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SQUID Studies of α,ω-Bis[(4,4′-cyanobiphenyl)oxy]alkanes and Elucidation of the Orientational Order Parameter

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ABSTRACT: The magnetic susceptibilities of dimer liquid crystals such as $NCPh_2O(CH_2)_nOPh_2CN$ (n = 9, 10) have been measured by a SQUID magnetometer. The anisotropies of the susceptibility, $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$, were found to increase abruptly at the isotropic to nematic transition (T_{NI}), followed by a gradual increase over the entire range of the nematic phase. At the onset of crystallization, a sharp decrease of the $\Delta\chi$ value was observed. The $\Delta\chi$ values in the very vicinity of T_{NI} were estimated by extrapolation from those obtained at stable nematic temperatures according to the empirical Haller equation: 0.889 and 1.062×10^{-9} m^3 kg^{-1}, respectively, for n = 9 and 10 at $T = T_{NI} - 0.5$ K. These results have been interpreted within the framework of the rotational isomeric state approximation, the effect arising from the conformational anisotropy of the flexible spacer being strictly taken into account. The order parameters of the mesogenic core axis thus estimated were found to be consistent with those directly observed at just below T_{NI} by the ^2H NMR technique using mesogen-deuterated samples.

Introduction

The ordering of anisotropic molecules is usually characterized by the orientational order parameter representing the distribution of the long molecular axis around the director of the mesophase. The Saupe matrix scheme[1] has been widely adopted in the mathematical description of such an orientational order. The structure of the mesophase can be conventionally characterized by the orientational order parameters $S_{\alpha\beta}$, which are defined as the elements of a second-rank Saupe ordering matrix. In the principal-axis system xyz, the observed anisotropy of the diamagnetic susceptibility, $\Delta\chi$, can be related to these order parameters by the expression[2]

$$\Delta\chi = \Delta\chi_0 S_{zz} + (1/2)(\chi_{xx} - \chi_{yy})(S_{xx} - S_{yy}) \qquad (1)$$

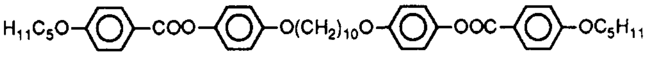
where

$$\Delta\chi_0 = \chi_{zz} - (1/2)(\chi_{xx} + \chi_{yy}) \qquad (2)$$

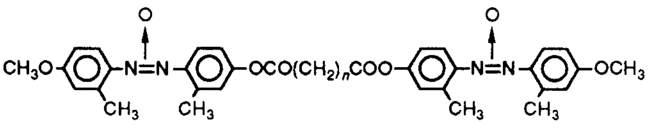
corresponds to the anisotropy of the susceptibility for the state in which the long molecular axes (z) are perfectly aligned along the director, and χ_{xx}, χ_{yy}, and χ_{zz} are the components of the molecular susceptibility tensor, χ. When molecules are cylindrically symmetric, the biaxiality term ($S_{xx} - S_{yy}$) vanishes, yielding a further simplification in the expression.

When the compound comprises a single mesogenic core unit, the definition of the molecular axis is relatively simple. de Jeu et al.[3] have studied magnetic properties of liquid crystals such as p,p'-di-n-alkyl- and p,p'-(di-n-alkyloxy)azoxybenzenes. In this work, they defined the molecular axis along the line connecting carbon atoms located at the 4- and 4′-positions. The $\Delta\chi_0$ values were estimated from the data reported for p-azoxyanisole in the crystalline state. The order parameters of the molecular axis thus defined were found to be consistent with those derived from other measurements.

Polymer liquid crystals (PLC) comprising a rigid mesogenic core and a flexible spacer in the repeat unit often exhibit a distinct odd–even oscillation in various thermodynamic quantities at the nematic–isotropic (NI) transition temperature.[4] The simplest example of such spacers may be of the type $-O(CH_2)_nO-$. In these systems, the orientational order parameter of the mesogenic core axis oscillates with the number of methylene units n,[5,6] suggesting that the order–disorder transition of the mesogenic core is coupled with conformational changes of the flexible spacer. Dimer liquid crystals (DLC) comprising two mesogenic units jointed by a single spacer also exhibit similar odd–even characteristics. As easily shown by an inspection of a molecular model, the molecular axis does not generally coincide with the mesogenic core axis. In this respect, PLC's as well as DLC's are very different from simple low molecular weight (monomer) liquid crystals. The ordering characteristics of the former systems require more elaborate treatment. Sigaud et al.[7] have measured the magnetic susceptibilities of a homologous series of monomer, dimer, and polymer liquid crystals. Their dimer has a structure such as



The $\Delta\chi_0$ values were estimated for the molecular axis defined along the direction connecting the two ether oxygens spanning the mesogenic core. Contribution from the spacer has been evaluated for two models: i.e., all-trans and random coil. The $\Delta\chi_0$ value corresponding to the average of these two extreme models was found to give the most satisfactory agreement with experiments. Recently, Esnault et al.[8,9] reported the results of SQUID measurements on some ester-type main-chain liquid crystals including the dimer models such as



n = 7 and 10

In their studies, ^1H and ^2H NMR methods were used in

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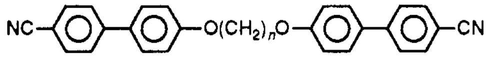
combination with the magnetic technique. A detailed analysis of the biaxiality inherent to these systems has been attempted.

The nematic conformations have been elucidated for several examples of PLC and DLC from the relevant ^{2}H NMR data.[10-12] Although the results reported from various laboratories seem to vary somewhat depending on the models adopted in the simulation of the spectra, all suggest that the flexible spacers prefer to take extended conformations in the nematic state. The orientational ordering of the mesogenic cores may thus be enhanced. These conclusions are also consistent with the results of a conformational analysis.[13] Abe and Furuya[14] have reported the results of rotational isomeric state (RIS) simulation of ^{2}H NMR spectra for PLC's and DLC's having deuterated spacers such as $-O(CD_2)_nO-$ with $n = 9$ and 10. In this treatment, the molecular axis (z) has been defined for each conformer along the direction parallel to the line connecting the centers of two neighboring mesogenic cores. Such simplification may be justified on the basis of the fact that the conformations permitted in the nematic state are all highly extended. In this manner, a distinction can be achieved between the external order parameter arising from the degree of rod-axis alignment with respect to the nematic director and the internal order parameter relating to the orientation of the bonds or groups with respect to the long molecular axis of the sequence. The ordering characteristics of the molecular axis thus defined can be described by the same formalism as those previously adopted for the low molecular weight analogue. The expressions given in eqs 1 and 2 are also valid except that the $\Delta\chi_0$ value is now given as a statistical mechanical average over all conformations permitted in the mesophase.

The diamagnetic susceptibility of liquid crystals has been measured by a variety of devices including the Faraday balance,[3,15,16] the Gouy balance,[17] and more recently by the SQUID method.[18,19] Among these techniques, SQUID allows in principle the highest sensitivity. In this paper, we have determined the magnetic susceptibilities of α,ω-bis[(4,4′-cyanobiphenyl)oxy]alkanes (CBA-n)



$n = 9$ and 10

by the SQUID method. The results have been analyzed within the frame work of the RIS model, the conformational flexibility of the spacer being taken into account. The orientational order parameters of the mesogenic core estimated therefrom are found to be consistent with those deduced from ^{2}H NMR by Emsley et al.[5]

Experimental Section

Samples, CBA-n ($n = 9$ and 10), were synthesized as prescribed by Emsley et al.[20] All samples prepared exhibited an enantiotropic nematic phase by the polarizing microscopic examination. The observed phase-transition temperatures (°C) are as follows:

$$\text{CBA-9} \quad K \xrightarrow{134} N \xrightarrow{172} I$$

$$\text{CBA-10} \quad K \xrightarrow{165} N \xrightarrow{184} I$$

These values are in reasonable agreement with those reported by Emsley et al.[20] and Griffin et al.[21]

The magnetic susceptibility measurements were performed by using a SQUID magnetometer (S.H.E. Corp. VTS 909) equipped with an inset specially designed for high-temperature experiments.[19] Approximately 50 mg of sample was charged in a cryolite glass bulb for each run. Experiments were carried out by cooling the sample from the isotropic phase under an N_2 atmosphere. During the measurements, the magnetic field was kept at 5 T. To determine the contribution of the glass bulb, experiments were performed, prior to the real measurements, for an unloaded bulb as a function of temperature. The signals observed for the empty bulb were subtracted from the raw susceptibility data.

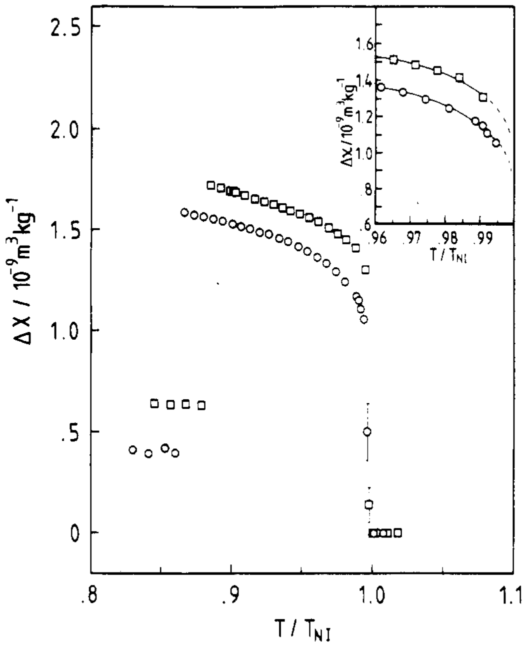


Figure 1. Observed anisotropies of the susceptibility, Δχ, plotted against the reduced temperature T/T_{NI} for CBA-n: CBA-9 (○) and CBA-10 (□).

Results

The anisotropy of the susceptibility, Δχ, for an aligned nematic state is defined as

$$\Delta\chi = \chi_{\parallel} - \chi_{\perp} \qquad (3)$$

where $\chi_{\parallel}$ and $\chi_{\perp}$ are, respectively, the components of the macroscopic susceptibility tensor, χ, parallel and perpendicular to the director. For the isotropic phase, χ_{iso} can be expressed as

$$\chi_{iso} = (1/3)(\chi_{\parallel} + 2\chi_{\perp}) \qquad (4)$$

Combining eqs 3 and 4, we obtain

$$\Delta\chi = (3/2)(\chi_{\parallel} - \chi_{iso}) \qquad (5)$$

In this study, the diamagnetic susceptibilities, χ_{iso}, in the isotropic phase were observed to be −8.132 and −8.071 × 10^{-9} m^3 kg^{-1} for CBA-9 and -10, respectively. These values are slightly lower (ca. 3%) than those calculated on the basis of the bond additivity rule by using Flygare et al.'s data:[22] −8.351 and −8.383 × 10^{-9} m^3 kg^{-1} for CBA-9 and -10, respectively.

In Figure 1, the observed anisotropies of the susceptibility Δχ are plotted against the reduced temperature (T/T_{NI}). The observed Δχ values increase abruptly at the isotropic–nematic transition. Due to a large fluctuation in the susceptibility, however, an accurate determination of the Δχ values was difficult in the immediate vicinity of T_{NI}. After such a discontinuous enhancement at T_{NI}, the Δχ value undergoes a more gradual increase over the rest of the entire range of the nematic phase. Around the crystallization temperature, the Δχ value decreases sharply. Similar trends have been reported for some monomer and dimer liquid crystals.[3,15-18] The Δχ values are somewhat higher for samples with $n = 10$ than those with $n = 9$. Variations of Δχ in the

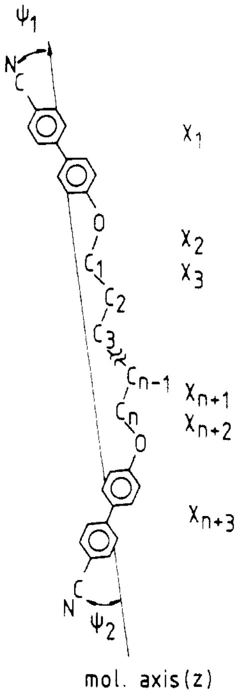


Figure 2. Schematic representation of CBA-*n*. Serial numbering of carbon atoms in the spacer and bond and group χ tensors are indicated.

neighborhood of T_{NI} are indicated on a large scale in the inset to Figure 1, where the solid curves were drawn by the least-squares fit for the empirical Haller equation[23]

$$\Delta\chi = C\,(1 - T/T_{NI})^{\gamma} \tag{6}$$

This expression reduces to an isotropic value ($\Delta\chi = 0$) at $T = T_{NI}$. Values of parameters C and γ obtained from the best fit plot are as follows: $C = 2.01$ and $\gamma = 0.118$ for CBA-9 and $C = 2.12$ and $\gamma = 0.100$ for CBA-10. In a later section, these results will be compared with those observed by the ^2H NMR technique at around T_{NI}. In consideration of the fact that the precision of the temperature control is usually of the order of 1 K in the ^2H NMR quadrupolar splitting measurements, it would be reasonable to adopt values at $T = T_{NI} - 0.5$ K ($T/T_{NI} = 0.999$) for the purpose of comparison. At this temperature, $\Delta\chi = 0.889$ and 1.062×10^{-9} m^3 kg^{-1} for CBA-9 and -10, respectively. The uncertainty involved in these estimates probably amounts to about 10%. For low molecular weight monomer liquid crystals, in which the isotropic–nematic transition takes place more sharply, the Haller equation is known to be valid at temperatures as high as $T/T_{NI} = 0.999$.[3,16-18]

RIS Analysis

In this section, we attempt to elucidate the orientational order parameters S_{zz} from the magnetic susceptibility data obtained by the SQUID measurements. In the first step, the $\Delta\chi_0$ values defined in eq 1 are estimated from the nematic conformation determined in the vicinity of T_{NI} by the ^2H NMR method.[14] To calculate S_{zz} from eq 1, in the second step, contribution from the biaxiality term is ignored for simplicity. The validity of such a simplification will be discussed in a later section.

Estimation of $\Delta\chi_0$. As shown in Figure 2, the magnetic susceptibility tensors are defined for the mesogenic units located at both terminals as well as for the individual bonds of the intervening spacer. The long molecular axis (z) is indicated by the solid line connecting the centers of the mesogenic units, ψ_1 and ψ_2 denoting the inclination of the mesogenic core axes with respect to the molecular axis.

Table I
Components of the Bond or Group Susceptibility Tensors[a]

	χ_{11}	χ_{22}	χ_{33}
biphenyl[b]	-64.7	-64.7	-183.8
C≡N[c]	-16.5	-11.6	-11.6
C—O[d]	-7.2	-6.7	-3.8
C—C[c]	-7.9	-0.2	-0.2
C—H[c]	-5.6	-3.1	-3.1

[a] Expressed in units of 10^{-6} erg G^{-2} mol^{-1}.[22] [b] Axes 1 and 2 are definded in the plane of biphenyl rings, two phenyl groups being taken to be coplanar. [c] The given bond is identified with axis 1. [d] Axis 1 is defined along the bond and axis 2 in the plane of the bond pair jointed by O.

Table II
Structural Parameters Used in the RIS Analysis[a]

bond	length, Å	bond angle	angle, deg	bond	rotational angle for gauche state, deg
O-C	1.40	∠C^{Ph}OC	120	CC-CC	±112.5
C-C	1.53	∠OCC	112	OC-CC	±117.0
		∠CCC	112		
		∠CCH	109		

[a] Reference 12.

According to Flygare et al.,[22] the magnetic susceptibility tensor of a molecule can be evaluated as the sum of contributions from the constituent bonds or groups. Values of the susceptibility used in the present treatment were taken from the literature and are summarized in Table I, where $\chi_{\alpha\alpha}$'s indicate the principal components of the tensor χ. The magnetic susceptibility tensor of the mesogenic unit, NCPh$_2$O, can be estimated according to

$$\chi_{NCPh_2O} = \chi_{CN} + \chi_{CC} + \chi_{Ph_2} + \chi_{CO} - 2\chi_{CH}$$

with χ values listed in Table I. Following the procedure adopted by Jernigan and Flory[24] in their treatment of the optical anisotropy of chain molecules, the tensors associated with a methylene unit $(CH_2)_i$ can be combined in the coordinate system defined on the C_i–C_{i+1} bond. For the C_n–H bonds of the terminal methylene groups, their tensors are expressed in the frame fixed on the C_n–O bond. For a given configuration (k), the magnetic susceptibility tensor may be expressed as[24]

$$\begin{aligned}\chi_k &= T_0\chi_1T_0^{\,t} + T_0T_1\chi_2T_1^{\,t}T_0^{\,t} + T_0T_1T_2\chi_3T_2^{\,t}T_1^{\,t}T_0^{\,t} + \dots \\ &= \sum_{i=1}^{n+3} T_0(T_1^{\,i-1})\chi_i(T_1^{\,i-1})^{t}T_0^{\,t}\end{aligned} \tag{7}$$

where T_0 is responsible for the transformation of the frame from bond 1 to the molecular axis (cf. Figure 2), T_i (with $i \geq 1$) transforms the coordinate system from i to $i - 1$, $T_i^{\,t}$ denotes the transpose of T_i, and $T_1^{\,i-1}$ represents the serial product comprising $i - 1$ factors. Geometrical parameters required for the description of given molecular configurations were adopted from the ^2H NMR work for consistency (Table II).[12]

The averaged value of $\Delta\chi_0$ can be obtained by

$$\Delta\chi_0 = (3/2)(\langle\chi_{zz}\rangle - \chi_{iso}) \tag{8}$$

and

$$\langle\chi_{zz}\rangle = Z^{-1}\sum_k \zeta_k\chi_{zz} \tag{9}$$

where χ_{zz} is the zz component of the magnetic susceptibility tensor defined by eq 7, ζ_k represents the statistical weight of the kth configuration, and Z is the conformational

Table III
Estimation of $\Delta\chi_0$ Values from the Nematic Conformation Derived from the ^{2}H NMR Analysis[a]

	model 1	model 2
CBA-9	1.18	1.38
CBA-10	1.87	2.20

[a] Units are 10^{-9} m^3 kg^{-1}.

Table IV
Order Parameters Estimated for CBA-*n* at $T = T_{NI} - 0.5$ K, the $\Delta\chi_0$ Values Being Taken from Table III

	CBA-9		CBA-10	
	model 1	model 2	model 1	model 2
S_{zz}	0.75	0.64	0.57	0.48
S_M	0.41	0.35	0.52	0.44
$S_{M,obs}$[a]	0.33 ± 0.02		0.50 ± 0.02	

[a] Derived from ^{2}H NMR measurements.[5]

partition function in the nematic state:

$$Z = \sum_k \zeta_k \qquad (10)$$

In the ^{2}H NMR studies on CBA's,[14] the conformation map, on which spatial arrangements of the configurations allowed in the free state are identified by their ψ_1 and ψ_2 values (cf. Figure 2), was used in the estimation of the nematic conformation. For a chosen ensemble of configurations, statistical weight parameters were so adjusted as to minimize the difference between the calculated and observed quadrupolar splittings. The best fit ensemble of configurations has been derived by repeating calculations iteratively. The results obtained around T_{NI} are as follows: $0 < \psi_1, \psi_2 < \psi_m$ with ψ_m = 35–45° for CBA-9; $0 < \psi_1, \psi_2 < \psi_m$ with ψ_m = 20–40° for CBA-10. The same conformation map was employed in the present estimation of $\Delta\chi_0$. The statistical weight parameters applicable to the nematic state were also adopted from the ^{2}H NMR work. Calculations were carried out for several representative sets of conformations chosen from the aforementioned range of ψ_m. In both CBA's, the $\Delta\chi_0$ values were found to be quite insensitive to small variations in the conformation set.[25] The values of $\Delta\chi_0$ thus estimated in the vicinity of the isotropic–nematic phase transition are tabulated in Table III (model 1). The role of the flexible spacer may be considered in two ways: (1) the effect on the orientational correlation between the terminal mesogenic core units and (2) a direct contribution to $\Delta\chi_0$ from the conformational anisotropy of the spacer. To elucidate the effect arising from the second factor separately, calculations were also performed for the model in which all χ matrices from $i = 2$ to $n + 2$ were assumed to be null (model 2): thus, in this model, all the contribution arises from the terminal mesogenic units. As shown by comparison, inclusion of the spacer contribution somewhat lowers the $\Delta\chi_0$ values (approximately 15% in both CBA's).

Estimation of the Order Parameters. The orientational order parameters of the molecular axis (S_{zz}) can be readily calculated from eq 1 by using $\Delta\chi_0$ values given in Table III. The S_{zz} values estimated for the temperature $T = T_{NI} - 0.5$ K are listed in the first row of Table IV, where the results are given for the two models employed in the estimation of $\Delta\chi_0$ values. The relative orientation of mesogenic core axes with respect to the long molecular axis conforms to the internal order parameter

$$P_2(\cos\psi) = (3\langle\cos^2\psi\rangle - 1)/2 \qquad (11)$$

where ψ is the angle between the mesogenic core and the molecular axis as defined in Figure 2, and $\langle\ \rangle$ denotes an average over conformations allowed in the nematic state. The values of $P_2(\cos\psi)$ have been estimated to be 0.55 for $n = 9$ and 0.92 for $n = 10$ in the vicinity of T_{NI}. The order parameter S_M defined by

$$S_M = S_{zz}P_2(\cos\psi) \qquad (12)$$

represents the orientational distribution of mesogenic core axes around the director of the nematic field. The values of S_M thus estimated are listed in the second row of Table IV. The same quantity is subject to a direct determination by using samples dueterated on the aromatic rings of the mesogenic core. Listed in the last row are the ^{2}H NMR results reported by Emsley et al.[5] The order parameter derived directly from the deuterium quadrupolar splitting measurements falls between the two calculated S_M values in both CBA's. The errors involved in our estimate may be of the order of 10%. The agreement is reasonable in both models. The preference between models 1 and 2 cannot be inferred from the present results.

Discussion

In the magnetic susceptibility studies of liquid crystals, the observed temperature dependence of $\Delta\chi$ values are conventionally analyzed according to the empirical Haller relation (eq 6). For simple liquid crystals, values of the parameter C obtained from this plot are often identified as $\Delta\chi_0$ and used in the determination of the orientational order parameter of the mesogenic core axis.[3,16,17] In DLC or PLC, as shown above, the molecule comprises two or more mesogenic units connected by flexible spacers. In such liquid crystals, the mesogenic core axes are usually tilted somewhat from the axis that represents the average orientation of the entire molecule. In the nematic state, the flexible spacers are allowed to take a variety of conformations. The disorientation angle of the mesogenic core axis also varies depending on the individual conformations. Although the Haller plot is still useful in treating the experimental data of these liquid crystals, the physical meaning of the parameters derived therefrom is somewhat obscure. In the present study, the values of C were found to be substantially larger than the $\Delta\chi_0$'s estimated by the RIS analysis. Correspondingly, the values of γ derived from the Haller plot were somewhat lower than usually observed for simple low molecular weight liquid crystals.

In the foregoing treatment, we have ignored the biaxiality of the system. Accordingly, the second term in the right-hand side of eq 1 was dismissed, and the treatment was greatly simplified. The first factor of the biaxiality term, $(1/2)\langle\chi_{xx} - \chi_{yy}\rangle$, may be estimated by knowing the conformations permitted in the mesophase. For the nematic conformations treated above, we calculate $(1/2)\langle\chi_{xx} - \chi_{yy}\rangle = 0.62$ and 0.31×10^{-9} m^3 kg^{-1} for CBA-9 and -10, respectively. If we tentatively adopt a value of 0.05 for the second term, $S_{xx} - S_{yy}$, as reported in the other measurements such as NMR, the contribution arising from the biaxiality term becomes of the order of 2% in the total estimate of $\Delta\chi$. With such a modification, the calculated values of S_M will be lowered by 0.01 from those listed in Table IV. The effect is therefore well within the error limit of the measurements.

Esnault et al.[8,9] have estimated the ratio $\Delta\chi/S_M$ for the ester-type DLC's depicted in the introductory part. The values were found to vary rather insensitively with temperature, suggesting that the contribution from the biaxiality term $S_{xx} - S_{yy}$ was small. They emphasized that the effect of biaxiality becomes more enhanced as the molecular weight of the sample increases.

Concluding Remarks

In this paper, we have determined the anisotropies of the magnetic susceptibility of α,ω-bis[(4,4'-cyanobiphenyl)oxy]alkanes by the SQUID method. The orientational order parameters of the nematic mesophase have been estimated by using $\Delta\chi_0$ values calculated on the basis of the group additivity assumption. Calculations were carried out for the nematic conformation derived from the analysis of the ^{2}H NMR data. In these treatments, the intramolecular orientational correlation between the mesogenic units located at both terminals of the spacer has been strictly taken into account within the framework of the RIS approximation. The order parameters of the mesogenic core axis elucidated from the SQUID data were shown to be consistent with those directly observed in the vicinity of T_{NI} by the ^{2}H NMR method. The procedure established in this work can be readily adopted to the analysis of magnetic susceptibility data of similar systems. Results obtained for some PLC's will be reported elsewhere.

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