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Orientational ordering of a nematic liquid crystal and its mixture with its chain-perfluorinated analogue

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The orientation of different segments of 4′-cyanophenyl 4-heptylbenzoate (7CPB) has been investigated using ^{13}C NMR. The method of proton-encoded local field (PELF) spectroscopy in combination with off-magic-angle spinning (OMAS) of the sample was used. High resolution 2D spectra were obtained, from which the order parameters were calculated. Linear relations between the obtained order parameters and anisotropic chemical shifts determined by 1D ^{13}C NMR were established and semi-empirical parameters were achieved. A 1:2 mixture of 7CPB and its chain-perfluorinated analogue (7PFCPB) showed interesting phase behaviour with the change of temperature. It was studied by the use of ^{13}C NMR and polarizing optical microscopy. The order parameters of 7CPB in the smectic A phase of the mixture were calculated using the semi-empirical parameters obtained from the 2D NMR method.

1. Introduction

Fluorinated liquid crystal materials have received much attention [1–3] because fluorine substitution can increase the impedance of liquid crystalline compounds and decrease in viscosity, making them advantageous in fabricating high performance thin film transistor (TFT) display devices. The presence of fluorine atoms can also change the polarity and phase behaviour of molecules. It has been shown that the replacement of a hydrocarbon chain in a liquid crystal by a perfluorinated or semi-perfluorinated chain highly favours the smectic A or smectic C phase [4–6]. The poor miscibility of hydrocarbon and fluorocarbon segments causes different parts in segmentally fluorinated alkanes to organize themselves in layered structures or microdomains of different compositions [7]. The same phenomena can be found in the crystalline state, where the molecular packing is controlled by the steric structure and intermolecular interactions [8]. Therefore, the phase behaviour of mixtures of liquid crystals with hydrocarbon and fluorocarbon chains should be different from that of normal hydrocarbon liquid crystal mixtures. However, it is surprising that there are not many studies of hydrocarbon/fluorocarbon liquid crystal mixtures.

Nuclear magnetic resonance (NMR) has many advantages in probing the ordering of liquid crystals [9] because it can determine the ordering and motion of individual parts of the molecules. The 2D SLF (separated local field)/VAS (variable angle spinning) NMR method has been proven to be especially effective in the determination of the ordering of liquid crystals [10]. A recent improvement of this technique increased the resolution of the 2D spectra [11–14], and it is now called proton-encoded local field (PELF) spectroscopy [15]. The combination of PELF with OMAS (off-magic-angle-spinning) [16] was used in this study. Because the order parameter can be related to the chemical shift in a semi-empirical way [17, 18], after the order parameters have been determined from 2D studies at a few different temperatures, it is possible to study the ordering of complicated liquid crystal systems with conventional 1D ^{13}C NMR over a wide temperature range. These systems include mixtures of a hydrocarbon liquid crystal and its chain-perfluorinated analogue.

2. Experimental

2.1. *Synthesis of 4′-cyanophenyl 4-heptylbenzoate (7CPB)*

4′-Cyanophenyl 4-heptylbenzoate was synthesized by following a general procedure [19]: A solution of 4-heptylbenzoyl chloride in 1,4-dioxan was added dropwise to a flask charged with a solution of 4-cyanophenol in pyridine, and the mixture was then heated at reflux for 5–6 h. After cooling, the reaction mixture was poured into a 1:1 mixture of ice and concentrated hydrochloric acid. Chloroform was added to dissolve the precipitate and the aqueous part was then extracted several times with chloroform. The organic portions were combined, washed with H_2O, 20% NaOH and H_2O successively and then dried over Na_2SO_4. After removal of the solvent,

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the solid was further purified by multiple recrystallization from a mixture of ethanol and water. The purity of the compound was checked by NMR spectroscopy.

2.2. *Synthesis of 4′-cyanophenyl 4-(perfluoroheptyl)benzoate (7PFCPB) (see the scheme)*

2.2.1. *4-(Perfluoroheptyl)benzoic acid* [20]

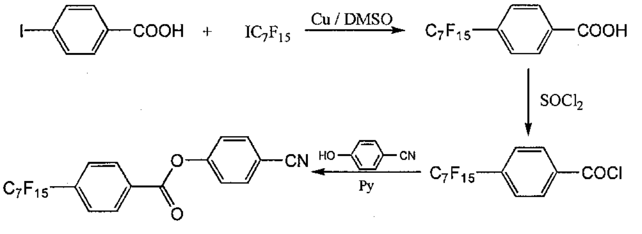
15.5 g (31.25 mmol) of $C_7F_{15}I$, 7.75 g (31.25 mmol) of 4-iodobenzoic acid, 10 g of freshly activated copper bronze [21] and 50 ml of freshly distilled dimethyl sulphoxide were charged into a 3-necked round bottom flask equipped with thermometer, condenser and nitrogen inlet. The reaction system was purged with N_2 and then heated at 110°C with stirring overnight.

After cooling to room temperature, 300 ml of ether was added; a precipitate was formed and then filtered off. The liquid part was treated with 200 ml water, and the resultant blue precipitate was separated and combined with the previous solid portion. The solids were treated with hydrochloric acid and then extracted several times with ether. All extracts were combined, washed with water until neutral and then dried over Na_2SO_4. 10.15g of solid (a mixture of 4-iodobenzoic acid and 4-(perfluoroheptyl)benzoic acid) was obtained after distillation of the solvent.

2.2.2. *4′-Cyanophenyl 4-(perfluoroheptyl)benzoate*

4.50 g (~ 9.2 mmol) of 4-(perfluoroheptyl)benzoic acid mixture was dissolved in about 70 ml of hot toluene. 1.5 ml of thionyl chloride was added dropwise to the solution and the reaction mixture was heated at reflux for 5 h. Toluene and excessive thionyl chloride were removed by rotary evaporation. The residual solid was washed with toluene, which was then removed under reduced pressure.

The resultant 4-(perfluoroheptyl)benzoyl chloride was dissolved in about 30 ml of 1,4-dioxan and the solution added dropwise to 30 ml of pyridine solution containing 1.29 g (10.8 mmol) of 4-cyanophenol. The mixture was then heated at 100°C for 15 h. The work-up procedure for this product was similar to that for 4′-cyanophenyl 4-heptylbenzoate (7CPB), except that it needed further column chromatographic separation using diethyl ether as eluent. 2.5 g of a white crystalline solid was obtained; the yield was 29% for the whole sequence.



Scheme. Synthetic route for 7PFCPB.

2.3. *Phase transition measurements*

The phase transitions of the two compounds were measured using a Perkin Elmer DSC7 differential scanning calorimeter. The liquid crystalline phases were observed under a polarizing microscope (Olympus BH-2).

2.4. *13C NMR*

^{13}C NMR experiments using the 2D PELF/OMAS technique were performed on 4′-cyanophenyl 4-heptylbenzoate with the use of a Varian UNITY/INOVA 400 NMR spectrometer equipped with a variable angle spinning probe. The PELF pulse was used with proton–carbon cross-polarization and the BLEW-48 [22] decoupling sequence. Temperature calibration was made by observing the temperature-dependent chemical shift change of ethylene glycol. Peak assignments of the ^{13}C NMR spectrum in the isotropic phase were made with the aid of the group contribution method.

The chemical shift determination of pure 4′-cyanophenyl 4-heptylbenzoate (7CPB) and a mixture of 7CPB and its fluorocarbon analogue 7PFCPB was conducted on the same spectrometer. An indirect detection probe manufactured by Narolac Corporation, Mastinez, CA, was used. The sample was first heated to above its clearing point and the chemical shift of the terminal methyl was set to be 14.05 ppm with respect to tetramethylsilane (TMS), so that the data were self-consistent. The chemical shift measurement was then made with decreasing temperature at 1°C intervals. To prevent rf overheating, a 1.6% decoupler duty cycle was used with a total cycling time of 3.558 s and a $\gamma B_2/2\pi$ value of 9.06 kHz.

3. Results and discussion

4′-Cyanophenyl 4-heptylbenzoate (7CPB) melts at 40.3°C to form a nematic phase, which then turns isotropic at 52.7°C. These transition temperatures are slightly different from the values reported previously [23]. Its chain-fluorinated analogue 7PFCPB melts at 107.5°C to form a smectic A phase, which becomes isotropic at 136.4°C.

The proton decoupled ^{13}C NMR spectra of 7CPB and 7PFCPB in their isotropic and liquid crystalline phases are shown in figure 1. As usual, the aromatic peaks shift down-field when the compounds are cooled from the isotropic phase to the liquid crystalline phase. The aliphatic peaks of 7CPB shift slightly up-field correspondingly, figure 1 (*b*), but the aliphatic peaks for 7PFCPB are too broad to be observed due to extensive ^{13}C–^{19}F coupling, figure 1 (*c*) and 1 (*d*). Even though the

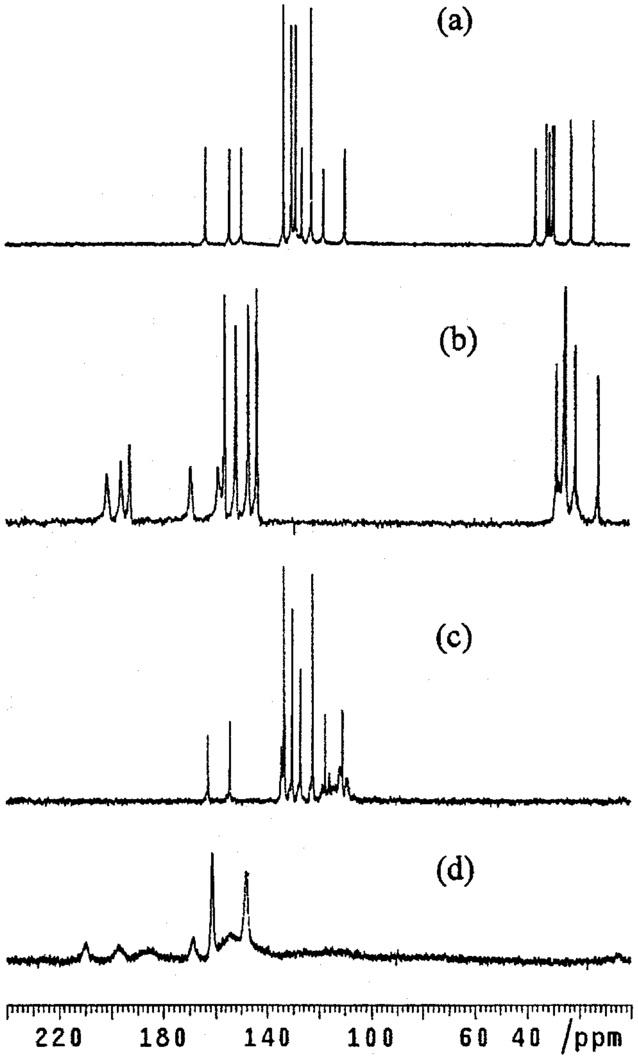


Figure 1. ^{13}C NMR spectra at 100.58 MHz for (*a*) 7CPB in the isotropic phase; (*b*) 7CPB in the nematic phase (at 43°C); (*c*) 7PFCPB in the isotropic phase; (*d*) 7PFCPB in the smectic A phase (at 128°C).

aromatic carbons have no directly bonded fluorine atoms, the ^{13}C–^{19}F dipolar couplings in the smectic A phase are large enough to cause broadening of the aromatic carbon peaks, figure 1 (*d*). The change in chemical shifts is due to incomplete averaging of the chemical shift tensors in the liquid crystalline phase. However, unless all the components of the tensors in the axis system of the ordering matrix are known, it is not possible to calculate the order parameters from the chemical shifts.

A more direct way to obtain the order parameters is to measure the C–H dipolar coupling constants using the 2D PELF/OMAS method. The sample was spun rapidly (~1 kHz) at an angle θ with respect to the magnetic field $\mathbf{B}_0$, which was chosen to be 47.58° in this experiment, to reduce the dipolar coupling and obtain sharp ^{13}C peaks. In the evolution period, the BLEW-48 decoupling sequence is used to remove proton–proton dipolar coupling so that first order C–H couplings can be observed in the ω_1 dimension. In the detection period, the SPINAL-64 broadband decoupling sequence [24] was used to obtain normal proton decoupled ^{13}C spectrum in the ω_2 dimension.

The 2D PELF/VAS spectra of 4′-cyanophenyl 4-heptylbenzoate at temperature $T/T_{NI} = 0.945$ are shown in figure 2. In the spectra, in the ω_1 dimension one-bond C–H coupling and some two-bond coupling can be observed. Each type of proton gives a doublet, and the central peaks are due to overlapping of many unresolved long range couplings. The quality of spectra in figure 2 is better than that obtained by the SLF/VAS method, in which 2-bond couplings can only be obtained by deconvolution of the overlapping peaks.

The method used to calculate order parameters from the C–H splittings is the same as the SLF/VAS method.

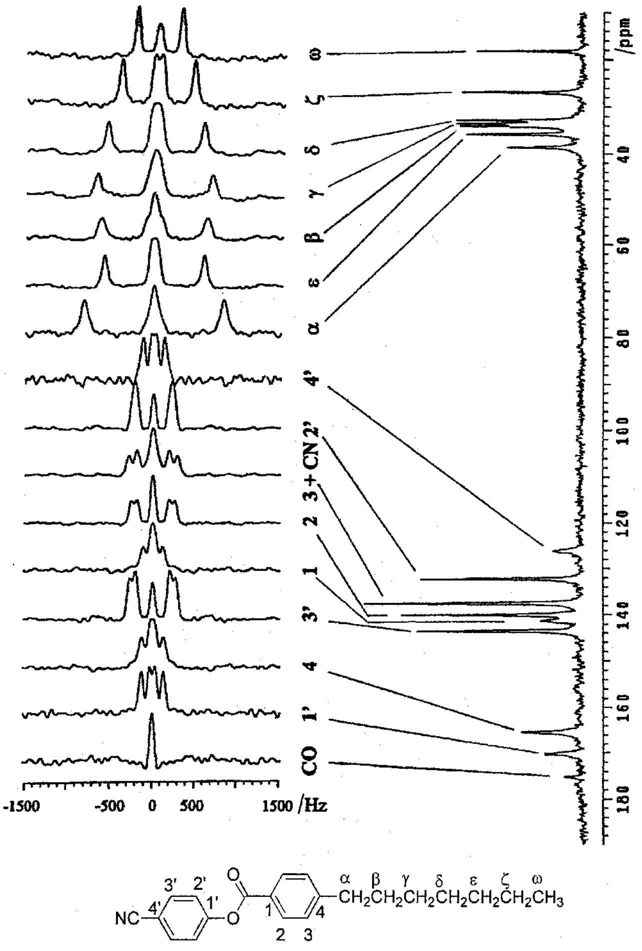


Figure 2. ^{13}C NMR spectra of 7CPB at $T/T_{NI} = 0.945$ with the sample spinning at a rate of about 1.0 kHz along an axis forming an angle 47.58° with respect to $\mathbf{B}_0$; presented together with traces in the ω_1 dimension in a 2D PELF experiment.

It has been described in detail previously [10], and will not be repeated here. For the phenyl ring carrying the aliphatic chain, the average values of the calculated angles are: ∠ H2–C2–C3 = 120.3 ± 0.4° and ∠ H3–C3–C2 = 119.8 ± 0.4°; for the phenyl ring bearing the cyano group, the angles are: ∠ H2′–C2′–C3′ = 120.8 ± 0.3° and ∠ H3′–C3′–C2′ = 120.1 ± 0.3°. These data are comparable to the previous results obtained with the SLF/VAS method [23].

To calculate the order parameters obtained from the 2D data with the ^{13}C chemical shifts (δ values), one can use the semi-empirical equation [17, 18]

$$\Delta\delta = aS + b \tag{1}$$

where $\Delta\delta = \delta_{ani} - \delta_{iso}$, and a and b are constants. For the phenyl rings, S refers to the order parameter of the two-fold axis of the ring; for the aliphatic carbons, S refers to the order parameters of the C–H axis.

In the present study, the PELF/OMAS technique was used to obtain the order parameters of 7CPB at four different temperatures. The values of $\Delta\delta$ for each carbon nucleus at these temperatures were then plotted against the order parameters to calculate the values of a and b. The results, together with the correlation coefficients, are given in tables 1 and 2. The high values of the correlation coefficients show that the data obey the linear relation expressed in equation (1) very well.

Once the values of a and b are determined, they can be used to calculate the order parameters from the chemical shift values, which can be measured more conveniently as a function of temperature using 1D data. The data for the aromatic and aliphatic carbons are presented in figures 3 and 4, respectively. They were fitted to the Haller equation [18, 25–27]

$$S(T) = S_0(1 - T/T^*)^F \tag{2}$$

where S_0 and F are empirical constants and T^* is a temperature at which the order parameter becomes zero. The calculated curves are represented as dashed lines in figures 3 and 4. Data for carbon atoms on the same ring are positioned on the same line. A good agreement between the experimental data and S by the theoretical calculation can be found in the plots.

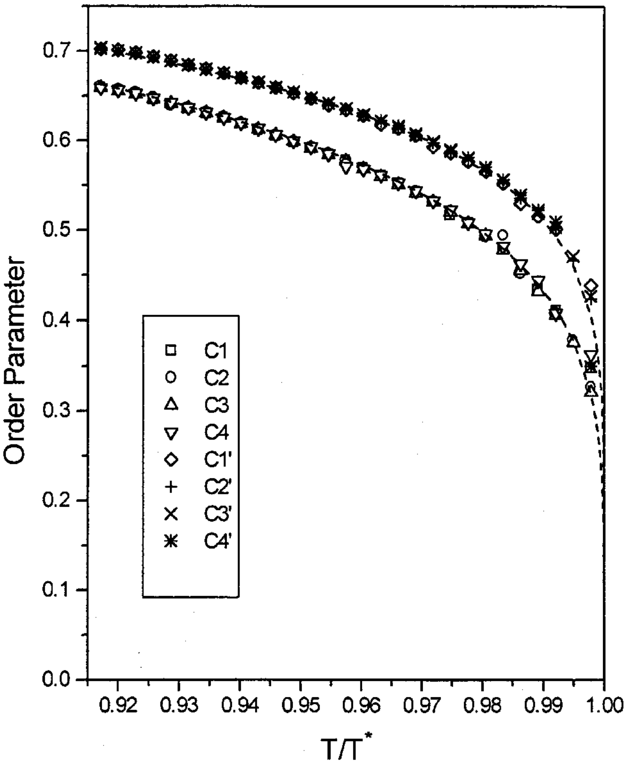


Figure 3. Plot of order parameters of the aromatic carbons of 7CPB against T/T^*.

Table 1. Semi-empirical parameters for the aromatic carbons of 7CPB.

	Carbon atom							
Parameter	1	2	3	4	1′	2′	3′	4′
a	74.7	34.6	29.3	51.7	94.3	40.8	45.1	106.9
b	10.1	6.44	5.56	20.4	− 6.91	− 0.02	− 0.68	− 7.10
Correlation coefficient	0.989	0.986	0.985	0.984	0.996	0.996	0.996	0.996

Table 2. Semi-empirical parameters for the aliphatic carbons of 7CPB.

	Carbon atom						
Parameter	α	β	γ	δ	ε	ζ	ω
a	42.9	31.6	33.5	38.6	46.7	14.8	48.3
b	0.22	− 1.89	− 0.32	− 0.54	0.12	− 0.55	0.32
Correlation coefficient	0.994	0.998	0.989	0.998	1.000	1.000	0.996

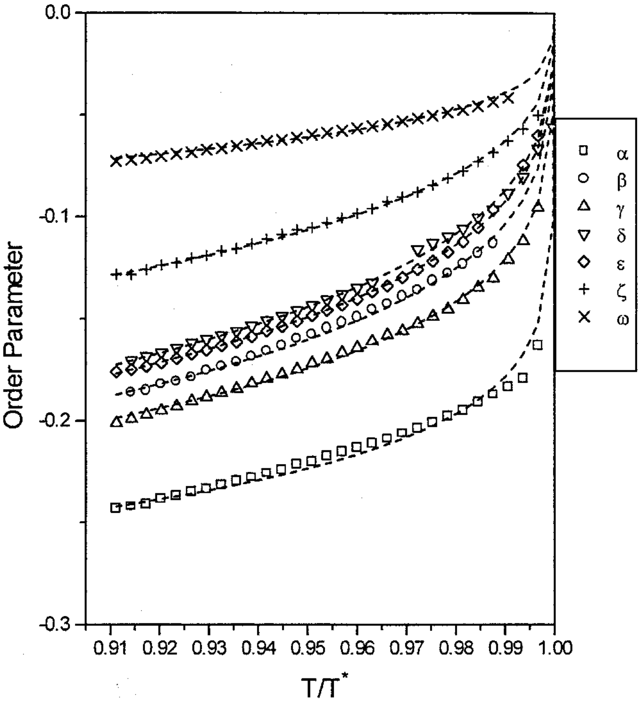


Figure 4. Plot of order parameters of the aliphatic carbons of 7CPB against T/T^*.

The S_0 and F values for the best fitting are listed in table 3, where Ring 1 refers to the phenyl ring containing the heptyl chain. T^* was initially treated as a variable parameter for fitting each curve; then, the average value of 324.7 K was used as a fixed parameter for all final fitting. It has been suggested that the numerical values of S_0 for the phenyl ring should be close to unity. Although a variety of experimental techniques used in the determinations of order parameters indicated that this is not always true [26], the values of S_0 for both phenyl rings in 7CPB are quite close to unity. For a perfectly aligned all-*trans* conformation of the aliphatic chain, S_0 for each C–H bond should be close to -0.333, i.e. $(3\cos^2 109°28' - 1)/2$. The values listed in table 3 for the first five carbon atoms agree with this estimation reasonably well. However, an obvious odd–even alternation trend can be observed in the table, indicating that the bond angles are not strictly 109°28′. The two outermost carbon atoms (i.e. ζ and ω) have S_0 values substantially less negative than the ideal value. This means that, in the theoretical state of perfect nematic ordering for the liquid crystalline core, the chain end would still undergo considerable motions. The parameter F is an indication of how fast a molecular segment approaches this perfect state with the lowering of temperature. The data in table 3 show that in general F increases gradually from the core to the chain. This is quite reasonable because in the nematic phase the motions of the core are more limited than those of the chain, and the 'freezing' of chain motions with the lowering of temperature is more pronounced.

Because of the lack of resolution in the ^{13}C spectrum of 7PFCPB in the smectic A phase, figure 1 (*d*), the order parameters could not be obtained with good accuracy. Nevertheless, a study of the ^{13}C spectra of mixture of 7PFCPB and 7CPB offers useful information on the phase behaviour of these systems.

Figure 5 shows the ^{13}C spectra of a mixture of 7PFCPB and 7CPB (mole ratio 2:1) at five different temperatures. At 137°C, which is higher than the clearing points of both compounds, the spectrum, figure 5 (*a*), is the sum of two isotropic spectra, figures 1 (*a*) and 1 (*c*). When the temperature is lowered, the spectrum consists of both isotropic and anisotropic peaks for both compounds, figure 5 (*b*). As the temperature is further lowered, the intensities of the isotropic peaks decrease, figure 5 (*c*). However, upon a further decrease of temperature, the intensities of the isotropic peaks increase substantially, figure 5 (*d*); in the mean time, the anisotropic peaks become very broad. Finally, at 48°C, the isotropic peaks disappear completely, while the anisotropic peaks sharpen again, but appear as partial powder pattern rather than single peaks.

This interesting sequence of spectral changes can be explained by the following. As the mixture is cooled from the isotropic phase, part of the sample turns into a smectic A phase. The smectic A phase seems to be well aligned in the magnetic field, so that the linewidths shown in figures 5 (*b*) and 5 (*c*) are comparable to those in the nematic phase, figure 1 (*b*). The two phases coexist for a fairly large temperature range (from *c.* 133 to 80°C), with the amount of isotropic phase diminishing. Further lowering of temperature reduces the solubility of 7PFCPB in 7CPB because the fluorocarbon chain is not compatible with the hydrocarbon chain. Then, the

Table 3. S_0 and F obtained by fitting the calculated order parameter of the Haller equation.

	Carbon atom/ring								
Parameter	Ring 1	Ring 2	α	β	γ	δ	ε	ζ	ω
S_0	1.09	1.02	-0.340	-0.360	-0.344	-0.366	-0.361	-0.282	-0.139
F	0.20	0.15	0.14	0.27	0.23	0.31	0.30	0.33	0.28

Table 4. Order parameters of the rings and aliphatic C-H bonds of 7CPB in the mixture of two temperatures.

	Carbon atom/ring								
Temperature/°C	Ring 1	Ring 2	α	β	γ	δ	ε	ζ	ω
114	0.65	0.70	− 0.19	− 0.15	− 0.13	− 0.13	− 0.15	− 0.068	− 0.057
104	069	0.72	− 0.20	− 0.18	− 0.14	− 0.14	− 0.16	− 0.075	− 0.061

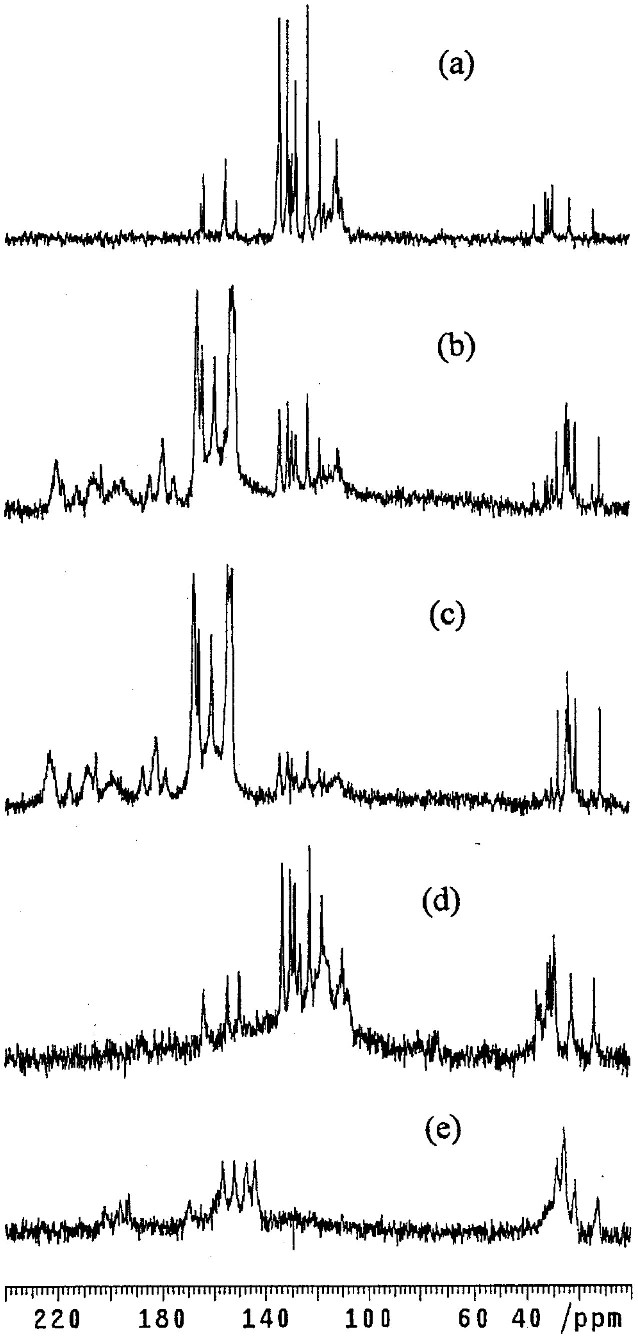


Figure 5. ^{13}C NMR spectra for a mixture of 7PFCPB and 7CPB at: (*a*) 137°C, (*b*) 114°C, (*c*) 104°C, (*d*) 78°C, (*e*) 48°C.

system, which has been mostly SmA with only a small amount of isotropic phase, turns into a mixture of isotropic and a higher order smectic phase. Judging from the characteristic of the spectrum, figure 5(*d*), the isotropic phase contains mostly 7CPB, with a small amount of dissolved 7PFCPB to keep it in the isotropic state. The director of the smectic phase does not have a unique orientation in the magnetic field, and the ^{13}C peaks are broad. Finally, at still lower temperatures, the isotropic portion freezes and the smectic phase has better ordering, showing partial powder patterns, figure 5(*e*). These explanations were substantiated by observations under the polarizing microscope, which showed the smectic A phase starting to appear at ~ 133°C and turning into a higher smectic phase at ~ 80°C.

In the smectic A phase, the order parameters of the rings and aliphatic C–H bonds in 7CPB can be calculated from equation (1) by using the data listed in tables 1 and 2. The results obtained at two temperatures are listed in table 4, where Ring 2 refers to the phenyl ring carrying the cyano group. As expected, the liquid crystal becomes more ordered with the decrease of temperature.

4. Conclusions

In conclusion, the orientational ordering of 4-cyanophenyl 4-heptylbenzoate (7CPB) has been studied by using the 2D PELF/OMAS method, which provides higher resolution than the previous SLF/VAS method and enables long range dipolar coupling to be directly visualized. Linear relations between chemical shifts and order parameters were established, and semi-empirical parameters were obtained to facilitate the study of the order behaviour of 7CPB over the entire nematic range by using 1D anisotropic ^{13}C chemical shift measurements. A 1:2 mixture of 7CPB with its chain-perfluorinated analogue has a very interesting phase behaviour with the change of temperature. The order parameters of 7CPB in the smectic A phase of the mixture were calculated from the ^{13}C chemical shifts.

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