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Molecular Ordering in Liquid Crystals Carrying Flexible Hydrocarbon Tails—A Rotational Isomeric State Analysis of D-NMR Data of Emsley et al. on 4-*n*-Alkyl-4′-Cyanobiphenyls (nCB)

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Deuterium NMR studies have been extensively carried out for 4-cyanobiphenyls carrying deuterated *n*-alkyl tails such as 4-*n*-pentyl-4′-cyanobiphenyl (5CB) and 4-*n*-octyl-4′-cyanobiphenyl (8CB) by Emsley et al. In this paper, we have performed a shape analysis of D-NMR spectra within the framework of the rotational isomeric state approximation, statistical weight parameters assigned to the individual bond rotations being treated as empirical variables. For simplicity, the molecular axis is taken to lie in the direction parallel to the line connecting both terminals of the molecule (Model II). Values of the statistical weight parameters thus deduced are used in the estimation of the distribution of conformers permitted in the nematic phase. The results obtained for 5CB and 8CB were found to be in reasonable agreement with those reported by Emsley et al. Our model is simpler, and it has an advantage in that no separate consideration for the external potential field is required. Application of our scheme to the dimer and polymer liquid crystals comprising mesogenic cores joined on both terminals of a soft-spacer should be straightforward.

INTRODUCTION

An anisotropic molecule comprising a rigid mesogenic core with a flexible hydrocarbon tail (or two tails extending in two opposite directions) has been shown to exhibit an odd–even oscillation in the isotropic–nematic transition temperature, and in the associated en-

thalpy and entropy changes when plotted against the number of carbon atoms in the flexible tail.[1,2] These observations indicate that the flexible hydrocarbon tail plays a role in determining the stability of the mesophase. To study the orientational ordering in these systems, British researchers[3] have extensively carried out D-NMR measurements on partially and fully deuterated samples. Typical examples are reported for a series of 4-*n*-alkyl-4′-cyanobiphenyls (nCB).[4–6] For 5CB and 8CB, the quadrupolar splitting $\Delta\nu$ originating from the deuterated flexible segment were analyzed and assigned to the respective segment positions. The variation of $\Delta\nu$ along the hydrocarbon sequence shows clearly that these tails are considerably flexible even in the nematic environment.

For these measurements, various statistical models and theories have been presented.[7–12] Following Emsley et al.'s formalism,[5] the quadrupolar splitting, $\Delta\nu_i$, for a rigid mesogene held in a uniaxial mesophase can be related to the ordering matrix S by

$$\Delta\nu_i = \sum_{\alpha,\beta}^{X,Y,Z} S_{\alpha\beta} q^i_{\alpha\beta} \tag{1}$$

where α,β represent principal axes X,Y,Z for S, and $q_{\alpha\beta}$ is the component of the deuterium quadrupolar tensor q^i for the i-th unit: q^i is usually assumed to be axially symmetric about the C–D direction. In the molecular system such as nCB with $n > 3$, the flexible hydrocarbon tail may assume various spatial configurations inasmuch as they are compatible with the nematic environment. In those cases where the orientational order of the mesogenic core is not affected appreciably by the conformational flexibility of the tail, we may still apply a single ordering matrix S to all the conformers. Then,

$$\Delta\nu_i = \sum_h \sum_{\alpha,\beta}^{X,Y,Z} P(h) S_{\alpha\beta} q^i_{\alpha\beta}(h) \tag{2}$$

where $P(h)$ is the probability that the molecule is in conformation h. Boden et al.[5] examined the validity of Equation (2) by using the rotational isomeric state (RIS) model[13] for the description of the conformation of the pendant alkyl chain in 8CB and 4,4′-di-*n*-heptyloxyazoxybenzene (HOAB). They failed in the interpretation of the D-NMR data, leading to the conclusion that the assumption of a single ordering matrix is invalid. Emsley et al.[6] have also reached the same conclusion from the D-NMR analysis of 5CB.

In a more elaborate model, the ordering matrix is taken to be conformation-dependent. Again, following Emsley et al.,[10]

$$\Delta\nu_i = \sum_h \sum_{\alpha,\beta}^{X,Y,Z} P(h)S_{\alpha\beta}(h)q^i_{\alpha\beta}(h) \tag{3}$$

On application of Equation (3) to the D-NMR data of nCB (n = 5 and 8), Emsley et al.[10] introduced a scheme in which the potential of the mean torque acting on the molecule varies with the spatial configuration of the hydrocarbon tail. The probability of occurrence of a given conformer, $P(h)$, is then expressed as a Boltzmann factor for the potential energy comprising the internal (or conformational) and external contributions. The elements of the Saupe ordering matrix, defined as a function of the external energy, were evaluated for the individual RIS configuration of the molecule. In this analysis, the values of the potential energy parameters were so adjusted as to reproduce the experimentally observed quadrupolar splittings, $\Delta\nu_i^{obs}$. A satisfactory agreement was attained for both 5CB and 8CB by using the same potential energy parameter set.

Samulski et al.[12,14] proposed another approach to the same problem. To account for the constraint imposed on molecules by the anisotropic environment, they introduced a hypothetical cylinder of radius r around the long axis of the molecule in a given configuration. Conformers with the tail extending outside across this cylinder wall are practically eliminated from the ensemble. In this model, the components of the ordering matrix, $S_{\alpha\beta}(h)$ in Equation (3), are estimated from the moment of inertia tensor of a given molecular geometry: the molecular axis (or the Z-axis) may be defined for each configuration of the flexible tail. Experimental observations were found to be reasonably reproduced by this model, with r being treated as an empirically adjustable parameter. The physical basis of such a hypothetical cylinder is somewhat obscure, however.

In this paper, we have developed a model based on the assumption that (1) the molecular axis lies in the direction parallel to the line connecting both terminals of the molecule; thus the Z-axis differs from one conformer to another (in a more elaborate scheme, this process may be replaced by Samulski et al.'s formula,[12] in which the principal axes are obtained by diagonalizing the moment of inertia tensor.), and (2) the molecules are approximately axially-symmetric around the Z-axis: the contribution from the asymmetric term, $S_{XX} - S_{YY}$, in the ordering matrix may be ignored, leading to the scheme in which the orientation of these anisotropic molecules can

be described by a single order parameter S_{ZZ}. In the following treatment, validity of the single-ordering-matrix scheme thus restored will be examined. It should be noted here that the entire concept involved in our scheme is quite different from those of Boden et al.[5] and Emsley et al.,[6] who have abandoned the single-ordering-matrix representation. Fractions of the conformer permitted in the nematic mesophase were determined by adjusting the conformational statistical weight parameter of each rotatable bond against experimental values of $\Delta\nu_i^{obs}$. Calculations were carried out by iteration until a favorable agreement was attained.

As described above, the aforementioned procedure does not require any separate consideration for the external potential energies characteristic to the nematic field. Our model is simple, and may be less rigorous than the more sophisticated models, but it does not contain any excessive number of adjustable parameters of unknown validity. The results of the present analysis are compared with those previously reported by Emsley et al.[10] and by Samulski et al.[12]

STRUCTURAL PARAMETERS

The bond lengths and bond angles used are listed in Table I. The cyanobiphenyl group is treated as a simple straight rod: the length spanning the rigid core, N≡C—ϕ—ϕ—C_1, is taken to be 10Å. The carbon atoms and C—C bonds comprising the alkyl chain flanking the biphenyl group are numbered as indicated in Figure 1. The bond angle ∠DCD was taken to be 107.9° as suggested from the electron diffraction studies on *n*-propane.[15] The angle ∠CCD listed in Table I was calculated by using this ∠DCD value. The rotation angle around the C^{ph}—C bond was fixed at 0°. The dihedral angle CC—CD is then calculated to be 121.7° for the molecular geometry given above. For the terminal C—C bond, a threefold symmetric rotational potential was assumed.

TABLE I

Geometrical Parameters Used for nCB

Bond	Length/Å	Bond angle	Angle/deg
C—C	1.53	∠C^{ph}CC	112.0
C—D	1.10	∠CCC	112.0
		∠CCD (CD_2)	109.2
		∠CCD (CD_3)	111.0

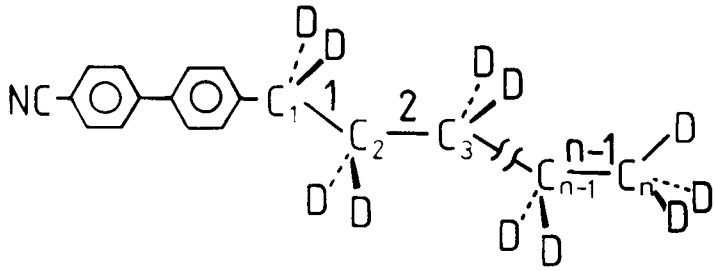

FIGURE 1 Schematic representation of *n*CB. The carbon atoms and C—C bonds in the terminal alkyl chain are numbered as indicated.

COMPUTATIONAL PROCEDURE

The quadrupolar splitting $\Delta\nu_i$ of the i-th C—D bond can be expressed in an analytical form such as

$$\Delta\nu_i = (3/2)(e^2qQ/h)S_{ZZ}\,(\langle 3\cos^2\theta_i\rangle - 1)/2 \qquad (4)$$

The contribution from the $S_{XX} - S_{YY}$ term is generally small, and for simplicity, neglected in this expression. In Equation (4), e^2qQ/h ($= 174$ kHz[16]) is the quadrupolar coupling constant; S_{ZZ} denotes the orientational order parameter of the molecular axis with respect to the director of the nematic domain; θ_i represents the angle between the C_i—D bond and the molecular axis; and the bracket indicates a statistical mechanical average over all allowed conformations. As stated in the introductory part, our model belongs essentially to the single-ordering-matrix scheme: the same value of S_{ZZ} is applicable to all the conformers in the mesophase. Comparison of the calculated and observed results may be facilitated by taking ratios such as

$$\Delta\nu_i/\Delta\nu_1 = (\langle 3\cos^2\theta_i\rangle - 1)/(\langle 3\cos^2\theta_1\rangle - 1) \qquad (5)$$

The experimental values of $\Delta\nu_i^{obs}$ reported in literatures are assembled in Table II, where the ratios expressed relative to the $\Delta\nu_1^{obs}$ value for the C_1—D bond are also included.

In this study, we have examined two models for the definition of the molecular axis:

Model I. The para-axis of the cyanobipheny group is defined as the Z axis of the molecular frame X,Y,Z. The same rule applies to all the conformers.

TABLE II

Summary of Experimental D-NMR Data for nCB Reported in Literature

Sample	Temp/K	Carbon number	$\Delta\nu_i^{obs}$/kHz	$\Delta\nu_i^{obs}/\Delta\nu_1^{obs}$	Ref.
5CB	307.5	1	32.3	1.0	
		2	20.9	0.647	
		3	22.7	0.703	6
		4	14.7	0.456	
		5	10.8	0.336	
8CB	306.0	1	47.6	1.0	
		2	34.4	0.723	
		3	38.0	0.799	
		4	31.1	0.654	5
		5	33.3	0.700	
		6	25.7	0.538	
		7	24.8	0.522	
		8	1.3	0.027	

Model II. The molecular axis is assumed to lie along the direction connecting the N atom of the cyano group and the terminal carbon of the hydrocarbon tail. In our treatment, it suffices to define the direction of the molecular axis, with which values of θ_i can be estimated.

In brief, Model II differs from I in that the orientation of the molecular axis is variable depending on the configuration of the tail when observed within the coordinate system fixed to the mesogenic core (cyanobiphenyl group). The prescription adopted in Model II will provide a basis for the treatment of the dimer liquid crystals in the following paper.[17]

With the molecular axis defined as above, the orientation of the individual C—D bonds, as expressed in terms of $\cos^2\theta_i$, may be calculated easily for all allowed spatial configurations. The relative importance of a given configuration can be customarily expressed by the product of statistical weight factors[13] assigned to the constituent bonds. In the anisotropic mesophase, the second-order interaction such as $g^{\pm}g^{\mp}$ should be largely suppressed, and thus the weight ω was set equal to zero. (This condition will be tentatively relaxed in the later section: the effect is indeed shown to be insignificant.) The statistical weight factor σ_i was assigned to the gauche state of the i-th C—C bond, the weight of unity being given to the corresponding trans state. The C^{ph}—C_1 bond is allowed to take one of the two isoenergetic states, and thus, the statistical weight factor around this bond is set equal to unity. In the actual calculation, statistical weight

factors σ_i's ($1 \leq i \leq n-2$) were treated as variables within the range of $0 < \sigma_i < 0.5$, the upper limit being set around the σ value in the isotropic phase. The use of Equation (4) may yield $\Delta\nu_i$ with either a positive or negative sign. Comparison with the observed splittings requires only absolute values of $\Delta\nu_i$. Computations were iteratively repeated until the calculated values of $|\Delta\nu_i/\Delta\nu_1|$ reproduced those observed. The best-fit set of σ_i should lead to an estimate of bond conformation for the hydrocarbon tail. The signs of $\Delta\nu_i$ may be determined concurrently.

RESULTS OF CALCULATIONS

Model I

Values of $|\Delta\nu_i/\Delta\nu_1|$ were calculated according to the prescription described above. The results are shown in Figure 2, where the ratios $\Delta\nu_i^{obs}/\Delta\nu_1^{obs}$ determined by the D-NMR measurements (*cf.* Table II) are also indicated (open circles). A similar RIS treatment based on an essentially identical model has been reported by Boden et al.[5] In agreement with their results, the observed ratios $\Delta\nu_i^{obs}/\Delta\nu_1^{obs}$ are well reproduced by the calculation except those for the terminal CD_3 group (*cf.* Figure 2). Values of the statistical weight σ_i obtained from this analysis are listed in Table III. A distinct odd–even oscillation is

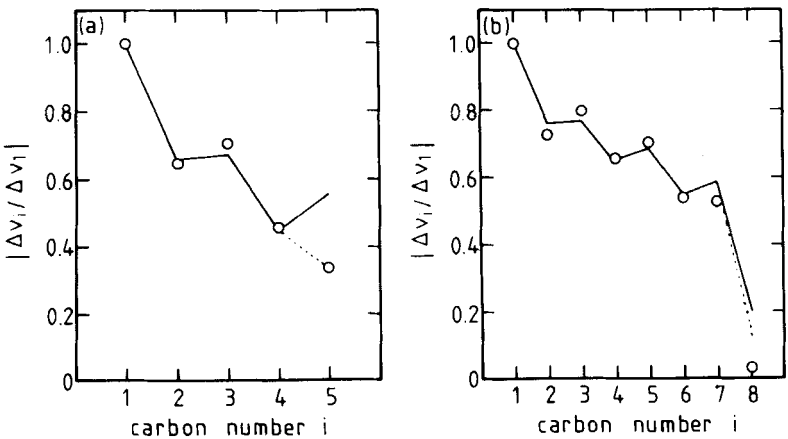

FIGURE 2 Ratios of the quadrupolar splitting $|\Delta\nu_i/\Delta\nu_1|$ plotted against carbon number i: (a) 5CB and (b) 8CB. Solid lines indicate the results calculated by using Model I. Observed values of the ratios $\Delta\nu_i^{obs}$ / $\Delta\nu_1^{obs}$ are shown by open circles. The dotted line indicates the improvement obtained by setting $\angle C_{n-1}C_nD = 116.0°$ for both 5CB and 8CB.

TABLE III

Values of the Statistical Weight Parameters Estimated from Model I and II for nCB

Statistical weight parameter	Model I	Model II
	5CB	
σ_1	0.129	0.188
σ_2	0.441	0.387
σ_3	0.119	0.188
	8CB	
σ_1	0.089	0.184
σ_2	0.446	0.298
σ_3	0.064	0.144
σ_4	0.323	0.275
σ_5	0.089	0.169
σ_6	0.446	0.234

observed in the σ values along the chain. These characteristic features of the hydrocarbon tail have been noted by several authors.[10,12,18,19]

The quadrupolar splitting of the terminal CD_3 group was found to vary rather sensitively with the bond angle $\angle C_{n-1}C_nD$ (or $\angle DC_nD$). In Figure 3, values of $|\Delta\nu_n/\Delta\nu_1|$ calculated for the CD_3 group are plotted as a function of this bond angle. Experimental values can be exactly reproduced when the angle $\angle C_{n-1}C_nD$ is set equal to 116.0°

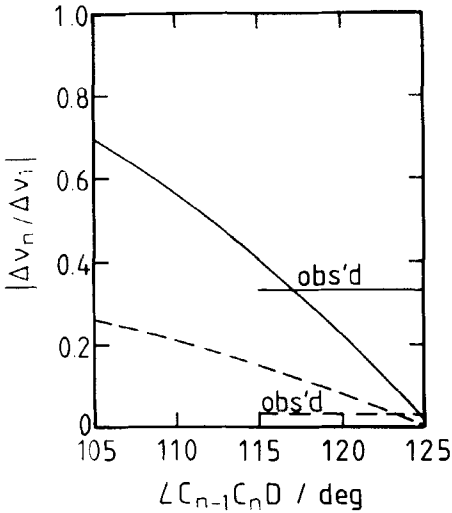

FIGURE 3 Variation of $|\Delta\nu_n/\Delta\nu_1|$ calculated according to Model I as a function of $\angle C_{n-1}C_nD$: solid curve for 5CB and broken curve for 8CB. Observed values $\Delta\nu_n^{obs}$ / $\Delta\nu_1^{obs}$ were indicated by the horizontal line.

for 5CB and 124.0° for 8CB. Alteration of the bond angle at the chain terminal should not affect the $|\Delta\nu_i/\Delta\nu_1|$ values of the preceding CD_2 groups ($i \leq n-1$). The improvement attained by setting $\angle C_{n-1}C_nD = 116.0°$ in both 5CB and 8CB is shown by the dotted lines in Figure 2. The values of $\angle C_{n-1}C_nD$ required to achieve an exact agreement are somewhat too large as compared with those generally adopted for relevant compounds, however.[15,20–22]

Model II

The model is introduced to account for the skewness in the molecular axis resulting from the spatial configuration of the hydrocarbon tail. Here the molecular axes are defined for the individual configurations of the alkyl chain. The treatment is otherwise the same as that of Model I. As stated earlier, the procedure is rather simple. The results derived from Model II are shown in Figure 4. The agreement with experimental values is nearly perfect for 5CB (Figure 4a). A small deviation in $|\Delta\nu_i/\Delta\nu_1|$ is noted for 8CB at C_5 and C_7-methylenes while the agreement is exact for the terminal CD_3 (Figure 4b). In general, experimental observations are well reproduced by the calculation based on Model II. The best-fit values of the statistical weight factor σ_i are compared with those of Model I in Table III. The odd–even oscillation of σ_i's becomes somewhat less marked in Model II.

The signs of the splitting $\Delta\nu_i$ were found to be negative in most cases. For the terminal group of 8CB, the magnitude of the splitting

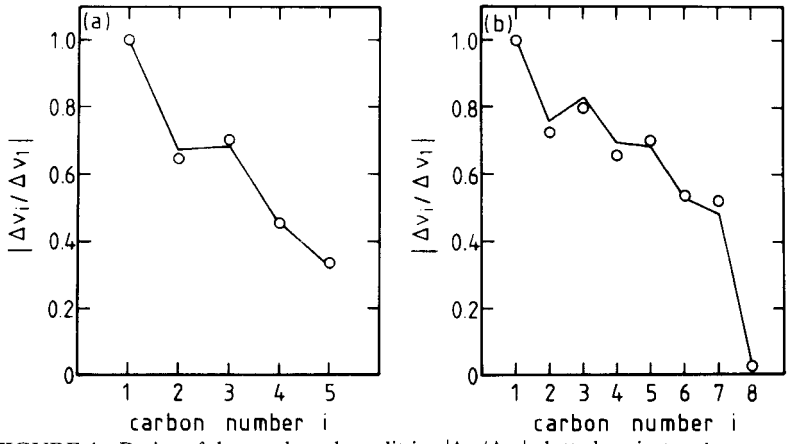

FIGURE 4 Ratios of the quadrupolar splitting $|\Delta\nu_i/\Delta\nu_1|$ plotted against carbon number i: (a) 5CB and (b) 8CB. Solid lines indicate the results calculated by using Model II. Observed values of the ratios $\Delta\nu_i^{obs}/\Delta\nu_1^{obs}$ are shown by open circles.

is small, and the sign of $\Delta\nu_8$ varies from positive in Model I to negative in Model II. These results are in agreement with those reported from the line shape analysis of the deuterium NMR spectra by Boden et al.[5] and Emsley et al.[6]: the sign of $\Delta\nu_8$ remains undetermined in the table given by the former authors.[5]

DISCUSSION

As illustrated above, the simulation based on Model I requires unrealistic values of the bond angle for $\angle C_{n-1}C_nD$. We have then examined a revised model which assumes a long molecular axis inclined at a given angle (α) with respect to the para-direction of the cyanobiphenyl group. This model has been used in the analysis of D-NMR spectra of *p*-alkoxybenzylidene-*p*-alkylaniline by Hsi et al.[19] In the present examples, calculations with α in the range 0 to 20° did not yield much improvement in the agreement with experimental data. After these trials, Model II was developed. As shown above, the observed D-NMR data are satisfactorily reproduced by the modifications assembled in this model. To assure the reliability of these results, computer simulations were carried out for all possible combinations of σ values. The best-fit values of σ_i were obtained as a unique solution in every calculation.

The bond conformations were estimated from the statistical weight factors determined above. Shown in Figure 5 are the fractions of the trans conformation (f_t) plotted against the C—C bond number along the hydrocarbon tail. The odd–even effect in f_t is less pronounced in Model II (open circles) as compared with Model I (filled circles) in both Figures 5a (5CB) and 5b (8CB). As inspection of a molecular model reveals, the C—C bond assigned an even number tends to take an orientation parallel to the para-axis of the biphenyl group in preferred conformations. Gauche rotations around the bond with an even number generally create kink-conformations which are seemingly incompatible with the one-dimensional nematic environment: thus in such a field, the gauche arrangement should be suppressed for this type of bond. With the same line of reasoning, conformations $g^{\pm}g^{\mp}$, characterized by the weight of ω, should occur rarely in the nematic field. Simplification ($\omega = 0$) adopted in the above simulation may be justified on this basis. In fact, it can be easily shown that use of a non-zero value for ω within the limit not exceeding that ($\omega = 0.038$) in the isotropic state does not appreciably alter the result: with $\omega = 0.038$, calculated values of $|\Delta\nu_i/\Delta\nu_1|$ are affected by the amount

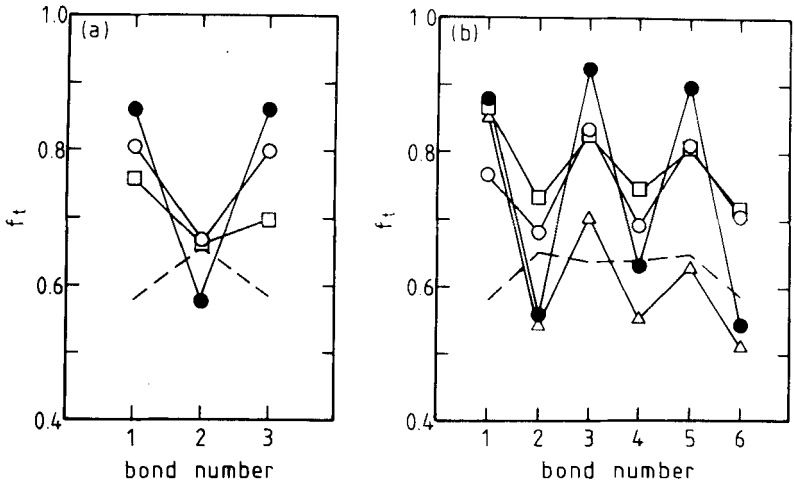

FIGURE 5 Bond conformation of the internal C—C bonds in the nematic phase. The fraction of trans conformer (f_t) was estimated for (a) 5CB and (b) 8CB. Calculated values are indicated by filled circles for Model I and by open circles for Model II. The broken lines indicate values of f_t calculated for the isotropic phase. Values of f_t estimated by Emsley et al. for 5CB and 8CB (open squares), and by Samulski et al. for 8CB (open triangles) are also included.

of less than 0.1%. For comparison, values of f_t calculated for the isotropic state (*i.e.*, free from any nematic constraint) are indicated by the broken lines in Figure 5. Also included in Figure 5 are the bond conformations for 5CB and 8CB (open squares) estimated by Emsley et al.,[10] and those for 8CB (open triangles) by Samulski et al.[12] The odd–even oscillations obtained by our analysis are close to those reported by Emsley et al. Samulski et al.'s treatment predicts an odd–even effect with somewhat lower values of f_t for all C—C bonds.

Thermal variation of the quadrupolar splitting has been reported for 5CB,[6,23] which exhibits a stable nematic mesophase over a substantial temperature range. These experimental data were analyzed in our scheme, and the statistical weight parameters σ_i (i = 1 to 3) were estimated at various temperatures. The results derived from Model II are plotted in Figure 6 against the temperature expressed relative to T_{NI}. All σ_i's increase gradually with temperature. The variation of σ_1 and σ_3 are nearly identical over the whole temperature range. The value of σ_2 increases a little more rapidly than σ_1 and σ_3 at lower temperatures. Also included in the figure are the variations of the order parameter S_{ZZ} for the long molecular axis. These values were estimated from $\Delta\nu_1^{obs}$ and the calculated average $(\langle 3\cos^2\theta_1\rangle - 1)/2$ according to the relation given in Equation (4). Values of S_{ZZ} may

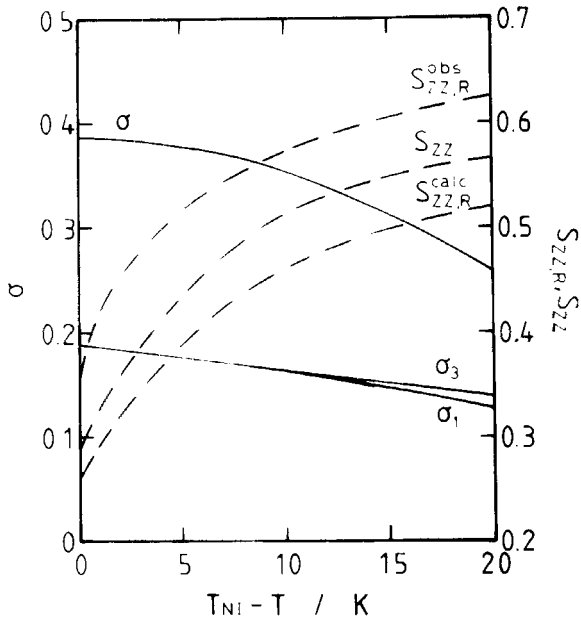

FIGURE 6 Variation of the statistical weight parameter σ_i plotted as a function of temperature $T_{NI} - T$ (solid curves). Temperature dependence of the order parameter for the molecular axis, S_{ZZ}, and that for the mesogenic core axis, $S^{calc}_{ZZ,R}$ are also indicated by broken curves. The observed values of $S^{obs}_{ZZ,R}$ were taken from Emsley et al.'s work.[6]

be converted to the order parameter of the para-axis of the cyanobiphenyl group by the expression

$$S_{ZZ,R} = S_{ZZ} (\langle 3\cos^2\theta_R \rangle - 1)/2 \quad (5)$$

where θ_R represents the disorientation angle of the long molecular axis relative to the para-axis of the cyanobiphenyl group, and the bracket denotes the average taken over all allowed conformations. Values of $S_{ZZ,R}$ thus derived are compared in Figure 6 with those directly determined by the D-NMR measurements of 5CB[6] with ring-protons deuterated. Experimental values of $S^{obs}_{ZZ,R}$ decrease very rapidly as the temperature approaches T_{NI}. Such an observed trend is reproduced by the calculation based on Model II, but with somewhat lower estimates of $S^{calc}_{ZZ,R}$: the difference amounts to *ca.* 0.08 at around T_{NI}.

The fraction of a given conformer may be calculated from the set of σ_i values determined above. In Table IV, fractions of some rep-

TABLE IV

Distribution of Conformers in the Nematic and Isotropic Phases[a]

(a) 5CB

Conformation	Fraction/%	
	Nematic	Isotropic
ttt	39.55(33.2)	18.21(22.7)
tg^+t	12.57(11.59)	8.03(8.35)
tg^-t	12.57(11.59)	8.03(8.35)
ttg^+	6.02(7.17)	8.03(8.35)
ttg^-	6.02(7.17)	8.03(8.35)
g^+tt	5.82(4.85)	8.30(8.35)
g^-tt	5.82(4.85)	8.30(8.35)
tg^+g^+	1.91(2.48)	3.54(3.07)
tg^-g^-	1.91(2.48)	3.54(3.07)
g^+g^+t	1.85(1.74)	3.66(3.07)
g^-g^-t	1.85(1.74)	3.66(3.07)
g^+tg^-	0.89(2.64)	3.66(3.07)
g^-tg^+	0.89(2.64)	3.66(3.07)
g^+tg^+	0.89(1.82)	3.66(3.07)
g^-tg^-	0.89(1.82)	3.66(3.07)
$g^+g^+g^+$	0.28(0.95)	1.61(1.13)
$g^-g^-g^-$	0.28(0.95)	1.61(1.13)

(b) 8CB

Conformation	Fraction/%	
	Nematic	Isotropic
ttttt	14.30(10.80)	3.70(5.54)
tg^+ttt	4.27(3.35)	1.63(2.04)
tg^-ttt	4.27(3.35)	1.63(2.04)
$tttg^+tt$	3.94(3.17)	1.63(2.04)
$tttg^-tt$	3.94(3.17)	1.63(2.04)
$ttttg^+$	3.35(3.35)	1.63(2.04)
$ttttg^-$	3.35(3.35)	1.63(2.04)
g^+tttt	2.63(1.14)	1.68(2.04)
g^-tttt	2.63(1.14)	1.68(2.04)
$tttg^+t$	2.43(2.29)	1.63(2.04)
$tttg^-t$	2.43(2.29)	1.63(2.04)
ttg^+ttt	2.06(1.48)	1.63(2.04)
ttg^-ttt	2.06(1.48)	1.63(2.04)
tg^+tg^-tt	1.17(1.16)	0.71(0.75)
tg^-tg^+tt	1.17(1.16)	0.71(0.75)
tg^+tg^+tt	1.17(1.16)	0.71(0.75)
tg^-tg^-tt	1.17(1.16)	0.71(0.75)
tg^+tttg^+	1.00(1.12)	0.71(0.75)
tg^-tttg^-	1.00(1.12)	0.71(0.75)

[a]Values in parentheses are those reported by Emsley et al.[10]

resentative conformers estimated by using Model II are listed. For comparison, values reported by Emsley et al.[10] are indicated in parentheses. Our calculations were carried out for the same temperatures as those employed in Emsley et al.'s treatment. The dominant fraction is due to the all-trans conformation in both schemes, but the weight is higher in our model (40% vs. 33% for 5CB, and 14% vs. 11% for 8CB). In 8CB, $tg^{\pm}ttt$ is more populated than $ttttg^{\pm}$ in our model while in Emsley et al.'s model, both exist in an equal amount. Except for this point, the rankings among one-gauche conformers are the same in the two models. Reversals of the order occur at several places among two-gauche conformers, but their population is generally low. It may be interesting to note that distributions of the conformer resemble each other, in spite of a large difference in the underlying concept of the models.

The nematic constraint vanishes at the nematic to isotropic phase transition temperature. The conformational distribution of the hydrocarbon tail should undergo a concomitant transition. Conformational contributions in the transition energy and entropy can be easily estimated from the conformer fraction, assuming that the conformation in the isotropic state is perfectly random. Conformational energies of the individual isomers were calculated by using the conventional values of the energy parameter such as $E_{\sigma 1} = 0.48$,[24] $E_{\sigma i} = 0.5$ with $i = 2$ to $n - 2$, and $E_{\omega} = 2.0$ for the second-order interaction involved in $CC^{ph}\,\circlearrowleft C\circlearrowleft\,CC$ and $CC\,\circlearrowleft C\circlearrowleft\,CC$, units being kcal mol^{-1}. Average energies, $\langle E\rangle_I$ and $\langle E\rangle_N$, were then evaluated from the conformational distributions of the respective phase. The energy ($\Delta\langle E\rangle_{NI,conf}$) and entropy changes ($\Delta S_{NI,conf}$) associated with the conformational transition can be estimated by

$$\Delta\langle E\rangle_{NI,conf} = \langle E\rangle_I - \langle E\rangle_N \tag{6}$$

and

$$\Delta S_{NI,conf} = -R \ln f_N + \Delta\langle E\rangle_{NI,conf}/T \tag{7}$$

where f_N represents the fraction of the conformer permitted in the nematic phase. The values of f_N derived from the D-NMR analysis are 0.54 in Model II and 0.57 in Emsley et al.'s scheme. The thermodynamic quantities calculated for 5CB (in Model II) near the transition temperature are as follows: $\Delta\langle E\rangle_{NI,conf} = 0.202$ kcal mol^{-1} and $\Delta S_{NI,conf} = 0.939R$ ($T = 307.5$ °K). Calculations based on the nematic fraction of Emsley et al. lead to a similar estimate: $\Delta\langle E\rangle_{NI,conf}$

$= 0.143$ kcal mol^{-1} and $\Delta S_{\mathrm{NI,conf}} = 0.800R$ ($T = 294$ °K). Conformational contributions estimated in this manner are considerably large as compared with the observed thermodynamic quantities such as $\Delta H_{\mathrm{NI}}^{\mathrm{obs}} = 0.12$ kcal mol^{-1} and $\Delta S_{\mathrm{NI}}^{\mathrm{obs}} = 0.200R$. (Here the correction required for the volume expansion is estimated to be on the order of 1×10^{-7} cal mol^{-1} deg^{-1} in $\Delta S_{\mathrm{NI}}^{\mathrm{obs}}$, and thus negligibly small.[25]) The calculation for 8CB in Model II yielded $\Delta\langle E\rangle_{\mathrm{NI,conf}} = 0.409$ kcal mol^{-1} and $\Delta S_{\mathrm{NI,conf}} = 2.025R$, which should be compared with the observed quantities such as $\Delta H_{\mathrm{NI}}^{\mathrm{obs}} = 0.212$ kcal mol^{-1} and $\Delta S_{\mathrm{NI}}^{\mathrm{obs}} = 0.341R$. The discrepancy becomes larger in 8CB. Steric interactions associated with the disorientation of rigid rods at N–I phase transition should produce a substantially negative contribution to ΔS_{NI}, partially compensating for the large positive value of $\Delta S_{\mathrm{NI,conf}}$. At this moment, we have no plausible explanation for the discrepancy noted in $\Delta H_{\mathrm{NI,conf}}$.

CONCLUDING REMARKS

The scheme (termed Model II) developed here gives a fair account of the quadrupolar splittings of deuterons incorporated in the hydrocarbon tails of 5CB and 8CB. In this scheme, we introduced an empirical rule for the definition of the molecular axis, keeping in mind that we are not attempting a rigorous analysis but simply trying to develop a scheme which is also applicable to dimer and polymer liquid crystals. The orientational order of alkyl cyanobiphenyls was treated by a single symmetric ordering matrix. The conformational distributions estimated for 5CB and 8CB in the nematic phase were shown to be rather close to those of Emsley et al.,[10] who assume the ordering matrix to be conformation-dependent.

Our scheme is simple, and it has an advantage in that any separate consideration for the external potential field is not required. The statistical weights assigned to the individual bond rotations can be directly elucidated from the observed quadrupolar splittings of the C—D bonds. The conformational distributions thus determined provide information regarding the intramolecular contribution to the energy and entropy change at the nematic–isotropic transition. Further refinement of the model is obviously needed, and now in progress. Application of our scheme to the dimer liquid crystals comprising mesogenic cores joined at both terminals of a soft-spacer will be described in a following paper.[17]

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