Conformational Anisotropy of *n*-Alkanes Dissolved in a Nematic Solvent: A Rotational Isomeric State Analysis of Proton–Proton Dipolar Coupling and Deuterium Quadrupolar Splitting Data

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(Received September 20, 1990)

ABSTRACT: Conformational anisotropy of *n*-alkane chains incorporated in a nematic environment has been investigated. Experimental values of proton–proton dipolar couplings of *n*-hexane [M. Gochin *et al.*, *Mol. Phys.*, **69**, 671 (1990)] and ²H-NMR quadrupolar splittings of a series of *n*-C_{*n*}D_{2*n*+2} (*n* = 5, 6, 7, 8, 10, and 16) [B. Janik *et al.*, *J. Phys. Chem.*, **91**, 1842 (1987); D. J. Photinos *et al.*, *J. Phys. Chem.*, **94**, 4688 (1990)] have been analyzed according to the model previously employed in the study of dimer and polymer main-chain liquid crystals. Our treatment proceeds as follows: 1. All possible configurations are enumerated for a free molecule within the framework of the RIS approximation. 2. For each conformer, the molecular axis is defined along the 'longest' principal axis of inertia. 3. Conformational statistical weight factors assigned to the individual bond rotations are adjusted according to the simplex method so as to reproduce the observations. The convergence of iteration was monitored by the reliability factor. The agreement between theory and experiment was found to be satisfactory in all examples. The bond conformations derived from the observed data were compared with those estimated for the free state. *n*-Alkane chains were found to be highly anisotropic in the nematic media.

KEY WORDS *n*-Alkane / Conformation / Liquid Crystal / Dipolar Coupling
/ Deuterium NMR Quadrupolar Splitting /

In the free state, *n*-alkane chains are flexible, a variety of spatial configurations being permitted. When such nonmesomorphic solutes are incorporated in liquid crystals, the normal isotropization temperatures are generally depressed, and two-phase regions are formed. Oweimreen and Martire^{1,2} have extensively studied thermodynamic aspects of solute-induced NI transitions as a function of size, shape, and flexibility of solute molecules. The slopes of the nematic and isotropic phase boundary lines have provided a measure of the nematic phase stability. In this work, *n*-alkane molecules (*n*-C₈H₁₈–*n*-C₁₄H₃₀) were found to be more compatible with, thus less destructive to the ordered nematic phase of *p*-methoxybenzylidene-*p*'-*n*-butylaniline (MBBA) as compared with some spherical or branched solutes

having similar hard core volumes. *n*-Alkanes exhibited an essentially identical behavior in *p*-*n*-pentyl-*p*'-cyanobiphenyl (5CB). In this respect Kronberg *et al.*'s NMR work³ is also suggestive. They studied the molecular ordering of nematic MBBA, MBBA + 5 mol% of *n*-hexane, *n*-hexadecane, and their branched isomers from the dipolar splitting due to the ortho protons of the benzene rings in MBBA. While *n*-C₆H₁₄ and *n*-C₁₆H₃₄ gave nearly superimposable order parameter vs. temperature curves, branched C₁₆H₃₄ was clearly more destructive, with lower solution order parameters, than *n*-C₁₆H₃₄. Martire suggested in his review² that the aligned environment should somewhat restrict the conformational freedom of the solute chains.

Samulski and his group^{4–7} have measured

the ^2H -NMR quadrupolar splittings of a series of perdeuterated n -alkanes $\text{C}_n\text{D}_{2n+2}$ ($n=5, 6, 7, 8, 10$, and 16) dissolved in a nematic solvent (Merck Phase V). In parallel to these studies, Gochin *et al.*^{8,9} have determined sixteen dipolar couplings between protons of partially deuterated n -hexane in a liquid crystal (Kodak EK11650) by means of two-dimensional NMR techniques. Under experimental conditions employed, various conformations exist in dynamic equilibrium, and one can only observe a weighted average of the ordering matrices¹⁰:

$$\langle S_{\alpha\beta} \rangle = \sum_g p^g S_{\alpha\beta}^g \quad (1)$$

where $S_{\alpha\beta}$ is the $\alpha\beta$ component of the ordering matrix, and p is the probability of conformer g . Experimental data points are however usually insufficient to determine both the probability and the ordering matrix independently. In an effort to elucidate the effect of the anisotropic field on the configuration of a flexible chain, Samulski *et al.*⁵ formulated the external mean-torque potential in two ways: (1) on the basis of the anisotropic-dispersion force and (2) on account of steric or excluded volume interactions, in which each conformer is treated as a rigid entity defined by its shape. Gochin *et al.*⁹ have also adopted the latter model in the analysis of their dipolar coupling data. The results of these analyses suggest that the probabilities of the more elongated conformers are somewhat enhanced in the liquid crystalline environment.

In recent papers,^{6,7} Photinos, Samulski, and Toriumi proposed a new model, in which the interaction with the external field is estimated as a sum of contributions from various segments of the conformer. The analysis obviously does not conform to eq 1. From this study, they concluded that a good fit to experimental couplings could be achieved on the basis of the conformer fractions nearly identical to those in the isotropic state.

In all of the aforementioned treatments, however, best-fit values of the conformer

probabilities were estimated by adjusting the interaction parameters characteristically defined in the individual theoretical models. The optimal values of these parameters determined by simulation usually elude verifications from other physical measurements.

On the other hand, a simpler model, so-called single-ordering-matrix scheme¹¹ is often useful in providing an approximate insight into the molecular ordering in liquid crystals. In this scheme, the orientational order parameters S defined in eq 1 are taken to be identical for all the conformers involved in the liquid crystalline environment. For the problem at hand, this assumption may be justified by the fact that major fractions are composed of conformations of moderately elongated forms even in the isotropic state. For given conformers, the axis of the principal moment of inertia tensor may be identified as the molecular axes. If a cylindrical symmetry can be assumed in the nematic system, the contribution arising from S_{zz} becomes foremost important. As pointed out by Photinos *et al.*,⁶ adoption of a single order parameter S in eq 1 possibly enhances the probabilities of more elongated conformers. This model has been examined by Gochin *et al.* in their earlier work.⁸ It is interesting to note that the results obtained by this simpler model are in good agreement with those derived from the more sophisticated approach.⁹

In our previous studies¹²⁻¹⁴ on the main-chain dimer and polymer liquid crystals, we have developed a simulation scheme on the basis of a single-ordering-matrix representation, which has been applied to the interpretation of ^2H -NMR quadrupolar splitting data of flexible spacers. The treatment can be easily extended to n -alkane molecules incorporated in a liquid crystalline system. Following Samulski *et al.*^{4,5} and Gochin *et al.*,^{8,9} we define molecular axis for each conformer in the direction along the principal axis of inertia with the minimum moment. In our scheme, statistical weight factors assigned to every rotatable bond are treated as variables in the

simulation of the observed data. The fraction of the nematic conformer can be easily estimated from the best-fit set of statistical weight parameters thus established. In small molecules such as *n*-hexane, the number of rotatable bonds is limited, and therefore the fraction of the individual conformers can be assessed more directly without partitioning of the weights. Then, the procedure is reduced to that of Gochin *et al.*⁸ In this work, we have first tested our scheme against the proton-proton dipolar coupling data of Gochin *et al.*^{8,9} The analysis has been extended later to include the deuterium quadrupolar splitting data of Samulski *et al.*^{5,6}

COMPUTATIONAL PROCEDURES

The structural parameters used in the calculation are listed in Table I. The bond angle $\angle$ DCD was taken to be 107.9° as suggested from the electron diffraction studies on *n*-propane.¹⁵ Bond angles $\angle$ CCD for methylene and methyl groups were calculated from the $\angle$ DCD value. For the bond rotation, a threefold potential with minima at $0, \pm 112.5^\circ$ was assumed.¹⁶ All possible configurations were enumerated for a free molecule within the framework of the RIS approximation.¹⁷

The observed dipolar coupling $\langle D_{ij} \rangle$ between protons *i* and *j* is given by¹⁸

$$\langle D_{ij} \rangle = (2/3) \sum_{\alpha\beta} \langle S_{\alpha\beta} D_{ij\alpha\beta} \rangle \quad (2)$$

The dipolar tensor component $D_{ij\alpha\beta}$ for a given conformer is expressed by

$$D_{ij\alpha\beta} = (-\gamma^2 h / 4\pi^2 r_{ij}^3) \times (3 \cos \theta_{ij\alpha} \cos \theta_{ij\beta} - \delta_{\alpha\beta}) \quad (3)$$

where r_{ij} is the internuclear distance, and $\theta_{ij\alpha}$ is the angle between the vector r_{ij} and the α axis of the molecule-fixed frame. On the basis of the single-ordering-matrix approximation, eq 2 can be rewritten as

$$\langle D_{ij} \rangle = (2/3) \sum_{\alpha\beta} S_{\alpha\beta} \langle D_{ij\alpha\beta} \rangle \quad (4)$$

Since the number of experimental data acquired from the deuterium quadrupolar splitting measurement is rather limited, it is more convenient to perform the simulation by using a simple expression such as

$$\Delta\nu_h = (3/2)(e^2 q Q / h) S_{zz} (\langle 3 \cos^2 \theta_h \rangle - 1) / 2 \quad (5)$$

where $e^2 q Q / h$ is the quadrupolar coupling constant, *z* represents the principal axis of the ordering matrix with the largest field gradient, and S_{zz} denotes the orientational order parameter of the *z* axis with respect to the nematic director. The molecular axis is defined along the *z* axis, and θ_h is the angle between the C_h -D bond and the molecular axis, and the bracket indicates an average over all allowed conformations. In the single-ordering-matrix scheme, the quadrupolar splitting ratio $\Delta\nu_h / \Delta\nu_k$ is free from the S_{zz} value. We thus have

$$\Delta\nu_h / \Delta\nu_k = (\langle 3 \cos^2 \theta_h \rangle - 1) / (\langle 3 \cos^2 \theta_k \rangle - 1) \quad (6)$$

To facilitate the analysis, *k* is taken to be the C-D bond of the central methylene unit(s), *i.e.*, $k = n/2$ (for even *n*) or $(n+1)/2$ (for odd *n*).

Table I. Geometrical parameters used for *n*-alkanes

Bond	Length	Bond angle	Angle
	Å		deg.
C-C	1.53	$\angle$ DCD	107.9
C-H	1.10	$\angle$ CCD (CD_2)	109.2
		$\angle$ CCD (CD_3)	111.0
		$\angle$ CCC	112.0

Figure 1. Schematic representation of an *n*-hexane molecule in its all-*trans* conformation. The carbon atoms and C-C bonds are numbered successively from one end to the other. The protons are numbered as indicated.

For large molecules, where plenty of conformers are permitted, a further approximation may be required. Following previous treatment,¹²⁻¹⁴ we adopt a scheme in which relative importance of a given conformer can be expressed as a product of statistical weight factors assigned to the constituent bonds. In this study, the statistical weight factor σ_h was assigned to the *gauche* state of the *h*-th C-C bond, the weight of unity being given to the corresponding *trans* state. The symmetry of *n*-alkane molecules dictates that $\sigma_h = \sigma_{n-h}$. For the terminal C-C bond, a threefold symmetric rotational potential was assumed: *i.e.* $\sigma_1 = \sigma_{n-1} = 1$. On the expectation that the second-order interaction such as $g^\pm g^\mp$ should be of rare occurrence in the nematic environment, the weight ω was set equal to zero. The validity of this assumption will be examined later.

Computations were iteratively repeated according to the simplex method¹⁹ until a satisfactory agreement between the calculated and observed values was attained. The convergence of the iteration was monitored by the reliability factor,

$$R(\%) = \left[\frac{\sum (A_{\text{calcd}} - A_{\text{obsd}})^2}{\sum (A_{\text{obsd}})^2} \right]^{1/2} \times 100 \quad (7)$$

where A stands for $\langle D_{ij} \rangle$ or $\Delta v_h / \Delta v_k$. The computations were carried out by using an ETA10 supercomputer.

The configuration of *n*-alkane chains may be restricted to some extent in the anisotropic environment. This effect may be examined on the basis of a simplified cylinder model, in which the axial ratio L/D provides a measure of the molecular asymmetry. The length L and diameter D of cylinders are estimated for the individual configurations by assuming van der Waals radii of the carbon and hydrogen atoms to be 1.70 and 1.20 Å, respectively.^{4,20} The conformers of contracted forms can be eliminated from the ensemble by setting a threshold value (cut-off axial ratio) of L/D .

RESULTS AND DISCUSSION

Proton-Proton Dipolar Couplings

A dipolar coupling depends on two configuration-sensitive parameters: r_{ij} and θ_{ij} . In particular, internuclear distance depends only on intramolecular structure. Gochin *et al.*^{8,9} have reported two sets of proton-proton dipolar coupling data on partially deuterated *n*-hexane dissolved in EK11650 (*ca.* 20 mol%): one by COSY and the other by INADEQUATE. Simulations were carried out according to eq 4 with resort to Gochin *et al.*'s COSY data. The results are shown in Table II. The R value was found to be minimized down to 2.2%, indicating that the experimental values are well reproduced by the calculation. The order parameters $S_{\alpha\beta}$ estimated concomitantly are given in the footnote to the table.

Table II. Results of the simulation for proton-proton dipolar couplings of *n*-hexane reported by Gochin *et al.*^a

<i>i-j</i>	$\langle D_{ij} \rangle / \text{Hz}$	
	Observed ^b	Calculated ^c
1-2	1876 (± 28)	1864
1-12	-206 (± 13)	-197
1-4	-386 (± 15)	-402
1-10	-322 (± 14)	-288
1-6	-1034 (± 25)	-948
1-8	-598 (± 15)	-643
4-5	3974 (± 34)	3975
4-10	-609 (± 14)	-595
5-10	-713 (± 18)	-777
6-7	4487 (± 34)	4485
6-8	43 (± 12)	101
7-8	-190 (± 12)	-206
4-6	186 (± 14)	193
5-6	81 (± 12)	88
4-8	-1616 (± 25)	-1661
5-8	-1086 (± 27)	-1042
$R/\%$	1.2	2.2

^a References 8 and 9.

^b Values reported on the basis of the COSY spectra.

^c Optimized values of the components of the ordering tensor are $S_{zz}=0.211$, $S_{xx}-S_{yy}=0.061$, $S_{xy}=0.036$, $S_{xz}=-0.040$, and $S_{yz}=0.013$.

Table III. Conformer probabilities of *n*-hexane estimated from the proton-proton dipolar coupling data

Conformation (Multiplicity)	Conformer probability/%				
	Our work	Gochin <i>et al.</i>			Free chain
		Single-ordering- matrix model ^a	Model A ^b	Model B ^c	
<i>ttt</i> (1)	32.8	37.0 (32.0)	30.4	30.3	18.9
<i>ttg</i> ⁺ (4)	8.5	7.3 (8.8)	8.3	8.3	8.2
<i>tg</i> ⁺ <i>t</i> (2)	7.7	8.5 (8.0)	8.3	8.3	8.2
<i>tg</i> ⁺ <i>g</i> ⁺ (4)	2.0	2.0 (2.0)	2.3	2.3	3.6
<i>g</i> ⁺ <i>tg</i> ⁺ (2)	2.2	0.5 (0.8)	2.3	2.3	3.6
<i>g</i> ⁺ <i>t</i> <i>g</i> ⁻ (2)	2.2	4.0 (3.6)	2.3	2.3	3.6
<i>g</i> ⁺ <i>g</i> ⁺ <i>g</i> ⁺ (2)	0.5	0.0 (0.0)	0.6	0.6	1.5

^a The values in parentheses were calculated by using the structural parameters in Table I.

^b After Samulski *et al.* (ref 5).

^c After Burnell *et al.* (ref 21).

The conformer probabilities calculated from the optimum values of the bond statistical weights are given in the second column of Table III, where Gochin *et al.*'s results^{8,9} obtained by using various models are also shown for comparison. Listed in the third column are the conformer probabilities reported by these authors on the basis of their single-ordering-matrix analysis.⁸ For a comparison purpose, we repeated their calculation by using structural parameters adopted in our work (*cf.* Table I). The values thus derived are indicated in parentheses in the same column. The components of the average order parameter elucidated in this manner are $S_{zz}=0.210$ (0.207), $S_{xx}-S_{yy}=0.066$ (0.056), $S_{xy}=-0.002$ (-0.003), $S_{xz}=-0.038$ (-0.015), and $S_{yz}=0.020$ (0.009), Gochin *et al.*'s values being cited in parentheses. The results obtained by using these two single-ordering-matrix schemes are favorably compared. On the assumption that excluded-volume-type steric interactions should affect the orientational ordering of solute molecules in the liquid crystalline environment, Gochin *et al.*⁹ have examined two theoretical approaches: Model A after Samulski *et al.*⁵ and Model B after Burnell *et al.*²¹ In these models, the total energy of a

solute conformer is defined as a sum of internal and external energies. The order parameter varies as a function of the size and shape of individual conformers. In this treatment, Gochin *et al.*⁹ also adjusted the *gauche* energy (an internal energy parameter) to achieve the best-fit simulation. The results of calculations are cited in the fourth and fifth columns. In terms of the conformer probabilities, the differences between the single-ordering-matrix and two excluded-volume models are trivial. In the last column of the table, the corresponding probabilities calculated by using conventional energy parameters for the isotropic state¹⁷ are listed.

Deuterium NMR Quadrupolar Splittings

In recent papers,^{6,7} Photinos *et al.* have reported experimental values of the quadrupolar splitting for *n*-decane-*d*₂₂ dissolved in nematic Phase V. Dipolar splittings due to geminal deuterium pairs were also measured. We have attempted to examine our scheme (eq 6) against these data. The adjustable parameters were fitted to the observed quadrupolar splitting ratios $\Delta\nu_h/\Delta\nu_k$ by minimizing the *R* factor. Numbers are given to each constituent bond from one terminal to the midpoint of the

Table IV. Results of the simulation for quadrupolar splitting ratios of *n*-decane- d_{22} reported by Photinos *et al.*^a

Number of allowed conformers	Carbon number	$\frac{\Delta\nu_h^b}{\Delta\nu_k} \left(\frac{D_h^b}{D_k} \right)$	Bond number	f_i	S_{zz}
577 (whole)	1	0.236			
	2	0.760 (0.78)	2	0.832	0.371
	3	0.895 (0.91)	3	0.887	
	4	0.965 (0.97)	4	0.910	
	5	1.000 (1.00)	5	0.887	
	<i>R</i> /%	0.000			
469 ^c	1	0.236			
	2	0.760 (0.78)	2	0.831	0.371
	3	0.865 (0.91)	3	0.885	
	4	0.965 (0.97)	4	0.909	
	5	1.00 (1.00)	5	0.883	
	<i>R</i> /%	0.000			
355 ^d	1	0.236			
	2	0.760 (0.78)	2	0.822	0.375
	3	0.895 (0.91)	3	0.874	
	4	0.965 (0.97)	4	0.898	
	5	1.000 (1.00)	5	0.870	
	<i>R</i> /%	0.000			
Observed	1	0.236			
	2	0.760 (0.80)			
	3	0.895 (0.90)			
	4	0.965 (0.95)			
	5	1.000 (1.00)			

^a Reference 6.^b Subscript *k* denotes the central methylene units.^c Conformers with $L/D < 1.50$ are omitted.^d Conformers with $L/D < 1.70$ are omitted.

chain. The results are shown in Table IV for the ensemble of whole conformers as well as two additional sets chosen on the basis of the asymmetry factor L/D . The observed quadrupolar splitting data are quantitatively reproduced by the simulation in all examples: $R=0.00$. The bracketed values are the ratios of the dipolar couplings calculated from the best-fit parameter set derived as above. Experimental values are listed in the last rows. The agreement for the dipolar coupling data is also satisfactory. Bond conformations

estimated on this basis are given in terms of the *trans* fraction (f_i). The analysis yields f_i values of about 90% for the internal C–C bonds, and slightly lower estimates for the terminals. The contribution arising from conformers of less elongated forms may be examined by eliminating these species from the ensemble. By setting the cut-off axial ratio at 1.50 and 1.70, the numbers of allowed conformers are reduced to 469 and 355, corresponding to a reduction of 19% and 38%, respectively. As shown in the table, the

Table V. Results of the simulation for quadrupolar splitting ratios of *n*-C_{*n*}D_{2*n*+2} (*n* = 5, 6, 7, 8, and 16) reported by Janik *et al.*^a

<i>n</i>	Carbon number	$\Delta\nu_h/\Delta\nu_k$		<i>R</i> /%	Bond number	<i>f_t</i>	<i>S_{zz}</i>
		Calcd	Obsd				
5	1	0.293	0.284	0.77	2	0.820	0.218
	2	0.949	0.955				
	3	1.000	1.000				
6	1	0.294	0.294	0.00	2	0.818	0.266
	2	0.888	0.888		3	0.833	
	3	1.000	1.000				
7	1	0.255	0.245	0.86	2	0.832	0.304
	2	0.844	0.851		3	0.858	
	3	0.954	0.947				
	4	1.000	1.000				
8	1	0.256	0.256	0.00	2	0.830	0.334
	2	0.813	0.813		3	0.873	
	3	0.943	0.943		4	0.898	
	4	1.000	1.000				
16	1	0.206	0.206	0.12	2	0.845	0.456
	2	0.677	0.678		3	0.896	
	3	0.799	0.799		4	0.922	
	4	0.878	0.879		5	0.939	
	5	0.935	0.934		6	0.963	
	6	0.972	0.973		7	0.953	
	7	0.989	0.987		8	0.949	
	8	1.000	1.000				

^a Reference 5.

experimental observations are equally well reproduced by either of these conformer sets. The *trans* fraction (*f_t*) around given C–C bonds tends to decrease slightly as conformers of smaller *L/D* are eliminated. These results indicate that contribution from less elongated forms are mostly suppressed in the simulation involving whole conformers.

We have further extended our treatment to include Janik *et al.*'s deuterium quadrupolar splitting data⁵ on *n*-alkanes with *n* = 5, 6, 7, 8, and 16. (*n*-Decane has already been treated above by using a newer set of experimental data). The measurements were carried out for a 0.5 mol% solution in Merck Phase V. The results of simulations are summarized in Table

V. As shown by comparison, the agreement with experiment is again quantitative (*R* < 1%). Especially in the case of *n*-C₆ and *n*-C₈, *R* values are minimized to 0.00. For *n*-C₁₆, the iterative calculation required a large computer time, and therefore it was terminated before the minimum *R*-value was attained. In Table V, the *trans* fractions estimated for the constituent bonds are listed. These results again suggest that *n*-alkane chains prefer to take *trans*-rich conformations to cope with the uniaxial environment. The populations of the all-*trans* conformation are estimated to be 66.0% for *n*-C₅, 53.8% for *n*-C₆, 48.9% for *n*-C₇, 45.3% for *n*-C₈, 38.3% for *n*-C₁₀, and 33.0% for *n*-C₁₆. It should be reminded here that these

Figure 2. Variation of the end-to-end dimension $[\langle r^2 \rangle / (n-1)]^{1/2}$ with n . The results derived from the deuterium quadrupolar splitting data of Janik *et al.*⁵ and Photinos *et al.*⁶ are indicated by open circles. Shown by filled circles are those estimated for the isotropic state. Values calculated for the all-*trans* form are also indicated for comparison (open squares).

values were derived from the measurements on the mixture containing 0.5 mol% of *n*-alkane solutes. As shown in Table III, a lower estimate (32.8%) is obtained for *n*-C₆ from the analysis of Gochin *et al.*'s data,^{8,9} for which a solution of *ca.* 20 mol% was employed.

The average dimension of a chain molecule is often expressed by the root-mean-square end-to-end distance $\langle r^2 \rangle^{1/2}$. The results of calculations for the nematic and isotropic states are indicated in Figure 2, where the ratio $[\langle r^2 \rangle / (n-1)]^{1/2}$ is plotted against n . All calculations were carried out by assuming that the chain dimensions were unperturbed by the long-range intramolecular interactions. *n*-Alkane chains are considerably elongated in the nematic field as compared with the arrangement in the random-coil state. The uppermost curve was derived for the all-*trans* planar conformation, setting the limiting values.

Throughout this paper, statistical weight factor ω for the g^+g^- conformation has been set equal to zero in the nematic medium on the expectation that such conformations should be largely suppressed. For *n*-pentane, we have attempted to treat the observed splitting ratios by using $\omega=0.035$, a value conventionally adopted for a free chain.¹⁷ The value of f_i thus determined is 0.820, which differs scarcely from that (0.822) previously obtained by setting $\omega=0$. The effect should be minor in the other *n*-alkanes as well.

From the definition of eq 5 and 6, the order parameter of the molecular axis may be calculated. The value of S_{zz} thus estimated are given in the last columns of Tables IV and V, the value of eq^2Q/h being set equal to 174 Hz.²² The order parameters of the nematic environment are not known in these instances, however. With such information, the reliability of the analysis may be further improved.

As described above, our scheme is admittedly simple. Our treatment rests on the assumption that the molecular axis of the chain should tend to align along the field. This assumption is consistent with Martire *et al.*'s thermodynamic observations^{1,2} as well as Kronberg *et al.*'s NMR work.³ The results of the analysis are however somewhat incompatible with the interpretation recently proposed by Photinos *et al.*^{6,7} For a more definite proof, the validity of the model may be hopefully tested against other conformation-dependent properties as well. Some efforts are in progress in our laboratory.

Acknowledgments. We wish to thank Prof. E. T. Samulski for his helpful discussions at an early stage of the work. This work was supported in part by a Grant-in-Aid for General Scientific Research (No. 02650642) from the Ministry of Education, Science, and Culture of Japan.

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