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High field carbon 13 relaxation of 5CB. Chemical shift anisotropy as a probe of nematic dynamics

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High field carbon 13 relaxation of 5CB

Chemical shift anisotropy as a probe of nematic dynamics

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The carbon 13 spin-lattice relaxation times of the ring carbons at 22·6 MHz in the nematic phase and at 20·0 MHz in the isotropic phase of 5CB have been published previously. An analysis of the results in the nematic phase based on diffusion constants obtained from deuteron relaxation was presented. In this paper measurements of the carbon 13 spin-lattice relaxation times of the ring carbons of 5CB at 125·6 MHz are given along with an analysis which makes use of the wide variation in the field to interpret the relatively simple relaxation of the protonated aromatic carbons. An effort to interpret the more complicated relaxation behaviour of the unprotonated carbons using the simplification in relaxation behaviour at high fields where chemical shift anisotropy dominates the relaxation is less successful. However, the conclusion that order director fluctuations account for almost 50 per cent of the relaxation rate in the nematic phase at high fields suggests that study of high field rotating frame relaxation for these carbons might be a rich source of information on critical fluctuations.

1. Introduction

The carbon 13 spin-lattice relaxation times of all the resolved resonances in both phases of 4-cyano-4′-*n*-pentylbiphenyl (5CB) at 22·6 MHz (nematic) and 20·0 MHz (isotropic) have been published previously [1]. The relaxation data for the protonated aromatic *ortho* carbons have been analysed [2] using Dong's results for deuterium relaxation in 5CB-d_{15} at 15·4 MHz [3]. The relaxation data for the unprotonated aromatic *para* carbons were analysed in the manner of Wittebort *et al.* [4], using spectral density expressions developed by Dong [3]. The results were satisfactory given the difference in frequency between the carbon 13 and deuterium data. The availability of high field NMR provides a test of relaxation theory that is even more impressive.

The carbon 13 spin-lattice relaxation times of all the resolved aromatic resonances in both phases of 5CB at 125·6 MHz have been measured and an analysis using the previous theory is presented. The conclusions are consistent with earlier results, and suggest that the study of relaxation due to chemical shift anisotropy at high fields is a promising but not a completely uncomplicated approach to studying dynamics in mesogens.

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2. Theory

We consider here only the case of relaxation of nuclei in a relatively rigid sub-unit of a molecule, and specifically ignore alkyl chain relaxation. In liquid crystal phases the primary source of relaxation of deuterium nuclei and of carbon 13 nuclei directly bonded to a proton is often the modulation of the appropriate interaction by molecular angular fluctuations (AFS) [5, 6]. Indeed, for the molecular geometries which occur in many liquid crystals, and especially in the biphenyls, molecular angular fluctuations may be the only source of relaxation. This situation may simplify the analysis of the relaxation of the nuclei in question, but may limit the usefulness of relaxation as a probe of molecular motion, in particular in the study of order director and order parameter fluctuations [7]. We limit our theory section to relaxation of carbon 13 nuclei, and consider only the simplest useful forms of the theory. We start with the case of a carbon 13 directly bonded to a proton.

If the sample's director is parallel to the magnetic field, then the carbon 13 Zeeman spin lattice relaxation rate ($R_{1ZC} = T_{1ZC}^{-1}$) due to AFS modulations of the dipole–dipole interaction of the carbon 13 with a single proton is

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

where the spectral densities $J_p(\omega)$ are defined below, ω_C is the ^{13}C resonance frequency, ω_H is the ^{1}H resonance frequency, and

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

where γ_C and γ_H are the ^{13}C and ^{1}H gyromagnetic ratios, respectively, $\hbar$ is Planck's constant divided by 2π, and r_{CH} is the ^{13}C–^{1}H distance of separation (for directly bonded protons, just the bond length) [7, 8].

In principle any interaction can be modulated motion and thus serve as a source of relaxation [8, 9]. The case of a relaxation contribution due to chemical shift anisotropy has been considered by Wittebort *et al.* [4]. The ^{13}C spin lattice relaxation due to chemical shift anisotropy can be expressed as

$$R_{1ZCSA} = A_{CSA} J_{1CSA}(\omega_C), \qquad (2)$$

with

$$A_{CSA} = \tfrac{3}{2}(\omega_C \sigma_{ZZ})^2,$$

where σ_{ZZ} is the component of the shielding tensor along the director. Other possible mechanisms include scalar coupling to nuclei involved in exchange processes (very unlikely for the situations considered here), scalar coupling to quadrupolar nuclei (a possibility for the carbon in the CN group), and relaxation by spin rotation (fluctuations of the angular momentum vector of the molecule—generally limited to small molecules, but a possibility at elevated temperatures). In principle it is possible to determine the portion of the relaxation due to the dipole–dipole interaction between a carbon 13 and a proton (R_{1ZC}) by measuring the NOE factor for which

$$R_{1ZC} = R_1 \times (\mathrm{NOE} - 1)/1{\cdot}988. \qquad (3)$$

We present the theory given by Dong [10] for rod-like mesogens for the case where the long molecular axis and the *para* axes of the rings coincide with the principal axis. The molecular dynamics are approximated by treating the molecule as a symmetric top with rotational diffusion constants $D_{\parallel}$ and $D_{\perp}$, about and of the molecular long axis, and with internal ring rotation uncorrelated to molecular tumbling and described by a rotational diffusion constant D_R for rotation about the *para* axis.

If internal ring rotation is ignored then the correlation times for the overall molecular motion is approximated by $\tau_{pq}^{-1} = (D_\perp/\beta_{pq}^2) + (D_\parallel - D_\perp)q^2$ where the β_{pq}^2 are functions of the order parameter $\langle P_2 \rangle$ which are given by Nordio and Segre [11]. Internal ring rotation can be included by taking the correlation times as

$$\tau_{pq}^{-1} = (D_\perp/\beta_{pq}^2) + (D_\parallel - D_\perp)q^2 + D_R(1 - \delta_{q0}), \tag{4}$$

with δ_{q0} is the Kronecker delta. The spectral densities can be written as

$$\begin{aligned} J_p(\omega) = {} & f_0\kappa(p,0)\tau_{p0}/(1+\omega^2\tau_{p0}^2) \\ & + 2f_1\kappa(p,1)\tau_{p1}/(1+\omega^2\tau_{p1}^2) \\ & + 2f_2\kappa(p,2)\tau_{p2}/(1+\omega^2\tau_{p2}^2), \end{aligned} \tag{5}$$

with

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

where the $D_{pq}^2(\Omega)$ are Wigner rotation matrices written as functions of the Euler angles Ω_0 which transform from the molecular to the director frame. The $\kappa(p,q)$ are given by Freed [7] as functions of $\langle P_2 \rangle = \langle D_{00}^2(\Omega_0) \rangle$ and $\langle P_4 \rangle = \langle D_{00}^4(\Omega_0) \rangle$.

For dipole–dipole interactions the f_n are given by

$$f_0, f_1, f_2 = (3\cos^2\beta_{1F} - 1)^2/4, (3\sin^2 2\beta_{1F})/8, (3\sin^4\beta_{1F})/8, \tag{7}$$

where β_{1F} is the angle between the local symmetry interaction (for quadrupolar and dipole–dipole interactions, the C–D and C–H bond, respectively) and the *para* axis of the ring. For chemical shift anisotropy the f_n are given by

$$f_0'\ f_1, f_2 = 1, 0, (1/6)\left(\frac{\sigma_{xx} - \sigma_{yy}}{\sigma_{zz}}\right)^2, \tag{8}$$

where σ_{xx} and σ_{yy} are the components of the shielding tensor perpendicular to the director [8].

The f_q for chemical shift anisotropy show that the contribution to relaxation from CSA does not depend on the τ_{p1}, and since in many cases $D_\parallel \gg D_\perp$, it is often true that chemical shift anisotropy relaxation depends only on two diffusion constants, $D_\perp$ and the effective diffusion constant $4D_\parallel + D_R$. For a symmetric chemical shift tensor, as is the situation in the present case for the carbon of the CN group, $f_2 = 0$ and the CSA relaxation depends only on $D_\perp$.

For the isotropic phase, we have $\kappa(p,q)$ $\kappa(p,q) = 0{\cdot}2$ and $\beta_{pq}^2 = 1/6$. Thus for the isotropic state in the present notation the label p can be dropped and we may write

$$\tau_q^{-1} = (6D_\perp) + (D_\parallel - D_\perp)q^2 + D_R(1 - \delta_{q0}) \tag{9}$$

and

$$\begin{aligned} J(\omega) = {} & f_0 0{\cdot}2\tau_0/(1+\omega^2\tau_0^2) \\ & + 2f_1 0{\cdot}2\tau_1/(1+\omega^2\tau_1^2) \\ & + 2f_2 0{\cdot}2\tau_2/(1+\omega^2\tau_2^2), \end{aligned} \tag{10}$$

and the conventional isotropic relaxation equations [9] are easily obtained.

Relaxation in the mesogenic phase can occur not only from modulations arising from angular fluctuations (AFS) but also from modulations arising from order director fluctuations (ODF) which can modulate any of the interactions considered above [3–5, 8]. The ODF contributions to the ^{13}C dipole–dipole and ^{13}C chemical shift anisotropy can be approximated with

$$R_{1ZC}^{\mathrm{ODF}} = A_{\mathrm{CH}} J_1^{\mathrm{ODF}}, \tag{11}$$

$$R_{1ZCSA}^{\mathrm{ODF}} = A_{\mathrm{CSA}} J_1^{\mathrm{ODF}}, \tag{12}$$

with

$$J_1^{\mathrm{ODF}} = \frac{3kT\langle P_2\rangle^2}{4\surd(2)\pi\surd(\omega_0)K(D+K/\eta)^{1/2}} f_0, \tag{13}$$

where k is Boltzmann's constant, K is the average elastic constant, D is the translational diffusion constant, and η is the rotational viscosity. As can be seen from equation (7) the ODF contribution to the dipole–dipole relaxation of a protonated carbon with a bond angle of 60° with the director is much smaller than the AFS contribution, while from equation (8) it can be seen that the ODF and AFS contributions to the chemical shift are similar. There are corrections to the above equations due to the high frequency cut-off [5, 7] and a cross term between ODF and AFS [5, 7], but both of these corrections are small in the present situation.

3. Experimental

The biphenyl samples were purchased from BDH Chemicals Ltd., Canada, and used without further purification. The N–I phase transition for 5CB was found to be 35·3°C. Samples were placed in both 5 mm and 7·5 mm tubes, and all samples except those used in the isotropic measurements at 20·0 MHz were degassed using the freeze–pump–thaw method and sealed under vacuum. The isotropic ^{13}C T_1 and NOE relaxation measurements at 20·00 MHz were made on a Varian CFT-20 spectrometer. The nematic ^{13}C T_1 relaxation measurements at 22·63 MHz were made with a Bruker SXP 4-100 spectrometer interfaced to a Nicolet 1180 computer, and with a proton decoupling field of approximately 10 G applied only during data acquisition to minimize sample heating [12]. This spectrometer was not equipped to measure NOEs. All relaxation measurements were made without sample spinning using the inversion recovery technique. We estimate that the relaxation times of the protonated and unprotonated carbons have an accuracy of 5 and 10 per cent, respectively. A gas flow system was used to control the temperature with a gradient of about 1°C across the sample. Temperatures were determined with a thermocouple in the absence of decoupling. The T_1 and NOE measurements at 125·8 MHz were all made on a Bruker Aspect 500 using WALTZ-16 decoupling. The isotropic measurements were made with continuous decoupling with an effective proton $\pi/2$ pulse of 105 μs while the nematic measurements were made with decoupling only during acquisition with an effective proton $\pi/2$ pulse of 9·5 μs. An effort was made to measure NOEs in the nematic phase, but the necessary compromise between sufficient power during recovery and avoidance of heating effects did not lead to convincing results.

4. Results and discussion

The ^{13}C NMR spectra and spin lattice relaxation times of 5CB at low field have been presented previously [1]. The spin lattice relaxation times at high field are given in

Table 1. Experimental relaxation times T_1 (ms) at 125·7 MHz.

T/K	C4	C8	C5	C2	C7	C3	C6	CN	C1
315	1017	901	1081	391	413	418	423	269	999
326	1244	1064	1390	587	583	601	589	315	1168
336	1477	1360	1615	751	751	780	765	370	1387
351	2451	1980	2428	1241	1131	1277	1153	570	2004
	C4, C8	C5	C1	C2	C7	C3	C6		
305·6	1199	1417	1041	309	347	332	316		
304·6	1172	1393	1023	308	336	327	321		
303·5	1174	1352	1021	298	324	328	320		
302·2	1226	1514	1305	303	320	321	316		
299·7	1268	1459	1453	281	304	302	300		

table 1. The spectra are essentially identical to those at low fields except that in the isotropic phase all four of the protonated lines are resolved. The NOEs at high field were, within experimental error, 2·0 for the unprotonated carbons (no dipole–dipole interaction), and 3·0 for the protonated carbons (only dipole–dipole interaction). The carbon relaxation times of all four of the protonated aromatic resonance lines differ by less than the experimental error, and so it is appropriate to average these for each molecule. In the isotropic phase the relaxation times of the unprotonated aromatic resonance lines, C1, C4 and C5 for each molecule agree within the experimental error while the relaxation time of C8 is shorter due to the neighbouring methylene protons. Unfortunately, in the nematic phase C4 and C8 overlap. Consequently, for the unprotonated case, only the average relaxation times of C1 and C5 are used in the analysis.

The averaged protonated aromatic ^{13}C spin lattice relaxation times are given in figure 1, along with the values found by doing a least squares fit [13] to the R_{1ZC} of the above theory in the isotropic and nematic phases separately. The values of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ were found from Dong's values for 5CB with the assumptions that $\langle P_2 \rangle$ are functions of $(T - T_{\mathrm{NI}})$. The three diffusion constants were assumed to have a temperature behaviour given by

$$D_i = A_i \exp(-E_i/T),$$

where T is the absolute temperature. In the fit the E_i and A_i were treated as variable parameters. In addition the separation r_{CH} was treated as a variable parameter. The parameters found are given in table 2, and the diffusion constants found are plotted in figure 2. The value of r_{CH} found in the fit was the same for both phases, and in agreement with the literature [14]. The values of A_i and E_i were found to be poorly determined, especially in the nematic phase with its small temperature width, but the resulting diffusion constants appear to be consistent to within 10 per cent or better for $D_\perp$ and 4 per cent or better for $D_\parallel$ and D_{R}. The activation energies for the nematic phase are in reasonable agreement with those obtained by Dong [3], as are the values for D_{R} and $D_\parallel$, but our values of $D_\perp$ are higher. The increase in value of $D_\perp$ in going from the isotropic phase to the nematic phase reflects a change in environment for motion about an axis perpendicular to the molecular long axis. This motion is constricted in the nematic phase, leading to a higher collision rate.

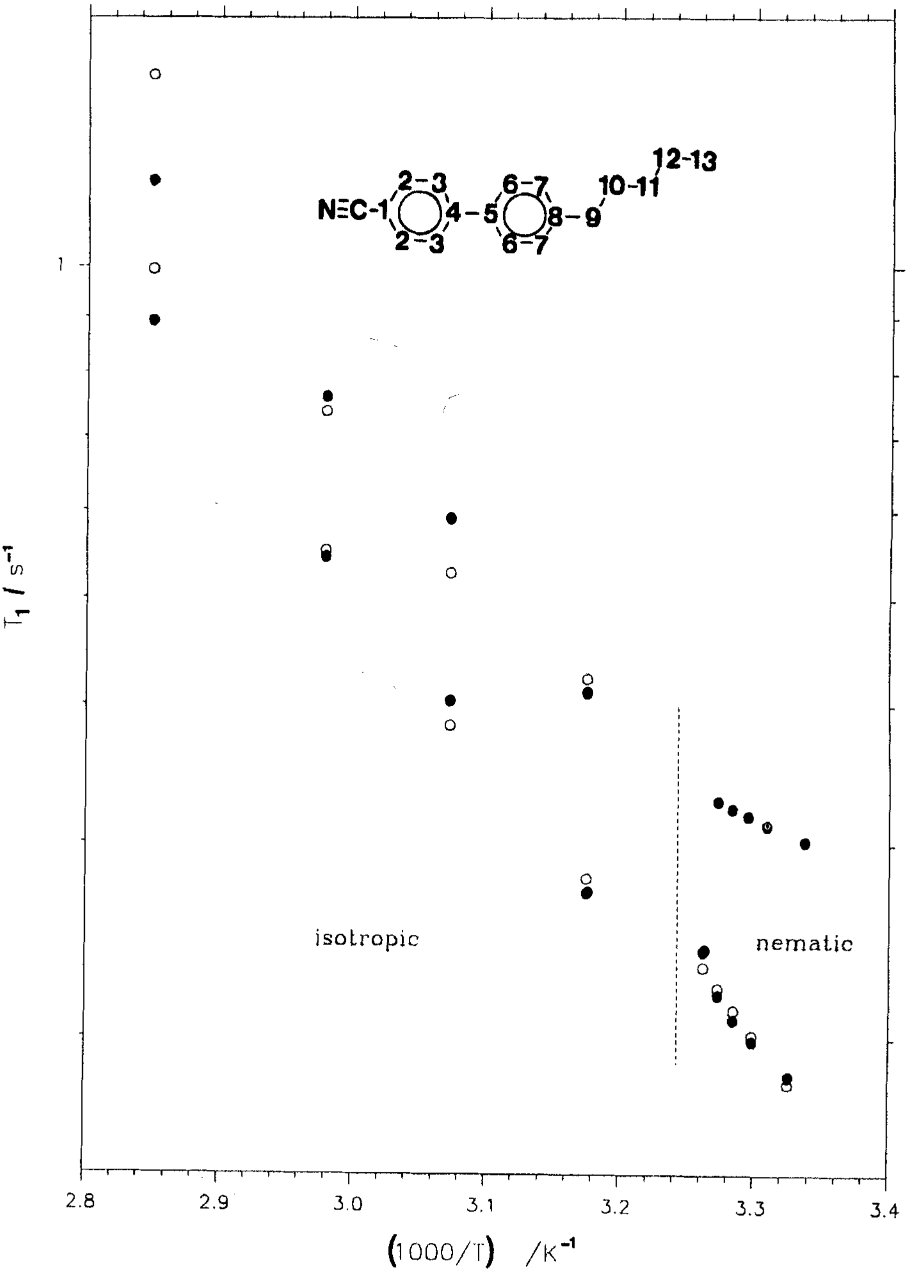

Figure 1. Plots of the averaged experimental (●) and calculated (○) ^{13}C spin lattice relaxation times for the protonated ring carbons of 5CB versus reciprocal temperature. For a given temperature, the longer relaxation time is the value for high field and the shorter relaxation time is the value for low field. Note that at high field in the nematic phase the agreement between theory and experiment is very close.

Table 2. Parameters for fit to protonated data

Phase	$A_\perp/\mathrm{s}^{-1}$	$E_\perp/\mathrm{K}$	$A_\parallel/\mathrm{s}^{-1}$	$E_\parallel/\mathrm{K}$	$A_\mathrm{R}/\mathrm{s}^{-1}$	E_R/K	$r/\mathrm{Å}$
Isotropic	$0{\cdot}55 \times 10^{11}$	2500	$0{\cdot}72 \times 10^{12}$	1720	$0{\cdot}13 \times 10^{23}$	9570	1·104
Nematic	$0{\cdot}52 \times 10^{14}$	3570	$0{\cdot}20 \times 10^{12}$	1760	$0{\cdot}73 \times 10^{24}$	10400	1·104

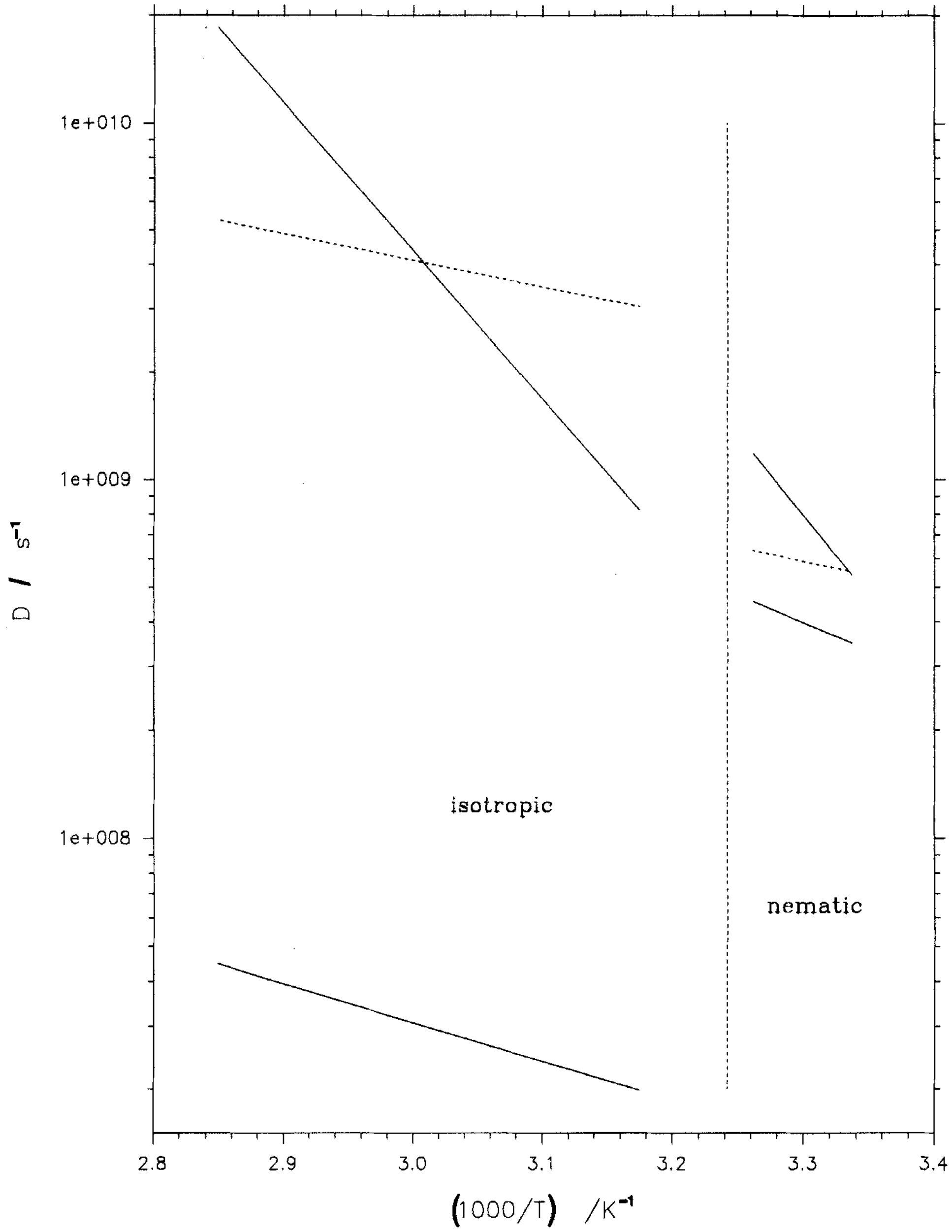

Figure 2. Plots of diffusion constants found for protonated ring carbons versus reciprocal temperature. Solid line is $D_\perp$, dashed line is $D_\parallel$ and dotted line is D_R.

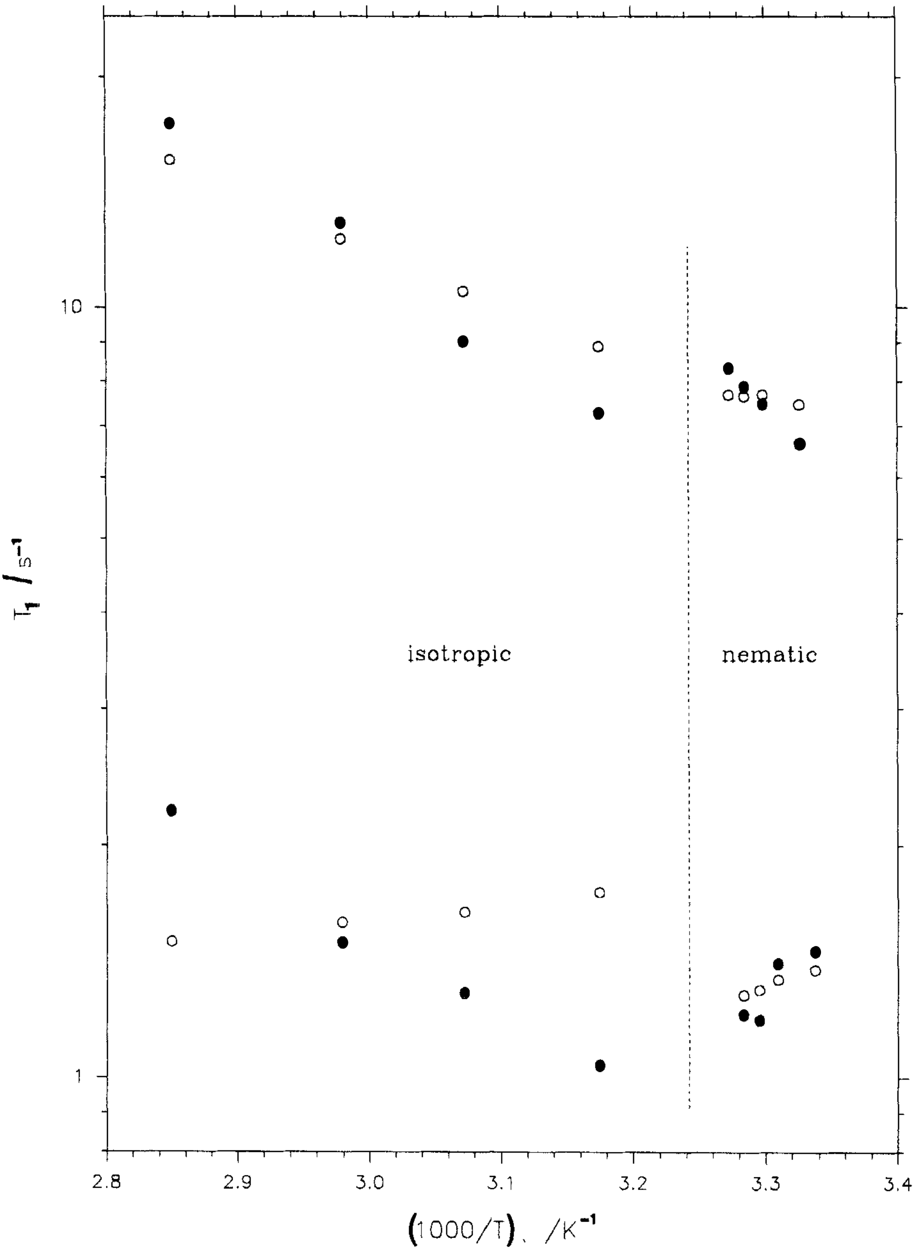

Figure 3. Plots of the averaged experimental (●) and calculated (○) ^{13}C spin lattice relaxation times for the unprotonated ring carbons of 5CB versus reciprocal temperature. For a given temperature, the longer relaxation time is the value for high field and the shorter relaxation time is the value for low field.

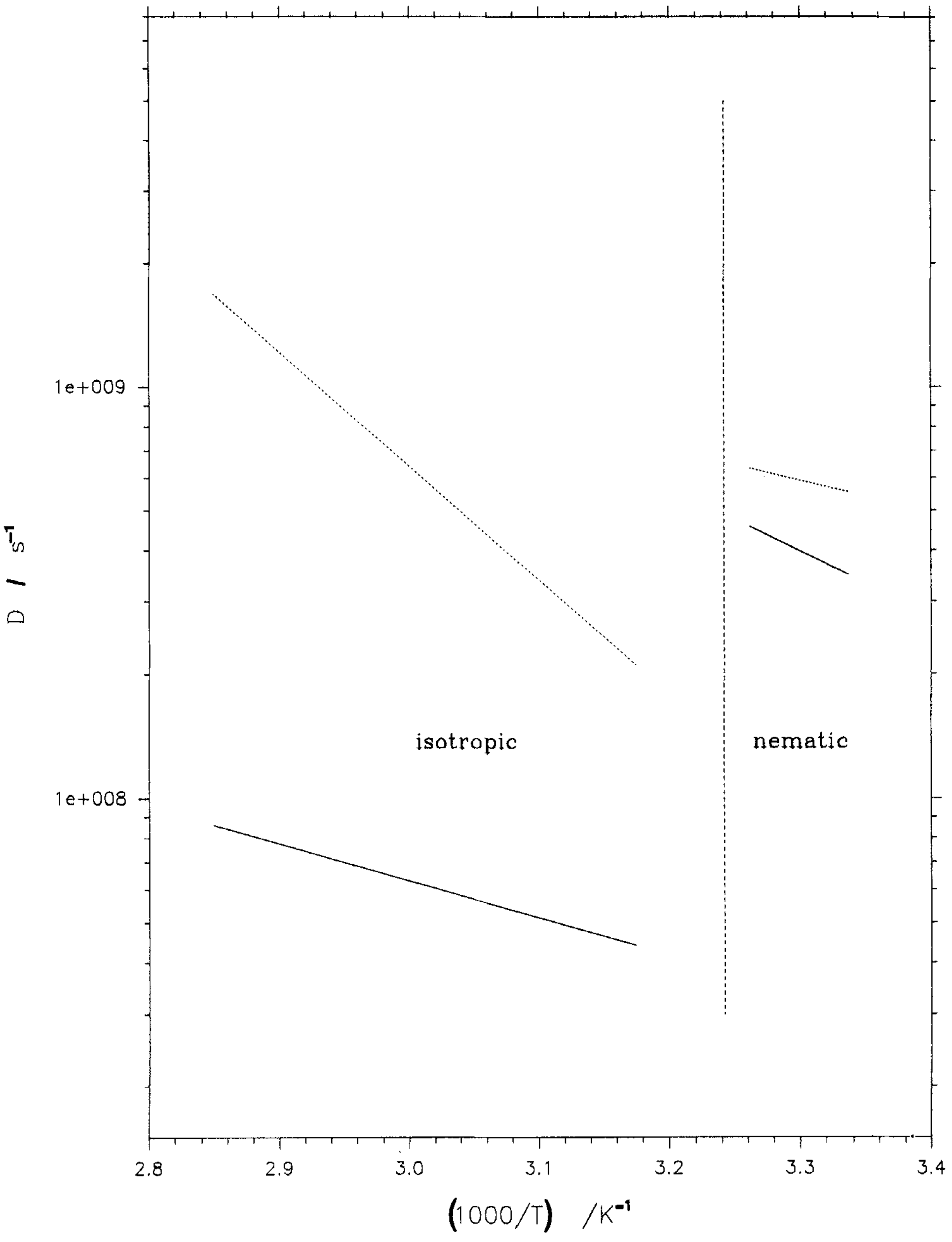

Figure 4. Plots of diffusion constants found for unprotonated ring carbons versus reciprocal temperature. Solid line is $D_\perp$, dashed line is $4D_\parallel + D_R$.

Table 3. Parameters for fit to unprotonated data.

Phase	$A_\perp/\mathrm{s}^{-1}$	$E_\perp/\mathrm{K}$	$A_{\mathrm{effective}}/\mathrm{s}^{-1}$	$E_{\mathrm{effective}}/\mathrm{K}$	amp
Isotropic	$0{\cdot}32\times10^{11}$	2080	$0{\cdot}145\times10^{18}$	6410	0·51
Nematic	$0{\cdot}18\times10^{14}$	4010	$0{\cdot}145\times10^{26}$	11700	0·39

The relaxation of the unprotonated carbons exclusive of proton–carbon dipole–dipole interactions, specifically the average of C1 and C5 with the low field values corrected by a factor of 2·5 [1], is given in figure 3. As all carbons in an aromatic ring are part of a rigid sub-unit of the molecule, it would be reasonable to assume that the motions causing the relaxation of the unprotonated aromatic ring carbons are the same as the motions causing the relaxation of the protonated ring carbons, and to use the diffusion constants obtained for the protonated carbons. However, the unprotonated carbons sample the motion in directions different from those of the protonated carbons, so we chose instead to perform an independent fit. The NOE studies indicate that there is no significant contribution to the relaxation of the unprotonated carbons by dipole–dipole interactions with distant protons at high field. We used the NOE measurements at low field to extract that portion of low field relaxation which is not due to dipole–dipole interactions, and treat it as a case of pure chemical shift anisotropy.

The director and molecular axes coincide for the unprotonated carbons, and the xx, yy, and zz components of the chemical shift tensor are taken as 99, 8, and -107 p.p.m., respectively [15]. The ODF terms were evaluated using the order parameters $\langle P_2 \rangle$ as found for the protonated case, and published values of K [16] and η [17] were used to construct power series in $\langle P_2 \rangle$ to interpolate values of K and η. For D we used the single value $0{\cdot}45 \times 10^6\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ as suggested by Dong [3]. For reasons given above, a model with only two diffusion constants and a parameter to vary the strength of the interaction was used. The experimental averaged values and the calculated relaxation times of the unprotonated ring carbons are given in figure 3. The parameter values are given in table 3 while the diffusion constants are plotted in figure 4. The strength factor differs by over 30 per cent between the nematic and isotropic phases which suggests that the theory used here is too naive for the physical situation. The fit to the data in the nematic phase is good, and in particular the opposite slopes of the high and low field data are given correctly. The fit to the high field isotropic data is reasonable but the fit to the low field isotropic data gives the negative of the correct slope. We hope to resolve this difficulty by studying the relaxation in the isotropic phase at a field between the fields used in the present work. Moreover an interpretation of the CN group carbon relaxation data, which was not possible with the data currently available, may be possible.

5. Conclusions

The ^{13}C spin lattice relaxation times of the protonated ring carbons of the 5CB over a very wide frequency range have been analysed. The agreement between experiment and theory appears satisfactory. The ^{13}C spin lattice relaxation times of the unprotonated ring carbons of 5CB have also been analysed but the agreement between experiment and theory is less satisfactory.

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