

Anti-Parallel Dimer Formation of 4-Cyano-4'-Alkyl Biphenyls in Isotropic Benzene Solution - Seeds of Liquid Crystalline Phases -

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The formation of anti-parallel (dipole) dimers of liquid crystalline phase forming 4-cyano-4'-alkyl biphenyls ($n = 5$ (pentyl) and $n = 8$ (octyl)) was examined in isotropic benzene solution. High frequency dielectric relaxation (DR) measurements up to 50 GHz were performed to probe molecular dynamic processes of n CB molecules and to evaluate a Kirkwood factor (g_K), a measure of orientational correlation between dipole moments of cyano ($-C\equiv N$) groups sensitive to the formation of the anti-parallel dimers, $(nCB)_2$, which shows $g_K < 1$. DR spectra for solutions at intermediate to high concentrations were decomposed into two relaxation modes. A fast dielectric mode with the relaxation time of ca. 100~120 ps was assigned to free rotation of monomeric n CB molecules, while the other slow relaxation mode with the relaxation time of ca. 400 ps tentatively to the dissociation process of $(nCB)_2$ dimers due to their lifetime. Infrared (IR) absorption spectra for the isotropic solution were also measured in a wavenumber range from 2200 to 2250 cm^{-1} corresponding to $C\equiv N$ stretching vibration mode to evaluate molar fractions of n CB molecules forming the $(nCB)_2$ dimers, since the stretching band slightly altered the peak wavenumber due to the formation of anti-parallel $(nCB)_2$ dimers. The results of both the DR and IR measurements revealed that the formation of $(nCB)_2$ dimers even in isotropic solution and the equilibrium constant of a chemical reaction, $2nCB \leftrightarrow (nCB)_2$, in benzene solution remarkably increased with increasing concentrations of n CB. Because most of n CB molecules form the anti-parallel dimers at moderate to high concentrations, the formation of the $(nCB)_2$ dimers is necessary for n CB to undergo a phase transition from isotropic to a nematic liquid crystalline phase in benzene solutions at higher concentrations and also in the bulk state.

Key Words: 4-cyano-4'-alkylbiphenyl / Anti-parallel dimer / Liquid crystal / Dielectric relaxation / Rotational diffusion

1. INTRODUCTION

We do not have to explain the importance of liquid crystalline (LC) materials in our daily life. Especially, without the application of liquid crystalline materials to display technologies in many practical tools such as television sets, personal computers, mobile phones, and so on, ubiquitous information technologies sustaining our convenient network societies are not considered.¹⁻⁵⁾ 4-cyano-4'-alkyl biphenyls (n CBs), such as 4-cyano-4'-pentyl biphenyl (5CB) and 4-cyano-4'-octyl biphenyl (8CB), have been well known as LC substances widely used in LC displays.^{6,7)} Pure 5CB is thermo-tropic LC substance, and demonstrates isotropic to nematic LC phase transition at $T_{I-N} = 35$ °C and nematic

LC phase to solid phase transition (melting point) at $T_M = 22.5$ °C.⁷⁾ On the other hand, pure 8CB possesses $T_{I-N} = 40$ °C, nematic LC to smectic LC phase transition at $T_{N-S} = 32.5$ °C and $T_M = 22$ °C.⁷⁾ In the case of a smectic LC phase formed by 8CB in a temperature range between T_{N-S} and T_M , it has been revealed via several scattering experiments⁸⁻¹⁰⁾ and scanning tunneling microscopic (STM) observation on a graphite surface¹¹⁾ that 8CB molecules form anti-parallel dimers and the formed dimers arranged in a direction (uni-axial director) and also form periodically well-defined layers that can slide over one another. The reason for the anti-parallel dimer formation should be the strong dipole-dipole interaction between cyano groups. Moreover, Smith et al.¹²⁾ reported that a solid phase structure of some longer n CBs ($n \geq 8$) deposited on flat graphite surfaces showed two-dimensional molecular arrangements constructed by the anti-parallel dimers. Consequently, an anti-parallel dimer, $(8CB)_2$, is an intrinsic

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unit element to form the smectic LC phase in 8CB. Since nematic LC phase has simpler characteristic structure than the smectic LC phase and possesses only a uni-axial director without periodic layers observed in the smectic LC phase, it is possible that the anti-parallel dimer is not an intrinsic unit element to form the nematic LC phase for *n*CB. Nevertheless, Leadbetter et al.¹⁰⁾ proposed the presence of local bilayer structure formed by anti-parallel dimers even in the nematic LC phase of 5CB using X-ray diffraction experiments.

More than a decade ago, the formation of excimers in pure 5CB, 6CB and 8CB was investigated over a temperature range from isotropic to crystalline state using steady state fluorescence spectroscopic methods and also time resolved fluorescence lifetime measurements.¹³⁻¹⁵⁾ Although monomer fluorescence was much stronger than excimer one in a temperature range lower than T_M , excimer fluorescence much stronger than monomer one was clearly observed irrespective of transition temperatures such as T_{I-N} and T_{N-S} in a range higher than T_M .¹³⁾ Because the speculated structure of excimers formed by *n*CB molecules possesses similar characteristics to that of anti-parallel dimers, it is expected that the substantial observation of excimer fluorescence reveals the presence of anti-parallel (*n*CB)₂ dimers not only in the smectic LC phase, but also in the nematic LC and isotropic phase. These considerations lead to an idea that anti-parallel (*n*CB)₂ dimers are necessary elements like seeds of the formation of nematic LC phases, and the anti-parallel dimers exist even in the isotropic phases of *n*CBs.

Molecular dynamics (MD) simulation study is one of useful, reliable methods to investigate intermolecular conformation formed in a tested system. Recently, Fukunaga et al.¹⁶⁾ carried out MD simulation study employing a coarse-grained model to clarify the static structure and some dynamic properties of 5CB in a nematic LC phase, and concluded that head-to-head, i.e. anti-parallel, intermolecular associations are formed locally.

Dielectric relaxation (DR) measurements are useful methods to examine the magnitude of dipole moments and their orientational dynamics in samples.¹⁷⁻¹⁹⁾ Because *n*CBs bear cyano ($-C\equiv N$) groups that have a relatively large intrinsic dipole moment of $4.1 \sim 4.3$ D²⁰⁾ at terminal points of molecules fixed parallel to the biphenyl group, a Kirkwood factor (g_K) defined as a ratio of the square of apparent dipole moment to that of the intrinsic dipole moment ($g_K = \mu_{app}^2 / \mu_0^2$) demonstrates the magnitude of orientational correlation between dipole moments in samples.²¹⁾ Then, the value of g_K is a useful, sensitive measure to discuss the presence of anti-parallel (*n*CB)₂ dimers; i) when $g_K > 1$, dipole moments in the

sample have a trend to align parallel, ii) when $g_K = 1$, dipole moments have no correlation in their orientation, iii) when $g_K < 1$, dipole moments have a trend to align anti-parallel. Furthermore, since the origin of dipole moments in *n*CB results from the presence of $-C\equiv N$ groups fixed parallel to biphenyl groups, DR modes observed in the *n*CB solutions should be assigned to the molecular motions related to changes of molecular orientation.

More than a decade ago, Shabatina²²⁾ found that infrared (IR) absorption spectra in a wavenumber ($\bar{\nu}$) range from 2200 to 2250 cm⁻¹ corresponding to a $C\equiv N$ stretching vibration mode slightly, but clearly alter the peak absorption wavenumber due to the formation of anti-parallel dimers. Then, IR measurements in the $\bar{\nu}$ range is a useful method to evaluate molar fractions of *n*CB molecules forming the anti-parallel (*n*CB)₂ dimers, if the obtained IR spectra are decomposed into two IR absorption modes related to $C\equiv N$ stretching vibration modes of monomeric *n*CB and anti-parallel dimeric (*n*CB)₂.

In this study, both the DR relaxation over frequency range up to 50 GHz and IR absorption measurements in the $\bar{\nu}$ range from 2200 to 2250 cm⁻¹ were employed to investigate the formation of the anti-parallel dimer of liquid crystalline forming 5CB and 8CB and not forming 4-cyano-4'-methylbiphenyl (1CB) in isotropic benzene solution. Based on the obtained DR and IR data, molecular dynamics of *n*CB molecules and the chemical equilibrium between monomeric *n*CB molecules and anti-parallel (*n*CB)₂ dimers in isotropic benzene solution was discussed in detail as functions of concentrations of *n*CB molecules. Consequently, we led to a conclusion that most of 5CB and 8CB molecules form anti-parallel dimers, (*n*CB)₂, even in isotropic benzene solution in a moderate to concentrated regime. Then, anti-parallel dimer formation is necessary for *n*CB molecules to undergo a phase transition from the isotropic to nematic LC phase.

2. EXPERIMENTAL

2.1 Materials

1CB (> 97 %), 5CB (> 97 %), and 8CB (> 97 %) were purchased from Wako Pure Chemical Industries Ltd. (Osaka) and were used without any further purification procedures. Highly dehydrated benzene (Bz) (> 99.5 %) was purchased from the same company and was used without purification. The concentration (*c*) of 1CB was ranged from 0.11 to 1.4 M because of its limited solubility in Bz. 5CB and 8CB were dissolved into Bz at several concentrations, *c*, ranged from 0.24 to 1.7 M (6.8 to 47 wt%) and 0.24 to 1.6 (8.9 to 51 wt%), respectively.

2.2 Methods

Dielectric relaxation, DR, measurements were performed at 25 °C in a frequency (ν) range from 1 kHz to 50 GHz using three distinct systems. In a lowest frequency range from 1 kHz to 2 MHz, a precise LCR meter (E4980A, Agilent Technologies, Santa Clara) equipped with a homemade electrode cell with a vacant electric capacitance of $C_0 = 4.8$ pF was used. In a medium frequency range from 1 MHz to 3 GHz, an RF LCR meter (4287A, Agilent Technologies, Santa Clara) equipped with a homemade electrode cell possessing a vacant electric capacitance of $C_0 = 0.23$ pF was used. In these two systems, the obtained electric capacitance (C) and conductance (G) were converted to real and imaginary parts of electric permittivity (ϵ' and ϵ'') as function of an angular frequency ($\omega = 2\pi\nu$) in the manner $\epsilon' = CC_0^{-1}$ and $\epsilon'' = (G - G_{DC})(C_0\omega)^{-1}$; G_{DC} means a direct current conductance due to the presence of ionic impurities in samples. Moreover, in the highest frequency range from 50 MHz to 50 GHz, a dielectric probe kit 8507E equipped with a network analyzer N5230C, ECal module N4693A, and performance probe 05 (Agilent Technologies, Santa Clara) was used for dielectric relaxation measurements. Three-point calibration using hexane, 3-pentanone, and water as standard materials was carefully performed prior measurements of sample solutions. In this highest frequency range, ϵ' and ϵ'' were automatically calculated by a program included in the dielectric probe system. Calibration procedure was described in detail elsewhere.^{18,19)} Temperature of the sample solutions was kept at 25 °C using a thermostating equipment for each system controlled by a Peltier device.

The IR spectra of n CB/Bz solutions were recorded with a Bio-Rad Excalibur FTS 3000 (Fourier Transform IR

spectrometer: Bio-Rad, Varian, Agilent, Santa Clara) equipped with a sandwich-type liquid cell constructed with two calcium fluoride (CaF_2) crystalline window plates with a diameter of 20 mm and a thickness of 2 mm separated by two types of spacer sheets with a thickness of ca. 0.01 or 0.02 mm. The thickness of the liquid samples was adequately modified via the appropriate choice of a spacer plate for each sample to produce high-quality absorption spectra for quantitative analysis. All of the IR measurements were performed at room temperature, ca. 25 °C.

3. RESULTS AND DISCUSSION

3.1 Dielectric Behavior in a Dilute Regime

As a typical experimental result in a dilute regime, dielectric spectra (ϵ' and ϵ'' vs ω) for Bz solution of 1CB and 5CB at $c = 0.24$ M (5.2 wt% and 6.8 wt% for 1CB and 5CB, respectively) are shown Figs. 1 (a) and (b). Dielectric spectra for both solutions were well described with Debye-type relaxation functions²³⁾ with a single set of relaxation time (τ_1) and strength (ϵ_1) as given by

$$\epsilon' = \frac{\epsilon_1}{1 + \tau_1^2 \omega^2} + \epsilon_\infty, \quad \epsilon'' = \frac{\epsilon_1 \tau_1 \omega}{1 + \tau_1^2 \omega^2} \quad (1)$$

where ϵ_∞ means the high frequency limiting electric permittivity.

Because 1CB does not possess a flexible alkyl chain, but a small, symmetric methyl group connected to a biphenyl group, one does not have to take account of the presence of a dipole moment perpendicular to the longer molecular axis and dielectric mode due to the rotational process around the longer axis in a dilute condition. A rotational process around

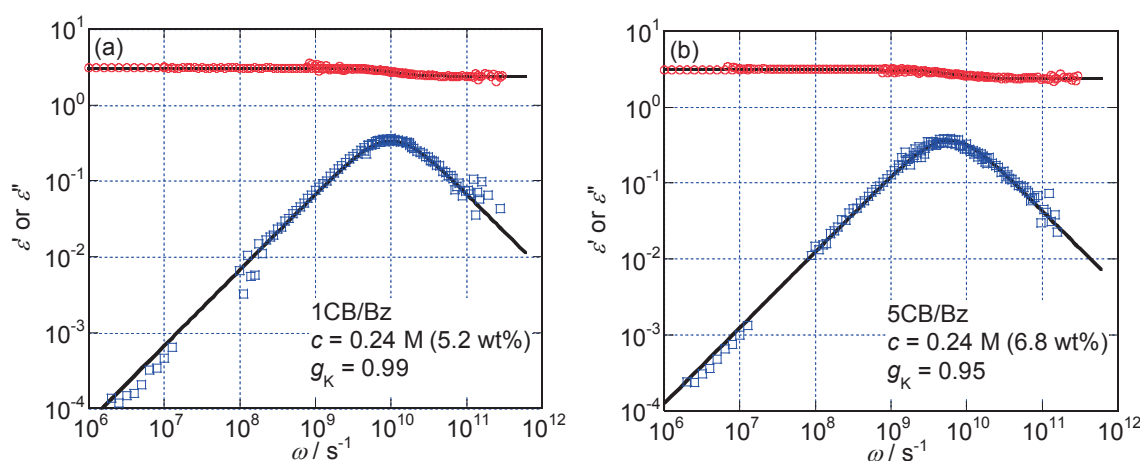


Fig. 1. Dielectric spectra (ϵ' and ϵ'' vs ω) for Bz solutions of 1CB (a) and 5CB (b) at $c = 0.24$ M.

a short axis is the only reason for the dielectric relaxation mode in 1CB as seen in Fig. 1 (a). Then, a single Debye-type relaxation mode observed in Fig. 1(b) suggests that 5CB has only one DR mode due to the rotational mode as well as 1CB. On the other hand, Kundu et al.²⁴⁾ reported dielectric spectra of Bz solutions of 5CB in both isotropic and LC regimes over a wide ω range and they decomposed the spectra into two Debye-type relaxation modes with two sets of relaxation parameters, τ_j and ε_j ($j = 1$ and 2) up to 2.6 M (70 wt%). They claimed that 5CB molecules have two kinds of DR processes related rotational motions around a longer and shorter molecular axes.²⁴⁾ According to their interpretation, 5CB molecules possesses a small permanent dipole moment perpendicular to the longer molecular axis because of presence of flexible pentyl group, and rotational motion around the longer molecular axis is dielectrically active. However, a single dielectric process observed in this study in dilute Bz solution of 5CB as seen in Fig. 1 (b) revealed that the dielectric process of 5CB in dilute solution was simply a single mode. Consequently, one does not have to consider the presence of a dipole moment perpendicular to the longer axis in *n*CB. In the case of a dilute Bz solution of 8CB at $c = 0.25$ M, dielectric spectra were not described with a single set of relaxation parameters, but with two sets of relaxation parameters. This difference found in the 8CB solution will be discussed in detail in a later section.

A Kirkwood factor (g_K) is defined as a ratio of the square of an apparent dipole moment (μ_{app}^2) to that of the intrinsic dipole moment (μ_0^2) of a tested substance; $g_K = \mu_{app}^2 \mu_0^{-2}$, and is a quantitative measure of orientational correlation between two dipoles (or molecular axes). When the determined g_K value is greater than unity, molecular dipoles possesses a trend to make parallel correlation between them. Moreover, when the g_K value is equal to unity, dipoles possess no orientational

correlation between them. Furthermore, when the g_K value is smaller than unity, dipoles possess a trend to make anti-parallel correlation between them. According to Kirkwood and Fröhlich, the square of apparent dipoles, μ_{app}^2 , is given by

$$\mu_{app}^2 = \frac{9(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)\varepsilon_v k_B T}{\varepsilon_0(\varepsilon_\infty + 2)^2 c N_A} \quad (2)$$

where ε_0 , ε_∞ , $k_B T$, and N_A represents the electric permittivity at $\omega = 0$ ($\varepsilon_0 = \varepsilon_1 + \varepsilon_\infty$ in the case of Figs. 1 (a) and (b)), the electric permittivity of a vacuum, the product of a Boltzmann constant and the absolute temperature, and Avogadro's number, respectively. The value of the intrinsic dipole moment has been reported to be $|\mu_0| = 4.1 \sim 4.3$ D²⁰⁾ for cyano group, $-\text{C}\equiv\text{N}$, connected to alkyl and phenyl groups. On the other hand, the intrinsic dipole moment of 5CB has been reported to be $|\mu_0| = 4.75$ D.²⁵⁾ It seems that the presence of a biphenyl groups enhances dislocation of electrons in a polar cyano group, $-\text{C}\equiv\text{N}$, of *n*CB. The evaluated g_K values noted in Figs. 1 (a) and (b) assuming $|\mu_0| = 4.7$ D were close to unity and led to weak orientational correlation between dipoles, in other words, molecular axes of both 1CB and 5CB in the dilute condition. Consequently, irrespective of the species of alkyl chains, *n*CB molecules demonstrated a dielectric process related to the rotational mode around the shorter molecular axes governed by free rotations proving the values of $g_K = 1$ in the dilute condition.

3.2 Dielectric Behavior in a Concentrated Regime

Figs. 2 (a) and (b) show dielectric spectra for Bz solutions of 5CB and 8CB at $c = 1.32$ (36.6 wt%) and 1.25 M (40.3 wt%), respectively as typical results in a concentrated regime. The dielectric spectra were no longer described with single Debye-type relaxations, whereas two sets, $j = 1$ and

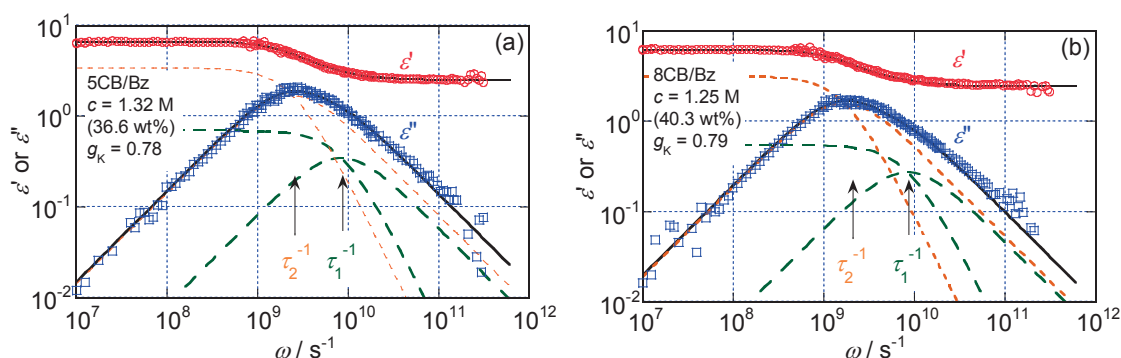


Fig. 2. Dielectric spectra for Bz solutions of 5CB (a) and 8CB (b) at $c = 1.3$ and 1.25 M, respectively. Solid lines mean the summation of constituent Debye-type functions, broken and dotted lines for the mode $j = 1$ and 2, respectively.

2, of relaxation parameters were necessary to reproduce the obtained dielectric spectra completely. Solid lines represent the summation of constituent Debye-type functions: broken and dotted lines in the figures for the mode $j = 1$ and 2, respectively. Contrary, Bz solutions of 1CB showed single Debye-type DR behavior over the concentration examined.

The dependencies of ε_j and τ_j ($j = 1$ and 2) on c for all the Bz solutions of n CB are shown in Figs. 3 (a) and (b). Since the presence of a fast relaxation mode $j = 1$ was recognized irrespective of the c values for all the n CB species, the mode was easily assigned to the rotational relaxation mode of monomeric n CB molecules. In the case of 1CB solution, DR strength of the mode $j = 1$, ε_1 , demonstrated increasing almost proportional to c as seen in Fig. 3 (a). However, the fact the ε_1 value deviated from increasing in proportion to c in a moderate to high c range for 5CB and 8CB solution clearly manifested that the amounts of n CB molecules behaving as free monomeric molecules do not simply increase in proportion to c and decreased in a high c range. The slow mode $j = 2$ observed obviously in a high c region irrespective of n CB species resulted from intermolecular interaction since the relaxation strength, ε_2 , abruptly increased with increasing c .

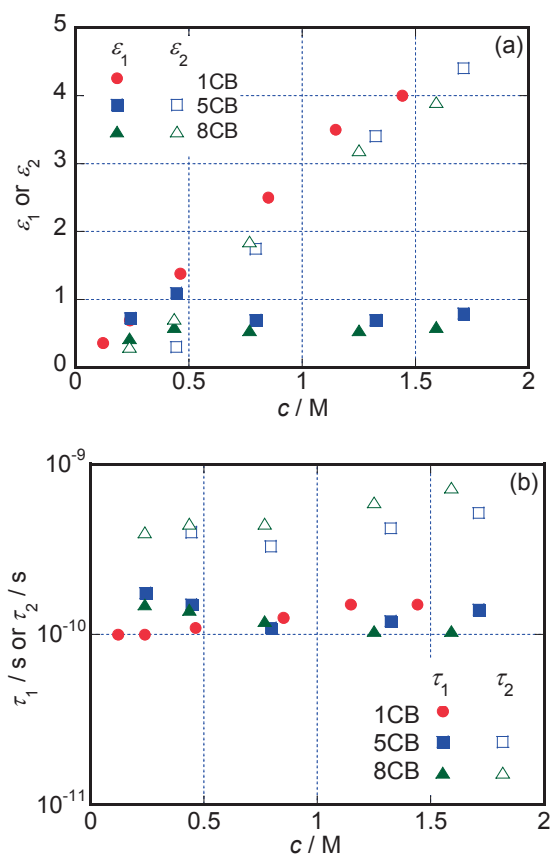


Fig. 3. Dependencies of relaxation strength, ε_1 and ε_2 (a), and times, τ_1 and τ_2 (b), on c for Bz solutions of 1CB, 5CB and 8CB.

Thus, either of the fast and slow modes observed in 5CB and 8CB should not be assigned to the rotational process around the longer molecular axis.

Two dielectric relaxation modes were previously observed in Bz solution of 5CB and attributed to rotational relaxation processes around longer and shorter molecular axes.²⁴⁾ The two relaxation modes correspond to the modes $j = 1$ and 2 in this study. The reported ε_1 and τ_1 values ($\Delta\varepsilon_2$ and τ_2 in the reference²⁴⁾) are smaller and shorter than the values seen in Figs. 3 (a) and (b) over entire c range. Additionally, the magnitude of ε_2 ($\Delta\varepsilon_1$ in the reference²⁴⁾) at $c = 0.36$ M (10 wt%) is much larger than the values in Figs. 3 (a) and (b). Then, the authors claimed that the value of g_K is obviously less than unity (meaning anti-parallel orientational interaction) at moderate and concentrated regimes as well as seen in Fig. 4, whereas the g_K value is of ca. 1.1 at $c = 10$ wt%. Although they used $|\mu_0| = 4.85$ D²⁴⁾, which is larger $|\mu_0|$ value than that used in this study, the large ε_2 led to such the illogically big g_K of 1.1 in a dilute regime. Consequently, it seems that their experimental results contain some problems especially in the low c regime.

The values of g_K calculated via eq 2 for Bz solutions of 5CB and 8CB at $c = 1.3$ and 1.25 M were noted in Figs. 2 (a) and (b), respectively. The g_K values ca. 0.78 revealed that both 5CB and 8CB molecules possessed a tendency to form an intermolecular conformation fixed anti-parallel in the concentrated regime where solutions were not in LC state, but still in isotropic one. The concentration, c , dependence of the g_K values for Bz solutions of 1CB, 5CB, and 8CB are shown in Fig. 4. A trend that the g_K value decreased from unity at $c = 0$ down to 0.6 ~ 0.65 at $c = 2$ M with increasing c was observed for both 5CB and 8CB. Urban et al.²⁵⁾ also reported the g_K value smaller than unity for pure 5CB in

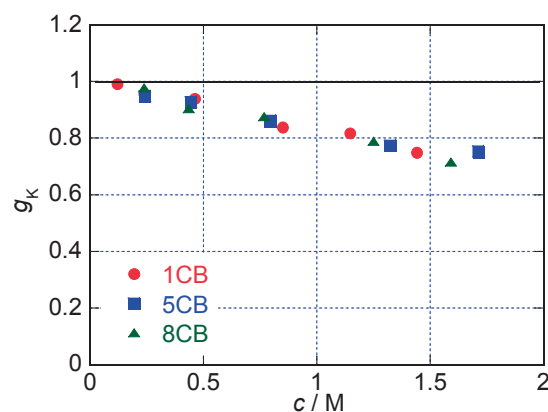


Fig. 4. Concentration, c , dependence of a Kirkwood factor, g_K , for Bz solutions of 1CB, 5CB, and 8CB.

isotropic state above T_{IN} , and they discussed the presence of anti-parallel $(5CB)_2$ dimers. Kundu et al.²⁴⁾ also pointed out the contribution of anti-parallel $(5CB)_2$ dimers to DR behavior. Interestingly, Bz solutions of 1CB showing simple single Debye-type DR behavior also demonstrated remarkable depression in the g_K value as observed in Fig. 4. This means that 1CB also possesses a tendency to make anti-parallel orientational correlation as well as 5CB and 8CB molecules. Similar dielectric behavior to Bz solutions of nCB molecules resulted to g_K smaller than unity has been observed in tetrachloromethane (CCl_4) solutions of dimethylsulfoxide (DMSO), which has large dipole moment of ca. 4.0 D as a small molecule and a strong tendency to form anti-parallel dimers.²⁶⁾

Here, we propose a simple model to describe the c dependence of g_K values based on a simple chemical reaction between monomeric nCB and anti-parallel dimeric $(nCB)_2$ governed by an equilibrium constant (K_d) as schematically depicted in Fig. 5.²⁶⁾ The equilibrium constant, K_d , given by forward (R_f) and backward (R_b) reaction rates is calculated as below using the concentration of monomeric nCB ($[nCB]$) and that of anti-parallel dimeric $(nCB)_2$ ($[(nCB)_2] = (c - [nCB])/2$)

$$K_d = \frac{R_f}{R_b} = \frac{[(nCB)_2]}{[nCB]^2} = \frac{c - [nCB]}{2[nCB]^2} \quad (3)$$

We simply assumed that the fast dielectric relaxation mode $j = 1$ was assigned to the rotational motion of monomeric nCB molecules, because the motion is the fastest dielectrically active mode. The values of τ_1 seem to range from 100 to 150 ps irrespective of the concentrations and species of nCB as seen in Fig. 3(b). On the other hand, the slow mode $j = 2$ was assigned to the dissociation process of anti-parallel dimers, $(nCB)_2$, governed by the lifetime of the dimer (τ_{life}). Because anti-parallel dimers possess no (total) dipole moments, rotations of the anti-parallel dimers are inert dielectrically

(cf. Fig. 5). After the dissociation process governed by τ_{life} , generated two monomeric nCB molecules are capable of quick rotation and would show a dielectric relaxation mode with a characteristic time of $\tau_2 (\sim \tau_{life} = R_b^{-1})$. According to this assumption, the lifetime, τ_2 , of anti-parallel dimers, $(8CB)_2$, looks not so different from that of $(5CB)_2$. As we described in the previous section, 1CB solution did show single Debye-type relaxation. This does not simply mean that 1CB does not form anti-parallel dimers in isotropic Bz solution. If 1CB forms the anti-parallel dimers and the τ_2 value is not sufficiently long, but close to τ_1 , its DR behavior should be observed as a single Debye-type relaxation mode.

In the case of neat 5CB in nematic LC state at 25 °C, a dielectric relaxation time of the longer relaxation mode, $\tau_2 \sim 20$ ns,²⁴⁾ well agrees with the fluorescence lifetime of excimers (τ_{ex}^{flu}).^{13,14)} The lifetime of excimers (anti-parallel dimers), τ_{life} , is reported to be close to τ_{ex}^{flu} .¹³⁾ Then, the fact of $\tau_2 \sim \tau_{ex}^{flu}$ in the nematic LC state of 5CB is one of substantial evidences for the assignment that the dielectric relaxation mode with a longer relaxation time, τ_2 , is the same as the dissociation process of the formed anti-parallel dimer.

Then, the relationship $\varepsilon_1 = \alpha_{MON}[nCB]$ was obtained, where α_{MON} means a proportional constant given by

$$\alpha_{MON} = \frac{(\varepsilon_\infty + 2)^2 N_A \mu_0^2 c - 27 \varepsilon_\infty \varepsilon_v k_B T + \sqrt{\left\{ (\varepsilon_\infty + 2)^2 N_A \mu_0^2 c - 27 \varepsilon_\infty \varepsilon_v k_B T \right\}^2 + 72 (\varepsilon_\infty + 2)^2 N_A \mu_0^2 \varepsilon_\infty \varepsilon_v k_B T c}}{36 \varepsilon_v k_B T c} \quad (4)$$

assuming $\mu_{app}^2 = \mu_0^2$, $g_K = 1$ for the monomeric nCB and $[nCB] = c$, i.e. $[(nCB)_2] = 0$, in eq 2. By use of eq 4 for α_{MON} , eq 3 is recast into

$$K_d = \frac{\alpha_{MON}^2 (c - \varepsilon_1 / \alpha_{MON})}{2 \varepsilon_1^2} \quad (3')$$

Using eq 3', the value of K_d was evaluable at each tested concentration, c . The obtained K_d values are plotted as functions of the concentration, c , for 5CB and 8CB in Fig. 6. A trend that K_d values increased with increasing c was apparent irrespective of the nCB species. This observation clearly suggests the tendency of anti-parallel dimer formation is remarkably enhanced by increasing c even in isotropic Bz solution especially in a low c range from the view point of DR data. Large amounts of nCB molecules form anti-parallel $(nCB)_2$ dimers at a high c range as shown in a molar fraction of anti-parallel $(nCB)_2$ dimer forming nCB ($f_D = 1 - [nCB]/c$) in Fig. 6, i.e., almost 5CB and 8CB molecules of 0.9 in the

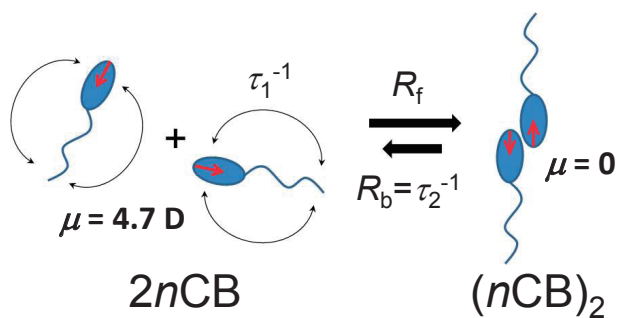


Fig. 5. Schematic depiction of chemical reaction between monomeric nCB and anti-parallel dimeric $(nCB)_2$.

molar fraction form anti-parallel $(n\text{CB})_2$ dimers at $c \geq 1.5$ M. The dependencies of K_d values on c seen in Fig. 6 strongly reveal that longer alkyl tails more effectively enhance the formation of anti-parallel dimers, $(n\text{CB})_2$. This is the reason for the fact that a Bz solution of 8CB did not show a single Debye-type DR process even in the dilute condition of $c = 0.24$ M.

A proportional constant, α_{DIM} , combining ε_2 and $[(n\text{CB})_2]$ was also defined and the α_{DIM} values were evaluable via an equation $\alpha_{\text{DIM}} = 2\varepsilon_2(c - [n\text{CB}])^{-1}$. The fact that the relationship $\alpha_{\text{MON}} > \alpha_{\text{DIM}}/2$ is responsible for the relationship $g_K < 1$ in Bz solutions of $n\text{CB}$ molecules. The K_d value is directly related to the Gibbs energy change resulted from the anti-parallel dimer formation. The reason for the c dependence of K_d in a dilute condition is possibly that the entropy change due to the anti-parallel dimer formation depends on the value of c .

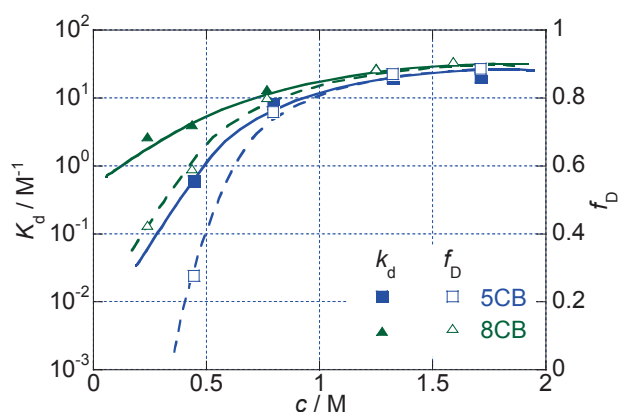


Fig. 6. Dependencies of K_d and $f_D (=1-[n\text{CB}]c^{-1})$ values (see text) on the concentration, c , for Bz solutions of 1CB, 5CB, and 8CB. Lines in this figure are guide for eyes.

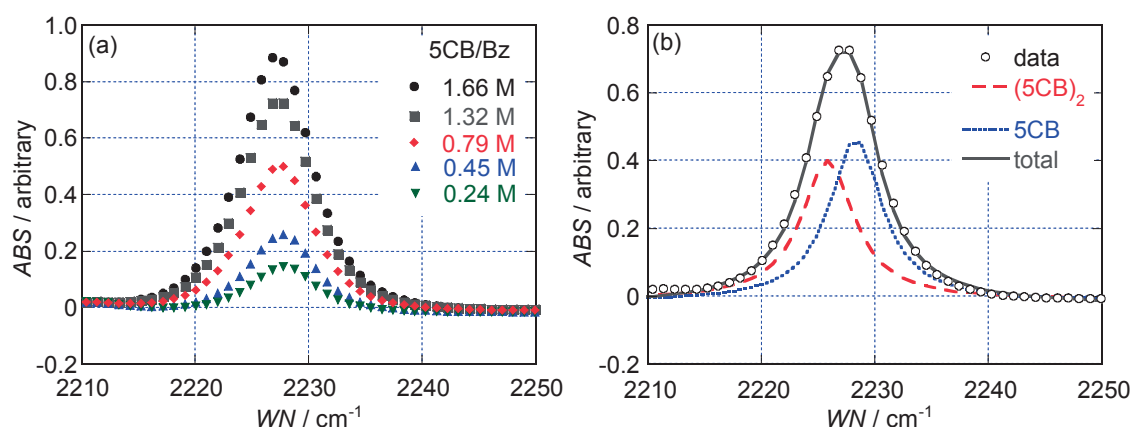


Fig. 7. (a): IR absorption spectra of Bz solutions of 5CB at several concentrations from 0.24 to 1.66 M in a wavenumber, WN , range from 2210 to 2250 cm^{-1} corresponding to the $\text{C}\equiv\text{N}$ stretching mode, (b): Decomposition of an IR spectrum of a solution of 5CB in Bz at 1.32 M into two Lorentz functions corresponding to monomeric 5CB and dimeric $(5\text{CB})_2$. Constituent dashed and broken lines possessing peak WN at 2229 and 2226 cm^{-1} represent the $\text{C}\equiv\text{N}$ stretching mode of monomeric 5CB and dimeric $(5\text{CB})_2$, respectively.

More than two decades ago, Kędziora and Jadżyn²⁷⁾ estimated the equilibrium constant, K_d , and reported to be $\sim 0.7 \text{ M}^{-1}$ for 5CB in benzene solution at 30 °C from the static electric permittivity, ε_0 , assuming the value is independent of the concentration, c . This K_d is smaller than the value evaluated in this study, $K_d \sim 30 \text{ M}^{-1}$. The reason for this discrepancy should be that the magnitude of relaxation strength for each dielectric mode corresponding to monomer and anti-parallel dimeric association was not evaluated directly from dielectric spectra, but ε_0 and the assumption of a constant K_d value independent of c .

3.3 IR Absorption Behavior

More than a decade ago, Shabatina²²⁾ demonstrated that a $\text{C}\equiv\text{N}$ vibrational stretching band observable around 2230 cm^{-1} slightly alters its peak wavenumber downwardly with increasing the molar fraction of (anti-parallel) dimer, $(n\text{CB})_2$. As seen in Fig. 7 (a), IR absorption spectra of Bz solutions of 5CB in a wavenumber, WN , range from 2210 to 2250 cm^{-1} obtained in this study slightly altered peak WN downwardly with increasing the concentration, c . According to Shabatina²²⁾, IR spectra for $\text{C}\equiv\text{N}$ stretching band were decomposed into two Lorentz functions corresponding to the $\text{C}\equiv\text{N}$ stretching mode of monomeric 5CB and dimeric $(5\text{CB})_2$ as seen in Fig. 7 (b) for data at $c = 1.32$ M as an example. Constituent broken and dotted lines possessing peak WN at 2226 and 2229 cm^{-1} represent the $\text{C}\equiv\text{N}$ stretching mode of monomeric 5CB and dimeric $(5\text{CB})_2$, respectively. Decomposing procedures of the IR spectra described above were also successfully performed at other concentrations.

Assuming chemical equilibrium between $n\text{CB}$ and

$(nCB)_2$ as seen in Fig. 5, the equilibrium constant, K_d , can be also determined from IR data as well as dielectric ones. Because absorption ($ABS_{MON} (= w_{1/2}^{MON} I^{MON})$) and $ABS_{DIM} (= w_{1/2}^{DIM} I^{DIM})$; $w_{1/2}^{MON}$ and I^{MON} represent a half-value width and intensity of a Lorentz-type absorption function for the monomer nCB) is proportional to the concentration, equations $ABS_{MON} = \alpha_{MON}[nCB]$ and $ABS_{DIM} = \alpha_{DIM}[(nCB)_2]$ are naturally obtained introducing absorption coefficients α_{MON} and α_{DIM} . Then, eq 3 can be recast into

$$\frac{c}{ABS_{MON}} = \frac{1}{a_{MON}} + \frac{2K_d ABS_{MON}}{a_{MON}^2} \quad (5)$$

$$\text{or } \frac{c}{\sqrt{ABS_{DIM}}} = \frac{1}{\sqrt{K_d} a_{DIM}} + \frac{2\sqrt{ABS_{DIM}}}{a_{DIM}} \quad (5')$$

These are the same equations described by parameters relevant to monomers or dimers

Because the thickness of sample solution was not exactly fixed at the identical value, an inner standard signal was necessary for quantitative analysis. Since a C-C stretching vibration band of phenyl rings found at 1600 cm^{-1} is not affected by the formation of anti-parallel dimers, $(nCB)_2$, this band at 1600 cm^{-1} ($ABS_0 = a_0 c$) was employed as the inner standard. Relative absorption intensities, $ABS_{MON-0} = ABS_{MON}(ABS_0)^{-1}$ and $ABS_{DIM-0} = ABS_{DIM}(ABS_0)^{-1}$, were determined. Then, eqs 5 and 5' are recast into

$$\frac{1}{ABS_{MON-0}} = \frac{a_0}{a_{MON}} + 2K_d \left(\frac{a_0}{a_{MON}} \right)^2 ABS_{MON-0} c \quad (6)$$

(for monomers)

$$\text{or } \sqrt{\frac{c}{ABS_{DIM-0}}} = \sqrt{\frac{1}{K_d} \left(\frac{a_0}{a_{DIM}} \right)} + 2 \left(\frac{a_0}{a_{DIM}} \right) \sqrt{ABS_{DIM-0} c} \quad (6')$$

(for dimers)

Figs. 8 (a), (b), and (c) show plots $(ABS_{MON-0})^{-1}$ vs $ABS_{MON-0} c$ and $\sqrt{c(ABS_{DIM-0})^{-1}}$ vs $\sqrt{ABS_{DIM-0} c}$ for Bz solutions of 1CB, 5CB, and 8CB, respectively. These plots provide K_d values resulted from IR data. Then, the K_d values obtained from slopes and intercepts are shown in these plots. Both the plots for monomers and dimers reasonably agreed with each other. In the case of 1CB solution, the K_d value of ca. 0.25 M^{-1} was obtained over the c range examined. This fact strongly suggests that 1CB showing a single Debye-type DR with the g_K factor remarkably decreasing with increasing c forms anti-parallel dimers, $(1CB)_2$, and the chemical equilibrium is controlled by the K_d value resulted from IR data. The

reason for the single Debye-type DR is that the lifetime, τ_2 , of the formed anti-parallel dimers should be short and not so different from τ_1 due to its short alkyl tail: a methyl group.

On the other hand, the obtained plots were not straight for Bz solutions of 5CB and 8CB as seen in Figs. 8 (b) and (c). Then, the K_d value was not determined exactly in a low c side, but was determined to be ca. 30 M^{-1} in a high c side for 5CB

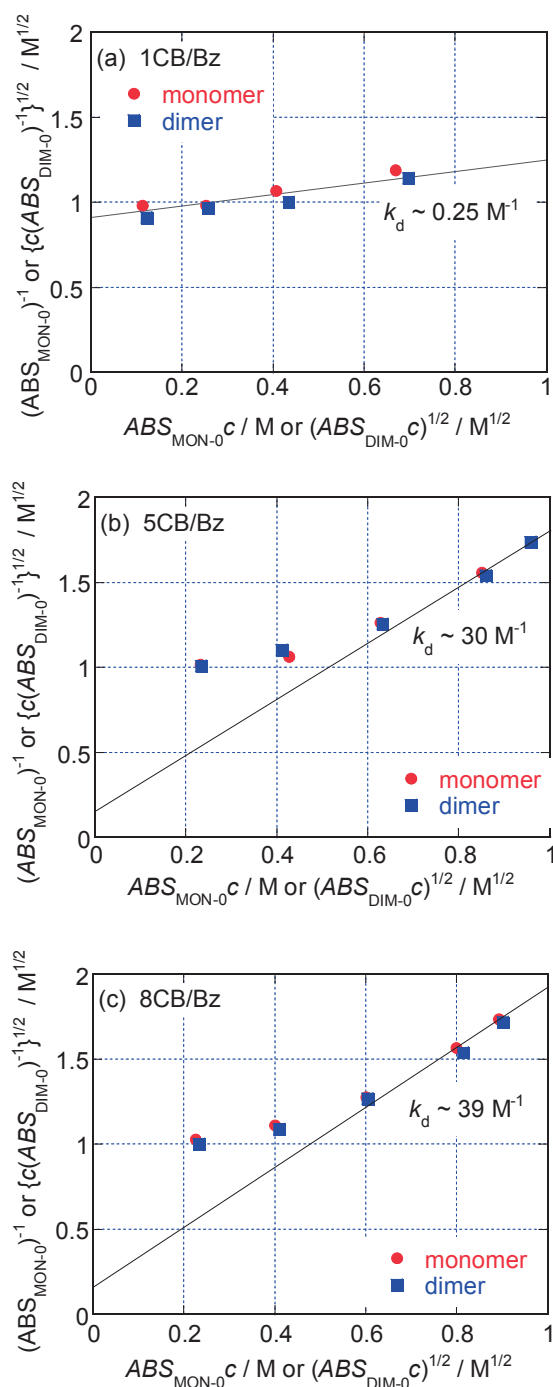


Fig. 8. Relationship between $(ABS_{MON-0})^{-1}$ and $(ABS_{MON-0})c$, and that between $\sqrt{c(ABS_{DIM-0})^{-1}}$ and $\sqrt{ABS_{DIM-0} c}$ (see text) for Bz solutions of 1CB (a), 5CB (b), and 8CB (c).

as seen in Fig. 8 (b). Slightly larger K_d value of ca. 39 M^{-1} in the high c region was also determined for 8CB (Fig. 8(c)). These K_d values for 5CB and 8CB reasonably corresponded to the values resulted from DR techniques shown in Fig. 6. Consequently, the validity of consideration based on the chemical equilibrium between $n\text{CB}$ and anti-parallel $(n\text{CB})_2$ in isotropic Bz solution (Fig. 5) was adequately proved by independent two experimental techniques. Then, we might conclude that there is chemical equilibrium between $n\text{CB}$ and anti-parallel $(n\text{CB})_2$ even in isotropic Bz solution at moderate concentrations.

From these considerations, the anti-parallel dimers, $(n\text{CB})_2$, formed in isotropic solution would be elemental seeds necessary for the formation of not only a smectic LC phase, but also a nematic LC phase. Moreover, molecular motions dielectrically observed in isotropic Bz solution of $n\text{CB}$ molecules which were attributed to the rotational process of monomeric molecules and the dissociation of anti-parallel dimers seem important also in LC phases formed at higher concentrations and in the bulk state.

4. CONCLUSIONS

Liquid crystalline phases forming (and not forming) 4-cyano-4'-alkylbiphenyls make anti-parallel dimers even in isotropic benzene solution irrespective of species of alkyl chains. The formation of anti-parallel dimers is well described with chemical equilibrium between monomers and dimers, and the equilibrium moves toward the dimer forming side with increasing concentration. Then, the formed anti-parallel dimers would be essential seeds of a nematic liquid crystalline phase formation observed at higher concentration and in the bulk state. Two kinds of molecular dynamic processes were dielectrically observed in isotropic benzene solution irrespective of species of alkyl chains. A fast relaxation mode was assigned to rotational relaxation mode of monomeric molecules, and the other slow mode which increased the magnitude of relaxation strength with increasing the concentration was tentatively attributed to the dissociation process of anti-parallel dimers. These dynamic processes would be important also in liquid crystalline phases used in many practical applications.

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