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NMR studies of a *D*-phase compound

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Proton NMR spectra and relaxation times (T_1s) at 60 MHz were obtained for the thermotropic compound 4′-*n*-hexadecyloxy-3′-nitro-biphenylcarboxylic acid, which, upon heating, has the sequence of phases: crystal→S_C→D (or smectic-D)→S_A→isotropic. The spectrum narrows over two orders of magnitude upon heating into the D phase, then broadens again in the S_A phase. The spectrum in the D phase is composed of a number of chemical shift peaks, the same as in the isotropic phase, except that the carboxylic acid peak is shifted further downfield in the D phase, evidence of intermolecular hydrogen bonding. In the smectic phases S_C and S_A the spectrum is super-Lorentzian with a width of around 2 kHz, considerably narrowed compared with the 36-kHz-wide spectrum of the solid. The relaxation times increase smoothly from 0.35 s at 124 °C to 0.73 s at 194 °C in the S_C and S_A phases. In the D phase, individual peaks have T_1s ranging from 0.18 to 1.1 s, with weighted averages agreeing with the trend of the data from the S_C and S_A phases. Measurements of spin echoes in the D phase without and with a field gradient gave values of about 50 ms for T_2 and 3×10^{-11} m^2/s for the diffusion coefficient. The data indicate that, in the D phase, the molecules sample enough orientations on the time scale of the NMR experiments to average out the dipolar couplings left after the motional narrowing that takes place in the S_C and S_A phases. This is accomplished by diffusion of molecules through regions having different directors.

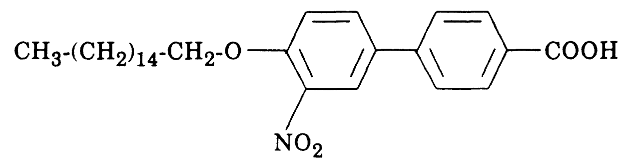
I. INTRODUCTION

The compound, 4′−*n*-hexadecyloxy-3′-nitro-biphenylcarboxylic acid (NHDBCA), first synthesized and studied by Gray and co-workers in 1957, is one of four similar compounds that have the optically isotropic D phase, also referred to as the smectic-D or S_D phase.[1−10] Recently, other optically isotropic phases have been observed in thermotropic liquid crystals.[11,12] Similar phases are found in lyotropic systems.[13,14] The x-ray scattering studies performed on the D phase have not yet given a complete picture of the molecular arrangement, but apparently the molecules form dimers about 7 nm in length that aggregate into micellarlike structures which are arranged into a cubic pattern having a lattice parameter of 7–10 nm.[4,5,7,9] The D phase may be the thermotropic equivalent of the viscous isotropic phase observed in lyotropic liquid crystals.[5] In NHDBCA, the D phase lies between two birefringent phases identified as S_C and S_A.[2] The S_A phase is only a few degrees wide. Supercooling of the transitions has been observed, as well as a metastable S_4 phase.[6,7] A tilt angle of 47° was measured in the S_C phase below the D phase in another compound.[9] NHDBCA decarboxylates at higher temperatures, increasing the difficulty of studying it. In this paper, we would like to report our preliminary observations of proton NMR spectra and relaxation times for this compound over the temperature range 125 to 195 °C and the diffusion coefficient measured at 181 °C in the D phase. These data are quite similar to that observed in cubic lyotropics.[15−19]

II. EXPERIMENTAL

The compound was synthesized at the Liquid Crystal Institute using the method described by Gray, Jones, and Marson[1] and recrystallized twice from absolute ethanol. The molecular formula and phase-transition temperatures observed by microscopy on heating at 2 °C/min are given in Fig. 1. The S_C-D transition was observed at temperatures as low as 170 °C in the NMR samples. Four samples were used in the NMR measurements. Sample 1 was evacuated for several hours at 90 °C and cycled several times through the crystal-S_C transition before sealing under a vacuum. Sample 2 was packed and sealed under nitrogen gas. Samples 3 and 4 were evacuated several hours at room temperature and sealed under vacuum. The spin-lattice relaxation measurements and some spectra were taken on samples 1 and 2. Samples 3 and 4 were used at Southeastern Massachusetts University (SMU) for T_2 and diffusion coefficient measurements and for better-resolved spectra.

When first heated in the NMR probe, sample 1 entered the D phase at 175 °C. It was then cooled to room tem-



$$\text{crystal} \xrightarrow{123^\circ\text{C}} S_C \xrightarrow{179^\circ\text{C}} D \xrightarrow{192^\circ\text{C}} S_A \xrightarrow{195^\circ\text{C}} I$$

FIG. 1. Molecular formula of NHDBCA and the sequence of phases upon heating.

perature. When reheated and studied the next day it did not transform into the D phase until 181 °C. When this process was repeated a third time, no D phase formed at all. Microscopic observations of a thin sample placed under a cover slip did not show such rapid deterioration. When the sample was heated and held in the isotropic phase, small regions formed in which the D phase was not observed and which looked slightly orange. These regions slowly grew from small nuclei. However, when the cover slip was removed before heating, the sample flowed as it reached the isotropic phase, forming drops and rapidly spreading the altered material uniformly throughout. The D phase was subsequently lost, as was eventually the case for the NMR samples.

Sample 2 entered the D phase at 170 °C and was slowly heated to the isotropic phase at 196 °C while taking relaxation data over several hours. Upon cooling it did not enter the D phase. Subsequent reheating from room temperature did not produce the D phase.

Sample 3 also entered the D phase at 170 °C and did reenter the D phase after cooling from the I through the S_A phase, probably because this process was carried out without a long time spent at high temperatures.

Most NMR measurements were performed at the U.S. Naval Research Laboratory (NRL), using a 60-MHz solid-state spectrometer rebuilt from a Bruker SXP with a Varian HO12A 12-in. magnet. The instrument is controlled by a Nicolet 293B pulse generator programmed with a Nicolet 1180 computer utilizing the GENT-1180 software from General Electric. Spectral and relaxation time measurements were performed with the GENT-1180 software. For the relaxation measurements, a π-τ-$\pi/2$ sequence was used. The sample temperature was regulated using a Bruker B-ST100/700 temperature controller and measured by lowering a thermocouple to the level of the sample either in a very thin glass tube immersed in the liquid crystal or between the sample tube and another, larger, concentric tube. The variation in temperature across the sample is estimated to be 1 °C. The statistical uncertainties in the fits to T_1 were typically 2% and range up to roughly 10% for the COOH proton T_1 in the D and isotropic phases.

Measurements were also made at 60 MHz at SMU using an NMR solid-state spectrometer consisting of the magnet and temperature controller from a JEOL C-60HL spectrometer, a Nicolet 1180E data acquisition system, an Arenberg PG-650 transmitter, and home-built radio-frequency gates, pulse generators, probe, and receiver. Spectra were taken again in the solid, S_C, and D phases. A simple spin-echo sequence ($\pi/2$-τ-π-echo) with and without a field gradient was used to get T_2 and the diffusion coefficient. The values of D were obtained from the slopes of plots of log (echo) versus $I^2\tau^3$, where I was the current in the gradient coils.[20] The coils were calibrated using a water sample at 24.5 °C and assuming $D = 2.24 \times 10^{-11}$ m^2/s.[21] This procedure was applied to an evacuated sample of glycerol and yielded a value of $D = 1.8 \pm 10^{-12}$ m^2/s, about 14% lower than the published value.[22] Unless otherwise stated, the data plotted in this manner fell on straight lines. These T_2 and D values are only preliminary measurements. The temperature varied by as much as 3 °C across the sample in this apparatus. In addition to the NMR measurements, microscopic observations were made at SMU with the aid of a home-built temperature controller and oven.

III. RESULTS

A. Spectra

NMR spectra typical of the solid, smectic, D, and isotropic phases are shown in Figs. 2–4. A unique feature of this compound is the dramatic narrowing of the spectrum by roughly two orders of magnitude when heated into the D phase, followed by a broadening and second narrowing as it is heated further through the S_A phase

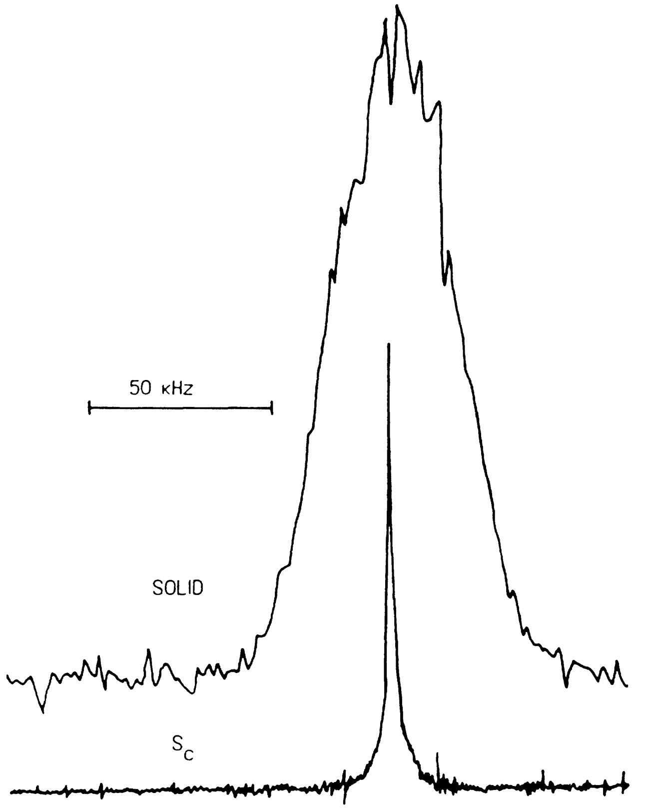


FIG. 2. Proton NMR spectra of NHDBCA in the solid and S_C phases.

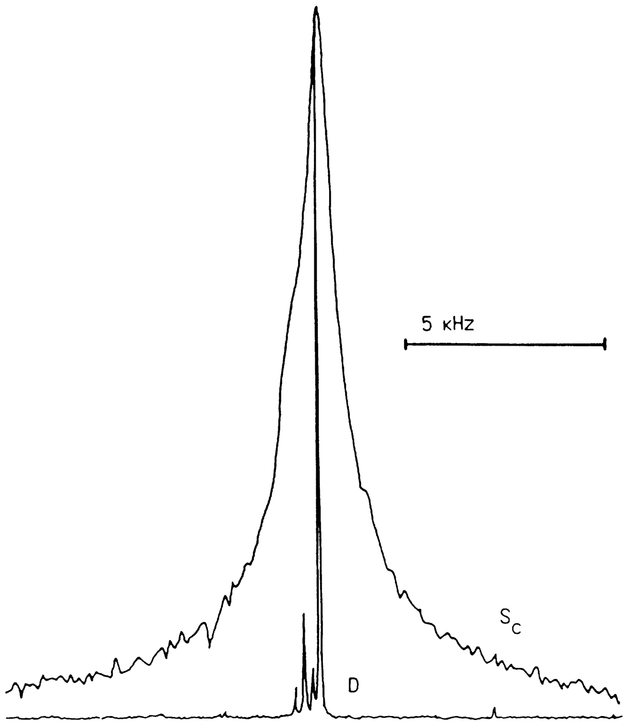


FIG. 3. Proton NMR spectra of NHDBCA in the S_C and D phases. The horizontal scale is expanded compared to Fig. 2. The spectrum in the S_A phase is essentially the same as the S_C spectrum shown here.

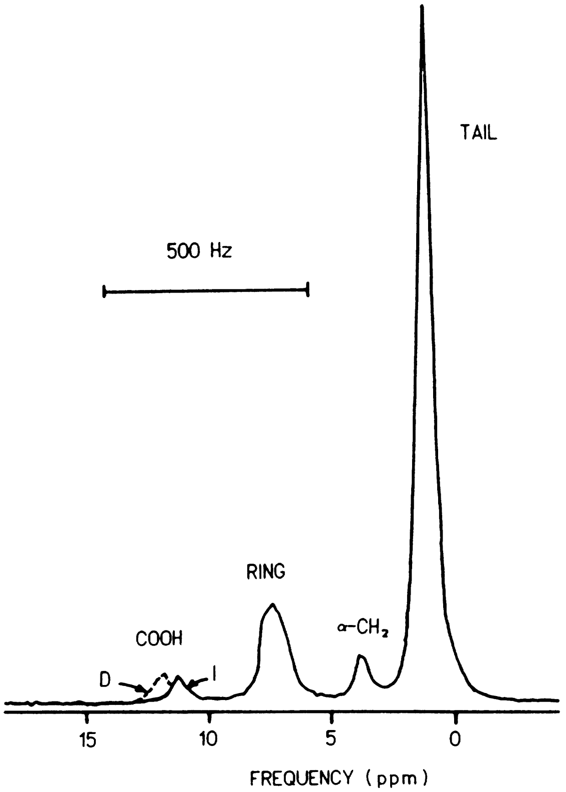


FIG. 4. Proton NMR spectra of NHDBCA in the D and isotropic phases. The horizontal scale has been expanded again. The two spectra are identical except for a shift in the COOH peak at the left, which is further to the left (downfield) in the D phase.

into the isotropic phase. The spectra had the same general appearance in both the S_C and S_A phases, a super-Lorentzian[15] several kHz full width at half maximum (FWHM) with a slight asymmetry that is probably due to chemical shifts. The spectra narrowed gradually as the temperature was increased. No change in the NMR signal was observed when a sample, cooled in the magnet from the isotropic phase to the smectic-*A* phase, was rotated by 90°, indicating a lack of alignment of the sample directors. The spectrum in the *D* phase was the same as the chemical shift pattern observed in the isotropic phase except that one of the peaks was shifted almost 1 ppm further downfield in the *D* phase. The narrowest lines were about 30 Hz FWHM in both the *D* and isotropic phases, possibly the resolution of our instrument (the samples were not spun). Four peaks were observed, for which we make the following identification, judging from their positions and areas on these spectra and from the high-resolution spectrum of NHDBCA and the methoxy precursor dissolved in dimethyl sulfoxide.

(1) The largest peak is due to the 31 methyl and methylene protons attached to the last 15 of the carbons on the chain. We have taken this peak to be centered at 1 ppm.

(2) The small peak at about 4 ppm is due to the a-CH_2 protons.

(3) The wide line at 6.5–8 ppm is due to the seven protons on the aromatic rings.

(4) The remaining small peak at 11–12 ppm is due to the carboxylic acid proton and is further downfield in the *D* phase than in the isotropic phase.

B. Spin-lattice relaxation rates

An Arrhenius plot of the spin-lattice relaxation rates is given in Fig. 5. In the smectic phases, the relaxation data (amplitude versus τ) follow single exponentials and give identical rates using any part of the spectra or free-induction decays (FID's). This was not true below the crystal-S_C transition. For the isotropic and *D* phases, the relaxation rates were determined separately for each peak. The α-CH_2 peak could not be resolved in most of these relaxation experiments. However, measurements at 181 °C are consistent with a value of around 2 s^{-1} for this peak.

Average relaxation rates were also calculated from the data in the *D* and isotropic phases by using the initial amplitudes of the FID's. For small values of the delay between pulses, this method yields the same value as the weighted average computed according to the formula

$$R_{\text{ave}} = \frac{(31R_{\text{tail}} + 2R_{\alpha} + 7R_{\text{ring}} + 1R_{\text{acid}})}{41} \ . \tag{1}$$

As seen in Fig. 5, these average values fall on the fit to the data in the S_C and S_A phases. This agreement shows that the motions responsible for T_1 at 60 MHz are insensitive to the differences between the S_C, S_A, D, and isotropic phases. The single-exponential character of the spin-lattice relaxation in the S_C and S_A phases is due to spin diffusion.[18] The dipolar couplings that give rise to the spin diffusion and to the wider spectra of the S_C and

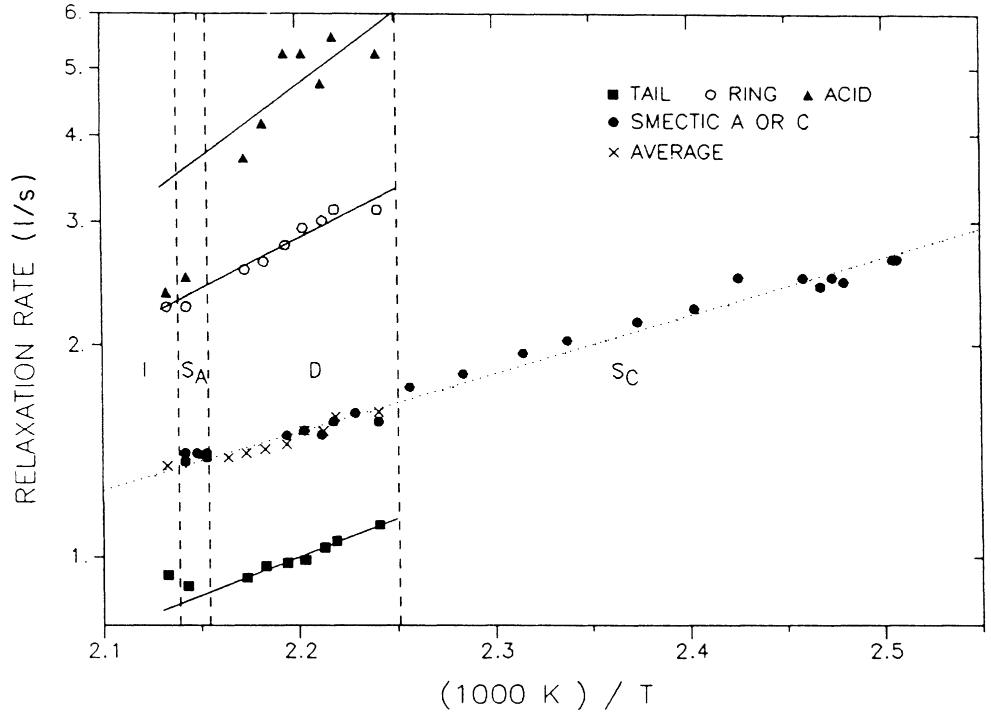


FIG. 5. Spin-lattice relaxation rates ($1/T_1$) vs inverse temperature for NHDBCA in the temperature range 125 to 196 °C. The dotted line indicates the trend of the data in the S_C and S_A phases. It corresponds to an activation energy of 3.7 kcal/mol. In the isotropic and *D* phases, T_1 values are plotted separately for the lines in the spectrum due to protons on the tail (■), in the rings (○), the COOH group (△), and the average (×). In the *D*-phase region, values are also given for data taken when the sample was in a smectic phase (●). The solid lines represent fits to the data in the *D* phase.

S_A phases are removed in the *D* and isotropic phases.

Four least-squares fits of the data to the form

$$R - R_0 \exp(E_A/kT) \qquad (2)$$

are shown in Fig. 5. The three solid lines are fits to the rates for the tail, ring, and acid protons in the *D* phase and correspond to activation energies of 4.9, 6.6, and 9.7 kcal/mol, respectively. The dotted line is a fit to the rates for samples in the S_C and S_A phases (solid circles). It corresponds to an activation energy of 3.7 kcal/mol. Measurements taken during the third heating of sample 1 gave values that are not shown on the graph. These measurements, taken over the temperature range 170 to 195 °C, parallel the data taken using fresher samples, lying about 5% below the data shown in the region corresponding to the *D* phase in a fresh sample. The data from the second heating of this sample (S_C to *D* transition around 180 °C) are included on the figure and appear as the solid circles in the *D*-phase region.

C. T_2 and *D*

As the observed linewidths in the *D* and isotropic phases were thought to be due to the magnet inhomogeneity, a simple $\pi/2$-τ-π-echo sequence was used to determine a value for T_2 in the *D* phase at 181 °C. The plot of the log of echo height versus 2τ curved upward with an initial relaxation time of ~50 ms and a value of about 80 ms at longer times. Assuming two exponents gave roughly 80 ms for the larger fraction (~60%) and 25 ms for the faster decay. Due to the poor quality of these data, only the fit to a single exponential will be used, giving a rough value of $T_2 = 53$ ms, which corresponds to a Lorentzian having a FWHM of $1/\pi T_2 = 6$ Hz. The longer relaxation time of 80 ms, corresponding to a FWHM of 4 Hz, may be a better value for the case of the methyl and methylene protons. The diffusion coefficient measured in the *D* phase in sample 3 at 186 °C was $2.8 \pm 0.3 \times 10^{-11}$ m^2 using $\tau = 80$ and 100 ms. The same measurement on sample 4 at 181 °C gave $3.1 \pm 0.4 \times 10^{-11}$ m^2/s. Attempts were made to obtain a value for *D* in the isotropic phase with poor results due to sample decomposition and poor temperature homogeneity. Sample 3 gave curved plots, showing a large range in diffusivity in the sample. At 205 °C the average value of *D*, taken from the slope of the graph at small values of $I^2\tau^3$, was $38 \pm 4 \times 10^{-11}$ m^2/s with a range from 10 to 100×10^{-11} m^2/s. At 214 °C, the average value increased to $\sim 200 \times 10^{-11}$ m^2/s. When sample D was studied at 210 °C, it gave a relatively straight line with a much lower slope, corresponding to $D = 6.3 \pm 0.6 \times 10^{-11}$ m^2/s. This sample was soon after removed and was seen to have uneven composition and bubbles, probably due to decarboxylation.

IV. DISCUSSION

A. Comparisons with NMR studies of other systems

In many respects, these data show a great similarity to earlier studies of lyotropic systems which included cubic phases.[15–18] The changes in spectral width with temperature parallel the changes in width with water concentration in a two-component lyotropic system (dimethyldodecylamine oxide plus deuterium oxide) studied by Lawson and Flautt.[17] Even the orders of magnitude of linewidths are the same. The shapes of the NHDBCA proton spectra in the S_C and S_A phases are very similar to the super-Lorentzian observed in the neat and middle phases. In the notation of Lawson and Flautt (Ref. 17, p. 2068), the S_C spectrum of Fig. 3 has a ratio (width at $\frac{1}{8}$ maximum to width at $\frac{1}{2}$ maximum) $R\,(\frac{8}{2})=3.6$, as opposed to their observation of 6.6 in the neat phase and a value of 2.6 for a pure Lorentzian. The smooth variation of T_1 (or the weighted average in the D phase) with temperature, showing no abrupt change at the S_C to D transition, corresponds to the observation of Charvolin and Rigny[18] that T_1 values at high frequencies, e.g., 60 MHz, were the same for the cubic and lamellar phases at the same temperature. In both the S_C phase of NHDBCA and the lamellar phase studied by Charvolin and Rigny[18,23] the T_1 measurements show a single exponential, indicating spin diffusion.

An abrupt increase in proton NMR linewidth upon warming, such as we see at the D to S_A transition, was also seen in the plastic crystal 2-methyl-2-propanethiol[24] (MPT) at the phase transition from phase II to phase I. This increase was explained in terms of a "quenching" of self-diffusion at the transition. However, unlike the abrupt decrease in linewidth seen upon warming NHDBCA through the S_C to D transition, in MPT the linewidth gradually decreases from around 13 kHz at 160 K to 400 Hz at 201 K. After the abrupt increase to around 8.5 kHz at the phase transition, the linewidth in MPT again smoothly decreases. The smooth decreases in linewidth in MPT were consistent with an Arrhenius-type temperature dependence of D inside each phase.

The spectra of NHDBCA in the S_C and S_A phases differ considerably from those seen in aligned shorter-chain liquid crystals such as terephthal-*bis*-butylaniline *n*-heptyloxazoxybenzene and (HOAB).[25] The HOAB spectrum in the S_C phase, Fig. 9 of Wise, Smith, and Doane,[25] is somewhat the same shape, although it is much broader, especially at the base. This difference is probably due at least in part to the alkyl chains on NHDBCA being considerably longer than those on HOAB, giving rise to a relatively larger contribution to the spectrum from the protons on the disordered portion of the tail.[26–28] The HOAB sample in this case was initially aligned by cooling in the magnetic field then rotating 55°, giving a distribution of directors.

B. Rapid molecular motions ($<10^{-8}$ s)

When a substance melts into a relatively disordered smectic phase (such as S_C or S_A) from the solid, its molecules acquire a number of motions that can significantly narrow an NMR spectrum. Translational diffusion, rotations about the long molecular axes, rapid reorientations of the long molecular axes about the director, and internal conformational motions take place on a time scale fast enough ($<10^{-8}$ s) to reduce the dipole-dipole interactions that give rise to the proton NMR spectrum and relaxation.[29,30] Especially at temperatures above 100 °C, the intermolecular interactions are effectively reduced to negligible amounts while intramolecular interactions are partially averaged such that the interactions are proportional to P_2 (cosθ), where θ is the angle between a local director and the magnetic field.[18,19,29,30] At a transition such as S_C to S_A, these relatively rapid motions typically show no sudden changes.[30–32] It is these motions that modulate the dipole-dipole interactions at rates giving rise to the smooth variation in spin-lattice relaxation times for NHDBCA in the S_C, D and S_A phases. Cooperative modes of oscillation, effective in proton spin-lattice relaxation in high-temperature nematics[30] may also contribute here. Due to the large number of possible motions giving rise to the proton T_1's, little can be deduced from these data about rapid motions other than that they are about typical for liquid crystals.

The observations of different T_1 values for different parts of the molecule in the D phase may be evidence that T_1 is dominated by intramolecular interactions. That is, the dipole-dipole interactions between a proton on one molecule and protons on nearest neighbors would have similar strengths and correlation times for all the protons. If anything, due to the concentration of protons in the tail region, one would expect intermolecular interactions to produce smaller, not greater, T_1 values in that region compared to the ring. The high relaxation rates of the COOH proton are evidence of dimerization of these molecules. The hydrogen bonding of two molecules provides each COOH proton with at least one neighboring proton around 2.3 Å away.[33]

C. Slow molecular motions

The motional narrowing of the proton NMR spectrum upon heating into the D phase, along with the lack of a corresponding change in T_1 show that relatively slow motions take place in this phase that do not occur in the adjacent S_C and S_A phases. As was seen to be the case for the cubic phase of potassium laurate in water,[18] these slow motions are reorientations of the molecules caused by translational diffusion of the molecules through areas having different directors. Although diffusion would be expected to take place at similar rates in the S_C and S_A phases, it would not modulate the interaction as much since the director is fixed over relatively longer distances in those phases. Assuming that the spectra are narrowed from widths of 2 kHz to lines having $T_2 \sim 50$ ms implies a correlation time for isotropic molecular reorientations roughly given by[34]

$$t_c \sim \frac{(1/T_2)}{(\gamma H_d)^2} \sim [(0.050\ \mathrm{s})(2\pi \times 10^3_{\mathrm{s}}\ ^{-1})^2]^{-1} \sim 0.5\ \mu\mathrm{s}\ . \quad (3)$$

These slow reorientations of a molecule could be due to translational diffusion through regions of differing director inside the cubic unit cell. Using a translational diffusion coefficient of 3×10^{-11} m^2/s, the rms distance traveled by NHDBCA molecules in t_c is about $\sqrt{6Dt_c}$ or 9.5 nm. Thus, in time t_c, the molecules would be expected to sample a wide variety of orientations by diffusing through roughly one unit cell. In the layered structures of the S_C or S_A phases, translational diffusion over such a distance would not usually involve reorientations. Another implication of the NMR measurement of the diffusion coefficient is that in 200 ms, the duration of the experiment, the root-mean-square displacement of the molecules (which is what the NMR measurement is sensitive to) is $\sqrt{6Dt}=6$ μm, that is, the molecules are not bound tightly to a small region such as the primitive cubic cell. It is possible that a measurement of the diffusivity on a much shorter time (and, correspondingly, length) scale would yield a higher value and that the NMR measurement gives a reduced value because the relatively large displacements require that the molecules move along highly convoluted surfaces. Such a reduction would occur if the diffusivity were highly anisotropic in the S_C and S_A phases, with low diffusivity normal to the smectic layers, and if the layered structure were retained on a short (<10 nm) scale in the D phase. In fact, our measured value for D seems low in comparison with measurements of $D_\parallel$ in S_A phases.[35–38] For example, Krüger, Spiesecke, and Weiss[35] measured values around 10^{-10} m^2/s in the S_A phase of p-dodecanoylbenzylidene-p'-aminoazobenzene at 160 °C. A study of twist-impeded self-diffusion has been made in a cholesteric material.[39] Our attempt to measure diffusivity in the isotropic phase was made to see if there was evidence of a restriction. Our initial measurement of $D\sim4\times10^{-10}$ m^2/s in the isotropic phase at 205 °C may be an indication that diffusion on a small distance scale (<10 nm) in the D phase does occur at a higher rate than that measured by the NMR experiment. Note that using the diffusivity measured in the D phase, the time to diffuse the molecular width of 0.5 nm is around 1 ns, a very effective time scale for spin-lattice relaxation.

The appearance of the COOH peak further downfield in the D phase compared to the isotropic phase is evidence of deshielding due to intermolecular hydrogen bonding, possibly the dimerization or even a larger networking of carboxylic head groups, as suggested by Lydon.[7,33] The high relaxation rates for this proton in the D phase support this idea. The few measurements in the isotropic phase appear to give lower rates than are predicted from the data in the D phase, possibly indicating less hydrogen bonding. The data are of poor quality, however.

V. CONCLUSIONS

In light of the above, we can draw a number of conclusions about the D phase that may serve to illucidate its structure.

(1) On a time scale of 200 ms, a typical distance traveled by a molecule along is 6 μm. The molecules are not fixed to one cell of the cubic lattice.

(2) On a time scale of 0.1 – 1 μs, the molecules sample a wide enough range of orientations to average the residual dipole-dipole interactions essentially to zero, giving rise to a proton NMR spectrum as if from an isotropic liquid. These reorientations are due to translational diffusion of the molecules across distances of about 10 nm through regions with widely different directors. This mechanism is not effective at reducing the linewidth in the S_C or S_A phases.

(3) These fluctuations in orientation do not occur on a short enough time scale to cause a significant difference in the (60 MHz) spin-lattice relaxation rates in the D phase in comparison with those observed in the S_C or S_A phases.

(4) Spin-lattice relaxation in all these phases is due to rapid ($<10^{-8}$ s) modulation of interactions by such motions as translational diffusion past neighboring molecules, rotations about the long molecular axes, rotations of the long molecular axes away from the director, and rapid conformational motion. Formation of dimers or even larger groups by hydrogen bonding of the carboxylic head groups provides a neighboring proton for each COOH proton giving it an efficient relaxation mechanism by modulation of the direction of the internuclear vector or by formation and breaking of the hydrogen bonds. These rapid motions are also responsible for the line narrowing in the S_C and S_A phases compared to the solid and change smoothly with temperature at the transitions.

(5) Intermolecular hydrogen bonding occurs in the carboxylic acid region of the molecule.

Note especially that the cubic structure does not involve relatively small variations in the director as seen, for instance, in the ripple phase,[40] but must include variations of director well past the "magic angle," 54.74°, where $P_2(\cos\theta)$ takes on a value of zero. This is consistent with the rotational symmetry of the phase.

A number of NMR (and other) experiments can be performed to get a better picture of the motions of molecules in the D phase. The slower motion can be studied in more detail by $T_{1\rho}$, T_{1D}, and low-frequency T_1 measurements. Such measurements would indicate whether the different lines in the D spectrum have similar correlation times. In particular, if the COOH proton is relaxed by making and breaking of hydrogen bonds in that region, it may have a different correlation time and, thus, a different frequency dependence than the tail and ring protons. Deuterium NMR spectra and relaxation rates would give much clearer information, especially as they are dominated by a single interaction, the quadrupole interaction. Measurements of diffusion coefficients versus temperature in the D and I phases and, if possible, the S_C and S_A phases might reveal more of the restrictions caused by the cubic structure in the D phase. Measurements on oriented samples would simplify a study of anisotropies in different properties. The D and other cubic phases can also be investigated in other materials and in mixtures of materials. Dielectric relaxation measurements would provide correlation times to compare with NMR measurements. Neutron and light scattering would also provide useful information.

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