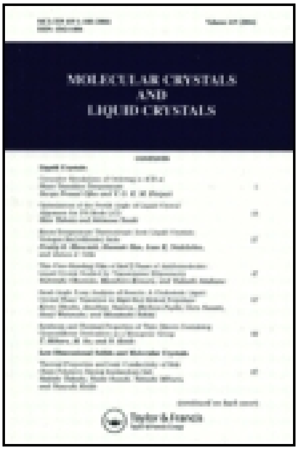

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

An NMR Study of the Smectic-A <—> Nematic Phase Transition of Alkyl Cyanobiphenyl

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To cite this article: H. Yoshida (1995): An NMR Study of the Smectic-A <—> Nematic Phase Transition of Alkyl Cyanobiphenyl, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 259:1, 55-74

To link to this article: http://dx.doi.org/10.1080/10587259508038673

Mol. Cryst. Liq. Cryst., 1995, Vol. 259, pp. 55–74
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An NMR Study of the Smectic-A ⟨–⟩ Nematic Phase Transition of Alkyl Cyanobiphenyl

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(Received May 6, 1994; in final form June 27, 1994)

The author reports for the first time that a critical feature arising from the fluctuations of the order parameter in the smectic-A ⟨–⟩ nematic (Sm-A ⟨–⟩N) phase transitions of 4-cyano-4′-n-octylbiphenyl (8CB) and 4-cyano-4′-n-nonanylbiphenyl (9CB) can be clearly observed from nuclear magnetic resonance (NMR) ^{13}C T_1 (spin-lattice) and T_2 (spin-spin) relaxation times.

By postulating that the Sm-A ⟨–⟩N phase transition is similar to the lambda transition in helium, and applying a static scaling relation to the correlation function, we show that the phase of the order parameter in both the Sm-A and N phases plays an identical role near the transition. The relaxation rates $(T_2)^{-1}$ against the reduced temperature in both the Sm-A and N phases exponentially diverge near the transition, while $(T_1)^{-1}$'s remain a constant. In fact the logarithmic plots of $(T_2)^{-1}$ versus the reduced temperature indicate being linearly increased near the transition. This fact suggests that we can study the critical phenomena on the Sm-A ⟨–⟩N phase transition by means of NMR techniques. Both critical exponents of the correlation lengths (ξ) in 8CB and 9CB are determined from these ^{13}C T_1 and T_2 relaxation times. The critical exponents for the correlation lengths, ξ, both in the Sm-A and N phase transitions of 8CB have been estimated as $\nu = \nu' = 1/2$, whose values are in accordance with the previous result in cyano-^{13}C T_1, T_2 for 8CB within experimental errors [H. Yoshida, *Phys. Lett. A*, **172**, 267 (1993)]. This result is consistent with the symmetry of the mean-field approximation.

On the other hand, the critical exponent for 9CB did not satisfy $\nu = \nu' = 1/2$, and showed somewhat smaller values ($\nu = \nu' = 0.45$) both in the Sm-A and N phases. These critical exponents for 8CB and 9CB do not satisfy de Gennes's prediction. These critical exponents are determined for the properties of particular atoms constituting the biphenyl core parts, which do not contain a flexible alkyl end-chain. But it should be noted that the exponents of 8CB and 9CB including both the core part and the flexible alkyl end-chain have been reported previously.

Keywords: NMR, relaxation times (T_1, T_2), phase transition, critical exponents, n-alkyl cyanobiphenyl

I. INTRODUCTION

The dynamic properties between the smectic-A and nematic (Sm-A and N) phases of liquid crystals have attracted considerable theoretical and experimental attention. Theoretical models of these phase transitions have been proposed, and it has been discussed[1,2] whether they are first order or second order phase transitions. The transition properties have been reported theoretically by de Gennes[3] on the basis that the free energy density between the Sm-A and N phases is isomorphic to that of the Ginzburg-Landau model of superconductivity.[4,5] Liquid crystals also have experimentally provided important information on the role of order-parameter symmetry and spatial dimensionality[6] at the Sm-A ⟨–⟩N phase transition, because no true long range order exists in the Sm-A phase,[7] and since these mesophases have been shown to be different universal classes for the critical exponent at the Sm-A ⟨–⟩N phase transition. Therefore, there has been considerable experimental investigation of the phase transition properties by X-ray scattering,[8–10] light scattering,[10,11] and calorimetric measurements,[12–14] etc.

In the past, the diffusive optical soft modes in the nematic phase described by order-director fluctuations have been studied by means of NMR techniques,[15,16] while the soft modes corresponding to the short range order fluctuations in the isotropic phase have also been examined by various kinds of measurements.[17–20] As pointed out by Blinc *et al.*,[21] and as reported by Dong and Tomchuck,[15] the diffusive optical soft modes in the nematic phase near the isotropic phase transition have been observed by NMR relaxation measurements. The NMR technique is a powerful tool to directly investigate both the critical dynamics near the phase transition and the properties of particular atoms constituting the compounds. Therefore the core part and the flexible alkyl end-chain can be individually observed by NMR technique. On the other hand, the properties of phase transitions other than those of the nematic ⟨–⟩ isotropic phase have not been studied by NMR measurements.

In a recent paper,[22] the author has reported that the critical behavior near the Sm-A⟨–⟩N phase transition can be observed from the carbon-13 spin-lattice and spin-spin relaxation times denoted as ^{13}C T_1 and T_2 by means of the NMR technique, and that the critical exponent for the correlation length can be determined by using the results. By postulating that the transition in the Sm-A ⟨–⟩N phase is similar to the lambda transition in helium, the phase of order parameter $|\Psi|$ near the transition plays an identical role in both the Sm-A and N phases under a scaling relation. It will be reported in this paper that both the critical exponents for the correlation lengths in 8CB and 9CB near the Sm-A ⟨–⟩N phase transition temperatures can be theoretically and experimentally determined by NMR measurements, and that 8CB and 9CB show different critical exponents for the correlation lengths.

II. THEORETICAL BACKGROUND

In this section, it will be described how to estimate the critical exponent for the correlation length near the Sm-A ⟨–⟩N phase transition by using the ^{13}C T_1 and T_2 relaxation times obtained from NMR measurements according to Ref..[15,16]

The Sm-A order parameter is described by the amplitude of a one dimensional density wave whose wave vector q_0 is parallel to the nematic director (n). Hence, the density distribution function is written as follows;

$$\rho(r) = \rho_0 \left[1 + R_e|\Psi(r)|e^{-iq_0 z}\right] \tag{1}$$

where $d = 2\pi/q_0$ is the smectic layer spacing, $|\Psi(r)| = |\Psi|e^{-iq_0 u}$ corresponds to a complex two-component order parameter and $q_0 u$ represents the phase of $|\Psi|$ whose u is the displacement of the smectic layers in the z-direction (z is normal to the smectic layers). The order-parameter near the Sm-A ⟨–⟩N phase transition temperature (T_c) can be expanded according to the Ginzburg-Landau form.[4,5] The symmetry properties of

$|\Psi|$ has enabled de Gennes to propose a free energy density of the Landau-Ginsburg form near the Sm-A ⟨–⟩ N phase transition;[6]

$$\Delta f = A_0|\Psi|^2 + \frac{1}{2}B_0|\Psi|^4 + \cdots + (\nabla\cdot\Psi^* + iq_0\,\delta n\Psi^*)\frac{1}{2M}(\nabla\cdot\Psi - iq_0\,\delta n\Psi)$$
$$+\frac{1}{2}[K_1(\nabla\cdot n)^2 + K_2(n\cdot\nabla\times n)^2 + K_3(n\times\nabla\times n)^2]$$
$$= \Delta f_{(GL)} + \Delta f_{(F)} \tag{2}$$

where $\Delta f_{(F)}$ stands for the elastic free energy density in the presence of elastic distortion. K_1, K_2 and K_3 are the splay, twist, and bend Frank elastic constants, δn represents the local director fluctuation, and Δf represents the free energy density. In the Sm-A phase, $\langle|\Psi|\rangle = (-A_0/B_0)^{1/2}$. If we assume that $\langle|\Psi|\rangle$ would be spatially uniform, then the free energy density in Equation (2) becomes,[10]

$$\Delta f = 1/2\{-A_0^2/B_0 + B(\partial u/\partial z)^2$$
$$+ D[(n_x + \partial u/\partial x)^2 + (n_y + \partial u/\partial y)^2] + K_1[(\partial n_x/\partial x)$$
$$+ (\partial n_y/\partial y)]^2 + K_2[(\partial n_y/\partial x) - (\partial n_x/\partial y)]^2$$
$$+ K_3[(\partial n_x/\partial z)^2 + (\partial n_y/\partial z)^2]\}. \tag{3}$$

Taking the Fourier transform of Equation (3), and applying the equipartition theorem, we can lead to expressions for the mean squared fluctuations in the phase of $|\Psi|$ and the director (n_0). If we choose the wave vector q to be along the x–z plane and n_0 to lie in the z-axis, we obtain equations as below;[6]

$$\langle|\Psi(q)|^2\rangle = kT/2V[A_0 + q_z^2/2M_V + (q_x^2 + q_y^2)/2M_T]; \quad T > T_c \tag{4a}$$

$$\langle n_x^2(q)\rangle = kT/[K_1q_x^2 + K_3q_z^2]; \quad T > T_c$$
$$= kT/[K_1q_x^2 + B(q_z/q_x)^2]; \quad T < T_c \tag{4b}$$

$$\langle n_y^2(q)\rangle = kT/[K_3q_z^2 + K_2q_x^2]; \quad T > T_c$$
$$= kT/[D + K_2q_x^2 + K_3q_z^2]; \quad T < T_c \tag{4c}$$

where the coefficients $B = |\Psi|^2q_0^2/M_V$ and $D = |\Psi|^2q_0^2/M_T$ correspond to the restoring forces for fluctuations in the phase of $|\Psi|$ and fluctuations in molecular orientation away from the normal to the layer, respectively. Equation (4) with $B = D = 0$ describes the usual director fluctuations in the nematic phase. The presence of fluctuations in the smectic-A phase short range order modulates the Frank elastic constant.

In the mean-field theory, the free energy density of Equation (2) yields correlation lengths near the N phase as follows;

$$\xi_{\parallel}^2 = 1/2A_0M_V; \quad \xi_{\perp}^2 = 1/2A_0M_T \tag{5}$$

where $\xi_{\parallel}$ and $\xi_{\perp}$ are the longitudinal and transverse correlation lengths. V is the volume of the sample, and A_0 is proportional to $T - T_c$ in the mean-field theory.

In the N phase, we can obtain Equation (4a) by including the second order space variation of $|\Psi|$ in $\Delta f_{(GL)}$. Whereas by postulating that the fluctuations of $\langle|\Psi|\rangle$ are similar to the lambda transition in helium,[23] it has been reported that the phase of the order parameter played an identical role in both the Sm-A and N phases.[24] Then, we can obtain $A_0 \simeq \xi^{-2+\zeta}$, and $1/M_V$, $1/M_T \simeq \xi^{\zeta}$ near the transition where ζ means the departure of the correlation function at the critical point from the prediction of the Ornstein-Zernicke theory. Applying a static scaling relation to the correlation function $\langle|\Psi(q)|\rangle$, then we can obtain a homogeneous function $q^p\Gamma(q, \xi)$; that is, $\langle|\Psi(q)|\rangle = q^p\Gamma(q, \xi)$, and this functional equation must be either identical zero or else a simple power of form, where the parameter p is generally called the degree of homogeneity.[25] Because of $\xi \simeq -\varepsilon^{-\nu}$ at $T < T_c$, $\xi' \simeq \varepsilon^{-\nu'}$ at $T > T_c$, and $\langle|\Psi(q)|\rangle \simeq q^{-2+\zeta}$ at $T = T_c$, we obtain the relation of critical exponents as follows, $\nu = \nu'$ as $\varepsilon \to 0^-$ $(T < T_c)$, $\varepsilon \to 0^+$ $(T > T_c)$ where $\varepsilon = |(T - T_c)|/T_c$ means a reduced temperature. That is, according to the static scaling hypothesis which asserts that the free energy is a generalized homogeneous function, the phase of the order parameter $\langle|\Psi(q)|\rangle$ near the critical point plays an identical role in both the Sm-A and N phases providing that Γ and q are scaled appropriately. Therefore, the scaling hypothesis enables us to have an identical correlation function in Equation (4a) in both the Sm-A and N phases near the critical point, and the critical exponents show the same values in both the Sm-A and N phases. However, in the case of Sm-A phase, we must include the fourth order space variation of $|\Psi|$ in $\Delta f_{(GL)}$, considering that $|\Psi|$ has a finite equilibrium value $(\Psi_0^2 = -A_0/B_0)$ in the Sm-A phase. Hence, we will substitute $2|A_0|$ for A_0 in Equation (4a) in the Sm-A phase. If the gaugelike coupling of $|\Psi|$ to n is taken into account, the Sm-A $\langle\text{-}\rangle$N phase transition will be a weak first order.[26] To estimate the relaxation data, however, we concentrate only on the correlation function $\langle|\Psi(q)|\rangle$; that is, fluctuations of the order parameter in Equation (4a).

NMR measurements have characteristic merits as compared with other tools, though they cannot provide two different correlation lengths observed from X-ray scattering, so we assume $q_z^2 \simeq q_x^2 + q_y^2 (\equiv q^2)$ and $1/AM_V \simeq 1/AM_T \equiv \bar{\xi}^2$, and then Equation (4a) is rewritten as follows;

$$\langle|\Psi(q)|^2\rangle = \frac{kT}{2VA_0(1 + \bar{\xi}^2 q^2)}. \tag{6}$$

It should be noted that Equation (6) is similar to the equation in the nematic phase near isotropic phase transition which is derived by Dong and Tomuchuk.[15] Therefore, we can lead to the relaxation equation

$$\begin{aligned} \frac{\partial\langle|\Psi(q)|\rangle}{\partial t} &= -\tau_q^{-1}\langle|\Psi(q)|\rangle = -\frac{1}{\eta}\cdot\frac{\partial\Delta f_{(GL)}}{\partial\langle|\Psi(q)|\rangle} \\ &\simeq -A_0|\Psi|/\eta \qquad (T > T_c) \\ &\simeq -2|A_0|\cdot|\Psi|/\eta \qquad (T < T_c) \end{aligned} \tag{7}$$

where η is the viscosity or diffusion constant for the nematic or the smectic phase, and $\tau_q = \eta/A_0(1+\bar{\xi}^2 q^2)$, $\eta/2|A_0|(1+\bar{\xi}^2 q^2)$ in the N and Sm-A phases, respectively. The relaxation rate increases infinitely in the vicinity of the phase transition temperature as T_c is approached because of $A_0 \propto |T - T_c|^\nu$ near the transition; i.e. critical slowing down of the optical soft mode. Physically, the diffusive optical soft modes describe fluctuations of the order parameters and condense at the stability limit T^+ or T^*, that is, T^+ and T^* mean the critical temperatures at the stability limits of the Sm-A and N phases, respectively. And ν, ν' are critical exponents for the correlation lengths in the Sm-A and N phases, respectively.

The following spin-lattice (T_1) and spin-spin (T_2) relaxation rates in the laboratory frame originate from fluctuations in the magnetic dipolar interaction of a spin-1/2 pair;

In the case of non-protonated ^{13}C;

$$(T_1)^{-1} = (9\gamma_C^4 \hbar^2/8r_{CC}^6)\,[J^{(1)}(\omega_C) + J^{(2)}(2\omega_C)] \tag{8}$$

$$(T_2)^{-1} = (9\gamma_C^4 \hbar^2/8r_{CC}^6)\,[\tfrac{1}{4}J^{(0)}(0) + \tfrac{5}{2}J^{(1)}(\omega_C) + \tfrac{1}{4}J^{(2)}(2\omega_C)] \tag{8$'$}$$

where r is the fixed C–C internuclear distance and ω_C is ^{13}C's Larmor frequency (67.9 MHz). γ_C is the gyromagnetic ratio for ^{13}C, and $J^{(i)}$ (ω) stands for the spectral density. Considering the facts that the relaxation process for non-protonated carbon is mainly originated from the resonance frequency (ω_C), and the temperature dependence of FWHM in the non-protonated C_5 carbon is nearly equal to the true $(T_2)^{-1}$, the relaxation process is considered to be stemmed from the ^{13}C–^{13}C nuclear interactions. For the protonated ^{13}C,

$$\begin{aligned}(T_1)^{-1} = (\gamma_C^2\gamma_H^2\hbar^2/8r_{CH}^6)[\tfrac{1}{2}J^{(0)}(\omega_H-\omega_C) + 9J^{(1)}(\omega_C)\\ + \tfrac{9}{2}J^{(2)}(\omega_H+\omega_C)]\end{aligned} \tag{9}$$

$$\begin{aligned}(T_2)^{-1} = (\gamma_C^2\gamma_H^2\hbar^2/8r_{CH}^6)[J^{(0)}(0) + \tfrac{1}{4}J^{(0)}(\omega_H-\omega_C) + 9J^{(1)}(\omega_H)\\ + \tfrac{9}{2}J^{(1)}(\omega_C) + \tfrac{9}{4}J^{(2)}(\omega_H+\omega_C)]\end{aligned} \tag{9$'$}$$

where r_{CH} is the fixed C–H internuclear distance, ω_H is ^{1}H's Larmer frequency (270 MHz), and γ_H is the gyromagnetic ratio for ^{1}H. The relaxation process of the protonated carbon is a sum of the C–H nuclear interactions. According to Dong and Tomuchuk,[15] we can obtain the following spectral densities:

$$J^{(M)}(M\omega) = \frac{M^2}{3\sqrt{2}\pi}\cdot\frac{kT\sqrt{\eta\cdot\tau_0}}{L^{3/2}}[\kappa(0,M)]^2 x[1+(1+M^2\omega^2\tau_0^2)^{1/2}]^{-1/2} \tag{10}$$

$$J^{(0)}(2\omega') = \frac{\sqrt{2}}{\pi}\cdot\frac{KT\sqrt{\eta\cdot\tau_0}}{L^{3/2}}[\kappa(0,0)]^2 x[1+(1+4\omega'^2\tau_0^2)^{1/2}]^{-1/2} \tag{11}$$

$$\kappa(0,M) = \langle D_{0M}^2 D_{M0}^{2*}\rangle - \langle D_{kM}^2\rangle\delta_{k,0}\delta_{M,0} \tag{12}$$

where τ_0 is $\tau_{q=0}$, $M = 0$, 1 or 2, D^1_{mn}: Wigner's rotation matrix, and $\langle\cdots\rangle$: orientational average.[27] L is an elastic constant in the Sm-A or N phase, which corresponds to $M_V^{-1} \simeq M_T^{-1} (\equiv M^{-1})$ in Equation (2). And ω' represents the locking frequency in the rotating frame. If $\omega' = 0$, we can obtain the spectral density, $J^{(0)}(0)$, appearing in the T_2 relaxation time.

III. EXPERIMENTAL SECTION

The samples of 4-cyano-4'-n-octylbiphenyl (8CB), and 4-cyano-4'-n-nonanylbiphenyl (9CB) used in this work were purchased from Merck Japan Ltd. and were used without further purification. 8CB exhibited smectic-A $\langle-\rangle$ nematic $\langle-\rangle$ isotropic phase transitions at 21.5°C $\langle-\rangle$33.5°C $\langle-\rangle$40.5°C, while those for 9CB occurred at 42.0°C$\langle-\rangle$ 47.9°C$\langle-\rangle$49.5°C. These specimens were sealed in 5 mm OD tubes.

All measurements of ^{13}C T_1(spin-lattice) and T_2 (spin-spin) relaxation times were carried out on a JEOL-GSXW 270 pulse FT NMR spectrometer, operating at 67.9 MHz with a deuterium internal lock system.

The T_1 and T_2 measurements were performed without sample spinning by using the inversion-recovery pulse sequence $(-\pi-\tau-\pi/2-)$, and the Carr- Purcell–Meiboom–Gill pulse sequence $(-\pi/2-[-\tau-\pi-]_n-\tau-)$, respectively. The relaxation experiments were carried out by 10 T_1 waiting time for both the non- and protonated carbons. The T_1's were obtained after averaging 150 FID signals, and the T_2's were acquired after averaging 300 FID signals both in the smectic-A and nematic phases. The data were treated with linear-least-square fits after carrying out the Fourier transfer.

The temperature in the samples was controlled within an accuracy of ± 0.05°C in the smectic-A and nematic phases, whose temperatures were determined by a copper–constantan thermocouple inserted into the samples. And the experiments were performed after reaching enough thermo-equilibria.

IV. RESULTS AND DISCUSSION

The para-^{13}C T_1 and T_2 in the smectic-A and nematic (Sm-A and N) phases of 8CB as functions of temperature are shown in Figure 1, where para-^{13}C represents non-protonated carbons designated as C_1, C_4, C_5, and C_8. Also ortho-^{13}C stands for protonated carbons of C_2, C_3, C_6 and C_7, as illustrated in Figure 2. T_1 is nearly independent of temperature in both the Sm-A and N phases, while the T_2's are constant until ~ 32.5°C and monotonously decrease as the temperature approaches T_c in the Sm-A phase. And a monotonous decrease in the T_2's is also found in the N phase as T_c is approached, where T_c means the Sm-A $\langle-\rangle$N phase transition temperature. The critical behavior of 8CB and 9CB near T_c is similar to that of proton $T_{1\rho}$ in the rotating frame which has been observed from PAA near T_{NI}, and the critical slowing down of the optical soft mode has been suggested.[15] However, the values of T_2's in this work are much smaller than those of $T_{1\rho}$. Dong and Tomchuk have pointed out in their paper[15] that the order-director fluctuations give only a nonzero $J^{(1)}(\omega)$ when the

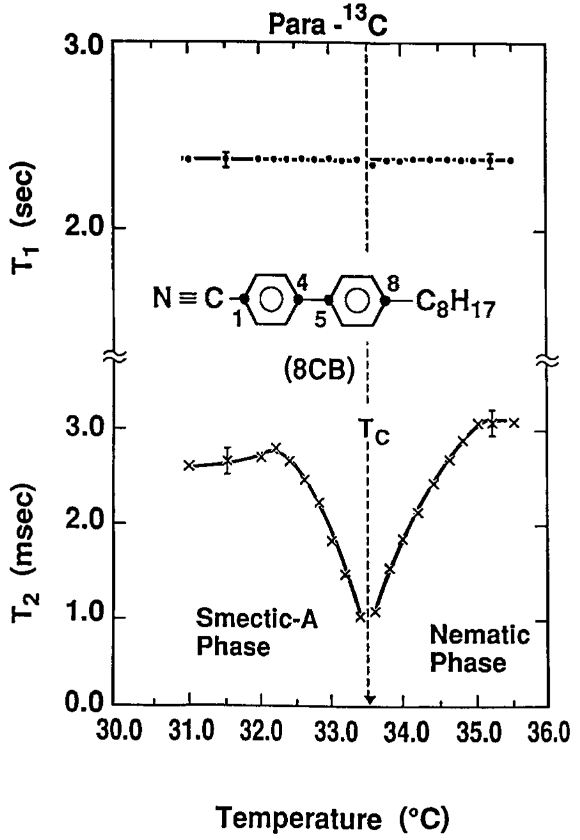

FIGURE 1 Mean values of C_1, C_4, C_5 and C_8 para-^{13}C T_1 and T_2 relaxation times in smectic-A and nematic phases of 8CB versus temperature.

director is aligned with the external magnetic field and thus $T_1/T_{1\rho} = 5/2$. According to Ref. [28], and as previously reported,[22] however, the relaxation rates should be dependent on all spectral densities. That is, it will not be necessary that T_1 equals $5/2 \cdot T_{1\rho}$ or $5/2 \cdot T_2$ even if the director is parallel to the external magnetic field. This fact demonstrates that the temperature dependence of the spectral full width at half maximum (FWHM) for the representative C_5 carbon arising from only a spectral density of $J^{(0)}(0)$ is qualitatively in agreement with the behavior of true $(T_2)_t$'s, as shown in Figure 3, where $\Delta\omega_{1/2}$ (FWHM) $= (T_2)_t^{-1} = (\pi T_2)^{-1}$. Hence, we can obtain the spectral densities as follows;

$$J^{(0)}(0) \propto [\kappa(0,0)]^2 T\eta\bar{\xi}/L^2 \tag{13}$$

and

$$J^{(M)}(\omega) \propto [\kappa(0,0)]^2 T(\eta/L)^{1/2}\omega^{-1/2} \tag{14}$$

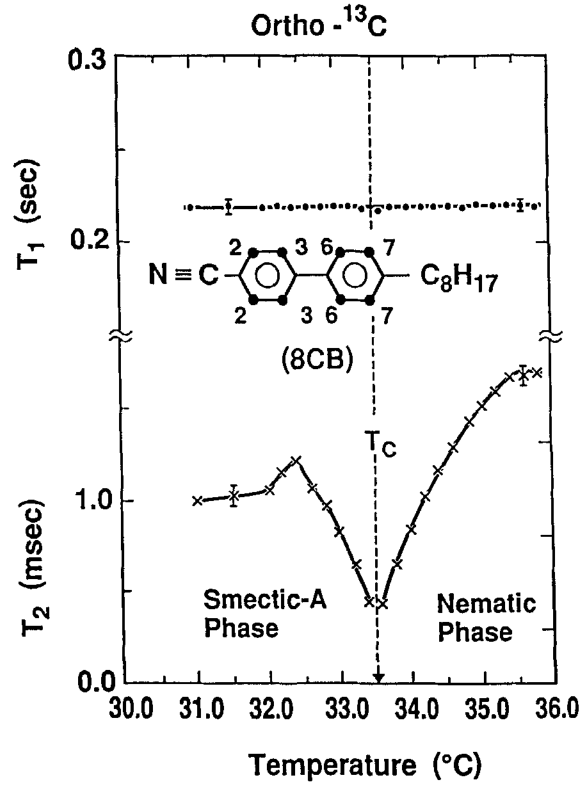

FIGURE 2 Mean values of C_2, C_3, C_6 and C_7 ortho-^{13}C T_1 and T_2 relaxation times in smectic-A and nematic phases of 8CB versus temperature.

where $M = 0, 1$ or 2 and $\omega = 1/2\,(\omega_H - \omega_C), \omega_C, 2\omega_C$ or $\omega_H + \omega_C$. Here, we find that the correlation length (ξ) appears only to the $J^{(0)}$ (0) term as seen in Equation (13). In fact, the relaxation rates $(T_2)^{-1}$ in 8CB against the reduced temperature in both the Sm-A and N phases exponentially diverge near the phase transition as shown in Figures 4(a) and 4(b), while $(T_1)^{-1}$'s are independent of the temperature. And the logarithmic plots of $(T_2)^{-1}$'s as a function of reduced temperature show to be linearly increase as shown in Figures 5(a) and 5(b). This fact suggests that NMR relaxation measurements enable us to study the critical phenomena on the Sm-A <-> N phase transition. In the case of ^{13}C T_1 and T_2, the measured T_1 and T_2 contain mainly an intramolecular contribution although the relaxation processes are mixed with the C–H nuclear interactions, i.e., intermolecular contribution is negligible for ^{13}C T_1 and T_2, while the protons T_1 and T_2 or $T_{1\rho}$ contain both intra- and intermolecular contributions so that intermolecular interaction considerably contributes to T_1 and $T_{1\rho}$.[26] In the case of the ^{13}C relaxation rates, therefore, we can safely assume $(T_1)_a^{-1} \gg (T_1)_r^{-1}$ and $(T_2)_a^{-1} \gg (T_2)_r^{-1}$, where the subscripts of "a" and "r" represent the intra- and intermolecular interactions, respectively. Thus,

$$(T_1)^{-1} \simeq (T_1)_a^{-1}, \quad (T_2)^{-1} \simeq (T_2)_a^{-1} \tag{15}$$

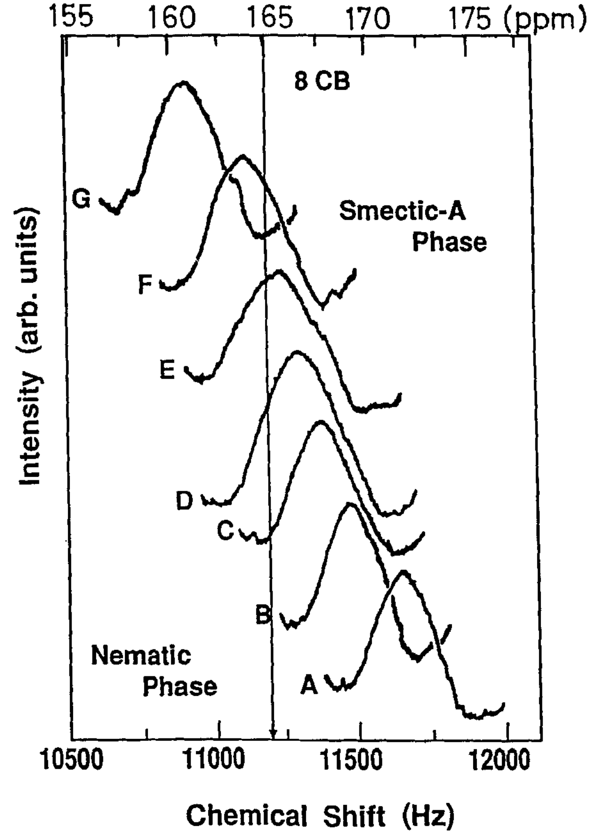

FIGURE 3 Temperature dependence of full width at half maximum (FWHM) and chemical shift for representative C_5 carbon in resolution of 2.82 Hz. (**A**): 240 ± 20 Hz at 31.5°C, (**B**): 210 ± 15 Hz at 32.0°C, (**C**): 250 ± 20 Hz at 32.5°C, (**D**): 330 ± 30 Hz at 33.0°C, (**E**): 390 ± 30 Hz at 33.3°C, (**F**): 290 ± 30 Hz at 34.0°C and (**G**): 250 ± 25.0 Hz at 34.5°C.

When Equations (13) and (14) are substituted into Equations (8) and (8′), and subsequently using Equation (15), we can obtain

$$(T'_2)_a^{-1} \simeq (T_2)_a^{-1} - f(s)(T_1)_a^{-1} = (9\gamma_C{}^4\hbar^2/32r_{CC}^6)J^{(0)}(o) \qquad (16)$$

where

$$f(s) = \frac{\frac{5}{2} + (1 - \frac{5}{4}S)^2/\sqrt{2}}{1 + 4(1 - \frac{5}{4}S)^2/\sqrt{2}},\ S(\equiv |\Psi| \text{ in Equation (2)})$$

$(T_2)_a^{-1} \gg f(s)(T_1)_a^{-1}$ are both in the Sm-A and N phases, hence we can approximate Equation (16) as follows,

$$(T'_2)_a^{-1} \simeq (T_2)_a^{-1} \simeq (9\gamma_C{}^4\hbar^2/32r_{CC}^6)J^{(0)}(0) \qquad (17)$$

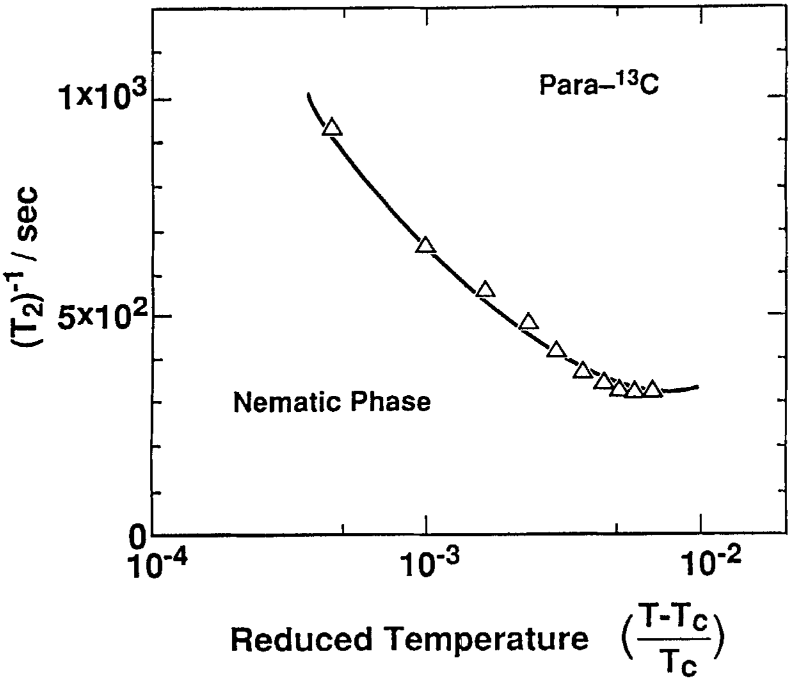

FIGURE 4(a) Plots of relaxation rates $(T_2)^{-1}$ against reduced temperature in the nematic phase of 8CB.

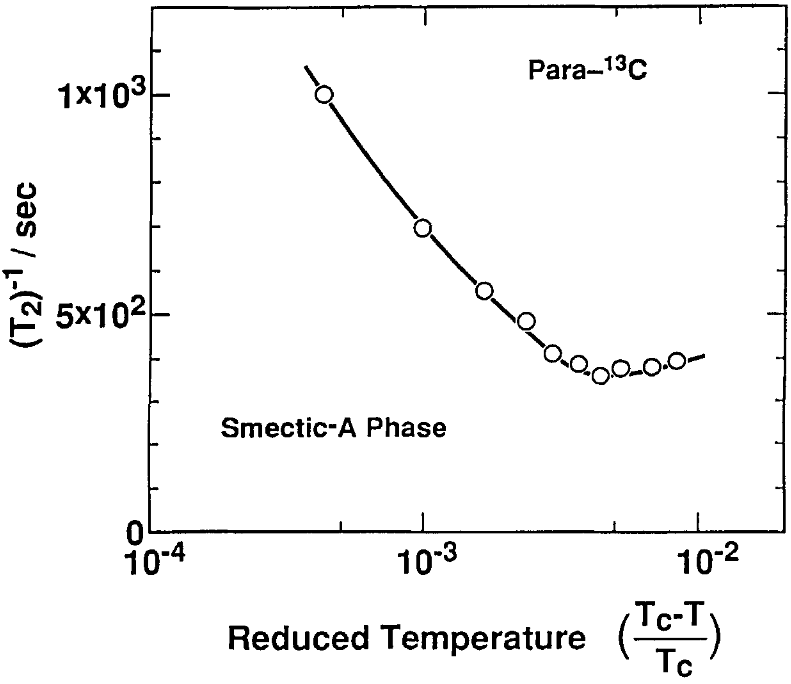

FIGURE 4(b) Plots of relaxation rates $(T_2)^{-1}$ against reduced temperature in the smectic-A phase of 8CB.

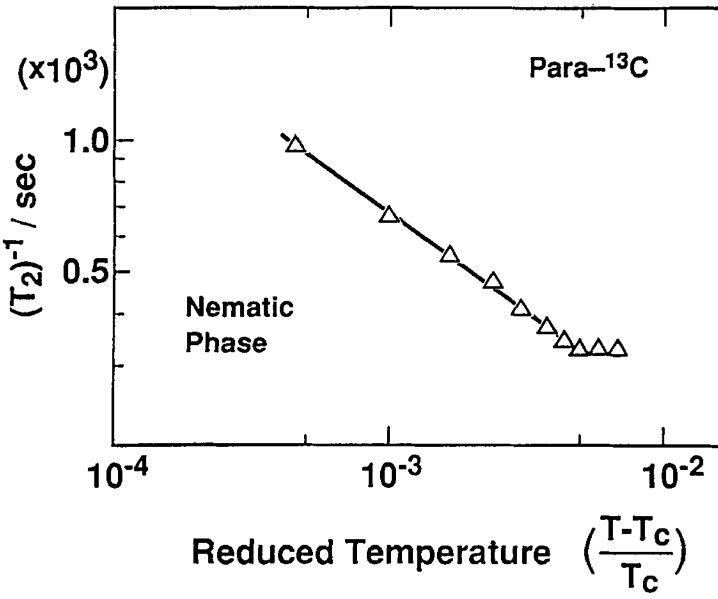

FIGURE 5(a) Logarithmic plots of relaxation rates $(T_2)^{-1}$ as a function of reduced temperature in the nematic phase of 8CB.

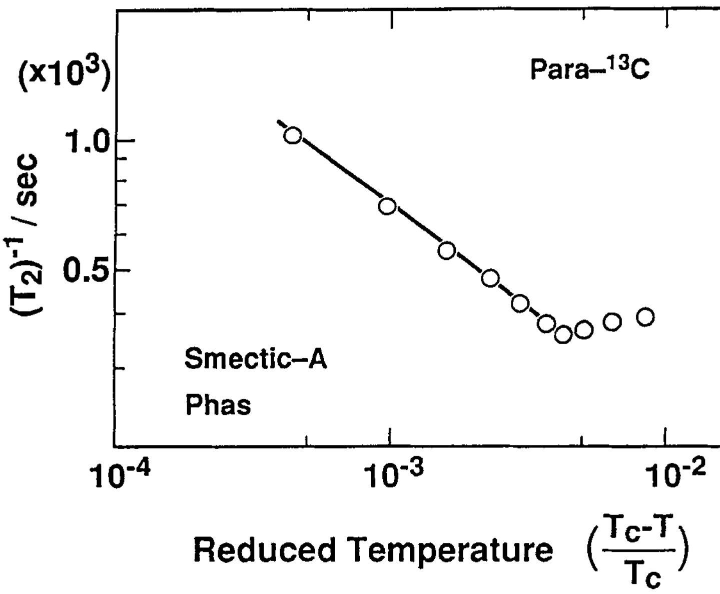

FIGURE 5(b) Logarithmic plots of relaxation rates $(T_2)^{-1}$ as a function of reduced temperature in the smectic-A phase of 8CB.

The S values used for $[\kappa(0,0)]$ are from NMR measurements of 8CB and 9CB.[30,31] Combining Equations (13) and (17) by using $\eta \propto e^{W/T}$, where W is the thermal activation energy, we obtain

$$(T'_2)_a e^{W/T}[\kappa(0,0)]^2 \propto (T^+ - T)^\nu \quad \text{(in the Sm-A phase)} \tag{18}$$

$$(T'_2)_a e^{W/T}[\kappa(0,0)]^2 \propto (T - T^*)^{\nu'} \quad \text{(in the N phase)} \tag{19}$$

where ν and ν' are the critical exponents for the correlation lengths near the Sm-A and N states, respectively. In calculating Equations (18) and (19), the activation energy ($W = 1.4\,\text{eV}$) will be adopted for the Sm-A <–> N phase transition found for another liquid crystal;[32] as far as the author knows, its values for the Sm-A and nematic phase transitions in 8CB have not yet been reported.

$(T'_2)_a$'s calculated from Equation (17) clearly show the critical behavior near T_c when T approaches T^* or T^+; then $(T'_2)_a \to 0$ as seen in Equations (18) and (19), and ξ increases infinitely at T_c, since $\xi \propto (T^+ - T)^{-1/2}, (T - T^*)^{-1/2}$. Although we cannot define clearly that this feature is the critical slowing down of the optical soft mode, the critical behavior is induced definitely from the critical phenomenon in the Sm-A <–> N phase transition.

Figures 6 and 7, respectively, show the linear-least-square fits the $(T'_2)_a$ data for $\nu = 1/2$ and $2/3$ in the Sm-A and N phases. The critical temperature of the Sm-A phase occurs at $T^+ - T_c = 0.18°\text{C}$ for $\nu = 2/3$, and at $T^+ - T_c = 0.01°\text{C}$ for $\nu = 1/2$, while the critical temperature T^* of the N phase is at $T_c - T^* = 0.18°\text{C}$ for $\nu' = 2/3$, and at $T_c - T^* = 0.02°\text{C}$ for $\nu' = 1/2$. Thus, it is reasonable that we adopt $\nu = \nu' = 1/2$ both in

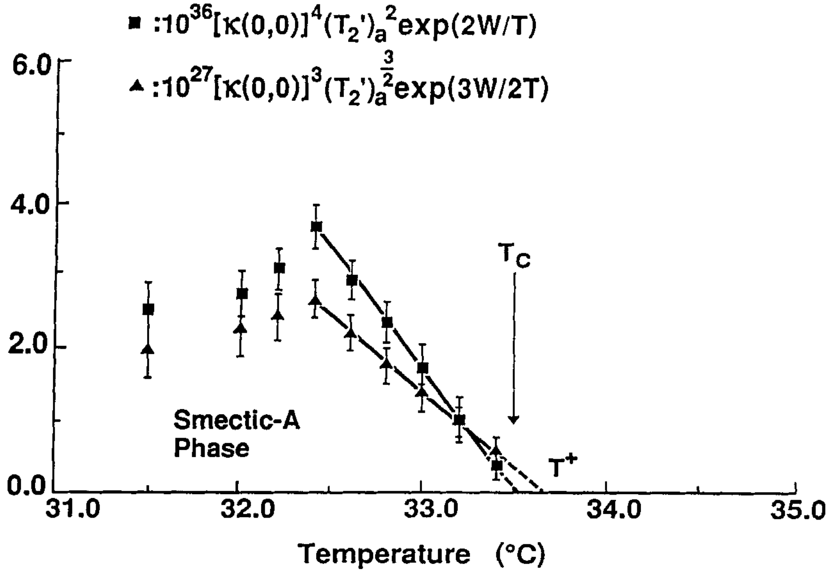

FIGURE 6 Critical temperature dependence of $[\kappa(0,0)]^4 \times (T_2')_a^2 \exp(2W/T)$ and $[\kappa(0,0)]^3 (T'_2)_a^{3/2} \exp(3W/2T)$ for para-^{13}C in smectic-A phase of 8CB.

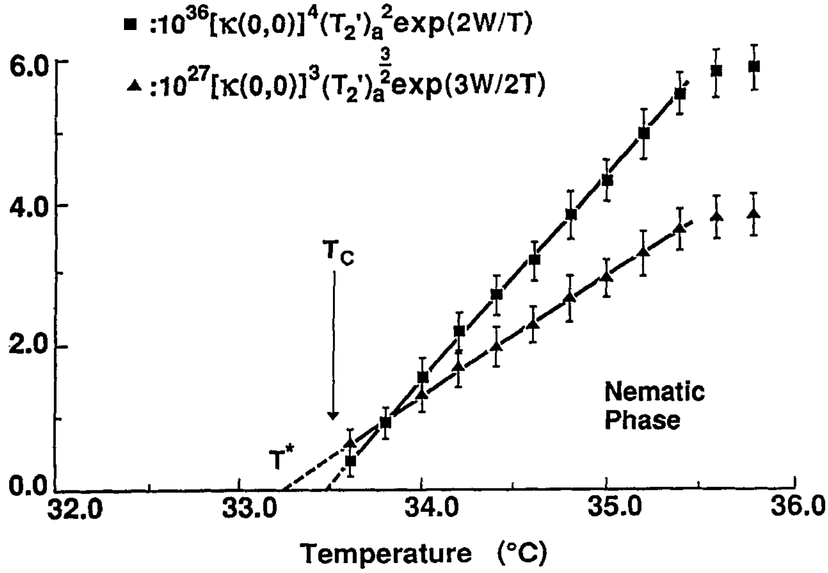

FIGURE 7 Critical temperature dependence of $[\kappa(0,0)]^4 \times (T'_2)_a^2 \exp(2W/T)$ and $[\kappa(0,0)]^3 (T'_2)_a^{3/2} \exp(3W/2T)$ for para-^{13}C in nematic phase of 8CB.

the Sm-A and N phase transitions of 8CB, considering the fact that T_c contains experimental errors within ± 0.05°C, and that the phase transition between the Sm-A and N phases which occurs at 0.01°C or higher temperature in the transition point should be theoretically and experimentally a weak first order.[26] In fact, the order parameters of 8CB show a slight discontinuity at the Sm-A<->N phase transition point.[30]

The critical exponent for the correlation length in ortho-^{13}C is also estimated by using Equations (18) and (19), because the ortho-^{13}C T_1 and T_2 rates are satisfied with Equation (15). Figure 2 shows the ortho-^{13}C T_1 and T_2 relaxation times both in the Sm-A and N phases of 8CB as a function of temperature. Also, the critical behavior is clearly shown near the Sm-A <->N phase transition. The linear-least-square fits the $(T'_2)_a$ data for $\nu = 1/2$ and $\nu = 2/3$ in the Sm-A and N phases are shown in Figures 8 and 9. In the Sm-A phase, the critical temperature dependencies of $\nu = 2/3$ and $\nu = 1/2$ are shown to be $T^+ - T_c = 0.15$°C and $T^+ - T_c = 0.02$ °C, respectively. Whereas, in the N phase, the dependence is indicated to be $T_c - T^* = 0.17$°C for $\nu' = 2/3$ and $T_c - T^* = 0.02$°C for $\nu' = 1/2$. Hence, in the case of ortho-^{13}C, we should adopt $\nu = \nu' = 1/2$ both in the Sm-A and N phases. These results are consistent with the symmetry of the mean-field prediction.

Also, the critical behavior in the para- and the ortho-^{13}C T_2 of 9CB are observed clearly in the vicinity of the Sm-A <->N phase transition temperature, as shown in Figures 10 and 11, respectively. The critical temperature dependence of the exponent in the Sm-A and N phases of 9CB can be determined in the same way as the estimation of 8CB, where we use the activation energy ($W' = 1.6$ Ev),[30] and the order parameters for

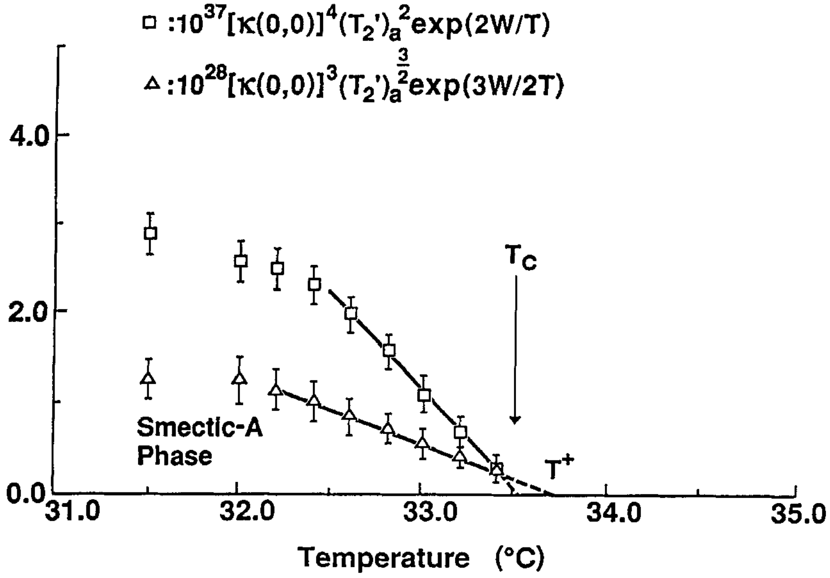

FIGURE 8 Critical temperature dependence of $[\kappa(0,0)]^4 \times (T'_2)_a^2 \exp(2W/T)$ and $[\kappa(0,0)]^3 (T'_2)_a^{3/2} \exp(3W/2T)$ for para-^{13}C in smectic-A phase of 8CB.

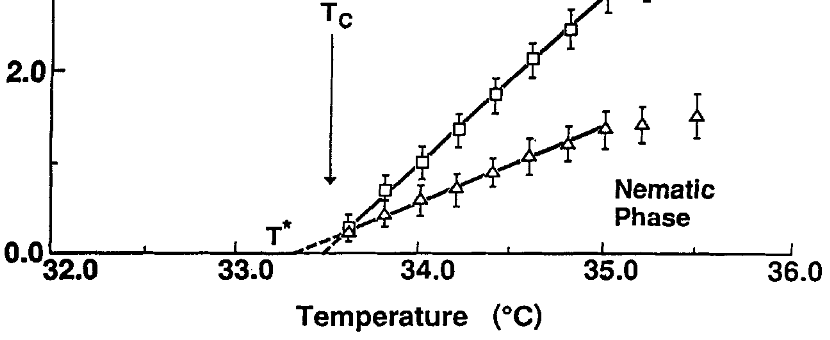

FIGURE 9 Critical temperature dependence of $[\kappa(0,0)]^4 \times (T'_2)_a^2 \exp(2W/T)$ and $[\kappa(0,0)]^{3/2} (T'_2)_a^2 \exp(3W/2T)$ for ortho-^{13}C in nematic phase of 8CB.

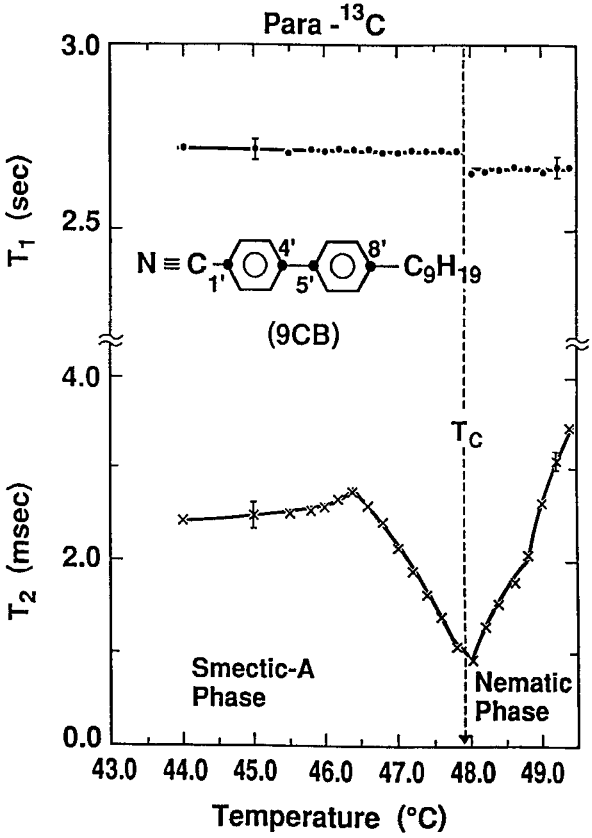

FIGURE 10 Mean values of C_1', C_4', C_5' and C_8' para-^{13}C relaxation times in smectic-A and nematic phases of 9CB versus temperature.

estimating $\kappa(0,0)$ are quoted from Ref. [31]. Figures (12–15) show the critical temperature dependence of the exponent in the para- and the ortho-positions, respectively.

In the case of para-^{13}C;

$(T^+ - T_c)^{-1/2} = 0.12°C$; $(T^+ - T_c)^{-0.45} = 0.02°C$ (in the Sm-A phase)

$(T_c - T^*)^{-1/2} = 0.08°C$; $(T_c - T^*)^{-0.45} = 0.01°C$ (in the N phase)

while, for ortho-^{13}C:

$(T^+ - T_c)^{-1/2} = 0.09°C$; $(T^+ - T_c)^{-0.45} = 0.01°C$ (in the Sm-A phase)

$(T_c - T^*)^{-1/2} = 0.28°C$; $(T_c - T^*)^{-0.45} = 0.02°C$ (in the N phase)

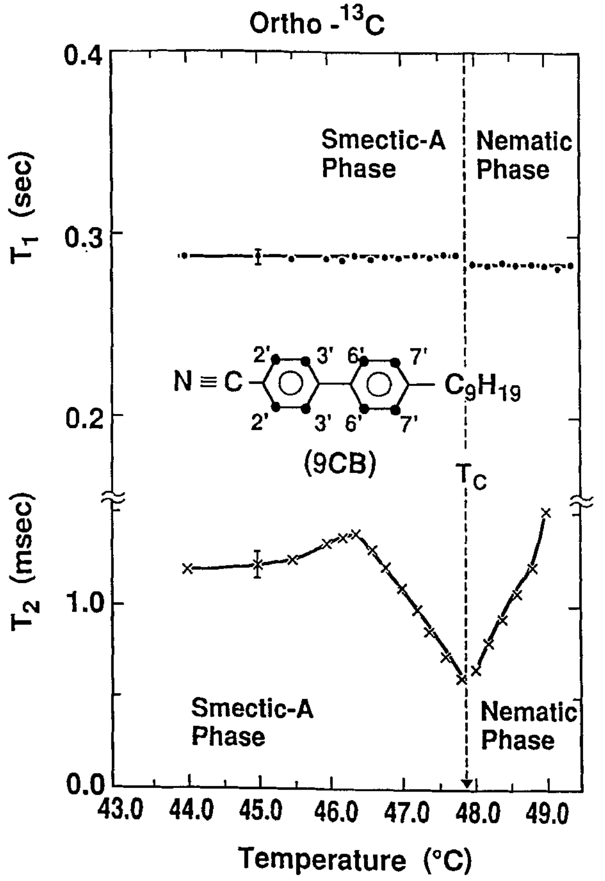

FIGURE 11 Mean values of C'_2, C'_3, C'_6 and C'_8 ortho-^{13}C relaxation times in smectic-A and nematic phases of 9CB versus temperature.

The above results lead to the conclusion that we should adopt the critical exponent of $\nu = \nu' = 0.45$ both in the para- and the ortho-^{13}C. This critical exponent is not consistent with the value of 8CB, and cannot be in agreement with any theoretically expected values although a symmetry, $\nu = \nu'$, is maintained between the Sm-A and N phases as predicted by the scaling hypothesis. The discrepancy in the universal class between the critical exponent of 8CB and that of 9CB may be responsible for the larger first-order phase transition as compared with 8CB. In fact, both the para- and the ortho-^{13}C T_1 relaxation times in 9CB are clearly discontinuous at T_c, as shown in Figures 10 and 11, so that the order parameters show a large discontinuity at the Sm-A ⟨–⟩N phase transition temperature of 9CB.[31]

In addition, it should be noted that these critical exponents are estimated from the carbon atoms composing the biphenyl core parts, which do not include a flexible alkyl end-chain in 8CB and 9CB. Hence, it may be reasonable that the critical exponents of 8CB and 9CB in this work are different from those of X-ray and DSC measurements.

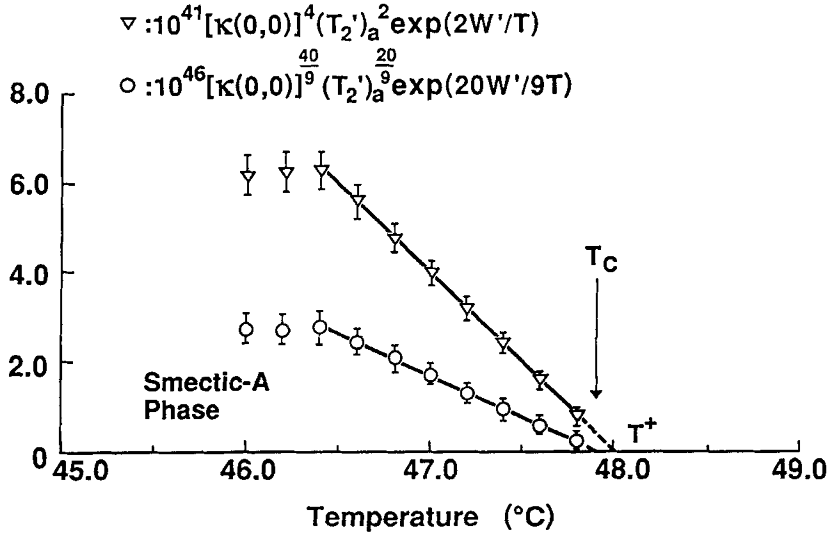

FIGURE 12 Plots of $[\kappa(0,0)]^4 \times (T_2')_a^2 \exp(2W'/T)$ and $[\kappa(0,0)]^{40/9} \times (T_2')_a^{20/9} \exp(20W'/9T)$ in para position vs. temperature in smectic-A phase of 9CB.

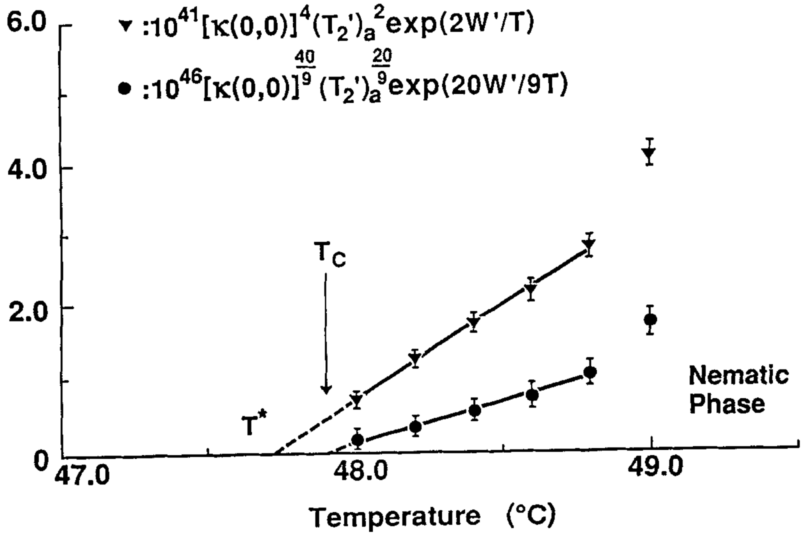

FIGURE 13 Plots of $[\kappa(0,0)]^4(T_2')_a^2 \exp(2W'/T)$ and $[\kappa(0,0)]^{40/9} \times (T_2')_a^{20/9} \exp(20W'/9T)$ in para position vs. temperature in nematic phase of 9CB.

5. CONCLUSION

The critical temperature behaviors of the smectic-A ⟨–⟩ nematic phase transitions in 8CB and 9CB have been investigated for the first time by NMR ^{13}C T_1 and T_2 relaxation measurements. The analysis of the relaxation rates estimated with $J^{(0)}(0)$ has

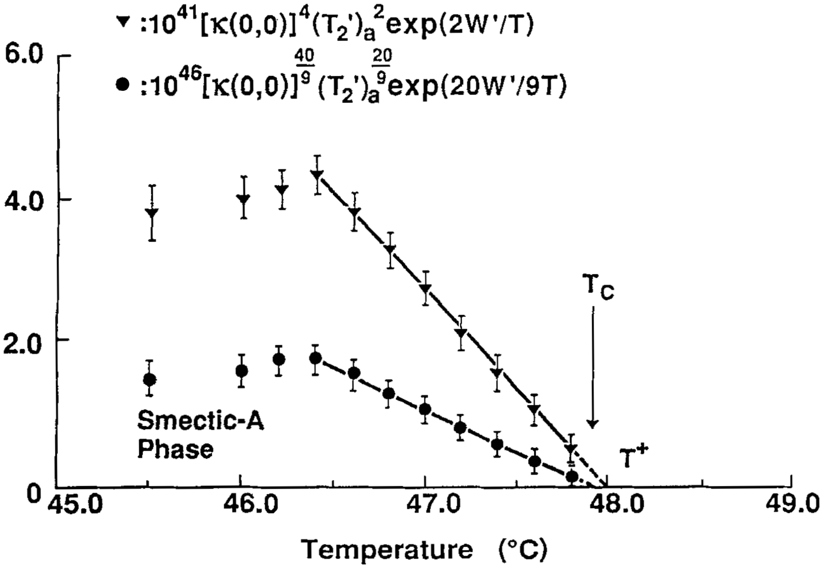

FIGURE 14 Plots of $[\kappa(0,0)]^4(T'_2)_a^2 \exp(2W'/T)$ and $[\kappa(0,0)]^{40/9} \times (T'_2)_a^{20/9} \exp(20W'/9)$ in ortho-position vs. temperature in smectic-A phase of 9CB.

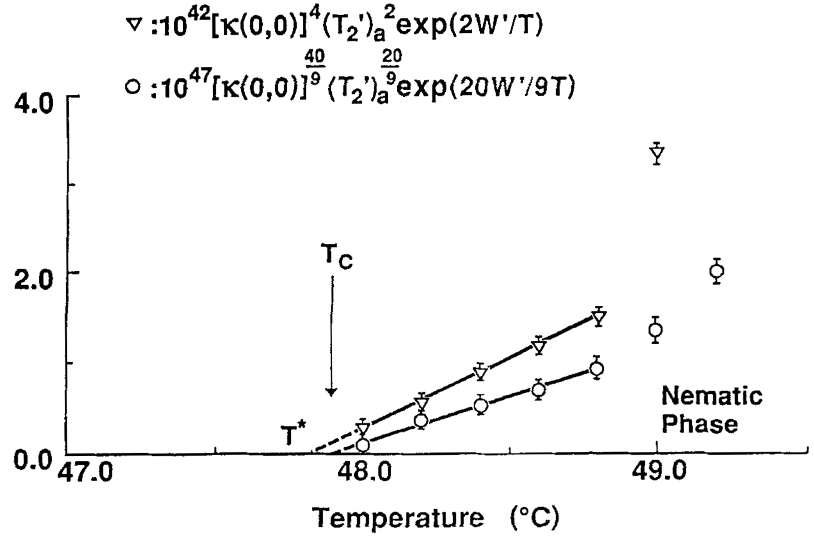

FIGURE 15 Plots of $[\kappa(0,0)]^4(T'_2)_a^2 \exp(2W'/T)$ and $[\kappa(0,0)]^{40/9} \times (T'_2)_a^{20/9} \exp(20W'/9)$ in ortho-position vs. temperature in nematic phase of 9CB.

been found to be essentially similar to these of protons T_1 and $T_{1\rho}$, as previously reported.[15] However, the estimation process of carbon-13 T_1 and T_2 was much simpler than that of protons T_1 and $T_{1\rho}$, because the ^{13}C-relaxation rates are negligible for intermolecular contribution, although the relaxation processes can be mixed with the C–H nuclear interactions. On the other hand, the proton T_1 and $T_{1\rho}$ rates have been found to contain both the inter- and intramolecular interactions. By postulating that the Sm-A $\langle - \rangle$ N phase transition is similar to the lambda transition in helium, and applying a static scaling relation to the correlation function, then the scaling hypothesis permits us to have the same correlation function $\langle |\Psi(q)| \rangle$ in both the Sm-A and N phases near the transition. The result for the Sm-A and N phases in 8CB clearly shows the critical phenomenon near the transition, and the relaxation rates $(T_2)^{-1}$ exponentially diverge near the transition. The critical exponent for $\bar{\xi}$ in 8CB has been estimated as 1/2 both in the Sm-A and N phases. This result suggests that a symmetry between the Sm-A and N phases exists near T_c, as predicted by the mean-field approximation. This critical exponent is coincident with the previously reported value.[22]

On the other hand, the critical exponent for $\bar{\xi}$ in 9CB has been found not to be satisfied with 1/2, which has been estimated as $v = v' = 0.45$ in both the Sm-A and N phases. This discrepancy in the critical exponents of 8CB and 9CB may be the reason why the Sm-A $\langle - \rangle$ N phase transition of 9CB is of a larger first order than that of 8CB. It should also be emphasized that these critical exponents are determined from the biphenyl core part, which do not contain a flexible alkyl end-chain, so that the exponents in this work are inconsistent with the results of X-ray and DSC measurements observed from the behavior of all liquid crystals, including both the core part and the flexible alkyl end-chain.

Acknowledgment

The author would like to thank Prof. S. Kobinata of The Toin University of Yokohama for his helpful advice and fruitful discussion. He is also indebted to Mr. F. Umibe, a consultant, for reviewing the original manuscript and suggesting revisions in the English text.

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