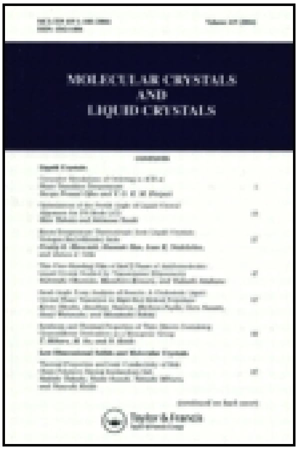

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Successive Excitation of Molecular Motion in a Nematic Liquid Crystalline Compound, HBAB, as Studied by Nuclear Magnetic Resonance

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Successive Excitation of Molecular Motion in a Nematic Liquid Crystalline Compound, HBAB, as Studied by Nuclear Magnetic Resonance†

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Successive excitation of molecular motion was studied, by proton NMR lineshape and relaxation measurements, in relation to the phase transitions of a nematic liquid crystalline compound, *p*-*n*-hexyloxybenzylideneamino-*p*′-benzonitrile (HBAB). The dynamical nature of the intercrystalline phase transition was investigated and the higher-temperature crystalline phase was revealed to be a motionally disordered phase with respect to conformation of the alkoxy chain. The difference between this phase and the general smectic phase in their motional aspects is pointed out. The second rank orientational order parameter in the nematic phase near T_c exhibits a steep descent toward a small critical value of 0.28 at T_c which cannot be explained by Maier-Saupe's mean field theory nor its modifications. A comparison of the behavior of *p*-*n*-hexyloxybenzylidene-*p*′-toluidine (HBT) with HBAB shows that the effect of the terminal substituent on the nematic order parameter is important. Molecular dynamics in the nematic phase is characterized by translational self-diffusion in the low-temperature region and by fluctuation of the order director near T_c. A strong correlation between the self-diffusion and a large amplitude rotational motion is suggested in the isotropic liquid phase.

I INTRODUCTION

Various mesomorphous states have been the subject of intensive study because of their unusual properties.[1-3] General macroscopic properties

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† This paper is based on part of the Ph.D. Thesis of one of the authors (S.M.).

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of liquid crystals have been successfully rationalized phenomenologically by the elastic continuum theory of liquid crystals.[1] On the other hand, the microscopic properties such as successive excitation of motional modes in such mesogen compounds have not been well understood up to the present. The study of molecular dynamics in liquid crystals will be of general interest because it will shed light on the successive excitation of motional modes in molecular crystals in relation to their phase transitions.

We have carried out NMR studies[4] of the three *p*'-substituted HBA (*p*-*n*-hexyloxybenzylideneaniline), i.e., HBAB (*p*-*n*-hexyloxybenzylideneamino-*p*'-benzonitrile), HBAC (*p*-*n*-hexyloxybenzylideneamino-*p*'-chlorobenzene), and HBT (*p*-*n*-hexyloxybenzylidine-*p*'-toluidine). The phase relations are illustrated in Figure 1, which shows that these compounds exhibit a wide variety of liquid crystalline polymorphism depending on the terminal atom or group. Hence one can systematically examine the relation of the motional modes with various phase transitions without altering the gross degrees of freedom of molecular motion. It is the purpose of this series of studies to investigate the dynamical properties of the various phases by applying the NMR technique. The present paper, the first one of the series, deals with HBAB. Its transition temperatures and the entropies of transitions[6] are shown in Table I.

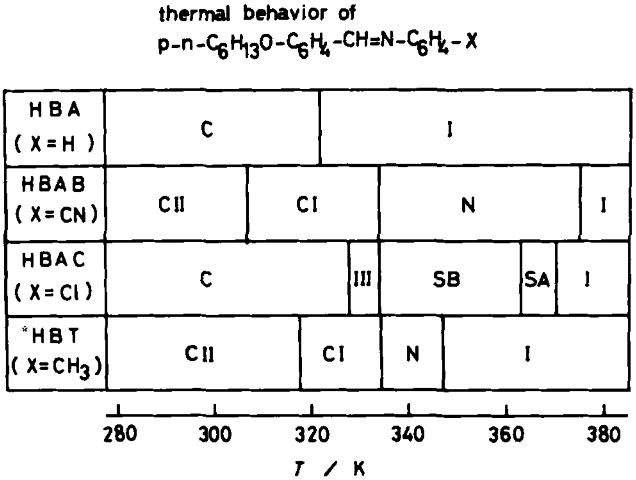

FIGURE 1 Thermal behavior of the three mesogen compounds together with the unsubstituted HBA.[5] The symbols C, CI, and CII represent the crystalline phases. N, SA, and SB represent the nematic, smectic A, and smectic B mesophases, respectively. The symbol I is for the isotropic liquid. The phase III in HBAC has not been identified.

* Although not shown in this figure, HBT is known to show two metastable phases[4,52] when cooled from N, which are identified as SB and CIII.

TABLE I

Transition temperatures and the entropies of transitions in HBAB measured by Tsuji *et al.*[6]

	T/K ΔS/J K^{-1} mol^{-1}					
CII	306.98 16.7	CI	334.05 71.2	N	375.11 3.2	I

The most noticeable feature of HBAB among its homologous series from the viewpoint of molecular structure is that HBAB has a large dipole moment along the long molecular axis due to the local dipole moment of the cyano substituent (ca. 4 D). In fact, the substitution at one end of the molecule has a large effect on the phase relations as seen in Figure 1. Arora and Fergason[19] discussed such substituent effect on the mesophase-forming tendency.

The nematic liquid crystal HBAB is one of the typical compounds which have been extensively studied by various experimental methods. In early 1970's, dielectric constant and relaxation[7] in the nematic phase, and the Kerr effect[8] in the isotropic phase were measured with special interest in its very strong positive dielectric anisotropy. HBAB also attracted interest of many scientists since Gähwiller discovered the hydrodynamic instability of this material under shear flow.[9] Some experimental as well as theoretical efforts[10-13] have been dedicated to this point, and it is now conceived phenomenologically that the flow instability is related to the change of sign of the Leslie viscosity coefficient α_3 at about 365 K, but the origin of this phenomenon on the molecular level has not been clarified. Gähwiller[9] suggested that the dimerization of the molecules in an antiparallel manner due to the large permanent dipole may occur in the nematic mesophase and that such dimerization could explain the difficulty in achieving the uniform alignment in the direction of the shear flow. He also suggested that measurements of the temperature-dependence of the orientational order parameter or of the low frequency dielectric relaxation will give us a clue to this problem. Schadt[7] measured the low frequency dielectric relaxation and pointed out that the static dipolar coupling between the molecules is weak in contradiction to Gähwiller's suggestion. Some other physical quantities such as density,[13] viscosity coefficients,[10,13,14] elastic constants,[15] magnetic anisotropy,[14] transition temperatures[16,17] were measured for the nematic HBAB. Recently temperature-dependence of IR spectra[18] of thin film of HBAB aligned on a solid surface was also reported.

The dynamical structure of the high-temperature crystalline phase (CI) is interesting because it should reflect one stage of successive excitation of molecular degrees of motion. Recently we studied the kinetics of the phase transition between the two crystalline modifications (CII/CI) of HBAB by NMR,[20] and discussed its rate of transformation on the basis of the homogeneous nucleation and growth mechanism.

The major objectives of the present study are (1) to find the difference in molecular motion between the two crystalline phases and to assess the type of disorder in CI if there is any, (2) to measure the temperature-dependence of orientational order parameter in the nematic phase, and to examine the applicability of the mean field theories for nematic liquid crystal, and (3) to determine what motional modes are responsible for nuclear spin-lattice relaxation in the nematic phase of HBAB.

II EXPERIMENTAL

The sample of HBAB was provided by Dr. K. Tsuji of Kwansei Gakuin University. The purity of the sample as determined by calorimetric technique near the melting point was 99.90%.[6] We further purified it by the molecular distillation method prior to experiment. The sample was sealed in a glass ampule under a pressure of 4 kPa of helium exchange gas after evacuation of ten hours with three freeze–pump–thaw cycles. No decomposition was observed during the experiments in the crystalline and the nematic phases, but when kept in the isotropic phase for more than five hours, the specimen decomposed to a small extent as evidenced by a narrow central component in the proton NMR spectrum even in the crystalline phases. Therefore, we repurified the sample as donated for the experiments on the isotropic phase.

The measurements on the crystalline phases were strongly affected by the large hysteresis effect associated with the phase transition from the phase CI to the phase CII. The transition from the phase CII to CI took place at 307 K on heating CII from 77 K and it was moderately rapid so that annealing at 325 K for two hours was sufficient to obtain pure CI. On cooling CI, on the other hand, it was readily undercooled down to 77 K without provoking the transition into CII. The transition rate from the undercooled state of CI to the stable phase CII was determined by our recent NMR experiment:[20] it took as long as 6.1×10^5 s (7.1 days) for half the CI to be transformed into CII at 293 K. A few weeks were necessary for completion of this transition at room temperature.

Proton NMR lineshape was measured by the continuous wave method by utilizing a Robinson-type spectrometer[21] working at 19.8 MHz. The external field was calibrated by monitoring the proton signal of Cu^{2+}-doped water at room temperature. The external field was modulated at 147 Hz. The second moment was determined by graphical integration with the correction, $H_m^2/4$, of the modulation width.[22] Temperature was controlled by use of a proportionally regulated heater system, and was measured by Chromel-P-Constantan thermocouples.†

Proton spin-lattice relaxation rates were measured by a pulse method. They were measured at three different Larmor frequencies ($\omega_0/2\pi$), 10.0, 20.5, and 40.5 MHz. Only the experiments at 10.0 MHz were done for the crystalline states. Details of the 10.0 MHz spectrometer were reported elsewhere.[23] A new variable-frequency spectrometer for the experiments at 20.5 and 40.5 MHz will be reported elsewhere.

Measurements for the nematic phase were done on the sample cooled from the isotropic liquid phase.

The comb-shaped $\pi/2$'s (total duration about 100 μs)-τ-$\pi/2$ pulse sequence was used for the experiments in the crystalline phases, whereas the $\pi/2$-τ-$\pi/2$ sequence was used in the nematic and the isotropic liquid phases. Free induction signals were observed by utilizing waveform recorders (Biomation Model 805 and Iwatsu Model DM 701). The magnetization recoveries were exponential in the crystalline and the nematic phases, for which well-defined T_1^{-1} values were obtained. In the isotropic liquid phase, however, the recovery was nonexponential; the T_1^{-1} was, therefore, defined by the inverse of the time for the magnetization to be recovered by the factor $1 - (1/e) = 0.63$. The T_1^{-1} thus defined accounts essentially for the fast relaxing component.

The maximum experimental uncertainties in T_1^{-1} were 10% for the crystalline phases, and 7 to 8% for the nematic and the isotropic phases.

III RESULTS AND DISCUSSION

III.1 The crystalline phases

III.1.1 Second moments The proton NMR lines showed Gaussian envelopes without any fine structures in the two crystalline phases. The second moments M_2 in these phases are shown in Figure 2 as a function of temperature. The second moment in CII showed narrowing around

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† These thermocouples were provided from the Chemical Thermodynamics Laboratory, Osaka University.

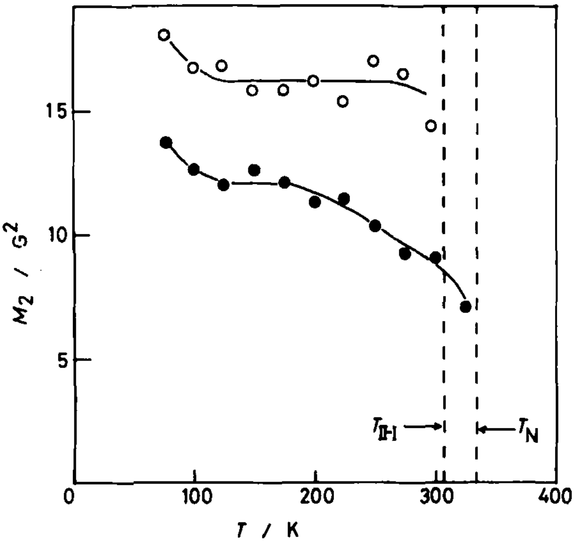

FIGURE 2 Second moments of proton NMR lines in the two crystalline phases of HBAB (● CI and ○ CII). The solid curves are drawn only for the guide of the eye.

100 K, and then assumed an almost constant value of 16 G^2 between 100 K and the transition point, T_{II-I}. On the other hand, the M_2 in CI showed narrowing around 100 K and further decreased gradually from 12.2 G^2 at 175 K to 7.2 G^2 at 325 K. In order to identify the motional modes responsible for the motional narrowing in the two phases, we attempted to make a model calculation of M_2 in the crystalline states. Since the structural data of HBAB are not available, we assumed that the molecular structure of HBAB can be represented by the combination of the reported molecular structure of benzylideneaniline[24] and *n*-alkanes[25] as shown in Figure 3, in which the planes of the two benzene

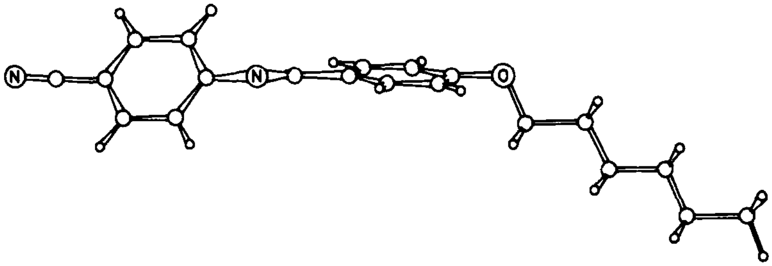

FIGURE 3 Assumed molecular structure of HBAB. Large and small circles represent carbon and hydrogen atoms, respectively. Nitrogen and oxygen atoms are indicated.

rings are twisted through 65.5° from each other. Taking into account all the pairwise dipole–dipole interactions between the twenty-two protons within a molecule and ignoring small contributions from the other magnetic nuclei, the intramolecular contribution to M_2 in the rigid lattice was calculated to be 17.2 G^2 for a powdered sample. Magnitudes of motional narrowing[26,27] were estimated for three different types of internal rotation which were considered possible in the crystalline states: (1) the terminal methyl rotation, (2) the reorientation of the ethyl group about the next-to-terminal C—C bond in addition to the methyl reorientation, and (3) the overall rotation of the hexyloxy chain about the bond between the ring carbon and the oxygen. The results are summarized in Table II. In the case (3), we assumed that only the methyl group rotates but that the rest of the hexyloxy group is rigid, and rotates as a whole about the C_{ring}—O bond without any internal segmental motion. Hence the value 4.8 G^2 in Table II will give the upper bound for the model (3).

Comparing the experimental results of Figure 2 with the calculated values, the following assignments can be made. (1) In CII, the narrowing below 100 K is due to the methyl reorientation, and this is the only mode that is seen by NMR in this phase. It follows from this assignment that intermolecular contribution to M_2 in the plateau region is 2 G^2 which is of reasonable magnitude. (2) In the undercooled CI, the narrowing below 100 K is brought about by the reorientation of the ethyl group. The gradual decrease in M_2 in the higher temperature region suggests that some modes of segmental motion of the chain are excited successively, but the overall rotation of the chain is not excited even in the vicinity of the melting point, T_N.

The fast rotational diffusion of the chain is excited in the nematic phase as can be recognized from the narrow central component of the NMR signal.

TABLE II

Calculated second moments of proton NMR lines (intramolecular contribution to a powder pattern).

Motional states	M_2/G^2
rigid lattice	17.2
terminal CH_3 reorientation	13.9
CH_3—CH_2 reorientation	11.4
overall chain rotation	less than 4.8

III.1.2 Spin-lattice relaxation rates The spin-lattice relaxation rates measured at 10.0 MHz in CII and CI are plotted against the reciprocal of temperature in Figures 4 and 5, respectively.

In CII, there is only one T_1^{-1} maximum in the temperature region studied; this fact, together with the result of the second moment, shows that the terminal methyl reorientation is the only mechanism responsible for spin-lattice relaxation. The spin-lattice relaxation rate due to methyl reorientation can be expressed by[27]

$$T_1^{-1} = AB(\omega_0\tau_c)\omega_0^{-1}, \quad A = \frac{3}{5}\gamma_H^4\hbar^2 r_m^{-6} I(I+1),$$

$$B(\omega_0\tau_c) = \frac{\omega_0\tau_c}{1+(\omega_0\tau_c)^2} + \frac{4\omega_0\tau_c}{1+4(\omega_0\tau_c)^2}, \quad (1)$$

where ω_0 is the angular Larmor frequency, τ_c is the correlation time of reorientation, r_m is the interproton distance within a methyl group, and γ_H, $\hbar$, and I have their usual meaning. Now, using A as an adjustable parameter and assuming a classical activation process of Arrhenius type,

$$\tau_c = \tau_0 \exp(\Delta H/RT), \quad (2)$$

the T_1^{-1} can be reproduced and is shown in Figure 4. The parameter

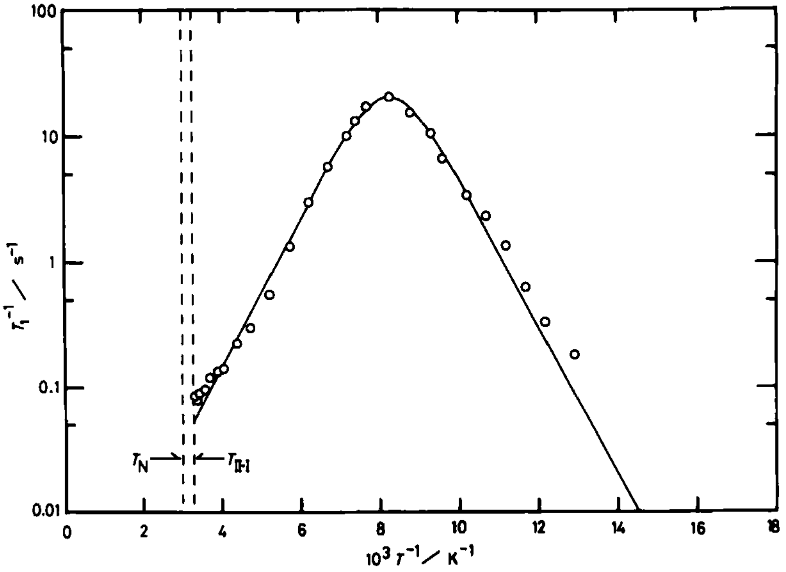

FIGURE 4 Proton spin-lattice relaxation rates at 10.0 MHz in CII of HBAB. The solid curve is the calculated one (see in the text).

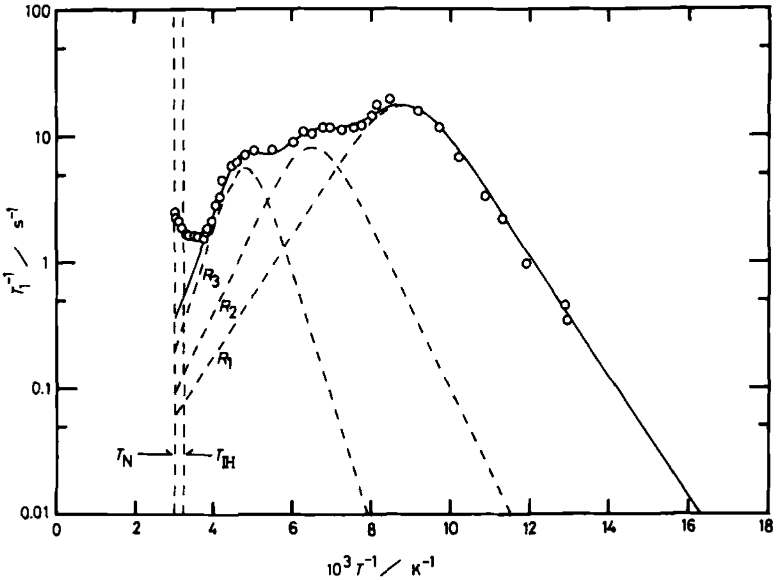

FIGURE 5 Proton spin-lattice relaxation rates at 10.0 MHz in the phase CI of HBAB. The broken curves R_1, R_2, and R_3 represent the contribution of each of the three modes of relaxation (see in the text and Table III). The solid curve shows the sum of them, $R_1 + R_2 + R_3$.

values, $A = 8.82 \times 10^8\ s^{-2}$, $\tau_0 = 1.53 \times 10^{-13}$ s, and the activation enthalpy, $\Delta H = 11.1$ kJ mol^{-1}, gave the best fit to the experimental data. The theoretical value of A was approximately estimated as follows. If we suppose that the spin temperature concept is valid in the whole system of protons and that the methyl-protons are the only protons which can transfer the energy of the spin system to the lattice, the energy of protons other than the methyl-protons will be transferred to the lattice through the methyl-protons via nuclear spin diffusion to methyl-protons. Based on this model, the value of A was estimated, by utilizing $r_m = 1.78 \times 10^{-10}$ m (from Ref. 25), as

$$A = 2 \times \left\{ \frac{3}{10} \gamma_H^4 \hbar^2 r_m^{-6} I(I+1) \right\} \times \frac{3}{22} = 1.10 \times 10^9\ s^{-2},$$

which is about 25% larger than the value determined empirically as mentioned above.

In CI (Figure 5), on the other hand, it can be seen that at least three relaxation processes (R_2, R_3, and the highest temperature branch) in addition to the methyl reorientation (R_1) are responsible for spin-lattice relaxation. As three of them (R_1, R_2, and R_3) have the maxima of their relaxation rates within the temperature range studied, a semiquantitative analysis can be made. Since the first process (R_1) is that of methyl reorientation, Eqs. (1) and (2) can be used to analyze the data. The successive processes R_2 and R_3 probably correspond to reorientational motions of larger segments like ethyl and propyl groups although rigorous treatment of such segmental motions of alkoxy chain needs a complicated calculation. For the present, let us assume an exponential time-correlation of a pair of spins for each reorientational mode (identified by the suffix j),

$$\langle F^{(p)*}(\boldsymbol{r}, 0)F^{(p)}(\boldsymbol{r}, t)\rangle = \langle |F^{(p)}(\boldsymbol{r}, 0)|^2\rangle \times \exp(-t/\tau_{cj}). \qquad (3)$$

Here, $F^{(p)}(\boldsymbol{r}, t)$ denotes the dipolar interaction tensor[27] for a pair of spins under consideration. The T_1^{-1} can then be described by a superposition of the power spectra, $B(\omega_0\tau_{cj})$, each of which corresponds to a particular reorientation mode, i.e.,

$$T_1^{-1} = \sum_{j=1}^{3} R_j = \omega_0^{-1} \sum_{j=1}^{3} A_j B(\omega_0\tau_{cj}). \qquad (4)$$

Assuming again the Arrhenius type activation processes for τ_{cj}'s and using A_j's as the adjustable parameters, T_1^{-1} can be reproduced and is drawn in Figure 5. The calculated curve explains the data fairly well except in the highest temperature region where a fourth process takes place. The parameters obtained are summarized in Table III.

TABLE III

Summary of motional data on HBAB.

phase	CII	CI		
mode	CH_3-reorientation	three rotational modes $R_1(CH_3$-)	$R_2(C_2H_5$-)	$R_3(C_3H_7$-)
ΔH_R/kJ mol^{-1}	11.1	9.1	12.4	19.0
τ_0/s	1.53×10^{-13}	6.13×10^{-13}	6.04×10^{-13}	1.65×10^{-11}
A/s^{-2}	8.82×10^{8}	7.35×10^{8}	3.53×10^{8}	2.48×10^{8}

phase	N	I
mode	translational self-diffusion	self-diffusion coupled with large-amplitude rotation
ΔH_D/kJ mol^{-1}	31.3	39.7
diffusion coefficient	$D_\perp^0 = 1.50 \times 10^{-10}$ m^2 s^{-1} at 345 K ($D_\perp^{00} = 8.25 \times 10^{-6}$ m^2 s^{-1})	$D > 3.0 \times 10^{-9}$ m^2 s^{-1} ($D^0 > 1.1 \times 10^{-3}$ m^2 s^{-1})

We can thus conclude that CI is a kind of dynamically disordered crystalline state with respect to conformation of the hexyloxy chain. However, it should be noted that melting of the chain does not take place until the transition point to the liquid crystalline phase is reached, where self-diffusion of molecules is also excited. Here lies a significant difference between this crystalline state and the smectic phases of HBAC and HBT, in which melting of the chain and excitation of molecular self-diffusion take place simultaneously.[4]

III.2 Orientational order in the nematic phase

The NMR absorption line in the nematic phase has a triplet structure, the outer doublets of which come from the dipole–dipole interaction of the adjacent proton pairs attached to the benzene ring, which is not averaged to zero owing to uniaxial orientational order. The width of the dipolar splitting is related to the orientational order parameter through the equation[28]

$$\delta H = 3\ \gamma_H \hbar r_b^{-3} \langle p_2(\cos\ \theta)\rangle p_2(\cos\ \Phi), \tag{5}$$

where r_b is the distance between the adjacent protons and $p_2(x)$ is the Legendre polynomial of the rank two. Here, Φ is the angle between the interproton vector and the long axis of fast rotational diffusion of molecules, and θ is the angle between the molecular axis and the nematic director, $\boldsymbol{n}$. The bracket denotes the ensemble average, and $\langle p_2(\cos\ \theta)\rangle$ (hereafter abbreviated as $\langle p_2\rangle$) is interpreted as the second rank orientational order parameter. If we take $\Phi = 10°$ and $r_b = 0.245$ nm on the basis of the molecular geometry,[24] the order parameter can be deduced from the experimental value of δH. The results are plotted in Figure 6 as a function of T^* ($T^* = T/T_c$; T_c is the clearing temperature). The order parameter exhibits a strong temperature-dependence near T_c and the value at the clearing point is estimated to be $\langle p_2\rangle = 0.28$, which is very small compared with the values that have been reported for other nematic systems.

Now, comparison of the experimental order parameter with the results of mean field theories of the nematic state will be made. The first successful molecular theories based on anisotropic intermolecular attractive forces is the theory developed by Maier and Saupe[29] (M–S), in which individual molecules are assumed to "feel" an intermolecular potential,

$$\phi_i(\cos\ \theta_i) = -\frac{K}{V^\gamma} p_2(\cos\ \theta_i)\ \langle p_2(\cos\ \theta)\rangle. \tag{6}$$

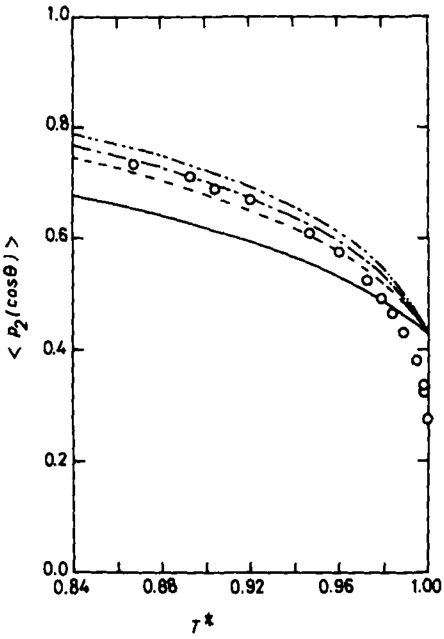

FIGURE 6 The second rank orientational order parameter in the nematic HBAB plotted against the reduced temperature ($T^* = T/T_c$). The theoretical curves are the solutions of the mean field theory for different values of γ: —— for $\gamma = 0$ (neglecting volume change), ---- for $\gamma = 2$ (Maier-Saupe), — — — for $\gamma = 3$ (Chandrasekhar-Madhsudana), and —-—-— for $\gamma = 4$ (Humphries-James-Luckhurst).

Here, θ_i is the angle between the long axis of the molecule i and the director. The molecular distribution function is assumed to be spherical and the volume dependence of the strength of interaction is taken to be $\gamma = 2$ because the major interaction between molecules is considered to be the London dispersion forces.

After the pioneer work by M–S, some careful analyses of experimental results were made using γ as an adjustable parameter. The values $\gamma = 3$ by Chandrasekhar and Madhusudana[30] and $\gamma = 4$ by Humphries, James, and Luckhurst[31] were shown to explain the experimental results better. However, it was shown later by Cotter[32] that theoretical consistency of the mean field approximation requires that $\gamma = 1$.

In the case of HBAB, precise density measurements were made by White *et al.*[13] By utilizing their data, $\langle p_2 \rangle$ was calculated by solving numerically the self-consistency equation,

$$\langle p_2 \rangle = \int_0^1 p_2(\cos\theta_i)\exp(-\phi_i/kT)\,\mathrm{d}(\cos\theta_i) \Big/ \int_0^1 \exp(-\phi_i/kT)\,\mathrm{d}(\cos\theta_i), \quad (7)$$

as a function of T^* and is shown in Figure 6 for some γ-values. It seems that with the values of γ such that $2 \lesssim \gamma \lesssim 4$, the mean field theory can reproduce the experimental data well in the region, $T^* \lesssim 0.94$. But, for $T^* \gtrsim 0.94$, our experimental data deviate significantly from the theory; a sharp descent of $\langle p_2 \rangle$ takes place towards 0.28, whereas the theory predicts that $\langle p_2 \rangle_c = 0.43$ irrespective of the choice of γ. The failure of the mean field theory near the clearing temperature is now evident.

The value of $\langle p_2 \rangle_c$ can be made somewhat smaller by applying some other statistical mechanical methods to Eq. (6), the M–S potential. For example, Sheng and Wojtowicz[33] found the value 0.38 by applying the cluster variation method and assuming the number of the nearest neighbors to be $z = 6$. Lebwohl and Lasher[34] and Jansen, Vertogen, and Ypma[35] found that $\langle p_2 \rangle_c = 0.33$ by the Monte-Carlo "experiments". Humphries, James, and Luckhurst,[31] on the other hand, modified the M–S potential by taking account of the effect of higher order terms in the expansion of intermolecular potential[36] and found that the term p_4, when its coefficient is taken to be negative, has the effect of decreasing $\langle p_2 \rangle$ in the mean field approximation. However, its effect must be small since the series, p_n, converges rapidly.

Although several theoretical attempts have been made to obtain smaller $\langle p_2 \rangle_c$ values than 0.43, any type of modifications of the M–S theory that have been proposed so far cannot explain the very small value of $\langle p_2 \rangle_c$ of HBAB. The molecular theories of nematic liquid crystal based on anisotropic dispersion forces have yielded some successful results for systems having weak dielectric anisotropy such as PAA (*p*-azoxyanisole).[31,33] But it seems difficult to apply the same type of theory to the quantitative understanding of molecular order in such a system having strongly positive dielectric anisotropy as HBAB.

A comparative experiment was attempted to examine the effect of the terminal polar group on the nematic order parameter. The most suitable nematogen for such a study is HBT (see Figure 1) in which the cyano end group of HBAB is replaced by a methyl group, thus forming an essentially nonpolar compound. It should also be noted that the melting points (CI → N) of the two compounds coincide to within 0.2 K (334.05 K for HBAB, and 334.26 K for HBT).[5] The temperature-

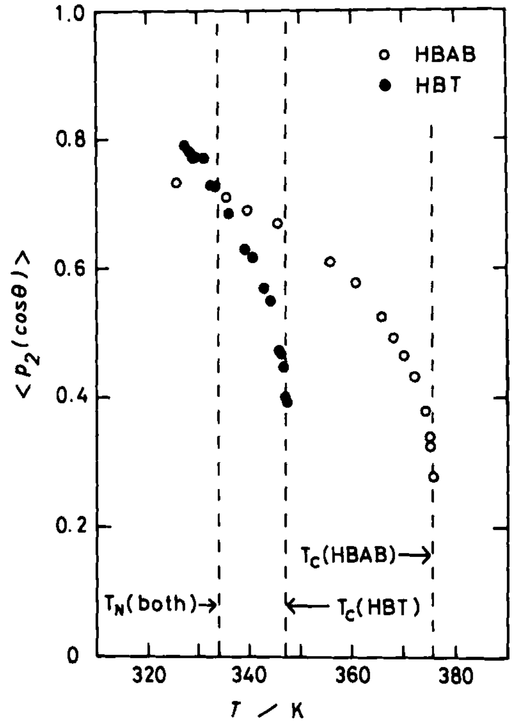

FIGURE 7 Comparison between the second rank orientational order parameters in nematic HBAB (O) and HBT (●).

dependence of $\langle p_2 \rangle$ in HBT[4] is plotted in Figure 7 together with that in HBAB in order to show that the behavior of $\langle p_2 \rangle$'s in the two nematogens is quite different. Although the value of $\langle p_2 \rangle$ is 0.71 at the melting points for both compounds, the value of $\langle p_2 \rangle$ at the clearing points are quite different from each other. The value of $\langle p_2 \rangle_c$ was found to be 0.39 in HBT, which is close to the mean field value.

There is a possibility of molecular association in HBAB due to the large dipole moment of the cyano end group, as suggested by Gähwiller.[9] It was shown by Sheng[37] that molecular association has an effect of decreasing $\langle p_2 \rangle_c$. The small value of $\langle p_2 \rangle_c$ in HBAB may at least partly be related to this effect. The difference in densities[13,38] between HBAB and HBT also supports this idea; the fact that HBAB is more closely packed than HBT in the nematic phase implies the possibility of molecular association in HBAB. It is also to be noted that Cladis[39-42] suggested that molecular association is closely related to the reentrant phenomenon which is one of the peculiar phenomena exhibited by the nematogens having the cyano end group. HBAB is in fact one of the constituents of the reentrant binary mixture first discovered in 1975.[39]

III-3 Molecular dynamics in the nematic phase

Spin-lattice relaxation rates T_1^{-1} in the nematic and the isotropic liquid phases are plotted in Figure 8 against the reciprocal temperature. The figure includes the data taken in the undercooled nematic region. The T_1^{-1} exhibited ω_0-dependence in the entire nematic region studied, and this fact is attributable either to (i) order director fluctuation (ODF) or to (ii) translational self-diffusion of molecules (TSD). The equation for the ODF-assisted spin-lattice relaxation rate for a pair of proton spins with a fixed internuclear distance was given by Pincus[43] and later modified by Ukleja, Pirs, and Doane[44] into the form,

$$T_1^{-1} = \langle p_2 \rangle^2 B\, \omega_0^{-1/2} \left\{ 1 - \frac{2\sqrt{2}}{\pi} \left(\frac{\omega_0}{\omega_c} \right)^{1/2} \right\}, \tag{8}$$

$$B = \frac{9}{8} \gamma_H^4 \hbar^2 r^{-6} \frac{1}{2\pi} \left(\frac{2\eta}{K_o^3} \right)^{1/2} kT.$$

Here, η is the apparent viscosity, K_o is the elastic constant under one elastic constant approximation (i.e., $K_o \equiv K_1 = K_2 = K_3$ is assumed), and ω_c denotes the higher cutoff frequency of the director fluctuation. Equation (8) was derived assuming that the molecules are aligned by

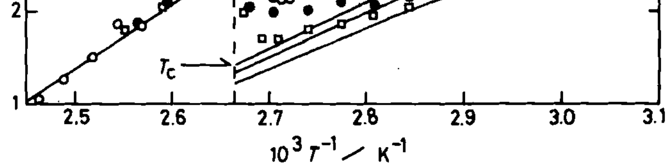

FIGURE 8 Proton spin-lattice relaxation rates in the nematic and the isotropic phases of HBAB. The experimental points ○, ●, and ☐ represent the data taken at 10.0, 20.5, and 40.5 MHz, respectively. The three curves in the N phase represent the theoretical curves for the three Larmor frequencies, based on Eqs. (9) and (11) with the parameters given in Table III. The solid line in the I phase corresponds to the activation enthalpy, 39.7 kJ mol^{-1}.

the external field. As the second term in Eq. (8) is usually small compared with unity, especially in a low viscosity system, the relation $T_1^{-1} \propto \omega_0^{-1/2}$ follows. The temperature-dependence of T_1^{-1} is weak except in the vicinity of T_c.

A theory of spin relaxation due to TSD was developed by Torrey[45] and Harmon and Muller[46] for isotropic liquids. Recently Žumer and Vilfan[47] modified this theory in order to apply it to the nematic liquid crystal system taking into account the effects of geometrical distribution of spins within a molecule, anisotropy of diffusion, and anisotropy of the molecular distribution in space. They found by numerical calculations that such effects could be as small as or smaller than the experimental uncertainty and that the equations of Torrey, Harmon, and Muller could also be applied to the nematic liquid crystal after certain modifications. So, we will apply the modified form of the approximate solution to the intermolecular spin-lattice relaxation rate given by Harmon and Muller in the limit of low but nonzero frequency,

$$T_1^{-1}(\omega_0, D_\perp^0) = \frac{C}{D_\perp^0}\left\{1 - 0.555\, d\left(\frac{\omega_0}{\omega_d}\right)^{1/2}\right\}. \tag{9}$$

The quantity d denotes the "hard sphere" diameter in the direction perpendicular to the long axis of the molecule, and $D_\parallel^0$ and $D_\perp^0$ represent the components of the diffusion coefficient tensor parallel and perpendicular to $\boldsymbol{n}$, respectively, on condition of perfect orientational order, and are related to the diffusion coefficient tensor in the real system through

$$\begin{aligned} D_\parallel &= \frac{1}{3}(1 + 2\langle p_2\rangle)\, D_\parallel^0 + \frac{2}{3}(1 - \langle p_2\rangle)\, D_\perp^0 \\ D_\perp &= \frac{1}{3}(1 - \langle p_2\rangle)\, D_\parallel^0 + \frac{1}{3}(2 + \langle p_2\rangle)\, D_\perp^0. \end{aligned} \tag{10}$$

By analyzing the ω_0- and T-dependences of the data in terms of Eqs. (8) and (9), we can conclude that TSD makes a dominant contribution to T_1^{-1} in the low temperature region of the nematic mesophase. According to the X-ray analysis by Leadbetter *et al.*,[51] d was evaluated to be 0.50 nm for a Schiff base and biphenyl-type nematic systems irrespective of the kind of materials. We therefore took the value $d = 0.50$ nm, and assuming that

$$D_\perp^0 = D_\perp^{0\infty} \exp(-\Delta H_D/RT), \tag{11}$$

we could obtain information concerning $D_\perp^0$ from the temperature- and frequency-dependences of the experimental T_1^{-1} by utilizing Eq. (9). The following parameters were thus derived for HBAB: $D_\perp^{00} = 8.25 \times 10^{-6}$ m^{-2} s^{-1}, $\Delta H_D = 31.3$ kJ mol^{-1}, and $C = 5.55 \times 10^{-10}$ m^2 s^{-2}. The theoretical curves of Eqs. (9) and (11) calculated from these parameters are shown in Figure 8, which demonstrate good agreement with experiment in the low frequency region.

The present stage of our knowledge on self-diffusion in HBAB is only preliminary; e.g., the anisotropy of diffusion coefficient tensor has not been determined experimentally. But, according to the data available now,[48-50] the relation $D_\parallel^0/D_\perp^0 \simeq 2$ seems to hold generally, being independent of substances as far as the shapes of the molecules are alike. Therefore it is probably not far from truth to derive $D_\parallel$ and $D_\perp$ from Eq. (10) by assuming $D_\parallel^0/D_\perp^0 = 2$. The following results were then obtained: $D_\parallel = 2.7 \times 10^{-10}$ m^2 s^{-1}, $D_\perp = 1.7 \times 10^{-10}$ m^2 s^{-1}, and $D_\parallel/D_\perp = 1.6$ at 345 K.

The deviation of the experimental T_1^{-1} data from the theory in the high temperature region will be due to the ODF mechanism. The relaxation enhancement near T_c indicates the excitation of long-wavelength modes of director fluctuation related to the phase transition. It is now accepted[28] that for high temperature nematics (which is less viscous) like PAA, ODF governs nuclear spin-lattice relaxation and that for low temperature nematics (which is more viscous) like MBBA (*p*-methoxybenzylidene-*p*′-butylaniline), TSD governs it. HBAB stands at an intermediate position between PAA and MBBA from the viewpoint of both its temperature range of existence and the magnitude of its rotational viscosity.[10] This point is consistent with our NMR observations.

III.4 Molecular dynamics in the isotropic liquid phase

The fast component of the spin-lattice relaxation rate in the isotropic liquid phase exhibited no appreciable dependence on ω_0. No effect was observed of critical fluctuation due to short range order in this phase as long as the dominant fast component was concerned. Assuming that TSD is the main mechanism for T_1^{-1} in this phase, we can estimate the value of D (scalar diffusion coefficient) by use of Harmon–Muller's equation if the frequency-dependence of T_1^{-1} may be determined experimentally. Only the lower bound of D, $D > 3 \times 10^{-9}$ m^2 s^{-1}, could be deduced in the present case because the T_1^{-1} observed at three different Larmor frequencies agreed to within 7% of their values which is within the limit of experimental accuracy of our apparatus. The diffusion coefficient D thus increases when the substance passes through the clearing point from N to I. But, the apparent activation enthalpy, ΔH_D, for isotropic diffusion obtained from the temperature-dependence of T_1^{-1} is 39.7 kJ mol^{-1}, a value greater than that in the nematic phase. In the isotropic phase in which the long range orientational order has vanished, it is expected that a large-amplitude rotation of the molecule about its short axis is excited and is strongly correlated with TSD. If it is the case, such a motion will be quite effective on the spin relaxation; the apparent ΔH_D will then correspond to the potential barrier restricting such a correlated motion and can become larger than ΔH_D in the nematic phase.

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