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Molecular Ordering in Dimer Liquid Crystals as Estimated by the Analysis of D-NMR Spectra of Deuterated Flexible Spacers

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Molecular Ordering in Dimer Liquid Crystals As Estimated by the Analysis of D-NMR Spectra of Deuterated Flexible Spacers

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An attempt has been made to elucidate molecular conformations of ether- and ester-type dimer liquid crystals (DLC) carrying deuterated soft-spacers by utilizing the information provided by the D-NMR method. The analysis has been carried out according to the following steps: 1. All possible configurations are enumerated for a free molecule within the framework of the RIS approximation. 2. Configurations which do not conform to the nematic ordering are discarded. 3. For the nematic ensemble thus selected, conformational statistical weight factors assigned to the individual bond rotations are adjusted so as to reproduce the observed profile of the D-NMR spectrum. In this treatment, following the scheme established in the preceding paper, the molecular axis of a conformer is defined along the line connecting the centers of the terminal mesogenic cores. The results of the analysis indicate that conformations permitted in the nematic state amount to 10 to 15% of the free molecule near the N–I transition temperature. The order parameters for the molecular axis are calculated to be 0.49 for the ether and 0.75 for the ester DLC. The order parameters for the mesogenic core are also estimated, and found to be reasonably consistent with those generally observed for relevant compounds.

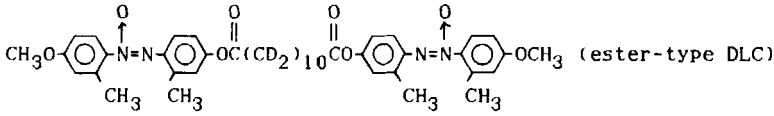
INTRODUCTION

Thermodynamic properties of polymer liquid crystals comprising a rigid mesogenic core and a soft spacer in a repeat unit have been

extensively investigated. Typical examples were reported for polyesters,[1,2] $[X\text{-}OC(O)(CH_2)_nC(O)O]_x$, and polyethers,[3,4] $[X\text{-}O(CH_2)_nO]_x$, with various mesogenic cores X. These polymers are known to exhibit an odd–even effect[1–3] in various thermodynamic quantities at the nematic–isotropic phase transition temperature with the number of methylene units n. A similar phenomenon has already been noted as early as 1927 by the work of Vorlander[5] on a series of low molecular weight dicarboxylic acid esters carrying the *p*-methoxy-azobenzene groups on both terminals (*i.e.*, a dimer model). The magnitude of odd–even oscillation in thermodynamic quantities such as ΔS_{NI} tends to be somewhat suppressed in these dimer liquid crystals (DLC). Nonetheless, they are often regarded as a prototype of polymer liquid crystals.

The odd–even oscillation mentioned above arises from the tetrahedral character of the sp^3 carbon atoms.[6,7] The conformational analyses have been carried out for these flexible spacers to elucidate the directional correlation between the terminal mesogens. When the number of methylene units in the flexible segment is even, the angles between the two successive mesogenic core axes are found to be distributed in the range 0° to 30° (*ca.* 30%) and 85° to 130° (*ca.* 70%). For the n = odd system, the major portion of the angle is located in the region 50° to 90° (*ca.* 90%), and to some degree (*ca.* 10%), orientations are also permitted in the range above 150°. In the n = even series, the parallel orientation of successive mesogenic cores is allowed, conforming more or less to the concept of an ordinary nematic ordering. In accord with these considerations,[6] the order parameter of the mesogenic core was found to be appreciably higher for the n = even series.

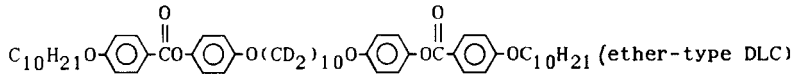
Some of the dimer and polymer liquid crystals have been investigated by the D-NMR technique to elucidate the conformation of the flexible spacer. Samulski *et al.*[8] studied a polyester such as $[C_6H_3(CH_3)\text{—}N(O)\text{=}N\text{—}C_6H_3(CH_3)OC(O)(CD_2)_{10}C(O)O]_x$, for which they observed a pair of quadrupolar splittings with the ratio of peak areas 1 : 4. A nearly identical spectrum has been reported for the corresponding dimer model compound by Martins *et al.*:[9]



(ester-type DLC)

Yoon and his collaborators[10,11] investigated a polyether, $[(CD_2)_{10}OC_6H_4C(O)OC_6H_4O(CD_2)_{10}OC_6H_4OC(O)C_6H_4O]_x$, where

the flexible spacer is joined by the ether linkage with the mesogenic cores. This polymer exhibits one doublet with broad peaks.[10,11] The quadrupolar splitting pattern of a dimer model of this polymer with $n = 10$ was reported by Griffin and Samulski:[12]



In contrast to the polymer, the low molecular weight analog exhibits three distinct doublets. Summarized in Table I are the results on the dimer model compounds, for which our present investigation is specifically focused. The quadrupolar splittings listed are those observed just below the N–I transition temperature. In the ester DLC, the outermost peaks exhibiting a larger splitting are known to arise from α-CD_2.[9] As the following analysis should eventually indicate, the largest $\Delta\nu$ value of the ether DLC is also due to the α-CD_2 groups. For the latter purpose, ratios expressed relative to the largest $\Delta\nu$ value are also included in the table.

Conformational analyses of the polyesters and polyethers mentioned above have been carried out by Samulski,[13] and Yoon and Bruckner,[7,10,11] respectively. Although the actual procedures are quite different between these two parties, the observed spectra for polymers with $n = 10$ are reasonably well reproduced within the framework of the rotational isomeric state (RIS) model. In both cases, an extension of the chain along the molecular axis expressed by the length spanning a repeat unit (or some closely related quantity) provides an empirical criterion to elucidate the nematic fraction.

Our approach to this problem has been outlined in the preceding

TABLE I

Summary of Experimental D-NMR Data Reported in Literature on Thermotropic Ether- and Ester-Type DLCs

DLC	Temp./K	$\Delta\nu^{obs}$/kHz	$\Delta\nu^{obs}/\Delta\nu_1^a$
ether[b]	409	47.4	1.0
		40.7	0.86
		37.4	0.79
ester[c]	367	72.4	1.0
		51.2	0.71

[a]Ratio of the splitting expressed relative to the value ($\Delta\nu_1$) of α-CD_2.
[b]Ref. 12.
[c]Ref. 9.

paper[14] (hereafter, referred to as Paper I). In conformity with the previous treatment, the molecular axis is defined along the line connecting the centers of two neighboring mesogenic cores. Numerical values of the conformational statistical weight factor assigned to each rotatable bond are elucidated so as to reproduce the observed D-NMR data listed above. The conformational partition function thus established can be used to estimate various average properties of the nematic ensemble.

THE RIS DESCRIPTION OF THE CHAIN

Geometrical data. For the purpose at hand, the mesogenic cores may be treated as a simple rod. The bond lengths and bond angles adopted are listed in Table II. The methylene carbons of the soft-spacer are numbered from one terminal to the other as illustrated in Figure 1, where the carbon and oxygen atoms constituting carbonyl groups are distinguished by an asterisk. In Table II, values of the bond length O—C_1 and bond angle $\angle C^{Ph}OC_1$ were chosen from the crystallographic data of 1,4-dimethoxybenzene[16] and the electron diffraction studies on anisole.[17] Bond angles $\angle OC_1D$ and $\angle CCD$ were calculated by assuming $\angle DCD = 107.9°$.[18] The corresponding values of the ester group were identical with those adopted in the previous paper.[6]

The torsional angle around the O—C_1 bond was taken to be zero (*i.e.* trans).[16,17,19,20] The rotational states for the OC_1—C_2C_3 bond

TABLE II

Geometrical Parameters Used for the Analysis of DLCs

Bond[a]	Length/Å	Bond Angle[a]	Angle/deg
		ether	
O—C_1	1.40	$\angle C^{Ph}OC_1$	120.0
C—C	1.53[b]	$\angle OC_1C_2$	112.0
		$\angle CCC$	112.0[b]
		$\angle OC_1D$	109.2
		$\angle CCD$	109.2[b]
		ester	
O—C*	1.35	$\angle C^{Ph}OC^*$	116.7
C*—C_1	1.53	$\angle OC^*C_1$	111.4
		$\angle C^*C_1C_2$	112.0
		$\angle C^*C_1D$	109.2

[a]The carbonyl carbons are indicated by an asterisk.
[b]The same values are used for the ester compound.

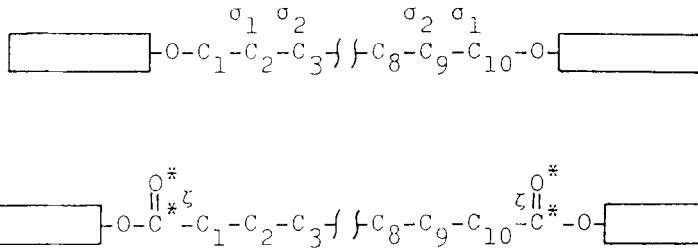


FIGURE 1 Schematic representation of DLCs, where rectangles represent mesogenic cores. Methylene carbons of the soft-spacer are numbered from left to right. Statistical weight parameters σ_i are defined as indicated.

were assumed[21] to occur at 0° and ±117.0°. The conformation of the ester group was taken to be trans. For the following bond, OC*—C_1C_2, the rotational states have been estimated to be 0° and 122.7°.[22,23] For the internal C—C bonds, we adopted conventional values[24] of 0° and ±112.5°. An accurate value of the dihedral angle CC—CD is required for the estimation of the spatial orientation of C—D bonds. For the molecular geometry given in Table II, the value is calculated to be 121.2°.

DEFINITION OF THE STATISTICAL WEIGHT FACTORS

In the RIS approximation, the weight of a given configuration may be expressed as a product of statistical weight factors assigned to the constituent bonds of the sequence. In this paper, 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 symmetry of the molecular system dictates that $\sigma_i = \sigma_{n-i}$. Thus, for the $n = 10$ dimer, statistical weight factors σ_i from $i = 1$ to 5 need to be defined (*cf.* Figure 1). Following the previous treatment,[14] the weight for the second-order interaction $g^{\pm}g^{\mp}$ was set equal to zero in the nematic state.

In the ether dimer, the conformation around C^{ph}—O was taken to be coplanar with the preceding phenylene ring.[25] The gauche arrangement for the O—C_1 bond involves repulsive steric interactions between the phenylene and methylene groups of three bond apart. Thus, this bond was fixed in the trans state. For the ester compound, the C^{ph}—O bond is known to exhibit four rotational minima. The dihedral angles between the ester plane and the phenylene ring have been estimated to be ±58.0° and ±122.0°.[25] As may be easily shown

by an inspection of a molecular model, the rotation around C^{ph}—O should not cause any effect on the conformation of the spacer. Within the scheme adopted in this work, detailed knowledge of the rotational potential is not necessary for this bond. Statistical weight factor ζ is assigned to the rotation around the C*—C_1 bond of the ester. Our recent analysis[23] on some dicarboxylic acid esters indicates that the trans form is more stable around this bond by *ca.* 1 kcal mol^{-1} than the gauche arrangement in the free state.

The same notations (σ_i) were used for the methylene sequence in the two DLCs. Since the conformational characteristics are in principle different between the ether and ester compounds, numerical values of σ_i should be variable depending on the system.

COMPUTATIONAL PROCEDURE

Quadrupolar splittings $\Delta\nu_i$ of the i-th C—D bond can be expressed by the conventional expression,

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

where e^2qQ/h (= 174 kHz[11,26]) is the quadrupolar coupling constant, S_{ZZ} denotes the orientational order parameter of the molecular axis (Z-axis) with respect to the director of the nematic domain, ϕ represents the angle between the C—D bond and the molecular axis, and the brackets denote the averaging over all allowed conformations. With the reason stated in paper I, the ratio between two different $\Delta\nu$ values should be free from the S_{ZZ} value (*cf.* eq. (5) of paper I). The observed ratios, $\Delta\nu^{obs}/\Delta\nu_1^{obs}$ are included in Table I.

In the nematic field, molecules tend to orient along a given director. In conformity with Model II of the previous treatment of nCB,[14] the molecular axis may be defined by the vector connecting the centers of two adjacent mesogenic cores. Figure 2 includes the definition of angle ψ for the inclination of a mesogenic core with respect to the molecular axis, and θ for the relative orientation of the two terminal mesogenic core axes. For simplicity, the mesogenic cores were taken to be a straight rod with the center at a distance of 5 Å from the oxygen atom (see Figure 2), the value roughly corresponding to the structure illustrated in the introductory part. Values of ϕ were calculated as the angle defined by the individual C—D bonds and the molecular axis.

From our previous analysis,[6] the distribution curve $P(\theta)$ vs. θ is

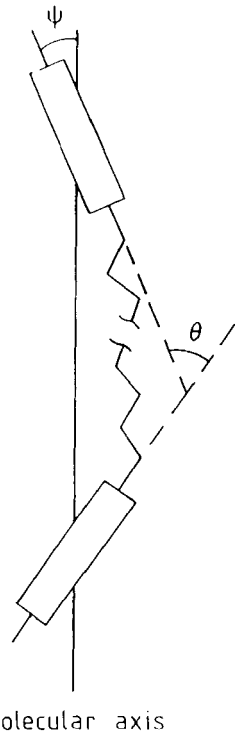


FIGURE 2 Definition of the molecular axis for a nematic conformation.

known to be bimodal in the free state, $P(\theta)$ indicating the fraction of conformers with an inclination angle θ. Under the nematic environment, distribution of angle θ should be restricted within a certain range. To save our computer time, conformers with angles θ which do not conform to the nematic concept were discarded. Values of $\cos^2\phi$ were calculated on this basis for all the spatial configurations permitted in the range, $0° \leq \theta \leq 20°$. In the computer simulation, statistical weight factors σ_i's as well as ζ were varied in an uncorrelated manner within the range from 0 to 1. Statistical weight factor σ_1 of the ether compound involves gauche interaction around the OC–CC moiety, for which the gauche form is known to be somewhat more stable in the free state. This factor was thus examined over a wider range (0 to 2.0). Use of Eq. 1 may yield $\Delta\nu_i$ with either a positive or negative sign. Comparison with experimental observations requires only absolute values of $\Delta\nu_i$. Computations were iteratively repeated until the calculated values of $|\Delta\nu_i/\Delta\nu_1|$ reproduced the observed profile

of the D-NMR spectrum. A unique set of statistical weight factors was successfully selected for each molecular system by this technique.

RESULTS AND DISCUSSION

The best-fit values of ζ and σ_i were explored by computer simulation according to the scheme described above. The results are illustrated in Figure 3a for the ether and Figure 3b for the ester dimer. Solid lines indicate variation of the calculated values of $|\Delta\nu_i/\Delta\nu_1|$ with carbon number i. The observed quadrupolar splittings may be assigned as indicated by open circles. On the right-hand-side of each figure,

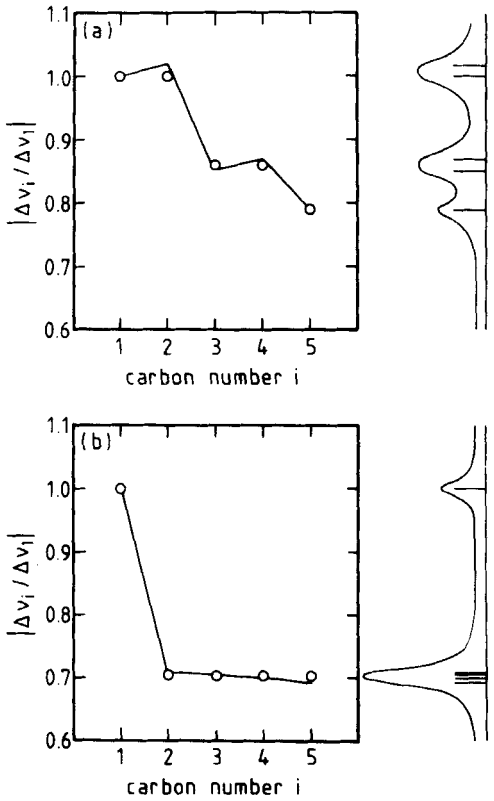


FIGURE 3 Variation of the ratio of the quadrupolar splitting $|\Delta\nu_i/\Delta\nu_1|$ as a function of carbon number i: (a) ether and (b) ester DLC. Solid lines represent the calculated values of $|\Delta\nu_i/\Delta\nu_1|$. Open circles indicate the ratios of the observed quadrupolar splitting $\Delta\nu_i^{obs}/\Delta\nu_1^{obs}$.

the results of calculations are illustrated by the stick diagram. The spectra calculated in this manner well reproduce those observed. The agreement is satisfactory in both examples. Values of the statistical weight parameter thus estimated are summarized in Table III. With values of σ_i's and ζ thus estimated, the statistical weight of any given conformer in the nematic state may be calculated. From the conformational partition function elucidated above, various average properties of the system may be calculated. Bond conformations, $f_t = 1 - f_g$, evaluated for the individual C—C bonds are plotted against the bond order in Figures 4a and 4b, respectively, for the ether and ester dimers. As has been noted by various workers,[7,8,10,11,13] the oscillation in f_t along the chain is the characteristic feature of the n = even system. The bond conformations in the isotropic state may be estimated by the conventional RIS model.[6,7] Conformational energy parameters required in the Boltzmann expression were taken from literature:[23,27] (ether) $E_{\sigma 1} = 0$, $E_{\sigma i} = 0.5$ with $i = 2$ to 5, $E_{\omega} = 2.0$ for the second-order interaction involved in CC$\overset{\curvearrowleft}{}C\overset{\curvearrowright}{}$CC, and $E_{\omega'} = 0.5$ for OC$\overset{\curvearrowleft}{}$C—$\overset{\curvearrowright}{}$CC; (ester) $E_{\zeta} = 1.0$, $E_{\sigma_i} = 0.5$ with $i = 1$ to 5, and $E_{\omega} = 2.0$ for the second-order interaction, all energies being in kcal mol^{-1}. Temperatures were taken to be the same as those listed in Table I. The f_t values thus obtained for the unconstrained state are indicated by broken lines in each figure.

From the information obtained above, various characteristic properties of the nematic phase can be evaluated. Some representative results are summarized in Table IV. The nematic fraction f_N is defined by the ratio z_N/z_I, where z_I represents the conformational partition function in the isotropic state. The results indicate that conformations permitted in the nematic state are 10% to 15% of the free molecule. The contribution to the latent energy ΔE_{NI} at the N–I phase transition may be estimated as the difference of the average energies between

TABLE III

Values of the Statistical Weight Parameter Estimated by the Analysis of D-NMR Data for Ether- and Ester-Type DLCs

Statistical weight parameter	Ether	Ester
ζ	—	0.259
σ_1	0.692	0.445
σ_2	0.259	0.509
σ_3	0.541	0.220
σ_4	0.335	0.509
σ_5	0.541	0.277

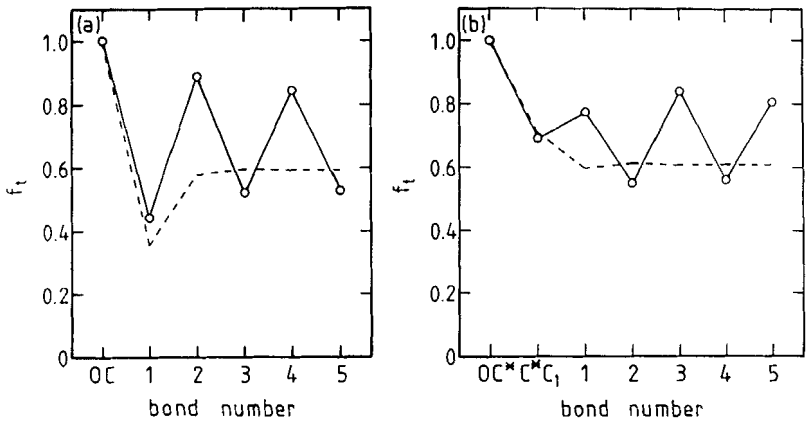


FIGURE 4 Bond conformation of the flexible spacer: (a) ether and (b) ester DLC. The trans fraction (f_t) was plotted against bond number: bond C_i—C_{i+1} is represented by i. Open circles indicate the f_t values calculated for the nematic fraction. The characteristic odd–even oscillation is illustrated by the solid lines. The results estimated for the unconstrained state are also indicated for comparison (broken lines).

the two phases. In these calculations, the energy difference between the gauche and trans state was taken to be invariant for a given bond in both the nematic and isotropic phases. The energy change estimated in this manner is of purely conformational origin. The values of $\Delta\langle E\rangle_{\mathrm{NI,conf}}$ are 0.65 for the ether and 0.48 kcal mol^{-1} for the ester. Variation of the conformational entropy at the transition was estimated by the formula $\Delta S_{\mathrm{NI,conf}} = -R\ln f_{\mathrm{N}} + \Delta\langle E\rangle_{\mathrm{NI,conf}}/T$ (R: the gas constant, T: temperature). The values of $\Delta S_{\mathrm{NI,conf}}$ thus obtained are around 6 for the ether and 5 cal mol^{-1} K^{-1} for the ester. Evidently, a large contribution arises from the conformational change of the flexible spacer at the N–I transition. In the real liquid crystal

TABLE IV

Characteristic Properties of the Nematic Phase[a] for Ether- and Ester-Type DLCs

	Ether	Ester
f_{N}/%	10.60	15.21
$\Delta\langle E\rangle_{\mathrm{NI,conf}}$/kcal mol^{-1}	0.65	0.48
$\Delta S_{\mathrm{NI,conf}}$/cal mol^{-1} K^{-1}	6.04	5.03
$P_2(\cos\psi)$	0.91	0.86
S_{ZZ}^{b}	0.49	0.75

[a]Calculated by using the parameters listed in Table III.
[b]Estimated from $\Delta\nu_1^{\mathrm{obs}}$ by using the relation given in Eq. 1.

system, a positive value of $\Delta S_{NI,conf}$ should be largely compensated for by a negative term intrinsic to the steric effect of rod-like segments. Included also in the table are the $P_2(\cos\psi)$ term for the orientation of the mesogenic core with respect to the molecular axis (*cf.* Figure 2). The order parameter S_{ZZ} of the molecular axis estimated from the observed $\Delta\nu_1$ value is listed in the last row. The order parameter of the mesogenic core given by the product, $S_{ZZ}(3\langle\cos^2\psi\rangle - 1)/2$, is 0.45 for the ether and 0.65 for the ester. Yoon *et al.*[28] obtained a value of 0.49 for the ether DLC by magnetic susceptibility measurements, while Blumstein *et al.*[9] reported 0.60 for the ester by using the D-NMR method. These results are also consistent with those generally observed in the NMR[9] as well as D-NMR measurements on related compounds.[29]

CONCLUDING REMARKS

In this work, an attempt has been made to elucidate the nematic conformation of a flexible spacer incorporated in a DLC from the observed profile of the D-NMR spectrum. The molecular axis is taken to lie along the direction connecting the center of the two neighboring mesogenic cores. Statistical weight factors assigned to the individual bond rotations are adjusted to reproduce experimental observations. It should be noted that this method does not require any information regarding the external potential field which should be responsible for the nematic ordering of the terminal mesogenes. This article is specifically addressed to the treatment of DLCs. Extension of the work to the polymer system will be the subject of the forthcoming paper.[15]

The results of the analysis indicate that orientation of mesogenic cores with respect to the molecular axis is restricted within a certain fractional range of angles. In view of the complexity associated with the spatial distribution profile, a description of the intermolecular interaction, which critically depends on the mutual orientation of mesogenic cores, may require some elaboration. Since the major purpose of the present work is to elucidate conformation of the soft spacer permitted in the mesophase, aspects involving the intermolecular interaction will be treated elsewhere.

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