Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Carbon-13 Study of Relaxation and Chemical Shifts in the Smectic Liquid Crystal 8CB

J. Bozek [a], H. M. Hutton [a], J. S. Lewis [b], E. Tomchuk [b] & E. Bock [c]

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

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

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

Version of record first published: 17 Oct 2011.

To cite this article: J. Bozek , H. M. Hutton , J. S. Lewis , E. Tomchuk & E. Bock (1985): Carbon-13 Study of Relaxation and Chemical Shifts in the Smectic Liquid Crystal 8CB, Molecular Crystals and Liquid Crystals, 122:1, 191-203

To link to this article: http://dx.doi.org/10.1080/00268948508074753

Mol. Cryst. Liq. Cryst., 1985, Vol. 122, pp. 191–203
0026-8941/85/1224–0191/0

Printed in the United States of America

Carbon-13 Study of Relaxation and Chemical Shifts in the Smectic Liquid Crystal 8CB†

J. BOZEK, H. M. HUTTON

Department of Chemistry, University of Winnipeg, Winnipeg, Manitoba, R3B 2E9, Canada

J. S. LEWIS, E. TOMCHUK

Department of Physics, University of Winnipeg, Winnipeg, Manitoba, R3B 2E9, Canada

and

E. BOCK

Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, R3T 2N2, Canada

(*Received August 20, 1984*)

The ^{13}C chemical shifts and spin-lattice relaxation times were obtained for all the resolved resonances in the isotropic, nematic, and smectic phases of 8CB. NOE measurements were also obtained for the isotropic phase. A study of these data reveal some inconsistencies with dielectric and deuterium NMR studies, but general agreement with a ^{13}C NMR study of 5CB. Discontinuities in relaxation times at both the nematic/isotropic and smectic/nematic phase transitions are observed for some of the carbon atoms. The difference between the components of the motionally averaged shielding tensor parallel and perpendicular to the long molecular axis is found for both the aromatic carbons and the first carbon of the octyl chain.

†Work supported by the Natural Sciences and Engineering Research Council of Canada.

INTRODUCTION

The ^{13}C chemical shifts and spin-lattice relaxation times were obtained for all the resolved resonances in the isotropic, nematic, and smectic phases of 4-cyano-4'-*n*-octylbiphenyl (8CB). NOE measurements were also obtained for the isotropic phase. The results are compared to our previous ^{13}C NMR results for 5CB,[1] to dielectric studies[2,3] of 5CB and 8CB, and to deuterium NMR studies of 8CB-d_{17}.[4,5,6,7] Using known values of the order parameter together with our measured chemical shifts, we determined the difference in the parallel and perpendicular components of the motionally averaged chemical shift tensor for the aromatic carbons and the inner alkyl carbon of 8CB.

EXPERIMENTAL

The isotropic measurements were performed on a Varian CFT-20 NMR spectrometer with gated proton decoupling. The nematic and smectic measurements were performed on a Bruker SXP-4-100 spectrometer at 22.632 MHz with proton decoupling (H_1 approximately 10 gauss) applied only during data acquisition. All measurements were made without sample spinning. The chemical shifts were measured with respect to benzene and converted to TMS using 128.7 ppm. Relaxation times were measured using the inversion–recovery method. The sample temperatures were controlled using gas flow systems, with a temperature gradient of about 1°C. The sample temperatures were measured using a copper–constantan thermocouple in the absence of decoupling, and rf heating effects were determined by observing the nematic/isotropic transition in the presence of decoupling. The T_1 measurements have an accuracy of about 5% for the protonated carbons and of about 10% for the unprotonated carbons. The accuracy in the NOE measurements is estimated to be about 10%. The 8CB sample was purchased from BDH Chemicals Canada, Ltd., and was found to have a clearing point at about 39.8°C (T_{NI}).

RESULTS AND DISCUSSION

Typical spectra are shown in Figures 1 and 2, and the structure of 8CB is given in Figure 2 where the phenyl and alkyl carbon atoms are

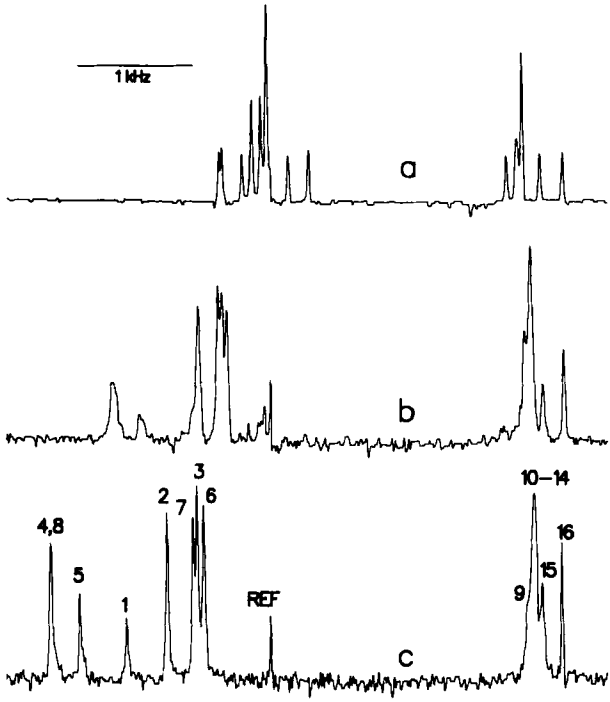
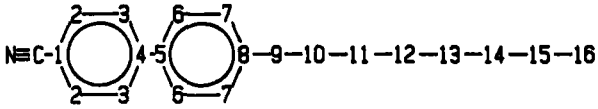


FIGURE 1 Carbon-13 Fourier transform NMR spectra of 8CB recorded on the Bruker SXP-4-100 spectrometer. (a) is a spectrum of isotropic 8CB at 46.5°C, (b) is a spectrum of nematic 8CB at 38.5°C, and (c) is a spectrum of smectic 8CB at 25.0°C. The spectral width is 5200 Hz. Line assignments correspond to the structural carbons, and the unshifted line is an external benzene reference.

numbered and the hydrogen atoms are omitted for clarity. The chemical shift assignments for the aromatic carbons follows from the results for 5CB,[1] while those for the alkyl carbons assume that the chemical shifts decrease along the chain and it is possible that C_{10} and C_{11} should be reversed. Figure 3 compares spectra from a relaxation experiment with vastly different recovery times at a temperature near T_{NI}, and the lack of shifts between the spectra indicates that the temperature is reasonably constant during the actual inversion–recovery sequences.

The spin-lattice relaxation times and apparent activation energies are given in Table I, and plots of $\log T_1$ vs $1/T$ are shown in Figures 4, 5, 6, and 7 for the ortho carbons C_2, C_3, C_6, C_7, "outer" para carbons C_1, C_8, "inner" para carbons C_4, C_5, and the alkyl chain $C_9 \rightarrow C_{16}$, respectively. The relaxation times are shorter than those for 5CB[1] at the same temperature, and the activation energies are in



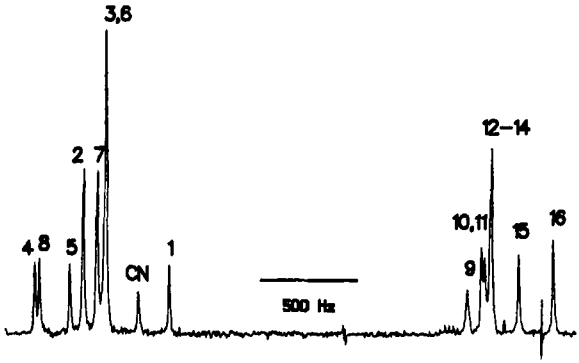


FIGURE 2 Carbon-13 Fourier transform NMR spectra of isotropic 8CB recorded on the Varian CFT-20 spectrometer at 45°C. The spectral width is 3000 Hz. Line assignments correspond to the structural carbons. The structure of 8CB is shown with the carbon atoms numbered and the hydrogen atoms omitted for clarity.

general smaller. This is in contrast to dielectric studies[2] which yield identical activation energies for 5CB and 8CB. In general the carbon relaxation times of the well-resolved resonance lines show a discontinuity at the nematic/isotropic transition temperature, but in some cases the discontinuity is less than the scatter in the relaxation times. C_9, which has a very dramatic discontinuity at the nematic/isotropic transition, also shows a distinct discontinuity at the smectic/nematic transition, and the data suggest a similar discontinuity for C_1 and C_5. Due to overlap of resonances in the nematic and smectic phases, the results for C_4 and C_8, and for C_{10-14}, are of limited significance. The relaxation times for C_{15} and C_{16} show suggestions of discontinuities at the phase transitions, but the data are not good enough to clearly establish such changes. The dielectric relaxation of 8CB[3] does show a distinct change at the smectic/nematic phase transition. The behavior of the 8CB relaxation times at the nematic/isotropic phase transition is in general consistent with that observed in 5CB relaxation times[1] provided that the poorer accuracy (due to low decoupling levels) of the latter results is considered. In particular, the dip in many of the

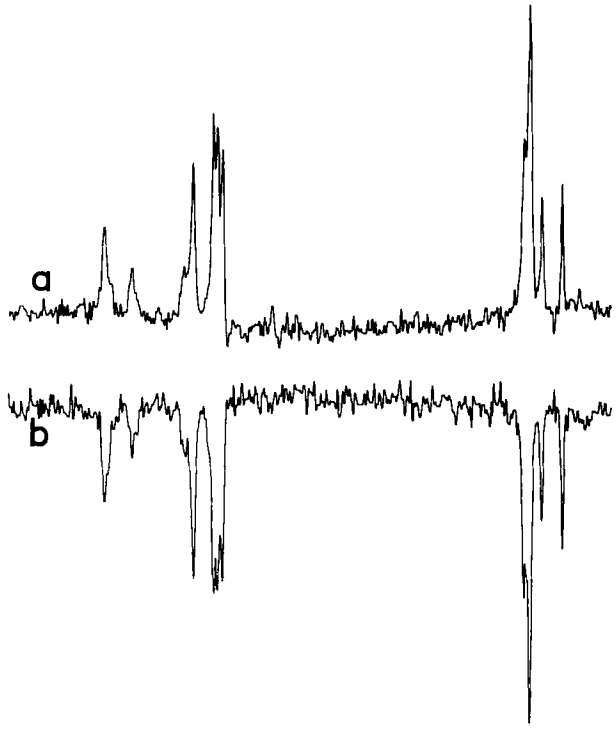


FIGURE 3 Partially relaxed carbon-13 Fourier transform NMR spectra of nematic 8CB at 38.8°C. (a) corresponds to a recovery time of 20 seconds and (b) corresponds to a recovery time of 10 milliseconds.

relaxation times in the isotropic phase near the nematic phase is confirmed, but the 5CB ^{13}C work will have to be investigated further with high power decoupling in the nematic phase before the comparison can be completed.

There is ample evidence to justify the assumption that the protons in the liquid crystal are sufficiently strongly coupled to each other that the relaxation of the (natural abundance) ^{13}C does not affect the protons. Then the ratio of ^{13}C relaxation due to dipole–dipole interaction with bonded ^{1}H, and the ^{2}D relaxation due to quadrupolar interactions of deuterium substituted for the bonded ^{1}H, should depend only on the deuterium quadrupolar coupling constant, the separation of the carbon and proton, and the number of bonded protons. Deuterium NMR T_1's of the alkyl chain of 8CB[4,5] indicate that the variation of relaxation times along the middle of the chain is not great (about 50%), which may explain why the recovery of the

TABLE I

Relaxation in 8CB, with T_1 (sec) as a function of temperature (activation energies in kJ/mol)

Temp.	Para aromatic				Ortho aromatic				
°C	C_1	C_4	C_5	C_8	C_2	C_3	C_6	C_7	CN
21.6	1.91	1.55	2.02	—	0.112	0.110	0.141	0.138	—
22.9	1.88	1.63	2.15	—	0.122	0.128	0.137	0.139	—
23.9	2.12	1.75	2.15	—	0.128	0.128	0.144	0.147	—
24.7	2.42	1.71	2.42	—	0.134	0.138	0.153	0.151	—
25.4	—	—	—	—	0.141	0.142	0.160	0.151	—
27.5	2.87	1.91	2.54	—	0.138	0.145	0.170	0.167	—
29.3	2.49	1.93	2.46	—	0.152	0.163	0.173	0.174	—
30.4	2.57	1.89	2.39	—	0.166	0.168	0.193	0.185	—
31.2	2.36	2.25	2.31	—	0.167	0.171	0.179	0.188	—
31.9	2.49	1.94	2.41	—	0.181	0.182	0.196	0.194	—
33.2	3.24	2.36	3.10	—	0.186	0.189	0.199	0.201	—
34.4	3.08	2.00	2.70	—	0.198	0.202	0.211	0.214	—
35.3	2.41	2.10	2.77	—	0.201	0.201	0.212	0.212	—
36.7	2.59	2.01	2.53	—	0.211	0.216	0.217	0.219	—
37.6	2.91	2.28	3.07	—	—	—	—	—	
38.1	4.07	2.52	3.63	—	0.241	0.226	0.232	0.237	—
38.9	3.74	2.32	3.15	—	0.258	0.228	0.234	0.234	—
39.6	4.49	2.33	4.60	—	0.296	0.238	0.239	0.266	—
E_a (Nem & Smec)	26.1 ± 4.7	16.4 ± 2.1	22.3 ± 4.1		35.6 ± 1.9	30.4 ± 0.9	23.9 ± 0.9	26.1 ± 0.8	
41.0	2.47	2.16	2.16	1.39	0.218	0.229	—	0.217	1.37
42.0	2.11	2.17	2.09	1.27	0.212	0.234	—	0.209	1.45
43.0	2.78	2.65	2.40	1.51	0.231	0.216	—	0.231	1.33
44.0	2.28	1.86	2.04	1.22	0.193	0.196	—	0.166	1.14
45.0	2.55	2.34	2.41	1.32	0.222	0.211	—	0.211	1.47
46.0	2.71	2.68	2.70	1.48	0.222	0.230	—	0.218	1.46
48.0	2.97	2.53	2.58	1.54	0.255	0.261	—	0.252	1.25
50.0	2.60	2.56	3.41	1.73	0.276	0.272	—	0.265	1.44
51.0	2.93	3.06	2.82	1.60	0.268	0.270	—	0.269	1.70
52.0	2.78	2.54	2.96	1.70	0.310	0.305	—	0.277	1.43
53.0	3.48	2.60	2.88	1.91	0.298	0.306	—	0.321	1.42
54.0	3.55	3.18	3.30	1.76	0.316	0.295	—	0.293	1.66
56.0	3.24	2.94	2.94	1.92	0.329	0.329	—	0.308	1.68
58.0	3.84	3.69	3.48	2.34	0.343	0.358	—	0.317	2.10
60.0	3.16	2.94	3.03	2.07	0.326	0.354	—	0.323	1.78
62.0	3.55	3.36	3.26	1.82	0.358	0.362	—	0.342	2.18
63.0	3.73	4.07	3.45	2.53	0.470	0.437	—	0.380	2.59
66.0	4.53	3.89	3.79	2.52	0.444	0.432	—	0.394	2.58
71.0	4.70	5.14	5.06	2.44	0.441	0.440	—	0.420	2.69
76.0	5.52	4.52	5.20	2.71	0.505	0.509	—	0.491	3.53
80.0	6.03	5.90	5.21	2.84	0.551	0.519	—	0.527	3.21
E_a (Isotropic)	21.8 ± 1.6	22.7 ± 2.0	21.3 ± 1.7	19.9 ± 1.7	24.5 ± 1.4	23.4 ± 1.3		23.4 ± 1.5	24.8 ± 2.1

Temp.	*n*-octyl chain					
°C	C_9	C_{10}	C_{11}	C_{12-14}	C_{15}	C_{16}
21.6	0.275	—	—	0.172	0.474	1.49
22.9	0.292	—	—	0.191	0.510	1.49
23.9	0.296	—	—	0.192	0.484	1.68
24.7	0.274	—	—	0.205	0.369	1.58
25.4	0.339	—	—	0.195	0.496	—
27.5	0.363	—	—	0.207	0.512	1.61
29.3	0.334	—	—	0.215	0.587	1.78
30.4	0.360	—	—	0.225	0.508	1.84
31.2	0.342	—	—	0.234	0.521	2.07
31.9	0.354	—	—	0.227	0.646	2.05
33.2	0.357	—	—	0.239	0.596	2.03
34.4	0.354	—	—	0.240	0.641	2.06
35.3	0.356	—	—	0.240	0.669	2.02
36.7	0.320	—	—	0.246	0.668	1.89
37.6	—	—	—	—	—	2.16
38.1	0.347	—	—	0.267	0.728	2.41
38.9	0.339	—	—	0.260	0.668	2.31
39.6	0.340	—	—	0.262	0.546	2.31
E_a (Nematic)	− 5.9 ± 6.9					
E_a (Smectic)	17.4 ± 3.8					
E_a (Nem & Smec)		—	—	16.2 ± 0.9	17.6 ± 3.7	18.7 ± 1.9
41.0	0.121	0.518	0.205	0.247	0.737	2.24
42.0	0.113	0.420	0.206	0.259	0.752	2.15
43.0	0.117	0.474	0.214	0.280	0.761	2.21
44.0	0.122	0.444	0.193	0.266	0.709	2.01
45.0	0.118	0.438	0.215	0.259	0.773	2.06
46.0	0.144	0.473	0.255	0.279	0.849	2.18
48.0	0.142	0.502	0.226	0.287	0.770	2.54
50.0	0.136	0.559	0.271	0.301	0.897	2.73
51.0	0.150	0.497	0.260	0.293	0.875	2.66
52.0	—	0.523	0.286	0.351	0.960	2.76
53.0	0.155	0.665	0.284	0.329	0.937	2.83
54.0	0.146	0.552	0.282	0.309	0.882	2.81
56.0	0.148	0.598	0.287	0.354	1.01	2.94
58.0	0.157	0.571	0.318	0.363	1.13	3.36
60.0	0.139	0.638	0.290	0.352	1.00	3.07
62.0	0.151	0.699	0.329	0.362	1.22	3.32
63.0	0.189	0.839	0.367	0.407	1.31	3.70
66.0	0.192	0.839	0.359	0.449	1.29	3.92
71.0	0.185	0.713	0.388	0.451	1.54	3.85
76.0	0.225	0.849	0.412	0.520	1.57	4.11
80.0	0.239	1.04	0.458	0.582	1.89	4.30
E_a (Isotropic)	15.9 ± 1.4	19.1 ± 1.8	19.5 ± 1.1	19.1 ± 0.9	22.4 ± 1.1	18.9 ± 1.2

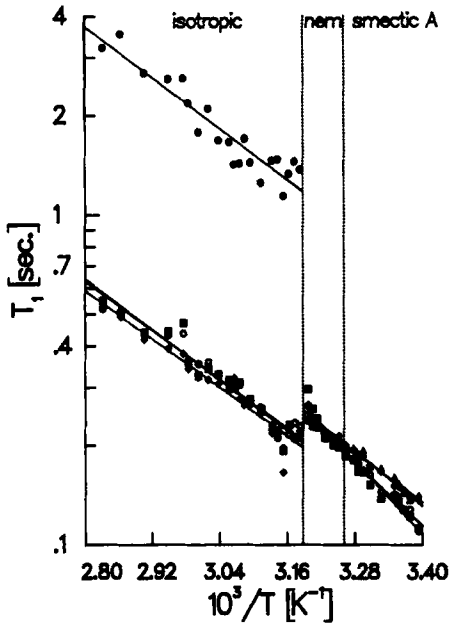


FIGURE 4 The temperature dependence of ^{13}C T_1's in the isotropic, nematic, and smectic phases of 8CB. The C_2, C_3, C_6, and C_7 ortho aromatic carbons are indicated by ■, ○, △, and ◊, respectively, and C ≡ N by ●. The straight lines represent the least square fit of the data.

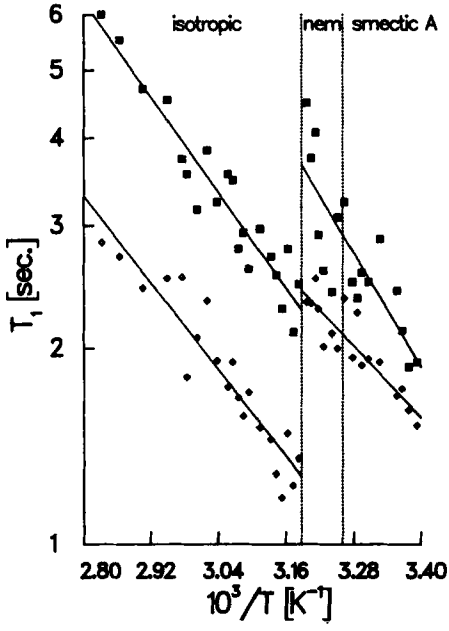


FIGURE 5 The temperature dependence of C_1 (■) and C_8 (◊) para ^{13}C T_1's of 8CB.

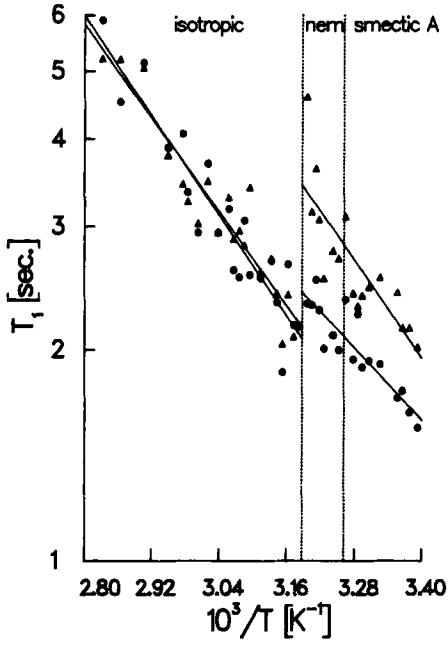


FIGURE 6 The temperature dependence of C_4 (●) and C_5 (△) para ^{13}C T_1's of 8CB.

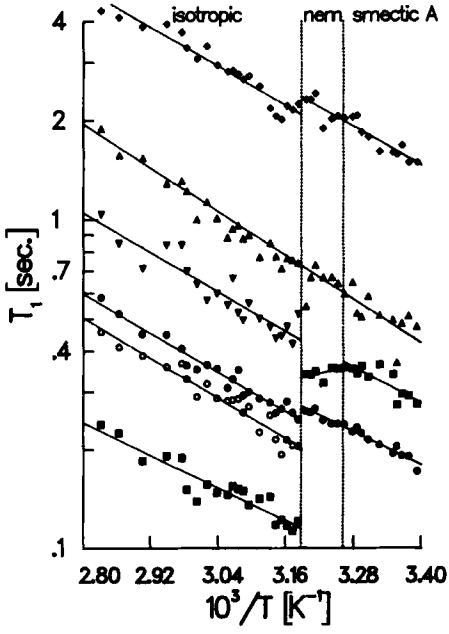


FIGURE 7 The temperature dependence of the octyl ^{13}C T_1's of 8CB. The C_9, C_{10}, C_{11}, and C_{12-14}, C_{15}, and C_{16} are indicated by ■, ○, ●, ▽, △, ◇, respectively.

TABLE II

NOE of 8CB in the isotropic liquid state at 76°C

n-octyl chain						
C_9	C_{10}	C_{11}	C_{12-14}	C_{15}	C_{16}	$C \equiv N$
2.36	2.56	2.48	2.58	2.54	2.42	3.00
ortho			para			
C_2	$C_{3,6}$	C_7	C_1	C_4	C_5	C_8
2.76	2.61	3.01	2.36	2.41	2.35	2.36

broad peak encompassing C_{10-14} appears to be well described by a single exponential. If the deuterium relaxation times[4] are divided into the product of the carbon relaxation times and the number of attached protons (at a particular site in the alkyl chain), the result is about 2×10^1 except for site 15 which yields about 4×10^1; the reason for the apparent anomaly at site 15 is not clear.

The NOE's were measured, and the results are given in Table II. The dipolar contribution to the relaxation times was calculated for 76°C using

$$1/T_{1d} = (\text{NOE} - 1)/(1.988 \times T_1),$$

and the results are plotted in Figure 8 as a function of carbon number (with the methyl result corrected by a factor of 3/2). The results are consistent with those obtained for 5CB.[1] Again it should be noted that C_{10} and C_{11} may be interchanged.

The chemical shifts, in ppm from TMS, are given in Figures 9 and 10. Within experimental error no change with transition was found in the isotropic phase, and the results are consistent with those for 5CB. The difference between the observed mesogenic chemical shift, σ_M, and isotropic chemical shift, σ_i, can be written as

$$\sigma_M - \sigma_i = (2/3)S(\bar{\sigma}_{\parallel} - \bar{\sigma}_{\perp})$$

where S is the order parameter and $\bar{\sigma}_{\parallel}$ and $\bar{\sigma}_{\perp}$ are the components of the motionally averaged tensor parallel and perpendicular to the long molecular axis. The order parameter S was taken from the work of Horn,[9] and the resulting values of $(\bar{\sigma}_{\parallel} - \bar{\sigma}_{\perp})$ for the aromatic carbons are given in Table III. The correlation coefficients found for these cases were all greater than 0.96. In the absence of a temperature dependence study of the order tensor for the two halves of the aromatic core, the above expression is the only practical one, but

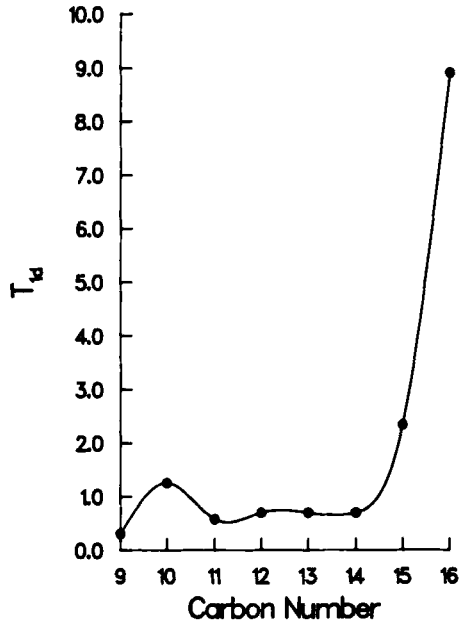


FIGURE 8 Plot of the *n*-octyl chain ^{13}C T_{1d} vs carbon number at 76°C. The T_{1d} for C_{16} is 3/2 times the observed value.

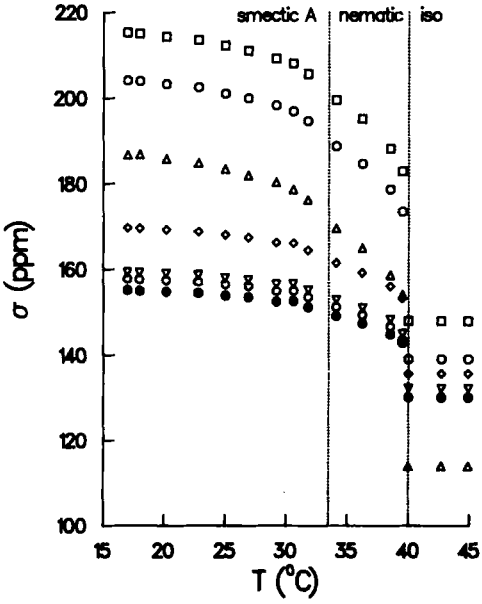


FIGURE 9 The temperature dependence of aromatic ^{13}C line positions in 8CB. Chemical shifts are given with respect to TMS. The C_1, C_2, C_3, $C_{4,8}$, C_5, C_6, and C_7 are indicated by △, ◇, ○, □, , ●, and ▽, respectively.

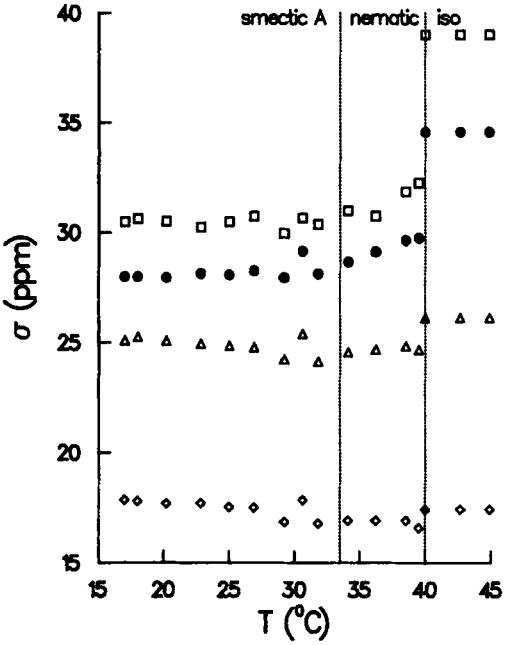


FIGURE 10 The temperature dependence of octyl ^{13}C line positions in 8CB. Chemical shifts are given with respect to TMS. The C_9, C_{10-14}, C_{15}, and C_{16} are indicated by ◇, △, ●, and □, respectively.

TABLE III

Calculated values of $(\bar{\sigma}_{\parallel} - \bar{\sigma}_{\perp})$ for the aromatic carbons of 8CB

Carbon	$(\bar{\sigma}_{\parallel} - \bar{\sigma}_{\perp})$ (ppm)	Type
$C_{4,8}$	181 ± 11	para
C_5	171 ± 12	para
C_1	185 ± 14	para
C_2	91 ± 6	ortho
C_7	78 ± 4	ortho
C_3	78 ± 5	ortho
C_6	69 ± 5	ortho

since the angle of the ^{13}C symmetry axis is close to that of the magic angle the approximation should be a good one.[6]

The ordering of the alkyl tail has been considered by Emsley[6] and Luckhurst.[7] The order parameters are given for three temperatures,[6] and for C_9 use of these with the above expression yields $(\bar{\alpha}_{\parallel} - \bar{\sigma}_{\perp}) = -16 \pm 3$ ppm with a correlation coefficient of 0.96, a result that is consistent with the results for the methylene carbons in hexaethyl

benzene.[10] The correlation between the chemicals shifts of C_{15} and the order parameter was less than 0.2, but this may be due to the very small shifts involved and to the partial overlap with C_{11-14}.

CONCLUSION

The temperature dependence of the ^{13}C NMR chemical shifts and relaxation times of 8CB have been measured. The results are consistent with a previous ^{13}C NMR study of 5CB, but apparently inconsistent with dielectric relaxation measurements. Comparison with deuterium NMR studies of 8CB allows a plausible determination of $(\bar{\sigma}_{\parallel} - \bar{\sigma}_{\perp})$ for C_9 the first carbon in the alkyl chain, but presents some apparent inconsistencies for both the chemical shifts and the relaxation times of the second last member, C_{15}. We suggest that more extensive temperature dependence studies of deuterium NMR of 8CB and high power decoupled ^{13}C NMR of 5CB would be useful in further evaluation of the present ^{13}C NMR results for 8CB.

References

1. J. S. Lewis, E. Tomchuk, H. M. Hutton, and E. Bock, *J. Chem. Phys.* **78**, 632 (1983).
2. B. R. Ratna and R. Shashidhar, *Mol. Cryst. Liq. Cryst.* **42**, 185 (1977).
3. C. Druon and J. M. Wacrenier, *Amm. Phys. (France)* **3**, 199 (1978).
4. J. W. Emsley, J. C. Lindon, and G. R. Luckhurst, *Molec. Phys.* **32**, 1187 (1976).
5. J. W. Emsley and D. L. Turner, *J. Chem. Soc., Faraday Trans. 2* **77**, 1493 (1981).
6. J. W. Emsley, "Measurement of Orientational Ordering by N.M.R.," presented at the NATO Advanced Institute of NMR of Liquid Crystals, 1983.
7. G. R. Luckhurst, "Molecular Field Theories of Nematics: Rigid and Non-Rigid Molecules," presented at the NATO Advanced Institute of NMR of Liquid Crystals, 1983.
8. A. Pines and J. J. Chang, *Phys. Rev. A* **10**, 946 (1974).
9. R. G. Horn, *J. de Physique* **39**, 105 (1978).
10. M. Mehring, *High Resolution NMR Spectroscopy in Solids*, (Springer-Verlag, Berlin, 1976), p. 185.