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J. S. Lewis [a] , E. Tomchuk [a] & E. Bock [b]

[a] Department of Physics, University of Winnipeg, Winnipeg, Manitoba, Canada, R3B 2E9

[b] Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, Canada, R3T 2N2

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^{13}C NMR Relaxation and Order in Neat 60CB and 80CB

J. 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

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We have recently considered the dynamics of the re-entrant 60CB/80CB using ^{13}C NMR relaxation,[1] and an analysis[2,3] based on ^{2}H relaxation.[4] Here we investigate the order parameters of neat 60CB and 80CB, as well as the dynamics of these materials, including the effect of chain deuteration on correlation time. The results are compared to those for 6CB and 8CB, and a quantitative assessment of the differences in motion is made. An attempt is also made to relate these results to the structure and dynamics of 60CB/80CB re-entrants.

Keywords: C-13, relaxation, NMR, 60CB, 80CB

INTRODUCTION

Nematic liquid crystals lack long range translational order, and on a macroscopic scale are fluids. Smectic liquid crystals possess long range translational order in at least one dimension, and on a macroscopic level are soap-like solids. The reentrant nematic (RN) phase, discovered by Cladis[5] in 1975, occurs at a temperature below the smectic (S) phase, and thus appears to violate the intuitive view of the relationship between conventional solid/fluid transitions and temperature changes, and so it is not surprising that a great deal of experimental and theoretical work has been devoted to such materials.[6]

Nuclear magnetic resonance (NMR) studies of static and dynamic properties of reentrant liquid crystals have proven particularly puzzling.[7–12] We have recently[1] studied the reentrant mixture 60CB/80CB by measuring the carbon-13 spin-lattice relaxation times of the protonated ring carbons of octyloxycyanobiphenyl (80CB) in a 26 wt% mixture of perdeuterated hexyloxycyanobiphenyl (60CB-d_{21}) in 80CB. It has been suggested[13] that a carbon-13 study of the individual 60CB and 80CB components of this reentrant might be of use in interpreting the carbon-13 study of the 60CB/80CB mixtures and this suggestion is pursued in the present work. In

previous works[2,3] we have been concerned that deuterated and undeuterated liquid crystals may have differing relaxation properties. In general deuterated and undeuterated species will have differing relaxation and spectral properties due to spin, but the concern here is with the spatial dynamic properties. With this in mind, we briefly consider the carbon-13 spectra and relaxation of the protonated core of the chain deuterated species 80CB-d_{17}.

The changes of the carbon-13 spectra of mesogens as a function of temperature can be used to provide some insight into changes in the order parameter with temperature, but for reasons given previously[14] no attempt will be made here to quantify these.

EXPERIMENTAL

The 80CB and 60CB samples were purchased from BDH Chemicals Canada, Ltd., and used without further purification. The 80CB-d_{17} sample was purchased from Merck Sharp and Dohme Canada Ltd. and used without further purification. The samples were placed in 7.5 mm o.d. NMR tubes and degassed. The sample tubes were glued in 10 mm o.d. NMR tubes which were in turn held in a holder which prevented sample rotation. The space between the tubes was filled with D_2O, and the temperature of this bath monitored with a copper-constantan thermocouple inserted before and after experiments. The temperatures of the bath were maintained by a nitrogen gas flow system with a resulting temperature gradient of less than 0.5°C across the sample.

The carbon-13 spin-lattice relaxation measurements were performed on a Bruker SXP 4-100 MHz spectrometer interfaced to a Nicolet 1180 computer. The carbon-13 channel operated at 22.632 MHz. The proton decoupler operated at 90 MHz with a B_1 decoupling field of approximately 10 gauss applied only during data acquisition so as to minimize sample heating.[15] All measurements were made without sample spinning, using the inversion recovery technique. All of the magnetization recovery curves appeared to be exponential within experimental error. The estimated error in the relaxation times is about 5%. The chemical shifts were measured with respect to a capillary of DMSO inserted in the bath. At low temperatures a capillary of ethanol was also used. The results are expressed with respect to TMS. All measurements were performed after cooling from the isotropic.

RESULTS AND DISCUSSION

Typical carbon-13 spectra of 80CB are given in Figure 1. The line labelled "REF" is due to a capillary of DMSO placed in the D_2O bath. These spectra are similar to those for 8CB,[16] but because of the oxygen atom the line labelled "d" (originating from the first carbon of the aliphatic tail) is shifted towards the aromatic region and the line labelled "c" (originating from the protonated aromatic carbons closest to the tail) has been shifted towards the aliphatic region. These correspond to lines

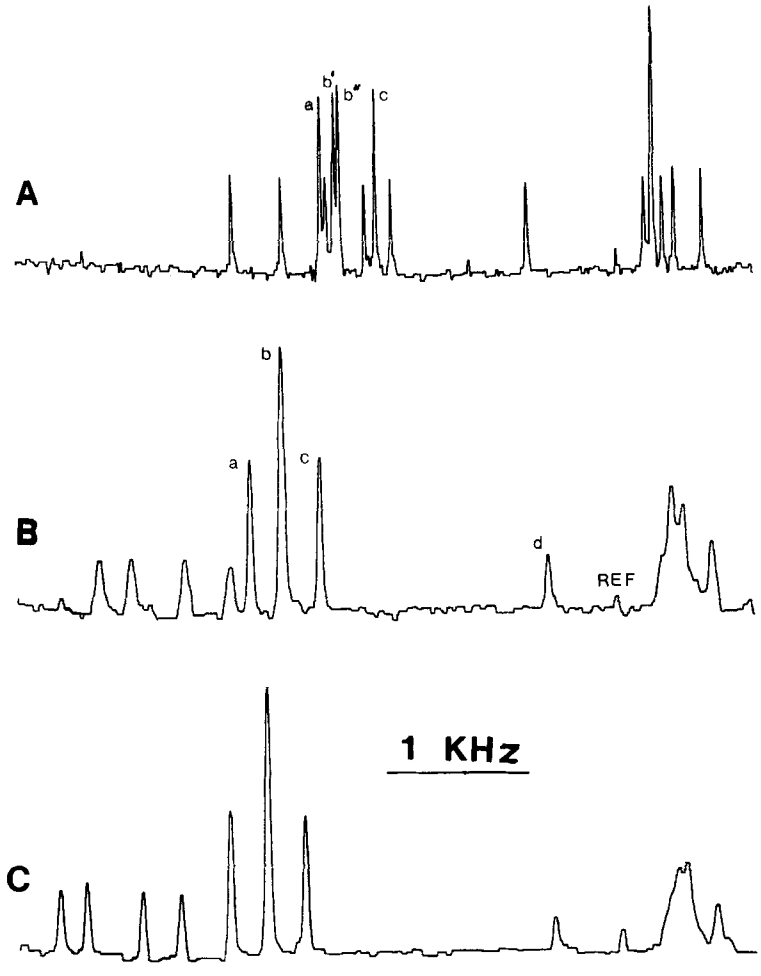

FIGURE 1 Carbon-13 spectra of 80CB. (A) is a spectrum of the isotropic phase at 83.9°C, (B) is a spectrum of the nematic phase at 74.2°C, and (C) is a spectrum of the smectic phase at 60.0°C. The lines originating from the ortho (protonated) aromatic carbon-13 are labelled by their order in the spectra. Labels "d" and "REF" are explained in the text.

9 and 7, respectively, of Reference 16. The effect of the oxygen atom on the unprotonated aromatic carbons is less clear. It appears that a line has shifted towards the aliphatic region, but it is not clear that this line is necessarily due to the carbon directly bonded to the oxygen. Line b can sometimes be resolved into two peaks, but in general our magnetic field homogeneity was not good enough to do this in a consistent manner. The spectra of 60CB are similar to those for 80CB.

Typical spectra for 80CB-d_{17} are shown in Figure 2. The aromatic portion of the isotropic spectra is essentially identical to that for 80CB. The aliphatic portion of the isotropic spectra differs from that of the 80CB because of two effects: (1) the deuterium are not being decoupled, and so the carbon spectra are affected by the

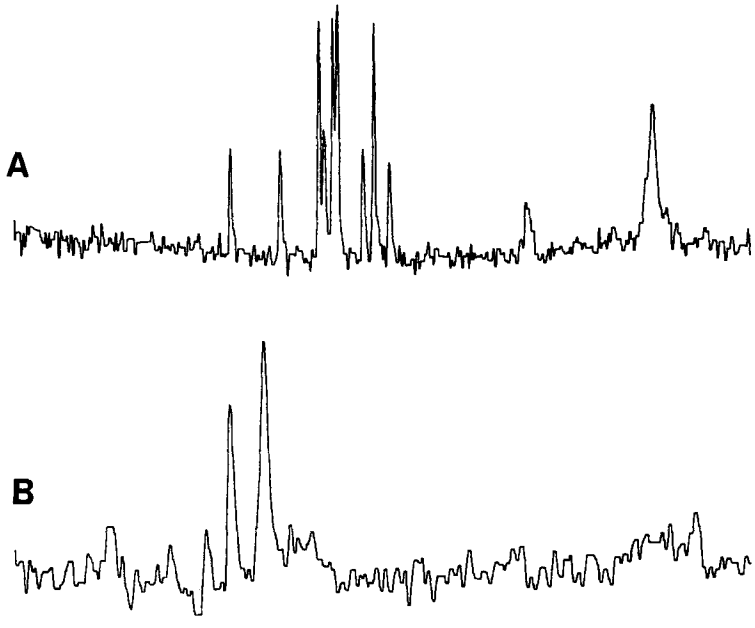

FIGURE 2 Carbon-13 spectra of 80CB-d_{17}. (A) is a spectrum of the isotropic phase at 85.6°C and (B) is a spectrum of the nematic phase at 71.3°C. The spectral width is as in Figure 1.

indirect spin-spin coupling between the carbon and the deuterium which is transmitted via the electrons of the molecules, and (2) the **direct** dipole-dipole interaction between the carbons and the deuterium is much weaker than that between the carbons and the protons and so the relaxation times of the deuterated chain carbons are much longer than those of the protonated chain carbons and consequently the deuterated carbons will be more prone to NMR saturation than the protonated carbons. The nematic phase spectra of 80CB and of 80CB-d_{17} are very different. The **direct** dipole-dipole interactions are no longer averaged to have no effect on the spectra. Moreover the **direct** interactions are much stronger than the **indirect** with the result that the absence of deuterium decoupling is much more severe in the nematic than in the isotropic phase. The aliphatic portion of the nematic phase spectra is now no longer identifiable since split lines may well extend a KHz from the original line position. The aromatic portion of the nematic phase spectra is also affected. It appears that the protonated carbons closest to the tail are being split by **direct** interactions with the deuterons of the tail, while the other protonated carbons are not. We suggest that a possible method of studying tail conformation is with carbon-13 NMR of liquid crystal molecules where only one carbon of the tail is deuterated.

The measured carbon-13 spin-lattice relaxation times for the protonated aromatic carbons for 60CB and for 80CB are given in Table I and Table II, respectively. The average relaxation times of the protonated aromatic carbons of 60CB and 80CB are plotted in Figure 3 as a function of reciprocal temperature, along with

TABLE I

Relaxation times in 60CB, with T_1 (sec.) as a function of temperature. Activation energies Ea in KJ/mole

Temp. °C	a	b	c
77.1	0.539	0.538	0.464
76.6	0.511	0.479	0.408
75.8	0.529	0.432	0.396
75.1	0.545	0.431	0.388
73.2	0.457	0.386	0.373
71.8	0.409	0.391	0.360
68.7	0.414	0.368	0.333
65.8	0.392	0.330	0.314
62.8	0.341	0.308	0.284
60.4	0.302	0.289	0.268
58.5	0.278	0.270	0.244
56.6	0.270	0.245	0.235
54.7	0.245	0.234	0.231
50.4	0.212	0.194	0.191
Ea	32.9	30.6	27.3
	±1.2	±1.4	±0.9

the corresponding average relaxation times of 80CB in a re-entrant mixture of 26 wt% of 60CB-d_{21} in 80CB.[1] It can be seen that any difference between the re-entrant 80CB and pure 80CB results is minor, and that the change in behavior of the relaxation times between the nematic and smectic phases of the pure 80CB is not great. The 60CB results are slightly larger at the higher temperature end of the graph. Indeed, if the averaged relaxation times are plotted versus $T\text{-}T_{NI}$, with the appropriate T_{NI} for each sample (78, 79 and 76.6°C for our particular re-entrant, 80CB, and 60CB samples) then the 60CB relaxation times merge very well with those of the other two samples.

The relaxation data for 80CB-d_{17} will not be given here, but we note that the ^{13}C spin-lattice relaxation times of 80CB-d_{17} are similar to those for 80CB. This suggests that the motions causing relaxation in the aromatic core of 80CB are not highly correlated with motions of the tail. This is consistent with the similarity between our 60CB and 80CB results.

It should be noted that we are dealing with three very different mesogenic states.

TABLE II

Relaxation times in 80CB, with T_1 (sec.) as a function of temperature. Activation energies Ea in KJ/mole

Temp. °C	a	b	c
78.9	0.515	0.474	0.473
77.7	0.550	0.422	0.355
76.5	0.517	0.435	0.438
75.1	0.414	0.419	0.370
73.0	0.411	0.392	0.346
70.7	0.386	0.360	0.318
68.2	0.352	0.348	0.307
Ea*	38.1	28.1	39.2
(nem.)	±8.1	±2.0	±6.7
63.5	0.302	0.287	0.280
61.4	0.283	0.281	0.257
59.2	0.266	0.249	0.239
57.5	0.252	0.236	0.215
55.6	0.228	0.233	0.218
Ea	31.5	27.7	31.7
(smec.)	±1.9	±3.3	±3.8
Ea*	32.4	29.9	28.9
(nem. & smec.)	±1.7	±0.8	±1.8

* Values at 78.9°C and 77.7°C excluded from activation energy calculation.

The 60CB is a nematic, the 80CB is a nematic at high temperatures and a smectic at lower temperatures (T_{NS} of about 66.5°C), and the re-entrant is a nematic in the temperature range considered here (N/S_A and S_A/RN transitions at approximately 46° and 28°C). We should note that the relaxation times of the re-entrant at lower temperatures does reflect the existence of phase transitions. The conclusion appears to be that, as far as the carbon-13 spin-lattice relaxation times of the protonated ring carbons is concerned, all three, the pure 80CB, the re-entrant 80CB, and the pure 60CB are identical. Presumably all three have similar molecular dynamics.

The situation is different for the case of the related molecules 6CB and 8CB.[14,16]

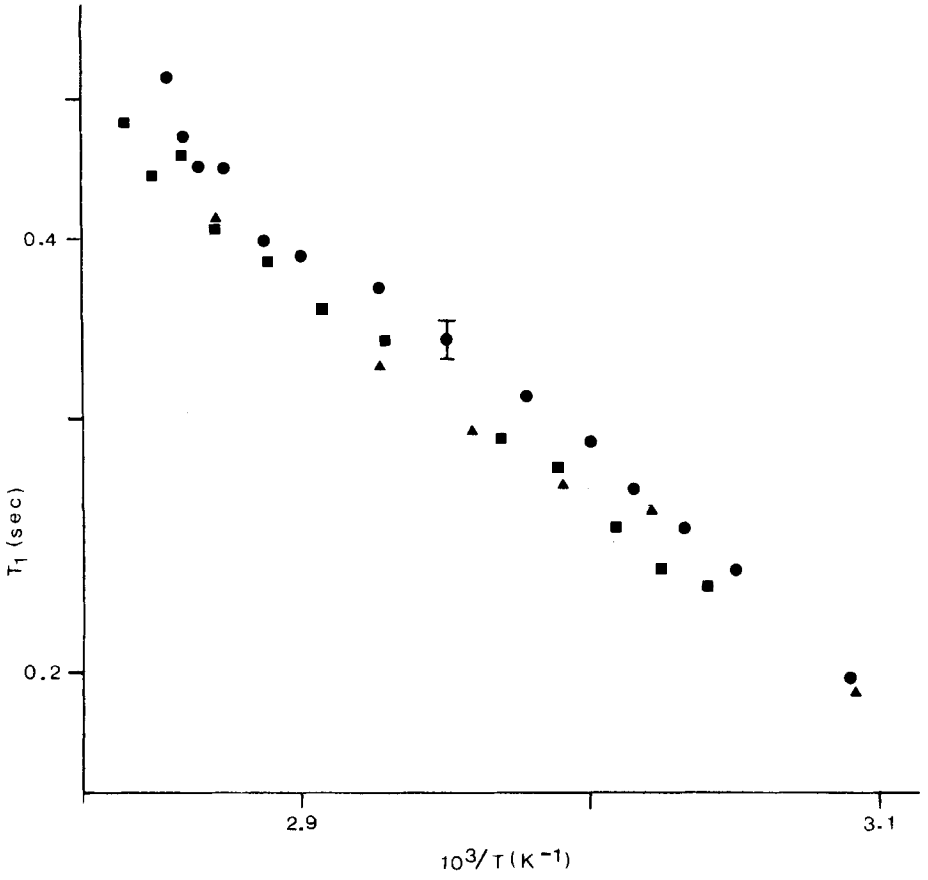

FIGURE 3 Plots of the average carbon-13 spin-lattice relaxation times of the protonated ring carbons of 60CB (●), 80CB (■), and of the 80CB of the reentrant 60CB-d_{21}/80CB (▲) versus reciprocal temperature.

The protonated aromatic carbon-13 spin-lattice relaxation times of 6CB and 8CB have similar activation energies, but even if the difference in clearing temperatures is taken into consideration (see Figures 12 and 13 of Reference 14) the magnitudes differ by about 20 to 30%. On the other hand, the protonated aromatic relaxation times of the nematic and smectic phases of 8CB appear to be continuous and in this sense the behavior resembles that of 80CB.

These results suggest that similar dynamical behavior of 60CB and 80CB in both the pure and mixed states is related to the formation of a reentrant phase in 60CB/80CB mixtures while dissimilar behavior of neat 6CB and neat 8CB prevents the formation of a reentrant phase in mixtures of these molecules.

The chemical shifts for the ortho protonated aromatic carbon-13 lines of 60CB and 80CB are given in Table III and Table IV, respectively. The difference between

TABLE III

Chemical shifts (ppm with respect to TMS) for ortho aromatic lines of 60CB. (estimated error ±0.1 ppm)

Temp. °C	a	b	c
79.6	132.4	128.0	115.3
		126.7	
75.8	149.1	140.2	128.8
71.8	154.4	144.9	133.1
68.7	156.2	146.4	134.5
65.8	157.0	146.7	135.0
62.8	158.9	148.1	136.7
60.4	159.1	148.3	136.8
58.5	159.9	149.1	137.4
56.6	160.5	149.4	138.0
54.7	160.9	149.9	138.3
50.4	162.0	150.9	139.1

TABLE IV

Chemical shifts (ppm with respect to TMS) for ortho aromatic lines of 80CB (estimated error ±01. ppm)

Temp. °C	a	b	c
83.9	132.3	127.8	115.2
		126.5	
77.7	151.2	142.0	130.3
76.5	152.9	143.5	131.7
74.2	154.4	144.5	132.7
73.0	155.9	145.9	134.2
69.6	157.6	147.0	135.4
67.3	158.5	147.7	136.0
65.2	160.4	149.2	137.5
64.0	160.6	149.3	137.6
63.2	161.3	150.0	138.4
62.0	161.0	149.5	137.8
60.5	162.3	150.8	139.1
60.0	162.3	150.8	139.1
59.2	162.1	150.5	138.8

the average of the protonated ring carbon line positions of the mesogenic (σ_M) and the isotropic (σ_I) phases for 60CB and 80CB are plotted in Figure 4 as a function of T-T_{NI}, where T_{NI} is the clearing temperature of the appropriate mesogen. In the simple case where a mesogen is uniaxial and has a negligible value of S_{xx}-S_{yy}, the plotted $\sigma_M - \sigma_I$ will be proportional to the order parameter S_{zz}.[16] This proportionality constant is difficult to determine but it is clear from the figure that the order behaves in a reasonable way. The order in 80CB is greater than that in 60CB, and the jump in order at the nematic/smectic phase transition of 80CB is clearly demonstrated.

CONCLUSION

The carbon-13 nuclear magnetic spin-lattice relaxation times and chemical shifts in the mesogenic phases of 60CB and 80CB have been measured as a function of temperature. The relaxation measurements have been compared with the corresponding results from the reentrant 60CB/80CB and from the mesogens 6CB and 8CB. Similarities and differences have been considered, in particular the remark-

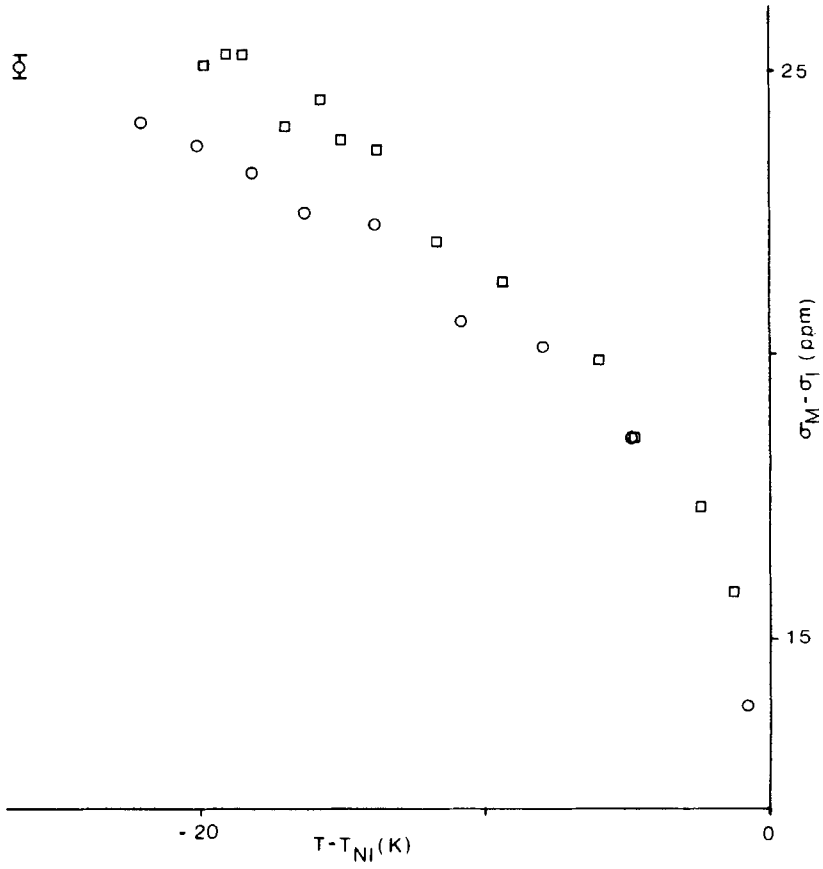

FIGURE 4 Plots of the difference between the average of the protonated ring carbon line positions of the mesogenic (σ_M) and the isotropic (σ_I) phases of 60CB (○) and for 80CB (□) as a function of T-T_{NI}, where T_{NI} is the appropriate clearing temperature.

able unity of 60CB and 80CB dynamic properties both in pure form and in mixture with each other. The usefulness of carbon-13 chemical shifts in monitoring the general order of the materials has been noted.

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