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Determination of the orientational ordering of 4′-cyanophenyl-4-alkylbenzoates by ^{13}C NMR

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The orientational ordering of three 4′-cyanophenyl-4-alkylbenzoates (with number of carbons in the alkyl chain, $n=6, 7$ and 8; hereafter abbreviated as n-CPBs) has been investigated by ^{13}C NMR. The order parameters of different molecular segments in the nematic phase of the n-CPBs were determined by the two-dimensional technique of separated local field (SLF) spectroscopy combined with off-magic-axis, variable-angle spinning (VAS) of the sample. The carbon-13 chemical shifts for each carbon nucleus in these compounds were determined by slowly spinning the sample parallel to the applied magnetic field. The order parameters obtained from SLF/VAS studies are linearly related to the corresponding anisotropic carbon-13 chemical shifts. These results provide a convenient way to obtain the order parameters for other homologous members of this liquid crystal series by direct measurement of only their carbon-13 chemical shifts in conjunction with the observed linear relationship between order parameters and chemical shifts.

1. Introduction

The presence of orientational ordering with no long range positional ordering is the characteristic feature of the nematic liquid-crystalline mesophase. The orientational ordering of liquid crystals can be probed by a variety of techniques [1] including dielectric relaxation, infrared spectroscopy, X-ray diffraction, electron spin resonance (ESR), and nuclear magnetic resonance (NMR). Among the variety of useful techniques, ^{13}C NMR has proved to be powerful for probing the orientational ordering of the individual molecular segments in liquid-crystalline phases [2–15]. The method employed in our study combines the two-dimensional separated local field (SLF) spectroscopy with variable angle spinning (VAS). Upon determining the order parameters of several compounds in this homologous series by a systematic variation of the temperature within their mesomorphic range, the results can then be correlated with the anisotropic ^{13}C chemical shifts of these compounds obtained from the corresponding one-dimensional spectra [11–15]. Because the order parameters in a homologous series have been shown to linearly depend on the corresponding anisotropic ^{13}C chemical shifts [15], the order parameters of other compounds in the same series not hitherto determined by SLF/VAS can be obtained from simple one-dimensional NMR with the use of these experimentally established linear correlations.

In this work, we have studied the orientational ordering of three 4′-cyanophenyl-4-alkylbenzoates and compared the results with the 4-alkyl-4′-cyanobiphenyl series, in order to evaluate the influence of the link on the ordering parameter of each fragment.

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2. Experimental

The compounds 4′-cyanophenyl-4-alkylbenzoates (n-CPBs, $n=6, 7$ and 8) were synthesized in this laboratory by following a procedure similar to that described by Kelly [16]. The synthesis involved the reaction of 1 : 1 mole ratio of 4-alkylbenzoyl chloride with 4-cyanophenol in dry pyridine at 80°C for approximately 2 h. Upon cooling the reaction mixture followed by acidification with cold dilute hydrochloric acid, the product was extracted with chloroform. The chloroform was then evaporated under reduced pressure and the product was filtered and washed with cold hexane and purified by multiple recrystallizations from ethanol. The purity of the compounds were established by NMR spectroscopy. The transition temperatures of the three compounds determined by polarizing microscopy are listed in table 1.

The ^{13}C NMR experiments using the VAS/SLF techniques were performed by using a Varian XL-300 NMR spectrometer equipped with a variable-angle spinning probe manufactured by Doty scientific, Columbia, South Carolina. The SLF pulse sequence was used with a ^{13}C spin echo and the BLEW-48 decoupling sequence. The details of the experimental technique have been described previously [10–15]. For the anisotropic carbon-13 chemical shift measurements, a Varian VXR-500 NMR spectrometer operating at 125·7 MHz was employed. Temperature scales were calibrated by observing the change in the ^{13}C spectrum of each compound at the isotropic to nematic transition temperature.

3. Results and discussion

3.1. *Determination of order parameters by 2D ^{13}C NMR*

In this laboratory, we have used two-dimensional ^{13}C NMR to study the orientational ordering of a large number of liquid crystals [3–15]. For the sake of completeness, the principles of the method are briefly reviewed below.

A nematic liquid crystal is spun rapidly at an angle β with respect to the magnetic field B_0 to orient the sample along the spinning axis and to obtain sharp ^{13}C peaks. The angle β in this work was chosen to be between 46° to 48° and was determined by measuring the ratio of the F–F dipolar coupling of 2,2-difluoro-1,1,1,2-tetrachloroethane partially oriented in the nematic phase of ZLI-1291 with and without sample spinning (spinning rate *c.* 1 kHz). In the 2D SLF method, an efficient proton–proton dipolar decoupling sequence BLEW-48 [17] is applied during the evolution period, so that first-order C–H couplings can be observed in the ω_1 dimension of the experiment; the methylene carbons are split into triplets, the methyl carbons are split into quartets, and the protonated aromatic carbons are split into doublet of doublets due to couplings with the *ipso* and *ortho* protons. As an example,

Table 1. The transition temperatures of the three n-CPB compounds. Heating rate 5°C min^{-1}. Cooling rate 5°C min^{-1}. * supercooled at room temperature.

n	C	→	N	→	I
6	●	42·3	●	46·7	●
		*	●	(46·7)	●
7	●	42·9	●	55·2	●
		*	●	(55·2)	●
8	●	46·3	●	52·5	●
		*	●	(52·5)	●

the spectra of 7-CPB at 48°C are shown in figure 1. The normal spectrum containing chemical shift information is obtained in the ω_2 dimension, shown at the bottom of figure 1. While the ^{13}C peaks for each of the aliphatic carbons at 75·4 MHz is not always fully resolvable, better resolution in the crowded aliphatic region can be obtained by performing the SLF/VAS experiments at 125·7 MHz. The assignment of the aromatic peaks was made using the group contribution method [18] and the assignment for the alkyl peaks follows that of the corresponding cyanobiphenyls [7].

The splittings ($\Delta\nu$) for the overlapping multiplets can be easily obtained by fitting the spectra into a sum of the suitable number of Gaussian peaks. The dipolar coupling constants D can then be calculated by using the equation

$$\Delta\nu = f[(3\cos^2\beta - 1)D + J]. \tag{1}$$

In equation (1), f is a scaling factor for the dipolar decoupling sequence $f = 0{\cdot}42$ for BLEW-48 [19]), and J is the scalar coupling constant. The experimental error on the absolute value of the dipolar coupling is estimated to be about 5 per cent.

The segmental order parameters of the phenyl rings can be calculated from the dipolar splittings with respect to their para axis, using well-known relations [2–15]. Because of internal rotation of the phenyl rings along their para axis, the effective symmetry of the phenyl rings is D_2. Then, only two order parameters S_{zz} and $S_{xx} - S_{yy}$

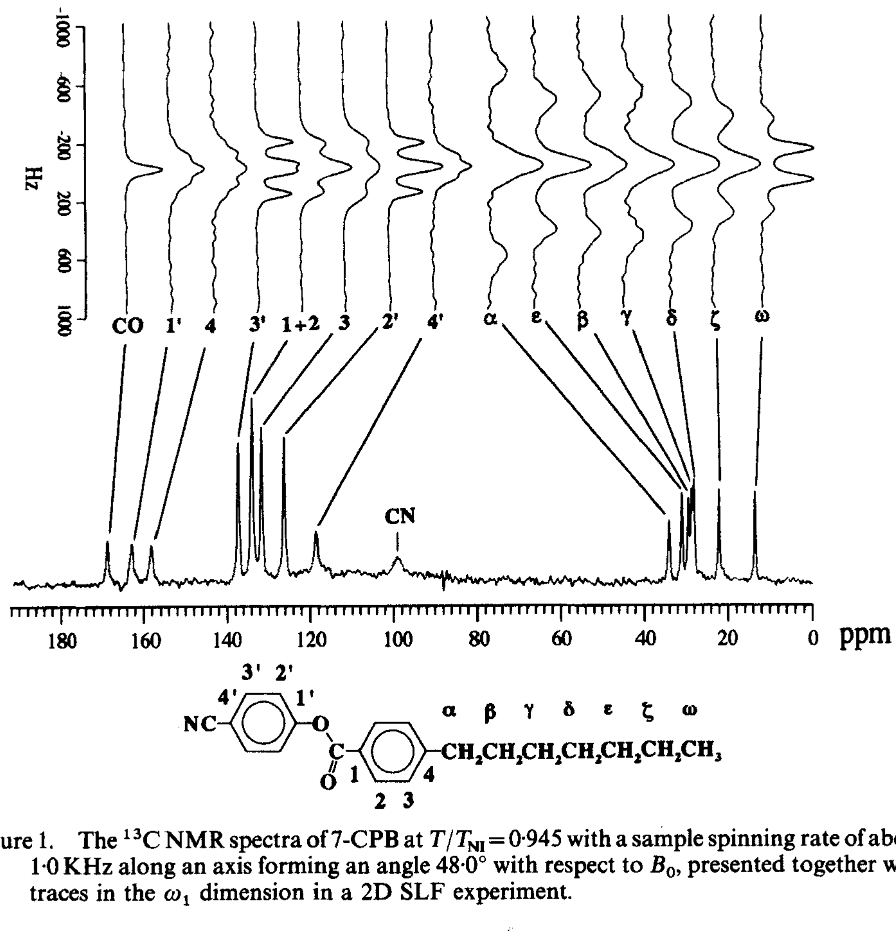

Figure 1. The ^{13}C NMR spectra of 7-CPB at $T/T_{NI} = 0{\cdot}945$ with a sample spinning rate of about 1·0 KHz along an axis forming an angle 48·0° with respect to B_0, presented together with traces in the ω_1 dimension in a 2D SLF experiment.

are required to describe the ring ordering. If we assume an hexagonal geometry for the phenyl ring, these two order parameters and the H–C–bond angles for each phenyl ring can be calculated from the experimentally observed six C–H dipolar coupling constants by the use of least squares analysis [2]; the convention of the axis system is such that the C_2 axis of each phenyl ring is defined as the z axis and the normal to the ring is defined as the y axis, while the x axis in the plane of the phenyl ring and perpendicular to the z axis. For the aromatic rings, the splitting pattern exhibited by each of the protonated carbons is an overlapping doublet of doublets arising from the dipolar coupling of these carbon nuclei to the directly bonded proton and as well as to the *ortho* proton. For the doublet of doublets, the large C–H splitting is assigned to the coupling with the *ipso* proton and the smaller coupling to the *ortho* proton. A genuine triplet is observed for the quarternary carbons, because rapid motional averaging of the phenyl rings makes the *ortho* protons identical. Since the component peaks within each group often overlap with each other, the multiplets were fitted to the sum of corresponding gaussian peaks. For the quarternary carbon (C4) in the phenyl ring directly attached to the alkyl chain, the triplet was found to be too broad to be accurately deconvoluted. One possible reason for this line broadening is presumably due to the further splitting of the quarternary carbon triplet signals by the adjacent methylene group protons in the alpha position of the alkyl chain. Furthermore, the signal of the other quarternary carbon of this phenyl ring is buried underneath that of a protonated carbon and is usually not resolved. Therefore only the two sets of the doublet splittings observed from the protonated carbons were utilized in the fitting program for the calculation of the core order parameters of the phenyl ring directly attached to the alkyl chain. For each phenyl ring, two bond angles and two order parameters were obtained by using a non-linear least-squares program to fit the experimental dipolar constants.

The results of the order parameters for each of the aromatic rings for 6-CPB, 7-CPB and 8-CPB are collected in table 2. The calculated value for each bond angle is essentially the same for all the compounds within the homologous series at different temperatures. For the phenyl ring containing the aliphatic chain, the averaged values of the bond angles are: $\angle$H3–C3–C2 = 118·8° ± 0·3°; $\angle$H2–C2–C3 = 120·0° (not varied). For the phenyl ring directly bearing the cyano group, the corresponding bond angles are $\angle$H2′–C2′–C3′ = 121·7° ± 0·3° and $\angle$C2′–C3′–H3′ = 120·9° ± 0·3°. It is interesting to note that the $\angle$H2′–C2′–C3′ bond angle is noticeably larger than 120°, presumably because the attractive interaction between the oxygen atom of the carboxylate group and H2′ might enlarge this bond angle. A similar result has been observed for liquid crystals containing a –CH=CH–COO– bridge connecting two phenyl rings [20].

For the alkyl chains, the order parameter of each C–H bond is a weighted average over all conformations, and is directly proportional to the corresponding C–H dipolar coupling constant [3]. An assumed value of 0·110 nm for the alkyl C–H bond distance, together with nuclear gyromagnetic ratios and the Planck's constant, yields the following simplified expression for the order parameters along the aliphatic carbon-hydrogen bonds

$$S_{\mathrm{CH}} = -(4\pi^2 r^3/\gamma_{\mathrm{C}}\gamma_{\mathrm{H}} h) D_{\mathrm{CH}} = -4{\cdot}407 \times 10^{-5} D_{\mathrm{CH}} \qquad (2)$$

where D_{CH} is expressed in Hz. The order parameters for the various aliphatic carbon atoms in 6-CPB, 7-CPB and 8-CPB at two temperatures are listed in table 3. Because 7-CPB has the largest nematic range and can be supercooled to a much lower temperature, the values of its S_{CH} for the aliphatic chain at five temperatures are plotted

Table 2. Order parameters for each of the phenyl rings in 6-, 7- and 8-CPB as a function of reduced temperature (T/T_{NI}).

Compound	T/T_{NI}	S_{zz}	$S_{xx}-S_{yy}$	S'_{zz}	$S'_{xx}-S'_{yy}$
8CPB	0·9475	0·525	0·035	0·586	0·029
	0·9567	0·514	0·046	0·565	0·032
	0·9790	0·479	0·054	0·502	0·032
7CPB	0·9450	0·615	0·055	0·637	0·017
	0·9633	0·557	0·066	0·558	0·026
	0·9908	0·444	0·048	0·454	0·017
6CPB	0·9779	0·481	0·055	0·503	0·019
	0·9970	0·404	0·047	0·419	0·017

Table 3. Order parameters for the aliphatic C–H segments of 6-, 7- and 8-CPB at $T_{NI}-T=4$ K and $T_{NI}-T=8$ K.

	6CPB		7CPB		8CPB	
Carbon	$T_{NI}-4$ K	$T_{NI}-8$ K	$T_{NI}-4$ K	$T_{NI}-8$ K	$T_{NI}-4$ K	$T_{NI}-8$ K
α	−0·211	−0·213	−0·222	−0·225	−0·211	−0·243
β	−0·134	−0·152	−0·151	−0·172	−0·136	−0·142
γ	−0·150	−0·164	−0·172	−0·182	−0·153	−0·182
δ	−0·114	−0·126	−0·134	−0·148	−0·136	−0·150
ε	−0·118	−0·130	−0·143	−0·154	−0·136	−0·164
ζ	—	—	−0·101	−0·108	−0·102	−0·126
η	—	—	—	—	−0·102	−0·122
ω	~0	~0	−0·056	−0·060	~0	~0

in figure 2, in which the well-known odd–even effect [21] is quite evident. Because of this effect, S_{CH} for the methyl group in the alkyl chain is close to zero for 6-CPB and 8-CPB, but rather appreciable for 7-CPB.

3.2. *Determination of order parameters from ^{13}C chemical shifts*

The 2D SLF/VAS technique is a reliable and convenient method to determine the orientational order parameters without the use of isotropic substitution (and by ^2H NMR) or spin probes which perturb the liquid crystal ordering. However, it is rather time consuming in terms of the prolonged spectrometer time needed for performing these experiments and the accompanying data processing involved. To study the temperature dependence of the order parameters of a large number of homologous compounds over wide temperature ranges, one can combine the SLF/VAS results with ^{13}C chemical shift data [11–15], which are readily obtained from one-dimensional NMR experiments.

Because of the anisotropic nature of the liquid-crystalline phase, the observed chemical shift is dependent on the order parameters [22]. For the phenyl group with effective D_2 symmetry, the chemical shift expression relating to order parameters is given by (3)

$$\delta_{LC}=\delta_{iso}+(2/3)S_{zz}[\sigma_{zz}-1/2(\sigma_{yy}+\sigma_{xx})]+(1/3)(S_{xx}-S_{yy})(\sigma_{xx}-\sigma_{yy}), \qquad (3)$$

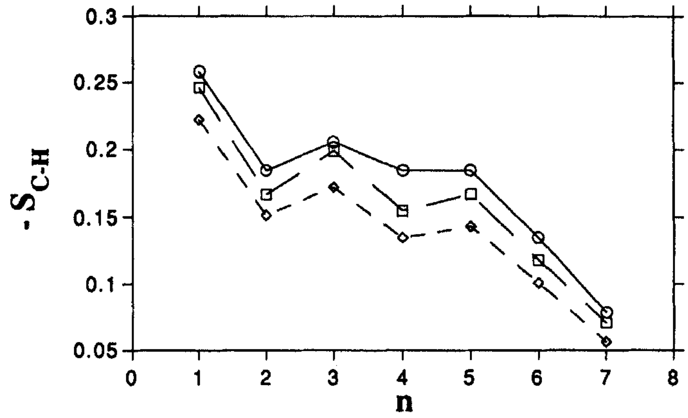

Figure 2. The values of S_{C-H} for the aliphatic chains in 7-CPB at $T_{NI}-T=20$ K (○), 12 K (□) and 4 K (◇).

where the σs are components of the chemical shift tensor along the major axes of the ordering matrix. In principle, the order parameters can be determined from the chemical shifts provided that the system has C_3 or higher symmetry and the values of σs are known. However, this is rarely the case. On the other hand, we have shown that a semi-empirical relation can be established for both the phenyl rings and the C–H bonds in the aliphatic chains [15]

$$\Delta\delta = a\cdot S + b \tag{4}$$

where $\Delta\delta = \delta_{LC} - \delta_{iso}$, and a, b are constants, and the subscript in S_{zz} for the phenyl rings or S_{CH} for the chains is omitted. It must be noted that equation (4) is strictly not applicable for temperatures close to the clearing point, at which both $\Delta\delta$ and S approach zero. With variable angle sample spinning, the anisotropic chemical shift is scaled by a factor of $(3\cos^2\beta - 1)/2$; therefore, the observed value of $\Delta\delta$ in equation (4) should be divided by this factor.

The value of anisotropic chemical shift for each carbon nucleus in the phenyl rings is plotted against S_{ZZ} obtained from the analysis of SLF/VAS data. For each type of carbon, all data from three members of this homologous series with different values of n are pooled in these plots for each of the phenyl rings. The resulting plots of $\Delta\delta$ against S for 6-CPB, 7-CPB and 8-CPB are shown in figures 3 and 4, and the values of a and b obtained from linear least squares fitting of these data are listed in table 4. These values offer a convenient data base for the determination of the order parameters of the n-CPB series from their anisotropic ^{13}C chemical shifts, which are obtainable from conventional one-dimensional experiments. It must be noted that for the phenyl rings, the slope of the linear equation, a is approximately equal to $[2\sigma_{zz} - (\sigma_{yy} + \sigma_{xx})]/3$. Since the major axes of the chemical shift tensors for the non-protonated carbons should nearly coincide with the principal axes of the order matrix [23, 24], the corresponding values of a are approximately equal to 2/3 times the chemical shift anisotropy. However, this is not the case for the other carbon atoms [15].

In order to test the appropriateness of utilizing tabulated values of a and b to calculate the order parameters of the aromatic core, calculated values of S from the chemical shifts of each of the carbon nucleus in the phenyl rings are compared with the experimental value of S_{ZZ}. The best fit of the data is represented by a solid line in figure

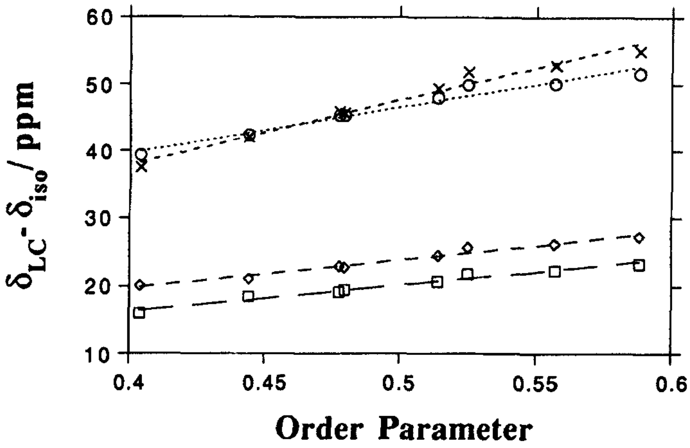

Figure 3. The values of $(\delta_{LC}-\delta_{iso})$ plotted against order parameters for the phenyl ring (labelled ring 1) attached to the aliphatic chain in *n*-CPB with $n=6$, 7 and 8 where (○) = C4, (□) = C3, (◇) = C2 and (×) represents C1.

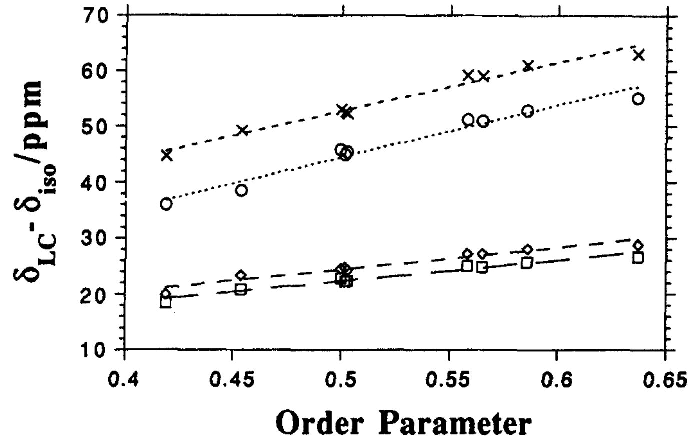

Figure 4. The values of $(\delta_{LC}-\delta_{iso})$ plotted against order parameter for the phenyl ring (labelled ring 2) attached to the cyano group in *n*-CPB with $n=6$, 7 and 8 where (○) = C1', (□) = C2', (◇) = C3' and (×) represents C4'.

Table 4. Calculated values of *a* and *b* (ppm) for each ^{13}C nucleus in the phenyl rings in *n*-CPBs. The ring attached to the alkyl ring is labelled ring 1 and the carbons in this ring indicated by unprimed numbering. The phenyl group attached to the cyano group is referred to as ring 2 and the corresponding carbons are indicated by primed numericals.

	1	2	3	4	1'	2'	3'	4'
a	97·5	41·5	39·0	68·9	93·4	37·7	39·9	88·3
b	−1·2	3·1	0·73	12·1	−2·3	3·4	4·4	8·5
Correlation coefficient	0·99	0·99	0·99	0·98	0·98	0·98	0·97	0·99

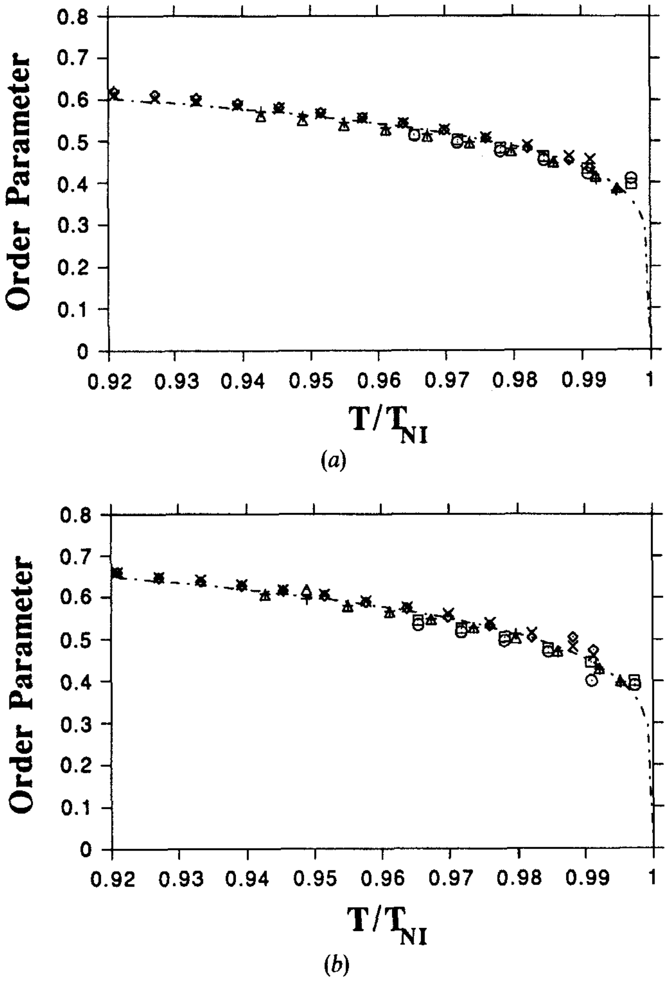

Figure 5. The core order parameter S calculated from equation (4) by the use of parameters listed in table 2 plotted as a function of the reduced temperature (T/T_{NI}) from the ^{13}C chemical shift of (*a*) the carbon atoms in the phenyl ring next to the aliphatic chain where (○) represents C2 and (□) C3 of 6CPB, (◇) C2 and (×) C3 of 7CPB, and (+) C2 and (△) C3 of 8CPB and (*b*) the carbon atoms of the phenyl ring attached to the cyano group where (○) represents C3′ and (□) C2′ of 6CPB, (◇) C3′ and (×) C2′ of 7CPB, and (+) C3′ and (△) C2′ of 8CPB. The dashed lines in both (*a*) and (*b*) represent the results of the nonlinear least squares fits of the calculated data to the empirical equation (5).

5, in which the order parameter depends on the reduced temperature according to the formula [25, 26]

$$S(T) = S_0(1 - T/T_+)^F. \tag{5}$$

In equation (5) S_0 and F are empirical constants. T_+ is a temperature slightly higher than T_{NI} at which the order parameter would reach zero if the continuous decrease of the order parameter was not aborted by the transition. As the experimental values of the order parameters are obtained relatively far from the transition, we have replaced T_+ by T_{NI} in equation (5). The values of S_0 and F obtained by fitting equation (5) to the order parameters calculated from chemical shifts are listed in table 5. They are in reasonable agreement with the corresponding values of the empirical constants obtained by utilizing the S_{ZZ} values directly determined from 2D SLF/VAS.

It has been suggested that the numerical value of S_0 in equation (5) should be close to one. However, this does not appear to be true as indicated by a variety of experimental techniques utilized in the determination of order parameters [26]. We suggest that the value of S_0 might indicate the maximum ordering possible in the nematic phase for a particular molecular fragment such as a phenyl ring. This value cannot be experimentally attained due to phase transitions. However, a comparison of S_0 values for two fragments of the molecule is relevant. Our results for the *n*-CPB series show that S_0 for the phenyl ring bearing the cyano group ($S'_0 = 0{\cdot}991$) is larger than that the phenyl ring containing the alkyl chain ($S_0 = 0{\cdot}880$). The difference in the order parameters S_{ZZ} and $S_{Z'Z'}$ and then in their limiting values results from the different orientations of the two para axes with respect to the director. S_{ZZ} and $S_{Z'Z'}$ are related by the formula

$$S_{ZZ}(3\cos^2\alpha - 1) = S_{Z'Z'}(3\cos^2\beta - 1), \tag{6}$$

where α, β are the angles between the director and the z, z^- axis respectively. If the angle ϕ ($\phi = \alpha + \beta$) between the z and z' axis is known, the position of the director can be estimated by solving equation (6) numerically. The crystal structure of 4'-cyanophenyl-4-octylbenzoate has been determined and gives a value of $\phi = 9{\cdot}7°$ [27]. The calculation was performed at $T/T_{NI} = 0{\cdot}92$, and the angle α was found to be equal to 12·7°. The accuracy of this value is limited by the experimental error in the order parameters and with the assumption that ϕ is the same in the solid and in the liquid crystal, but the nearly equal values of ϕ and α clearly indicate that the nematic director nearly coincides with the para axis of the most ordered fragment [28]. This is not surprising because the large dipole moment of the cyano group is expected to promote a head to tail arrangement of the molecules. This head to tail arrangement should enforce the director to be nearly aligned with the para axis of the phenyl ring bearing the cyano

Table 5. Comparison of S_0 and F values obtained by fitting the experimental and the calculated values of the order parameters to the empirical equation (5).

	$S_{0\,\mathrm{cal}}$	$S_{0\,\mathrm{exp}}$	F_{cal}	F_{exp}
Ring 1	0·880	0·803	0·150	0·125
Ring 2	0·991	0·895	0·169	0·141

Table 6. Comparison between the calculated order parameters for 4-alkylcyanobiphenyls and 4'-cyanophenyl-4-alkylbenzoates at different reduced temperature.

		n-CPB	
T/T_{NI}	*n*-CB	Ring 1	Ring 2
0·92	0·661	0·604	0·651
0·94	0·619	0·578	0·617
0·96	0·575	0·544	0·574
0·98	0·482	0·488	0·450

group. Therefore the order parameters calculated for the ring bearing the cyano group in the *n*-CPBs compare favourably with that obtained for the two aromatic rings in the 4-*n*-alkyl-4′-cyanobiphenyls (*n*-CB) in which we can assume the director to be parallel to the para axis (see table 6).

4. Conclusions

In conclusion, a combination of our 2D VAS/SLF results in conjunction with the anisotropic chemical shift measurements from one dimensional experiments confirms the linear correlation between the chemical shifts and the order parameter. This method is therefore capable of providing a useful database for the determination of order parameters of the members of the *n*-CPB homologous series. Furthermore, in this work, it has been observed that the order parameter of the phenyl ring attached to the cyano group in this homologous series exhibits a larger ordering than the phenyl ring attached to the alkyl chain. The evolution of the order parameter as a function of reduced temperature in accordance with the empirical equation (5) indicates that the ordering behaviour of the phenyl ring bound to the cyano group in the *n*-CPB appears to be comparable to the corresponding trends for the *k*-CB series studied previously [16]. However, the phenyl ring attached to the alkyl chain in the *n*-CPB series appears to be less ordered when compared with the orientation of the corresponding ring in the *k*-CB series. This experimental finding is due to the non-colinearity of the para axis of the two phenyl rings. At $T/T_{NI}=0{\cdot}92$, the director was found to be nearly aligned with the para axis of the more ordered fragment, and to be 13° apart from the para axis of the phenyl ring bearing the alkyl chain.

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