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# Nematic ordering and crystal structure of liquid crystals containing a 4-chlorophenyldifluoroethylene unit

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Partially fluorinated liquid crystals have many desirable properties such as high impedance and low viscosity. The compounds *trans*-1-(*trans*-4-alkylcyclohexyl)-2-(4-chlorophenyl)-difluoroethylene have very low viscosities and reasonable nematic ranges, and are very suitable for electro-optic displays. The crystal structure of a compound in this homologous series has been determined by X-ray diffraction. The orientational ordering for this compound and for another homologue in their nematic phases has been studied by the use of one and two dimensional $^{13}$C NMR. The proton-decoupled $^{13}$C spectra are complex due to splittings from the two F-19 nuclei, but they have been analysed by combining chemical shift anisotropy and variable angle spinning studies. Carbon–proton and carbon–fluorine dipolar coupling constants were obtained, and the order parameters for the two conjugated molecular segments (the chlorophenyl ring and the difluoroethylenic link) were calculated from the dipolar coupling constants. The temperature dependences of the local order parameters of each fragment were studied.

## 1. Introduction

Due to their unique physical and material properties, fluorinated liquid crystals (LCs) are of great interest for electro-optical applications such as twisted nematic (TN) or supertwisted nematic (STN) displays, especially with the use of thin film transistor (TFT) technology [1–5]. Therefore, investigations of the oriential ordering of such compounds are important.

Compared with ordinary LCs, the proton-decoupled $^{13}$C spectra of fluorinated LCs are much more complex because each of the $^{13}$C peaks is split into doublets by the fluorine nucleus due to $^{13}$C–$^{19}$F coupling. The complication is two-fold. First, long-range scalar C–F couplings are usually observed for conjugated fluorinated molecules; for example, $^{10}J_{C\text{–}F}$ has been determined for *trans*-4-fluorostilbene dissolved in a deuteriated solvent [6]. Second, because dipolar couplings are rather large in liquid crystals, long range couplings through space can also be appreciable. Thus, the assignment of the $^{13}$C spectra of fluorinated LCs is difficult due to many splittings and strong overlappings.

Variable angle spinning combined with separated local field spectroscopy (VAS/SLF) has been proven to be a powerful 2D $^{13}$C NMR method for the determination of the local ordering parameters of numerous liquid crystals [7, 8]. VAS/SLF is a useful technique to reduce the magnitude of coupling constants and enhance the resolution of the spectrum in the dipolar dimension. Combined with the measurement of chemical shift anisotropy, the $^{13}$C signals can be assigned and the order parameter calculated.

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In this paper, we present the study of the orientational ordering of two mesogens containing a chlorophenyldifluoroethylene moiety, labelled DFHP-3Cl and DFHP-5Cl (figure 1), and the crystal structure of DFHP-3Cl. They are promising materials for STN displays due to their high contrast and rapid response time [9]. These rather simple compounds contain four different parts: a rigid *para*-disubstituted phenyl ring, a rigid double bond bearing two fluorine substituents, a cyclohexane ring, and an alkyl chain containing three or five carbons.

The $^{13}$C NMR of these two compounds in the nematic phase has been studied. The investigation was focused at the phenyl ring and the difluoroethylene linkage, for which the $^{13}$C signals are well resolved. To extract the order parameters from the experimental NMR data, the geometry of the molecule is needed. Therefore, the X-ray structure of DFHP-3Cl was also studied, and the molecular geometry obtained for the solid state was used to evaluate the order parameter of individual segments in the nematic phase of both compounds. The comparison of the order parameters of the two molecular segments offers an interesting insight into the ordering of the whole molecule in the nematic phase.

## 2. Experimental

### 2.1. *Materials*

The compounds DFHP-3Cl and DFHP-5Cl were synthesized and characterized in the laboratories of the Ashai Glass Co. [9]. The nematic ranges of the compounds were determined by using an Olympus BH-2 polarizing microscope equipped with a Linkam PR-600 heating stage. The results are shown in figure 1.

### 2.2. *X-ray data collection and structure resolution*

Single crystals of DFHP-3Cl were grown from $CHCl_3$ solution at room temperature. The cell parameters were obtained and data collection was performed on a Siemens P4 diffractometer. The data collection conditions and the refinement characteristics are given in table 1. The crystal structure was solved by using the XP Molecular Graphics 5.03 package [10]. The final reliability factors were $R = 0.0548$ and $wR = 0.1434$ with a goodness of fit of 0.986.

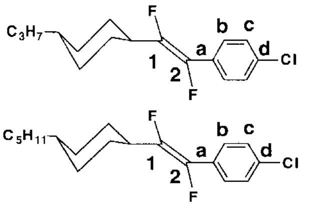
### 2.3. *NMR experiments*

The $^{13}$C chemical shift experiments on the liquid crystals were performed at 125.71 MHz ($B_0 = 11.70$ T) on a Varian VXR-500S NMR spectrometer equipped with an indirect detection probe manufactured by Narolac Cryogenic Corporation, Martinez, CA (USA). This probe maximizes the efficiency of proton decoupling and provides a temperature control of 0.1 K. The sample was put in a standard 5 mm tube and spun at a slow rate (12 Hz) along the magnetic field. To avoid radio frequency overheating, a 0.8% decoupler duty cycle was used.

The 2D variable angle spinning (VAS)–separated local field (SLF) [6, 7] experiments were made using a Varian XL-300 NMR spectrometer operating at 75.43 MHz ($B_0 = 7.05$ T). A variable angle spinning probe, from Doty Scientific, Columbia, SC (USA) was used. The angle between the spinning axis and the magnetic field was set at $\theta = 44.8°$; the calibration of the angle was made by using a standard method [11]. Details of experimental conditions and data processing have been described elsewhere [7, 8].

**DFHP-3Cl**

**DFHP-5Cl**



Cr (320.5) N (334.1) I

Cr ( < 298 ) N (341.5) I

Figure 1. Structural formulae of the compounds investigated including the labelling of the fragments studied.

Table 1. Crystal data collection and refinement characteristics.

| | | | |
|---|---|---|---|
| *Data collection conditions* | | | |
| Radiation | MoK$_\alpha$ | Wavelength/Å | 0.71073 |
| Temperature/K | 295 | $\theta$ range/° | 1.89–20.99 |
| $h_{min}$, $h_{max}$ | − 10, 0 | Absorption correction | none |
| $k_{min}$, $k_{max}$ | − 10, 11 | | |
| $l_{min}$, $l_{max}$ | − 15, 15 | | |
| Reflections collected | 3540 | Independent reflections | 3295 |
| *Refinement* | | | |
| Refinement mode | Full-matrix-block least-square on $F^2$ | | |
| Final $R$ indices | 0.0548 | $wR$ | 0.1434 |
| Goodness of fit | 0.986 | Number of refined parameters | 361 |

For both 1D and 2D NMR experiments, the temperature calibration was made by observing the nematic to isotropic transition.

## 3. Results and discussion

### 3.1. *X-ray analysis*

The crystal data for DFHP-3Cl are listed in table 2. The crystal contains two independent molecules **1** and **2**. The fractional coordinates and the $U_{eq}$(Å$^2$) factors for non-hydrogen atoms are given in table 3. The labelling of non-hydrogen atoms of both independent molecules is presented with the thermal ellipsoids in figure 2. The DFHP-3Cl molecules have a *trans*-configuration relative to the ethylenic bonds C7–C8 and C24–C25. The bond lengths in the central chain of atoms C4–C7–C8–C9/C21–C24–C25–C26 (table 4) are in agreement with those found in difluorostilbene derivatives (C–C 1.46 Å and C=C 1.33 Å) [12, 13]. The lengths of the C–F bonds are also close to those obtained in related compounds (C–F 1.34 Å) [12, 13].

The phenyl rings in both molecules 1 and 2 are perfectly planar. It is well known [14] that for compounds of the stilbene type, the steric hindrances between carbon atoms in the ideal molecular model (all angles 120° and benzene rings in the plane of the central chain of bonds) can be eliminated either by rotating of the benzene rings from the plane of the central ethylene system or by increasing the angle of C–C=C. In *trans*-stilbene, a considerable increase in the C–C=C angle to 130° is observed and the approximately flat molecular shape is explained by conjugation of the central double bond with the phenyl rings [15]. In the DFHP derivatives, the interatomic angles (table 5) and dihedral angles (table 6) in the fluorinated link differ from the ideal model of the molecule, and hence both types of aforementioned deformations are observed in these compounds. Thus the angle C–C=C is in the range 131° (molecule 1) to 134° (molecule 2) and the rotation of the benzene ring changes from 1° for molecule 1 to 8° for molecule 2. The C–F bond deviates from the plane by less than 3°. Therefore the steric hindrances in the DFHP molecules lead to an important increase in the valency angle C–C=C and to a slight deviation of the coplanar character of the molecule due to rotation of the benzene rings. The terminal alkyl chains have a *trans*-conformation.

The projection of the structure along the *a* axis is presented in figure 3. The molecular arrangement is typical of a nematogenic compound. The crystal cohesion is probably assured by dipolar interactions between polar groups, helped by the overlapping of the aromatic rings and also very weak van der Waals interactions between neighbouring molecules.

### 3.2. *Chemical shifts*

Figure 4 shows the unsaturated part of the proton-decoupled $^{13}$C spectrum of DFHP-3Cl in the nematic

Table 2. Crystal data for DFHP-3Cl.

| *Crystal data* | | | |
|---|---|---|---|
| Chemical formula | $C_{17}H_{21}ClF_2$ | MW (g mol$^{-1}$) | 298.79 |
| Crystal system | Triclinic | Space group | $P1$ |
| $a$/Å | 10.4434 | $\alpha$/° | 113.043 |
| $b$/Å | 12.3114 | $\beta$/° | 92.740 |
| $c$/Å | 14.9168 | $\gamma$/° | 110.826 |
| Volume of cell/Å$^3$ | 1610.1 | Number of molecules per unit cell ($Z$) | 4 |
| Density/g cm$^{-3}$ | 1.233 | Absorption/mm$^{-1}$ | 0.246 |
| Crystal shape | Needle | Crystal colour | transparent white |

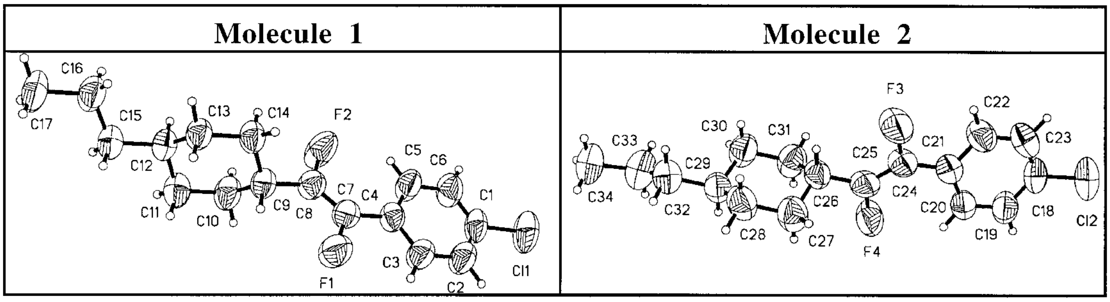


Figure 2. Independent molecules of DFHP-3Cl presented with the thermal ellipsoids.

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathrm{\AA}^2 \times 10^3$) in DFHP-3Cl. $U$(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| Atom | $x/a$ | $y/b$ | $z/c$ | $U$eq/$\mathrm{\AA}^2$ |
|---|---|---|---|---|
| Cl(1) | 1863(2) | 641(2) | 1392(1) | 119(1) |
| F(1) | 7276(3) | 2291(3) | − 634(2) | 117(1) |
| F(2) | 4542(3) | 405(3) | − 2727(2) | 127(1) |
| C(1) | 3027(5) | 867(4) | 625(3) | 80(1) |
| C(2) | 4413(5) | 1608(4) | 1033(3) | 86(1) |
| C(3) | 5349(4) | 1813(4) | 444(3) | 81(1) |
| C(4) | 4910(4) | 1270(4) | − 581(3) | 67(1) |
| C(5) | 3493(5) | 503(4) | − 987(3) | 87(1) |
| C(6) | 2561(5) | 306(5) | − 381(4) | 91(1) |
| C(7) | 5933(4) | 1522(4) | − 1185(3) | 72(1) |
| C(8) | 5855(4) | 1178(4) | − 2135(3) | 73(1) |
| C(9) | 6943(4) | 1483(4) | − 2706(3) | 68(1) |
| C(10 | 6799(4) | 2393(4) | − 3129(3) | 85(1) |
| C(11) | 7894(4) | 2669(4) | − 3740(3) | 83(1) |
| C(12) | 7882(4) | 1461(4) | − 4561(3) | 69(1) |
| C(13) | 8042(4) | 576(4) | − 4132(3) | 70(1) |
| C(14) | 6941(4) | 272(4) | − 3526(3) | 74(1) |
| C(15) | 8976(4) | 1777(4) | − 5168(3) | 78(1) |
| C(16) | 8920(4) | 642(4) | − 6080(3) | 90(1) |
| C(17) | 9935(5) | 1015(5) | − 6711(3) | 105(2) |
| Cl(2) | − 7970(2) | − 3636(2) | 6715(1) | 129(1) |
| F(3) | − 5689(3) | − 5814(2) | 2601(2) | 122(1) |
| F(4) | − 3349(3) | − 2594(3) | 3789(2) | 131(1) |
| C(18) | − 7074(5) | − 3934(5) | 5749(4) | 86(1) |
| C(19) | − 5819(5) | − 3014(5) | 5827(3) | 95(1) |
| C(20) | − 5135(5) | − 3220(4) | 5061(3) | 87(1) |
| C(21) | − 5690(4) | − 4359(4) | 4188(3) | 70(1) |
| C(22) | − 6963(5) | − 5301(4) | 4136(4) | 91(1) |
| C(23) | − 7635(5) | − 5076(5) | 4924(4) | 100(1) |
| C(24) | − 5051(4) | − 4585(4) | 3327(3) | 75(1) |
| C(25) | − 3998(4) | − 3845(4) | 3097(3) | 79(1) |
| C(26) | − 3455(4) | − 4114(4) | 2174(3) | 77(1) |
| C(27) | − 1892(5) | − 3808(5) | 2374(3) | 102(2) |
| C(28) | − 1373(5) | − 4137(5) | 1413(4) | 99(1) |
| C(29) | − 1634(4) | − 3460(4) | 829(3) | 82(1) |
| C(30) | − 3172(5) | − 3716(5) | 651(3) | 100(1) |
| C(31) | − 3724(5) | − 3398(5) | 1609(3) | 97(1) |
| C(32) | − 1085(5) | − 3838(5) | − 136(3) | 98(1) |
| C(33) | − 1041(6) | − 3091(6) | − 689(4) | 123(2) |
| C(34) | − 344(6) | − 3417(6) | − 1577(4) | 125(2) |

Table 4. Interatomic distances (Å) in the fluorinated link in DFHP-3Cl.

| Molecule **1** | | Molecule **2** | |
|---|---|---|---|
| F(1)–C(7) | 1.370(4) | F(3)–C(24) | 1.355(4) |
| F(2)–C(8) | 1.365(5) | F(4)–C(25) | 1.357(5) |
| C(4)–C(7) | 1.457(5) | C(21)–C(24) | 1.451(6) |
| C(7)–C(8) | 1.300(5) | C(24)–C(25) | 1.314(6) |
| C(8)–C(9) | 1.482(5) | C(25)–C(26) | 1.476(6) |

Table 5. Interatomic angles (°) in the fluorinated link in DFHP-3Cl.

| Molecule **1** | | Molecule **2** | |
|---|---|---|---|
| C(3)–C(4)–C(7) | 119.5(4) | C(20)–C(21)–C(24) | 123.6(4) |
| C(5)–C(4)–C(7) | 122.9(4) | C(22)–C(21)–C(24) | 119.3(4) |
| C(8)–C(7)–F(1) | 112.5(4) | C(25)–C(24)–F(3) | 113.3(4) |
| C(8)–C(7)–C(4) | 134.2(4) | C(25)–C(24)–C(21) | 133.5(4) |
| F(1)–C(7)–C(4) | 113.3(3) | F(3)–C(24)–C(21) | 113.2(4) |
| C(7)–C(8)–F(2) | 115.4(4) | C(24)–C(25)–F(4) | 115.5(4) |
| C(7)–C(8)–C(9) | 131.6(4) | C(24)–C(25)–C(26) | 130.8(4) |
| F(2)–C(8)–C(9) | 113.0(3) | F(4)–C(25)–C(26) | 113.5(4) |

phase, with normal slow spinning (12 Hz) of the sample along the axis of the magnetic field; spectra obtained for DFHP-5Cl are similar. The complexity of the spectrum is due to many splittings resulting from C–F couplings. Thus, each $^{13}$C nucleus which is coupled to two fluorine nuclei gives rise to four peaks, i.e. doublets of doublets, which may not have the same height or linewidth due to the effect of chemical shift anisotropy on relaxation [16]. By assuming that the $^{13}$C nuclei of the chlorophenyl ring (Ca, Cb, Cc, Cd) are also split by the two fluorine nuclei into doublets of doublets, at the most 24 peaks are expected for the chlorophenyldifluoroethylene unit. Experimentally, 19 peaks are present in figure 4. To decipher this complex spectrum, we used the following method for spectral assignment.

In a liquid crystal, the splitting due to heteronuclear coupling is [17]:

$$\Delta \nu = 2D + J \qquad (1)$$

where $D$ is the dipolar coupling constant, and $J$ is the scalar coupling constant. The value of $J$ can be measured from the isotropic spectrum, and its anisotropy is assumed to be negligible for C–H and C–F couplings [18]. For the DFHP compounds, the indirect coupling constants $J_{\mathrm{C-F}}$ (in Hz) are: C1–F1 = − 222.7, C1–F2 = 45.3; C2–F1 = 54.6; C2–F2 = − 250.6; Ca–F1 = 6.2; Ca–F2 = 25.7; Cb–F1 = 7.4; Cb–F2 = 9.4; Cc–F2 = 2.0; Cd–F2 = 3.5. The signs of these splittings were assigned by comparison with similar compounds, and the values for the splittings agree well with those of similar compounds [19, 20].

When broad band proton decoupling is used to study the $^{13}$C spectra in the nematic phase, only the $^{13}$C–$^{19}$F couplings need to be considered. For the two fluorine nuclei in the DFHP compounds, the $^{19}$F chemical shift difference is 6.59 ppm (3100 Hz at 11.74 T), and $J_{\mathrm{F-F}}$ = 122 Hz. Therefore, their couplings to each $^{13}$C nucleus can be treated as independent of each other, namely as an AMX system. As a result, in the presence of two fluorine nuclei F1 and F2, each $^{13}$C peak is split into four peaks with line positions described by the

Table 6. Dihedral angles (°) in the fluorinated link in DFHP-3Cl.

| Molecule **1** | | Molecule **2** | |
|---|---|---|---|
| C3–C4–C7–C8 | 179.09 (0.45) | C20–C21–C24–C25 | – 8.13 (0.75) |
| C3–C4–C7–F1 | 1.01 (0.54) | C20–C21–C24–F3 | 173.20 (0.38) |
| F1–C7–C8–F2 | 179.74 (0.34) | F3–C24–C25–F4 | 178.22 (0.35) |
| F1–C7–C8–C9 | – 0.82 (0.66) | F3–C24–C25–C26 | 3.30 (0.68) |
| C4–C7–C8–C9 | 179.28 (0.41) | C21–C24–C25–C26 | – 175.37 (0.42) |
| C12–C15–C16–C17 | 174.73 (0.37) | C29–C32–C33–C34 | 173.82 (0.44) |

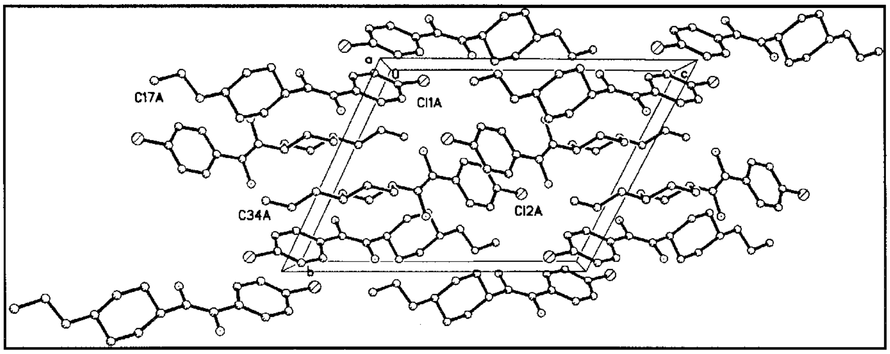


Figure 3. Projection of the DFHP-3Cl crystal structure on the $(y0z)$ plane.

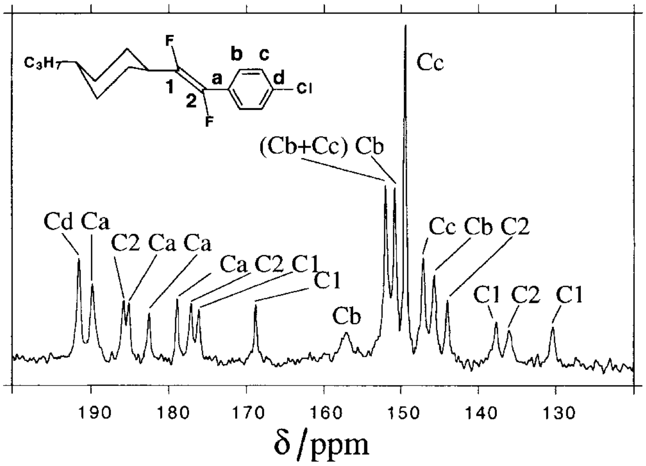


Figure 4. The low-field portion of the $^{13}$C NMR spectrum of DFHP-3Cl in the nematic phase at $T/T_{\mathrm{NI}} = 0.961$.

following equations:

$$\delta^1_{\mathrm{obs}} = \delta_{\mathrm{iso}} + \delta_{\mathrm{aniso}} + (D_1 + {}^1J_{\mathrm{C\text{-}F1}}/2) + (D_2 + {}^2J_{\mathrm{C\text{-}F2}}/2) \tag{2}$$

$$\delta^2_{\mathrm{obs}} = \delta_{\mathrm{iso}} + \delta_{\mathrm{aniso}} + (D_1 + {}^1J_{\mathrm{C\text{-}F1}}/2) - (D_2 + {}^2J_{\mathrm{C\text{-}F2}}/2) \tag{3}$$

$$\delta^3_{\mathrm{obs}} = \delta_{\mathrm{iso}} + \delta_{\mathrm{aniso}} - (D_1 + {}^1J_{\mathrm{C\text{-}F1}}/2) + (D_2 + {}^2J_{\mathrm{C\text{-}F2}}/2) \tag{4}$$

$$\delta^4_{\mathrm{obs}} = \delta_{\mathrm{iso}} + \delta_{\mathrm{aniso}} - (D_1 + {}^1J_{\mathrm{C\text{-}F1}}/2) - (D_2 + {}^2J_{\mathrm{C\text{-}F2}}/2) \tag{5}$$

where $\delta_{\mathrm{iso}}$ is the isotropic line position, and $\delta_{\mathrm{aniso}}$ is the anisotropic line position in the absence of $^{13}$C–$^{19}$F coupling. The combination of these four equations results in a simple relation

$$(\delta^1_{\mathrm{obs}} + \delta^4_{\mathrm{obs}}) - (\delta^2_{\mathrm{obs}} + \delta^2_{\mathrm{obs}}) = 0. \tag{6}$$

With the aid of this useful relation and the group contribution method [19], the assignment of the complex spectrum shown in figure 4 was possible. For the carbon nuclei under consideration, C1, C2, Ca and Cb show four peaks each, which is expected. The Cc carbon exhibits a triplet because the two dipolar coupling constants are nearly equal, and the $J$ values are small. The Cd carbon is far away from the two fluorines, and shows only a singlet because the splittings are unresolved. Furthermore, one of the peaks from Cb and one from Cc overlap with each other. Therefore, a total of 19 peaks is observed in this region.

Figure 5 shows the temperature dependence of the line positions for the aromatic and ethylenic carbons of DFHP-5Cl. The evolution of the chemical shifts of the aromatic carbons follows the normal trend of non-fluorinated liquid crystals [21], namely their values increase with decrease in temperature. However, two peaks of C1 and two peaks of C2 in the ethylenic link decrease with decrease in temperature. This is due to the presence of large one-bond C–F dipolar coupling constants: in equations (4) and (5), $D_1 > \delta_{\mathrm{aniso}}$ and has a larger temperature dependence, while the temperature effect of $D_2$ is relatively unimportant, and the

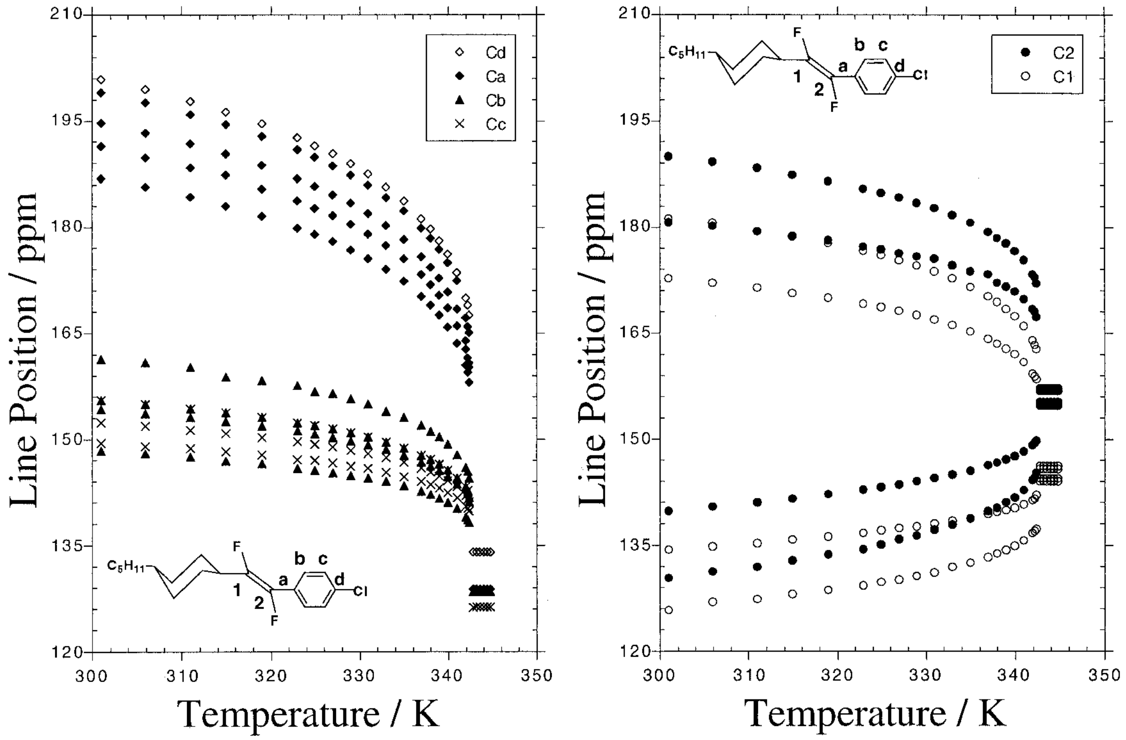


Figure 5. Temperature dependence of the line position for the aromatic and the ethylenic carbons (C1 and C2) in DFHP-5Cl.

temperature dependence of the $J$ terms are usually negligible.

### 3.3. *Order parameter of the phenyl ring*

A well established method to obtain the order parameter of phenyl rings and other molecular segments in a liquid crystal is to study $^{13}$C NMR using the VAS/SLF technique to determine the $^{13}$C–$^{1}$H splitting of each pair [7, 8]. As an example, the spectra of DFHP-5Cl at 331 K are displayed in figure 6.

The normal proton-decoupled 1D spectrum is obtained in the $\omega_2$ dimension. In this region many overlappings between aromatic and ethylenic carbon signals are observed. The assignments of the peaks were made based on the carbon–fluorine splittings and the group contribution method, as discussed in the previous section; however, all dipolar couplings are reduced by a factor of $(3\cos^2\theta-1)/2$, where $\theta$ is the angle between the spinning axis and the magnetic field. The intensities of the Cb and Cc peaks are enhanced due to the NOE effect [19].

First order C–H couplings are observed in the $\omega_1$ dimension of the experiment, but only the resolved aromatic peaks can be used for the determination of the C–H couplings and the calculation of the order parameters. Therefore only the slices of the Cb and Cc carbons are displayed. In the nematic phase, the phenyl ring has an effective $D_2$ symmetry because it undergoes rapid jumps about its *para*-axis, inducing an equivalence between the two *ortho*- and the two *meta*-positions. For each of the protonated aromatic carbons, the pattern in the second dimension is then a doublet of doublets due to splittings by the directly bonded proton and the *ortho*-proton. The doublet of doublets for Cb and Cc are broadened due to unresolved couplings, and the $\Delta\nu$ values of the two splittings for each carbon were obtained by a numerical lineshape fitting [8]. For the SLF/VAS technique, equation (1) becomes [8]:

$$\Delta\nu = f[(3\cos^2\theta-1)D+J] \tag{7}$$

where $f$ is a scaling factor, and is equal to 0.42 when the proton–proton dipolar coupling sequence BLEW-48 is used [22], and $\theta$ is the angle between the spinning axis and the magnetic field $B_0$. The $\Delta\nu$ values obtained from the spectra and the dipolar coupling constants $D$ deduced from them are gathered in table 7.

From the dipolar coupling constants, the order parameters of various molecular segments can be obtained. For a group with $C_s$ symmetry, the dipolar coupling constant is related to the order parameters $S_{\alpha_\beta}$ by [23]:

$$\begin{aligned} D_{ij} = -\frac{\gamma_i\gamma_j h}{8\pi^2 r_{ij}^3}[&(3\cos^2\theta_{ijz}-1)S_{zz} \\ &+(\cos^2\theta_{ijx}-\cos^2\theta_{ijy})(S_{xx}-S_{yy}) \\ &+4\cos\theta_{ijx}\cos\theta_{ijz}S_{xz}] \end{aligned} \tag{8}$$

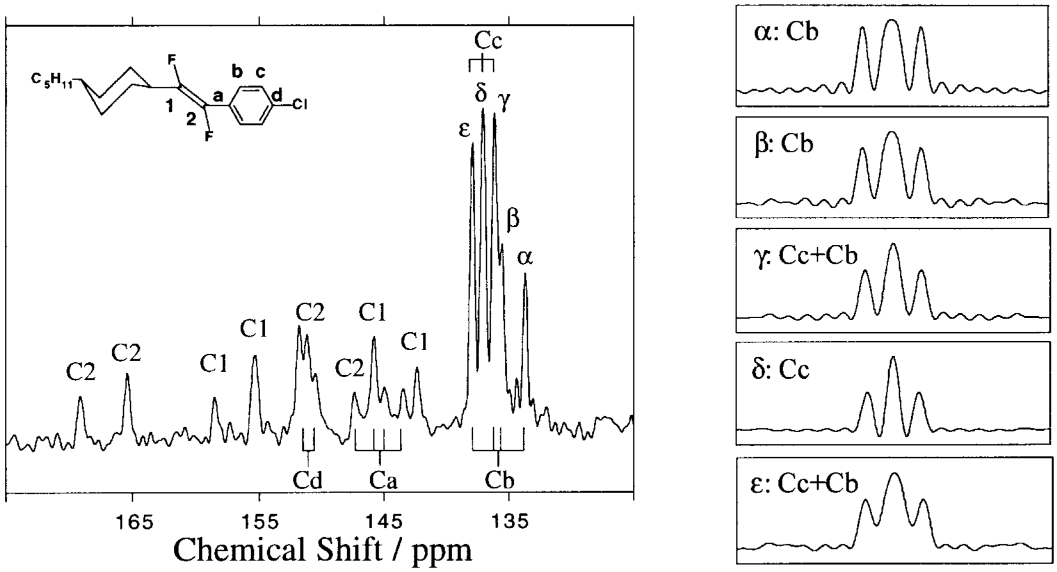


Figure 6. $^{13}$C SLF/VAS spectra of DFHP-5Cl at 75.43 MHz at 331 K. The sample was spun at a rate of 1 kHz along an axis forming an angle of $\theta = 44.8°$ with respect to the magnetic field. Only the conjugated part is displayed. The normal proton decoupled 1D spectrum obtained in the $\omega_2$ dimension is presented on the left side. The spectra in the $\omega_1$ dimension obtained for the lines α–ε are shown on the right side, the spectral width of which is 3000 Hz. The traces α and δ are pure doublets of doublets and were used for the dipolar coupling constant calculations. The other traces correspond to overlapping peaks of two carbons.

Table 7. $\Delta\nu$ values (Hz) of the two splittings for carbons Cb and Cc obtained by a numerical lineshape fitting, and dipolar coupling constants $D$ (Hz) deduced from them using equation (7) at different values of $T/T_{\mathrm{NI}}$.

| $T/T_{\mathrm{NI}}$ | $\Delta\nu_{\mathrm{Cb-Hb}}$ | $D_{\mathrm{Cb-Hb}}$ | $\Delta\nu_{\mathrm{Cb-Hc}}$ | $D_{\mathrm{Cb-Hc}}$ | $\Delta\nu_{\mathrm{Cc-Hb}}$ | $D_{\mathrm{Cc-Hb}}$ | $\Delta\nu_{\mathrm{Cc-Hc}}$ | $D_{\mathrm{Cc-Hc}}$ |
|---|---|---|---|---|---|---|---|---|
| 0.973 | 245.30 | 827.35 | 215.70 | − 1004.1 | 216.00 | − 1005.5 | 319.80 | 1181.5 |
| 0.961 | 265.40 | 921.83 | 233.40 | − 1087.3 | 227.10 | − 1057.7 | 339.10 | 1272.2 |
| 0.950 | 280.70 | 993.76 | 242.60 | − 1130.6 | 235.60 | − 1097.6 | 356.50 | 1354.0 |
| 0.926 | 305.80 | 1111.7 | 271.60 | − 1266.9 | 254.70 | − 1187.4 | 391.90 | 1520.4 |
| 0.903 | 322.30 | 1189.3 | 290.00 | − 1353.4 | 282.20 | − 1316.7 | 429.60 | 1697.7 |

where $\gamma_i$ and $\gamma_j$ are the magnetogyric ratios of the nuclei $i$ and $j$, respectively, $r_{ij}$ is the internuclear distance, and $\theta_{ij(x,y,z)}$ is the angle between the vector of $r_{ij}$ and the $x$, $y$, $z$ axis of the coordinate system. Equation (8) refers to groups of interacting nuclei, so the order parameters $S_{zz}$, $S_{xx} - S_{yy}$, and $S_{xz}$ describe only the orientation of the rigid fragment of the DFHP compounds, not the entire liquid crystal molecule. For the *para*-disubstituted phenyl ring, the $z$ axis is taken to be through the Ca and Cd 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 $y$ and $z$ axes. Because of the effective $D_2$ symmetry of the ring, the $S_{xz}$ term becomes zero, and only the $S_{zz}$ and $S_{xx} - S_{yy}$ terms are necessary to describe the orientational ordering. Once the splittings are assigned, the order parameters and the bond angles can be calculated from the observed dipolar couplings with a non-linear least squares fit to equation (8). In the first step of the calculation, the C–C–H aromatic bond angles were treated as variables at every temperature for each compound. Their average values were Hb–Cb–Cc 119.3° ± 0.3° and Cb–Cc–Hc 120.7° ± 0.3°; the value used for the C–H bond length was 0.109 nm. To refine the order parameter calculation, these angles were treated as constants. The results for DFHP-3Cl and DFHP-5Cl are listed in table 8.

The data in table 8 show that the order parameters of the two compounds are nearly equal at the same reduced temperature. To examine further the temperature dependence of the order parameters, we use the chemical shift data for the slow-spinning samples. It has been shown that the $^{13}$C chemical shift changes obey the semi-empirical equation [24]:

$$\delta_{\mathrm{obs}} = \delta_{\mathrm{iso}} + aS + b \tag{9}$$

where $a$ and $b$ are constants related to the chemical shift tensor components and are supposed to be independent of temperature, and $S$ is the $S_{zz}$ component of the

Table 8. Order parameters for the phenyl rings of DFHP-3Cl and DFHP-5Cl at different values of $T/T_{NI}$; the absolute error of the SLF/VAS technique is estimated at 5%.

| DFHP-3Cl |  |  | DFHP-5Cl |  |  |
|---|---|---|---|---|---|
| $T/T_{NI}$ | $S_{zz}$ | $S_{xx}-S_{yy}$ | $T/T_{NI}$ | $S_{zz}$ | $S_{xx}-S_{yy}$ |
| 0.961 | $0.477 \pm 0.024$ | $0.047 \pm 0.002$ | 0.903 | $0.612 \pm 0.031$ | $0.044 \pm 0.002$ |
| 0.970 | $0.450 \pm 0.023$ | $0.046 \pm 0.002$ | 0.926 | $0.560 \pm 0.028$ | $0.041 \pm 0.002$ |
| 0.979 | $0.411 \pm 0.021$ | $0.045 \pm 0.002$ | 0.950 | $0.508 \pm 0.025$ | $0.039 \pm 0.002$ |
| 0.988 | $0.363 \pm 0.018$ | $0.041 \pm 0.002$ | 0.961 | $0.489 \pm 0.024$ | $0.041 \pm 0.002$ |
|  |  |  | 0.973 | $0.459 \pm 0.023$ | $0.042 \pm 0.002$ |

aromatic ring or the order parameter of the C–H bond in the aliphatic chain. By using equation (9), the constants $a$ and $b$ can be determined from chemical shifts and the values of $S_{zz}$ obtained at different temperatures. If it is assumed that, in a homologous series, the number of carbons in the terminal alkyl chain does not change the chemical shift anisotropy tensor values of the aromatic carbons, data for different compounds in the same series can be pooled. In figure 7, the anisotropic chemical shifts of the two compounds are plotted versus the order parameters obtained by the VAS/SLF method. A single linear relationship is observed for each aromatic carbon of both compounds. From the $a$ and $b$ values obtained, the values of $S$ at other temperatures can be calculated from the chemical shifts. This allows a large amount of data to be obtained, which tends to moderate the uncertainties of $S_{zz}$ measurements by the VAS/SLF method. The data are then fitted using the Haller equation [25]:

$$S(T) = S_0(1 - T/T^{\dagger})^F \tag{10}$$

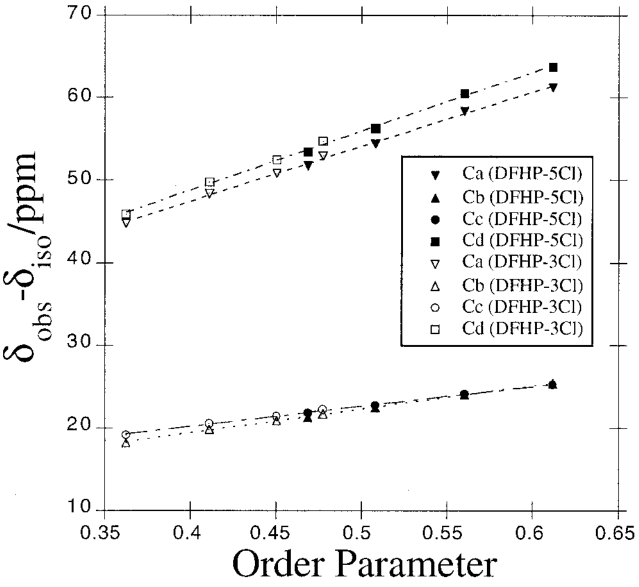


Figure 7. Linear correlation between the chemical shifts of the aromatic carbons and $S_{zz}$ for the phenyl ring in DFHP-3Cl and DFHP-5Cl.

where $T^{\dagger}$ is the reduced temperature, and $S_0$ and $F$ are empirical parameters. The experimental data and the best fit curves are represented together in figure 8, and the values obtained from the least squares fit are given in table 9.

It should be pointed out that equation (10) is an empirical relation which may be regarded as a special case of the Landau–de Gennes theory in describing the molecular ordering for isotropic–nematic transitions

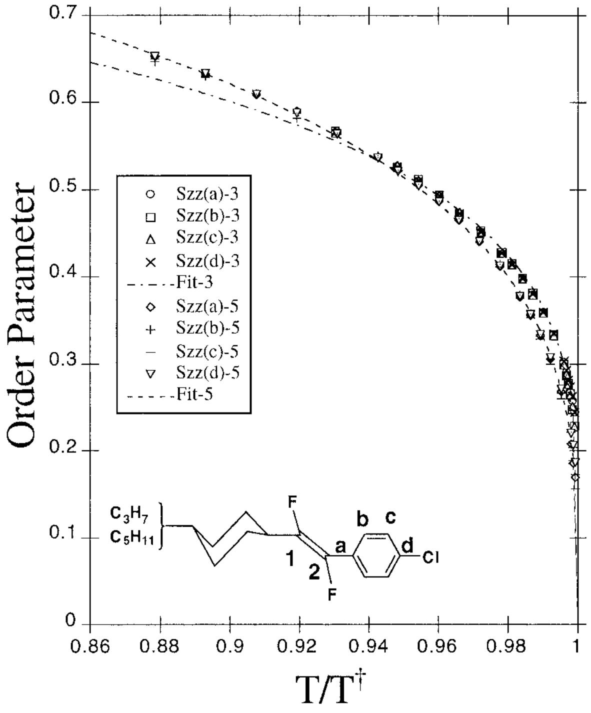


Figure 8. The temperature dependence of $S_{zz}$ for the phenyl ring in DFHP-3Cl and DFHP-5Cl.

Table 9. Parameters for the temperature dependence of $S_{zz}$ for the phenyl rings obtained from fitting the experimental data to equation (10). $R$ is the correlation factor.

|  | $T^{\dagger}$ | $S_0$ | $F$ | $R$ |
|---|---|---|---|---|
| DFHP-3Cl | 346.65 | 0.987 | 0.216 | 0.9986 |
| DFHP-5Cl | 334.25 | 1.164 | 0.273 | 0.9993 |

[21], but it is not strictly valid near the clearing temperature [25]. The physical meaning of the parameters $S_0$ and $F$ are quite simple: $S_0$ is the limit of the order parameter with decreasing temperature, and $F$ may be considered as an indication of how quickly a molecular segment reaches the limit of the order parameter as a function of change in temperature. Experimentally, the limiting value of the order parameter, $S_0$, cannot be reached due to phase transition of the liquid crystal into a solid. The $S_0$ value of DFHP-5Cl is found to be larger than 1, which is physically impossible, but the accuracy of this value is comparable to that of the order parameter (i.e. 5%). The $F$ values obtained are rather high compared with values usually observed for similar molecular segments in liquid crystals based upon, for example, cinnamates or propenimines [26, 27]. This implies that the phenyl fragment in the DFHP compounds would reach the limiting value of the order parameter more slowly. It is known that the parameter $F$ in the Haller equation depends on the rigidity of the molecular fragment [26, 28]. The chlorophenyldifluoroethylene segment is highly conjugated, leading to an enhancement of the rigidity in the phenyl fragment and to high $F$ values.

### 3.4. *Order parameter of the ethylenic link*

Because the C–F splittings for the C1, C2 and Ca carbons are fairly large and the peaks do not overlap under the condition of broad band proton decoupling (figure 4), analysis of the 1D $^{13}C$ spectra using equations (2–5) yields the values of $\Delta\nu$ directly. However, the signs of $\Delta\nu$ cannot be determined from the experimental spectra. In order to use equation (1) to calculate the C–F dipolar coupling constants, the following consideration is made. From the crystal structure presented in §3.1, the angles between the molecular long axis and the four C–F vectors are larger than the magic angle, leading to positive dipolar coupling constants (in equation (8), the contribution of the $S_{zz}$ term is the largest). Thus, using the experimental values of $\Delta\nu$ at each temperature and the $J_{C\text{–}F}$ values listed in §3.2, the C–F dipolar coupling constants can be calculated. From these dipolar coupling constants the three order parameters $S_{zz}$, $S_{xx}-S_{yy}$, and $S_{xz}$ can be computed using equation (8). The $z$ axis is taken to be through the Ca and C2 carbons, the $y$ axis is normal to the ring, and the $x$ axis is in the plane of the double bond. The results are plotted in figure 9.

As already observed in many compounds having an ethylenic double bound conjugated with an aromatic ring, $S_{xz}$ is negative and $S_{xx}-S_{yy}$ is positive [26, 27]. Even though the last two terms in equation (8) have opposite signs, the last term is actually larger, giving a non-negligible contribution to the dipolar splitting. The values of $S_{zz}$ are considerably higher than those for the phenyl ring (figure 8), and seem to be unusually large for a nematic liquid crystal. Although we cannot offer a good explanation for this result, it should be noted that the ethylenic linkage is not uniaxial, and the $z$ axis of the double bound does not coincide with the two-fold axis of the phenyl ring. When a Haller type equation is used to fit the temperature dependence of these three order parameters, the values of $F$ obtained were $0.21 \pm 0.02$, $0.19 \pm 0.02$, and $0.22 \pm 0.02$, respectively. Although the accuracy of these values is not very high, it is comforting to note that the three order parameters seem to have the same thermal evolution and are close to that for the aromatic ring in the same compound (table 8).

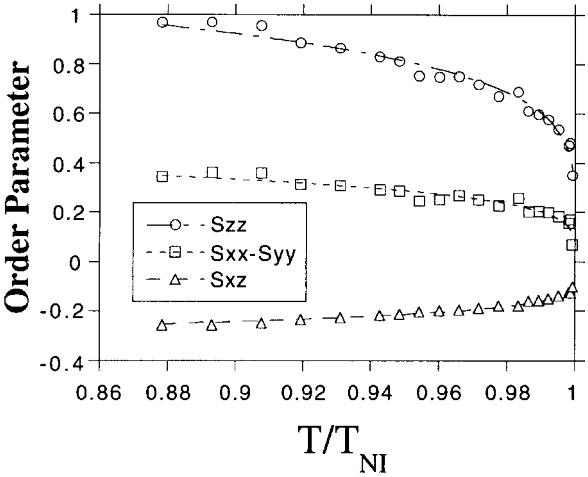


Figure 9. The temperature dependence of the order parameters for the ethylenic linkage in DFHP-3Cl.

For the phenyl ring, the semi-empirical equation (9) was used to correlate the $^{13}C$ chemical shift and the order parameter of the phenyl ring. Because the ethylenic linkage is not uniaxial, and the principal axes of the chemical shift tensor may be quite different from the axis system of the chemical bonds, this equation may not be applicable. When the $^{13}C$ chemical shift data of the ethylenic linkage were fitted to a Haller-type equation, the $F$ values obtained were about 0.4, quite different from those obtained from fitting the order parameters. Therefore, we conclude that equation (9) is not valid for the ethylenic linkage.

## 4. Conclusion

The X-ray structure of *trans*-1-(*trans*-4-propylcyclohexyl)-2-(4-chlorophenyl)difluoroethylene has been obtained. The main feature in the structure is the strong steric hindrance between the *ortho*-hydrogen with respect to the double bond and the first fluorine attached to that bond. This induces a large C–C=C valence angle and causes the planes of the phenyl ring and the double bond to be non-coplanar. The orientational ordering of two liquid crystals containing the 4-chlorophenyldifluoroethylene unit has been studied by the use of one and two dimensional $^{13}$C NMR. By combining chemical shift anisotropy and variable angle spinning studies, the complex $^{13}$C spectra were analysed. The order parameters for the two conjugated molecular segments were calculated using the carbon–proton and carbon–fluorine dipolar coupling constants and X-ray structural data.

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