Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

A carbon-13 study of relaxation in the mesophases of 5O·7 and the 5CB homologous series

John S. Lewis[a]; E. Tomchuk[a]; E. Bock[b]
[a] Department of Physics, University of Winnipeg, Winnipeg, Manitoba, Canada [b] Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, Canada

To cite this Article Lewis, John S. , Tomchuk, E. and Bock, E.(1989) 'A carbon-13 study of relaxation in the mesophases of 5O·7 and the 5CB homologous series', Liquid Crystals, 5: 3, 1033 — 1044

To link to this Article: DOI: 10.1080/02678298908026407

URL: http://dx.doi.org/10.1080/02678298908026407

LIQUID CRYSTALS, 1989, VOL. 5, NO. 3, 1033–1044

A carbon-13 study of relaxation in the mesophases of 5O·7 and the 5CB homologous series

by JOHN S. LEWIS and E. TOMCHUK
Department of Physics, University of Winnipeg, Winnipeg, Manitoba, Canada R3B 2E9

and E. BOCK
Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2

Carbon-13 spin–lattice relaxation times of the protonated ring carbons have been measured at 22·6 MHz in the nematic and all four smectic phases of 5O·7 (4-*n*-pentyloxybenzylidene-4′-*n*-heptylaniline). Dong has obtained the deuterium spectral densities J_1 and J_2 at 15·4 MHz for the deuterated aniline ring of 5O·7-d_4, and has presented and applied a theory in which the spectral densities are expressed in terms of the diffusion constants $D_\parallel$ and $D_\perp$. His results are used to calculate ^{13}C relaxation times from the spectral densities J_0, J_1 and J_2. The calculated ^{13}C spin–lattice relaxation times are then compared with our experimental values to test the theory. The ^{13}C spin–lattice relaxation times of all the resolved resonances in the various phases of the first four members of the 5CB homologous series have been published previously. Dong has also published an analysis of 5CB deuterium data, and we use his results for the diffusion constants $D_\parallel$ and $D_\perp$ to calculate ^{13}C relaxation times of the protonated aromatic carbons of 5CB, 6CB, 7CB and 8CB. The ^{13}C relaxation times of the unprotonated aromatic carbons of the 5CB series are calculated in the manner of Wittebort *et al.*, but using the spectral density expressions developed by Dong. The calculated ^{13}C spin–lattice relaxation times of the 5CB homologous series are then compared with our experimental values to test the theory for the protonated and unprotonated ring carbons.

1. Introduction

One powerful test of the validity of N.M.R. theories of relaxation in liquid crystals [1] is to compare deuterium relaxation with the carbon-13 relaxation of a carbon bound to the equivalent proton in an undeuteriated molecule [2]. The two cases are indeed different: the deuteron is relaxed by the nuclear quadrupole–electric field gradient interaction, whereas the carbon is relaxed by its dipole–dipole interaction with the bound proton. Basic relaxation theory leads to expressions which are distinctly different combinations of spectral densities, so agreement between ^{13}C and deuterium N.M.R. (D.M.R.) 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 (5O·7) in the nematic, smectic A, smectic C, smectic B and smectic G phases are reported here and the results are compared with those calculated from Dong's deuterium relaxation studies of 5O·7-d_4 [3, 4]. The carbon-13 spin–lattice relaxation times of all the resolved resonances in the various phases of 4-cyano-4′-*n*-pentylbiphenyl (5CB), 4-cyano-4′-*n*-hexylbiphenyl (6CB), 4-cyano-4′-*n*-heptylbiphenyl (7CB) and 4-cyano-4′-*n*-octylbiphenyl (8CB) have been published previously [5, 6]. The relaxation data for the protonated aromatic *ortho*-carbons are analysed using Dong's results for deuterium relaxation in 5CB-d_{15} [7]. The relaxation data for the unprotonated aromatic *para*-carbons are analysed in the manner of Wittebort *et al.* [8], but using spectral density expressions developed by Dong.

2. Theory

For the situations considered in this paper, the primary source of both deuterium and carbon-13 relaxation is the modulation of the appropriate interaction by molecular angular fluctuations (AFs) [1].

If a sample's director is parallel to the magnetic field, then the deuterium Zeeman (R_{1ZD}) and the deuterium quadrupole (R_{1QD}) spin–lattice relaxation rates are

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

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

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

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

where e^2qQ/h is the quadrupole coupling constant [3]. One of the advantages of deuterium relaxation is that R_{1ZD} and R_{1QD} can be measured simultaneously [9], and as equations (1) and (2) are two equations in two unknowns, the measured R_{1ZD} and R_{1QD} are easily solved to yield $J_1(\omega_0)$ and $J_2(2\omega_0)$, providing only that A_D is known.

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 directly bonded proton is

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

where 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 bond length [10, 11].

In the case where the carbon is not directly bonded to a proton, there is still dipole–dipole relaxation with neighbouring protons, but it is necessary to include an additional relaxation contribution due to chemical shift anisotropy. The ^{13}C spin–lattice relaxation due to chemical shift anisotropy is

$$R_{1ZCSA} = A_{CSA}J_{1CSA}(\omega_C), \qquad (4)$$

with

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

where σ_{zz} is the component of the shielding tensor along the director.

We present Dong's theory [3] for rod-like mesogens for the special case where the long molecular axis and the *para*-axes of the rings coincide with the principal axis. The molecular dynamics are assumed to be adequately described by treating the molecule as a symmetric top with rotational diffusion constants $D_\parallel$ and $D_\perp$ about and of the long molecular 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 time for the overall molecular motion is

$$\tau_{pq}^{-1} = (D_\perp/\beta_{pq}^2) + (D_\parallel - D_\perp)q^2, \tag{5}$$

where the β_{pq}^2 are functions of the order parameter $\langle P_2 \rangle$ which are given by Nordio and Segre [13]. Internal ring rotation can be included by adding a term in D_R so that equation (5) becomes

$$\tau_{pq}^{-1} = (D_\perp/\beta_{pq}^2) + (D_\parallel - D_\perp)q^2 + D_\mathrm{R}(1 - \delta_{q0}), \tag{6}$$

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

$$\begin{aligned} J_p(\omega) = {} & f_0\kappa(p, 0)\tau_{p0}/(1 + \omega^2\tau_{p0}^2) + 2f_1\kappa(p, 1)\tau_{p1}/(1 + \omega^2\tau_{p1}^2) \\ & + 2f_2\kappa(p, 2)\tau_{p2}/(1 + \omega^2\tau_{p2}^2), \end{aligned} \tag{7}$$

with

$$\kappa(p, q) = \langle [D_{pq}^2(\Omega_0)]^2 \rangle - |\langle D_{pq}^2(\Omega_0) \rangle|^2 \delta_{p0}\delta_{q0}, \tag{8}$$

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 to the director frame. The $\kappa(p, q)$ are given by Freed [11] 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 both quadrupole and dipole–dipole interactions the f_n are

$$\left.\begin{aligned} f_0 &= [d_{00}^2(\beta_\mathrm{IF})]^2 = (3\cos\beta_\mathrm{IF} - 1)^2/4, \\ f_1 &= [d_{10}^2(\beta_\mathrm{IF})]^2 = (2\sin^2 2\beta_\mathrm{IF})/8, \\ f_2 &= [d_{20}^2(\beta_\mathrm{IF})]^2 = (3\sin^4\beta_\mathrm{IF})/8, \end{aligned}\right\} \tag{9}$$

where β_IF 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

$$f_0 = 1, \quad f_1 = 0, \quad f_2 = \tfrac{1}{6}\left(\frac{\sigma_{xx} - \sigma_{yy}}{\sigma_{zz}}\right)^2, \tag{10}$$

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

Relaxation can occur not only from modulations arising from AFs but also from modulations arising from order director fluctuations (ODF) which can modulate any of the interactions considered above [1, 7, 8, 10]. The ODF contributions to the ^{13}C dipole–dipole and ^{13}C chemical shift anisotropy can be approximated by

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

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

with

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

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 (9), 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, and from equation (10) it can be seen that the ODF and AFs contributions to the chemical shift are similar. There are corrections to equations (11) and (12) due to the high frequency cutoff [1, 11] and a cross term between ODF and AFs [1, 11], but both of these corrections are small in the present situation.

3. Experimental

The 5O·7 sample was purchased from Frinton Laboratories (Vineland, New Jersey, U.S.A.) and purified by crystallization 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 transitions were found to be 38, 51·3, 55·6, 63·6 and 77·0°C, respectively, in good agreement with Dong's 5O·7-d_4 values. The biphenyl samples were purchased from B.D.H. Chemicals Canada, Ltd, and were used without further purification. The N–I phase transitions for 5CB, 6CB, 7CB and 8CB were found to be 35·3, 29·0, 42·8 and 39·8°C, respectively, and the S_A–N phase transition for 8CB was 33·8°C. All samples were degassed using the freeze–pump–thaw method, and were sealed under vacuum.

The ^{13}C relaxation measurements were made at 22·63 MHz 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 [14]. 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.

4. Results and discussion

Typical ^{13}C N.M.R. spectra of the aromatic region of 5O·7 in the isotropic, N, S_A, S_C, S_B and S_G phases, along with line assignments and a carbon numbering diagram, are given in figure 1. The diagram is based on X-ray data for the homologue 4O·8 [15] and shows the second molecule of the unit cell projected on a plane whose axes are the two larger principal axes of the molecule in the solid phase. Line assignments are based on carbon-13 studies of the homologues MBBA-d_1 [16] and 5O·7-d_1 [17]. The protonated aromatic carbon lines remain resolved in all four phases. The lines C7 and C8 correspond to Dong's aniline deuterium lines [3]. That each pair of *meta*-protonated carbons gives a single spectral line is consistent with the assumption that the rings undergo rapid internal rotation independent of the overall motions of the molecule.

Plots of $\log T_{1ZC}$ versus $1/T$ for the protonated aromatic carbons of 5O·7 are shown in figure 2. Straight lines are obtained in the nematic and smectic phases with the slopes in the nematic significantly smaller than in the smectic phases. Activation energies in the nematic and smectic phase are $23{\cdot}2 \pm 6{\cdot}7$ and $41{\cdot}2 \pm 2{\cdot}9\,\mathrm{kJ\,mol^{-1}}$ for the benzilidene ring carbons and $12{\cdot}6 \pm 4{\cdot}6$ and $37{\cdot}7 \pm 1{\cdot}7$ for the aniline ring carbons. The lower relaxation times for the benzilidene ring carbons indicate either slower motions or additional relaxation pathways for this ring.

Our average values for the aniline ^{13}C relaxation times, T_{1ZC}, are shown in figure 3 along with the calculated T_{1ZC} values. The calculated values were obtained using equation (5), and Dong's $\langle P_2 \rangle$, $\langle P_4 \rangle$, $D_\parallel$ and $D_\perp$ data for the deuteriated aniline ring of 5O·7-d_4 with the assumption that the proton–carbon distance r_{CH} is 1·084 Å.

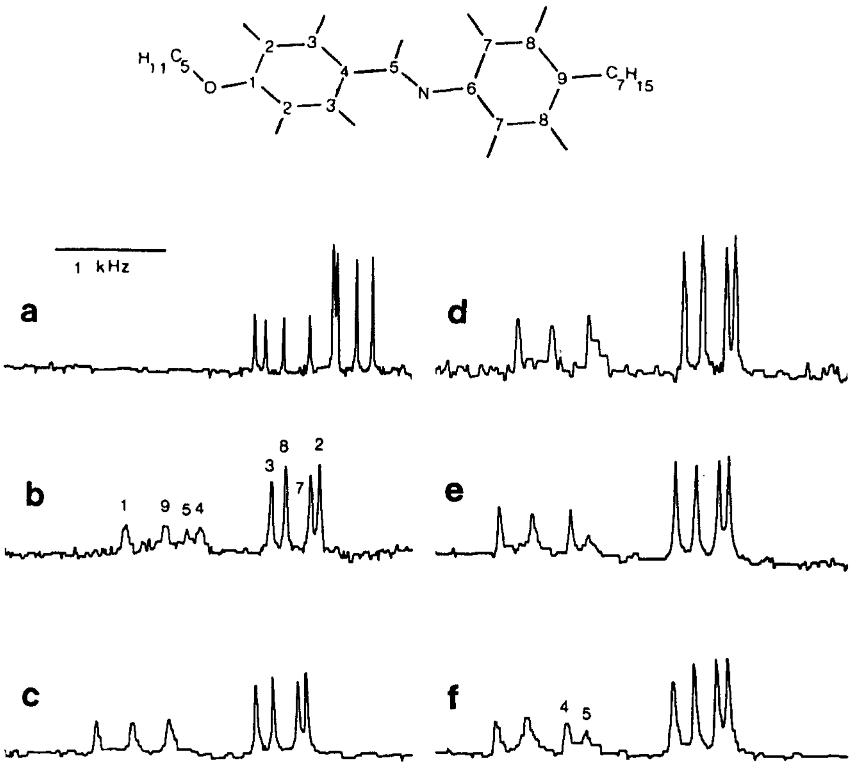

Figure 1. Carbon-13 N.M.R. spectra of the aromatic region of 5O·7. (*a*) Isotropic phase (79·6°C), (*b*) nematic phase (69·6°C), (*c*) smectic A phase (62·3°C), (*d*) smectic C phase (54·0°C), (*e*) smectic B phase (48·4°C) and (*f*) smectic G phase (31·9°C).

Also shown are calculated values of T_{1ZC} for the extreme narrowing approximation where all the $\omega\tau_{pq}$ are set to zero. It can be seen that the extreme narrowing results reproduce the shape of the experimental curve reasonably well, but that the curve for the full expression diverges from this shape in the high temperature end of the nematic region. The divergence between the two calculated curves is considered elsewhere [18].

Using equation (6) Dong [4] has obtained some new but preliminary values for $D_{\parallel}$, $D_{\perp}$ and D_{R}. Using these values we have recalculated the ^{13}C relaxation times which are also shown in figure 3. It can be seen that the magnitude of the ^{13}C relaxation is correctly predicted, but the shape of the curve is suspect.

The ^{13}C N.M.R. spectra and spin–lattice relaxation times of 5CB, 6CB, 7CB and 8CB have been presented previously [5, 6]. 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 average protonated aromatic ^{13}C spin–lattice relaxation times for the *n*CB series are given in figures 4 and 5, along with the values calculated from equation (6)

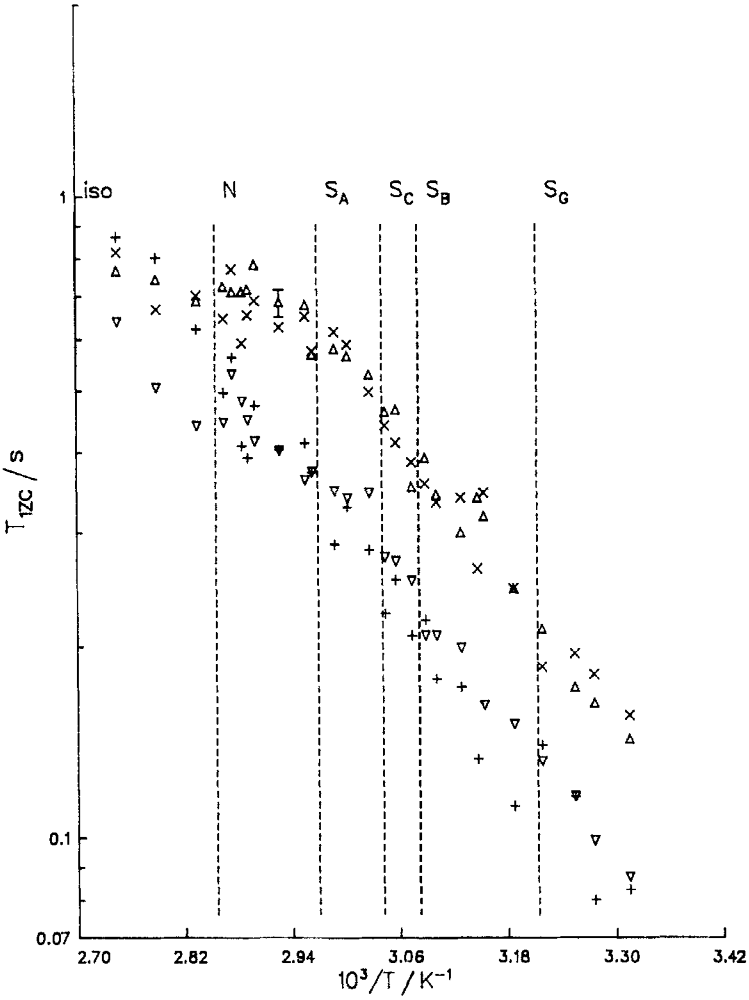

Figure 2. Carbon-13 relaxation times of the protonated carbons of the aromatic rings of 5O·7 versus reciprocal temperature. (▽) C2, (+) C3, (△) C7 and (×) C8.

using $D_\parallel$, $D_\perp$ and D_R obtained by Dong [7] from his analysis of the deuterium relaxation of 5CB. The extreme narrowing results for the *n*CB cases differ by less than 1 per cent and are not shown. The procedure used to extend the 5CB results to the *n*CB series is given below.

The values of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ for 6CB, 7CB and 8CB were found from Dong's $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values for 5CB with the assumption that $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are functions of $(T - T_{NI})$. The appropriate diffusion constants $D_\parallel$, $D_\perp$ and D_R were obtained from

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

where the A_i and E_i were found from Dong's figure 3 [7] and are listed in the table.

Dong's 5CB paper does not lend itself to an estimate of the error in our calculated ^{13}C relaxation times, but it is reasonable to assume that they are similar to those for

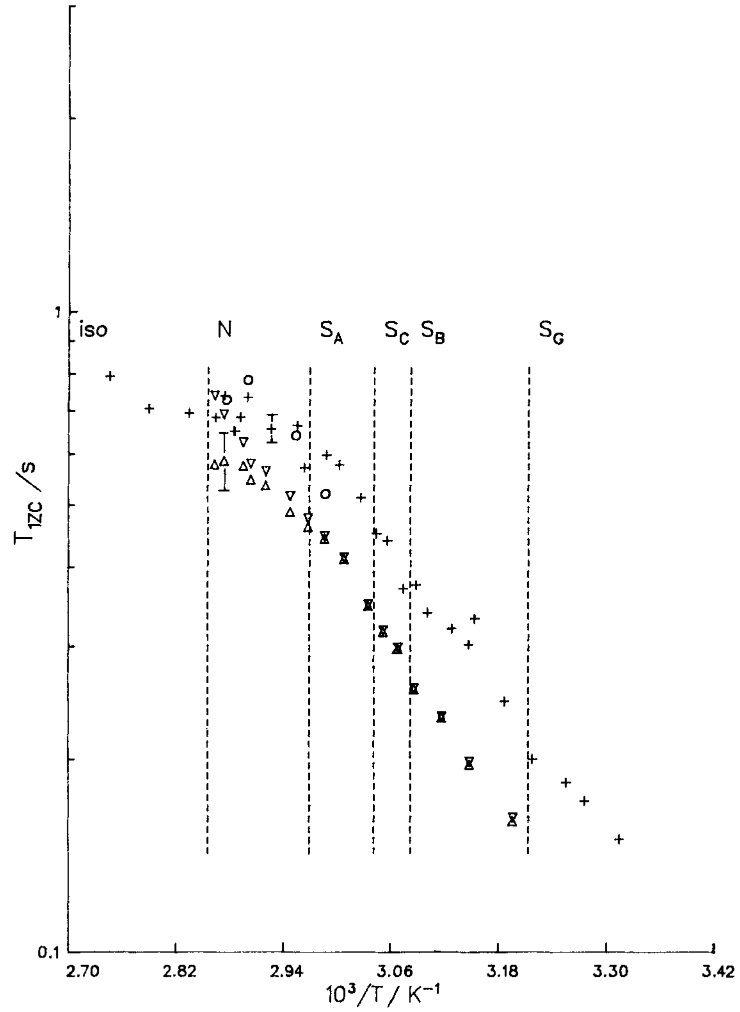

Figure 3. Plots of (+) experimental ^{13}C relaxation times for the 5O·7 aniline ring, (△) extreme narrowing and (▽) full expression calculations versus reciprocal temperature. Calculated values using new diffusion data are indicated by ○.

Parameters used to calculate diffusion constants in *n*CB, using $D_i = A_i \exp(-E_i/T)$.

i	A_i/s^{-1}	E_i/K
$\parallel$	$4{\cdot}86 \times 10^{11}$	1800
$\perp$	$2{\cdot}91 \times 10^{13}$	3870
R	$3{\cdot}06 \times 10^{23}$	10 120

5O·7, i.e. twice the experimental error. If this estimate is accepted, then the agreement between the calculated and experimental values for the *n*CB ^{13}C spin–lattice relaxation times is in fact satisfactory for the case of the protonated aromatic sites, and thus the theory must be regarded as giving a satisfactory description of both deuterium and carbon-13 relaxation of the aromatic rings of the *n*CB series. The extension of this analysis to protonated chain carbons, as well as the

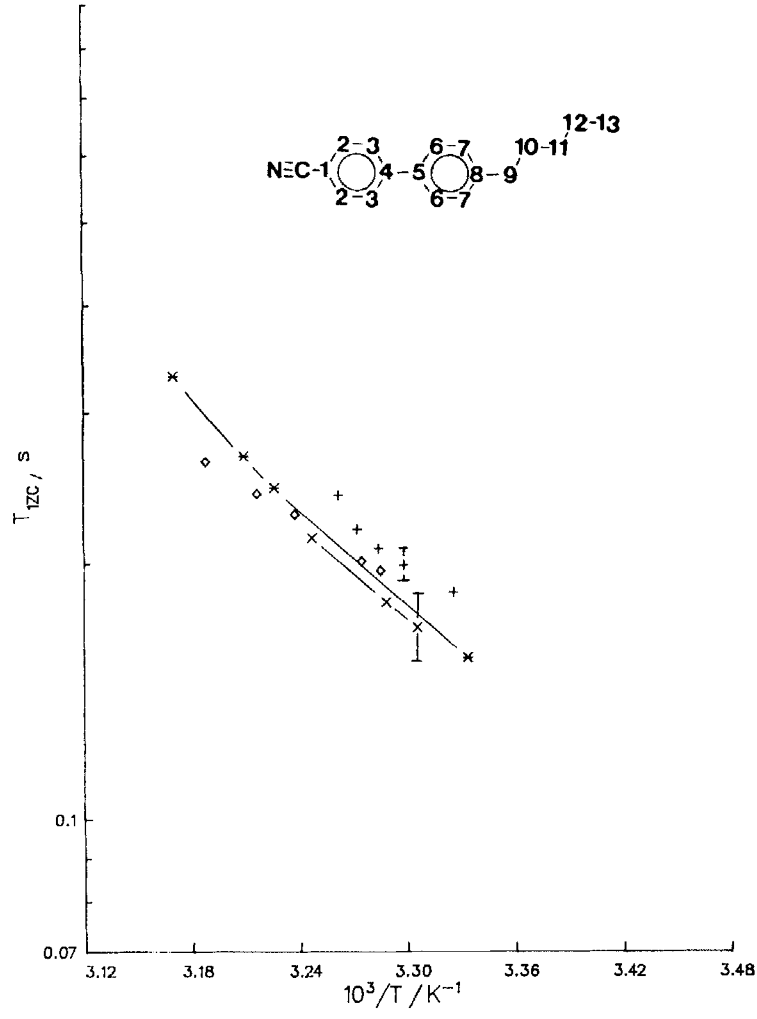

Figure 4. Plots of the experimental ^{13}C spin–lattice relaxation times for the protonated ring carbons of (+) 5CB and (◇) 7CB versus reciprocal temperature. Calculated values for (x) 5CB and (∗) 7CB are indicated. The hydrogen atoms are omitted for clarity. Lines are drawn through calculated values to aid the eye.

possible effects of order director fluctuations on ^{13}C relaxation, will be considered in a future paper.

We now consider the relaxation of the unprotonated carbons, specifically C1 and C5. As all carbons in an aromatic ring are part of a reasonably rigid subunit of an otherwise 'floppy' molecule, it is reasonable to assume that the motions causing the relaxation of the unprotonated aromatic ring carbons will be the same as the motions causing the relaxation of the protonated ring carbons. Of course, the ways in which these motions affect the relaxation may and do differ appreciably. We take as a starting point the approach of Wittebort *et al.* [8], which is to assume that the unprotonated carbons are relaxed by two pathways: (*a*) by dipole–dipole interactions with nearby protons on the same molecule and (*b*) by the chemical shift anisotropy mechanism. We assume that the primary intramolecular dipole–dipole interaction of

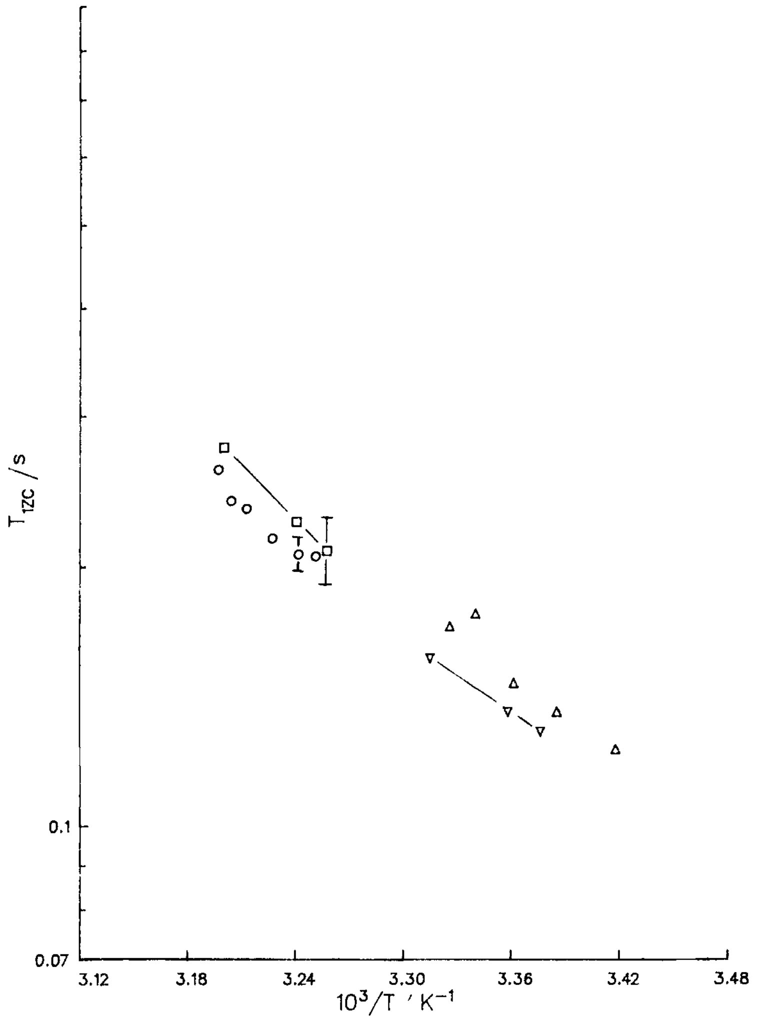

Figure 5. Plots of the experimental ^{13}C spin–lattice relaxation times for the protonated ring carbons of (△) 6CB and (○) 8CB versus reciprocal temperature. Calculated values for (▽) 6CB and (□) 8CB are indicated. Lines are drawn through calculated values to aid the eye.

each unprotonated carbon is with the protons of the two adjacent protonated carbons. Using distances of 1·4 Å [19] and 1·084 Å for the C–C and C–H bonds, respectively, we find r_{CH} to be 2·15 Å and β_{1F} to be 94·1°. The *xx*, *yy* and *zz* components of the chemical shift tensor are given by Wittebort *et al.* as 22, −112 and 90 p.p.m., respectively. The ODF terms were evaluated using the order parameters $\langle P_2 \rangle$ from above, and published values of K [20] and η [21] for the *n*CB series. For D we used the single value $0{\cdot}45 \times 10^6\,cm^2\,s^{-1}$ as suggested by Dong [7]. The calculated relaxation times of the unprotonated ring carbons are given in figures 6 and 7. The calculated AFs chemical shift anisotropy is about one-third of the calculated AFs dipole–dipole interaction and so is a significant source of relaxation for unprotonated carbons even at the relatively low frequencies used in the present work. The ODF chemical shift anisotropy is about three times as large as the ODF dipole–dipole

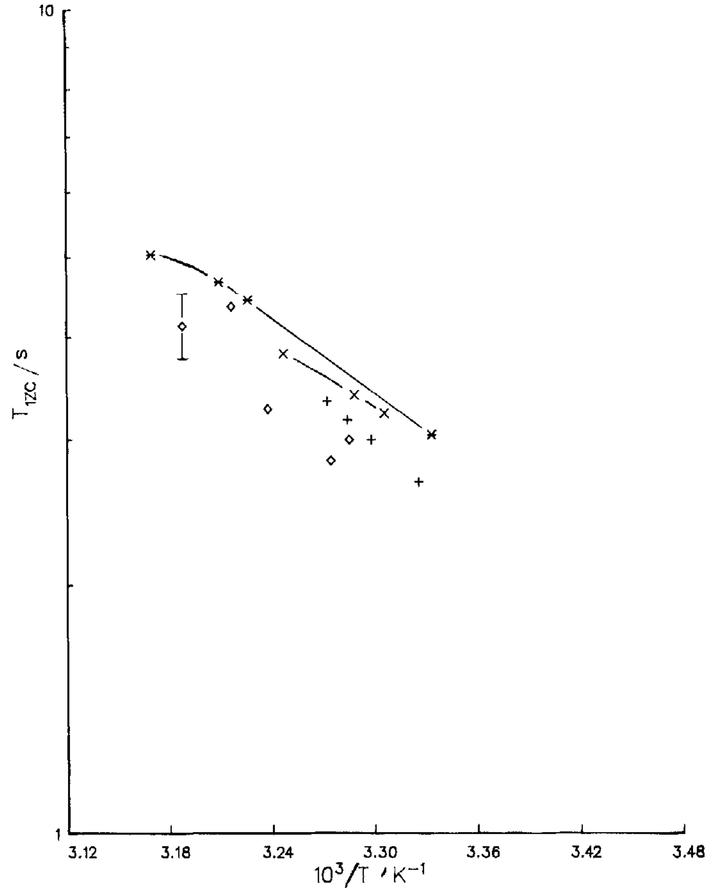

Figure 6. Plots of the experimental ^{13}C spin-lattice relaxation times for the unprotonated ring carbons of (+) 5CB and (◇) 7CB versus reciprocal temperature. Calculated values for (x) 5CB and (*) 7CB are indicated. Lines are drawn through calculated values to aid the eye.

term. In general the total AFs contribution is between one and two times the total ODF contribution. With the exception of 8CB, the calculated and experimental relaxation times of the unprotonated ^{13}C agree within the error. We suggest that the difficulty with 8CB is perhaps due to the onset of the smectic phase, and we note that the divergence of the average elastic constant K [20] is in the wrong sense to explain the relaxation times of the unprotonated ring carbons in 8CB.

5. Conclusions

The ^{13}C spin–lattice relaxation times of the protonated aniline ring carbons of 5O·7 and of the protonated ring carbons of the *n*CB series have been analysed using the results of deuterium relaxation. The agreement between experiment and theory appears satisfactory. The ^{13}C spin–lattice relaxation times of the unprotonated ring carbons of the *n*CB series have also been analysed but in the manner of Wittebort *et al.* With the exception of 8CB, the agreement between experimental and theory is also satisfactory.

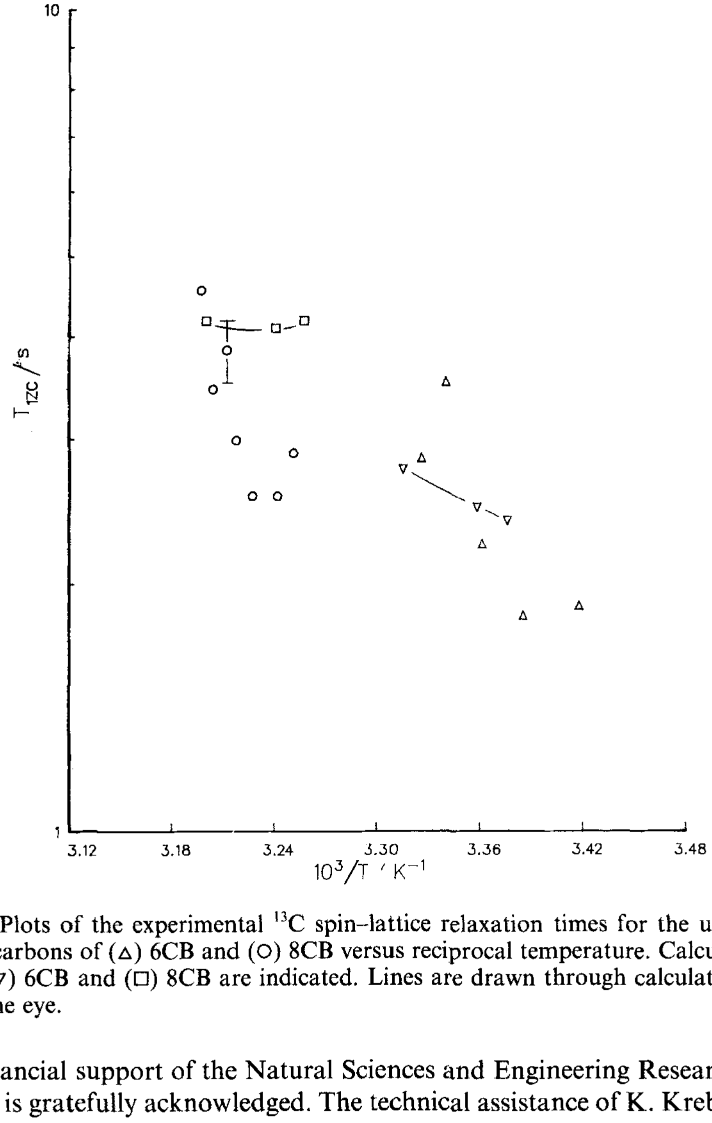

Figure 7. Plots of the experimental ^{13}C spin–lattice relaxation times for the unprotonated ring carbons of (△) 6CB and (○) 8CB versus reciprocal temperature. Calculated values for (▽) 6CB and (□) 8CB are indicated. Lines are drawn through calculated values to aid the eye.

The financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. The technical assistance of K. Krebs is greatly appreciated. We also thank Dr R. Y. Dong of Brandon University for many valuable discussions.

References

[1] Doane, J. W., 1979, *Magnetic Resonance Studies of Phase Transitions*, edited by F. J. Owens, C. P. Poole, Jr and H. A. Farach (Academic Press), p. 171.

[2] Vold, R. R., 1985, *Nuclear Magnetic Resonance of Liquid Crystals*, edited by J. W. Emsley (D. Reidel), p. 280.

[3] Dong, R. Y., 1986 *Molec. Crystals liq. Crystals*, **141**, 349.

[4] Dong, R. Y. (private communication).

[5] Lewis, J. S., Peeling, J., Tomchuk, E., Danchura, W., Bozek, J., Hutton, H. M., and Bock, E., 1987, *Molec. Crystals liq. Crystals*, **144**, 57.

[6] Bozek, J., Hutton, H. M., Lewis, J. S., Tomchuk, E., and Bock, E., 1985, *Molec. Crystals liq. Crystals*, **122**, 191.

[7] Dong, R. Y., 1988, *J. chem. Phys.*, **88**, 3962. We thank Dr Dong for a preprint of this paper.

[8] WITTEBORT, R. J., SUBRAMANIAN, R., KULSHRESHTHA, N. P., and DUPRE, D. B., 1985, *J. chem. Phys.*, **83**, 2457.
[9] VOLD, R. L., DICKERSKON, W. H., and VOLD, R. R., 1981, *J. magn. Reson.*, **43**, 213.
[10] ABRAGAM, A., 1961, *The Principles of Nuclear Magnetism* (Oxford University Press), p. 295.
[11] FREED, J. H., 1977, *J. chem. Phys.*, **66**, 4183.
[12] LYERLA, J. R., JR, and LEVY, G. C., 1974, *Topics in Carbon-13 NMR Spectroscopy*, Vol. 1, edited by G. C. Levy (Wiley), p. 79.
[13] NORDIO, P. L., and SEGRE, V., 1979, *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic Press), p. 411.
[14] LEWIS, J. S., TOMCHUK, E., and BOCK, E., 1988, *J. magn. Reson.*, **78**, 321.
[15] LEADBETTER, A. J., and MAZID, M. A., 1981, *Molec. Crystals liq. Crystals*, **65**, 265.
[16] HÖHENER, A., MÜLLER, L., and ERNST, R. R., 1979, *Molec. Phys.*, **38**, 909.
[17] LEWIS, J., CHAN, P., TOMCHUK, E., and BOCK, E. (to be published).
[18] LEWIS, J., SHAMS, Z., TOMCHUK, E., and BOCK, E. (to be published).
[19] WEAST, R. C. (editor), 1968, *CRC Handbook of Chemistry and Physics*, 49th edition (The Chemical Rubber Co.), p. F-154.
[20] BRADSHAW, M. J., RAYNES, E. P., BUNNING, J. D., and FABER, T. E., 1985, *J. Phys., Paris*, **46**, 1513.
[21] SIEDLER, L. T. S., HYDE, A. J., PETHRICK, R. A., and LESLIE, F. M., 1983, *Molec. Crystals liq. Crystals*, **90**, 255.