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^{13}C Relaxation Times Study of Liquid Crystalline *p*-Methoxybenzylidene-*p*-Butylaniline†

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The ^{13}C relaxation times T_1 and T_2 for all resolved carbon lines are reported as a function of temperature in the nematic and isotropic phases of MBBA. Also the NOE measurements were performed in the both nematic and isotropic phases.

The discontinuity of ^{13}C T_2's was observed at the nematic-isotropic transition point. From T_1 and T_2 data, it is shown that a short range order remains in the small temperature range just above the isotropic-nematic transition point.

The region of small temperature dependence was found in the plots of ^{13}C T_1 vs reciprocal temperature. The rotational motion around the molecular axis was estimated to be three orders faster than the motion around the axis perpendicular to the molecular axis.

INTRODUCTION

As well known, nuclear relaxation times of the liquid crystal compounds gives the important information about the molecular motion. The nematic liquid crystal *p*-methoxybenzylidene-*p*-*n*-butylaniline (MBBA) has been studied by using NMR methods. Pines and Chang[1] have studied the phase transition in MBBA by using ^{13}C NMR technique. Hutton and co-workers[2] have reported on the molecular motion of MBBA by observing the ^{13}C-relaxation time T_1.

In this paper the ^{13}C spin-lattice relaxation time T_1 and the ^{13}C spin-spin relaxation time T_2 of MBBA were observed. This paper would be the first mea-

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surements of ^{13}C T_2 in MBBA as a function of temperature. From the ^{13}C relaxation data, the molecular motion of MBBA is discussed.

EXPERIMENTAL

MBBA is sealed in a 10 mm OD sample tube and used without degassing. Measurements of ^{13}C relaxation times were performed on JEOL FX-100 FT NMR spectrometer operating at 25.05 MHz with a deuterium external lock. The ^{13}C T_1 measurements were done with proton noise decoupling using 180°-τ-90° pulse sequence with an accuracy of about 5%.

The ^{13}C T_2 measurements were performed using 90°-(τ-180°)n-τ pulse sequence under proton CW decoupling.

The accuracy in T_2 measurements is about 15%.

The relaxation times were observed in the both nematic and isotropic phases by varying the temperature from 20°C to 100°C. ^{13}C NMR spectra were obtained without sample spinning after averaging 4 and 50 FID signals for the isotropic and the nematic phases, respectively.

RESULT AND DISCUSSION

^{13}C NMR spectra of MBBA in the isotropic and nematic phases are shown in Figure 1. In the isotropic phase, ^{13}C NMR spectrum of MBBA consists of 14 lines arising from 14 chemically nonequivalent carbons, while only 12 lines are observed in the nematic phase due to overlapping of signals. 0-1, 0-2, 0-3, and 0-4 lines in Figure 1 originated from the 4 pairs of protonated ortho aromatic carbons.

The temperature dependences of ^{13}C T_1 and T_2 of the ortho aromatic carbons and azomethine carbon are shown in Figure 2. T_1's of the ortho aromatic and azomethine carbons increase with arise of temperature. However, it is found that the temperature dependence in the region between 34°C and 43°C is very small. The T_2 of the ortho aromatic carbons exhibits a remarkable change at the isotropic-nematic transition point. In the low temperature range of the isotropic phase, T_2 is not completely equal to T_1. However, T_2 is equal to T_1 at near 80°C. The 0-1 and 0-2 lines are not shown in Figure 1. Because the 0-1 line gives almost same plots with the 0-4 line as a function of temperature. The plots of log T_1 vs reciprocal temperature of the 0-2 line is also similar to the plots of 0-3 line.

Figure 3 shows the temperature dependence of ^{13}C T_1 and T_2 in the methoxy and methyl carbons in the both end-chain of MBBA. The T_1 increases with a rise of temperature. But the region of small temperature dependence is found in the both carbons just alike with that observed in the ortho aromatic car-

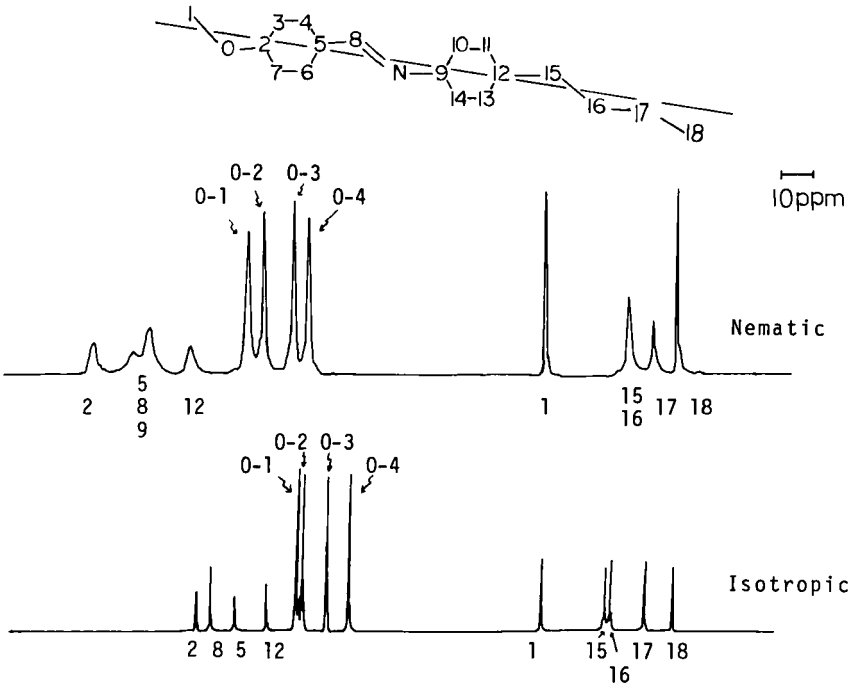

FIGURE 1 ^{13}C NMR spectra of MBBA.

bons. An obvious discontinuity is also observed in the T_2 of the both carbons. In the isotropic phase, the T_2 of the methyl carbon is not agree with T_1 in the low temperature range below 80°C.

Figure 4 shows the temperature dependence of the T_1 and T_2 in the methylene carbons of *n*-butyl chain. The T_1 increases with a rise of temperature and a discontinuity in T_2 is observed at the iostropic-nematic transition point. Again the T_2 is not equal to the T_1 in the small temperature region just above the isotropic-nematic transition point.

The temperature dependence of T_1 and T_2 for the quartanary carbons is shown in Figure 5. The region of small temperature dependence of T_1 is also observed in these carbons. In this case, the T_2 is not equal to the T_1 up to 80°C as observed in other carbons.

This experimental fact observed in the low temperature range of the isotropic phase indicates that a short range order remains in this temperature region between 34°C and 43°C.

In order to estimate the contribution of dipole-dipole relaxation mechanism to $^{13}CT_1$, ^{13}CNOE was measured in the isotropic and the nematic phases. In the isotropic phase, all protonated carbons have an NOE over 2.7. In the

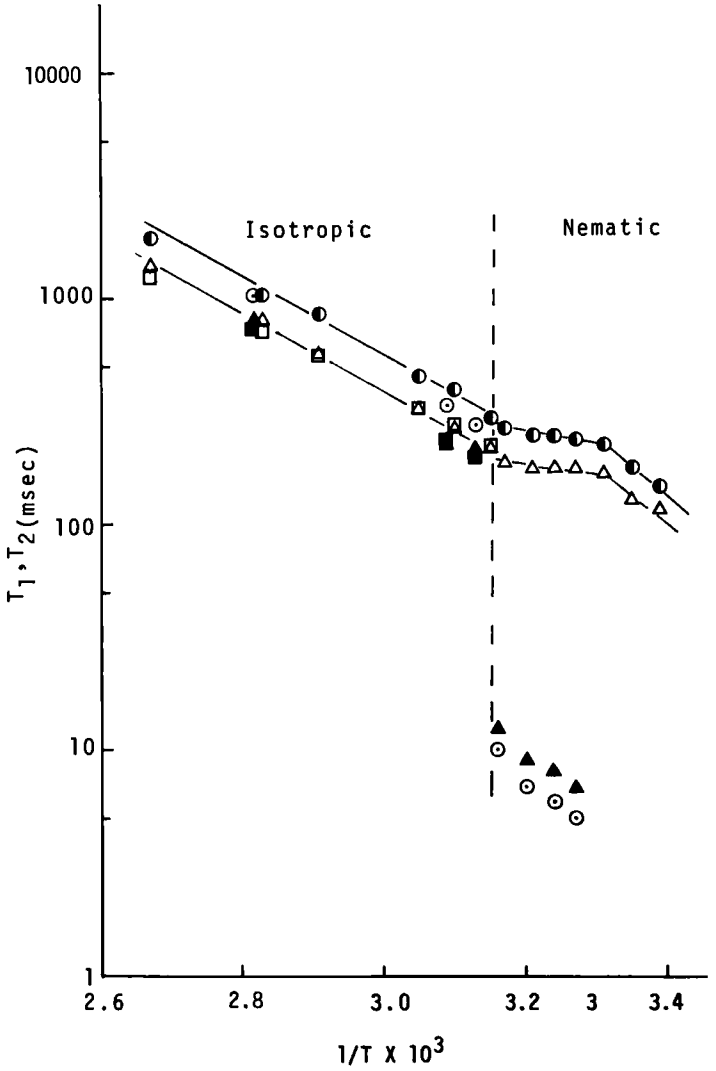

FIGURE 2 The temperature dependence of ^{13}C T_1 and T_2 of the ortho aromatic and azomethine carbons in the nematic and isotropic phases. ◐: 0–3 . . T_1, ⊙: 0–3 . . T_2, △: 0–4 . . T_1, ▲: 0–4 . . T_2 □: C_8 . . . T_1, ■: C_8 . . . T_2.

nematic phase, the ortho aromatic and the mothoxy carbons have an NOE of about 2.5. The NOE enhancements of the other carbons are lower than 2.0. Therefore the relaxation mechanism for the ortho aromatic and methoxy carbons would be mainly a dipolar relaxation in the both isotropic and nematic phases.

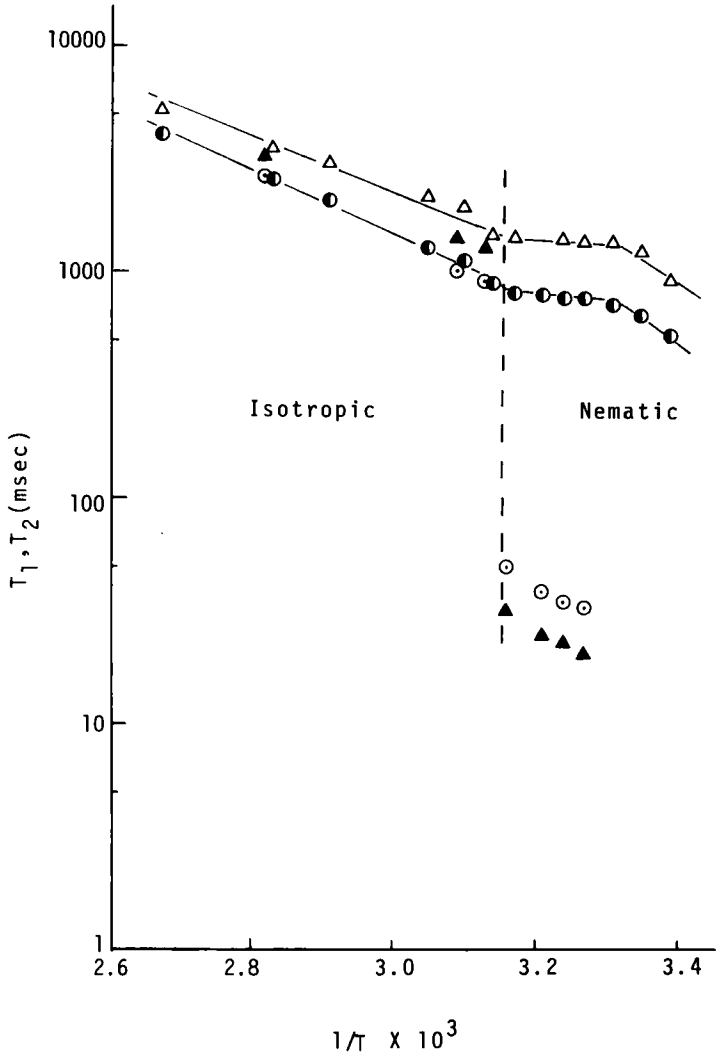

FIGURE 3 The temperature dependence of ^{13}C T_1 and T_2 of the methoxy and methyl carbons in the nematic and isotropic phases. ◐: C_1 . . . T_1, ⊙: C_1 . . . T_2, △: C_{18} . . . T_1, ▲: C_{18} . . . T_2.

The region of small temperature dependence in the nematic phase is found by the detailed measurements of ^{13}C T_1 of MBBA. Such region has not been found in the previous work[2] on the ^{13}C T_1 relaxation of MBBA. The ^{13}C T_1 relaxation mechanism for ortho aromatic and methoxy carbons of MBBA is mainly contributed by the dipole-dipole interaction in the both isotropic and nematic phases. In liquid crystal compounds, it is considered that the ^{13}C dipo-

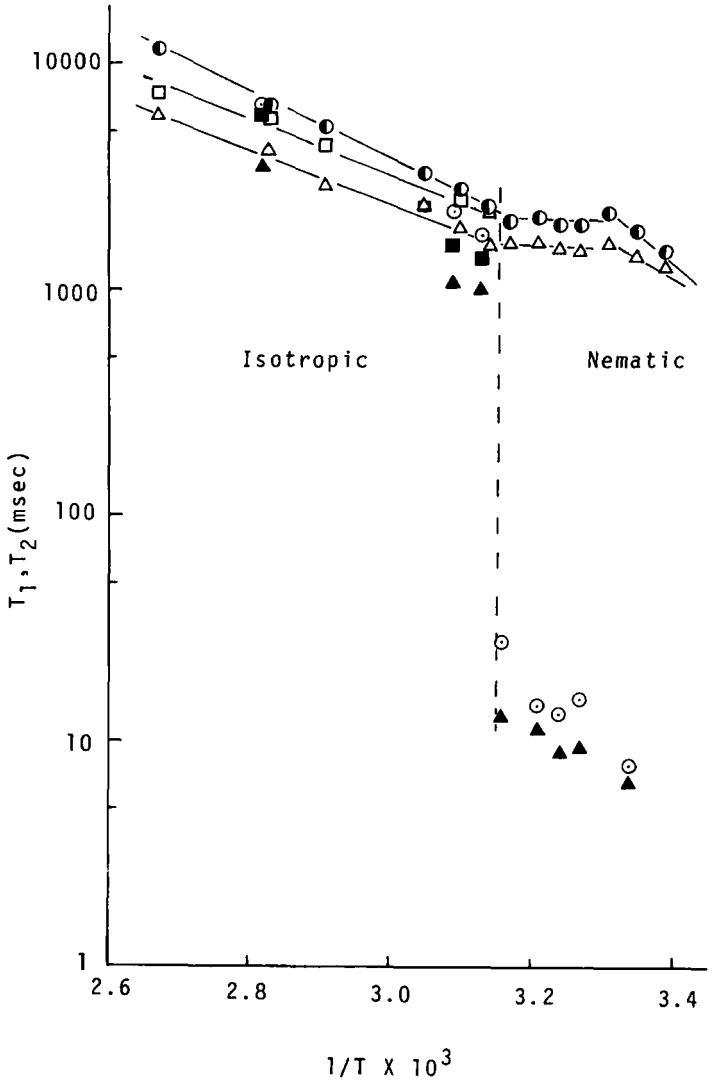

FIGURE 4 The temperature dependence of ^{13}C T_1 and T_2 of the methylene carbons in the nematic and isotropic phases. ◐: C_{17} . . . T_1, ⊙: C_{17} . . . T_2, △: C_{15} . . . T_1, ▲: C_{15} . . . T_2, □: C_{16} . . . T_1, ■: C_{16} . . . T_2.

lar relaxation is mainly governed by the anisotropic rotational diffusion of entire molecule.[2,3] The existence of the region of small temperature dependence in the ortho aromatic and methoxy carbon, however, may indicate that there is a molecular motion represented by another correlation time besides the anisotropic entire motion. The conclusive mechanism of such a molecular motion is not clear, at present. If the mechanism in question is effective in the ^{13}C

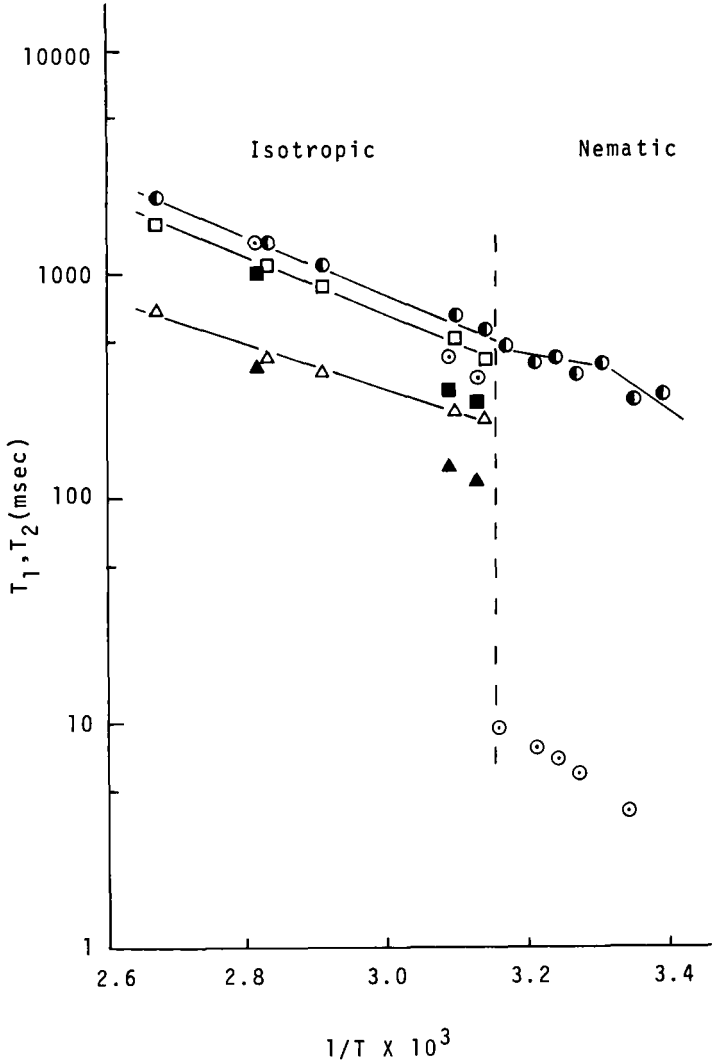

FIGURE 5 The temperature dependence of ^{13}C T_1 and T_2 of the aromatic quartanary carbons in the nematic and isotropic phases. ◐: C_2 . . . T_1, ⊙: C_2 . . . T_2, △: C_5 . . . T_1, ▲: C_5 . . . T_2, □: C_{12} . . . T_1, ■: C_{12} . . . T_2.

dipolar relaxation process, the observed relaxation rate can be the sum of the relaxation rate of two mechanism.

We roughly assume that the ^{13}C T_1 relaxation of MBBA in the region below 30°C is mainly contributed by the anisotropic rotation of entire molecule. While the ^{13}C T_1 relaxation of MBBA in the region above 50°C is mainly contributed by the molecular motion in question. The dipole-dipole relaxation

rate $(1/T_{1d})_{Me}$ for the methoxy carbon of PAA (*pp'*-azoxyaniline) has been derived by Hayamizu and Yamamoto.[3] In their study, it is considered that possible mechanisms which are effective in the ^{13}C relaxation process for the methoxy carbon of PAA are molecular entire reorientation and fast internal rotations. $(1/T_{1d})_{Me}$ is given by

$$(1/T_{1d})_{Me} = \frac{3\,\gamma_H^2\gamma_C^2\hbar^2}{2r^6} \times 3\left[\frac{1}{6D_\perp}\left(\frac{3\cos^2\theta - 1}{2}\right) + \frac{1}{2D_\perp + 4D_\parallel}\sin^4\theta\right] \times\left(\frac{3\cos^2\theta' - 1}{2}\right)\cdot\left(\frac{3\cos^2\theta^{\parallel} - 1}{2}\right) \quad (1)$$

where $D_\parallel$ is the rotational diffusion constant for the motion about the molecular symetry axis. $D_\perp$ is the rotational diffusion constant for the motion about an axis perpendicular to the molecular axis. θ is the angle between the molecular axis and C-O axis, θ' is the angle $\angle$COC and $\theta^{\parallel}$ is the angle $\angle$OCH. Even though θ is assumed to be 8°, the contribution to dipolar relaxation rate from the $D_\parallel$ term is negligibly small owing to the $\sin^4\theta$ factor. If the same expression is applied to the methoxy carbon of MBBA, the $D_\perp$ can be determined from the dipolar relaxation time $(1/T_{1d})_{Me}$ and the geometric factors of MBBA. The $(1/T_{1d})_{Me}$ value at 29°C is obtained from observed T_1. The geometric factors for MBBA are assumed to be $\theta = 8°, \theta' = 118°, \theta^{\parallel} = 109.5°$ and $r = 1.09$ A°. Thus, the $D_\perp$ at 29°C is determined to be 4.4×10^7 sec^{-1}.

The $(T_{1d})_{Me}$ at 80°C is obtained as 5 sec^{-1} by extrapolating the linear line region below 30°C, up to 80°C (Figure 6). Thus, the $D_\perp$ at 80°C is calculated to be 2.4×10^{-8} sec^{-1}. This value is five times larger than the $D_\perp$ value of MBBA obtained by Hutton and co-workers.[2] Such difference would be coming from the assumption that our experimental relaxation rate of MBBA is the sum of the relaxation rate of two mechanisms to explain the existence of the region of small temperature dependence in the T_1 data.

Huntress[4] has derived the following expression for the dipole relaxation rate $(1/T_{1d})$ of carbon-proton pair in a symmetric rotor undergoing anisotropic diffusional rotation:

$$(1/T_{1d}) = \frac{3\,\gamma_H^2\gamma_C^2\hbar^2}{2r^6}\,\frac{1}{6D_\perp}\left[1 + \frac{3\,(D_\perp - D_\parallel)}{5D_\perp + D_\parallel} \times \sin^2\alpha\left(1 + \frac{3\,(D_\perp - D_\parallel)}{2\,(D_\perp - 2D_\parallel)}\sin^2\alpha\right)\right]$$

where, α is the angle between the molecular axis and the C—H bond of interest. To determine $D_\parallel$, this equation is applied to the ortho aromatic carbons and the azomethine carbon of MBBA. In the ortho aromatic carbons, 59° is used for the angle α as an average for two C—H bonds.

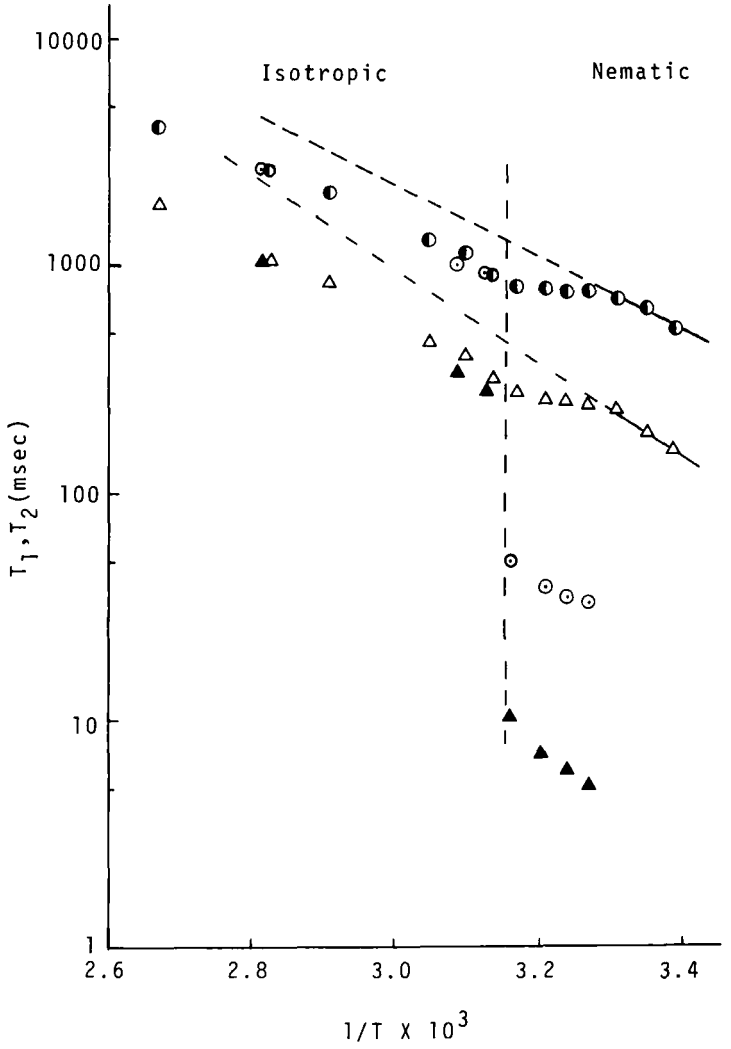

FIGURE 6 To obtain the T_{1d} of the methoxy and ortho aromatic carbons at 80°C for the anisotropic rotational mechanism, the linear line in the region below 30°C is extrapolated up to 80°C. ◐: C_1 . . . T_1, △: 0-3 . . T_1.

Using the $D_\perp$ determined above, the $D_\parallel$ from the ortho aromatic carbon (the 0-3 line) is determined to be 5.3×10^{10} sec^{-1} and 1.1×10^{10} sec^{-1} at 80°C and 29°C, respectively, as shown in Table 1. The $D_\parallel$ of MBBA as found to be three orders larger than the $D_\perp$. This fact almost agrees with the result obtained from ^{13}C T_1 of MBBA in the previous work.[2]

Mascicki and co-workers[6] reported 1.6×10^{-10} sec and 1.2×10^{-10} sec as the dielectric times of MBBA at 305 K and 335 K, respectively. The correlation

TABLE I

Rotational Diffusion Constant of MBBA

Temperature	$D_\perp$	$D_\parallel$
29°C (nematic)	4.4×10^7	1.1×10^{10}
80°C (isotropic)	2.4×10^8	5.3×10^{10}

times obtained from our $D_\parallel$ almost agree with those estimated dielectric relaxation measurement.

For the azomethine carbon, geometric factors[5] found in *N*-(*p*-chlorobenzylidene)-*p*-chloroaniline are used. The angle is equal to 68.4°, which means 60.4° + α, and r is equal to 0.91 A°. Thus the $D_\parallel$ is found to be negative at 80°C. The $D_\parallel$ from azomethine carbon may be found to be positive by larger $D_\perp$ value. A larger $D_\perp$ value, however, would lower the $D_\parallel/D_\perp$ as pointed out by Hutton and co-workers.[2] The $D_\perp$ obtained from Eq. 1 may be estimated to be somewhat small due to the assumption of fast internal rotations. On the other hand, the $D_\parallel$ value of azomethine carbon is very sensitive to the magnitude of the angle α (namely θ). A smaller value makes the direction which gives a positive $D_\parallel$ from the azomethine carbon.

It is necessary to consider the geometric factors of MBBA in the isotropic phase in addition to the consideration of the $D_\perp$ value and the $D_\parallel/D_\perp$ ratio in anisotropic rotation.

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