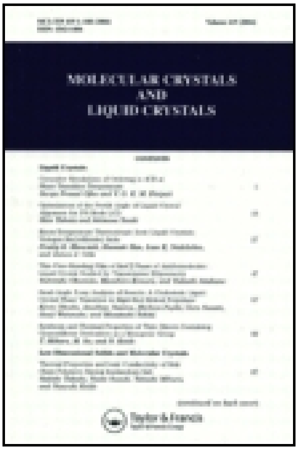

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Anisotropic Translational Diffusion of Methane in N-(4-n-pentyloxybenzyl dene)-4-n-hexylaniline (50.6)

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Anisotropic Translational Diffusion of Methane in N-(4-n-pentyloxybenzylidene)-4-n-hexylaniline (50.6)

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The temperature dependence of the translational diffusion coefficients is reported for methane dissolved in the thermotropic liquid crystal N-(4-n-pentyloxybenzylidene)-4-n-hexylaniline (50.6). The general features of methane diffusion behavior in the N, S_A and crystal S_B phases of 50.6 are quite similar, with respect to the magnitude of the rates and corresponding anisotropies, to those found in the homolog 40.6. The mutual characteristics are: that considerable smectic character ($D_\parallel < D_\perp$) exists in the nematic phase, that $D_\parallel \ll D_\perp$ with $E_\parallel \gg E_\perp$ in the S_A phase because of increasing layer definition and of methane expulsion from the cores to the chains and that $D_\perp/D_\parallel \sim 30$ (with $E_\parallel \sim E_\perp$) in the crystalline S_B phase. Methane behavior in the S_F phase of 50.6 is very unusual, showing a slight decrease in $D_\perp$ and large increases in $D_\parallel$ upon decreasing temperature with $D_\perp/D_\parallel$ values of from 10 to 5. This is possibly the result of the decrease in the close-packed core thickness coupled to increase in the disorder (loss of 3-d correlation) within the layer in the S_F phase. The diffusion behavior in the S_G phase is similar to that found in the S_B phase. The factor of three larger $D_\parallel$ values in S_G over S_B is thought to be the result of persistance of disordered regions remaining from the S_F phase.

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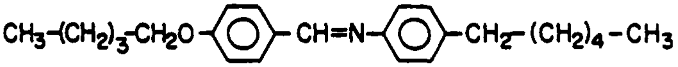
INTRODUCTION

Of the many homologs belonging to the alkoxybenzylidene- alkylaniline family of liquid crystalline compounds (the n0.m series),[1,2] the homolog 50.6



has been of perhaps the greatest interest[3-6] in that it displays a variety of liquid crystalline phases: nematic and five smectic phases A, C, B, F and G. Much interest has been centered on the occurance of the recently-identified[3] smectic F (S_F) phase, which was found to possess a lower 2-dimensional order between two smectic phases, S_B and S_G of higher 3-dimensional order.[3,5] Although the S_F phase has been identified as such, not much is actually known about the molecular order and distribution within the phase.

This communication reports measurements of the translational diffusion of methane (CH_4), dissolved in 50.6, along and perpendicular to the liquid crystal molecular director, by the pulsed magnetic field gradient spin echo NMR technique. In previous studies,[7-8] methane has proven to be a suitable solute probe in liquid crystals; it is small, yet sensitive to the different chemical environments within the phase and is essentially non-perturbing to the phase, in that no appreciable phase transition temperature depressions are observed (at typical pressures of 8–15 atmospheres). Much concerning the nature of a phase can be deduced from the diffusion behavior of a suitable probe. In the N, S_A and S_B phases of a close homolog, 40.6, methane diffusion behavior was phase-dependent.[7] It was deduced that in the N phase of 40.6 there was a sizeable presence of pretransitional smectic order. The layer-like smectic order was found to greatly impede diffusion along the director, $D_\parallel$, while promoting transverse diffusion $D_\perp$, to a degree strongly dependent on the ordered arrangement of the liquid crystal molecules within the lamellar layer. Typical anisotropies were of the order of $D_\perp/D_\parallel = 30$ in the S_B phase. As the ordering of the smectic layering increases in the S_A phase, methane is expelled from the close-packed polar aromatic cores into the more flexible non-polar aliphatic chains between the layers. Methane (CH_4) proton dipolar and CH_3D deuterium quadrupolar splittings were very helpful in formulating the above model of methane behavior in nematic and smectic phases. Similar measurements were also used in the present study to complement the information derived from the diffusion measurements.

EXPERIMENTAL

Methane and dideuteromethane (CH_2D_2) were purchased from Merck. The compound 50.6 was synthesized in a similar manner described in Ref. 9, from the condensation of n-pentyloxybenzaldehyde and n-hexylaniline in absolute ethanol. The crystals were washed repeatedly and recrystallized five times from absolute ethanol. The phase transition temperatures of the purified 50.6 were then determined from thermal microscopy measurements made with the sample on a clean glass slide covered with a glass slip in a Bausch and Lomb polarizing microscope equipped with a Mettler FP52 microfurnace and the Mettler FP5 temperature control unit. All six liquid crystalline phases were observed, with characteristic focal, broken and checkered fan textures that were very similar to the texture photographs of 50.6 in the literature.[2,3,10] At the S_B-S_F transition, the checkered texture was only faintly seen, which later annealed at the S_G transition temperature. The observed transition temperatures (°C) were as follows:

$$\begin{array}{ccccccccccccc} \mathrm{I} & - & N & - & S_A & - & S_C & - & S_B & - & S_F & - & S_G \\ & 72.7 & & 60.6 & & 51.9 & & 50.3 & & 41.8 & & 38.5 & \end{array}$$

and are very close to previously published values.[1-6,11-12]

The lineshape and diffusion measurements were made in the same manner as those described earlier.[7] Separate samples of CH_4 and CH_2D_2 (8 atm) were prepared as before. In the lineshape studies, the proton and deuterium spectra of CH_2D_2 observed in the different phases of 50.6 appeared as relatively broad doublets, without fine structure.[14]

RESULTS AND DISCUSSION

Arrhenius plots of the translational diffusion coefficients, $D_\parallel$ and $D_\perp$, of methane in 50.6 are shown in Figure 1. Within the accuracy of the NMR temperature controller (±1°C), the phase transition temperatures observed in the CH_4-50.6 and CH_2D_2-50.6 samples were identical to those obtained from the thermal microscopy experiments.

For methane dissolved in liquid crystals[7] exhibiting only nematic phases, such as p-heptylcyanobiphenyl (7CB), p-methoxybenzylidene-p-butylaniline (MBBA) and the alkyl azoxybenzene mixture (Merck Licrystal Phase 5), it is observed that $D_\parallel > D_\perp$, in that translation of methane through the phase is less hindered parallel to the direction of the liquid crystalline long axes (the director) than perpendicular to it. However, methane diffusion in the N phases of the liquid crystals 40.6 and p-

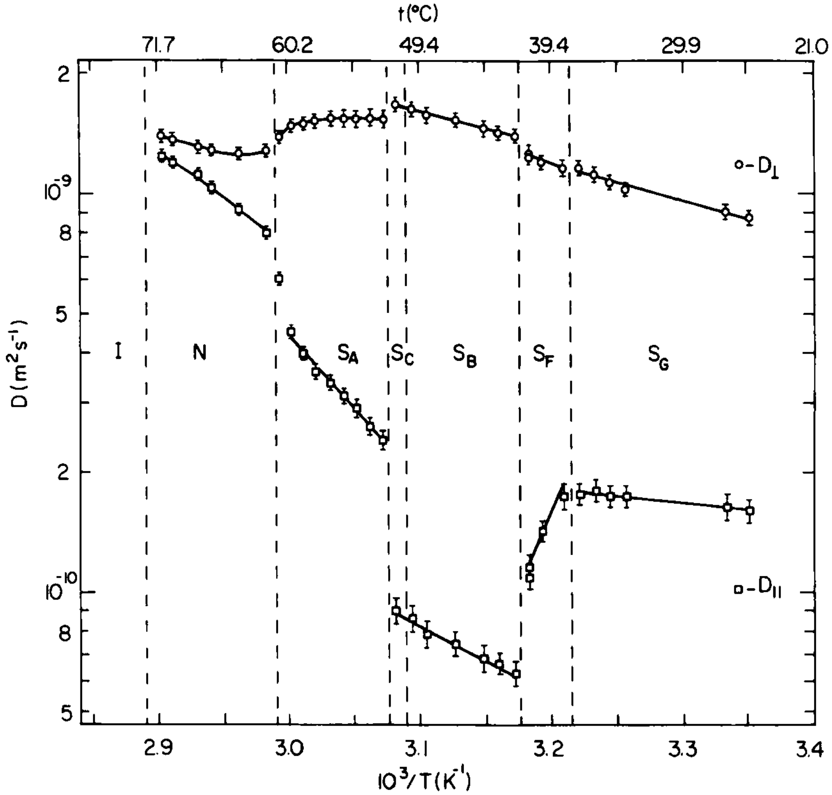


FIGURE 1 Arrhenius plots of methane diffusion in 50.6. The diffusion coefficients parallel and perpendicular to the director are denoted as $D_{\|}$ (squares) and $D_{\perp}$ (circles) respectively. The phase transition temperatures are indicated by the vertical broken lines. The lines drawn through the experimental points are only to aid the eye.

octylcyanobiphenyl (8CB), both having smectic phases below the nematic phase, is such that $D_{\|} < D_{\perp}$. The conclusion drawn is that local smectic order exists far into the nematic phase of these compounds. The methane diffusion rates in the N phases of 50.6 and 40.6 are of the same magnitude with a larger activation energy in 50.6. The N-S_A phase transition in 50.6 has a larger effect on the diffusion rates than in 40.6 and may be related to the 40% larger transition enthalpies and entropies in 50.6.[2-3,11-12] The more energetic transition in 50.6 may explain what seems to be more sudden methane expulsion effect in 50.6 than in 40.6. The proton dipolar and deuterium quadrupolar splitting of CH_2D_2 in the N and S_A phases of 50.6 are shown in Figure 2 and Figure 3 respectively. The behavior is very similar to that found in 40.6 and strengthens the conviction that methane

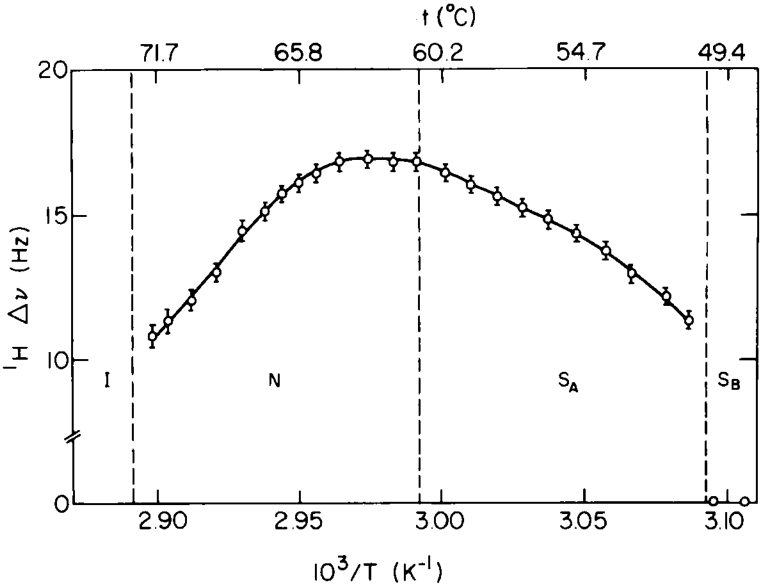


FIGURE 2 Temperature dependence of the proton splittings, ^{1}HΔν, of CH_2D_2 in the *N* and S_A phases of 50.6. The splitting is defined as the frequency difference in Hz between the signals in the 1:1 doublet (see text).

is indeed being sterically expelled from the polar cores to the non-polar chain ends. Longitudinal methane diffusion in the S_A phase of 50.6 is characteristic of that found for a variety of small probes in this phase with large diffusional activation energies on the order of 20-30 kcal/mole.[15] For methane, this is probably a consequence of the increasing definition of the layer structure with decreasing temperature and the increasing concentration of methane in the chain end region where transverse diffusion is much faster than the longitudinal diffusion.

Because the S_C range in 50.6 is so short and the transition energies for the nearby S_C–S_B transition are so large, it is certain that the large decrease in $D_\parallel$ around 51°C is due to the onset of the S_B phase and not to the S_C phase. Although the broken fan texture of the S_C phase is clearly visible in the microscopy measurements, no specific S_C effects on the diffusion rates could be attributed to the S_C layer tilting but rather is masked by the dramatic effects from the S_B phase. Longitudinal diffusion in the crystal[16] S_B phase of 50.6 is very slow and is most likely a permeation process; the low diffusion rates through the aromatic core sheet are a function of the crystal-like orientational order of the 3-dimensional molecular close-packing within the layer of cores where the molecular centers of mass are

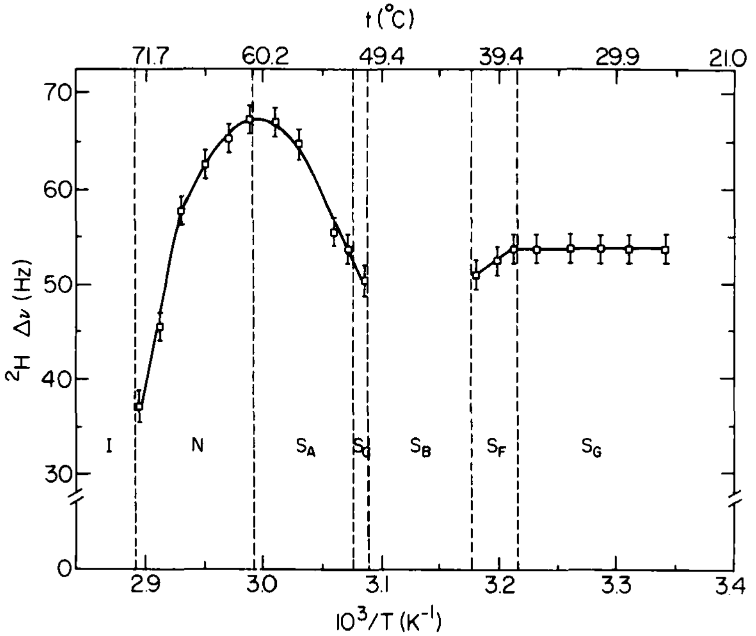


FIGURE 3 Temperature dependence of the deuterium splitting, ${}^2H\Delta\nu$, in CH_2D_2 in 50.6, where the splitting is the frequency difference in Hz between the signals in the 1:1 doublet (see text). The splitting in the S_B phase was less than the line broadening (10-15 Hz).

highly aligned. The abrupt decrease of $D_{\parallel}$ is a consequence of the strongly first-order S_A–S_B transition. This is also apparent in the collapse of the CH_2D_2 proton dipolar and deuterium quadrupolar splittings at the transition (Figures 2 and 3). Any quadrupolar splittings present in the S_B phase were less than the 10-15 Hz line broadening factor used. In the S_B phase then, the methane molecules are most likely concentrated in the extreme chain end region, experience very little orientational order and translate almost exclusively between the layers, in a liquid-like environment.

As mentioned earlier, among the n0.m's, 50.6 is unique in the formation of a new smectic phase in between a S_B and S_G phase. This S_F phase, identified from diffraction and miscibility experiments has been described by a lack of 3-dimensional long-range order (no correlation of molecular arrangement within the lamellar layer), a slight layer tilt (24°) and the presence of both considerable regions of disorder and extensive layer dislocation.[3,5] Although the S_B–S_F transition enthalpy and entropy is quite small,[2-3] the effect on the diffusion of methane is very pronounced and is indicative of a first-order transition. From Figure 1, this is seen as a significant decrease in $D_\perp$ together with an abrupt doubling in the magnitude of $D_\parallel$. This behavior can be interpreted as a sudden "breaking-up" of the crystalline S_B ordered layer structure in such a way that the clearly-defined layering is changed to one which now slightly impedes transverse diffusion with significantly faster longitudinal diffusion. The sudden reappearance of the quadrupolar splittings in the S_F phase (Figure 3) indicates that methane is being ordered to a similar degree as that observed in the S_A phase, which is possible only if methane is found near or within the more rigid aromatic center of the layers. The picture of relatively fast methane diffusion through and presence of methane among the aromatic cores is reasoned to be due to the loss of positional correlation within the layers as the three-dimensional crystal S_B order decays to two-dimensional order in the S_F phase.[17]

Another interesting aspect of methane behavior in the S_F phase is the continued increase in $D_\parallel$ with decreasing temperature, implying in view of the above picture, an increase in the layer disorder as the phase is cooled. A possible interpretation of the behavior in the S_F phase concerns the reported decrease in the layer thickness from 27Å to 24Å at the $S_B - S_F$ transition.[4] Assuming the $D_\parallel$ process in the S_B phase is one of permeation of methane (with a diameter of 3.5Å) through "holes" in the S_B crystal lattice of roughly 5Å in diameter and 27Å in length,[4] then at the $S_B - S_F$ transition a decrease in the hole "length" coupled with randomly larger hole diameters (as the lattice is destroyed) would tend to allow methane a faster permeation rate and access to the more-ordered aromatic centers. Further, the layer thickness in the S_F phase decreases slightly with decreasing temperature,[4] which may help explain the increase in $D_\parallel$ as the temperature is lowered.

The trend of increasing $D_\parallel$ with decreasing temperature in the S_F phase ceases at the $S_F - S_G$ transition, which is possibly a consequence of the reappearance of 3-d order of hexagonal packing in the S_G cores.[3,5]

The fact that $D_\parallel$ in the S_G phase is considerably faster than in the S_B phase and that the quadrupolar splittings in the S_G phase are larger implies that, the layer definition and molecular packing order within the smectic layers is not as great as in the S_F phase. Strong diffuse X-ray diffraction observed in the 50.6 S_G phase indicates considerable disorder in this phase.[3,5] The relative loss of order in 50.6 upon going from S_B to S_G is apparent from simple visible inspection of the S_B, S_F and S_G phases as the sample is cooled in the magnetic field. While the S_B phase is clear and glass-like to the eye, there is a considerable amount of light-scattering and visible striations in the S_G phase, which persist indefinately, if the sample is left undisturbed.

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