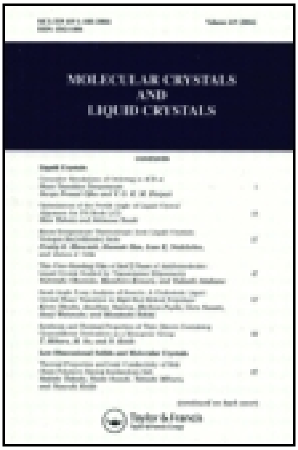

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Carbon-13 Study of Relaxation in the 5CB Homologous Series

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Carbon-13 Study of Relaxation in the 5CB Homologous Series

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The carbon-13 chemical shifts and spin-lattice relaxation times were obtained for all the resolved resonances in the isotropic and nematic phases of 5CB, 6CB, and 7CB. NOE measurements were also obtained for the isotropic phases of 5CB, 6CB, 7CB, and 8CB. These results and those previously obtained by us for 8CB and for the isotropic phase of 5CB, demonstrate that even-odd effects occur for the carbon-13 spin-lattice relaxation times which cannot be explained by the differences in the nematic-isotropic transition temperatures. It is observed that the temperature dependence of the NOE's is significantly different for the protonated and unprotonated aromatic carbons.

Keywords: NMR, liquid crystals, biphenyls, relaxation, homologous, carbon-13

INTRODUCTION

The carbon-13 chemical shifts and spin-lattice relaxation times were measured for all of the resolved resonances in the nematic and isotropic phases of 4-cyano-4′-n-pentylbiphenyl (5CB), 4-cyano-4′-n-

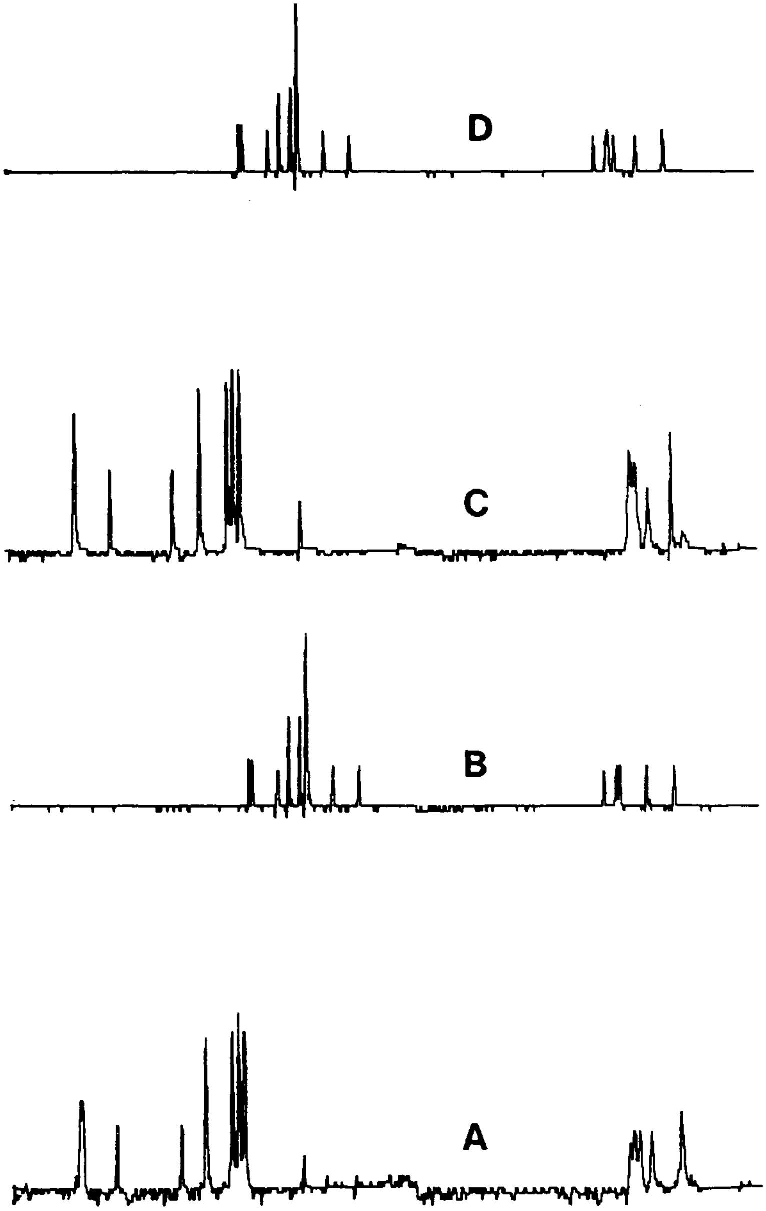

FIGURE 1 Carbon-13 Fourier transform NMR spectra recorded on the Bruker SXP-4-100 spectrometer. (A) is a spectrum of nematic 5CB at 27.6 °C, (B) is a spectrum of isotropic 5CB at 37.5 °C, (C) is a spectrum of nematic 6CB at 17.6 °C, and (D) is a spectrum of isotropic 6CB at 31.2 °C. The spectral width is 5200 Hz. The spectra baseline have been corrected to remove instrumental distortions.

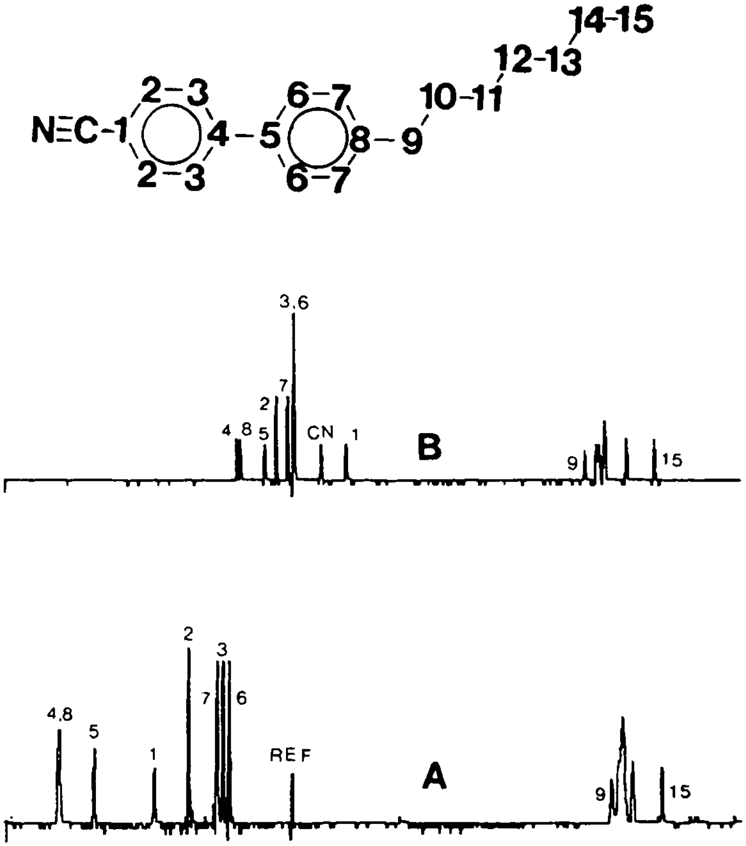

FIGURE 2 Carbon-13 spectra. (A) is a spectrum of nematic 7CB at 32.2 °C, (B) is a spectrum of isotropic 7CB at 44.0 °C, conditions as for Figure 1. The line assignments correspond to the structural carbons. The structure of 7CB is shown with the carbon atoms numbered and the hydrogen atoms omitted for clarity. See text for discussion of assignments of the alkyl spectra lines.

hexylbiphenyl (6CB), and 4-cyano-4'-n-heptylbiphenyl (7CB). NOE measurements were also obtained for the isotropic phase of these compounds and of 4-cyano-4'-n-octylbiphenyl (8CB). The results are compared to our previous carbon-13 results for 8CB[1] and for the isotropic phase of 5CB[2]. The study of trends in this homologous series reveals some even-odd effects for the spin-lattice relaxation times that cannot be explained by the differences in the nematic-isotropic transition temperatures. The temperature dependence of the NOE measurements is also considered.

TABLE

Relaxation times in 5CB, with T_1 (sec) as a function

Temp.	para aromatic				ortho aromatic			
°C	C1	C4	C5	C8	C2	C3	C6	C7
78.0	7.15	7.22	6.80	4.77	0.900	0.900	0.900	0.870
72.5	6.69	6.93	6.71	4.05	0.770	0.690	0.690	0.720
67.5	5.26	5.49	6.59	3.64	0.670	0.590	0.590	0.590
62.5	5.23	4.86	5.13	3.23	0.570	0.560	0.560	0.490
50.0	3.14	3.35	3.38	2.18	0.380	0.370	0.370	0.350
46.0	3.01	3.02	2.84	1.88	0.310	0.290	0.290	0.320
40.5	2.76	2.55	2.41	1.74	0.260	0.240	0.240	0.240
39.5	2.72	2.89	2.87	1.78	0.240	0.280	0.280	0.260
38.0	2.08	1.64	1.84	1.43	0.180	0.180	0.180	0.160
62.0	5.02	4.76	5.10	3.01	0.498	0.485	0.485	0.483
58.5	4.08	4.30	4.77	2.57	0.464	0.457	0.457	0.445
52.5	3.97	3.45	3.27	2.37	0.413	0.417	0.417	0.370
48.5	2.19	2.32	2.37	1.77	0.311	0.300	0.300	0.345
42.0	2.93	2.09	2.91	1.76	0.281	0.265	0.265	0.273
36.0	2.69	2.45	3.16	2.00	0.305	0.255	0.255	0.314
E_a	24.7	28.1	25.8	23.2	29.9	29.5	29.5	28.1
	±2.4	±2.6	±2.9	±1.8	±2.1	±1.8	±1.8	±2.6
(Iso)								
33.4	—	—	—	—	0.272	0.228	0.223	0.236
32.4	3.35	2.28	3.33	2.28	0.225	0.216	0.207	0.227
31.3	3.48	2.25	2.85	2.25	0.198	0.201	0.214	0.220
30.0	3.16	2.17	2.84	2.17	0.192	0.190	0.208	0.204
27.5	2.71	2.19	2.62	2.19	0.183	0.183	0.186	0.188
E_a	37.3	6.8	32.7	6.8	46.2	28.8	20.4	30.1
	±7.1	±2.6	±8.5	±2.6	±11.8	±4.0	±4.2	±1.3
(Nem)								

EXPERIMENTAL

The isotropic measurements were performed on a Varian CFT-20 NMR spectrometer with gated proton decoupling. Four of the spin-lattice relaxation time measurements (2 for 6CB and 2 for 7CB) and four of the NOE measurements (3 for 5CB and 1 for 7CB) were performed on a Bruker WH-90 with gated proton decoupling. It was possible to resolve the resonances of all non-equivalent carbon-13 sites with this instrument and the use of suitable averages gave results which were consistent with those obtained on the CFT-20. The nematic 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 (except for those on the WH-90) 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

I

of temperature. (Activation energies in kJ/moles)

Temp.	CN	pentyl chain				
°C	CN	C9	C10	C11	C12	C13
78.0	5.110	0.440	0.920	1.230	2.100	3.260
72.5	4.810	0.410	0.740	0.910	1.820	3.100
67.5	3.930	0.390	0.660	0.820	1.620	2.850
62.5	3.820	0.370	0.590	0.740	1.450	2.390
50.0	2.170	0.310	0.450	0.530	0.970	1.590
46.0	1.760	0.230	0.360	0.500	0.820	1.510
40.5	1.630	0.240	0.300	0.460	0.740	1.380
39.5	1.700	0.200	0.350	0.390	0.750	1.440
38.0	1.200	0.130	0.220	0.310	0.560	1.170
62.0	3.550	0.265	0.538	0.622	1.260	2.310
58.5	2.650	0.276	0.523	0.582	1.141	1.910
52.5	2.310	0.280	0.447	0.533	1.090	2.000
48.5	1.660	0.206	0.398	0.467	0.931	1.640
42.0	1.640	0.195	0.321	0.396	0.737	1.500
36.0	1.330	0.183	0.286	0.379	0.630	1.150
E_a	31.3	20.8	25.7	24.2	26.5	22.4
	±1.7	±2.6	±1.6	±1.7	±1.1	±1.1
(Iso)						
33.4	—	0.249	0.249	0.306	0.633	1.248
32.4	—	0.269	0.269	0.309	0.637	1.399
31.3	—	0.286	0.181	0.368	0.679	1.445
30.0	—	0.289	0.193	0.304	0.663	1.291
27.5	—	0.311	0.189	0.268	0.527	1.319
E_a	—	−26.6	42.4	19.9	22.7	10.2
	—	±3.8	±19.0	±14.3	±10.9	±8.9
(Nem)						

using the inversion-recovery method. The sample temperatures were controlled using gas flow systems, with a temperature gradient 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 was determined by observing the nematic-isotropic transition in the presence of decoupling. The relaxation time measurements have an accuracy of about 5% for the protonated carbons and of about 10% for the unprotonated carbons. The accuracy of the NOE measurements is estimated to be about 10%. All samples were purchased from BDH Chemicals Canada, Ltd., and used without further purification.

RESULTS AND DISCUSSION

The spectra of 5CB and 6CB are shown in Figure 1 and that of 7CB, with assignments, is given in Figure 2. The numbering of the carbon atoms for 7CB is shown in Figure 2 and the hydrogen atoms are

TABLE

Relaxation times in 6CB, with T_1 (sec) as a function

Temp.		para aromatic				ortho aromatic		
°C	C1	C4	C5	C8	C2	C3	C6	C7
60.0	3.66	3.30	3.83	2.64	0.355	0.372	0.372	0.318
57.0	3.33	2.99	3.29	2.05	0.338	0.342	0.342	0.315
54.0	2.83	2.89	2.78	1.94	0.292	0.330	0.330	0.288
52.0	3.06	2.32	2.67	2.13	0.261	0.296	0.296	0.267
47.5	2.58	2.49	2.26	1.46	0.233	0.264	0.264	0.213
44.0	2.16	2.08	2.18	1.41	0.212	0.228	0.228	0.223
41.0	2.38	2.34	2.08	1.60	0.170	0.191	0.191	0.192
37.0	2.07	1.65	1.78	1.31	0.163	0.179	0.179	0.200
34.4	2.65	2.51	2.67	1.64	0.202	0.193	0.193	0.194
31.1	2.71	2.45	2.45	1.47	0.180	0.190	0.190	0.185
E_a	10.5	10.5	12.9	15.1	21.7	22.7	22.7	17.1
	±3.5	±4.1	±4.4	±3.6	±3.1	±2.1	±2.1	±1.9
(Iso)								
27.5	2.74	2.08	2.95	2.08	0.188	0.169	0.155	0.170
26.2	3.94	1.65	3.11	1.65	0.203	0.170	0.159	0.175
24.3	2.45	1.68	2.02	1.68	0.145	0.144	0.147	0.150
22.2	1.86	1.55	1.79	1.55	0.134	0.130	0.136	0.144
19.4	1.79	1.43	1.97	1.43	0.122	0.123	0.123	0.125
E_a	59.2	28.1	46.8	28.1	46.0	32.4	23.1	29.8
	±18.9	±6.6	±15.1	±6.6	±8.6	±4.0	±2.5	±3.4
(Nem)								

omitted for clarity. The chemical shift assignments for the aromatic carbons in both phases and the alkyl carbons in the isotropic phase follow from the results for 5CB[2], with the sequence along the chain being C9, C11, C10, C12, C13, etc. In the nematic phase of 5CB the relaxation times suggest that the C10 and C11 order is reversed; this is reasonable, as the C10 and C11 lines are very close to each other in the isotropic phase, and the carbons closer to the aromatic core should be more highly ordered in the nematic phase and thus the C10 line should be shifted more than the C11 line at the phase transition. The assignment of the alkyl line with the largest chemical shift as being due to C9 is questionable for the nematic phase, but this assignment will be retained in this work. For the alkyl chain, the resonances of C9, the terminal carbon, and the next to terminal carbon are all resolved in this series, but there is significant overlap for the other carbons in the chain so that the physical significance of the results for these lines is questionable.

The spin-lattice relaxation times (T_1's) for 5CB, 6CB, and 7CB are presented in Tables I, II, and III, along with the activation energies, and in Figures 3 through 11. The solid lines give the least square fit

II

of temperature. (Activation energies in kJ/moles)

Temp.	CN	pentyl chain				
°C	CN	C9	C10,11	C12	C13	C14
60.0	2.280	0.184	0.359	0.389	1.010	3.220
57.0	2.320	0.185	0.391	0.396	0.968	2.710
54.0	2.040	0.204	0.497	0.358	0.874	2.370
52.0	1.650	0.142	0.336	0.333	0.800	2.300
47.5	1.420	0.136	0.264	0.295	0.776	1.840
44.0	0.955	0.123	0.275	0.229	0.598	1.780
41.0	1.530	0.121	0.249	0.211	0.672	1.710
37.0	1.130	0.122	0.243	0.243	0.559	1.610
34.4	1.292	0.126	0.334	0.267	0.534	1.866
31.1	1.244	0.151	0.286	0.245	0.515	1.854
E_a	20.2	11.6	11.8	16.2	20.6	16.0
	±4.9	±3.8	±4.8	±3.4	±1.5	±3.3
(Iso)						
27.5	—	0.214	0.237	0.237	0.498	1.642
26.2	—	0.247	0.194	0.194	0.414	1.397
24.3	—	0.239	0.261	0.261	0.427	1.368
22.2	—	0.190	0.190	0.190	0.478	1.363
19.4	—	0.177	0.169	0.169	0.350	1.132
E_a	—	25.3	26.3	26.3	20.9	27.5
	—	±9.2	±13.5	±13.5	±10.5	±5.3
(Nem)						

of a straight line to ln (T_1) as a function of $1000/T$, so that the slopes provide a graphical representation of the activation energies. The corresponding results for 8CB have been given previously.[1]

The comments made previously[1] on the comparison of the carbon-13 8CB relaxation times to the results of dielectric studies[3,4] of 5CB and 8CB and to the results of deuterium NMR relaxation studies of 8CB[5,6] remain valid when the carbon-13 relaxation times of the whole series 5CB, 6CB, 7CB, and 8CB are considered and will not be repeated here. Instead we wish to emphasize the changes within the homologous series and especially the existence of even-odd effects. For simplicity, we will exclude the smectic region of 8CB from the discussion.

A distinct even-odd effect is observed in the isotropic phase for the protonated (ortho) aromatic relaxation times, as is illustrated for C2 in Figure 12. Clearly the odd (5CB and 7CB) members have similar relaxation times, as do the even (6CB and 8CB) members, but the odd and even have relaxation times distinctly different from each other. This effect is still evident when the data are shifted along the temperature axis so that the nematic-isotropic transition temperatures

TABLE III

Relaxation times in 7CB, with T_1 (sec) as a function of temperature. (Activation energies in kJ/moles)

Temp.		para aromatic				ortho aromatic		
°C	C1	C4	C5	C8	C2	C3	C6	C7
69.8	6.62	7.16	6.07	3.34	0.669	0.647	0.599	0.610
57.7	4.18	3.88	3.38	2.41	0.439	0.434	0.434	0.378
52.0	3.20	2.95	3.12	2.05	0.369	0.361	0.361	0.366
50.3	3.53	3.46	3.23	2.09	0.358	0.358	0.341	0.339
45.0	2.72	2.79	2.89	1.68	0.273	0.279	0.279	0.275
E_a	32.2	34.8	27.0	24.4	31.7	30.0	27.7	27.7
	±2.6		±4.4	±1.2	±1.2	±1.1	±0.7	±2.5
(Iso)								
40.5	4.64	2.82	3.62	2.82	0.261	0.259	0.271	0.262
37.7	5.24	2.49	3.48	2.49	0.237	0.245	0.239	0.243
35.7	3.42	2.36	3.11	2.36	0.228	0.220	0.231	0.231
32.2	2.81	2.12	2.85	2.12	0.193	0.193	0.209	0.210
31.2	3.10	2.10	2.89	2.10	0.186	0.191	0.203	0.203
E_a	47.4	25.0	21.5	25.0	29.2	28.0	23.5	21.5
	±12.3	±1.7	±2.5	±1.7	±1.5	±1.7	±1.5	±0.2
(Nem)								

Temp.	CN	pentyl chain				
°C	CN	C9	C10,11	C12,13	C14	C15
69.8	3.650	0.267	1.049	0.616	1.922	3.981
57.7	2.260	0.142	0.410	0.456	1.200	2.560
52.0	1.920	0.177	0.331	0.372	1.110	2.160
50.3	1.883	0.168	0.581	0.361	1.050	2.331
45.0	1.540	0.132	0.234	0.317	0.876	1.860
E_a	31.2	21.9	47.2	24.9	27.9	27.1
	±1.5	±6.6	±12.8	±0.8	±2.0	±2.5
(Iso)						
40.5	—	0.421	0.204	0.312	0.764	1.776
37.7	—	0.433	0.171	0.285	0.697	1.774
35.7	—	0.369	0.191	0.277	0.691	1.580
32.2	—	0.371	0.230	0.230	0.617	1.596
31.2	—	0.358	0.223	0.223	0.573	1.627
E_a	—	15.2	−15.9	29.4	22.7	9.2
	—	±4.1	±8.4	±2.1	±2.2	±3.3
(Nem)						

of the different species coincide, as is illustrated in Figure 13 (where the common transition temperature has been taken as that of 5CB). Therefore the effect does not appear to be explained by the different transition temperatures. The situation for the nematic phase is less clear, and will be considered in a later work; here, we restrict comments to the isotropic phase. This effect is pervasive in this homol-

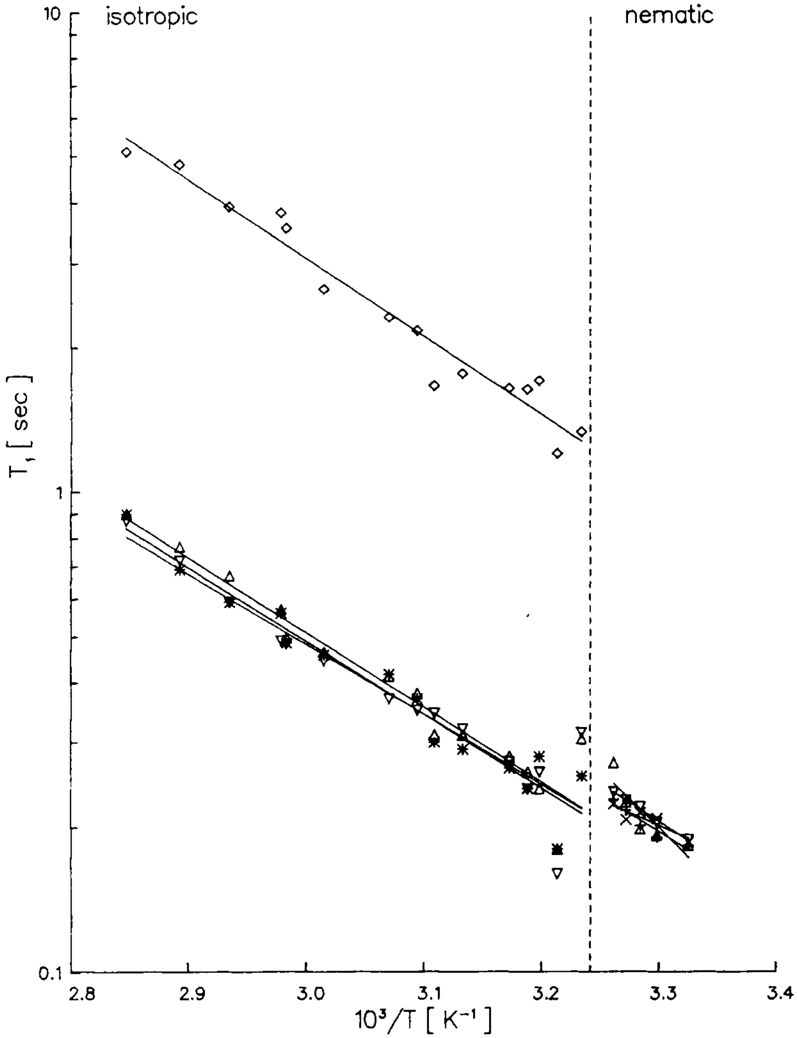

FIGURE 3 The temperature dependence of carbon-13 spin-lattice relaxation times in the isotropic and nematic phases of 5CB. The C2, C3, C6, and C7 ortho aromatic carbons are indicated by Δ, +, ×, and ∇ respectively, and CN by ◇. The straight lines represent the least square fit to the data.

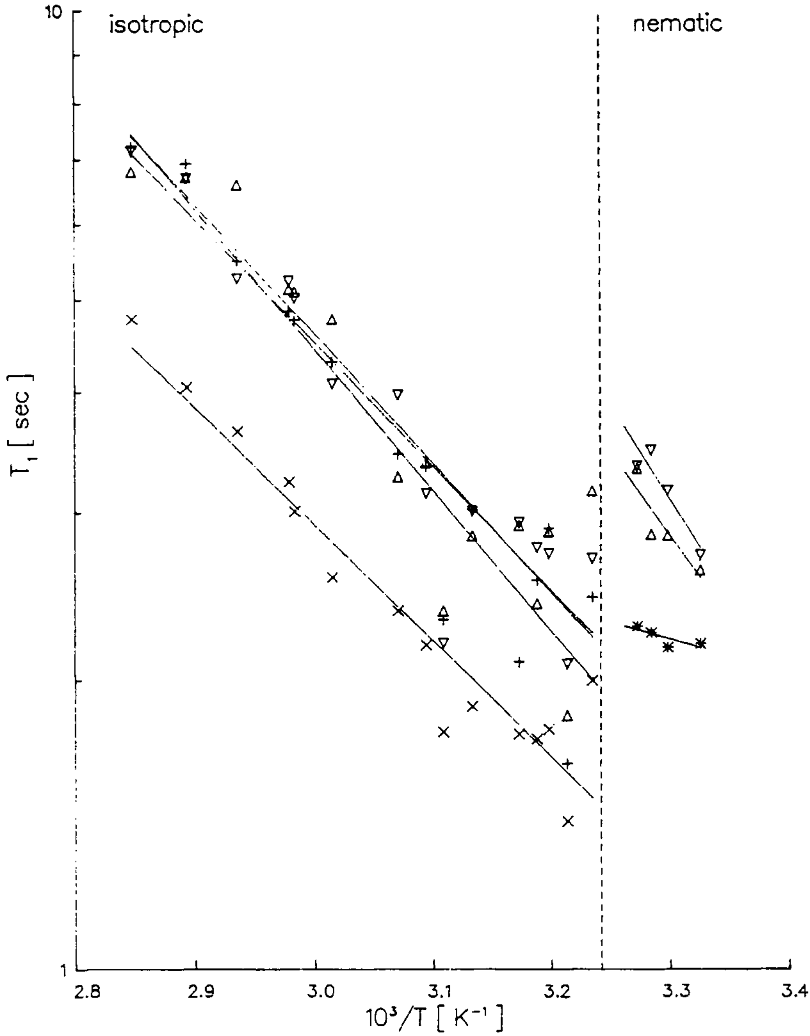

FIGURE 4 The temperature dependence of C1 (∇), C4 (+), C5 (Δ), and C8 (×) para aromatic relaxation times of 5CB.

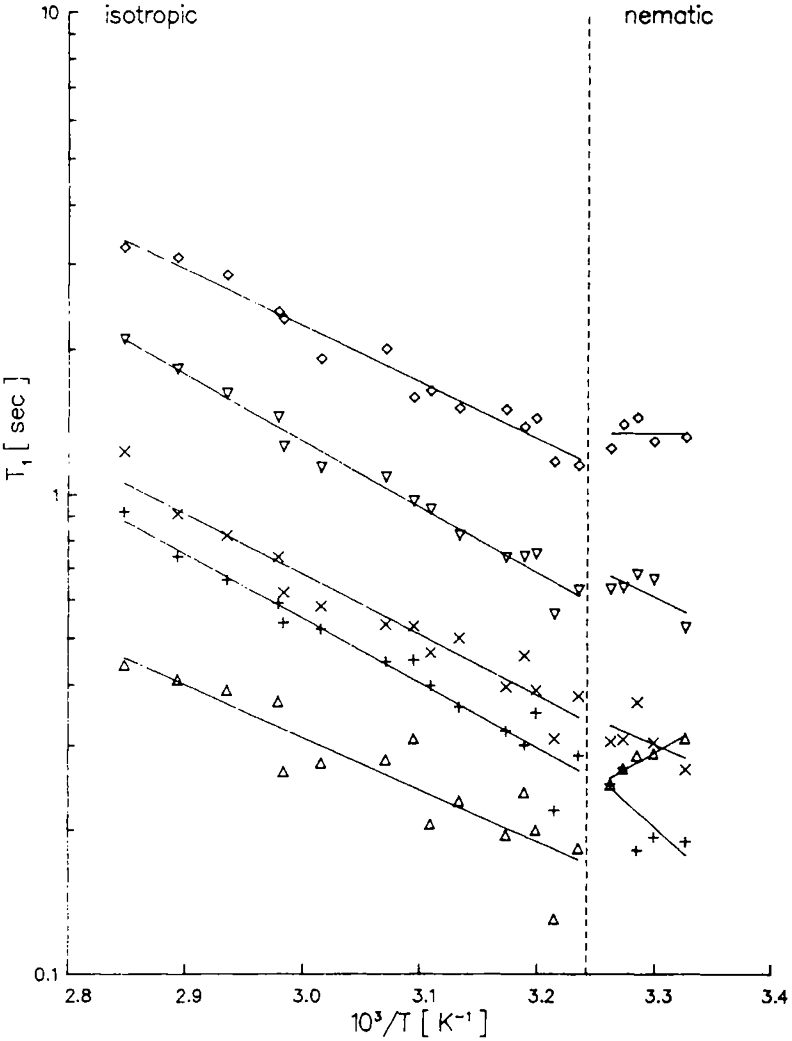

FIGURE 5 The temperature dependence of C9 (Δ), C10 (×), C11 (+), C12 (∇), and C13 (◇) alkyl relaxation times of 5CB.

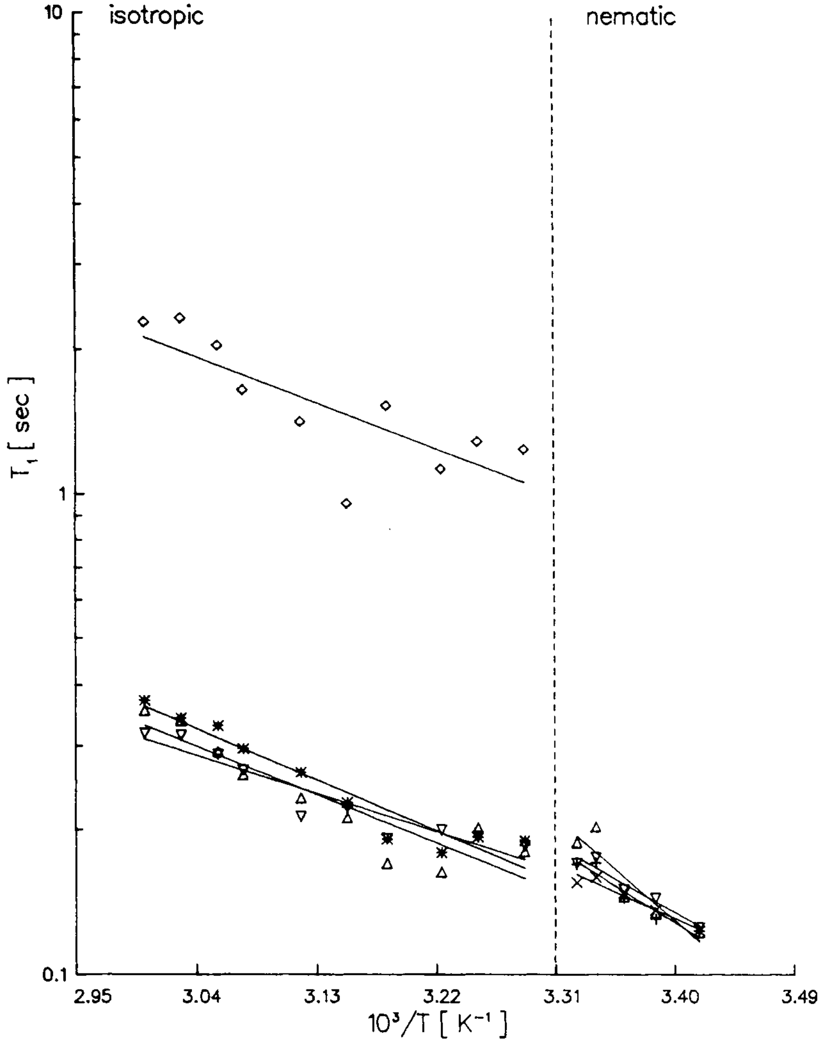

FIGURE 6 The temperature dependence of the ortho aromatic and CN relaxation times of 6CB. Symbols as in Figure 3.

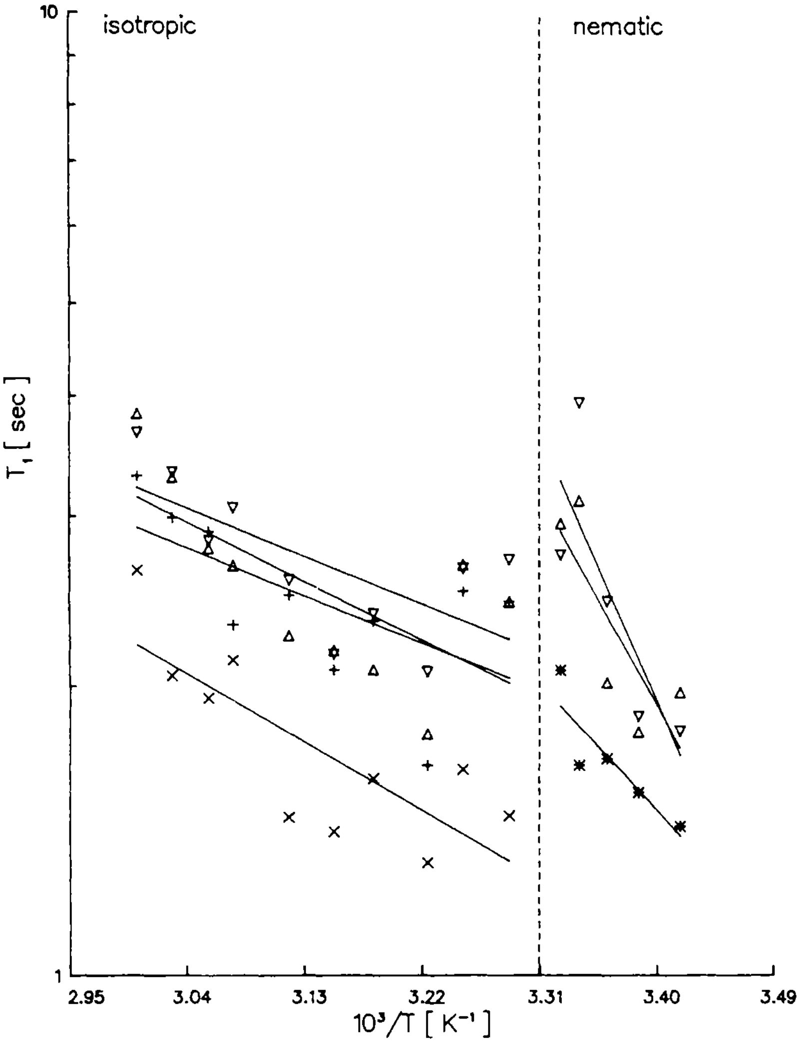

FIGURE 7 The temperature dependence of the para aromatic relaxation times of 6CB. Symbols as in Figure 4.

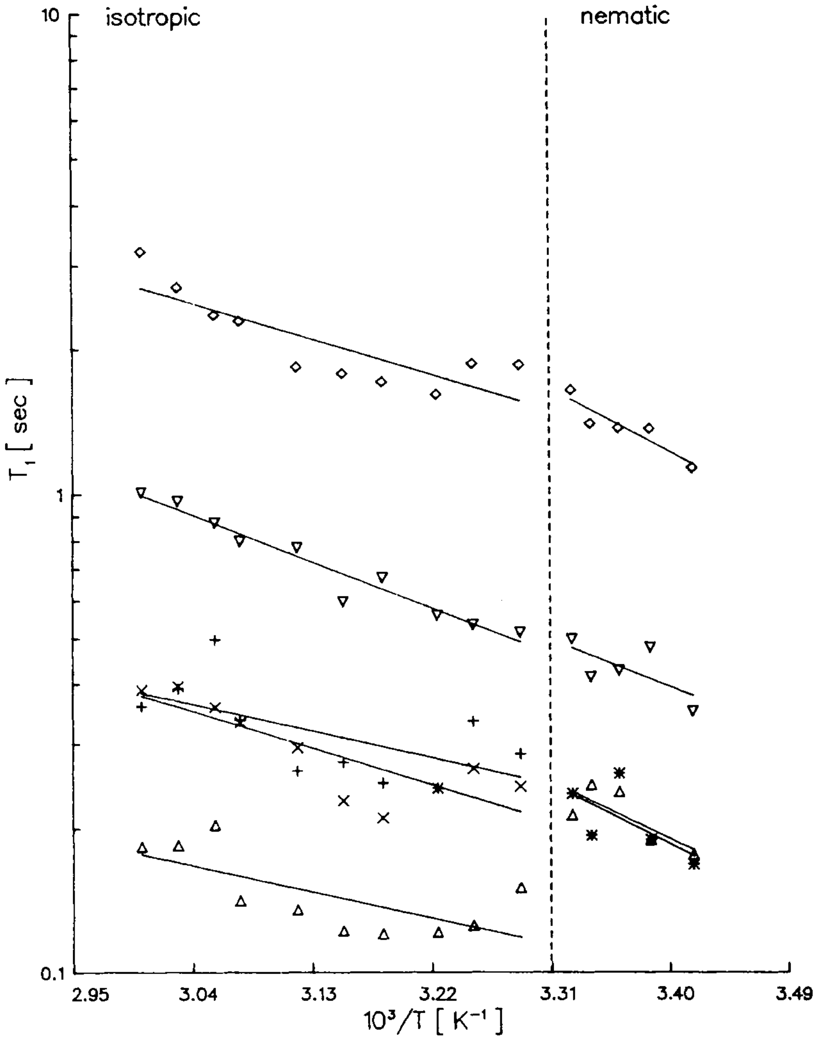

FIGURE 8 The temperature dependence of the alkyl relaxation times of 6CB. The C9, C10,11, C12, C13, and C14 are indicated by Δ, +, ×, ∇, and ◇, respectively.

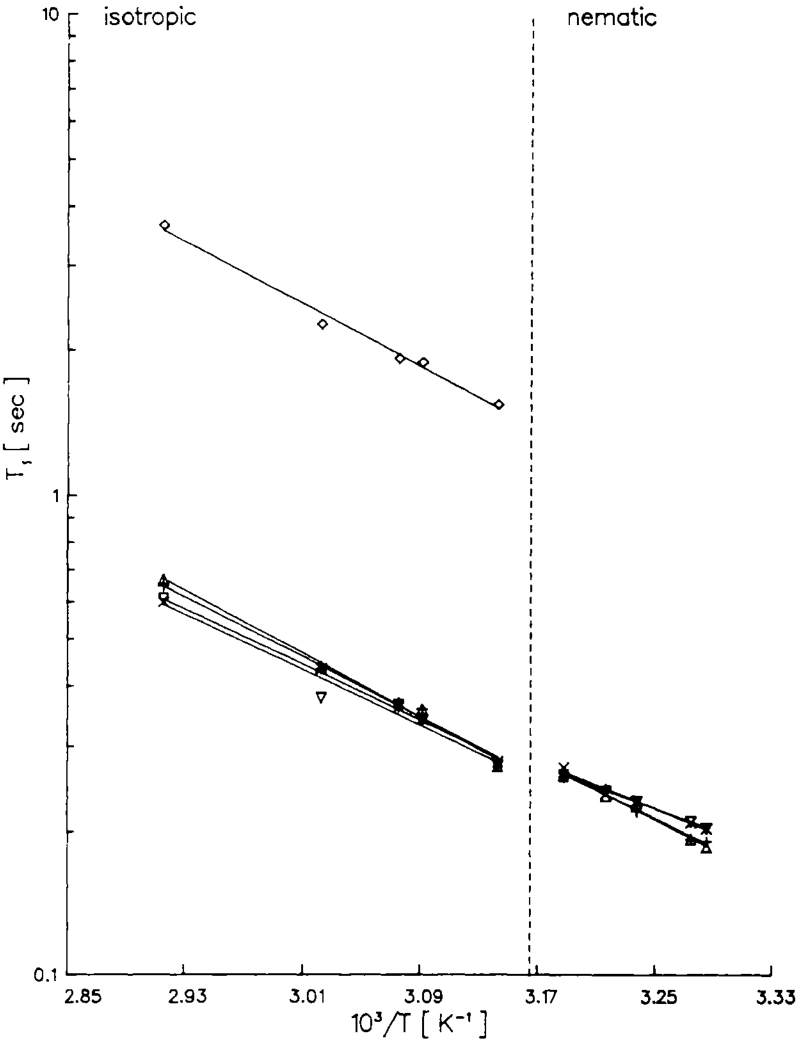

FIGURE 9 The temperature dependence of the ortho aromatic and CN relaxation times of 7CB. Symbols as in Figure 3.

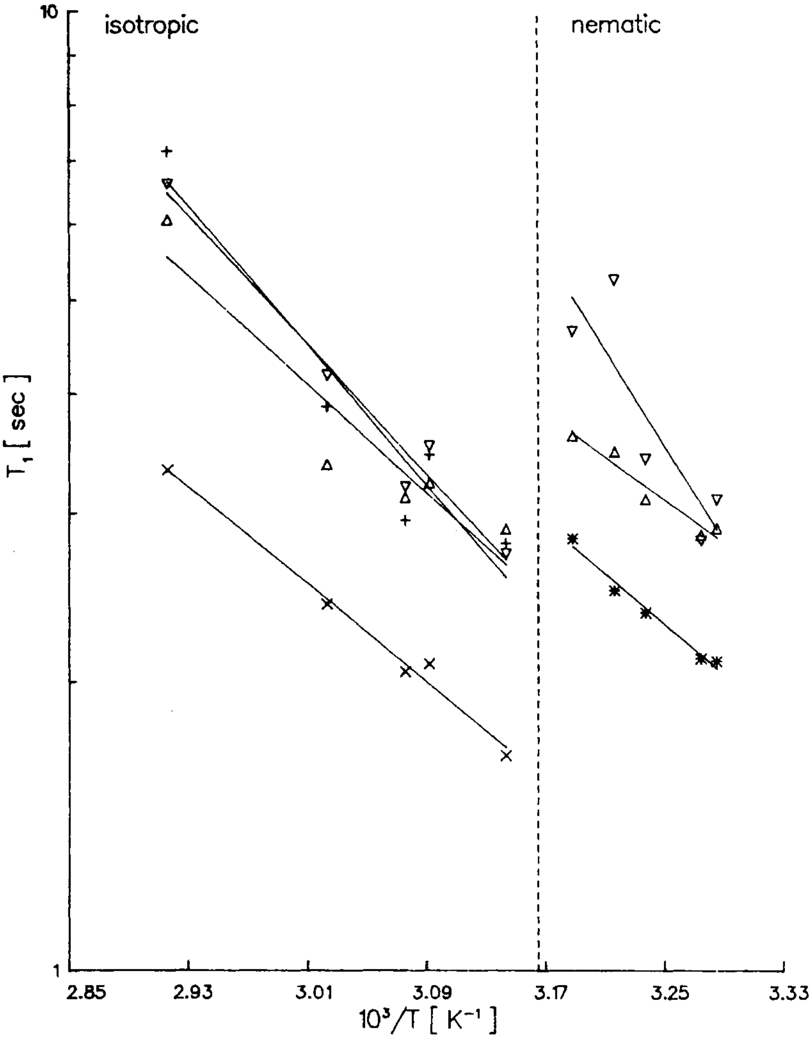

FIGURE 10 The temperature dependence of the para aromatic relaxation times of 7CB. Symbols as in Figure 4.

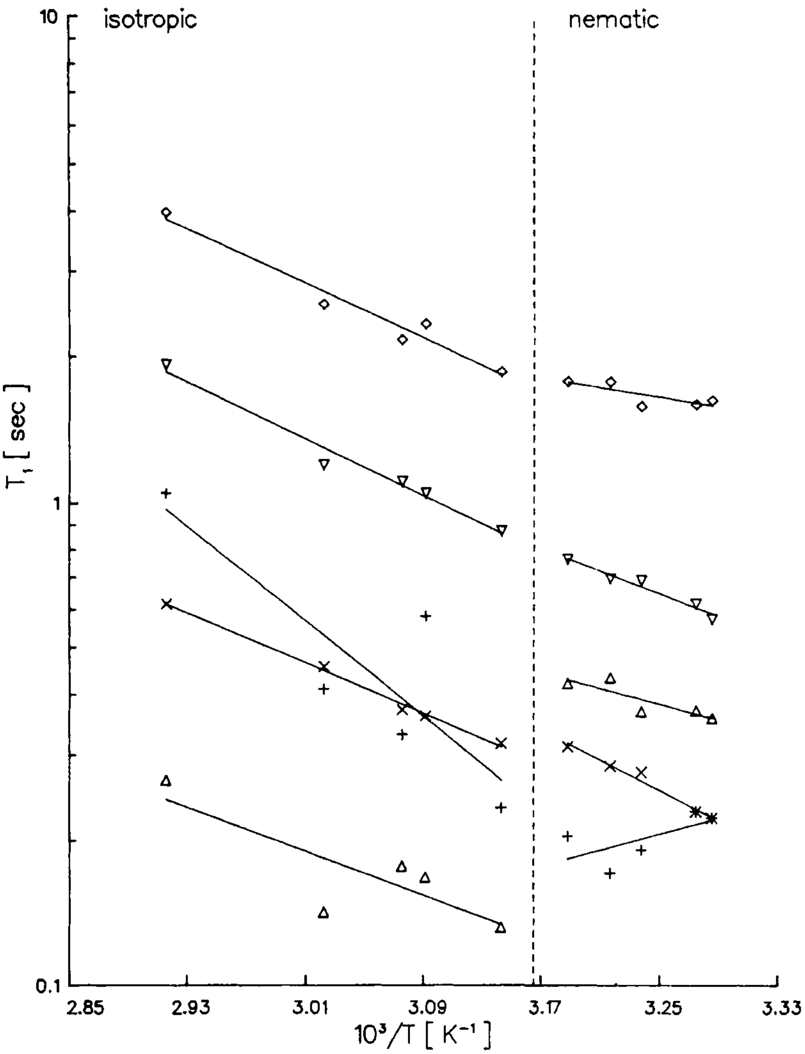

FIGURE 11 The temperature dependence of the alkyl relaxation times of 7CB. The C9, C10,11, C12, 13, C14, and C15 are indicated by Δ, +, ×, ∇, and ◇, respectively.

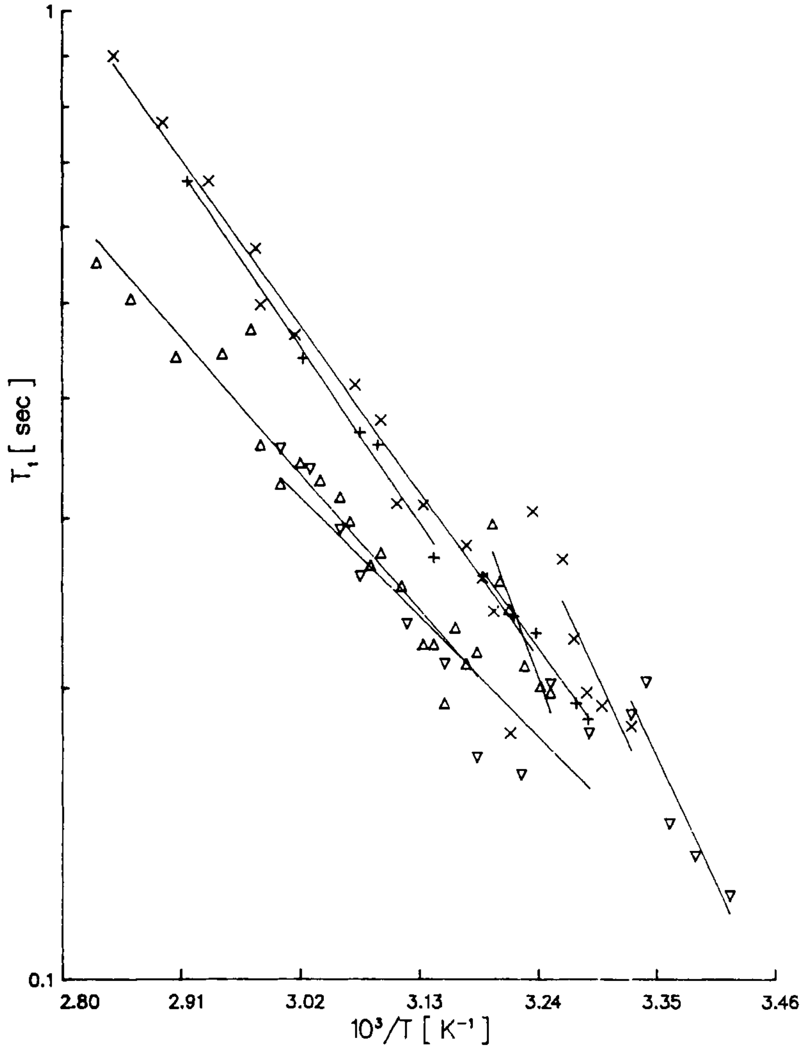

FIGURE 12 The temperature dependence of the ortho aromatic C2 relaxation times for 5CB (×), 6CB (▽), 7CB (+), and 8CB (Δ).

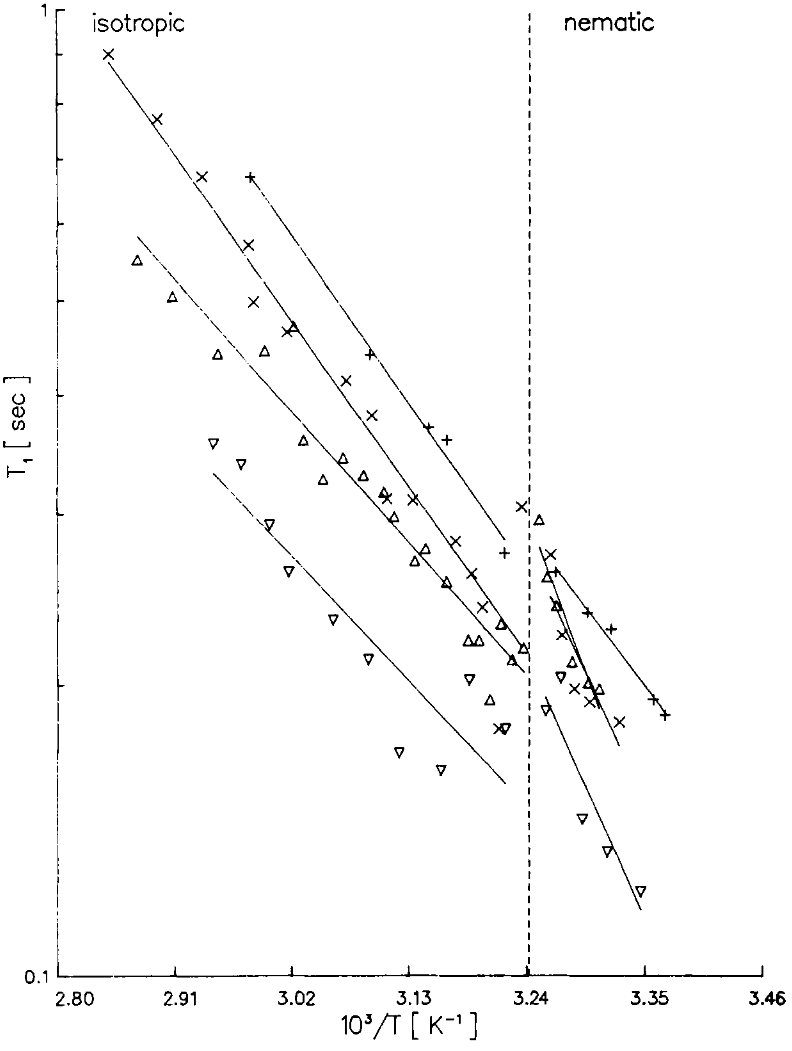

FIGURE 13 The relaxation times of the ortho aromatic C2 as a function of shifted temperatures (see text), symbols as in Figure 12.

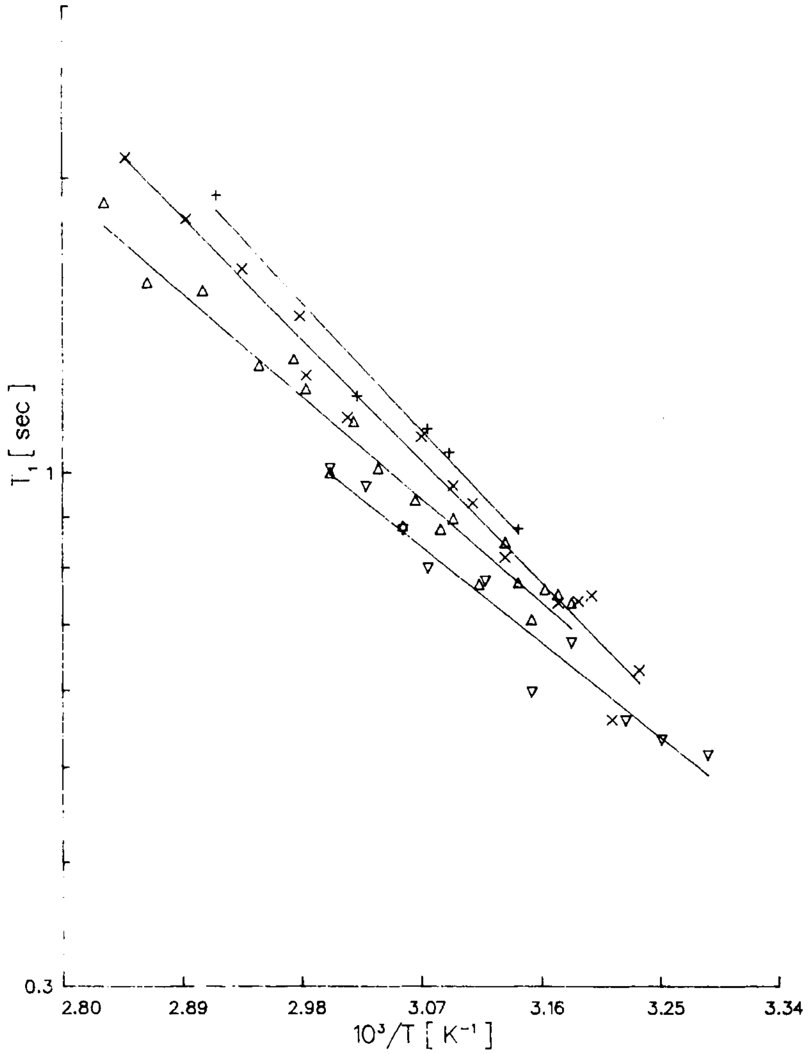

FIGURE 14 The temperature dependence of the next to last carbon of the alkyl chains in the isotropic phase. Symbols as in Figure 12.

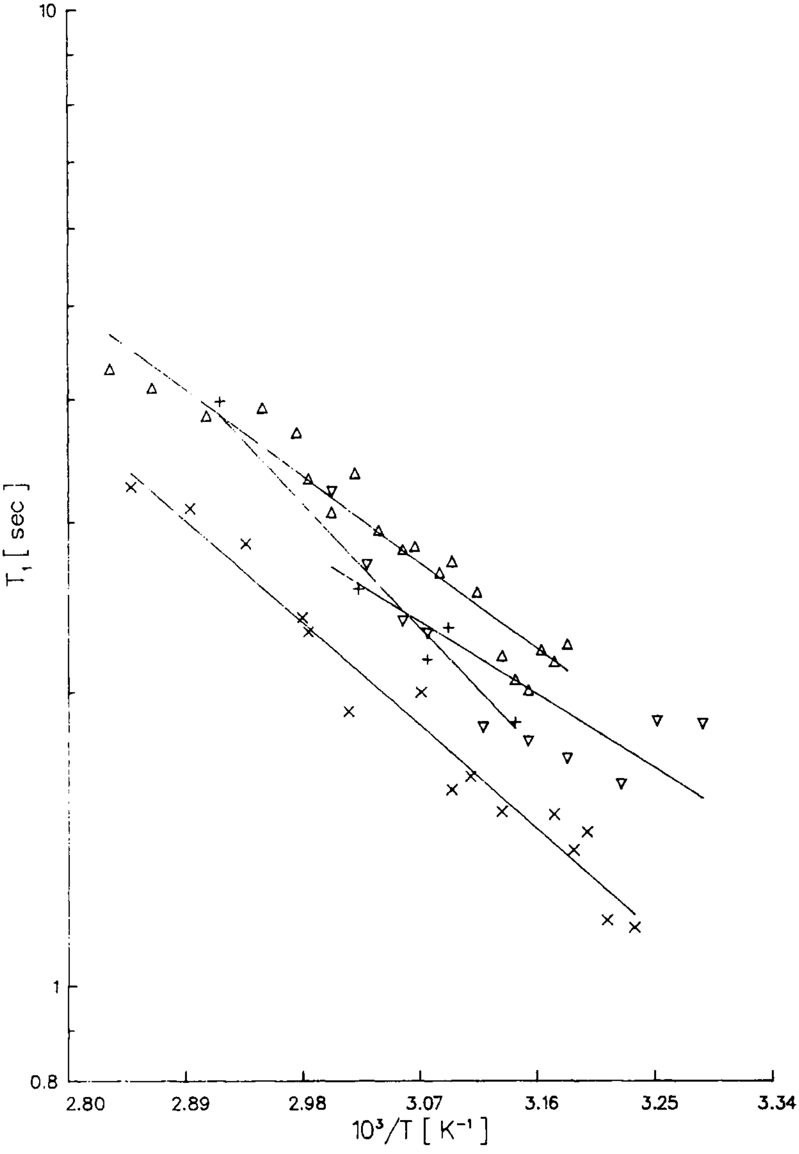

FIGURE 15 The temperature dependence of the last carbon of the alkyl chains in the isotropic phase. Symbols as in Figure 12.

ogous series and can be observed—albeit less clearly—for the unprotonated carbon-13 relaxation times as well.

The situation for the alkyl tails is less straightforward. For line C9, 5CB has a distinctly longer relaxation time than the other members of the series, but this could reflect an error in assignments. It is difficult to compare the relaxation times along the middle of the chains, especially as line overlap obscures the situation. The next to last carbon of the alkyl chains shows a mild even-odd effect (Figure 14), whereas the last carbon of the chains (Figure 15) has values for 5CB that are a bit shorter than for other members of the series. The results for C9 and for the last carbon of the chain can perhaps be rationalized by noting that the longer relaxation time corresponds in the present case to faster random motions. The final carbon of the pentyl chain can be regarded as being less independent from the rest of the molecule than is the case for the longer chains. The C9 of 5CB is nearer the final carbon of the pentyl chain and so is able to share in the free motions more completely than is the case for longer chains. However, the magnitude of the even-odd effect for the next to last carbon appears to be inconsistent with the behaviour of both C9 and of the last carbon of the chain.

The NOE's at representative temperatures for 5CB, 6CB, and 7CB are given in Table IV (aromatic) and Table V (alkyl chain). The NOE's of 8CB as a function of temperature are given in Table VI

TABLE IV

Aromatic NOE's for 5CB, 6CB, and 7CB

	Temp. (°C)	C4	C8	C5	C1	C2	C7	C3,6	CN
5CB									
	48.1	2.2	2.3	2.3	2.0	2.9	2.8	2.8	1.3
	56.0	2.2	2.4	2.3	2.2	2.7	2.7	2.8	1.3
	59.0	2.3	2.3	2.2	2.2	2.9	2.8	2.8	1.2
	69.8	2.4	2.5	2.2	2.2	2.9	2.7	2.8	1.2
6CB									
	38.5	2.1	2.1	2.1	1.9	2.5	2.7	2.6	1.1
	48.7	2.3	2.6	2.5	2.3	2.9	2.9	2.8	1.3
	58.0	2.3	2.6	2.3	2.2	2.9	2.8	2.9	1.3
7CB									
	48.5	2.1	2.2	2.1	2.1	2.8	2.8	2.7	1.2
	56.8	2.2	2.3	2.1	2.1	2.7	2.7	2.8	1.1
	59.0	1.8	1.9	1.7	1.9	2.7	2.4	2.5	0.8

TABLE V

Alkyl NOE's for 5CB, 6CB, and 7CB

5CB	Temp. (°C)	C9	C10	C11	C12	C13
	48.1	2.8	2.5	2.8	2.7	2.6
	56.0	2.5	2.5	2.6	2.5	2.5
	59.0	2.7	2.8	2.7	2.7	2.4
	69.8	2.8	2.8	2.8	2.8	2.7
6CB		C9	C10,11	C12	C13	C14
	38.5	2.1	2.4	2.2	2.3	2.8
	48.7	2.5	2.8	2.6	2.7	3.0
	58.0	2.6	2.7	2.6	2.7	3.0
7CB		C9	C10,11	C12,13	C14	C15
	48.5	2.3	2.5	2.4	2.5	2.5
	56.8	2.4	2.4	2.5	2.6	2.6
	59.0	2.3	2.2	2.6	2.0	2.4

(the NOE for the 8CB CN carbon at 76 degrees Celsius given in our earlier work[1] is a misprint; this should read 1.09, not 3.00). In Figure 16 the averages of the NOE's of the protonated and unprotonated aromatic Carbon-13 lines are given. The NOE's do not generally have a strong temperature dependence, except for the unprotonated aromatic carbon-13 NOE's which do increase with temperature. As the relaxation pathways for the unprotonated carbons may be complex, involving dipolar coupling to several protons as well as chemical shift anisotropy, this result may not be easy to interpret in detail.

The chemical shifts as a function of temperature are given in Tables VII, VIII, and IX, and for 5CB in Figures 17 and 18. The CN Carbon-13 is not included and the C4 and C8 shifts in the isotropic phase are averaged for comparison to the nematic C4,8 shift. In our previous Carbon-13 studies[1,2] we have used such data to determine values of the difference of the motionally averaged chemical shift tensors parallel and perpendicular to the long molecular axis. The validity of this procedure, based on questions of the relevant time averages of the order parameter tensor and the chemical shift tensor, has recently been questioned.[7] For the present we simply note that the para carbon-13 shifts vary more with temperature than the ortho carbon-13 shifts. This is expected as the symmetry axis of the para carbon chemical shift tensors lie along the axis through the biphenyl group (passing through the CN, C1, C4, C5, and C8 carbons) and this axis

TABLE VI

NOE's of 8CB as a function of temperature

Temp.		para aromatic			ortho aromatic			CN
°C	C1	C4	C5	C8	C2	C3,6	C7	CN
43.0	2.07	2.06	2.25	2.12	2.94	2.83	2.84	1.20
45.6	2.09	2.26	2.16	1.99	2.91	2.83	2.82	1.26
48.0	2.02	2.07	2.00	2.00	2.81	2.80	2.81	1.20
49.9	2.07	1.98	2.10	2.10	2.75	2.71	2.77	1.20
50.9	1.96	2.21	2.26	2.05	2.98	2.78	2.86	1.17
53.0	1.93	1.97	1.95	2.04	2.57	2.62	2.56	1.08
54.0	2.16	2.23	2.11	2.32	2.84	2.68	2.82	1.17
56.0	2.13	2.23	2.17	1.93	2.92	2.80	2.86	1.22
58.0	1.83	2.00	2.15	1.98	2.75	2.73	2.62	1.23
62.4	2.27	2.45	2.23	2.46	3.12	3.24	3.07	1.26
63.0	2.10	2.17	2.16	2.35	2.81	2.75	2.83	1.19
66.0	2.12	2.10	2.09	2.28	2.81	2.72	2.89	1.36
68.8	2.28	2.31	2.36	2.53	3.10	3.11	3.02	1.32
71.0	2.42	2.61	2.53	2.38	2.99	2.67	2.97	1.15
73.3	2.17	2.69	2.44	2.55	3.05	3.01	3.16	1.38
76.0	2.24	2.41	2.35	2.35	2.75	2.65	3.01	1.09
76.9	2.66	2.58	2.59	2.56	3.02	3.06	3.04	1.24
80.0	2.41	2.53	2.44	2.12	2.75	2.98	2.99	1.32

Temp.	pentyl chain					
°C	C9	C10	C11	C12–14	C15	C16
43.0	2.26	2.52	2.48	2.44	2.55	3.02
45.6	2.29	2.63	2.57	2.47	2.59	3.02
48.0	2.19	2.52	2.47	2.47	2.48	2.92
49.9	2.27	2.40	2.40	2.43	2.43	2.89
50.9	2.41	2.48	2.50	2.51	2.58	3.09
53.0	2.20	2.25	2.37	2.39	2.43	2.57
54.0	2.36	2.62	2.60	2.36	2.61	3.09
56.0	2.43	2.54	2.60	2.58	2.45	2.99
58.0	2.37	2.28	2.40	2.52	2.51	2.73
62.4	2.76	2.75	2.63	2.84	2.89	3.18
63.0	2.27	2.65	2.58	2.49	2.31	2.73
66.0	2.73	3.16	2.79	2.62	2.59	2.97
68.8	2.75	3.00	2.80	2.97	3.13	3.19
71.0	2.34	2.86	2.67	2.67	2.64	2.79
73.3	2.68	2.94	2.71	2.79	2.93	2.96
76.0	2.36	2.56	2.48	2.58	2.54	2.43
76.9	2.87	3.08	2.87	2.86	2.98	3.15
80.0	2.42	2.80	2.53	2.80	2.74	2.73

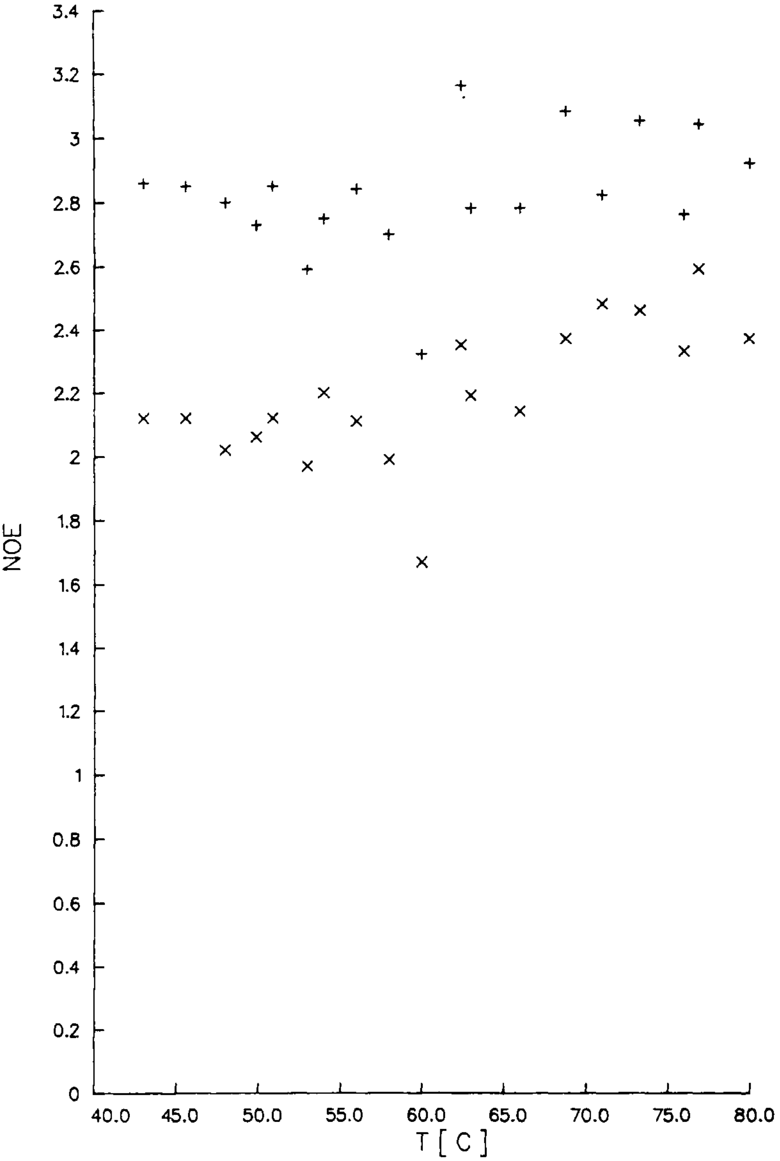

FIGURE 16 The temperature dependence of the averaged NOE's of 8CB for the ortho (+) and para (×) carbons.

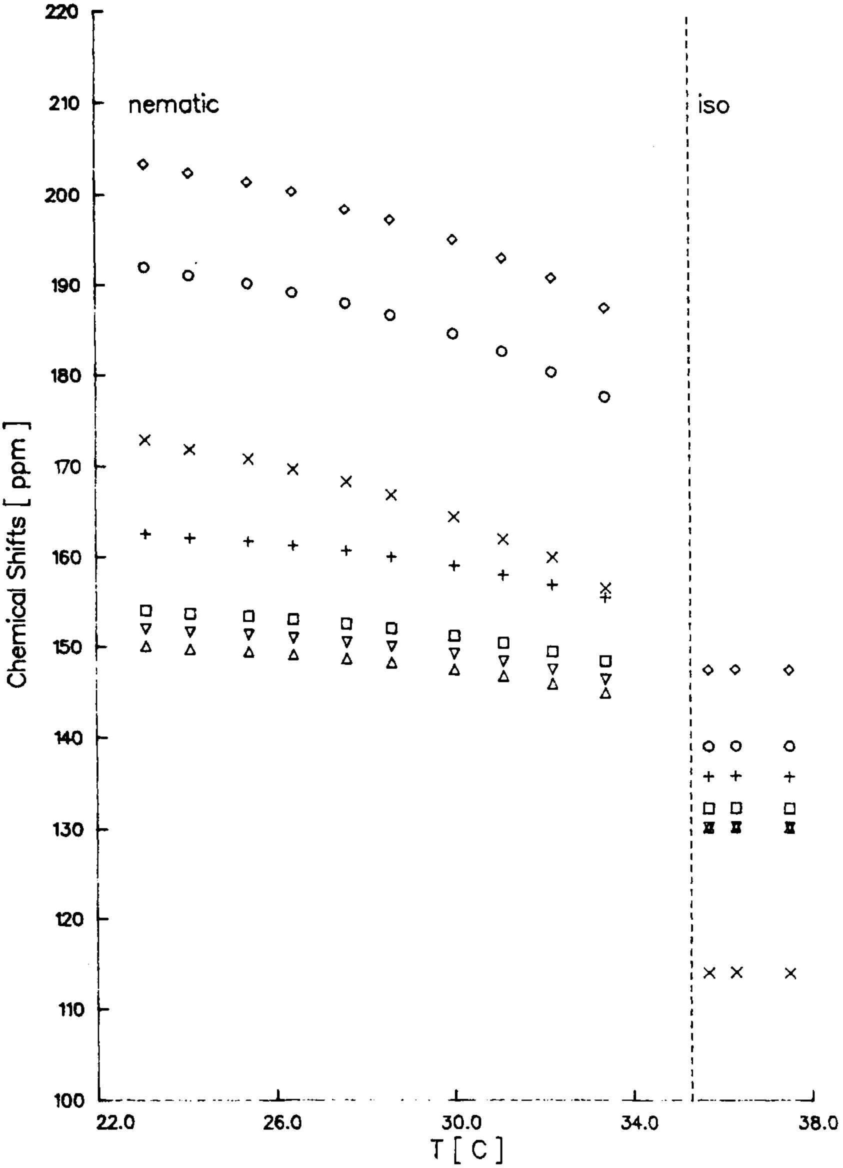

FIGURE 17 The temperature dependence of the aromatic carbon-13 line positions in 5CB. Chemical shifts are given with respect to TMS. The symbols used are C4,8 (◇), C5 (○), C1 (×), C2 (+), C7 (□), C3 (▽), and C6 (△).

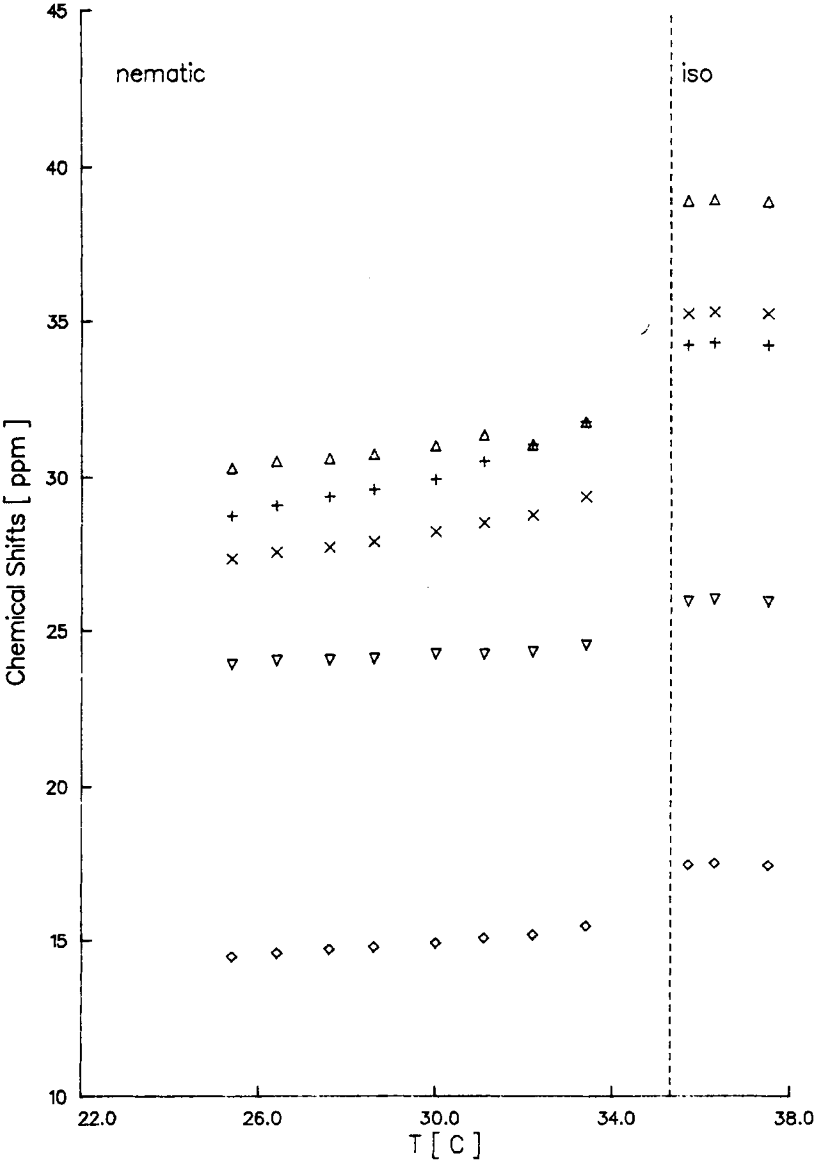

FIGURE 18 The temperature dependence of the alkyl carbon-13 line positions in 5CB. Chemical shifts are given with respect to TMS. The Symbols used are C9 (Δ), C10 (×), C11 (+), C12 (∇), and C13 (◇).

TABLE

Chemical shifts (ppm with respect to TMS) for 5CB

Temp.		para aromatic			ortho aromatic		
°C	C1	C4,8	C5	C2	C3	C6	C7
37.5	114.033	147.475	139.129	135.771	130.246	130.246	132.338
36.3	114.115	147.545	139.152	135.850	130.306	130.306	132.397
35.7	114.073	147.476	139.105	135.789	130.240	130.240	132.335
33.4	156.568	187.491	177.685	155.493	146.407	144.940	148.440
32.2	160.010	190.820	180.369	156.931	147.546	145.941	149.534
31.1	162.013	193.039	182.641	158.071	148.428	146.814	150.478
30.0	164.507	195.047	184.580	159.061	149.244	147.518	151.247
28.6	166.894	197.241	186.622	160.037	150.040	148.250	152.058
27.6	168.351	198.375	187.939	160.710	150.526	148.710	152.560
26.4	169.731	200.372	189.150	161.275	150.987	149.137	153.040
25.4	170.814	201.406	190.116	161.713	151.326	149.458	153.389

TABLE

Chemical shifts (ppm with respect to TMS) for 6CB

Temp.		para aromatic			ortho aromatic		
°C	C1	C4,8	C5	C2	C3	C6	C7
31.2	114.004	147.408	139.060	135.731	130.197	130.197	132.276
30.0	113.977	147.375	139.050	135.720	130.179	130.179	132.248
27.6	150.938	183.685	173.464	153.264	144.474	142.963	146.329
26.4	154.994	186.989	176.522	155.107	145.994	144.406	147.808
25.4	158.630	189.569	179.160	156.338	146.986	145.213	148.803
24.1	160.874	191.560	181.095	157.285	147.742	145.918	149.566
23.1	162.697	193.264	182.693	158.070	148.340	146.491	150.188
22.1	164.326	194.788	184.174	158.803	148.935	147.033	150.769
21.2	165.535	195.862	185.221	159.310	149.343	147.411	151.182
20.4	166.600	196.841	186.174	159.749	149.667	147.724	151.517
19.2	167.236	197.850	187.150	160.236	150.023	148.064	151.894
18.1	168.783	198.849	188.105	160.705	150.391	148.405	152.265
17.6	169.318	199.306	188.563	160.931	150.573	148.577	152.446
16.7	170.042	199.990	189.206	161.247	150.812	148.808	152.672

corresponds closely to the axis of rotation of the molecule, whereas the symmetry axis for the ortho carbons is at sixty degrees to the para symmetry axis and thus at roughly sixty degrees to the axis of rapid rotation.

CONCLUSION

The temperature dependence of the carbon-13 NMR chemical shifts, NOE's, and spin-lattice relaxation times of the first four mesogenic members of the 5CB homologous series have been measured. The

VII

as a function of temperature

Temp. °C	pentyl chain C9	C10	C11	C12	C13
37.5	38.887	34.216	35.237	25.932	17.422
36.3	38.948	34.299	35.299	26.020	17.506
35.7	38.903	34.226	35.238	25.950	17.456
33.4	31.770	31.770	29.352	24.525	15.462
32.2	31.039	31.039	28.751	24.307	15.180
31.1	31.349	30.498	28.502	24.229	15.075
30.0	31.008	29.919	28.205	24.241	14.915
28.6	30.744	29.588	27.896	24.093	14.786
27.6	30.610	29.357	27.709	24.053	14.710
26.4	30.522	29.069	27.549	24.033	14.589
25.4	30.303	28.727	27.334	23.916	14.470

VIII

as a function of temperature

Temp. °C	pentyl chain C9	C10,11,12	C13	C14
31.2	39.008	33.811	26.185	17.483
30.0	38.957	33.781	26.142	17.436
27.6	31.334	29.457	24.132	16.418
26.4	30.884	28.930	23.874	16.305
25.4	30.463	28.597	23.723	16.224
24.1	30.152	28.320	23.524	16.177
23.1	29.832	27.992	23.414	16.082
22.1	29.634	27.881	23.338	16.106
21.2	29.468	27.772	23.301	16.145
20.4	29.296	27.588	23.194	16.062
19.2	29.108	27.430	23.149	16.015
18.1	28.997	27.340	23.093	16.026
17.6	28.889	27.389	23.073	16.036
16.7	28.788	27.270	23.092	16.012

differences in the relaxation times as a function of temperature, and especially the even-odd effects found to exist, require explanation—perhaps using deuterium NMR—but enough data exist so that computer simulations in the isotropic phase should be useful.

Acknowledgments

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TABLE IX

Chemical shifts (ppm with respect to TMS) for 7CB as a function of temperature

Temp.	para aromatic			ortho aromatic			
°C	C1	C4,8	C5	C2	C3	C6	C7
44.0	114.100	147.451	139.147	135.731	130.231	130.231	132.301
40.4	160.959	191.594	181.008	157.235	147.643	145.774	149.410
39.4	164.449	194.615	184.228	158.579	148.774	146.845	150.569
37.5	166.624	196.801	186.082	159.526	149.494	147.505	151.275
36.5	168.134	198.088	187.395	160.115	149.941	147.909	151.722
35.7	169.514	199.355	188.683	160.699	150.390	148.350	152.208
34.5	170.920	200.713	189.917	161.385	150.919	148.840	152.746
33.4	172.115	201.825	190.995	161.926	151.354	149.242	153.186
32.2	173.268	202.904	192.002	162.424	151.730	149.620	153.597
31.1	174.893	203.747	192.933	162.893	152.114	149.949	153.971

Temp.	pentyl chain				
°C	C9	C10,11	C12,13	C14	C15
44.0	39.006	34.976	32.835	26.115	17.453
40.4	31.114	30.118	28.086	23.995	15.075
39.4	30.813	29.606	27.724	23.828	14.915
37.5	30.568	29.039	27.363	23.731	14.754
36.5	30.420	28.612	27.136	23.646	14.634
35.7	30.185	28.352	26.892	23.524	14.438
34.5	30.109	28.091	26.772	23.504	14.379
33.4	29.912	27.827	26.617	23.498	14.369
32.2	29.854	26.561	26.561	23.441	14.274
31.1	29.813	26.492	26.492	23.549	14.379

the limitations on the usefulness of chemical shifts for determining order tensor components and is gratefully acknowledged.

References

1. J. Bozek, H. M. Hutton, J. S. Lewis, E. Tomchuk and E. Bock, *Mol. Cryst. Liq. Cryst.*, **122**, 191 (1985).
2. J. S. Lewis, E. Tomchuk, H. M. Hutton and E. Bock, *J. Chem. Phys.*, **78**, 632 (1983).
3. B. R. Ratna and R. Shasidhar, *Mol. Cryst. Liq. Cryst.*, **42**, 185 (1977).
4. C. Druon and J. M. Wacrenier, *Amm. Phys.*, (France) **3**, 199 (1976).
5. J. W. Emsley, J. C. Lindon and G. R. Luckurst, *Molec. Phys.*, **32**, 1187 (1976).
6. J. W. Emsley and D. L. Turner, *J. Chem. Soc.*, *Faraday Trans.*, **2 77**, 1493 (1981).
7. B. M. Fung, private communication.