Oblate Hexaalkoxytriphenylene Solutes in a Prolate Nematic Solvent: A Deuterium NMR Study of Alkyl Chain Ordering

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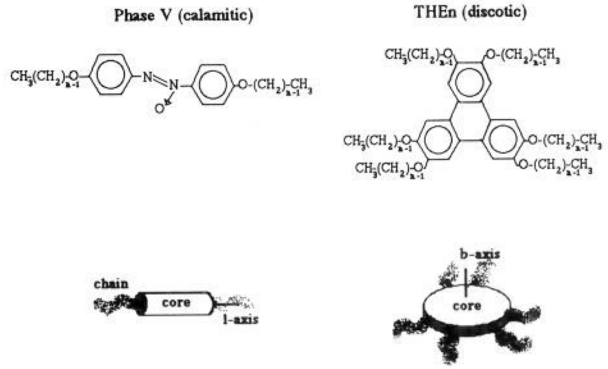
Abstract: We present deuterium NMR spectra of a series of hexaalkoxytriphenylene solutes (THE*n*, where $n = 5$, 6, 7, and 8 is the number of carbons in the labeled alkoxy chains) dissolved in the calamitic solvent phase V. The observed methylene quadrupolar splitting patterns (segmental order profiles) are markedly different from those obtained in the neat columnar discotic phases of the THE*n* mesogens; they also differ significantly from order profiles of alkoxy chains attached to calamitic mesogens. Theoretical simulations of the spectra give the assignment of the splittings and, moreover, enable studies of the accommodation of the oblate THE*n* solute in the calamitic solvent's orientationally biased mean field. The chord model with the rotational isomeric state description of the THE*n*'s six alkoxy chains quantitatively describes this unusual mixture of oblate and prolate molecules. The model shows that the accommodation of the THE*n* mesogenic core in the calamitic solvent's mean field does not favor maximum extension of the chains: The oblate THE*n* disk is tangent to the solvent director, and consequently, the radial disposition of extended chain contours on the periphery of the THE*n* disk is frustrated by the excluded volume interactions that constitute the solvent's mean field.

I. Introduction

Liquid crystallinity is exhibited by both oblate (discotic) and prolate (calamitic) mesogens when the shape anisotropy of a variety of (low-melting) organic molecules exceeds some critical aspect ratio.[1] The shape anisotropy of both kinds of thermotropic mesogens is derived from the structural definition of the molecular framework known as the "mesogenic core". In calamitics the prolate mesogenic core usually comprises *para*-linked aromatic rings in a rectilinear configuration. In typical discotics, a single aromatic ring or several fused rings make up the oblate core. Generally the (aromatic) cores of both types of mesogens are rigid, but there are also some nonaromatic and nonrigid examples of calamitics and discotics.[2] In the mesophases the global (anisometric) mesogen shapes are ordered by efficient intermolecular packing governed primarily by short-distance repulsions commonly referred to as excluded volume interactions. These packing constraints induce the well-known, long-range molecular orientational order wherein the principal axes of these two types of molecules (the minor *b*-axis of the oblate mesogen and the long molecular *l*-axis of the prolate mesogen) retain some degree of parallelism in their respective mesophases.

Scheme I



In mixtures of oblate and prolate mesogens, excluded volume interactions impose a tendency toward mutually perpendicular arrangements of the rod and disk *l*- and *b*-axes, respectively. Accordingly, it was believed that in such mixtures the ordered fluid phase would adopt a biaxial supramolecular organization[3] over a certain range of composition. There were also theoretical arguments indicating that the formation of such biaxial nematic phases is thermodynamically unstable relative to uniaxial phase separation.[4] A decade ago some of us[5] attempted to experimentally test these ideas by using deuterium NMR to monitor mixtures of the deuterium-labeled, discotic mesogen hexaalkoxytriphenylene (THE*n*, where *n* is the number of carbon atoms in the alkoxy chains) dissolved in the calamitic mesophase phase V (Scheme I). However, poor mutual solubility of this particular pair of mesogens restricted measurements to low concentrations (1–5 wt %) of the THE*n* "*solute*" in the calamitic phase V "*solvent*". Although we failed to detect evidence for biaxial phases, these mixtures nevertheless exhibited rather intriguing NMR data: The quadrupolar splittings obtained from the deuterium-labeled alkoxy chains of the THE*n* solutes exhibited patterns that were *qualitatively* different from those exhitibed by the neat columnar phases of the THE*n* series[6] and also very different

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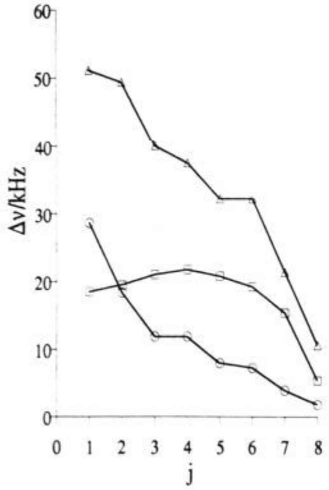

Figure 1. Deuterium NMR quadrupolar splittings for perdeuteriated octyloxy chains in a variety of mesophases wherein the director is parallel to the spectrometer magnetic field. The magnitudes of the full quadrupolar splittings $\Delta\nu^j$ (eq 2) at roughly the same reduced temperature ($T \approx T_c - 5$ K) are plotted versus j, the location of the labeled segment in the chain: (a) THE8 dissolved in phase V (squares);[5] (b) the columnar phase of THE8 (circles);[6] (c) (octyloxy)cyanobiphenyl calamitic nematic phase (triangles).[8]

from the patterns found for similar alkoxy chains in related calamitics.[7] As an example, we show in Figure 1 the magnitudes of the full quadrupolar splittings—$\Delta\nu^j$ vs j, the location of the segment in the chain—for three different cases: the THE8 solute in the phase V solvent (squares), the neat columnar discotic phase of THE8 (circles), and the neat calamitic nematic phase of (octyloxy)cyanobiphenyl (triangles).

In the latter cases of neat mesophases, the dramatically different segmental order parameter profiles observed for the calamitic nematic phase[7,8] and the columnar discotic phase[6] can be qualitatively explained[9] by the orientation of the chain–core junction relative to the mesogen principal axis: In the THE*n* series this junction (the C_{ar}–O bond) is perpendicular to the *b*-axis, whereas in calamitics this bond is nearly parallel to the long molecular *l*-axis. However, in addition to these qualitative differences between the segmental order profiles of *neat* discotic and calamitic phases (Figure 1), there are heretofore unencountered aspects of the averaging mechanism for the THE*n solutes* in a calamitic nematic solvent. For example, the symmetry of the arrangement of alkoxy chains on the periphery of the THE*n* solute's mesogenic core—six chains radially directed from the circumference of the discotic core—ensures that, in all solute orientations relative to the solvent director, most of the alkoxy chain contours conflict with the excluded volume interactions constituting the calamitic's (uniaxial) mean field (see sketch in Figure 2).

In this article we try to understand how the calamitic mean field produces the observed deuterium NMR segmental order profiles of the THE*n* solutes in the nematic solvent phase V, e.g., data in Figure 1 (squares). We do this by calculating these profiles within a modeling approach that has been successfully used to describe the orientational potential of pendant alkoxy chains of calamitics in the neat nematic phase[10] and also of *n*-alkane solutes in nematic solvents.[11] The approach is based on the construction of the molecular orientational potential (of mean torque) by additively combining contributions from submolecular modules.[12] Here we use a particularly simple formulation of this approach whereby the modular contributions to the orientational potential come from two sources: the rigid aromatic core of the THE*n* molecule and the chord segments (segments joining the midpoints of successive C–C bonds) of the pendant chains. This formulation, the "chord model" for brevity, has been shown to be particularly efficient in conveying the excluded volume aspect of the ordering mechanism of flexible prolate molecules[10–13] since it minimizes the necessity for introducing orientational correlations among pairs of submolecular modules.[12] The resulting molecular orientational potential can then be satisfactorily approximated by a direct superposition of uncorrelated terms describing the potential energy of the rigid core and the individual chords. We show that, by supplementing this simple model with the standard rotational isomeric state (RIS) methodology[14] of conformation generation, it is possible to account for the unusual order parameter profiles of the THE*n* molecules in the calamitic solvent and thereby gain physical insight into the ordering mechanism of pendant chains under the conditions of frustrated packing prevailing in this mixture.

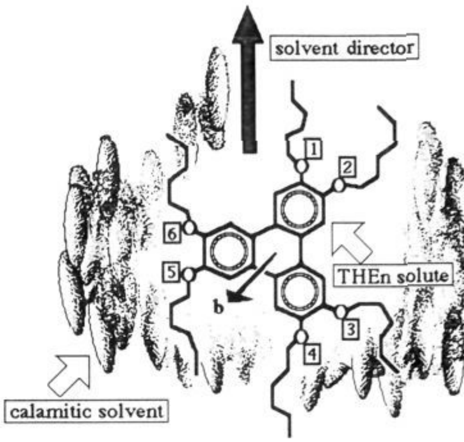

Figure 2. Schematic representation of the THE*n* solute's orientation relative to the calamitic solvent's director; $m = 1$–6 numbers the alkoxy chains on the solute.

II. Deuterium NMR Measurements

The deuterium-labeled THE*n* compounds were the same as those used in ref 6; details about the synthesis are given in refs 6 and 15. Typical deuterium NMR spectra[5] of the THE*n* homologues with fully deuteriated alkoxy chains for $n = 5$–8 dissolved (~3 wt %) in the nematic solvent phase V recorded at 9 K below the clearing temperature $T_c \approx 335$ K of the solution are shown in Figure 3. Figure 4b shows the quadrupolar splittings of the THE6 labeled at the aromatic proton site on the rigid core and at the α-position on the alkoxy chains; a typical spectrum of the selectively labeled THE6 is contrasted with that having a perdeuteriated chain as shown in Figure 4a (at $\sim T_c - 9$ K). The temperature dependent values of the quadrupolar splittings of the selectively labeled THE6 solute, $\Delta\nu_Q^{ar}$ (solid circles) and $\Delta\nu_Q^{\alpha}$ (open circles), are shown in Figure 5.

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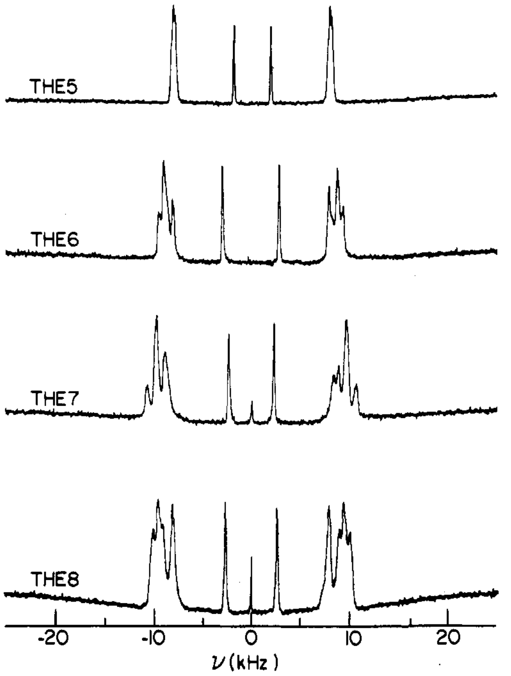

Figure 3. Deuterium NMR spectra of the THE*n* solutes dissolved in phase V and recorded at $T = T_c - 9$ K.

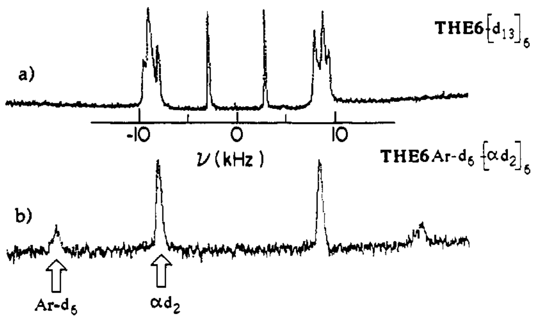

Figure 4. Deuterium NMR spectra of selectively labeled THE6 solutes dissolved in phase V at $T = T_c - 9 \pm 1$ K (a) perdeuteriated hexyloxy chains; (b) deuterium labels are at the aromatic proton site and the α-methylenes on the hexyloxy chains.

III. Calculation of Order Parameter Profiles

The order parameter of the discotic triphenylene core is defined by $S_b = \langle P_2(\cos\theta_b)\rangle$, where θ_b is the angle between the principal *b*-axis of the solute molecule and the nematic director of the solvent; $P_2(x) = (3x^2 - 1)/2$ is the rank-two Legendre polynomial, and the ensemble averaging indicated by the angular brackets is carried over all the orientations ω and conformations $\{n\}$ of the solute molecule. The order parameter S_b is readily obtained from the splittings of the aromatic deuterons $\Delta\nu_Q{}^{ar}$ if a rigid and planar structure of perfect trigonal geometry is assumed for the triphenylene core: Since the electric field gradient tensor interacting with the deuteron quadrupole moment is to a good approximation uniaxial with its symmetry axis along the C–D bond which, in turn, is perpendicular to the *b*-axis, it is straightforward to show that S_b and $\Delta\nu_Q{}^{ar}$ are related as follows:

$$\Delta\nu_Q{}^{ar} = \frac{3}{2}\nu Q[P_2(\cos\pi/2)]S_b = -\frac{3}{4}\nu_Q S_b \tag{1}$$

where ν_Q ($\approx$190 kHz) is the quadrupolar coupling constant for aromatic deuterons.

Similarly, the splittings of the deuteriated sites on the alkoxy chain are related to the order parameters of the respective C–D bonds according to

$$\Delta\nu^j = \frac{3}{2}\nu_Q\langle P_2(\cos\theta^j)\rangle \tag{2}$$

where ν_Q = 163 kHz, and θ^j is the angle between the *j*th C–D bond and the nematic director.

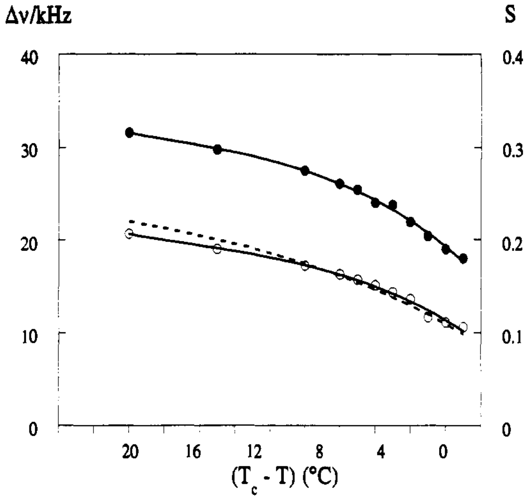

Figure 5. Temperature dependence of the deuterium quadrupolar splittings of the selectively labeled THE6 solute dissolved in phase V: (filled circles) aromatic deuterons; (open circles) α-methylenes; (dotted line) calculated (see text).

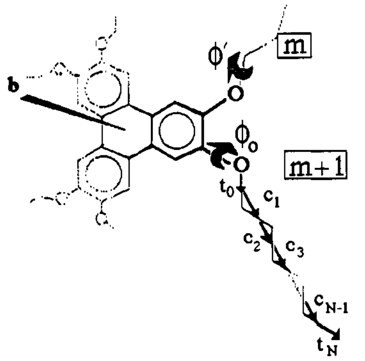

Figure 6. Schematic illustration of the THE*n* solute as depicted in the chord decomposition.

In order to relate the order parameters pertaining to the various segments of a THE*n* solute—the respective quadrupolar splittings in the deuterium NMR spectrum—to the basic quantities governing the orientational ordering and the conformational statistics of the solute, we make the following postulates regarding the orientation–conformation distribution function $f(\omega,\{n\})$ of the THE*n* homologues:

(i) The distribution is obtainable from a "potential of mean torque" $V(\omega,\{n\})$, which is made up from independent, additive contributions from the oblate mesogenic disk, $V_{disk}(\omega)$ (accounted for by a virtual segment directed along the *b*-axis), and the six alkoxy chains, $V_{chain}(\omega,n_m)$, where n_m is the conformation label for the *m*th alkoxy chain (m = 1, 2...6; refer to Figures 2 and 6). In the spirit of the modular formulation,[12] each of the six V_{chain} terms is assumed to be further decomposable into additive contributions from rigid chain segments (chords) as described in iii below. Thus, the orientational ordering of the entire flexible solute molecule is regarded as the result of the individual alignment of its (properly chosen) rigid submolecular units. Furthermore, each of the six alkoxy chains is assumed to attain all of its possible conformations relative to the discotic core independently of the conformations of the other five chains, and thus the conformation energy of the entire molecule is simply assumed to be the sum of the conformation energies $E_{conf}(n_m)$ of the individual chains. Accordingly, $f(\omega,\{n\})$ is of the form

$$f(\omega,\{n\}) = \zeta^{-1}\exp[-\{V_{disk}(\omega)+\sum_{m=1}^{6}[V_{chain}(\omega,n_m)+E_{conf}(n_m)]\}/kT] \tag{3}$$

where ζ is a normalization factor. An obvious consequence of the absence of any interchain terms in this expression is that some energetically forbidden conformations (because of excluded volume intersections between neighboring chains) are in fact not discarded. However, the effects of such spurious conformations on the results of the averaging have been analyzed quantitatively[16] and found to be quite tolerable for the purpose of the present calculations, particularly in view of the great computational simplification brought about by the assumption of conformational independence among the six alkoxy chains. The simplification lies in the fact that the absence of interchain correlations in eq 3 makes it possible to carry out the averaging by effectively generating the conformations of a single chain, as opposed to generating the conformations of the entire molecule (six chains simultaneously). The latter task is rather demanding and has been circumvented in previous studies by means of Monte Carlo sampling[17] or by rejection of a large number of conformations.[7] For the same reasons of computational efficiency, the rotational kinetic energy factor[10] is not included in eq 3. Although these simplifications affect the probabilities of individual conformations, they are not expected to influence critically the end result of the ensemble average.

(ii) The rigid, discotic core contribution to the potential of mean torque is given by

$$V_{\mathrm{disk}}(\omega) = -\tilde{W}P_2(\cos\theta_b) \qquad (4)$$

where the effective coupling parameter $\tilde{W}$ is anticipated to be negative, as the most favorable packing of the oblate solute in the calamitic occurs for $\theta_b \approx \pi/2$. Also, $\tilde{W}$ depends on the degree of ordering in the solvent and is therefore temperature dependent.

(iii) For the contribution $V_{\mathrm{chain}}(\omega,n_m)$ of the *m*th alkoxy chain (extending from the oxygen atom to the methyl group, the C_{ar}–O bond being understood to belong to the rigid core), we use the chord model expression[10–12]

$$V_{\mathrm{chain}}(\omega,n_m) = -\tilde{w}\{2\sin^2(\alpha_v/2)\sum_{c=1}^{N-1}P_2(\cos\theta_c) + [P_2(\cos t_0) + P_2(\cos t_N)]/2\} \qquad (5)$$

where θ_c denotes the angles of the chords—the segments joining the midpoints of successive C–C bonds—relative to the director; t_0 and t_N denote the angles of the chain end-segments (directed respectively along the O–C bond and the terminal C–CH_3 bond) relative to the director (refer to Figure 6). The angle α_v is the C–C–C (or O–C–C) valence angle, and $\tilde{w}$ is the single coupling parameter measuring the strength of alignment of chain segments in this minimal formulation of the chord model. By analogy with $\tilde{W}$, $\tilde{w}$ is temperature dependent. The ratio $\tilde{w}/\tilde{W}$ is, however, essentially temperature independent (the mean field approximation).[10,11]

(iv) Aside from the C_{ar}–O–C linkage, the conformations of the alkoxy chain are generated according to the standard three-state RIS model.[14] The gauche states are generated by discrete dihedral angle rotations with ϕ_g = 113° at the internal C–C bonds. Their respective energy is higher than that of the trans states by E_{tg} (≈0.5 kcal/mol). All of the conflicting g^+g^- sequences (the "pentane effect"[14]) are discarded and so are all conformations that lead to longer range self-intersections of the chain.

(v) The rotational energetics within the C_{ar}–O–C linkage are perturbed by the proximity to the rigid core and therefore are treated separately from the rest of the chain. As suggested by simple inspection of the possibilites of steric intersections between vicinal chains (consider rotations about C_{ar}–O and O–C bonds for neighboring pairs of chains attached to the same phenyl ring), a detailed treatment of this problem can be achieved only by considering the conformational interdependences[16] among such pairs of chains. In the present simplified framework of effectively independent chain motions, we assume that the gauche states of the O–C bond are obtained with rotations by $\phi'_g \approx 100°$, in accordance with the results of a structural study of 1-chloro-4-ethoxybenzene.[18] We also assume that the rotational isomeric states of the dihedral angle ϕ_0 (about the C_{ar}–O bond; see Figure 6) are restricted to the values of 0°, corresponding to the planar configuration, and ±90° for the two configurations where the C_{ar}–O–C plane is normal to the triphenylene plane.[19] The value of ϕ_0 = 180°, giving the other planar configuration, leads to excluded volume overlapping of the vicinal chains and is omitted altogether. For the energy values E'_{tg} of the gauche states of the O–C bond as well as for the energy difference ΔE_0 between the ϕ_0 = 0° and ϕ_0 = ±90° states of the C_{ar}–O bond, there are no directly transferable values in the literature, and therefore the estimates used in the present study are suggested by the analysis of the NMR data as discussed below.

(vi) In the calculations, we have assumed that the rings forming the THE*n* core are perfectly hexagonal and coplanar. This results in a planar core with trigonal symmetry having the C_{ar}–O bonds directed radially. The geometrical data used in the calculations are α_v = 112° for the C–C–C and O–C–C valence angles, 118° for the C_{ar}–O–C angles, and 109° for the D–C–D angles of the methylene segments. In order to detect self-intersections of the alkoxy chain, the C–C bond lengths were set at 1.53 Å and those of the C–O bonds at 1.40 Å. The value of 1.7 Å was used for the effective van der Waals radii of the CH_2 and CH_3 groups as well as for the oxygen atoms.

It is apparent from the nature of postulates i–vi that the emphasis is placed on depicting, in a physically simple and computationally straightforward way, the essence of the structure and the ordering mechanism rather than on an accurate account of the structural and conformational details of the system, an endeavor for which the present set of limited data is not well suited.

IV. Results and Discussion

The CD_3 splittings are readily assigned to the most intense and innermost peaks in the deuterium spectra of the THE*n* series in Figure 3. The magnitudes of the CD_2 splittings can be estimated from the resonance maxima within the envelope of the methylene resonances (Figure 3). A direct assignment of the CD_2 splittings is not possible even with the help of the spectra of the selectively deuteriated THE6 presented in Figure 4b because of the strong overlap of the methylene spectral lines and the experimental uncertainty in the temperature (±1 K) and, consequently, different degrees of orientational order S_b for the two labeled THE6 solutions (Figure 4). The assignments are therefore made using the conformation–orientation model described in the preceding section.

The values of the coupling parameters $\tilde{W}$ and $\tilde{w}$ in eqs 4 and 5 are determined by requiring that the calculated core order parameters and methyl splittings coincide with the experimental ones and also by requiring that the largest and smallest calculated splittings for the CD_2 groups corresond with the outer and inner edges of the group of overlapping CD_2 resonances for each spectrum in Figure 3. This optimization procedure is carried out with the restriction that the ratio $\tilde{W}/\tilde{w}$ be identical for all the simulated spectra of the THE*n* series. Although all the spectra in Figure 3 refer to the same temperature and therefore the calculated profiles for the different THE*n* members should be characterized by the same value of $\tilde{W}$, the optimization procedure allowed for small variations of $\tilde{W}$ from one member to another in order to cover uncertainties alluded to above in the temprature ($T = T_c - 9$ K).

This optimization procedure showed that (with $E_{tg} \approx 0.5$ kcal/mol) the best agreement with experiment is obtained for $E'_{tg} \approx 0.3$ kcal/mol, and $\Delta E_0 \approx 0.6$ kcal/mol with $\tilde{w}/\tilde{W} = -0.13$. The final optimization was made for each THE*n* member by keeping $\tilde{w}/\tilde{W}$ (=–0.13) constant and varying $\tilde{W}$ to improve the fit to the peak assignment implied by the preliminary simulations. The calculated splittings are shown in Figure 7; the optimal values of $\tilde{W}$ for all members of the THE*n* series remained essentially constant (–0.83 kcal/mol with a variation of only ±0.02), confirming theoretical expectations. The negative sign of $\tilde{W}$ is in accord with alignment of the discotic *b*-axis perpendicular to the nematic director (see Figure 2).

Aside from small odd–even oscillations in the $\Delta\nu^j$ with carbon number, a monotonic decrease in the order profile is typically the observed trend for alkoxy chains in the neat phases of both the THE*n* discotic mesogens and a variety of calamitic mesogens (see Figure 1). The essential feature in the profiles of Figure 7 is that the variation of the $\Delta\nu^j$ vs *j* profile is not monotonic with the position *j* along the chain. Because some of the splittings are very close to one another, it is possible to interchange the assignment among such splittings by moderate variations in the basic conformation parameters. For example, it was found that

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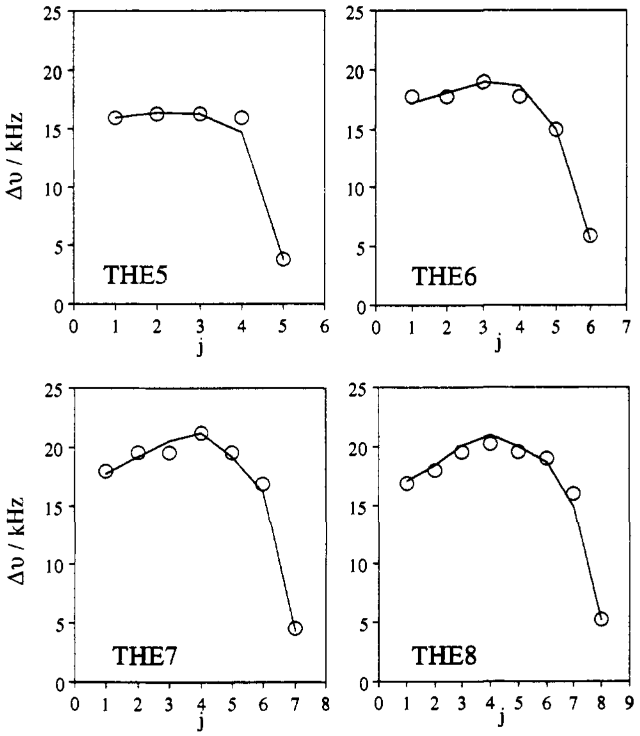

Figure 7. Comparison of experimental (open circles) and calculated (solid lines) segmental order profiles for THE*n* solutes in phase V (at $T = T_c - 9$ K).

by increasing E'_{tg} the assignment would tend toward a monotonic decrease of the splitting from the chain–core junction, i.e., from the α-methylene ($j = 1$) to the methyl group ($j = n$): For $E'_{tg} > 1$ kcal/mol, the calculated $\Delta\nu^j$ vs j profile becomes monotonic. At the same time, however, the overall agreement with measurement becomes rather poor. An analogous behavior is obtained on varying ΔE_0. On the other hand, the trend of the profiles remains essentially unaffected on increasing the value of E_{tg} from the nominal value of 0.5 kcal/mol (used in the calculations of the splittings in Figure 7) to the perhaps more relevant value of 0.68 kcal/mol obtained for hexane in the environment of a calamitic solvent.[20] The agreement with experiment is the same with either value of E_{tg}, but the optimal values of $\tilde{W}$ are somewhat larger and those of $\tilde{w}$ are smaller for the larger E_{tg} value. Similar behavior is observed on further elevating E_{tg} to the value of 0.8 kcal/mol suggested recently for liquid alkanes.[21] Finally, a reproduction of the spectral patterns was attempted for a fixed dihedral angle ϕ_0 between the C_{ar}–O–C and the triphenylene planes. It was found that the agreement with experiment is unacceptable for all values of the dihedral angle ϕ_0 between 0° and 90°, with the smallest disagreement obtained around 45°.

For the simulation of the temperature dependence of the aromatic and α-deuteron splittings shown in Figure 5 for selectively labeled THE6 solute, the same values of E'_{tg}, ΔE_0, and $\tilde{w}/\tilde{W}$ were used as for the fully deuteriated solute (i.e., the simulations in Figure 7), but the value of $\tilde{W}$ at each temperature was determined by requiring that the calculated aromatic splitting coincide with the experimental one. This $\tilde{W}$ value was then used to calculate the α-deuteron splitting at each respective temperature. The so calculated α-deuteron splittings (dotted line) are shown together with the experimental ones (open circles) in Figure 5. We note a small but systematic deviation from the experimental splittings. This is probably due to the effective character of the conformational parameters E'_{tg} and ΔE_0 and to the neglect of deviations from the planar hexagonal core geometry, i.e., no averaging of the C_{ar}–D bond's orientation over fluxional modes within the triphenylene core.

The consistent reproduction of the segmental order profiles and the temperature dependence of ordering in the THE*n* solutes in phase V using the chord model description and also the study of the factors that affect the ordering trend along the pendant chains suggests the following explanation for the qualitative differences between the spectral patterns in neat phases and discotic solutes in calamitic solvents (Figure 1): Consider first a neat calamitic phase. The core *l*-axis (Scheme I) and its pendant chain are aligned by excluded volume interactions with the rigid cores of the surrounding molecules toward the same direction, i.e., the nematic director. Since the pendant chain's contour for the calamitic mesogen extends essentially along the core *l*-axis, the ordering of the core of a calamitic cooperates with, and enhances, the ordering of the chain segments. As a result of chain flexibility (accessible conformational states), this *intramolecular* core–chain coupling is weakened by the increasing degrees of motional freedom of the more distant segments (for increasing *j* values). Hence, one gets the observed monotonic decrease (aside from small site-parity effects) of deuterium splittings on moving away from the calamitic core–chain junction toward the outer segments. The orientation mechanism in calamitics is also operative in the neat discotic columnar phases, only there, the ordering of both the discotic core and the pendant chains takes place in the plane normal to the discotic director.

For the present case of a discotic solute in a calamitic solvent, the solute chains are aligned along the director by the solvent molecules (uniaxial excluded volume interactions) while the plane of the solute core is aligned tangent to the director (Figure 2) so as to avoid intersections with the long axes of the solvent molecules. Such an arrangement, however, cannot simultaneously be favorable for the alignment of all six chains. For example, chains 1 and 4 in the orientation of the THE*n* shown in Figure 2 have their contours propagating along the director, while the contours of chains $m = 2, 3, 5$, and 6 are frustrated by the calamitic's mean field. In the case of chains 1 and 4, the ordering of the inner segments will be reinforced by the ordering of the discotic core and, similar to chains attached to calamitics, this reinforcement will be reduced for the outer segments (larger *j* values) due to chain flexibility. For the remaining (frustrated) chains, the ordering of the inner segments as a consequence of their proximity to the core (the tendency toward radial propagation of the contours of chains $m = 2, 3, 5$, and 6 in Figure 2) will be suppressed by the solvent's mean field, whereas for the outer segments of those chains, their flexibility provides the requisite motional freedom for a more favorable alignment of the outer portions of these contours along the director. On average, all THE*n* solute chains will sample both favorable and frustrated orientations in the calamitic solvent. As a consequence, the central portion of the chain appears to maintain a relatively high degree of ordering because it has both motional freedom and orientational coupling to the core. Accordingly, these central segments can receive intramolecular ordering enhancement from the core not only when the chain contour is favorably propagating along the director but also when the contour is frustrated as these segments are free enough to conform to the calamitic intermolecular excluded volume constraints.

V. Concluding Remarks

Quantifying the ordering of the alkyl chains in mesophases can provide a powerful window into a mesophase's orientational potential (potential of mean torque). In all cases reported to date (neat calamitic phases and neat columnar phases), the NMR studies of chain ordering have been dominated by the ordering of the mesogenic core. For the THE*n* solutes in a calamitic nematic solvent examined here, more subtle insights into the nature of the forces constituting the nematic mean field can become

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apparent by quantitatively modeling the effect of this field on the solute's radially disposed chains. This approach to characterizing the mean field is possible because of a delicate interplay between frustrated dispositions of the THE*n* chain contours (when the discotic core is optimally aligned) and their inherent flexibility. As can be seen from Figure 7, the theoretical reproduction of the experimental order parameter profiles is essentially exact within experimental error for all four THE*n* solutes. Hence, the chord model continues to faithfully represent the (dominant) excluded volume interactions operative in neat mesophases and in these mixtures of oblate and prolate mesogens. The picture of chain averaging that emerges from this unusual mixture of oblate solutes in the prolate mesogen solvent is one where the contour of the chain attached to the THE*n* solute must compromise the radial extension propagating from intramolecular (dihedral angle energetics and steric) interactions coming from the discotic core and those intermolecular (excluded volume) interactions emanating from the solvent. As a result of this frustration, the chains show maximum segmental orientational order for centrally located ($j \approx 3$ to $[n - 2]$) chain segments.

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