

# Dielectric Behaviors of Typical Benzene Monosubstitutes, Bromobenzene and Benzonitrile

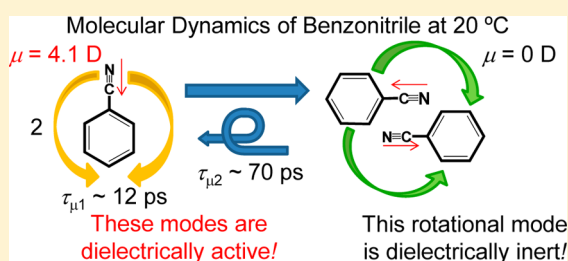
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**ABSTRACT:** The dielectric behaviors of typical benzene monosubstitutes, bromobenzene (Br-Bz) and benzonitrile (NC-Bz), were investigated up to 3 THz in the pure liquid state over a temperature range from 10 to 60 °C to understand differences in molecular motions of these simple, planar molecules bearing rather different electric dipole moments: 1.72 and 4.48 D for Br-Bz and NC-Bz in gaseous state, respectively. Temperature dependence of spin–lattice relaxation time ( $T_1$ ) for  $^{13}\text{C}$  NMR and viscosities for these liquids were also determined to obtain information for molecular motions. Moreover, depolarized Rayleigh scattering (DRS) experiments were carried out for both liquids at 20 °C to determine frequency dependencies of optical susceptibilities up to 8 THz directly relating to rotational motions of their molecular planes. Most Br-Bz molecules rotate freely over a temperature range examined, showing a Kirkwood correlation factor close to  $g_K \sim 1.0$  at dielectric Debye-type relaxation times (ca. 18 ps at 20 °C) essentially identical to microscopic (dielectric) relaxation times evaluated from  $T_1$   $^{13}\text{C}$  NMR data. A small amount of Br-Bz molecules forms dimeric intermolecular associations in an antiparallel configuration of dipole moments. On the other hand, NC-Bz molecules form stable dimers in the antiparallel dipole configuration at a population much higher than that of Br-Bz because of a markedly greater dipole moment than that of Br-Bz. A major dielectric relaxation mechanism for NC-Bz found at ca. 70 ps at 20 °C results from the dissociation process of dimers with a lifetime longer than a rotational relaxation time, observable as a minor dielectric relaxation mechanism at ca. 12 ps at 20 °C, of individual monomeric NC-Bz molecules without the formation of dimers. The formation of stable dimers in an antiparallel configuration is responsible for the observed small  $g_K$  values, ca. 0.5, and disagreement between major (or minor) dielectric relaxation times and microscopic dielectric relaxation times over the entire temperature range examined.



## INTRODUCTION

This year (2012) is the 100th anniversary of the publication of Debye's famous paper<sup>1</sup> on the presence of permanent dipoles in molecules due to anisotropic localization of electric charges. At present, there is no room for doubt that many polar molecules and chemical groups possess their characteristic permanent dipoles depending on their structure. The concept of permanent dipole can explain large, temperature-dependent electric susceptibilities that have been observed in many polar materials. Debye's second prominent work in dielectrics was his theory of dielectric (DE) relaxation behavior. He assumed a spherical molecule possessing a permanent dipole moment rotates freely feeling friction due to viscosities caused by the surrounding other molecules.<sup>2</sup> His model explains widely observed (Debye-type) DE relaxation behavior in many kinds of polar molecules. His relaxation model has only one set of a relaxation time ( $\tau_D$ ) and strength ( $\epsilon$ ) as described by eq 1 in the form of real and imaginary parts ( $\epsilon'$  and  $\epsilon''$ ) of electric permittivity as functions of angular frequency ( $\omega = 2\pi\nu$ ,  $\nu$ ; frequency in units of Hz)

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

where  $\epsilon_{\infty a}$  represents the apparent limiting electric permittivity observed at a sufficiently high frequency side. In the case of nonspherical molecules, additional relaxation modes are observable depending on the direction of permanent dipole moments fixed in the molecules. Perrin<sup>3</sup> extended the Debye-type dielectric relaxation model for spherical molecules to spheroidal (prolate and/or oblate) molecules and calculated multimodal dielectric relaxations as a function of the ratio of a long molecular axis to short one.

In general, a summation of Debye relaxation models bearing a necessary number of relaxation times and strengths is able to describe any kind of complicated DE behavior.<sup>4,5</sup> The application of Debye's model to real polar materials requires explicit expression for the relationship between the applied external electric

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field and the local electric field felt by a tested molecule. Onsager<sup>6</sup> has proposed a formula that precisely connects the external and local electric fields. Onsager's formula is useful for polar media consisting of polar molecules and more general than a formula proposed by Lorentz,<sup>7</sup> which is applicable only to nonpolar liquid media. Kirkwood<sup>8,9</sup> and Fröhlich<sup>4,5</sup> modified the formulas proposed by Debye and Onsager and obtained a general expression useful for any kinds of molecules that relates a relative static electric permittivity ( $\epsilon_0$ ) and the square of the dipole moment ( $\mu^2$ ) of a constituent molecule in the isolated state as follows

$$\Delta\epsilon = \epsilon_0 - \epsilon_{\infty a} = \frac{\epsilon_0(\epsilon_{\infty a} + 2)^2 \phi N_A \mu^2 g_K}{9(2\epsilon_0 + \epsilon_{\infty a})\epsilon_v k_B T} \quad (2)$$

where  $\phi$ ,  $N_A$ ,  $g_K$ ,  $\epsilon_v$  and  $k_B T$  represent the molar concentration of molecules in units of mol cm<sup>-3</sup>, Avogadro's number, the Kirkwood correlation factor, the electric permittivity in a vacuum, and the product of the Boltzmann constant and absolute temperature, respectively.<sup>10</sup> The Kirkwood correlation factor,  $g_K$ , provides a quantitative value showing the orientational correlation between the dipoles of each constituent molecule.<sup>8,9</sup> When  $g_K = 1$ , molecules rotate freely without any intermolecular orientational correlation. Under a condition of  $g_K > 1$ , molecules possess dipolar orientational correlation in a parallel fashion, whereas they exhibit antiparallel-type orientational correlation when  $g_K < 1$ .

The combination of the Debye-type relaxation model (eq 1) and the expression of the static electric permittivity given by eq 2 leads to the idea that polar molecules obey the Debye-type relaxation behavior with only one set of a relaxation time,  $\tau_D$ , and strength,  $\epsilon$ , governed by eq 2;  $\epsilon = \epsilon_0 - \epsilon_{\infty}$ . The Debye-type dielectric relaxation time,  $\tau_D$ , is a macroscopic relaxation time for the total dipole moment, which contains the information on complicated dipole–dipole correlation in general. The  $\tau_D$  value can be converted into a (microscopic) single molecule dipole relaxation time ( $\tau_\mu$ ) using proposed theoretical equations.<sup>11,12</sup> On the other hand, the value of  $\tau_\mu$  is evaluable from spin–lattice relaxation times ( $T_1$ ) of nucleus determined by nuclear magnetic resonance (NMR) experiments.<sup>13</sup>

In particular, the observed DE relaxation time,  $\tau_D$  (or  $\tau_\mu$ ), should be controlled by the viscosity of the tested liquid and temperature because polar molecules of  $g_K = 1$  show free rotation and feel friction controlled by the Stokes–Einstein–Debye (SED) relationship. We have referred to such polar molecules that satisfy these three criteria of single Debye-type relaxation,  $g_K = 1$ , and the SED relationship as *ideal polar molecules*.<sup>14</sup> In our previous study, we investigated the dielectric behavior of some small, symmetric ketones like acetone and 3-pentanone in the pure liquid state at several temperatures and compared the dielectric behavior of the ketones with that of ideal polar molecules.<sup>14</sup> Then, the presence of ideal polar molecules was clearly confirmed not only as a conceptual model for theoretical discussion but also in practice.

Benzene monosubstitutes, such as bromobenzene (Br-Bz) and benzonitrile (NC-Bz), are small, planar, dipolar molecules showing liquid phases over a relatively wide temperature range at 1 atm. Selection of substituting chemical groups provides a variety of combination of benzene monosubstitutes bearing similar molecular sizes but with rather different dipole moments. In the case of a combination of Br-Bz and NC-Bz, the values of dipole moments are 1.72 D<sup>15</sup> and 4.48 D<sup>16</sup> for Br-Bz and NC-Bz, respectively, both in the gaseous state. The contribution of a difference in the value of dipole moments more than twice to DE behavior should be clearly observed. Especially, the formation of

intermolecular associations due to strong dipole–dipole interaction between large dipole moments mainly governs DE behavior of NC-Bz without doubt.<sup>14,17,18</sup> Nevertheless, the importance of dipole–dipole interaction to the formation of intermolecular associations has not been discussed in detail so far in Br-Bz. If Br-Bz does not make (stable) intermolecular associations because of a not so large dipole moment of 1.72 D, the molecule rotates freely to demonstrate the Debye-type DE relaxation behavior. Even in the case, SED relationship is not anticipated in Br-Bz because it has been well-known that the activation energy of a microscopic relaxation time,  $\tau_\mu$ , evaluated from NMR techniques is not identical to that of viscosity as in benzene and its derivatives possessing weak intermolecular interactions. The reason for this disagreement in the activation energies is assigned to anisotropic rotations of such the planar molecules.<sup>19</sup> Consequently, benzene monosubstitutes do not show the DE behavior of ideal polar molecules as small ketones like acetone. DE measurements over a wide frequency range from 50 MHz up to ~3 THz, which are realized by a combination of reflection coefficient measurements using a network analyzer and THz range time domain reflectometric spectroscopy, reveal clearly DE behaviors of Br-Bz and NC-Bz in the liquid state.

Depolarized Rayleigh scattering (DRS) techniques sensitively provide information on rotational motions of molecular planes for benzene derivatives like Br-Bz and NC-Bz.<sup>20</sup> DRS precisely detects all the motions related to changes of the direction of molecular plains either accompanying dipole moment alternations, which is dielectrically detectable, or not. Therefore, a comparison between DRS and DE spectra clarifies which molecular motions in benzene derivatives are responsible for dielectric dispersions.

In this study, we combined several experimental techniques such as DE spectroscopy over a wide frequency range from 50 MHz up to 3 THz, DRS from 0.5 GHz up to 8 THz,  $T_1$  <sup>13</sup>C NMR measurements at the resonant frequency of 150 MHz, and viscosity measurements for Br-Bz and NC-Bz to obtain full understanding of their molecular motions in the pure liquid state. The results are quite useful to predict molecular dynamic characteristics for other small, planar solvent molecules bearing strong (or weak) intermolecular interaction due to large (or small) dipole moments because of attached dipolar chemical groups.

## ■ EXPERIMENTAL SECTION

**Materials.** Highly purified bromobenzene, Br-Bz (purity >99.5%), and benzonitrile, NC-Bz (>98%), were purchased from Sigma-Aldrich (St. Louis, MO) and Wako Pure Chemical Industries (Osaka), respectively, and used without further purification.

**Methods.** A dielectric-probe kit (8507E, Agilent Technologies, Santa Clara, CA) equipped with a PNA-L network analyzer (N5230C, Agilent Technologies) and a 50 GHz performance probe was employed to measure the real and imaginary parts,  $\epsilon'$  and  $\epsilon''$ , of the relative electric permittivity over a frequency,  $\nu$ , range from 50 MHz to 50 GHz ( $3.14 \times 10^8$  to  $3.14 \times 10^{11}$  s<sup>-1</sup> in angular frequency,  $\omega$ ). The three-load calibration process was performed at each temperature prior to the dielectric measurements for samples using three load liquids (*n*-hexane, 3-pentanone, and water) as described in detail elsewhere.<sup>17</sup> This measurement system performed dielectric (DE) measurements on the sample liquids with an uncertainty of less than 2.0%, at least in the range of  $\omega > 10^9$  s<sup>-1</sup>. The temperature,  $T$ , of the samples was adjusted to 10 to 60 °C with an accuracy of  $\pm 0.1$  °C using a temperature-control system equipped with a Peltier device.

A TR-1000 system (Otsuka Electronics, Osaka), a time-domain reflectometry spectroscopic system for the THz region utilizing a femtosecond laser, was used to measure  $\epsilon'$  and  $\epsilon''$  of Br-Bz and NC-Bz in the pure liquid state at  $T = 20^\circ\text{C}$  in a frequency range of  $\nu = 100\text{ GHz}$  to  $3\text{ THz}$  ( $\omega = 6.28 \times 10^{11}$  to  $1.88 \times 10^{13}\text{ s}^{-1}$ ). Liquid samples were sandwiched between two quartz window plates with an 8 mm aperture radius and a thickness of 1.0 mm using an O-ring-type spacer of 1.0 mm thickness. The refractive index ( $n$ ) and the absorption coefficient ( $\alpha$ ) were automatically calculated as functions of  $\omega$  via the standard software installed on the TR-1000 system and were converted to  $\epsilon'$  and  $\epsilon''$  using the relationships  $\epsilon' = n^2 - (\alpha c \omega^{-1})^2/4$  and  $\epsilon'' = n \alpha c \omega^{-1}$ , where  $c$  is the velocity of light.<sup>10</sup>

For spin–lattice relaxation time ( $T_1$ ) measurements for the  $^{13}\text{C}$  nuclei of Br-Bz and NC-Br, a Varian 600 NMR system (Agilent Technologies, Santa Clara, CA) was operated with a field/frequency lock in a temperature range of  $T = 10$ – $60^\circ\text{C}$  and at a resonance frequency of 150.8 MHz for  $^{13}\text{C}$  nuclei. A small amount of deuteriochloroform shielded in a thin glass capillary was inserted in a sample tube of 5 mm in a diameter for a field/frequency lock. A conventional inversion recovery pulse sequence was employed to determine  $T_1$  values. Nuclear Overhauser effect (NOE) enhancement factors ( $f_{\text{NOE}}$ ) for the  $^{13}\text{C}$  nuclei of Br-Bz and NC-Br were evaluated at each temperature by using the gated decoupling technique.

The viscosities and densities of Br-Bz and CN-Bz were measured as functions of  $T$  using a Stabinger SVM3000 (Anton Paar, Graz) viscosity–density meter.

Depolarized Rayleigh scattering, DRS (in other words, depolarized Raman scattering), in an ultralow frequency range measurements were performed at a scattering angle of  $90^\circ$  and  $T = 20^\circ\text{C}$  in both Br-Bz and CN-Bz. A rectangular quartz cell (10 mm  $\times$  10 mm  $\times$  height of 40 mm in size) with a shieling cap was used, which was kept at the set temperature with an accuracy of  $\pm 0.1^\circ\text{C}$ . A double-grating monochromator (Jovin-Yvon U-1000, Horiba, Kyoto) with a resolution of  $1\text{ cm}^{-1}$  and an Ar ion laser (S-P2016, Spectra-Physics, Santa Clara, CA) at a wavelength of 488.0 nm as an incident light source were employed in a frequency range higher than  $10^{12}\text{ s}^{-1}$ . Moreover, a Sandercock-type tandem Fabry–Perot interferometer TFP-1 (JRS Scientific Instruments, Zwillikon) with a free spectral range from 30 to 300 GHz and a single mode Ar ion laser (SP2060, Spectra-Physics) at a wavelength of 514.5 nm were used in a frequency range lower  $10^{13}\text{ s}^{-1}$ . The measurable differential cross section,  $\partial^2\sigma/\partial\Omega\partial\omega_2$ , of spontaneously scattered light from a sample is given by

$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega_2} \propto \omega_1\omega_2^3 I(\omega) \quad (3)$$

where  $\sigma$  represents the total scattering cross section,  $\omega = \omega_1 - \omega_2$ , and  $\omega_1$  and  $\omega_2$  are the frequencies of incident and scattered light, respectively,  $\Omega$  is the solid angle, and  $I(\omega)$  is the Raman scattering spectrum.<sup>21</sup> Frequency,  $\omega$ , dependencies of optical susceptibility ( $\chi''$ ) were calculated from  $I(\omega)$  under the depolarized condition via the equation

$$\chi'' = \frac{I(\omega)}{BE(\omega) + 1} \quad (4)$$

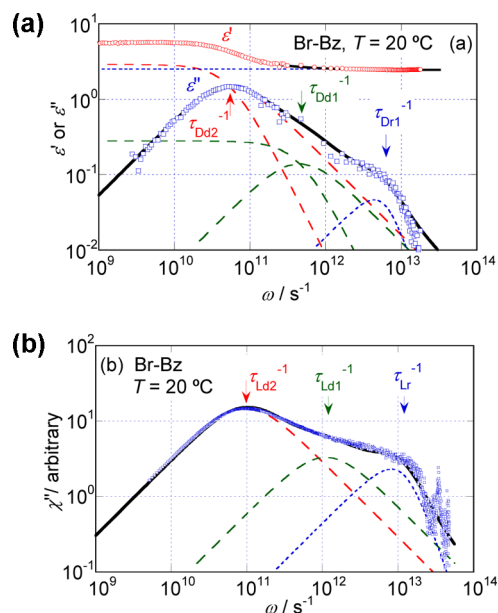
where  $BE(\omega)$  represents a Bose–Einstein factor. Since the Bose–Einstein factor is given in this manner  $BE(\omega) = [\exp\{h\omega/(2\pi k_B T)\} - 1]^{-1}$ , where  $h$  and  $k_B T$  represent Planck's constant and the product of Boltzmann constant and the absolute

temperature, respectively,<sup>22</sup> the expression of  $\chi''$  is simply casted in this form

$$\chi'' = I(\omega) \left\{ 1 - \exp\left(-\frac{h\omega}{2\pi k_B T}\right) \right\} \quad (4')$$

## RESULTS AND DISCUSSION

**Dielectric Behaviors of Bromobenzene.** The angular frequency,  $\omega$ , dependencies of  $\epsilon'$  and  $\epsilon''$  for Br-Bz determined at  $T = 20^\circ\text{C}$  are presented in Figure 1a as examples of the typical



**Figure 1.** (a) Frequency,  $\omega$ , dependencies of  $\epsilon'$  and  $\epsilon''$  and (b)  $\omega$  dependence of optical susceptibility,  $\chi''$ , for bromobenzene (Br-Bz) at  $T = 20^\circ\text{C}$  in the pure liquid state. Bold solid lines indicate the summation of constituent Debye-type relaxation (DR) functions (broken lines) and damped harmonic oscillation (DHO) functions (dotted lines).

dielectric (DE) behaviors at several temperatures. The DE spectra were reasonably decomposed into three constituent functions as given by eqs 5; the first and second components are Debye-type relaxation (DR) functions, and the third one is a damped harmonic oscillation (DHO) function that shows resonance characteristics

$$\epsilon' = \frac{\epsilon_{\text{Dd1}}}{1 + \omega^2 \tau_{\text{Dd1}}^2} + \frac{\epsilon_{\text{Dd2}}}{1 + \omega^2 \tau_{\text{Dd2}}^2} + \frac{A_{\text{Dr}} \omega_{\text{Dr}}^2 (\omega_{\text{Dr}}^2 - \omega^2)}{(\omega_{\text{Dr}}^2 - \omega^2)^2 + \omega^2 \gamma_{\text{D}}^2} + \epsilon_{\infty} \quad (5a)$$

and

$$\epsilon'' = \frac{\epsilon_{\text{Dd1}} \omega \tau_{\text{Dd1}}}{1 + \omega^2 \tau_{\text{Dd1}}^2} + \frac{\epsilon_{\text{Dd2}} \omega \tau_{\text{Dd2}}}{1 + \omega^2 \tau_{\text{Dd2}}^2} + \frac{A_{\text{Dr}} \omega_{\text{Dr}}^2 \omega \gamma}{(\omega_{\text{Dr}}^2 - \omega^2)^2 + \omega^2 \gamma_{\text{D}}^2} \quad (5b)$$

where  $\epsilon_{\text{Ddj}}$  and  $\tau_{\text{Ddj}}$  represent the relaxation strength and time ( $\tau_{\text{Dd2}} > \tau_{\text{Dd1}}$ ) of the DR function. Moreover,  $A_{\text{Dr}}$ ,  $\omega_{\text{Dr}}$ , and  $\gamma_{\text{D}}$  represent the resonance amplitude, frequency, and the damping constant of the DHO function, respectively, and  $\epsilon_{\infty}$  is the



$\omega$ -independent constant of electric permittivity. Because the value of  $\omega_{Dr} = 6.0 \times 10^{12} \text{ s}^{-1}$  ( $= 32 \text{ cm}^{-1}$  in wavenumbers) was identical to the peak frequency of a broad absorption band of Br-Bz in the far-infrared region related to vibrational motions of permanent dipoles i.e., Br-Bz molecules,<sup>23</sup> this DHO mode was assigned to a libration motion of Br-Bz molecules in cages formed by the surrounding other Br-Bz molecules. The determined relatively large damping constant,  $\gamma_D$ , of  $9 \times 10^{12} \text{ s}^{-1}$  ( $\sim 1.5\omega_{Dr}$ ) corresponded well to the broad absorption band that bears a half-width value of  $\sim 48 \text{ cm}^{-1}$ . The half-width value for the absorption band, which has been assigned to the intramolecular out-of-plane deformation band of Br–C connection observed at  $185 \text{ cm}^{-1}$ :<sup>24</sup> a needle-like small signal observed at  $3.5 \times 10^{13} \text{ s}^{-1}$  in an optical susceptibility spectrum seen in Figure 1b and discussed in detail later was evaluated to be ca.  $18 \text{ cm}^{-1}$  and was smaller than that observed at  $\omega_{Dr}$ . The origin of the DHO mode at  $\omega_{Dr}$  therefore appears to be different from the ordinal intramolecular vibration modes, such as the bending mode at  $185 \text{ cm}^{-1}$  and other many intramolecular vibration modes. Intramolecular vibration modes also contribute to the dielectric spectra as DHO modes with damping constants much smaller than the values of the mode at  $\omega_{Dr}$ . The value of  $\epsilon_\infty$  includes the summation of the amplitudes of these fast, sharp, intramolecular DHO modes.

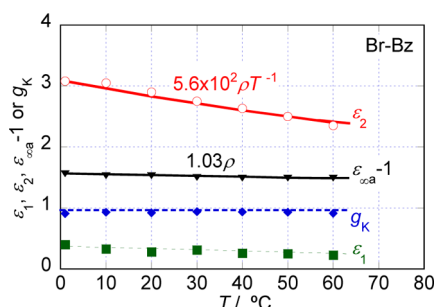
So far, few dielectric spectra for benzene monohalo derivatives covering up to a THz region were reported.<sup>25</sup> Therefore, the dielectric spectra seen in Figure 1a are one of reliable data for Br-Bz covering frequency up to 3 THz at present. Vij et al.<sup>26–28</sup> systematically discussed DHO resonance modes in small dipolar ketone homologues and their solutions dissolved in cyclohexane in detail. Vij's dielectric data on small ketones would be very good references to be compared with the data of Br-Bz in this study. They concluded that the DHO mode found in the ketone is attributed to a libration modes and the amplitude,  $A_{Dr}$ , is governed by the magnitudes of the dipole moment and the inertia moment of the ketone molecule. The resonance frequency,  $\omega_{Dr}$ , is proportional to  $(V_0 I_r^{-1})^{1/2}$ , where  $V_0$  and  $I_r$  represent the height of a local energy barrier of a cage surrounding a ketone molecule and the reduced inertia moment of the molecule, respectively.

Although the DR and DHO functions in eq 5 are derived from fundamentally different physical origins, the  $\omega$  dependence of the DHO function becomes similar to that of the DR function when the value of the damping factor,  $\gamma_D$ , is significantly large. However, in the case of Br-Bz, the  $\omega$  dependence of the third term of the dielectric response in eq 5 was obviously resonant and was still described with the DHO function. This observation means that librational intermolecular motions of Br-Bz molecules in cages formed by other molecules are highly restricted by strong restoring forces due to the potential energy,  $V_0$ . Therefore, rotational (relaxing) molecular motions of Br-Bz molecules occur in the frequency range much below  $\omega_{Dr}$ .

With respect to the Kirkwood correlation factors,  $g_K$ , which are a measure of the orientational correlation of dipole moments, i.e., molecular axes, over the entire frequency range, the precise value of an apparent high-frequency limiting electric permittivity,  $\epsilon_{\infty a}$ , is significantly important. The  $g_K$  factor is evaluable via eq 2 using the dipole moment,  $|\mu|$ , of Br-Bz in the isolated state. It is well known that the  $|\mu|$  values of benzene monohalo substitutes, e.g. Br-Bz, determined in the gas state,  $1.72 \text{ D}$ ,<sup>15</sup> are rather different from the values determined in the dilute solutions, ca.  $1.55 \text{ D}$ .<sup>29</sup> Then, we attempted to determine the  $|\mu|$  value of Br-Bz in solutions of benzene (Bz) and tetrachloromethane ( $\text{CCl}_4$ ) via dielectric measurements using the system consisting of a network analyzer. The obtained dielectric spectra showed single-mode

Debye-type relaxations, which were described with parameters:  $\epsilon_{D1}$ ,  $\tau_{D1}$ , and  $\epsilon_{\infty a}$  ( $= \epsilon_\infty + A_{Dr}$ ), for both Bz and  $\text{CCl}_4$  solutions at the Br-Bz composition less than 0.5 in mole fraction. The  $|\mu|$  value of Br-Bz was determined to be  $1.44 \text{ D}$  from the data in dilute conditions irrespective of the solvents and was used for calculations of  $g_K$  values of Br-Bz in the pure liquid state.

Since the  $g_K$  factor includes only information related to the rotational relaxation modes, the relationship  $\epsilon_{\infty a} = \epsilon_\infty + A_{Dr}$  was assumed for the evaluation of  $g_K$  values as in the previous study on small ketones.<sup>14</sup> The determined  $g_K$  values of Br-Bz in the pure liquid state seemed to demonstrate the relationship  $g_K \sim 1.0$  irrespective of temperature as seen in Figure 2. This observation



**Figure 2.** Temperature,  $T$ , dependence of Kirkwood factors,  $g_K$ , and magnitudes of dielectric relaxation strength for each mode,  $\epsilon_1$ ,  $\epsilon_2$ , and  $\epsilon_{\infty a} - 1$  for Br-Bz in the pure liquid state. Solid lines represent curves calculated from equations shown in the figure, and broken lines are guides for the eyes.

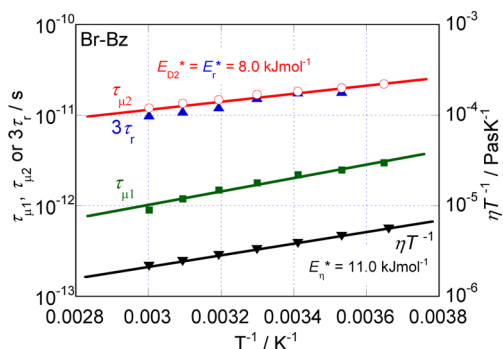
suggests that Br-Bz exhibits almost free rotation because of not so large dipole moment of  $1.44 \text{ D}$ .

Because the  $\epsilon_{\infty a}$  value was not correctly determined due to technical reasons for many substances, the conventional approximate expression of  $\epsilon_{\infty a} = 1.05n^2 \sim 1.1n^2$  and  $n = 1.559$  for Br-Bz at  $20^\circ \text{C}$  has been used in many studies; this expression leads to  $\epsilon_{\infty a} = 2.55\text{--}2.67$ . This value is slightly greater than the directly obtained value of  $2.53 (= 1.04n^2)$  at  $20^\circ \text{C}$  in this study (cf. Figure 1a). Consequently, the approximate expression for  $\epsilon_{\infty a}$  is incidentally useful for Br-Bz.

The simple but vague approximate expression for  $\epsilon_{\infty a}$  explained above leads to  $g_K$  values close to unity for dimethyl sulfoxide (DMSO) both in the pure liquid state and in solution, whereas DMSO obviously forms dimeric molecular associations in an antiparallel configuration, and the correct  $\epsilon_{\infty a}$  values determined at sufficiently high frequencies lead to  $g_K \sim 0.5$ . This value of  $g_K$  reveals the presence of dimers.<sup>17,18</sup> Then, researchers should be very careful when they encounter situations in which they must use the approximate expression for  $\epsilon_{\infty a}$  to evaluate  $g_K$  values.

The dependencies of dielectric relaxation strength,  $\epsilon_{D1}$ ,  $\epsilon_{D2}$ , and  $\epsilon_{\infty a} - 1$ , on  $T$  for Br-Bz are also plotted in Figure 2. The  $T$  dependencies of  $\epsilon_{D1}$ ,  $\epsilon_{D2}$ , and  $\epsilon_{\infty a} - 1$  are slightly different, as seen in the figure. An increase in  $T$  decreased all, however, decreased  $\epsilon_{D2}$  markedly. According to theoretical considerations of the dielectric behavior of a polar molecular liquid, the dielectric relaxation strength,  $\epsilon_{D2}$ , decreases with increasing  $T$  in proportion to  $\rho T^{-1}$ , where  $\rho$  is the density of the sample liquid, if the polar molecules behave like ideal polar particles that show free rotation without the formation of intermolecular associations.<sup>1,5,10</sup> The solid line in the figure represents the  $T$  dependence of  $5.6 \times 10^2 \rho T^{-1}$  and coincides well with the experimental  $\epsilon_{D2}$  data. On the other hand, the  $T$  dependence of  $\epsilon_{\infty a} - 1$

almost constant irrespective of  $T$  is typical for liquid substances. The parameter  $\epsilon_{\infty} - 1$  represents the dielectric contribution resulted from both the intramolecular vibration modes in the infrared (IR) range and the librational intermolecular mode observed at  $\omega_{D1}$  as described above. The magnitude of  $\epsilon_{\infty} - 1$  might be governed by the density of constituent molecules,  $\rho$ , as precise investigations in nonpolar liquids,<sup>30</sup> such as *n*-hexane, confirmed the relationship. The broken line in Figure 3 indicates the value proportional to  $\rho$ ,



**Figure 3.** Dependencies of relaxation times,  $\tau_{\mu 1}$ ,  $\tau_{\mu 2}$ , and  $3\tau_r$  and the temperature reduced viscosity,  $\eta T^{-1}$ , on the reciprocal of the absolute temperature,  $T^{-1}$ , for Br-Bz in the pure liquid state. Activation energies for each relaxation time calculated from solid lines are shown in the figure.

which are almost constant over the examined temperature range. Because the magnitude of  $\epsilon_{D1}$  is much small than that of  $\epsilon_{D2}$ , the importance of this dielectric mode seems to be low. However, the presence of this mode is not negligible and reveals that the DE behavior of Br-Bz is not classified into that of the ideal polar molecules. This minor DE mode found at  $\tau_{D1}$  will be discussed in detail later in conjunction with the obtained susceptibility spectrum.

For the analysis of relaxation times determined using different experimental methods, the (macroscopic) dielectric relaxation times,  $\tau_{D1}$  and  $\tau_{D2}$ , should be converted to microscopic dielectric relaxation times,  $\tau_{\mu 2}$  and  $\tau_{\mu 1}$ , which corresponds to a characteristic decay time of single molecular dipole using eq 6 proposed by Kivelson et al.<sup>12</sup>

$$\tau_{Dj} = F \frac{g_K}{\dot{g}} \tau_{\mu j} \quad (j = 1 \text{ and } 2) \quad (6)$$

where  $F$  and  $\dot{g}$  represent a local electric field correction, e.g.,  $F = 3\epsilon_0(2\epsilon_0 + \epsilon_{\infty})^{-1}$ ,<sup>11</sup> and a dynamic correlation factor, respectively. However, the relationship  $\tau_{D2} = g_K \tau_{\mu 2}$  simpler than eq 6 has been used in many studies<sup>31</sup> because  $\dot{g}$  has not been obtained in an explicit form. Then, we used this simpler relationship in this study, i.e., approximately  $\tau_{D2} = \tau_{\mu 2}$ , because  $g_K \sim 1$  for Br-Bz in the pure liquid state as described above. The relationship between the microscopic dielectric relaxation times,  $\tau_{\mu 2}$ , and  $T^{-1}$  for Br-Bz is shown in Figure 3. The slope of the plot represents the activation energies ( $E_{D2}^*$ ) for the microscopic dielectric relaxation time,  $\tau_{\mu 2}$ , ca. 8.0 kJ mol<sup>-1</sup> for Br-Bz.

The rotational relaxation time ( $\tau_r$ ) of molecules determined using NMR relaxation time measurements is classified as a second rank rotational correlation times. The quantity of  $3\tau_r$  has the same physical meanings as the microscopic dielectric relaxation time,  $\tau_{\mu 2}$ , i.e., the first rank rotational correlation time, if the molecules rotate freely without the formation of molecular associations.

In general, the experimental spin–lattice relaxation time,  $T_1$ , of a para-<sup>13</sup>C nucleus of Br-Bz includes a few kinds of contributions such as dipole–dipole (dd) interaction between <sup>13</sup>C and adjacent <sup>1</sup>H nuclei, spin rotation, scalar coupling, chemical shift anisotropy, and so on, in the manner of  $T_1^{-1} = T_{1dd}^{-1} + T_{1sr}^{-1} + T_{1csa}^{-1} + \dots$ . The most important contribution resulted from the dd interaction,  $T_{1dd}$ , is approximately evaluable using an NOE enhance factor ( $f_{\text{NOE}}$ ) via the relationship  $T_{1dd} = 1.998 T_1 f_{\text{NOE}}^{-1}$ .<sup>13</sup> Then, the  $T_{1dd}$  value is directly related to the rotational relaxation time,  $\tau_r$ , of the molecule, Br-Bz in this case, as given by

$$\frac{1}{T_{1dd}} = \frac{\gamma_H^2 \gamma_C^2 \hbar^2}{40\pi^2 r_{CH}^6} \left( \frac{\tau_r}{1 + 9(\omega_C \tau_r)^2} + \frac{3\tau_r}{1 + (\omega_C \tau_r)^2} + \frac{6\tau_r}{1 + 25(\omega_C \tau_r)^2} \right) \quad (7)$$

where  $\gamma_H$ ,  $\gamma_C$ ,  $\omega_C$ , and  $r_{CH}$  represent gyromagnetic ratios of <sup>1</sup>H and <sup>13</sup>C nuclei, the resonance angular frequency of <sup>13</sup>C in and distance between <sup>1</sup>H and <sup>13</sup>C, ca. 0.11 nm in this case, respectively.<sup>32</sup>

The temperature dependence of the  $3\tau_r$  values determined for para-<sup>13</sup>C of Br-Bz evaluated from the  $T_1$  and  $f_{\text{NOE}}$  values is also shown in Figure 3. The agreement between the  $3\tau_r$  and  $\tau_{\mu 2}$  data for Br-Bz looks perfect. This agreement between the  $3\tau_r$  and  $\tau_{\mu 2}$  reveals that the evaluated activation energy ( $E_r^*$ ) of  $3\tau_r$  are identical to that ( $E_{D2}^*$ ) of  $\tau_{\mu 2}$ . Consequently, these observations suggest that Br-Bz approximately behaves like ideal polar molecules that show free rotation without the formation of intermolecular associations in both the parallel and antiparallel configurations.

In the case of ideal polar molecules showing a free rotational relaxation mode without the formation of intermolecular associations, the microscopic dielectric relaxation time,  $\tau_{\mu}$ , is described by the Stokes–Einstein–Debye (SED) relationship given by

$$\tau_{\mu} \propto \frac{V\eta}{k_B T} \quad (8)$$

where  $V$  and  $\eta$  represent the effective molecular volume and the viscosity of the liquid, respectively.<sup>1,5,10</sup> Because  $V$  should be a weak function of  $T$ , the quantity of  $\eta T^{-1}$  exhibits the same  $T$  dependence as  $\tau_{\mu}$ . Figure 3 also show the relationship between  $\eta T^{-1}$  and  $T^{-1}$ , which provides an activation energy ( $E_{\eta}^* = 11$  kJ mol<sup>-1</sup>) of the  $\eta T^{-1}$  that is not identical to the  $E_{D2}^*$  value. The reported activation energy of the  $\eta$  for Br-Bz, ca. 8.54 kJ mol<sup>-1</sup>, in the literature<sup>19</sup> is coveted to be  $E_{\eta}^* = 10.4$  kJ mol<sup>-1</sup>, which is close to the value obtained in this study. This disagreement between  $E_{\eta}^*$  and  $E_{D2}^*$  reveals that Br-Bz does not hold the SED relationship. Consequently, Br-Bz does not satisfy the criteria for the behavior of ideal polar molecules in the view points of the SED relationship and also single-DR behavior.

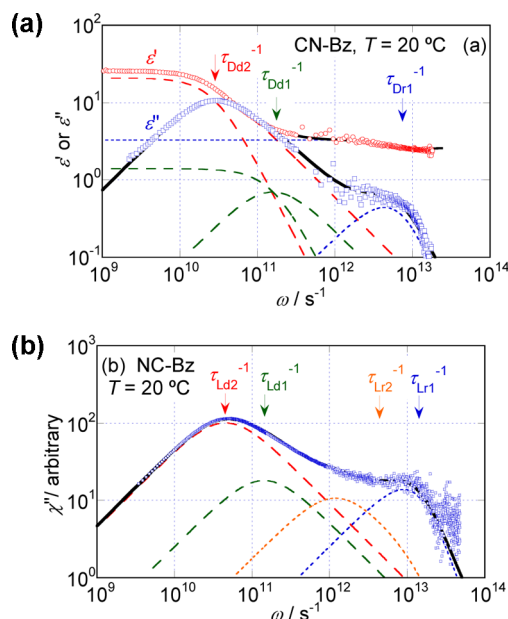
Disagreement between activation energies of  $E_{\eta}^*$  ( $= 10.6$  kJ mol<sup>-1</sup>) and  $E_r^*$  ( $= E_{D2}^* = 7.7$  kJ mol<sup>-1</sup>) has been well-known in benzene (Bz) in the pure liquid state.<sup>33</sup> The reason for the disagreement has been recognized to be the contribution of anisotropic rotational motions of planar Bz molecules.<sup>33</sup> In the case of Br-Bz, anisotropic rotational motions not so different from those in Bz molecules should occur naturally in also Br-Bz molecules. Thus, the reason why the  $E_{\eta}^*$  and  $E_{D2}^*$  values are not coincident is not attributed to the formation of intermolecular associations.

An optical susceptibility spectrum ( $\chi''$  vs  $\omega$ ) obtained from depolarized Rayleigh scattering (DRS) experiments for Br-Bz at 20 °C in the pure liquid state is shown in Figure 1b for the comparison with the  $\omega$  dependence of  $\epsilon''$  seen in upper Figure 1a. The  $\chi''$  spectrum was reasonably decomposed into three constituent modes as well as the dielectric spectrum: two DR modes designated by parameters,  $\tau_{Ld1}$  and  $\chi_{Ld1}$ ,  $\tau_{Ld2}$  and  $\chi_{Ld2}$ , and one DHO mode with  $\chi_{Lr}$  and  $\tau_{Lr}$ . Although intensity ratios between the magnitudes of strength for the corresponding modes  $\chi_{Ld1}\epsilon_{Dd1}^{-1}$ ,  $\chi_{Ld2}\epsilon_{Dd2}^{-1}$ , and  $A_{Lr}A_{Dr}^{-1}$  are not identical to each other, the ratios between characteristic times  $\tau_{Ld1}\tau_{Dd1}^{-1}$ ,  $\tau_{Ld2}\tau_{Dd2}^{-1}$ , and  $\tau_{Lr}\tau_{Dr}^{-1}$  look almost constant, ca. 0.5, irrespective of kinds of component modes. These reveal that the obtained DE and  $\chi''$  spectra exhibit the contribution of the same molecular motion at different strengths depending on the mode. Moreover, a coincident molecular motion is always observed at a higher rate by DRS than DE measurements. A ratio of the characteristic correlation times for the same molecular motion depending on the used observation techniques, DE and DRS, in which the second rank rotational correlation time is determined, is theoretically described with the number density of the molecule,  $N$ , in this manner;  $3\tau_{Ld2}\tau_{\mu 2}^{-1} (= 3g_K\tau_{Ld2}\tau_{Dd2}^{-1} \sim 3\tau_{Ld2}\tau_{Dd2}^{-1}) = (1 + g_L N)(1 + \dot{g}_L N)^{-1}$ , where  $g_L$  and  $\dot{g}_L$  represent the static and dynamic orientational pair correlation factors of molecular plane of Br-Bz, respectively.<sup>34</sup> However, since it has been well-known that the  $\dot{g}_L$  value is close to zero, the equation of the  $\tau_{Ld2}\tau_{Dd2}^{-1}$  ratio has been recasted approximately into relationship  $3\tau_{Ld2}\tau_{Dd2}^{-1} = 1 + g_L N$ . The experimental ratios of  $3\tau_{Ld2}\tau_{Dd2}^{-1} = 1.53$ ,  $3\tau_{Ld1}\tau_{Dd1}^{-1} = 1.23$ , and  $3\tau_{Lr}\tau_{Dr}^{-1} = 1.47$  were obtained from Figure 1a,b. These mean that the quantity  $g_L N$  is a positive small value, ca. 0.23–0.53, then, the tendency to possess weak static orientational pair correlation of the molecular plane in parallel is recognized for Br-Bz in the pure liquid state.

When we compare the relaxation time,  $\tau_{Ld2}$ , for the major relaxation mode found in DRS spectra and the rotational relaxation time,  $\tau_r$ , obtained from  $T_1$   $^{13}\text{C}$  NMR experiments, the relationship  $\tau_{Ld2}\tau_r^{-1} \sim 1.74$  is obtained. Because the ratio,  $\tau_{Ld2}\tau_r^{-1}$ , is also related to the parameter,  $g_L N$ , in the manner  $\tau_{Ld2}\tau_r^{-1} \sim 1 + g_L N$ , it is confirmed that  $g_L N$  is of a small value, ca. 0.74, meaning weak static orientational pair correlation of the molecular plane of Br-Bz in parallel.

**Dielectric Behavior of Benzonitrile.** In the case of benzonitrile, NC-Bz, so many researchers have concluded that NC-Bz forms intermolecular dimeric associations in liquid and gaseous state based on reliable experimental results, such as linear and nonlinear dielectric spectroscopies,<sup>35,36</sup> laser-induced fluorescence spectroscopic measurements in a free jet,<sup>37</sup> and DRS techniques.<sup>38</sup> Moreover, X-ray scattering experiments also revealed the presence of the intermolecular dimeric associations in the pure liquid state.<sup>39</sup> Then, one does not have to doubt the formation of intermolecular dimeric association. Here, we demonstrate the presence of dimeric associations of NC-Bz and the lifetime of the dimers based on the DE spectra obtained in this study.

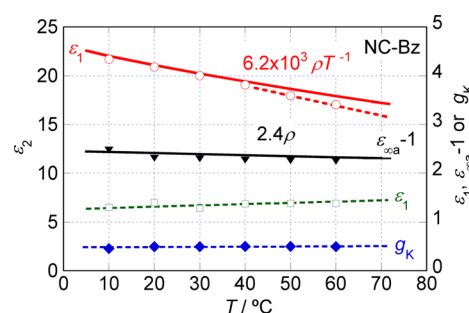
Figure 4a represents  $\omega$  dependence of DE spectra for NC-Bz at 20 °C. The DE spectra were reasonably decomposed into three constituent modes as given by eq 5. The first and second components are DR functions, and the third one is the DHO function as well as the case of Br-Bz. Because NC-Bz has intermolecular dimeric associations, either a slow DR mode observed at  $\omega = 2.9 \times 10^{10} \text{ s}^{-1}$  (or  $\tau_{Dd2} = 35 \text{ ps}$ ) or a fast one at  $1.6 \times 10^{11} \text{ s}^{-1}$  (or  $\tau_{Dd2} = 6.3 \text{ ps}$ ) seen in Figure 4a results from the dissociation process of dimeric associations according to the



**Figure 4.** (a)  $\omega$  dependencies of  $\epsilon'$  and  $\epsilon''$  and (b)  $\omega$  dependence of optical susceptibility,  $\chi''$ , for benzonitrile (NC-Bz) at  $T = 20$  °C in the pure liquid state. Bold solid lines indicate the summation of constituent DR functions (broken lines) and DHO functions (dotted lines).

consideration in the previous studies on dipolar associating molecules like DMSO<sup>17,18</sup> and ketones.<sup>14</sup>

In the case of NC-Bz, it has been also reported that the  $|\mu|$  value alters depending on the measuring condition. In the gaseous condition, the relationship  $|\mu| = 4.48 \text{ D}$  (or  $4.52 \text{ D}$ ) was reported,<sup>16,40</sup> while  $|\mu| = 4.05$  in dilute solutions.<sup>41</sup> Then, we tried to determine the  $|\mu|$  value in dilute benzene solutions at concentrations lower than 0.5 M using a measuring system consisting of a network analyzer and obtained the value of 4.1 D identical to that in the literature.<sup>41</sup> The temperature dependence of the Kirkwood factor,  $g_K$ , evaluated for NC-Bz via eq 2 under the assumptions that  $\epsilon_{\infty a} (= \epsilon_{\infty} + A_{Dr})$ , e.g., 3.31 at 20 °C (cf. Figure 4a), and  $|\mu| = 4.1 \text{ D}$  is shown in Figure 5. Because



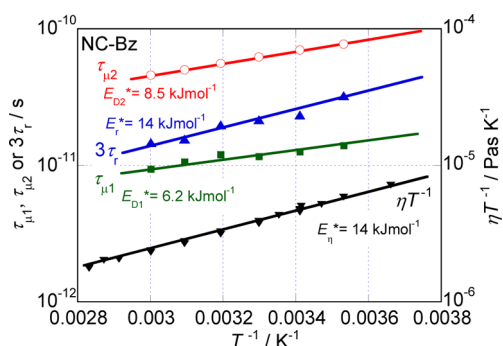
**Figure 5.**  $T$  dependence of  $g_K$ ,  $\epsilon_1$ ,  $\epsilon_2$ , and  $\epsilon_{\infty a} - 1$  for NC-Bz in the pure liquid state. Solid lines represent curves calculated from equations shown in the figure, and broken lines are guides for the eyes.

the obtained  $g_K$  values are of ca. 0.5 almost irrespective of temperature,  $T$ , this small  $g_K$  value reveals that intermolecular associations of NC-Bz are in the antiparallel cyclic configuration. Figure 5 also shows the dependence of  $\epsilon_{Dd1}$ ,  $\epsilon_{Dd2}$ , and  $\epsilon_{\infty a} - 1$  on  $T$  for NC-Bz. The behavior of  $\epsilon_{\infty a} - 1$  appears normal and is proportional to the density,  $\rho$ , over the entire examined temperature range. The Debye relaxation (DR) mode of  $\epsilon_{Dd2}$  observed over the entire temperature range will be assigned to



the contribution of dimeric NC-Bz associations. In the case of  $\varepsilon_{\text{Dd2}}$ , the relationship  $\varepsilon_{\text{Dd2}} \propto \rho T^{-1}$  shown by a solid line in Figure 5 holds over a wide  $T$  range examined. However, the  $\varepsilon_{\text{Dd2}}$  data downwardly deviated from the  $\rho T^{-1}$  line in a temperature range above 50 °C as indicated by a dotted line. This deviation indicates that the number density of dimeric NC-Bz associations decreases with increasing  $T$  and is responsible for a slight increasing in the  $\varepsilon_{\text{Dd1}}$  value (as indicated by a dotted line), since the fast DR mode designated by  $\varepsilon_{\text{Dd1}}$  and  $\tau_{\text{Dd1}}$  will be assigned to the rotational relaxation mode of monomeric CN-Br molecules. Because the conventional approximate relationship of  $\varepsilon_{\infty} = 1.05n^2 \sim 1.1n^2$  leads to an  $\varepsilon_{\infty}$  value of 2.45–2.57 due to  $n = 1.528$  at 20 °C, which does not agree with the experimental  $\varepsilon_{\infty}$  value of 3.31 for NC-Bz, the conventional relationship is not useful for the evaluation of  $g_K$ , as in the case of Br-Bz.

The temperature dependencies of microscopic dielectric relaxation times,  $\tau_{\mu 1}$  and  $\tau_{\mu 2}$ , which were converted from  $\tau_{\text{Dd1}}$  and  $\tau_{\text{Dd2}}$  using the relationship  $\tau_{\text{Dd1}} = g_K \tau_{\mu 1}$  and  $\tau_{\text{Dd2}} = g_K \tau_{\mu 2}$ , are shown in Figure 6. In a low  $T^{-1}$  (high  $T$ ) region, both the  $\tau_{\mu 1}$  and



**Figure 6.** Dependencies of relaxation times,  $\tau_{\mu 1}$ ,  $\tau_{\mu 2}$ , and  $3\tau_r$  and the temperature reduced viscosity,  $\eta T^{-1}$ , on the reciprocal of the absolute temperature,  $T^{-1}$ , for NC-Bz in the pure liquid state. Activation energies for each relaxation time calculated from solid lines are shown in the figure.

$\tau_{\mu 2}$  data obeyed an Arrhenius-type temperature dependence, with an activation energy of  $E_{\text{Dd1}}^* = 6.2 \text{ kJ mol}^{-1}$  and  $E_{\text{Dd2}}^* = 8.5 \text{ kJ mol}^{-1}$ , respectively. The physical meaning of the fast mode of  $\tau_{\mu 1}$  should be the rotational relaxation process of monomeric NC-Bz molecules, as discussed below. However, the origin of the slow mode of  $\tau_{\mu 2}$  would be related to the lifetime of the formed intermolecular dimeric associations if the dimeric associations have perfect antiparallel cyclic configurations that possess a total dipole moment of zero, as in the case of DMSO<sup>17,18</sup> and some small ketones.<sup>14</sup> The perfect antiparallel cyclic dimers possessing zero total dipole moment exhibit a dielectric relaxation process only when they dissociate into NC-Br monomers which quickly rotate after the lifetime of the dimers.

The  $3\tau_r$  values determined for para-<sup>13</sup>C nucleus of NC-Bz evaluated from the  $T_1$  <sup>13</sup>C NMR data and  $f_{\text{NOE}}$  values directly showing a microscopic dielectric relaxation time are also plotted in Figure 6. The  $3\tau_r$  values neither agreed with  $\tau_{\mu 1}$  nor  $\tau_{\mu 2}$  data for NC-Bz in the pure liquid state. Moreover, it seems that the  $3\tau_r$  are always the intermediate values between the  $\tau_{\mu 1}$  and  $\tau_{\mu 2}$  data. These behaviors completely different from those observed in Br-Bz seen in Figure 3, i.e., the found relationship  $\tau_{\mu 2} = 3\tau_r$  means free rotation like behavior, reveal that microscopic (dielectric) relaxation time  $3\tau_r$  determined from NMR data corresponds to the mean quantity determined as the average of the DR times of  $\tau_{\mu 1}$  and  $\tau_{\mu 2}$  depending on the population belonging to each DR

mode, 1 and 2. Here, we assume that the fast and slow DR modes of  $\tau_{\mu 1}$  and  $\tau_{\mu 2}$  correspond to the rotational mode of monomeric NC-Bz molecules and dissociation process of dimeric intermolecular associations possessing the antiparallel dipole configuration, respectively. Because the population of intermolecular dimers decreases with increasing  $T$  in general,  $T$  dependencies of relaxation times and strength for NC-Bz observed in Figures 5 and 6 are systematically explained by the assumption.

The evaluated activation energy,  $E_r^*$ , of  $3\tau_r$  are not identical to the  $E_{\text{d1}}^* = 6.2 \text{ kJ mol}^{-1}$  for  $\tau_{\mu 1}$  and  $E_{\text{d2}}^* = 8.5 \text{ kJ mol}^{-1}$  for  $\tau_{\mu 2}$ , respectively, as seen in Figure 6. The  $\eta T^{-1}$  values obtained from the viscosity measurements are also plotted in the same figure. Both the  $\eta T^{-1}$  and  $3\tau_r$  data show Arrhenius-type temperature dependencies over the entire examined  $T^{-1}$  range, and the activation energies for both the quantities,  $E_{\eta}^*$  and  $E_r^*$ , are almost identical to the value of  $14 \text{ kJ mol}^{-1}$ . These manifest that NC-Bz molecules have a planar (and anisotropic) shape as well as Br-Bz molecules; however, they form intermolecular (antiparallel) dimers at a high population as easily detected by DE experiments over the wide temperature range, and then, the average rate of all molecular motions observed in NC-Bz molecules even in monomeric and dimeric configuration possesses the activation energy values close to that of the temperature reduced viscosity,  $\eta T^{-1}$ . It is interesting to note that the agreement between  $E_{\eta}^*$  and  $E_r^*$  (not  $E_{\eta}^*$  and  $E_{\text{d2}}^*$ ) suggests the validity of the SED relationship (cf. eq 8) apparently, whereas this incidental agreement does not mean free rotation-like dynamic properties of NC-Bz molecules in the pure liquid state. In the case of free rotation, agreement among  $E_{\eta}^*$ ,  $E_r^*$ , and  $E_{\text{d2}}^*$  ( $= E_{\text{d1}}^*$ ) is required as observed in the ideal polar molecules like acetone and 3-pentanone.<sup>14</sup>

Dannhauser et al.<sup>35</sup> investigated temperature dependencies of the dielectric constant,  $\varepsilon_0$  ( $\varepsilon'$  at  $\omega = 0 \text{ s}^{-1}$ ), of some liquid nitriles including NC-Bz over a wide temperature range and determined equilibrium constants of dimerization reaction for the nitrile samples. To calculate the equilibrium constants from the obtained Kirkwood factors,  $g_K$ , they assumed a model in which intermolecular dimers are in antiparallel dipole configuration and show neither dielectric dispersions nor dipole moments and concluded the antiparallel dipole configuration model is rather reasonable. However, the contribution of dissociation process of the formed dimeric associations after their lifetime to dielectric behavior was not taken into account at all. Firman et al.<sup>42</sup> investigated dielectric behavior of NC-B up to 88 GHz at 25 °C. They found that the dielectric spectrum was not perfectly described with a single DR function; however, they did not take account of the formation of intermolecular association in NC-Bz. Barthel et al.<sup>43</sup> investigated dielectric spectra of NC-Bz up to 100 GHz ( $6.28 \times 10^{11} \text{ s}^{-1}$ ) over a wide temperature range. They found that NC-Bz possesses two kinds of DR modes fairly corresponding to our DR modes with relaxation times of  $\tau_{\text{Dd1}}$  and  $\tau_{\text{Dd2}}$ . However, they concluded that NC-Bz forms no intermolecular dimeric associations and the alternation from molecular dynamics governed by free rotation to rotational diffusion is observed by the two DR modes. Consequently, all dielectric studies reported so far did not support the presence of intermolecular dimeric associations.

An optical susceptibility spectrum,  $\chi''$  vs  $\omega$ , obtained from depolarized Rayleigh scattering (DRS) experiments for CN-Bz at 20 °C in the pure liquid state is shown in Figure 4b for the comparison with the  $\omega$  dependence of  $\varepsilon''$  seen in Figure 4a. The  $\chi''$  spectrum is reasonably decomposed into four constituent

modes contrary to the dielectric spectrum with three modes: two DR modes with  $\tau_{\text{Ld1}}$  and  $\tau_{\text{Ld2}}$  and two DHO modes with  $\omega_{\text{Lr1}} = 1.4 \times 10^{13} \text{ s}^{-1}$  ( $\tau_{\text{Lr1}} = 71 \text{ fs}$ ) and  $\omega_{\text{Lr2}} = 4.5 \times 10^{12} \text{ s}^{-1}$  ( $\tau_{\text{Lr2}} = 0.22 \text{ ps}$ ). This behavior is different from that of Br-Bz seen in Figure 1a,b. The ratios between characteristic times were calculated to be  $\tau_{\text{Ld1}}\tau_{\text{Dd1}}^{-1} = 1.1$ ,  $\tau_{\text{Ld2}}\tau_{\text{Dd2}}^{-1} = 0.63$ , and  $\tau_{\text{Lr1}}\tau_{\text{Drl}}^{-1} = 0.53$ .

According to the discussion for Br-Bz molecules above, the obtained DE and  $\chi''$  spectra exhibit the contribution of the same molecular motion at different strengths depending on the mode. Although the same molecular motion is always observed at a higher rate by DRS than DE measurements in the case of Br-Bz system, in the NC-Bz system the two DR modes were observed at similar frequencies in both DRS and DE spectra. The ratio of the characteristic times for the same molecular motion depending on the used observation techniques, DE and DRS, is described in this manner;  $3\tau_{\text{Ld2}}\tau_{\mu 2}^{-1} = 3g_{\text{K}}\tau_{\text{Ld2}}\tau_{\text{Dd2}}^{-1} = 1 + g_{\text{L}}N$ , as described above. The experimental ratios of  $3g_{\text{K}}\tau_{\text{Ld1}}\tau_{\text{Dd1}}^{-1} = 1.65$ ,  $3g_{\text{K}}\tau_{\text{Ld2}}\tau_{\text{Dd2}}^{-1} = 1.0$ , and  $3g_{\text{K}}\tau_{\text{Lr1}}\tau_{\text{Drl}}^{-1} = 0.80$  were obtained from Figure 4a,b. These mean that the  $g_{\text{L}}N$  for each mode are of small values, such as 0.65, 0.0, and  $-0.20$ , respectively. This trend to possess small (positive)  $g_{\text{L}}N$  values in the two DR modes of  $\tau_{\text{Ld1}}$  (or  $\tau_{\text{Dd1}}$ ) and  $\tau_{\text{Ld2}}$  (or  $\tau_{\text{Dd2}}$ ) means weak orientational pair correlation of the molecular plane of CN-Bz molecules in the pure liquid state. This observation reveals the formation of intermolecular dimers in the antiparallel dipole configuration does not so much influence the orientational pair correlation of the molecular planes.

On the other hand, comparing the relaxation time,  $\tau_{\text{Ld2}}$ , of a major mode found in the DRS spectrum and the rotational relaxation time,  $\tau_{\text{r}}$ , determined from  $T_1$   $^{13}\text{C}$  NMR data provides the relationship  $\tau_{\text{Ld2}}\tau_{\text{r}}^{-1} = 1 + g_{\text{L}}N \sim 2.79$  for the NC-Bz system. This leads to that relationship  $g_{\text{L}}N \sim 1.79$ , meaning much stronger orientational correlation of the molecular plane in parallel than that evaluated from relaxation times of each relaxation mode above. It seems that this contradiction in the value of  $g_{\text{L}}N$  results from the fact the rotational relaxation time,  $\tau_{\text{r}}$ , is the average value of two relaxation modes: the rotational relaxation mode of monomers,  $j = 1$ , and dissociation process of intermolecular dimeric association,  $j = 2$ , respectively.

The  $g_{\text{L}}N$  value for the DHO mode of  $\tau_{\text{Lr1}}$  (or  $\tau_{\text{Drl}}$ ) assigned to the libration of NC-Bz molecules in cages formed by other molecules had a small negative value of  $-0.2$ , which is rather different from the value, ca. 0.47, determined in the Br-Bz system. Because the Kirkwood factor,  $g_{\text{K}}$ , calculated from the  $\epsilon_0$  and  $\epsilon_{\infty}$  values via eq 2 is meaningful only in a frequency range lower than HDO modes, ca.  $\omega < 10^{13} \text{ s}^{-1}$ , taking the same  $g_{\text{K}}$  value in a frequency range of the librational DHO mode does not make sense. At present, although the  $g_{\text{K}}$  values effective in the frequency range of the librational DHO mode are not known for both Br-Bz and NC-Bz, the values should not be so different from each other. Here, we assume the relationship  $g_{\text{K}} = 0.1$ , which means anticipated strong intermolecular orientational correlation in the antiparallel dipole configuration in the libration mode of both the systems; then the static correlation factor,  $g_{\text{L}}N \sim -0.85$ , is obtained for both the system. The negative  $g_{\text{L}}N$  value reveals that the libration mode in the system is correlated in antiparallel in the viewpoint of molecular plane orientation irrespective of magnitudes of dipole moments of molecules. However, this result is contrary to the fact that X-ray diffraction experiments<sup>39</sup> and quantum chemical calculations<sup>44</sup> manifested that the intermolecular dimeric associations of NC-Br molecules formed in the pure liquid state possess *antiparallel dipole* and *parallel molecular plane* configuration. Consequently, such an

estimation method of the correlation factor,  $g_{\text{L}}N$ , quite useful in DR modes is not probably available in librational DHO modes.

A DHO mode of  $\tau_{\text{Lr2}}$  found only in DRS, but not in DE measurements, is explained by the presence of librational molecular motion without alternation of electric dipole moments. Because the intermolecular dimeric associations in the antiparallel configuration do possess zero total dipole moment, the librational motion of the dimers does not show any dielectric dispersion. In the case of the Br-Bz system, a small amount of intermolecular dimeric associations also present with a short lifetime close to  $\tau_{\text{Dd1}} = 2.2 \text{ ps}$  at  $20^\circ\text{C}$  (Figure 1a), while a DHO mode corresponding to the mode of  $\tau_{\text{Lr2}}$  found in the NC-Bz system was not observed clearly. The short lifetime and a low population of the dimers should be the reason for the absence of the additional DHO mode,  $j = 2$ , in the DRS spectrum of the Br-Bz system in the pure liquid state.

## CONCLUSIONS

Most bromobenzene (Br-Bz) molecules rotate freely over a temperature range from  $10$  to  $60^\circ\text{C}$  showing a Kirkwood correlation factor close to  $g_{\text{K}} = 1.0$  at dielectric Debye-type relaxation times, e.g.,  $\sim 18 \text{ ps}$  at  $20^\circ\text{C}$ , identical to microscopic dielectric relaxation times evaluated from  $T_1$   $^{13}\text{C}$  NMR data. A small amount of dimeric intermolecular associations of Br-Bz molecules forms in an antiparallel configuration of dipole moments. However, since the lifetime of the dimer is shorter than the rotational relaxation time of monomeric Br-Bz molecules, the rotational relaxation time of Br-Bz molecules is observed as the longest dielectric relaxation time. On the other hand, benzonitrile (NC-Bz) molecules form stable dimers in the antiparallel dipole configuration at a population much higher than that of Br-Bz molecules because of a markedly greater dipole moment than that of Br-Bz. In NC-Bz, a major dielectric relaxation mode resulted from the dissociation process of the dimer was observed as the slowest mode, and the other minor dielectric relaxation mode assigned to rotational relaxation of individual monomeric NC-Bz molecules was observed. The formation of dimers in an antiparallel configuration is responsible for the observed small  $g_{\text{K}}$  values, ca. 0.5. Because relatively broad resonant-type dielectric dispersions were observed at characteristic times, e.g.,  $\sim 0.15 \text{ ps}$  at  $20^\circ\text{C}$ , in both the systems, these resonance-type dielectric dispersions were assigned to librational motions of individual molecules in cages formed by other molecules. Additional resonant-type much broad molecular motion was found only in the NC-Bz system by using a depolarized Rayleigh scattering technique at characteristic times, e.g.,  $\sim 0.22 \text{ ps}$  at  $20^\circ\text{C}$ , which was attributed to librational motions of intermolecular dimers possessing no dipole moment due to antiparallel configuration.

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### Notes

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