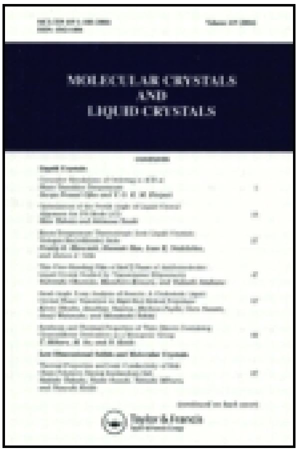

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Molecular Dynamics and Carbon-13Relaxation in the Nematic and Smectic A, C, and B Phases of 50.7

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Molecular Dynamics and Carbon-13 Relaxation in the Nematic and Smectic A, C, and B Phases of 50.7

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The carbon-13 nuclear magnetic resonance spin-lattice relaxation times of the protonated ring carbons of 4-*n*-pentyloxybenzylidene-4′-*n*-heptylaniline (50.7) have been measured in the nematic, smectic A, smectic C and smectic B phases. The results and theory presented in a recent deuterium magnetic resonance study of 50.7-d_4 are used to calculate expected carbon-13 relaxation times, which are then compared with our experimental values. The agreement is good enough to suggest that the molecular dynamics of the molecular core are reasonably well understood in the phases considered here.

Keywords: liquid crystals, NMR, carbon-13

I. INTRODUCTION

The study of nuclear magnetic resonance relaxation provides, in principle, a powerful means of studying the moelcular dynamics of liquid crystals.[1,2] In particular, with NMR the experimentalist has the unique ability to observe the dynamical behavior of individual atomic sites in a molecule. To interpret these observations requires theories which explain not only the general but also the detailed features of the molecular dynamics involved. One powerful test of theory is to compare deuterium relaxation with the carbon-13 relaxation of a carbon bound to the equivalent proton in an undeuterated molecule.[3] The two cases are indeed different: the deuteron is relaxed by motions of the nuclear quadrupole-electric field gradient interaction whereas the carbon is relaxed by motions of the dipole-dipole interaction of the ^{13}C and the bound ^{1}H. Basic relaxation theory leads to expressions which are distinctly different combinations of the spectral densities, and agreement between ^{13}C experiments and ^{2}H experiments will require a theory giving the correct combinations. Carbon-13 spin-lattice relaxation times (T_{1ZC}) of the protonated ring carbons of 4-*n*-pentyloxybenzylidene-4′-*n*-heptylaniline (50.7) in the nematic, smectic A, smectic C and smectic B phases are reported here and analyzed using the results and theory reported in recent deuterium relaxation studies of 50.7-d_4.[4,5]

II. THEORY

If a sample's director is parallel to the magnetic field **B**, then the deuterium Zeeman (R_{1ZD}) and quadrupole (R_{1QD}) spin-lattice relaxation rates are given by[4]

$$R_{1ZD} = A_D[J_1(\omega_0) + 4J_2(2\omega_0)] \tag{1}$$

$$R_{1QD} = 3A_DJ_1(\omega_0) \tag{2}$$

where the spectral densities $J_p(\omega)$ are defined below, ω_0 is the ^2H resonance frequency, and

$$A_D = (3\pi^2/2)(e^2qQ/h)^2$$

with e^2qQ/h the quadrupole coupling constant. One of the advantages of deuterium relaxation is that R_{1ZD} and R_{1QD} can be measured simultaneously,[6] and as Equations (1) and (2) are 2 equations in 2 unknowns, the measured R_{1ZD} and R_{1QD} are easily solved to yield $J_1(\omega_0)$ and $J_2(2\omega_0)$, providing that A_D is known.

The carbon-13 spin-lattice Zeeman relaxation rate ($R_{1ZC} = T_{1ZC}^{-1}$) due to the dipole-dipole interaction of the ^{13}C with a single directly bonded proton is[7,8]

$$R_{1ZC} = A_{CH}[J_0(\omega_C - \omega_H) + 3J_1(\omega_C) + 6J_2(\omega_C + \omega_H)] \tag{3}$$

where ω_C and ω_H are the ^{13}C and ^1H resonance frequency respectively, and

$$A_{CH} = \frac{1}{2}(\gamma_C\gamma_H\hbar/r_{CH}^3)^2.$$

γ_C and γ_H are the respective ^{13}C and ^1H gyromagnetic ratios, $\hbar$ is Planck's constant divided by 2π, and r_{CH} is the $^{13}C - {}^1H$ bond length. Additional relaxation mechanisms are possible for ^{13}C relaxation,[9] but in the present case are not required to explain the relaxation rates of the protonated carbons of the aniline ring.

One equation in 3 unknowns is not solvable, so carbon-13 relaxation (Equation (3)) can be far more difficult to interpret than quadrupolar relaxation (Equations (1) and (2)). In the extreme narrowing limit where the spectral densities are independent of frequency, Equations (1), (2) and (3) become 3 equations in 3 unknowns, and now it is possible to use ^2H and ^{13}C relaxation rates to obtain all three spectral densities J_0, J_1 and J_2. The drawbacks of this procedure are (1) that the value of J_0 depends on the validity of applying the extreme narrowing approximation to the specific case under consideration, and (2) that the procedure for measuring J_0 involves subtracting two nearly equal numbers producing large errors in J_0. The procedure followed here is to use the theory presented by Dong,[4] together with the parameters determined by him for 50.7-d_4, to calculate R_{1ZC}. The calculated and experimental values of R_{1ZC} are then compared to test the theory.

The notation $J_p(p\omega_0)$ used by Dong[4,5] is suitable for conventional R_{1ZD} and R_{1QD} experiments, but is unwieldy for the terms $J_2(\omega_C + \omega_H)$ and $J_0(\omega_C - \omega_H)$. Consequently we present his theory here using the notation $J_p(\omega)$. It is assumed that the long molecular axis coincides with the molecular principal axis, and that a cylindrical symmetry axis of the interaction of interest (quadrupolar or dipole-dipole) exists and makes an angle of 60° with the principal axis. These assumptions are in fact approximations made in the absence of sufficient information, but appear to be suitable for the case under consideration.[4,5] The molecular dynamics are assumed to be adequately described by treating the molecule as a symmetric top with rotational diffusion constants $D_\parallel$ for rotation about the long molecular axis, $D_\perp$ for rotations about any axis perpendicular to the long molecular axis, and with internal ring rotation uncorrelated to molecular tumbling and described by a rotational diffusion constant D' for rotation about the ring C1-C4 axis (see Figure 1).

The correlation times for the ring rotation of these rod-like mesogens are then given by

$$\tau_{pq}^{-1} = (D_\perp/\beta_{pq}^2) + (D_\parallel + D' - D_\perp)q^2 \tag{4}$$

where $p, q = 0, 1, 2$, and where β_{pq}^2 are functions of the order parameter $\langle P_2 \rangle$ and are taken from Nordio and Segre.[10] The spectral densities can be written as

$$\begin{aligned} J_p(\omega) = {} & [\kappa(p, 0)\tau_{p0}/(1 + \omega^2\tau_{p0}^2) \\ & + 36\kappa(p, 1)\tau_{p1}/(1 + \omega^2\tau_{p1}^2) \\ & + 27\kappa(p, 2)\tau_{p2}/(1 + \omega^2\tau_{p2}^2)]/64 \end{aligned} \tag{5}$$

with

$$\kappa(p, q) = \langle [D_{pq}^2(\Omega_0)]^2 \rangle - |\langle D_{pq}^2(\Omega_0) \rangle|^2 \delta_{p0}\delta_{q0} \tag{6}$$

where the $D_{pq}^2(\Omega_0)$ are Wigner rotation matrices written as functions of the Euler angles Ω_0 which transform from the molecular frame to the director frame. The $\kappa(p, q)$ are tabulated by Freed[8] as functions of $\langle P_2 \rangle = \langle D_{00}^2(\Omega_0) \rangle$ and $\langle P_4 \rangle = \langle D_{00}^4(\Omega_0) \rangle$. The values of $\langle P_2 \rangle$, $\langle P_4 \rangle$, $D_\parallel$, and $D_\perp$ characterize the relaxation and are taken from Dong[4] where they are given in graphical form. All have associated experimental errors, but additional errors can arise from reading the graphs. We verified that the values of the parameters taken from the graphs could be used to calculate the original ^2H spectral densities. These calculated deuterium spectral densities were consistently 15% higher than the experimental values[4] but still well within the combined experimental errors. In general D' is not the same for deuterated and undeuterated rings, and in the absence of additional information $D_\parallel$ and D' cannot be separated so that $D_\parallel + D'$ is treated as an effective $D_\parallel$.

III. EXPERIMENTAL

The 50.7 sample was purchased from Frinton Laboratories (Vineland, N.J., U.S.A.) and purified by recrystallization from ethanol. The transition temperatures for the S_G–S_B, S_B–S_C, S_C–S_A, S_A–N, and N–I phase transitions were found to be ~38, 51.3, 55.6, 63.6 and 77.0°C, respectively, in good agreement with Dong's 50.7-d_4 values.[4] The sample was degassed by the freeze-pump-thaw method, and sealed under vacuum. The ^{13}C relaxation measurements were performed at 22.632 MHz on a Bruker SXP 4-100 spectrometer interfaced to a Nicolet 1180 computer. All measurements were made without sample spinning with a proton decoupling field of approximately 10 gauss applied only during data acquisition. The sample temperatures were controlled using a gas flow system, which produced a temperature gradient across the sample of about one degree celsius. The sample temperatures were measured using a copper-constantan thermocouple in the absence of decoupling, and the rf heating effect determined by observing the nematic-isotropic transition in the presence of decoupling. The validity of this procedure has been discussed previously.[11] The relaxation times were obtained from a standard 3-parameter fit to the inversion-recovery data, and have an estimated accuracy of 5%.

IV. RESULTS AND DISCUSSION

Typical ^{13}C NMR spectra of the aromatic region of the 50.7 sample in the N, S_A, S_C and S_B phases, along with line assignments, are given in Figure 1. The molecular diagram is based on x-ray data for the homologue 40.8[12] while the line assigments are based on carbon-13 studies of the homologues MBBA-d_1[13] and 50.7-d_1.[14] The spectral lines assigned to the protonated carbon-13 ring sites remain resolved in all four phases. The deuterium lines studied by Dong[4] arise from deuterium atoms bonded to the aniline carbons C2 = C6 and C3 = C5 which produce the carbon-13 spectral lines of interest. The fact that each pair of symmetrically equivalent carbons gives a single spectral line is consistent with the assumption that the rings undergo rapid internal rotation.

The measured relaxation times $T_{1ZC} = 1/R_{1ZC}$ for the protonated aromatic ring carbons of 50.7 are shown in Figure 2 as plots of log T_{1ZC} versus inverse absolute temperature. The straight line plots were obtained by least squares fits to the data and have significantly smaller slopes in the nematic phase than in the smectic phases. The corresponding activation energies obtained from the slopes in the nematic and smectic phases for the protonated ring carbons are listed in Table I. The carbons of the oxybenzylidene ring have shorter relaxation times than those of the aniline ring, which could indicate that there are either slower motions or additional relaxation pathways for the oxybenzylidene ring.

Since the differences in the relaxation times of the protonated aniline ring carbons C2 = C6 and C3 = C5 at any temperature are less than the experimental errors, it is appropriate to use the average value. These average values are shown as plots of log T_{1ZC} versus inverse absolute temperature in Figure 3. The straight line plots

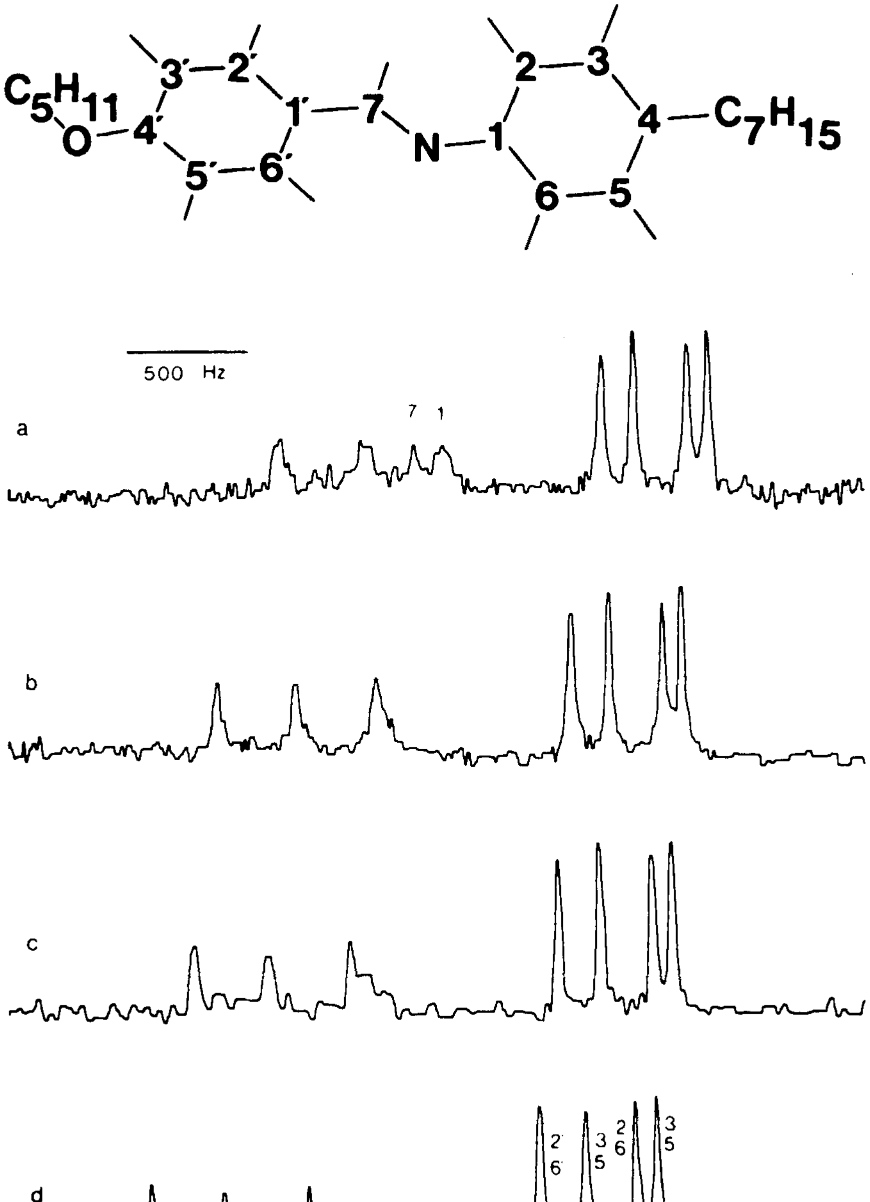

FIGURE 1 ^{13}C NMR spectra of the aromatic region of 50.7 for (a) Nematic phase (69.6°C), (b) Smectic A phase (62.3°C), (c) Smectic C phase (54.0°C), and (d) Smectic B phase (48.4°C).

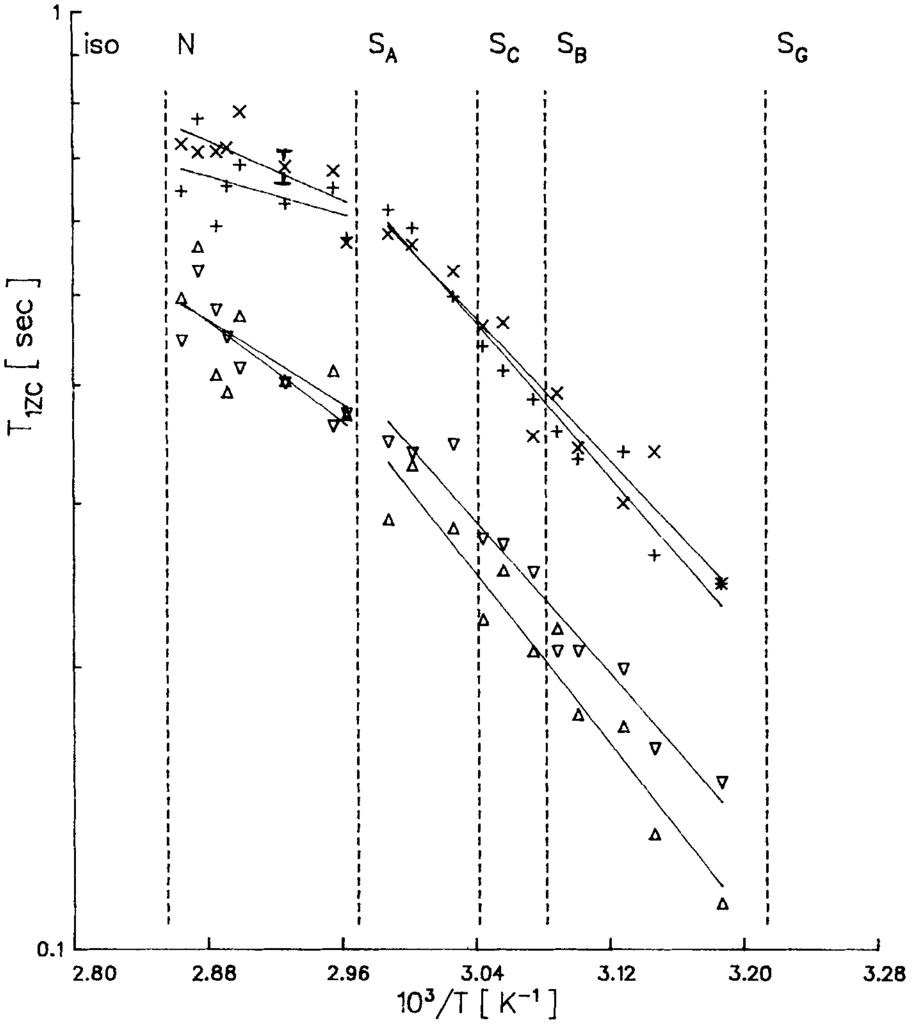

FIGURE 2 ^{13}C relaxation times T_{1ZC} for the protonated aromatic rings versus reciprocal temperature. The straight lines are based on least square fits, and the corresponding activation energies are given in Table I. The measurements are △ = C2′ = C6′, ▽ = C3′ = C5′, + = C3 = C5 and × = C2 = C6.

TABLE I

Activation energies for ^{13}C relaxation in the Nematic and Smectic phases.

Carbon	Nematic (kJ/mole)	Smectic (kJ/mole)
C3 = C5	10.0 ± 6.3	39.3 ± 2.1
C2 = C6	15.1 ± 5.0	36.0 ± 2.9
aniline*	12.6 ± 4.6	37.7 ± 1.7
C2′ = C6′	21.3 ± 8.4	43.5 ± 3.3
C3′ = C5′	25.1 ± 5.0	38.9 ± 2.5

*T_{1ZC} for C3 = C5 and C2 = C6 averaged before least square fitting.

in Figure 3 were obtained by least squares fits to the data and the corresponding activation energies listed in Table I. Figure 3 also displays our calculated values of T_{1ZC} for the case where the complete expression for the spectral densities, Equation (5), is used, and for the case of extreme narrowing where all the $\omega\tau_{pq}$ are set to zero in Equation (5).

In his deuterium study of 50.7-d_4 Dong[4] assumed that extreme narrowing was a valid approximation. Our T_{1ZC} values were calculated using a proton-carbon distance of 1.084Å[15] and Dong's $\langle P_2\rangle$, $\langle P_4\rangle$, $D_\parallel$ and $D_\perp$ values for the deuterated aniline ring of 50.7-d_4. While the calculated T_{1ZC} are on average 25% less than the ex-

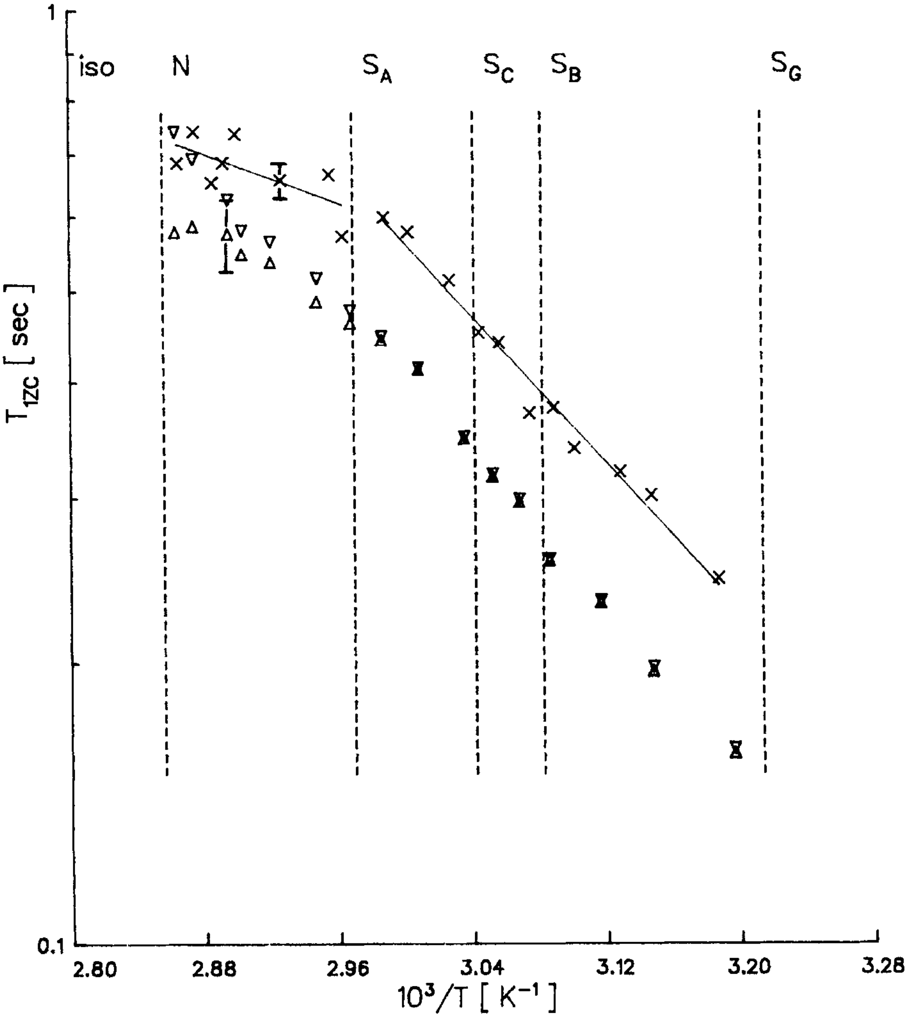

FIGURE 3 Plots of (×) experimental ^{13}C relaxation times for the aniline ring, and corresponding theoretical (Δ) extreme narrowing and (∇) full expression values calculated with r_{CH} = 1.084 Å versus reciprocal temperature.

perimental values it can be seen that the extreme narrowing calculations do reproduce the shape of the experimental curve reasonably well but that the values calculated with the full expression diverge from the curve at the high temperature end of the nematic region.

To show that the extreme narrowing theory does indeed reproduce the shape of the experimental curve, we selected a set of effective proton-carbon distances, r_{eff}, and recalculated the ^{13}C relaxation times for the entire temperature range. Figure 4 shows the extreme narrowing calculations for an r_{eff} value of 1.14Å along with the averaged experimental ^{13}C relaxation times for the aniline ring. As can be seen

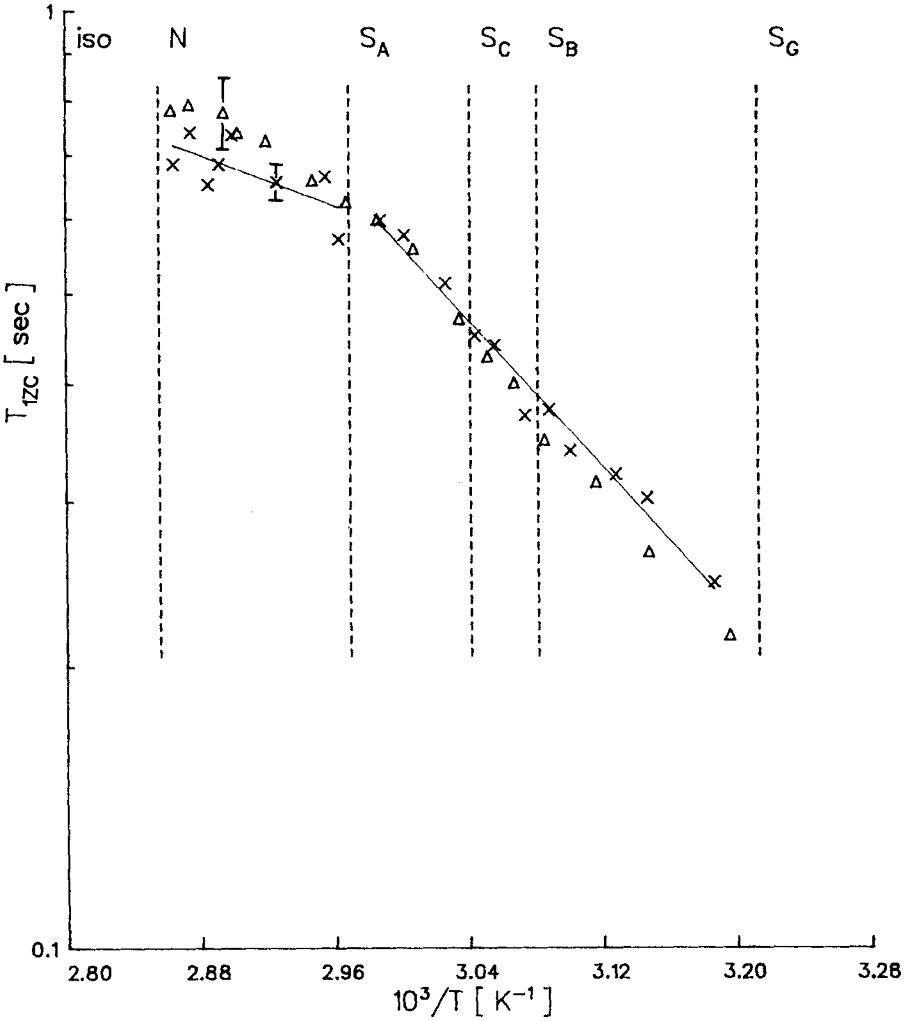

FIGURE 4 Plots of experimental (x) ^{13}C relaxation times for the aniline ring, and corresponding theoretical (△) extreme narrowing values calculated with r_{CH} = 1.14 Å versus reciprocal temperature.

the experimental and theoretical curves do coincide well within the experimental error.

The discrepancy in magnitude between the extreme narrowing calculated and experimental values arises in part from the difference in moments of inertia of the aniline rings of 50.7-d_4 and undeuterated 50.7. Spies *et al.*[16] have shown that the correlation time for angular reorientation in a small rigid molecule is directly proportional to the moment of inertia of the molecule. The moment of inertia of the whole 50.7 structure, and thus $D_{\|}$ and $D_{\perp}$, will not be greatly affected by the d_4-deuteration, but the moment of inertia of the aniline ring, and thus D', which is inversely proportional to the moment of inertia, will be greatly affected. Using conventional bond lengths and atomic masses[15] we find that the ratio of the moments of inertia about an axis through the two unprotonated carbons of the deuterated and undeuterated aniline rings to be 1.23. A crude approximation to the effect of deuteration can be obtained by assuming that the correlation times are simply inversely proportional to D', that is taking both $D_{\|}$ and $D_{\perp}$ to be zero. The ratio of the correlation times of the deuterated to the undeuterated molecule is then 1.23. For the extreme narrowing limit, the increase in our calculated relaxation times is then 11% at the highest temperature and 16% at the lowest temperature, corresponding to r_{eff} values of 1.10 Å and 1.11 Å, respectively. While the effect of deuteration is in the desired direction, the inclusion of nonzero $D_{\|}$ and $D_{\perp}$ tends to decrease this correction. Furthermore, as noted previously, our calculated deuterium spectral densities were consistently higher than Dong's experimental values. If the diffusion constants $D_{\|}$ and $D_{\perp}$ are simply multiplied by 1.15 to compensate for this systematic error, then our calculated T_{1ZC} values are increased by this factor. This correction is also in the desired direction and if combined with the deuteration effect produces excellent agreement between the calculated and experimental T_{1ZC} curves.

The extreme narrowing assumption requires comment. The original calculation[4] of the relaxation parameters was based on the measured deuterium $J_1(\omega_0)$ and $J_2(2\omega_0)$, using the extreme narrowing approximation. The application to carbon-13 involves larger frequencies, and it is possible that the extreme narrowing approximation may succeed with ^2H and fail with ^{13}C. The spectral densities J_p, given by Equation (5), are functions of the correlation times τ_{pq},

$$J_p = f(\tau_{pq}),\ q = 1, 2, 3.$$

The τ_{pq}, given by Equation (4), are functions of β_{pq}^2, $D_{\perp}$ and $D_{\|}$. The $D_{\|}$ are much greater than the $D_{\perp}$, with the ratio $D_{\|}/D_{\perp}$ being ~240 near the isotropic phase and ~34 in the S_B phase. The nematic region has $\langle P_2 \rangle$ values of ~0.4 to ~0.7, for which the β_{pq}^2 are in the range of ~0.1 to ~0.2. Thus, in the nematic region the τ_{pq}^{-1} will be approximated by $(D_{\|} + D')q^2$ unless $q = 0$, in which case τ_{p0}^{-1} is given by $D_{\perp}/\beta_{p0}^2$. In this region $D_{\|}$ decreases while $D_{\perp}$ increases with decreasing temperature so that τ_{p1} and τ_{p2} increase while τ_{p0} decreases as the temperature decreases. Numerical calculation confirms this behavior over the entire temperature range. The result is that in the nematic region the various $\omega\tau_{p1}$ and $\omega\tau_{p2}$ are much less than unity, but the various $\omega\tau_{p0}$ are approximately unity, for example, $(\omega_H - \omega_C)\tau_{00}$

$\sim$ 1.6, $\omega_C\tau_{10} \sim 0.5$, and $(\omega_C + \omega_H)\tau_{20} \sim 1.9$ at 76.1°C. The situation at lower temperatures is more complex. The $\omega_C\tau_{p1}$ and $\omega_C\tau_{p2}$ are in the range 0.02 to 0.06, but the other terms range from 0.1 to 0.6, and the extreme narrowing approximation is valid to within about 2 or 3 percent. Thus at lower temperatures the use of the extreme narrowing approximation seems reasonable. However, calculation shows that the extreme narrowing assumption at the high temperature end of the nematic region is not a valid assumption for both the carbon-13 and deuterium experiments. In using this assumption in the deuterium work erroneous parameters have been generated resulting in the fortuitous agreement of the extreme narrowing calculations with the ^{13}C data and the deviation of the T_{1ZC} values calculated with the full expression.

Recently Dong[17] has studied the relaxation of a ^2H attached to C7 of 50.7, and carried out an initial analysis using $r_{CH} = 1.084$ Å which does predict the correct magnitude of the ^{13}C relaxation in the nematic phase. This result suggests that a T_{1ZC} study of the C7 carbon would be desirable, but, as can be seen in Figure 1, the overlap of C7 with C1′ over a portion of the temperature region could present difficulties.

V. CONCLUSIONS

The ^{13}C spin-lattice relaxation times of the protonated aniline ring of 50.7 in the nematic and smectic A, C, and B phases have been measured and analyzed using results from a deuterium relaxation study. The agreement is good enough to suggest that the molecular dynamics of the molecular core are reasonably well described by the existing theory.

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