

of a rotational correlation time, θ^* . θ^* is related to a molecular volume, v , and viscosity, η , as follows:

$$\frac{1}{\theta^*} = \frac{k_B T}{v \eta} \quad (12)$$

Using the values of θ^* , $k_B T$ and η , we are able to obtain the molecular volume, v , and radius, a , assuming a rotational rigid sphere for the n CB molecules. The values of θ^* for 1CB and for 6CB are listed in Tables 3 and 4, respectively. As can be seen from these Tables, the error for θ^*

Fig. 6 Time Dependence of Overall Fluorescence Intensity ($I_T(t) = I_{VV}(t) + 2I_{VH}(t)$), Difference in Fluorescence Intensity between Vertically and Horizontally Polarized Emitted Light ($I_D(t) = I_{VV}(t) - I_{VH}(t)$) and Time Resolved Fluorescence Anisotropy, $r^*(t)$, for 6CB in Glycerol at 50.9°C.

decreases with the increase in temperature, and hence, the values of θ^* become considerably reliable at high temperature region. The temperature dependence of the θ^* values for 1CB and 6CB indicates that the rotational diffusions for these compounds increase with increasing temperature.

Tables 3 and 4 also present the values of v and a derived from θ^* . In order to make the molecular radius profiles more clear, the obtained radii are plotted against temperature as shown in Fig. 7. The each radius versus temperature profile does not simply obey the smooth viscosity change associated with the temperature rise. Namely, there exist three stages: the first stage is below 10°C; the second one, between 10–30°C for 1CB and 10–40°C for 6CB; the third one, above 30°C for 1CB and 40°C for 6CB. In the

Table 3 Rotational Correlation Time θ^* , Rotational Effective Molecular Volume, v , and Spherical Radius, a , for 1CB in Glycerol at Various Temperatures Obtained by Assuming Rigid Spherical Model.

Temperature/°C	$\eta/\text{Pa s}^a$	θ^*/ns	volume, $v/10^{-30} \text{ m}^3$	radius, $a/10^{-10} \text{ m}$
3.4	8.1237	21.4 ± 18	10.1 ± 8.3	1.34 ± 0.36
10.1	3.8554	10.8 ± 6.9	11.0 ± 9.1	1.38 ± 0.37
20.3	1.3833	16.1 ± 8.7	47.2 ± 25.5	2.24 ± 0.40
30.4	0.5791	11.5 ± 5.6	83.2 ± 41.0	2.71 ± 0.44
40.7	0.2716	4.57 ± 2.5	72.9 ± 40.1	2.59 ± 0.47
50.6	0.1436	2.54 ± 1.4	79.1 ± 42.2	2.66 ± 0.47
60.8	0.0793	1.43 ± 0.78	83.1 ± 44.8	2.71 ± 0.48

^a values interpolated from the reference data⁹⁾

Table 4 Rotational Correlation Time θ^* , Rotational Effective Molecular Volume, v , and Spherical Radius, a , for 6CB in Glycerol at Various Temperatures Obtained by Assuming Rigid Spherical Model.

Temperature/°C	$\eta/\text{Pa s}^a$	θ^*/ns	volume, $v/10^{-30} \text{ m}^3$	radius, $a/10^{-10} \text{ m}$
1.7	9.8891	58.3 ± 36	22.4 ± 14.1	1.75 ± 0.36
9.9	3.9392	25.8 ± 17	25.6 ± 17.1	1.83 ± 0.40
30.7	0.5655	9.27 ± 5.2	68.8 ± 38.5	2.54 ± 0.47
39.9	0.2869	14.1 ± 4.7	212.4 ± 70.8	3.70 ± 0.41
49.9	0.1499	5.37 ± 2.0	159.8 ± 60.3	3.37 ± 0.42
60.2	0.0820	3.67 ± 1.3	205.9 ± 72.7	3.66 ± 0.43

^a values interpolated from the reference data⁹⁾ **Fig. 7** Rotational Spherical Radius, a , for 1CB and 6CB in Glycerol at Various Temperatures.

Open circles denote 1CB and closed circles, 6CB, respectively.

low temperature region (the first stage), the rigid sphere radii are almost constant and average at $1.3 \times 10^{-10} \text{ m}$ for 1CB and $1.8 \times 10^{-10} \text{ m}$ for 6CB, whereas in high temperature region (the third stage: 1CB, 30–60°C; 6CB, 40–60°C), larger constant radii are obtained; i.e., $2.7 \times 10^{-10} \text{ m}$ for 1CB and $3.6 \times 10^{-10} \text{ m}$ for 6CB. It is noted that the values obtained in the high temperature region are in good agreement with those obtained by using steady-state exciting light, $2.9 \times 10^{-10} \text{ m}$ (1CB) and $3.4 \times 10^{-10} \text{ m}$ (6CB), respectively. This indicates that the rigid-sphere model is sufficiently applicable to the rotating n CB molecules regardless of the length of alkyl-chain attached to cyanobiphenyl part in the high-temperature region.

The increase in radius of rotational diffusion in the intermediate temperature region (the second stage) suggests that the rotational movement changes in this temperature region. In the case of cyanobiphenyl molecules, the rotation about the axes other than the long axis of cyanobiphenyl part play a dominant role for the decay of fluorescence anisotropy, $\bar{r}$. It is noted that the tempera-

ture of intermediate region is close to the phase-transition temperature (the phase-transition temperature between the nematic liquid-crystal and isotropic liquid for 6CB is ca. 29°C)², however, it is not likely that the rotational movements of n CB are specifically changed across the intermediate temperature region. Therefore, the relatively steep increase in their radii should be attributable to the enhancement of rotational fluctuations of n CB molecules, which lead to spherical-rigid rotation. Remarkable increase of a radius observed in 6CB rather than 1CB implies that the movements of hexyl-chain are much more enhanced in high temperature, and effectively reflected to the increase in radius of more randomized rotational diffusion.

4 CONCLUSION

The cyanobiphenyl part in 4- n -alkyl-4'-cyanobiphenyl molecule shows intense absorption due to the (π , π^*) transition in the ultraviolet region and emits a very strong fluorescence in the visible region. Absorption and fluorescence spectra, fluorescence lifetimes, and steady-state and time-resolved fluorescence anisotropies were measured for 4-methyl-4'-cyanobiphenyl (1CB) and 4-hexyl-4'-cyanobiphenyl (6CB) in glycerol at various temperatures. The wavenumbers and intensities of the absorption and emission bands for 1CB and 6CB were almost equal to each other. The fluorescence lifetimes for 1CB and 6CB were about 1.0 ns and did not depend on temperature. Thus, the cyanobiphenyl part in n CB molecule has own property which is not affected by the chain length of the alkyl group. Time-resolved fluorescence anisotropies indicated that the molecules of 1CB rotate more rapidly than those of 6CB in glycerol. The rigid-sphere radii for 1CB and 6CB obtained by using the pulsed exciting light were evaluated as $1.3 \times 10^{-10} \text{ m}$ (1CB) and $1.8 \times 10^{-10} \text{ m}$ (6CB) in the low temperature region (2–10°C), whereas $2.7 \times 10^{-10} \text{ m}$ (1CB) and $3.6 \times$

10^{-10} m (6CB) were obtained in the high-temperature region (1CB, 30-60°C ; 6CB, 40-60°C), which were in good agreement with those obtained from the Perrin-Weber plots, 2.9×10^{-10} m for 1CB and 3.4×10^{-10} m for 6CB, respectively. From these results, it is concluded that the rigid-sphere model is acceptable for the rotating 4-methyl-4'-cyanobiphenyl and even for 4-hexyl-4'-cyanobiphenyl. An increase in a rotational radius across the intermediate temperature region was notably observed in 6CB rather than 1CB. The movements of hexyl-chain effectively affect the enhancement of rotational fluctuations and yields increase in radius of rotational diffusion. The relatively large increase in radii attributable to the enhancement of vigorous movements of peripheral alkyl-chain in liquid-crystal molecules is important for the phase transition from liquid crystal to isotropic liquid of 4-alkyl-4'-cyanobiphenyls, hence, the changing to less vigorous movements of the peripheral alkyl-chain is thought enough to contribute to the liquid-crystal formation of 6CB molecules.

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