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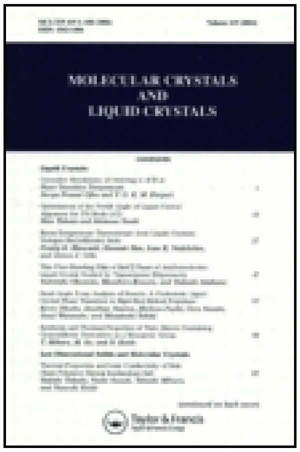

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D. J. Photinos [a]

[a] Department of Physics, University of Patra Patra Greece and Liquid Crystal Institute, Kent State University, Kent, Ohio, 44242, USA

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Determination of Alkyl Chain Orientational Order from Deuterium Magnetic Resonance Spectra of Liquid Crystals

D. J. PHOTINOS

Department of Physics, University of Patra, Patra Greece and Liquid Crystal Institute, Kent State University, Kent, Ohio 44242, USA

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The energies of interaction of alkyl chain segments with the nematic and smectic C medium are determined from analysis of the DMR spectra of 70BA, 80BA, and HOAB. The orientational order of the outer segments is found to result mainly from direct intermolecular interactions. A linear relation is obtained between the orientational and conformational energy of the chain.

INTRODUCTION

The orientational order of alkyl end chain segments of liquid crystal molecules can be understood as the combined result of the direct segmental interaction with the anistropic medium and of the coupling with the orientational order of the rigid molecular core through intramolecular interaction. Due to this coupling the orientational motion of the molecule becomes correlated to its conformational state. Accordingly, the segmental orientational order of the chain reflects the strength of core-medium, segment-medium, and segment-core interactions. This work is concerned with the determination of the characteristic energies of these interactions from DMR measurements in the nematic and smectic C phase.

Data[1-5] on 70BA, 80BA and HOAB are used for this analysis. The first two compounds are chosen because they have symmetric molecules and also because the spectra of the deuterated sites in the

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linkage group allow a direct determination of the order parameter of the aromatic core. HOAB is suitable for studying aromatic core asymmetry and internal rotations. Results of measurements on biaxial order parameters are also available for these compounds.

CALCULATION OF ORDER PARAMETERS

The orientational averages are calculated by the effective potential approach and by the correlation function approach. The effective potential used is basically of the form introduced by Emsley, Luckhurst, and Stockley[6]

$$V(\omega_1,\omega_2 . . . \omega_i . . .) \equiv V(\omega,n) = E_n + F^2_m \sum_i q^i Y^2_m(\omega_i) \qquad (1)$$

where ω_i denotes the orientation of the i^{th} molecular segment relative to the macroscopic frame, ω is the orientation of the molecular frame (taken to be rigidly attached to the aromatic core), n is the conformation index, E_n is the effective conformational energy, F^2_m are the components of the rank 2 mean field tensors, q^i are segmental coupling parameters and Y^2_m are the spherical harmonics. The i summation is over all molecular segments. Summation over the repeated tensor index m is implied.

In the mean field approximation, F^2_m is expressed in terms of the order parameters as follows,[7]

$$F^2_m = W \sum_i q^i \langle Y^{2*}_m(\omega)\rangle . \qquad (2)$$

Here, however, they are treated as parameters to be determined by fitting the data. For simplicity we consider only interactions of the aromatic core, with coupling q^a, and of the alkyl C—C bonds, with couplings q^c independently of their position on the chain.

In the correlation function approach, the single molecule probability distribution is written as

$$P(\omega,n) = f(\omega)h(n)(1 + g(\omega,n)) \qquad (3)$$

where

$$f(\omega) = \sum_n P(\omega,n) \qquad (4)$$

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is the orientational distribution function of the molecular frame, and

$$h(n) = e^{-\beta E_n} \Big/ \sum_n e^{-\beta E_n} \tag{5}$$

For $g(\omega,n)$ we use the leading terms in the expansion

$$g(\omega,n) = G(l,m,m';l_{\{i\}}m_{\{i\}})D^l_{mm'}(\omega)[\prod_i Y^l_{m_i}(\hat{\imath}_n) - \langle \prod_i Y^l_{m_i}(\hat{\imath}_n)\rangle] \tag{6}$$

Here $\hat{\imath}_n$ represents the orientation of the i segment relative to the molecular frame for a molecule in the n^{th} conformation and $D^l{}_{mm'}(\omega)$ are the rotation matrices. The coefficients G are treated as fitting parameters.

The results obtained by retaining just the $l = 2$, $l_{\{i\}} = 2$ term are essentially the same as those obtained with the effective potential of Eq. (1). For small values of $q^c F^2_m$ the two approaches are identical. Inclusion of correlation terms with $l > 2$ does not significantly affect the interaction energy values. This suggests that Eq. (1) gives a realistic description of the intermolecular interactions.

The conformational energy levels E_n are determined according to Flory's rotameric state model,[8] with two energy parameters $E_{g\pm g\mp}$ and with a four-bond interaction range. It is assumed that the geometry of all C—C and C—D bonds is tetrahedral and that the $g\pm$ states are obtained by ±120° rotations about the C—C bond. The angle COC_{ar} that specifies the direction of the chain relative to the core is also taken to be 120°.

In this simplified model the three quantities that essentially determine the orientational ordering of the flexible molecule are $F_{A(C)} \equiv (5/4\pi)^{1/2} q_{A(C)} F^2_o$ and E_g. The fields F_A, F_C represent the orientational energy of the core and of the chain segments respectively, and E_g is a measure of the rigidity of the molecule. These are the basic parameters used to fit the DMR data. The calculations show that the biaxial components of the field tensor and the conformational energy parameter $E_{g\pm g\mp}$ do not have significant effects on core-chain orientational correlation.

In the case of HOAB an additional energy parameter is required to account for internal rotations of the core and also a geometrical parameter to describe the inequivalence of the end chains. The latter is chosen to be the angle between the directions of the two $O—C_{ar}$ bonds in the extended molecular conformation. The value of 10° is used for this angle.

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The assignments of splittings used for the 70BA and 80BA spectra are $\Delta\nu_1 > \Delta\nu_2 > \Delta\nu_4 > \Delta\nu_3 > \Delta\nu_5 \geqq \Delta\nu_6 > \Delta\nu_7$. The assignment for HOBA is that of ref. (5).

RESULTS AND DISCUSSION

Calculations were performed by specifying a value of F_C and determining the values of F_A and E_g that produce the best fit to the data. The quality of the fits, expressed as the percent rms value of the difference between calculated and measured methylene splittings, improves continuously as F_C is increased from 0 to some optimum value $\bar{F}_C$. The fit quality at $F_C = 0$ is about 8 ~ 10% and becomes 2% or better near $\bar{F}_C$. It is, however, relatively insensitive to variations of F_C about its optimum value. The fits of methyl group splittings are much less accurate (~20%).

The values of $\bar{F}_C/kT$ found for 70BA (80BA) are .60(.47) near $T_{\mathrm{N-I}}$ and drop from .56(.43) to .44(.35) across the N—S_C phase transition. The corresponding optimum values $\bar{E}_g$ are nearly temperature independent with values (in kJ/mole) of 3.9(4.8) in the nematic and 4.3(5.4) in the S_C phase.

The substantially different values $\bar{F}_C$ and $\bar{E}_g$ in the two compounds indicate that these quantities depend on chain length. According to the mean field prediction of Eq. (2) F_C depends on chain length and exhibits an even-odd effect. The small drop of E_g across the N—S_C phase transition suggests that the conformation mechanism is basically the same in the two phases. The values of $\bar{E}_g$ and $\bar{F}_C/kT$ are in agreement with results of analogous calculations of 8CB.[6,9]

The optimum ratios of q_c/q_a are slightly larger in 70BA (~.24) than in 80BA (~.21). They show considerable temperature dependence, which is partly due to their sensitivity in variations of F_C. Because of the uniaxiality assumed for the core, the molecular order parameter $S_{zz}^{xx} - S_{zz}^{yy}$ vanishes at $F_C = 0$ and grows up to $-.08$ near $\bar{F}_C$. Estimates of the biaxial segmental order parameters using Eq. (2) suggest that the observation of significant biaxial order[2] only in the methyl group of 70BA is consistent with $S_{yz}^{yz} \sim .03$ and much smaller values for all the other biaxial order parameters.

The spectra of the nematic phase of HOAB can be reproduced to comparable accuracy and with basically the same values for F_o^C and E_g as for 70BA, using a planar model for the core whereby in addition to the extended conformation, the molecule can assume conforma-

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tions obtained by 180° flips about the N-phenyl bonds.[10] The total probability of such flips is ~.2. The S_C data of HOAB can be reproduced accurately enough by assuming a rigid core.

A measure of the effects produced on the segmental order parameters by the conformation dependence of the molecular orientational order is provided by the correlation factors

$$C_i = -\frac{\langle D^2_{om}(\omega)\rangle\langle Y^2_m(\hat{\imath}_n)\rangle}{\langle Y^2_0(\omega_i)\rangle} + 1. \qquad (7)$$

For $F_C = 0$ the correlation factors of all chain segments vanish, since according to Eq. (1) correlations are produced entirely by F_C. These factors increase very rapidly with F_C and at $\tilde{F}_C$ their values are as high as .4 for the innermost segments and nearly 1 for the outermost. Calculations performed with E_g varying along the chain give somewhat smaller values for C_i but the spectra of the outer 2 or 3 segments of the chain appear to be always dominated by their direct interaction with the anisotropic medium.

The study of conformational correlations in the orientational order reveals a particularly simple linear relation between the E_g and F_C of the form

$$\frac{F_c}{Z_1} + \frac{E_g}{Z_2} = kT \qquad (8)$$

with Z_1, Z_2 temperature independent parameters. Z_1 is independent of chain length but shows a small change across the N—S_C phase transition and Z_2 depends on chain length. It is found that $Z_1 \approx 1$ in the nematic and $Z_1 \approx .9$ in the smectic phase and $Z_2 \approx 2.75$ for 7OBA and HOAB and $Z_2 \approx 2.85$ for 8OBA, Eq. (8) reproduces fairly accurately the dependence of E_g and F_C at all temperatures and nearly in the entire range from $F_C = 0$ to $\tilde{F}_C$. This relation basically reflects the fact that the anisotropy of the medium and the effective part of the conformational energy are produced by the same intermolecular interaction.

A detailed exposition of the results on the temperature dependence of the energy parameters and the theoretical implications of Eq. (8) are given in a forthcoming publication.

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