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Orientational ordering of liquid crystals containing a difluoro-substituted phenyl ring

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Orientational ordering of liquid crystals containing a difluoro-substituted phenyl ring

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The orientational ordering of several liquid crystals containing a difluorosubstituted phenyl ring has been studied through the use of C-13 NMR. The fluorinated phenyl ring of these liquid crystals have C_s symmetry, so three order parameters are required to completely describe the ordering of this ring. All three of these order parameters have been calculated from carbon–fluorine dipolar coupling constants obtained from the carbon–fluorine splittings in the C-13 NMR spectra. Because of the complexity of the fluorine-coupled spectra, variable angle spinning (VAS) was used to resolve the carbon–fluorine splittings. In order to study the orientational ordering over wide ranges of temperature, we have developed an empirical correlation between the order parameter and the value of a carbon–fluorine dipolar coupling constant. This enabled us to study the change in the order parameter with temperature. The results of applying this method to several structurally similar liquid crystals containing the same type of difluorinated phenyl ring are presented. A comparison is made to a similar mono-fluorinated liquid crystal.

1. Introduction

The substitution of one or more fluorine atoms on to the phenyl ring in a liquid crystal alters the physical and material properties of the liquid crystal significantly [1–3]. Because fluorinated liquid crystals have high resistivity, they are useful in electro-optical displays that use thin-film transistors (TFTs). Therefore, studies of the orientational ordering of fluorinated liquid crystals are important. Such studies have been carried out recently by the use of deuterium, F-19, and C-13 NMR [4–6].

We have shown that the order parameters of a monofluoro-substituted liquid crystal can be determined from the carbon–fluorine dipolar coupling constants measured in the 1-D C-13 NMR spectrum [6]. This method was convenient and produced values of the order parameters which agreed with those determined through deuterium NMR and 2-D C-13 NMR. In the present study, we extend the use of this method to liquid crystals in which one phenyl ring is asymmetrically substituted with two fluorine atoms, and determine the order parameters of the fluorinated rings through the measurement of C–F dipolar coupling constants.

For a *para*-monofluoro-substitution [6], the phenyl ring has effective D_{2h} symmetry, and two order parameters are needed to describe the orientation of the phenyl ring. There are four magnetically non-equivalent C-13 nuclei, so eight peaks result from carbon–fluorine coupling. For a phenyl ring disubstituted with fluorine atoms in the *para*- and *ortho*-positions, the symmetry is reduced to C_s, and three order parameters are needed to describe the orientation of the phenyl ring. The complexity of the C-13 NMR spectrum is greatly increased because there are six magnetically non-equivalent C-13 nuclei, resulting in 24 aromatic C-13 peaks due to the coupling between each C-13 with two fluorine nuclei.

The order parameters may be calculated from the carbon–fluorine dipolar coupling constants [6] determined from the C-13 1-D NMR spectrum. However, in a C-13 1-D NMR spectrum of difluoro-substituted compounds, some of the 24 aromatic carbon peaks overlap, reducing the resolution and making the assignment of the coupling constants ambiguous. We have therefore used variable angle spinning (VAS) to reduce the magnitude of the coupling constants to enhance the resolution of the spectrum, which allows determination of all three order parameters from carbon–fluorine splittings. While in some cases more than two order parameters have been determined for solutes dissolved in liquid crystal, we believe

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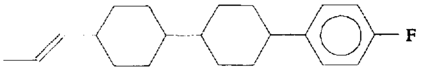
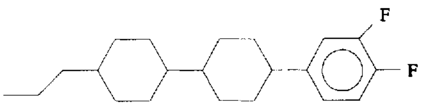
that our study is the first to calculate three order parameters for a liquid crystal molecular segment with C_s symmetry.

The method of observing carbon–fluorine dipolar coupling with VAS was applied to three difluorinated liquid crystals which have been the object of extensive studies of their material properties [1, 3]. The order parameters of these difluorinated liquid crystals are compared to those of a structurally similar mono-substituted liquid crystal. Structures of these liquid crystals are shown below. Details of their nomenclature are found elsewhere [1].

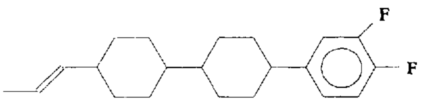
1d$_1$CCPF



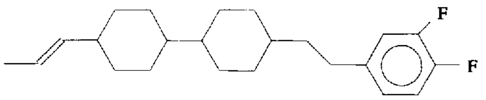
3CCP$_F$F



1d$_1$CCP$_F$F



1d$_1$CCAP$_F$F



2. Experimental

Details of the synthesis of 1d$_1$CCPF, 3CCP$_F$F, 1d$_1$CCP$_F$F, and 1d$_1$CCAP$_F$F have been described previously [1, 2]. The nematic ranges of these compounds were 105–194°C, 46–122°C, 64–159°C, and 64–137°C, respectively. 1d$_1$CCP$_F$F also has a smectic B range between 49–64°C [2]. The upper limit of the nematic range of the value for 3CCP$_F$F, determined with an Olympus BH-2 microscope equipped with crossed polarizers and a Linkham PR-600 heating stage, was slightly different from that previously observed [3], but the other values were the same.

The order parameters of the difluorinated compounds were determined using variable angle spinning (VAS) probes. For 3CCP$_F$F, the order parameters were determined on a Varian VXR-300 spectrometer. For 1d$_1$CCP$_F$F and 1d$_1$CCAP$_F$F, a Varian VXR-500S spectrometer was used because the VAS probe for this instrument could reach higher temperatures than the probe for the VXR-300 spectrometer. The experiments were performed at a spinning angle between 46–47°. In order to study the order parameter as a function of temperature, an indirect detection probe manufactured by Nalorac Cryogenic Corporation, Martinez, California, was used because it provides better temperature control than the VAS probes.

3. Results and discussion

Figure 1 shows the aromatic portion of the C-13 NMR spectrum of 3CCP$_F$F when the sample was spinning rapidly at 1200 Hz. The excellent resolution results from a narrowing of the linewidth caused by the reduction of the dipolar couplings and the scaling of the spinning chemical shift by a factor of $(3\cos^2\theta - 1)/2$ [7], where θ is the spinning angle. The spinning angle was determined accurately by standard means [8]. The spectra of the other liquid crystals are similar to figure 1. The principal

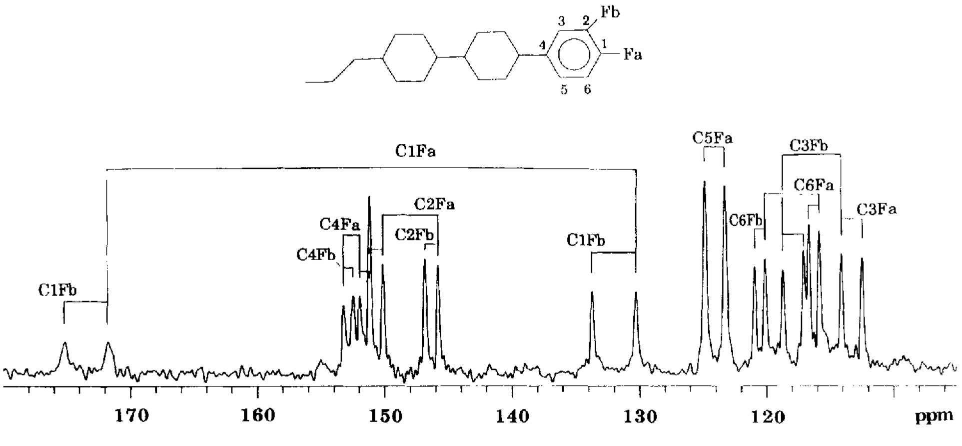


Figure 1. C-13 NMR spectra of the aromatic range of 3CCP$_F$F at 75·429 MHz and at a temperature of 60°C; sample spinning at 1600 Hz at an angle of 47·3° relative to the magnetic field. The splittings between the carbon and fluorine nuclei refer to the assignment in the structure at the top. Thus, C1Fb refers to the splitting between carbon 1 and fluorine b, etc.

difference for the other difluorinated liquid crystals, which all contain C–C double bonds, is that the alkenyl peaks overlap with one of the C5 peaks.

The assignments of the peaks were made based on the carbon–fluorine splittings (see figure 1) and confirmed by the carbon–proton splittings. The latter were observed through the use of two-dimensional separated local field spectroscopy (SLF) combined with variable angle spinning (VAS), which allows the carbon–proton splittings of each carbon peak to be individually resolved. It is possible to determine the order parameter of the ring with SLF/VAS, and we used this technique to study a large number of liquid crystal systems [7–13]. However, for fluorine-containing liquid crystals, we have shown that using carbon–fluorine dipolar couplings is as accurate as SLF/VAS and requires substantially less spectrometer and processing time [6].

It is straightforward to assign the peaks based on the carbon–proton splitting patterns and the magnitude of these splittings. For example, the C3 peak is split into a doublet by the directly bonded proton. This peak is easily differentiated from the C6 peak, which is split into a doublet of doublets by the directly bonded proton and the proton on the neighbouring carbon. The assignment of some peaks, such as those for the C5 and C6 carbons, makes use of the differing magnitudes of the carbon–fluorine splittings because the magnitude of the C5 splitting is expected to be smaller than that of the C6 carbon.

The splitting, $\Delta\upsilon$, between two nuclei spinning rapidly about an axis at an angle θ with respect to the magnetic field, is given by [14]

$$\Delta\upsilon = f[(3\cos^2\theta - 1)D + J] \qquad (1)$$

where f is a scaling factor, which is unity for broadband proton decoupling, D is the dipolar coupling constant, and J is the scalar coupling constant, which was measured for the liquid crystal in deuteriated chloroform. In principle, the J value may be anisotropic in liquid crystal systems, but the anisotropy is probably negligible [15] in the calculation of the dipolar coupling constants from equation (1). The structure of 1d$_1$CCP$_F$F is similar to 3CCP$_F$F, and the values of J do not change within experimental error. Due to the extra alkyl linkage, the J couplings of 1d$_1$CCAP$_F$F show minor differences.

The dipolar coupling for a group with C$_S$ symmetry is given by [15]

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

where γ is the magnetogyric ratio of the nuclei and i and j are the coupled nuclei, i.e. C, F, or H. The z axis is taken to be through the C1 and C4 carbons, the y axis is normal to the ring, and the x axis is in the plane of the ring and is perpendicular to both the y and z axes. r_{ij} is the internuclear distance, and $\theta_{ij(x,y,z)}$ is the angle which r_{ij} forms with the x, y, or z axis of the coordinate system. Equation (2) refers to groups of interacting nuclei, so the order parameters S_{zz}, S_{xx}–S_{yy}, and S_{xz} describe only the orientation of difluoro-substitued phenyl ring, not the entire liquid crystal molecule. The values of r_{ij} and θ_{ij} were based on an X-ray crystallography structure of a structurally similar compound [16]; they are not expected to differ appreciably among the compounds.

It is also possible to calculate the order parameters of the monofluorinated liquid crystal, 1d$_1$CCPF, through the use of equation (2). In this case, the D$_{2h}$ symmetry of the monofluorinated phenyl ring causes S_{xy} term of the equation to become zero, so only the S_{zz} and S_{xx}–S_{yy} terms are necessary to describe the orientation order. The geometric parameters and J coupling constants were obtained from a previous study of a monofluorinated liquid crystal [6] and are not expected to differ within experimental error.

Once the splittings were assigned, the values for S_{zz}, S_{xx}–S_{yy}, and S_{xz} may be readily calculated from the observed dipolar couplings with a non-linear least squares fit of equation (2). In practice, because of overlap of some of the peaks, not all 12 dipolar coupling constants were used to fit the data. Due to uncertainties in the geometry and the sensitivity of equation (2) to small changes in these geometric parameters, C2Fb and C3Fb (see figure 1) were not used in the calculation. Also, the C5Fb splitting is too small to be resolved. Thus, fitting with up to nine dipolar couplings was possible for 3CCPF$_F$. For the other difluorinated liquid crystals, however, C4Fa and C4Fb sometimes are not well resolved, and the C5Fa splitting overlaps with alkenyl peaks present in these compounds. Therefore, only six splitting are available from which to

Table 1. The orientational order parameters of 3CCP$_F$. The upper row for each temperature was calculated using 6 dipolar coupling constants discussed in the text. The values in the second row, given in parentheses, were calculated using the nine dipolar coupling constants discussed in the text.

T–T_{NI}	S_{zz}	S_{xx}–S_{yy}	S_{xz}
30 K	0·580 ± 0·001	0·059 ± 0·009	0·017 ± 0·008
	(0·580 ± 0·001)	(0·061 ± 0·008)	(0·014 ± 0·007)
45 K	0·612 ± 0·001	0·062 ± 0·007	0·017 ± 0·006
	(0·612 ± 0·001)	(0·063 ± 0·006)	(0·015 ± 0·005)
80 K	0·665 ± 0·001	0·061 ± 0·008	0·012 ± 0·008
	(0·665 ± 0·001)	(0·063 ± 0·008)	(0·008 ± 0·007)

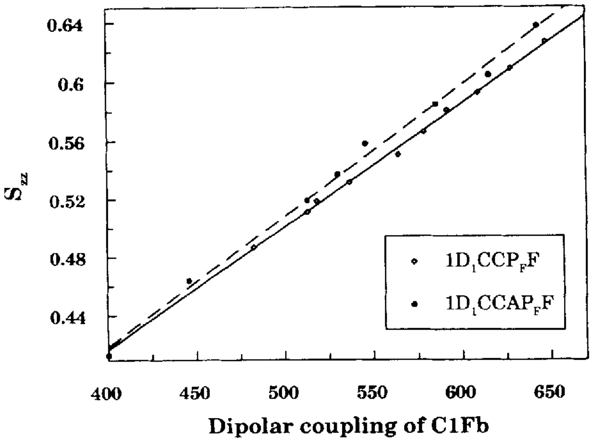


Figure 2. The linear correlation between the C1Fb dipolar coupling and the order parameter of the phenyl ring.

calculate the order parameter. Table 1 compares the order parameters of 3CCPF$_F$ calculated from nine splitting with those calculated from six. The error listed in the table are the errors in the calculations, and the amount of relative error increases with the decrease in the size of the order parameter from S_{zz} to S_{xz}. The actual experimental error resulting from systematic error is probably around 5 per cent. The differences between the order parameters calculated from the six dipolar coupling constants and nine dipolar coupling constants are small and within experimental error, which indicates the reliability of using six dipolar coupling constants instead of nine. The order parameters of the other compounds therefore were calculated with 6 dipolar coupling constants, and similar results were obtained.

The measured temperature for the variable angle spinning probes is not very reliable for the spinning rates used here because the centrifugal force acting on the sample tends to reduce the macroscopic alignment of the nematic phase [17]. However, the relationship between the dipolar couplings and the order parameters is determined microscopically, and is not expected to be affected by the spinning rates. We therefore studied the temperature dependence of the order parameters of these liquid crystals through the use of a linear correlation between the dipolar coupling, D, and S_{zz}. Assuming that S_{xx}–S_{yy} and S_{xz} are independent of temperature, equation (2) may be expressed as

$$D_{C\ F} = aS_{zz} + b \qquad (3)$$

where a and b are empirical constants.

The C2Fb splitting is well resolved in the C-13 NMR VAS spectra (see figure 1), and it is present with sufficient signal-to-noise to obtain reliable results. Figure 2 shows excellent linear relationships (correlation coefficient, $R > 0{\cdot}99$) between the S_{zz} order parameter and the C2Fb dipolar coupling for two of the compounds. The 3CCP$_F$F correlation is very similar to the correlation for 1d$_1$CCP$_F$F and is omitted to avoid crowding. For the higher symmetry 1d$_1$CCPF, there was no need to simplify the C-13 NMR spectrum by the use of VAS, and the order parameters were calculated directly from splittings measured in the regular C-13 NMR spectrum [6] by using equations (1) and (2).

Once the constants a and b are determined from measurements of a carbon–fluorine dipolar coupling and order parameters with the VAS probe, the order parameters can be calculated at any temperature from the carbon–fluorine dipolar couplings measured with the regular NMR probe through the use of equation (3). Because the carbon–fluorine dipolar couplings can be determined quickly and accurately as a function of temperature with the regular NMR probe, it is possible to obtain an experimental curve of the order parameters as a function of temperature.

Figure 3 shows the variation in the order parameter with temperature for the four liquid crystals studied. The entire nematic range of the liquid crystals is not shown because of the temperature limits of the NMR probes. The smectic B range, beginning at about T–T_{NI} = 90 K, of 1d$_1$CCPF$_F$ is not shown. The order parameter data were fitted to the empirical Haller equation [18]

$$S = S_0\left(1 - \frac{T}{T^{\dagger}}\right)^f \qquad (4)$$

where S_0, $T^{\dagger}$, and f are constants. $T^{\dagger}$ is slightly above the

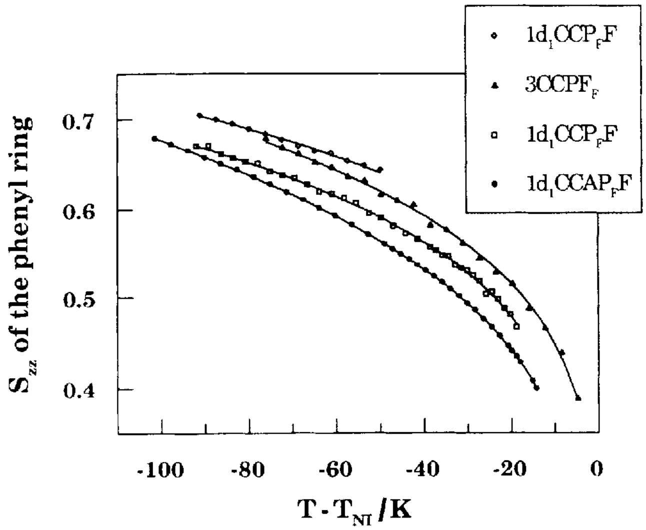


Figure 3. The variation in the order parameter of the phenyl ring with temperature for the liquid crystals studied. The legend identifies the respective compounds, and the solid lines are discussed in the text.

Table 2. The parameters result from the fit of the experimental order parameter data to equation (4). The errors listed are the errors in the calculations. Because temperature limitations of the NMR probes prohibited the acquisition of points very near T_{NI} (see figure 3) for three of the compounds, the values for 3CCP$_F$F are probably the most reliable. 1d$_1$CCPF was fit assuming that $T^{\dagger}$–T_{NI} = 1 K because its data were collected in a small temperature range.

Parameter	1d$_1$CCPF	3CCP$_F$F	1d$_1$CCPF$_F$	1d$_1$CCAP$_F$F
S_0	0·92 ± 0·01	0·94 ± 0·01	0·90 ± 0·01	0·97 ± 0·01
f	0·17 ± 0·01	0·18 ± 0·01	0·20 ± 0·01	0·25 ± 0·01
$T^{\dagger} - T_{NI}$(K)	—	0·3 ± 0·1	4 ± 1	2 ± 1

nematic to isotropic transition temperature, and f is related to how quickly the order parameter changes with temperature. This relation provides a good fit through the data and the solid lines calculated from equation (4) effectively guide the eye but the values of the variables calculated (see table 2) should not be regarded as exceedingly accurate because part of the temperature range of the liquid crystals was inaccessible to the NMR probes. Nevertheless, the value of f for 1d$_1$CCAP$_F$F differs substantially from 1d$_1$CCP$_F$F and the other compounds (see table 2). Because it is known that the parameter f in the Haller equation depends on the rigidity of the molecular fragment [19], this difference is likely caused by the reduction in the rigidity of the core by the extra alkyl linkage in 1d$_1$CCP$_F$F. The differences between the f values for the other compounds are less pronounced, and their structures do not contain as flexible a group as the alkyl linkage of 1d$_1$CCP$_F$F.

The temperature dependence of the order parameter (see figure 3) correlates with the structures of liquid crystals. For example, of the four compounds studied, 1d$_1$CCPF shows the highest order parameters at the same T–T_{NI} values. The absence of a lateral substituent and subsequently increased rigidity most likely is responsible for its high order parameter. The extra alkyl linkage of 1d$_1$CCAP$_F$F reduces the rigidity of the mesogenic core, and, consequently, the order parameter of the phenyl ring in this compound is the lowest of the four at the same values of T–T_{NI}. For some non-laterally substituted liquid crystals, double bonds adjacent to the cyclohexyl ring tend to increase the order parameter of the aromatic core because the double bond causes a decrease in the orientational freedom of the liquid crystal [20]. However, for the difluorinated liquid crystals, the phenyl ring with an adjacent double bond (in 1d$_1$CCP$_F$F) has a lower order parameter than that with an alkyl chain (in 3CCP$_F$F). It should be noted that, in addition to the presence of a lateral substituent, these difluorinated liquid crystals contain an extra cyclohexyl ring in the core of the liquid crystal. This situation has not been thoroughly investigated. Future studies of liquid crystals with various combinations of rings and lateral substituents, both fluorinated and non-fluorinated, may shed some more light on this subject.

4. Conclusions

The orientational ordering of the difluorinated compounds has been investigated through the calculation of the three order parameters of the phenyl ring from carbon–fluorine dipolar couplings. Some differences in the temperature dependence of the orientational order can be attributed to the molecular structure of the liquid crystal. Other differences point to the importance of the structure and in particular of lateral fluorinated substituents.

This study demonstrates that complicated fluorine-coupled C-13 NMR spectra can be simplified through the use of rapid spinning and that the order parameters of individual fluorinated segments may be conveniently calculated. This should prove useful for future studies of fluorinated liquid crystals, many of which display potentially useful material properties.

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