N.M.R. study of segmental molecular interactions in liquid crystals

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N.M.R. study of segmental molecular interactions in liquid crystals

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A simple statistical model of interacting non-rigid molecules, based on a perturbation expansion of the pair correlation function and the additivity of segmental interactions, is applied to the study of orientational order as measured by N.M.R. in the nematic and S_A phases of 4-n-alkyl-4'-cyanobiphenyls (N-CB, N = 5 to 8), the nematic and S_C phases of 4-n-alkyloxybenzoic acids (N-OBA, N = 7, 8) and the D_{h0} columnar discotic phase of hexa-alkyloxytriphenylenes (N-THE, N = 5 to 8). The order parameters of each homologous series are correctly described in terms of two isotropic and two anisotropic segmental coupling constants. The model predicts certain relations among coupling constants pertaining to different homogous series. These predictions are supported by the results obtained for the three types of compounds studied.

1. Introduction

The statistics of molecular conformations in the condensed state may be regarded as the combined result of intra- and intermolecular interactions. The former of these interactions produce the purely conformational energy term which can be determined theoretically from the quantum mechanics of the free molecule and experimentally from measurements in the gas phase. The effects of the intermolecular interaction are usually described in terms of a number of interaction parameters assumed to be the basic quantities in the context of some statistical mechanics approximation scheme. The measurement of segmental, orientational order by N.M.R. spectroscopy offers a powerful means for the experimental determination of certain of these parameters.

Several approaches [1–11], ranging from entirely phenomenological considerations to more systematic approximations of the exact formulation, have been developed for the purpose of relating the measured segmental order to the basic molecular and/or mesophase properties. In this paper we apply the method of a perturbation expansion in the long range correlation potential [11] to determine the interaction parameters associated with the conformational statistics and the orientational order as measured by N.M.R. in three different types of mesogens. In particular we apply the single order parameter model in the mean field approximation, as specified in the next section, to the analysis of: D-N.M.R. and C^{13}-N.M.R. data [6, 12, 13] in the nematic (N) and smectic A (S_A) phase of 4-n-alkyl-4'-cyano-biphenyls (N-CB); D-N.M.R. data [14] in the N and S_C phases of 4-n-alkyloxybenzoic acids (N-OBA); D-N.M.R. data [15, 16] in the D_{h0} columnar discotic phase of hexa-alkyloxytriphenylenes (N-THE).

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This set of compounds was chosen for the study because it furnishes a variety of core structures, pendant chain numbers and lengths thus providing suitable testing grounds of the range of applicability of the model and also of the transferability of certain interaction parameters. Furthermore it offers the possibility of studying the effects of different core structures and mesophase symmetries on the alkyl chain conformation mechanism.

2. The conformation-orientation probability distribution in the single order parameter model

For a spatially uniform, axially symmetric, apolar phase the effective molecular potential $V_1(\omega, n)$, where n is the conformation index and ω denotes the Euler angles describing the orientation of the rigid core relative to the macroscopic frame, is given [11] in the single order parameter approximation by

$$V_1(\omega, n) = E_0(n) + V(n) - \bar{u}_2 \sum_i h_i^2 \langle S \rangle Y(\mathbf{w}_i . \mathbf{N}). \tag{1}$$

Here $E_0(n)$ is the conformational energy of the free molecule and $V(n)$ represents the isotropic contribution of the intermolecular interaction. The anisotropic part is assumed to result from the direct superposition of the interactions of uniaxial segments, labelled by i, into which the molecule is properly subdivided. The respective coupling constants are written in the form of the products $\bar{u}_2 h_i^2$, where $\bar{u}_2$ is a parameter that sets the scale of the strength of the second rank anisotropic interactions and the factors h_i^2 measure the relative strength of the coupling of the various molecular segments. The unit vectors $\mathbf{w}_i$, $\mathbf{N}$ denote the directions of the principal axis of the ith segment and of the symmetry axis of the phase respectively, and

$$Y(\mathbf{w}_i . \mathbf{N}) = (3(\mathbf{w}_i . \mathbf{N})^2 - 1)/2.$$

The temperature dependence of $V_1(\omega, n)$ is contained in the single molecular order parameter

$$\langle S \rangle = \sum_i h_i^2 \langle Y(\mathbf{w}_i . \mathbf{N}) \rangle, \tag{2}$$

where the averaging over conformations and orientations is performed with the distribution function

$$P_1(\omega, n) = (1/Z_1) \exp \{ - V_1(\omega, n)/kT \}. \tag{3}$$

The general theory and the details of the derivation of equations (1) and (2) can be found elsewhere [11]. Here we shall briefly state the steps and mention the basic assumptions and approximations leading to these equations. They are as follows.

(*a*) The interaction mechanism and parametrization is introduced through the two-molecule potential $u(\mathbf{R}; \omega, n, \omega', n')$, which describes the effective intermolecular interactions in excess of the forces preventing molecular overlap. The effects of these forces are introduced through $g_0(\mathbf{R}; \omega, n, \omega', n')$ which represents the short range (excluded volume) factor of the pair correlation function $g = g_0 g_{1r}$. Here $\mathbf{R}$ is the intermolecular position vector and

$$g_{1r} = \exp(- W_{1r}(\mathbf{R}; \omega, n, \omega', n')/kT)$$

is the factor describing longer ranged pair correlations.

(*b*) The correlation function g is approximated by its first order perturbation expansion with respect to the long range correlation potential W_{1r}. In this approximation

$V_1(\omega, n)$ is given by

$$V_1(\omega, n) = E_0(n) + \sum_{n'} \int g_0(\mathbf{R}; \omega, n, \omega', n')u(\mathbf{R}; \omega, n, \omega', n')P_1(\omega', n')d\mathbf{R} \, d\omega'/V_s,$$

$$(4)$$

where V_s is the sample volume. This equation, in conjunction with equation (3), expresses the self consistency condition of the theory.

(*c*) For simplicity, the effective pair potential is assumed to be second rank anisotropic and segmentwise additive with factorizable coupling constants, i.e. to be of the form

$$u(\mathbf{R}; \omega, n, \omega', n') = -\sum_{ii'} \{h_i^0 h_{i'}^0 u_0(R_{i,i'}) + h_i^2 h_{i'}^2 u_2(R_{i,i'})Y(\mathbf{w}_i \cdot \mathbf{w}_{i'})\},$$

$$(5)$$

where $\mathbf{R}_{i,i'}$ are intersegmental position vectors and i, i' run over all intermolecular segmental pairs. Note that a single function u_0 (or u_2) is used to describe the spatial dependence of the isotropic (or anisotropic) interactions between all segmental pairs and that the entire set of the respective coupling constants is obtained in terms of the products of the coupling factors h_i^0 (or h_i^2) and the overall strength parameters understood to be included in u_0 (or u_2).

(*d*) The excluded volume factor g_0 is taken to be isotropic and conformation independent, $g_0 \simeq g_0(R)$, thus accounting for the effective size of the molecules but neglecting the short range effects of molecular shape and of its variation with conformation. The molecular potential $V_1(\omega, n)$ does however include the long range contributions of shape effects. These are reflected in the positional integrations of equation (4), which in view of equation (5) are of the form

$$I_k(r_{ii'}) = \int g_0(R)u_k(|\mathbf{R} + \mathbf{r}_{ii'}|)d\mathbf{R}/V_s.$$

$$(6)$$

Here $k = 0, 2$ and $\mathbf{r}_{ii'} = \mathbf{r}_i - \mathbf{r}_{i'}$, with $\mathbf{r}_i$ denoting the segmental positions relative to the molecular centre of interaction which is conveniently defined by the condition

$$\sum_i h_i^k \mathbf{r}_i = 0.$$

$$(7)$$

(*e*) The lengths $r_{ii'}$ depend on the specific pair ii' considered and on the conformations of the two molecules but are always smaller than the effective molecular diameter D_0 (by definition of the latter). Furthermore, for any physically acceptable form of g_0 and u_k, both the integrand of equation (6) and I_k are finite functions of $r_{ii'} < D_0$. It is therefore meaningful to express I_k as a power series in $r_{ii'}$,

$$I_k(r) = \sum_m u_k^{(m)} r^{2m}.$$

$$(8)$$

For example, if for g_0 we use a hard sphere function ($g_0(R) = 0$ or 1 for $R < D_0$ or $R > D_0$ respectively) and takes $u_k(R) \sim R^{-6}$, equation (8) gives

$$I_k(r_{ii'}) = (1/2)u_k^{(0)} \sum_{m=0}^{\infty} (m + 1)(m + 2)(r_{ii'}/D_0)^{2m}.$$

$$(9)$$

This suggests that for $r_{ii'}$ sufficiently smaller than D_0 the series can be reasonably approximated by the first few terms.

The single order parameter approximation is obtained by neglecting all but the constant term in the expansion of I_2 and also all the terms with $m > 1$ in the I_0

expansion. In that case equations (1), (2), (4) and (8) lead to the identifications

$$\bar{u}_2 \; = \; u_2^{(0)} \tag{10}$$

and

$$V(n) \; = \; u_0^{(1)} \left(\sum_{i'} h_{i'}^0 \right) \left(\sum_{i} h_i^0 r_i^2 \right) \tag{11}$$

According to equations (6) and (8), truncation of I_0 at the constant term amounts to ignoring the variation of the isotropic potential over distances of the order of the molecular size. In that case $V(n)$ reduces to an additive constant ($\sim u_0^{(0)}$) and the isotropic part of V_1 consists of just the conformational energy of the free molecule $E_0(n)$ [6, 8, 10]. Accordingly $u_0^{(1)}$ is the lowest non-trivial term in I_0 and in that sense the truncation at $u_0^{(1)}$ and $u_2^{(0)}$ represents the minimal inclusion of the effects of intermolecular interactions in V_1.

Retaining higher order terms in the expansions of I_0 and I_2 leads to the appearance of additional isotropic as well as anisotropic terms in V_1 and additional order parameters. However, going beyond the single order parameter approximation does not necessarily lead to a more accurate description since the neglect of shape effects in g_0 could be more serious than the neglect of higher order terms in equation (8). In any case the construction of V_1 by starting from the pair distribution and improving the approximations regarding the g_0 and u and the number of terms to be retained in I_k, offers a way of obtaining a more realistic singlet distribution without increasing the number of fundamental parameters and also offers a basis of assessing the nature and significance of the terms retained or neglected. Obviously these possibilities are not available in phenomenological direct constructions of V_1 by inclusion of ad hoc terms or constraints.

To proceed with the evaluation of orientation-conformation averages we make a definite subdivision of the molecule into rigid segments and assign the respective coupling factors h_i^0, h_i^2. These, along with $u_0^{(1)}$ and $\bar{u}_2$ form the complete set of interaction parameters of the model. It should be noted that the subdivision into segments and the respective coupling factors pertaining to the isotropic interaction are in general different from those of the anisotropic. Specific examples of this procedure are given in the next section.

The $E_0(n)$ term consists of the free alkyl chain energy, for which the rotational isomeric approximation is applied in the calculations, and of the core–chain and chain–chain (for molecules with more than one chain) interaction part. This part includes overlap terms (OT), which are taken into account by rejecting all the conformations that produce core–chain or chain–chain overlap, and also rotational terms $J_1(a_L)$, $J_2(a_L, a_{L'})$, . . . , where a_L denotes the angle of rotation about the linkage bond of the Lth chain chain relative to the core. Accordingly, we have for $E_0(n)$ the general form

$$E_0(n) \; = \; \sum_L \{N_g^L E_g + N_{(+/-)}^L E_{(+/-)}^L + J_1(a_L)\} + \sum_{LL'} J_2(a_L, a_{L'}) + \text{OT}, \tag{12}$$

where N_g^L, $N_{(+/-)}^L$ are the numbers of $g^\pm$, $g^\pm g^\mp$ segments in the Lth chain, E_g, $E_{(+/-)}$ are their respective energies and the L summation runs over all the alkyl chains in the molecule.

3. Calculation of interaction parameters

In this section we apply equations (4) and (12) to specific representative examples of core structure and chain arrangement. The values of the basic parameters are determined by fitting the segmental averages calculated with the distribution of equation (3) to the values implied by the N.M.R. spectra. The fitting procedure is based on minimizing the quantity

$$D_s = \left\{ \sum_i ((2(s^i_{TH} - s^i_{EX})/(s^i_{TH} + s^i_{EX}))^2)/M(M - 1) \right\}^{1/2}, \tag{13}$$

where s^i_{EX} and s^i_{TH} are the experimental and theoretical values of the splitting of the *i*th segment and M is the total number of inequivalent splittings involved in the simulation. Methyl groups exhibiting $s^i \simeq 0$ in certain homologues are not taken into account in equation (13).

The acceptable range of an interaction parameter is defined for each type of compound so as to contain the respective parameter values for which the splittings of any of the studied homologues can be reproduced to an accuracy corresponding to $D_s < 5$ per cent and with the correct sequence of relative magnitudes.

The same form of $V_1(\omega, n)$ can be used to describe the orientational order in spatially non-uniform phases in the limit where the effective single molecule potential can be separated into a purely positional part and a position independent part $V_1(\omega, n)$. Calculations based on such separable potentials produce very good simulations of the N.M.R. splittings in the smectic phase.

In all cases the value of $2 \, kJ \, mol^{-1}$ is used for E_g and that of $12 \, kJ \, mol^{-1}$ for $E_{(+/-)}$. The isotropic segmental interaction of the alkyl chain is attributed to effective atoms located at the carbon sites. Similarly, to describe the anisotropic interaction, the chain is subdivided into uniaxial segments coinciding with the respective C–C bonds. All the effective atoms and the C–C bonds are assumed to be equivalent with respect to their couplings, i.e. $h^0_i = h^0$ and $h^2_i = h^2$ when i refers to a chain segment.

The details of the rigid core interactions and the particular forms of the rotational terms J_1, J_2 used in this calculation depend on the molecular structure of the compound. These are as follows.

N-CB. The core interactions are assumed to result from the isotropic interactions of two effective atoms located at the ring centres and of a uniaxial tensor with its principal axis parallel to the long axis of the core. We may take, without loss of generality, $h^0_i = h^2_i = 1$ when i refers to a core segment. In that case $u^{(1)}_0$ and $\bar{u}_2$ represent the core–core coupling constants for the isotropic and anisotropic interactions, respectively. The J_2 term is not applicable here since there is only one chain in the molecule. The J_1 term cannot be defined for a cylindrically symmetric core. If however a transverse direction were singled out by allowing for core biaxiality, the principal Fourier component of this term would be

$$J_1(a) = B_1 \cos(2a), \tag{14}$$

where a is the dihedral angle formed by the C_{AR}–C_1–C_2 plane (the chain plane) and the symmetry plane of the core (i.e. the plane bisecting the dihedral angle formed by the two ring planes). The B_1 parameter gives in this case a measure of the possible inequivalence between states in which the chain plane coincides with the core symmetry plane ($a = 0$), and those in which the two planes are mutually perpendicular. The simulations of the N.M.R data in the nematic phase do not reveal any substantial core biaxiliaty and thus such inequivalences cannot be clearly detected.

The ranges of the interaction parameters h^0, h^2, $\bar{u}_2$ and $E_0^1 = u_0^{(1)}d^2$, where d is the C–C bond length, shown in the table were obtained by fitting the N.M.R. data in the nematic phase of N-CB, for N = 5, 6, 7, 8 assuming a uniaxial core. Although the values and ranges of these parameters are determined by imposing $D_s < 5$ per cent for any compound or temperature in the nematic range, the accuracy of most of the simulations is 2 $\sim$ 3 per cent and there are also some instances of exact (to within experimental error) simulations.

It is worth noting that the value of E_0^1 found here is nearly half of that found in a similar calculation [11] in which the isotropic interaction of the core was attributed to a single effective atom located at the core centre and furthermore core–chain overlap terms, $E_{(+/-)}$ terms as well as differences between h^0 and h^2 were not taken into account. This result, in connection with the fact that the two calculations show much smaller differences with respect to the other parameters, suggests the approximate validity of ring additivity of the isotropic core interactions.

Fitting the N.M.R. data in the S_A phase of 8-CB give practically the same values as in the nematic for all four parameters.

N-OBA. The core interactions are described in terms of a uniaxial tensor along the core axis and three isotropic effective atoms located one at each ring centre and one at the core centre. For simplicity we take the central atom to be equivalent to the ring atoms. In the absence of core biaxiality, the J_1 rotational terms cannot be defined. A J_2 term is, however, meaningful and its leading Fourier component is

$$J_2(a_1, a_2) = A_2\cos(a_1 - a_2), \qquad (15)$$

Here a_1, a_2 are the angles of rotation of the two chains about the respective C_{AR}–O bonds, with the values $a_1 = a_2 = 0$ corresponding to the transposed configuration shown in figure 1. The D-N.M.R. spectra do not allow sensitive determination of A_2. They indicate, however, that it is of the order of magnitude of E_g or smaller. In calculations where the angle $a = a_1 - a_2$ is allowed to take only four values (0, 90°, 180°, 270°) it is found that the probability of $a = 0$ is twice to three times larger than that of $a = 180°$, whereas the sum of these two planar probabilities is 0·3 to 0·45. These effects cannot of course be attributed directly to the parameter A_2 as they are produced from the interaction of the entire molecule.
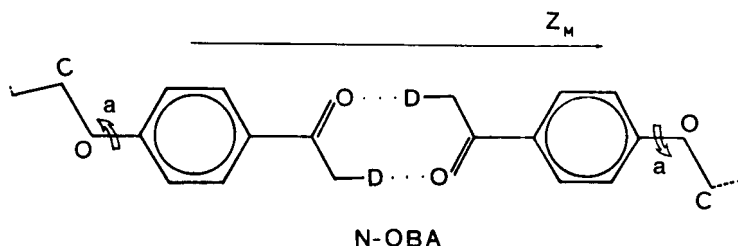

N-OBA

Figure 1. Molecular structure of the N-OBA core and inner segments of the alkoxy chains in the transposed configuration. Z_M gives the principal direction of the uniaxial tensor describing the anisotropic interaction of the core.

The results obtained for the coupling constants from fitting the D-N.M.R. data in the nematic and S_C phases of 7 and 8-OBA are shown in the table. The general quality of the simulations is the same as for the N-CB. In the S_C calculations the energy contributions of the biaxial order parameters were ignored.

Average values and acceptable ranges of interaction parameters determined from fits to N.M.R. data on N-CB (N = 5, 6, 7, 8), N-OBA (N = 7, 8) and N-THE (N = 5, 6, 7, 8) using the single order parameter approximation.

	h^0	h^2	$E_0^1/\text{kJ mol}^{-1}$	$u_2/\text{kJ mol}^{-1}$
N-CB	0·28 ± 0·06	0·18 ± 0·04	0·16 ± 0·06	7·6 ± 1
N-OBA				
N	0·26 ± 0·03	0·17 ± 0·03	0·19 ± 0·06	10·6 ± 2
S_C	0·25 ± 0·02	0·22 ± 0·03	0·18 ± 0·06	9·1 ± 1
N-THE	0·22 ± 0·06	−0·16 ± 0·04	0·13 ± 0·06	11 ± 2·2

N-THE. The interactions of the core are assumed to be described by four effective isotropic atoms located at the ring centres and by four uniaxial tensors, one with its principal axis normal to the core plane and three with their axes along the directions joining the central ring to the peripheral ones. If by h_N^2 and h_P^2 we denote the (positive) coupling factors associated with the non-planar tensor and with the three equivalent planar tensors respectively, the total anisotropic core interaction is characterized by the coupling factor $h_E = h_N^2-(3/2)h_P^2$. Setting $(h_E)^2 = 1$, in which case $\bar{u}_2$ represents the effective core–core coupling constant, the coupling factors of the chain segments, h^2, could be either positive or negative depending on whether these segments are more strongly aligned by the non-planar tensor ($h_E > 0$) or by the planar ones ($h_E < 0$).

For the (leading) rotational energy terms we have from each chain a contribution of the form

$$J_1(a_L) = B_1 \cos(2a_L) \tag{16}$$
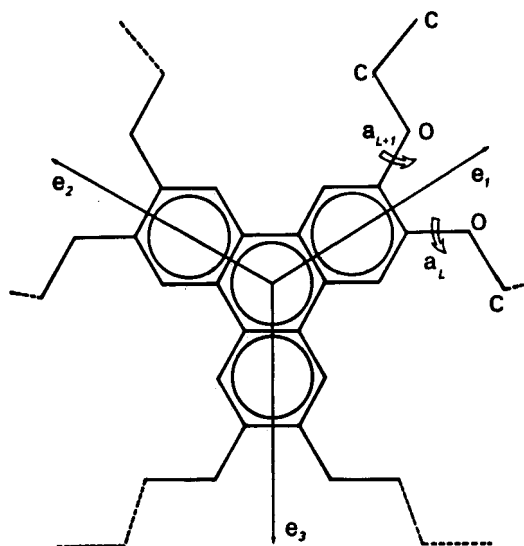
N-THE

Figure 2. Molecular structure of the N-THE core and inner segments of the alkoxy chains in the full extended configuration. The three vectors give the principal directions of the planar uniaxial tensors describing the anisotropic interaction of the core.

and from each pair of chains attached to the same ring, a contribution of the form

$$J_2(a_L, a_{L+1}) \;=\; A_2\{\sin(a_L/2)\sin(a_{L+1}/2)\}^2. \tag{17}$$

The angles a_L describing the rotations about the C_{AR}–O bonds are chosen so that the arrangement of figure 2 correspond to $a_L = 0$ for all chains.

Due to the presence of a very large number of conformations the simulation was performed with the Monte Carlo method. As a result, the ranges of variation of the interaction parameters are somewhat wider than in the previous compounds. This procedure could not give sharply defined values for the parameters B_1, A_2, it did however predict A_2 to be positive and of the order of magnitude of E_g.

There is some ambiguity concerning the signs of the deuterium order parameters of the alkyl chain. The results shown in the table are obtained from simulations of the D-N.M.R. splittings of 5,6,7,8-THE that give the same (positive) sign for all the deuterium order parameters. However, because of the relatively large number of parameters involved in the fitting, it is possible to obtain simulations, of comparable accuracy, in which some of the order parameters are negative. This ambiguity was not resolved conclusively in the present study.

4. Discussion

It is evident from the table that the four basic interaction parameters can be reasonably regarded as characteristic constants within each of the homologous series. In considering possible relations between values corresponding to different homologous series it should be noted that:

(*a*) Although the cores are of different sizes and shapes their subdivision into similar elements (benzene rings) allows their isotropic segmental interactions to be described by nearly the same values of h^0, E_0^1. The differences observed in the table, particularly for E_0^1 are not entirely attributable to a possible failure of exact additivity since according to equations (7) and (9) $u_0^{(1)}$ and $\bar{u}_2$ depend implicitly on the overall molecular size.

(*b*) The $\bar{u}_2$ parameter reflects the anisotropy of the core and thus is expected to be different for cores of different shapes. It is interesting, however, to observe that $\bar{u}_2$ of THE is approximately 3/2 times that of CB, suggesting that each of the three planar tensors of the THE core is roughly equivalent to the CB core tensor and that the non-polar tensor is of negligible coupling constant.

(*c*) The coupling constant of the anisotropic interaction of the C–C bonds of the chain is $\bar{u}_2 h^2$. Ignoring variations of $\bar{u}_2$ with molecular size, all the compounds in the table should exhibit the same (absolute) value for this parameter. This condition is reasonably satisfied within the acceptable range of the parameters.

Part of the effects of intermolecular interaction on the statistics of the alkyl chain are illustrated in figure 3, where the probability $p_T(i)$ of the ith C–C bond being in the trans state is plotted for the 7-membered homologues of the three series. The 7-THE plot is obtained from the results of the simulation with positive deuterium order parameters. On the same diagram a plot of $p_T(i)$ of the free chain, at the same temperature, is given for comparison with all the other plots which exhibit higher trans probabilities for the odd segments ($i = 0$ for the C_{AR}–O(C) bonds). The two plots on the 7-OBA diagrams refer to temperatures in the nematic and the S_C ranges
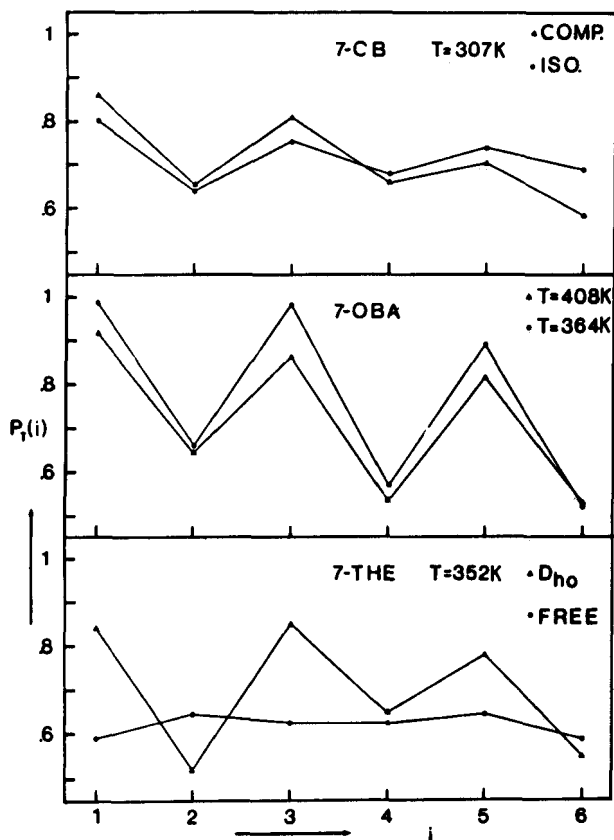
Figure 3.   Plots of the trans state probability versus the segment position showing the statistical profiles of the free chain and of the fully interacting chain in the D_{ho} columnar discotic phase, in the nematic and S_C phase of 7-OBA and in the nematic phase of 7-CB where the profile obtained with the complete interaction potential is compared to that obtained with just the isotropic part.

and show that the $p_T(i)$ profiles do not differ qualitatively in the two phases. To estimate the relative effects of the anisotropic interaction on the chain conformations we have plotted on the 7-CB diagram, along with the profile resulting from the complete effective potential of equation (1), the profile obtained from just the isotropic part, i.e. $E_0(n) + V(n)$. By comparing the isotropic plot to that of the free chain it follows that the $V(n)$ term favours the more elongated conformations of the molecule and thus enhances the effects of the anisotropic interaction. It is worth noting that this behaviour cannot be obtained if the effects of the isotropic interaction are accounted for by a uniform rescaling of the value of E_g everywhere along the chain [6, 8, 10, 17]. Accordingly, the concept of a single (possibly rescaled) E_g parameter for the entire alkyl chain may not be adequate to describe the conformational statistics in liquid crystal systems of the type considered in this study.

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