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Determination of order parameters from carbon–fluorine dipolar couplings

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A convenient NMR method for the determination of the order parameters for liquid crystals containing a fluorinated phenyl ring is described. The technique consists of measuring the carbon–fluorine dipolar coupling constants in the one-dimensional C-13 spectrum of the molecule. The order parameters may then be calculated for the fluorine-containing ring with a high degree of precision because of the excellent resolution afforded by the 1-D C-13 spectra. The method is used to determine the core order parameters for 4-*n*-hexyloxybenzilidene-4′-fluoroaniline (FAB-OC6). The results of the carbon–fluorine dipolar coupling method are compared with two established methods for determining the core order parameters of phenyl rings, namely deuterium NMR spectroscopy and SLF/VAS, a two-dimensional C-13 NMR spectroscopy. Some comments about the orientational properties of the fluorinated liquid crystal FAB-OC6 are made.

1. Introduction

Fluorinated liquid crystals have recently attracted attention due to their unique physical properties, which differ from their non-fluorinated counterparts [1–4]. Several members of the homologous series incorporating 4-*n*-hexyloxybenzilidene-4′-fluoroaniline (FAB-OC*n*) have been the object of studies by polarizing microscopy, X-ray diffraction [4], and deuterium and fluorine NMR spectroscopy [2]. These studies revealed a surprising and interesting physical property, namely some of the highest measured order parameters for the smectic liquid crystalline phases. Because the order parameter is the most important parameter to characterize the orientational ordering of liquid crystals, this unusual property of fluorinated liquid crystals merits further investigation.

Several methods exist for determining the microscopic order parameter of a liquid crystal system. Nuclear magnetic resonance (NMR) has the advantage of being able to study individual molecular segments of liquid crystal molecules. There are two commonly used NMR techniques for determining the order parameters of liquid crystals. The first one calculates the order parameters for the quadrupolar and deuterium–proton dipolar splittings observed in the deuterium NMR spectrum [2, 5–7]. This technique has proven to be very effective, but requires the synthesis of deuteriated liquid crystals. The other technique, which we have developed and used extensively, is a two-dimensional C-13 NMR technique called SLF/VAS [8–13]. It is a combination of separated local field spectroscopy (SLF) [14, 15] and variable angle spinning (VAS) [16, 17]. The order parameters are calculated from C–H dipolar couplings. Liquid crystals with C-13 in natural abundance are used, but the experiment is two-dimensional, and as such requires more spectrometer time.

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For liquid crystals containing fluorine atoms, the problems of synthesizing deuteriated liquid crystals and a lengthy two-dimensional acquisition can be avoided by exploiting the spin properties of the fluorine nucleus, which has a nuclear spin of 1/2. The carbon–fluorine splittings can be readily measured in the one-dimensional proton-decoupled C-13 spectrum. The dipolar couplings may be calculated from the splittings, allowing the order parameters to be quickly and routinely calculated. This yields the same kind of information about the fluorinated segment as other NMR methods and is very precise and convenient. The excellent resolution of the 1-D C-13 spectra contributes considerably to the precision of these calculations.

Broadband decoupling of the carbon–proton couplings is necessary for the method, but lower decoupler powers are required than for the SLF/VAS method. This reduces temperature gradients due to radio-frequency (RF) heating and enables fluorinated liquid crystals with very small nematic ranges to be studied. The results of applying this technique to FAB-OC6 are presented. The technique of using carbon–fluorine dipolar couplings is compared with other NMR techniques which may be used to calculated the order parameter for fluorinated ring sytems. Since measurements on the same compound have been made by different techniques, some conclusions about the orientational properties of the FAB-OC6 liquid crystal systems can be drawn.

2. Experimental

FAB-OC6 was prepared by directly mixing an excess of *p*-hexyloxybenzaldehyde with 4-fluoroaniline at room temperature. The product was purified by recrystallization three times from hexane. The phase transitions were observed in a Olympus BH-2 microscope equipped with cross polarizers and a Linkam PR-600 heating stage. FAB-OC6 shows a nematic, a smectic A, and a smectic B phase. The transition temperatures between the phases, C (47·7°C) S_B (55·0°C) S_A (61·5°C) N (63·0°C) I, were determined by polarizing microscopy. The values were somewhat higher than those reported in previous studies of this compound [2, 4], and the smectic A range was slightly wider. The microscope temperatures were calibrated with a standard, and the sharp transitions indicated a high purity for our sample.

All NMR experiments were performed at 125·697 MHz on a VXR-500S Varian spectrometer. An indirect detection probe from Nalorac Cryogenic Corporation, Martinez, California, was used to acquire the one-dimensional carbon-13 spectra. The inverse geometry of the probe provides superior decoupling efficiency compared to a normal geometry probe. Slow sample spinning (10 Hz) was used to avoid sample vortex. To perform 2-D VAS/SLF experiments, a variable angle spinning probe manufactured by Doty Scientific, Columbia, South Carolina, was used, and the experiments were performed at a spinning angle of 44–46° and a spinning rate of 1800 Hz. The duty cycle was kept at less than 2 per cent to avoid RF heating [18]. The sample was cooled at a rate of 0·1 K every 10 min in the NMR probe to avoid supercooling.

3. Results

The results of the calculation of order parameters of the fluoroaniline ring of FAB-OC6 by the measurement of the carbon-fluorine dipolar couplings in the one-dimensional C-13 NMR spectrum will be presented first. Then, these results will be discussed and compared in the next section with the order parameters calculated from deuterium NMR and SLF/VAS 2-D C-13 NMR.

Figure 1 (*a*) shows the nematic spectrum of FAB-OC6 obtained under the condition of slow sample spinning at 10 Hz. The aromatic peaks for the ring without fluorine were

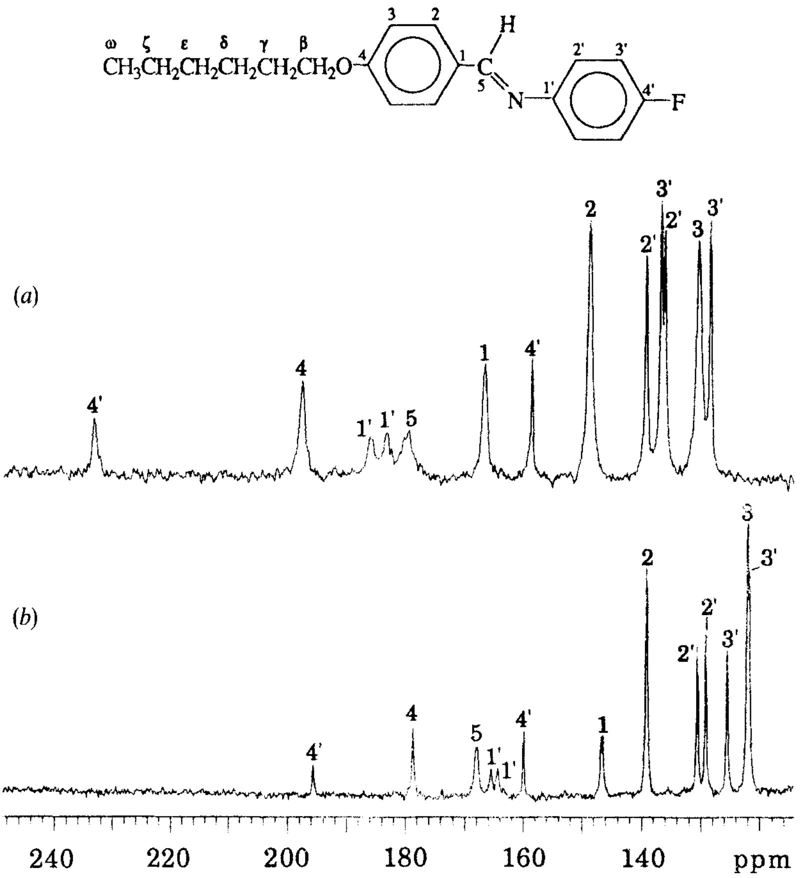

Figure 1. C-13 NMR spectra of FAB-OC6. (*a*) Nematic phase at $T-T_{NI}=0{\cdot}6$ K; spinning at 10 Hz and $\theta=0°$. (*b*) Smectic A phase at $T-T_{NI}=2{\cdot}8$ K; spinning at 1800 Hz and $\theta=45{\cdot}4°$.

assigned by comparison with the benzylidene ring of similar compounds containing alkoxy chains instead of fluorine—the 4-*n*-alkoxybenzylidene-4′-*n*-alkylanilines (*n*O.*m*) [12]. The aromatic peaks of the fluoroaniline ring were assigned based on the expected splitting of the carbon signals caused by the fluorine nucleus as described in the following paragraph. The peaks of the doublets may not have the same height or linewidth due to the effect of chemical shift anisotropy on relaxation [19].

To assign the carbon signals of the fluoroaniline ring, it is noted that when carbon-13 nuclei are split into doublets by the fluorine nucleus, the splitting between the fluorine and a carbon nucleus, $\Delta\nu$, is given by [8]

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

where f is a scaling factor, which is 1 for broadband proton decoupling, and equal to 0·42 when the proton–proton dipolar coupling sequence BLEW-48 is used [20, 21] in SLF/VAS experiments. θ is the angle between the liquid crystal director and the magnetic field, B_0, D is the dipolar coupling constant between carbon and fluorine, and J is the corresponding scalar coupling constant. For slow spinning along an axis parallel to B_0, the director aligns along B_0 and $\theta=0°$. The values for J used for equation (1) measured from the 1-dimensional spectrum of FAB-OC6 dissolved in deuteriated chloroform, and were −237 Hz, 22 Hz, and 8 Hz for F–C4′, F–C3′, and F–C2′, respectively. The signs of these splittings were assigned by comparison with similar compounds [22], and the values for the splittings agree well with those of similar compounds. The *J* value for F–C1′ values was small and difficult to determine accurately from the 1-D spectrum. For this, a *J* value of 3 Hz was assigned, based on comparison with a similar compound [22]. The values of the dipolar couplings calculated from equation (2) may be affected by an anisotropic *J* value for F–C4′. However, the anisotropy in the *J* value for direct C–F couplings is probably very small [23]. Due to the much larger size of the dipolar coupling constant relative to the *J* coupling constant, any contribution to the error in the dipolar coupling constant will be smaller than the error of the technique.

Because of the rapid internal rotation of the phenyl rings in the FAB-OC6 molecule, they have an effective D_{2h} molecular symmetry. Therefore, only two order parameters, S_{zz} and $S_{xx}-S_{yy}$, are needed to describe their orientational ordering. The order parameters for the fluoroaniline ring can be calculated from the four C–F dipolar coupling constants by the use of least squares analysis [10], and those for both phenyl rings may be calculated in a similar fashion from the C–H dipolar coupling constants, as was performed for the similar *n*O.*m* compounds [12]. The calculation of the order parameters of each ring is aided by defining one set of axes for each ring; the convention of the axis systems is such that the C_2 axis is defined as the *z* axis, and the normal to the ring is defined as the *y* axis. The assignment of a separate axis system to each ring prevents the mathematical complications of transforming the molecular coordinates to a single axis system encompassing both rings.

The dipolar coupling in the fluoroaniline ring between nuclei *i* and *j* is expressed by [23]

$$D_{ij}=\frac{-\gamma_F\gamma_C h}{8\pi^2 r_{ij}^3}[(3\cos^2\theta_{ijz}-1)S_{zz}+(S_{xx}-S_{yy})(\cos^2\theta_{ijx}-\cos^2\theta_{ijy})], \qquad (2)$$

where γ_F is the magnetogyric ratio of fluorine and γ_C is the magnetogyric ratio of carbon. The *z* axis is the twofold axis of the ring, and the *y* axis is normal to the ring. r_{ij} is the internuclear distance, and θ_{ijz} is the angle which the internuclear vector along r_{ij} forms with the *z* axis. S_{zz} and$S_{xx}-S_{yy}$ are the order parameters of the ring only, not the order parameters of any groups attached to the ring, because equation (2) is applicable to rings with effective D_{2h} molecular symmetry.

The values of r_{ij} used were based on a microwave spectroscopy study [20] of the geometry of fluorobenzene, which should be structurally similar to the fluorophenyl ring of FAB-OC6. The $r_{F-C1'}$ distance was taken to be 0·135 nm, the $r_{C4'-C3'}$ to be 0·138 nm, and ∠F–C4′–C3′ to be 118·3°. These values are similar to the results of averaging the X-ray diffraction results from several hundred compounds containing fluorine rings. The other geometry was similar to the benzene bond angle and bond distances, so the other ∠C3′–C2′–C1′ angle was taken to be 120·0°, and $r_{C1'-C2'}$ to be 0·140 nm. It must be noted that equation (2) is very sensitive to the geometry parameters chosen. However, since the geometry is assumed to be constant, the relative precision of the results is not compromised.

In the smectic A or smectic B phases of FAB-OC6, the C–H dipolar couplings are too large to be broadband decoupled without suffering the effects of excessive RF heating [18]. Therefore, rapid variable angle spinning was used to scale the splittings [8], as given in equation (1). On the other hand, the scaling of the splittings caused several peaks to overlap in the nematic phase, making the accurate measurement of

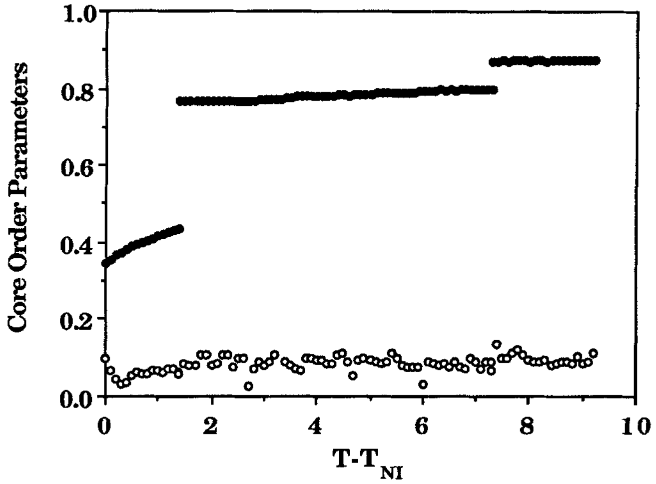

Figure 2. Core order parameters versus temperature determined by carbon–fluorine dipolar couplings. ● stands for S_{zz} and ○ denotes $S_{xx}-S_{yy}$. Note the large change in S_{zz} in the nematic phase, the gradual change in the smectic A phase, and the lack of change in the smectic B phase.

the carbon–fluorine splittings difficult. Therefore, the condition of $\theta = 0°$ was used for the nematic phase.

Figure 1 (*b*) is a spectrum of the smectic A phase obtained under conditions of rapid variable angle spinning (1400 Hz), with $\theta = 45{\cdot}4°$. The peak assignments were made according to the scheme discussed above for the nematic phase. This assignment was confirmed by a SLF/VAS experiment, which will be discussed in a later section. The smectic B spectra differ from the smectic A in their peak positions, especially for the down field 4′ peak, but appear otherwise similar to the smectic A spectrum.

The carbon-13 spectra were recorded at temperatures from the isotropic phase to several degrees below the transition to the smectic B phase. It was necessary to perform the experiments with cooling from the nematic to the smectic phase so that the sample would align with the spinning axis [21]. Each 1-D spectrum was used to calculate four dipolar coupling constants using equation (1). These four coupling constants were fitted by a least squares routine to equation (2) to obtain the S_{zz} and $S_{xx}-S_{yy}$ values for the fluorinated ring at each temperature. The resulting order parameters are shown in figure 2 as a function of reduced temperature. Errors on the calculation of S_{zz} were about 2 per cent and for $S_{xx}-S_{yy}$ about 20 per cent. The relative errors in the $S_{xx}-S_{yy}$ are larger due to the small values of $S_{xx}-S_{yy}$. The first three nematic points shown in figure 2 have slightly larger $S_{xx}-S_{yy}$ values because in the 1-D spectra, one of the peaks of the 2′ doublet was not resolved because of overlap with the peak from the 3′ carbon. This resulted in error due to difficulties in accurately determining the position of the 2′ peak.

4. Discussion

4.1. *Comparison of the order parameters with those calculated from deuterium NMR*

The order parameters for FAB-OC6 have been determined from deuterium NMR [2] by measuring the D–H dipolar splittings, $\Delta\nu_{\mathrm{DH}}$, which are related to the S_{zz} order parameter [23]

$$\Delta\nu_{\mathrm{DH}} = -\left(\frac{\gamma_{\mathrm{D}}\gamma_{\mathrm{H}}h}{4\pi r^3}\right)S_{zz}. \tag{3}$$

The deuterium quadrupolar splittings, $\Delta\nu_q$, are also related to the order parameters [5]

$$\Delta\nu_q = \frac{3e^2qQ}{4}\left\{S_{zz}[3l_{zb}^2 - 1 + \eta(1 - l_{zb}^2)] + (S_{xx} - S_{yy})\left[1 - l_{zb}^2 + \frac{\eta}{3}(1 + l_{zb}^2)\right]\right\}, \qquad (4)$$

where e^2qQ is the quadrupolar coupling constant and η is the asymmetry parameter. l_{zb} is the direction cosine of the principal axis, b, of the quadrupole tensor, which is usually along the C–D bond direction.

In general, order parameters determined by deuterium NMR and C–F dipolar couplings have similar values to within the experimental error, when errors caused by the assumptions about the geometry used in equations (1–4) are taken into account. Like the data shown in figure 2, the deuterium method [2] also shows a rapid increase in the order parameter in the nematic range and a highly first order nematic to smectic A transition. Also, in both methods, the $S_{xx} - S_{yy}$ value does not change very much with temperature. Relative errors in $S_{xx} - S_{yy}$ are also high in the deuterium method, again due to the small values for these parameters. However, the results of the deuterium NMR differ from the C–F dipolar coupling method in several respects. First, the deuterium results indicate that both S_{zz} and $S_{xx} - S_{yy}$ remain constant throughout the entire smectic A range. By contrast, the data in figure 2 indicate that S_{zz} increases slightly over the smectic A range. It has been shown that for most liquid crystals, S_{zz} does increase with decrease in temperature [9, 11, 12]. It may be reasonable to expect a similar type of behaviour in their fluorinated counterparts, which is what we found. A second difference between the deuterium results for FAB-OC6 and the present method is that the former shows that the order parameter suddenly decreases at the smectic A to smectic B transition, so that S_{zz} for the smectic B phase is less than that for the smectic A, which is a very perplexing result. The order parameter S_{zz} determined from the deuterium results of the smectic B phase then quickly increases linearly to a maximum value of the smectic B phase [2]. By contrast, figure 2 shows that the order parameter S_{zz} determined in this work does not have this anomaly; it has a sudden increase at the transition from the smectic A phase to the smectic B phase, and then stays constant within experimental error.

4.2. *Comparison with SLF/VAS results*

When variable angle spinning (VAS) [16, 17] is used to reduce carbon–proton dipolar couplings, their values may be accurately measured by separated local field spectroscopy (SLF) [14, 15]. The detailed examples of SLF/VAS may be found elsewhere [8–13]. The spectra in the ω_1 dimension appear as overlapping multiplets for each C-13 peak and the pattern is related to the number of protons coupled to the carbon. These multiplet patterns may be used to assign peaks in the ω_2 dimension which confirmed the assignment given in figure 1 (*b*). The dipolar couplings are calculated by equation (1) with $f = 0{\cdot}42$, which is the scaling factor introduced by the BLEW-48 decoupling sequence [24, 25] used during the evolution period of the 2-D SLF/VAS experiment.

Six dipolar coupling constants are fitted with a least squares program to solve equation (2) (γ_F is replaced with γ_H) for S_{zz}, $S_{xx} - S_{yy}$, the $C_2C_3H_3$ angle, and the $C_3C_2H_2$ angle where H_n is the proton attached to carbon n, C_n. In practice, it is physically meaningful to average the angles calculated from several experiments and then fix the averaged angles in the final calculation of the order parameter. The averaged angles for the fluoroaniline ring were $\angle C_{2'}C_{3'}H_{3'} = 119{\cdot}9 \pm 0{\cdot}5°$ and

Core order parameters for both rings of FAB-OC6 at several temperatures. The errors listed are the errors of the calculations; the error of the SLF/VAS technique itself is about 5–10 per cent.

	From C–H dipolar couplings				From C–F dipolar couplings	
$T-T_{NI}$/K	S_{zz}	$S_{xx}-S_{yy}$	$S_{zz'}$	$S_{xx'}-S_{yy'}$	$S_{zz'}$	$S_{xx'}-S_{yy'}$
2·6	0·67±0·03	0·05±0·01	0·72±0·02	0·09±0·01	0·767±0·001	0·05±0·01
3·8	0·70±0·03	0·05±0·01	0·68±0·04	0·06±0·02	0·774±0·001	0·05±0·01
7·0	0·72±0·04	0·04±0·02	0·74±0·04	0·06±0·02	0·799±0·001	0·04±0·02

$\angle C_{3'}C_{2'}H_{2'}=120{\cdot}5\pm0{\cdot}3^\circ$ and for the benzylidene ring the angles were $\angle C_2C_3H_3=119{\cdot}9\pm0{\cdot}8^\circ$ and $\angle C_3C_2H_2=120{\cdot}3\pm0{\cdot}7^\circ$. The angles are typical for this type of compound [12].

The SLF/VAS experiment requires the use of considerable decoupler power ($\gamma B_2/2\pi\sim20$ kHz in our case), which leads to a small temperature gradient caused by R.F. heating [18]. In the nematic phase, especially near the clearing point, the order parameters are strongly dependent on temperature, and the temperature gradient contributes to 5–10 per cent experimental error. The nematic range of FAB-OC6 is only 1·5 K, and it is not proper to use the SLF/VAS technique to determine the order parameters. In practice, near the clearing temperature, within the nematic range, the spectrum indicates a mixture of nematic and isotropic phases due to a temperature gradient caused by brief periods of RF heating developed in the SLF/VAS method. For the smectic phases, the results of applying the SLF/VAS procedure to FAB/OC6 at several temperatures are given in the table. For comparison, the order parameters calculated from the C–F splittings are also listed in the same table. The percentage difference is 5–15 per cent depending on the temperatures, which is comparable to the error in the SLF/VAS. Also contributing to the difference are the errors in the values for the geometry parameters.

The SLF/VAS method was used to study the orientation of the non-fluorinated ring and the aliphatic carbons of FAB-OC6. As shown in the table, the S_{zz} order parameters of the non-fluorinated ring are about the same as for the fluorinated ring. The S_{zz} values for the *n*O.*m* compounds, which are structurally similar to FAB-OC6, showed [12] the same effects, namely that the two rings have comparable order parameters to within experimental error. This is expected since both rings are rigidly bound in the mesogenic core.

For the aliphatic carbons of FAB-OC6, it is possible to calculate a bond order parameter, S_{C-H}, for the C–H bond of the methyl and methylene groups [8–13] from the aliphatic carbon–proton splittings, $\Delta\nu_{C-H}$, measured with SLF/VAS.

$$S_{C-H}=-\frac{4\pi^2r^3}{\gamma_C\gamma_H h}D_{C-H}, \tag{5}$$

where D_{C-H} is the dipolar coupling constant calculated from equation (1) and r is the C–H distance. Figure 3 shows the bond order parameter, S_{C-H}, of the aliphatic chain in FAB-OC6 at three different temperatures in the smectic A range as a function of the carbon number away from the aromatic core. The aliphatic peak assignments were made in accordance with *n*O.*m* (12).

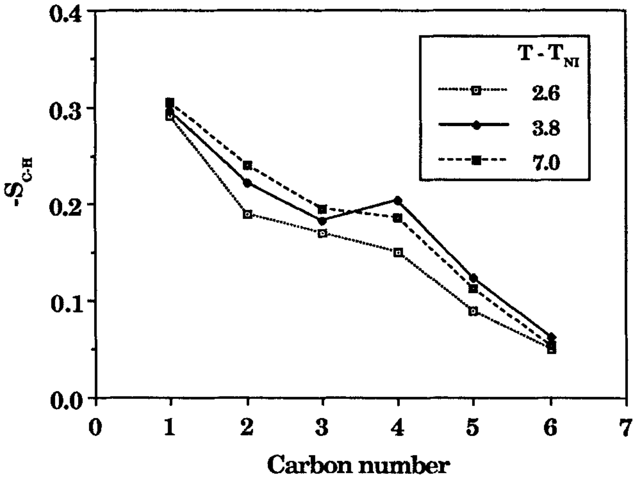

Figure 3. The bond order parameters for the aliphatic chain of FAB-OC6 determined by the SLF/VAS method at three different temperatures.

4.3. *Advantages and challenges of using carbon–fluorine dipolar couplings*

The study of FAB-OC6 has indicated that this system is a good one for comparison of the three methods discussed. For FAB-OC6, the nematic range is very small (1·5 K). The temperature gradient makes the SLF/VAS results unreliable within the short nematic range. On the other hand, the broadband proton decoupling power during measurement of carbon–fluorine couplings was about 60 per cent of the power used for the SLF/VAS experiments. The temperature gradients were not too deleterious, as evidenced by the smooth change in the order parameters in the nematic range (see figure 2). In fact, both the carbon–fluorine method and the deuterium method allow the calculation of order parameters at a large number of temperatures within the whole nematic and smectic ranges.

The three techniques discussed result in comparable order parameters for the liquid crystal phases of FAB-OC6 studied by each. All three techniques require that some assumptions be made about molecular properties–bond lengths, bond angles, and for the deuterium, asymmetry parameters. It is refreshing to note that results for all three techniques are generally comparable in spite of the error that the geometrical assumptions cause in the final error of the calculation. Another source of error in the calculation of the order parameter is the accuracy with which the peak positions may be measured from the spectra recorded by the respective NMR methods. The C-13 spectra presented in figure 1 show that excellent resolution is achieved, which contributes to the accuracy of the measurement of the peak frequencies. On the other hand, deuterium spectra tend to be broader. This sometimes results in peaks overlapping, which can contribute to inaccurate peak frequency measurements and order parameter calculations.

The use of carbon–fluorine couplings produces quantitative results which agree with the orientational behaviour observed in non-fluorinated liquid crystals. The agreement is greater than for the other methods discussed. The primary and obvious drawback seems to be that the calculation of order parameters fails for molecules lacking a fluorine nucleus. Deuterium NMR and SLF/VAS, on the other hand, can study rings with or without a fluorine atom. Another consideration is that the simplicity of the calculations of S_{zz} and $S_{xx}-S_{yy}$ by the carbon–fluorine dipolar coupling method are contingent on the molecule having no lower than C_{2v} symmetry [23]. If the molecule has the fluorine atom substituted at a location other than the *para*-position, the symmetry decreases, and more order parameters are needed to describe the orientation. Then, the difficulty of the problem is greatly increased. This is a limitation, but many of the new interesting fluorinated liquid crystals are *meta*-substituted [1, 3], and further investigations are warranted.

4.4. *The orientational properties of FAB-OC6*

In the course of comparing the various NMR methods for studying fluorinated liquid crystals, many data have been obtained about the orientation properties of FAB-OC6. As in other liquid crystals, the rapid change in S_{zz} in the nematic region of FAB-OC6 as the temperature decreases (see figure 2) is quite typical for nematic ordering near the clearing point. The abrupt change in the magnitude of S_{zz} at the nematic to smectic A phase transition is the characteristic of a first order transition, which is favoured for liquid crystals with short nematic ranges, as predicted by the theory of de Gennes [26]. The smectic A phase is more highly ordered and $S_{zz}(0{\cdot}7–0{\cdot}8)$ is larger than that for non-fluorinated compounds with similar structures [12], such as 4-*n*-alkoxybenzylidene-4′-*n*-alkylanilines (*n*O.*m*; $S_{zz} \sim 0{\cdot}55–0{\cdot}65$). In general, the high degree of ordering causes the liquid crystal molecules to have a greatly reduced translational motion in the smectic A phase, and to have very little changes in the order parameter throughout the entire smectic A range. This is also true for FAB-OC6 (see figure 2). Only at the smectic A to smectic B transition does the order parameter slightly increase, revealing a phase with even more restricted motions. X-ray diffraction studies [4] indicate that in the smectic B phase, FAB-OC6 is fully extended to its physically allowable maximum. Any further extension of the smectic B phase after the transition temperature therefore seems unlikely, and the order parameter in the smectic B phase does not change with temperature (see figure 2).

The order parameter $S_{xx} - S_{yy}$ seems to have a small increase on going from the nematic to the smectic A phase, but does not change much after that. This is a typical result for the biaxial order parameters of most liquid crystals and indicates that there is very little change in the alignment along the short axes of the liquid crystal molecules. The size of this order parameter is also typical of non-fluorinated liquid crystals, indicating that the presence of the fluorine does not greatly influence the out-of-plane alignment of this system.

For the aliphatic chain, the absolute values of the bond order parameter, S_{C-H}, decrease along the chain as expected. Like the *n*O.*m* series [12], the change does not show an obvious odd–even alternating effect as for the cyanobiphenyls [9, 10], but the decrease is nevertheless not monotonic. The S_{C-H} values for the carbons in the β and γ positions are higher than those for the *n*O.*m* compounds [12]. This is to be expected since the C–H segments are in part ordered by their physical connection to the highly ordered phenyl ring. The irregularity for the data at $T - T_{NI} = 3{\cdot}8$ K is probably not significant, because the differences of the order parameters for the three temperatures are generally within the range of the error of the technique.

The above discussions provide a somewhat complete picture of the ordering of FAB-OC6 as a function of phase. However, it is not clear to us how the fluorine atom is able to exert such a significant effect on the orientational properties of this liquid crystal, making the order parameters higher than those of other liquid crystals with similar structures. This is probably related to the effect of fluorine substitution on other physical properties of fluorinated liquid crystals [1, 3]. Therefore, we are continuing to study other fluorinated compounds to investigate further the significant influence of fluorine substitution on the material properties of liquid crystals.

5. Conclusions

We have studied the orientational ordering of liquid crystals with *para*-fluorinated phenyl rings by using carbon–fluorine couplings. We have shown that calculating the order parameters from the observed splittings in the one-dimensional spectrum is convenient, straightforward, and reliable, mainly because of the excellent resolution of the carbon-13 spectra. Another positive aspect of using the carbon–fluorine couplings is that, since the RF heating and temperature gradient are kept to a minimum by using moderate decoupler power, it is possible to study liquid crystals with a very large change in order parameters within small temperature ranges. On the other hand, the more general SLF/VAS technique is needed to determine the order parameters of the non-fluorinated ring and the alkyl chains.

In many respects, the fluorinated liquid crystal, FAB-OC6, appears to behave very similarly to non-fluorinated liquid crystals in terms of general trends of the change in the order parameter as a function of temperature. The value of the order parameter, S_{zz}, in the smectic phase, however, is much larger than that in similar non-fluorinated systems. This type of structure–material relation is very interesting and needs to be further studied.

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