Similarities and Differences Between Molecular Order in the Nematic and Twist-bend Nematic Phases of a Symmetric Liquid Crystal Dimer

by

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Abstract

The order parameter, S_{zz} , where *z* is the *para* axis of the difluoroterphenyl groups in DTC5C9, have been obtained from chemical shift anisotropies measured by ¹³C – {¹H} NMR experiments at temperatures throughout the nematic, N_U, and twist-bend nematic, N_{TB}, phases shown by this compound. The order parameter temperature profiles are unusual in having a maximum value in the N_U phase and then decreasing until the N_{TB} phase is reached. There is a small discontinuity (~2%) in S_{zz} at $T_{NN_{TB}}$ and then a gradual decrease until a new phase appears. This behaviour is interpreted as revealing a temperature-dependent tilting of local directors in both phases this tilt is consistent with the structure of the phase as a helical arrangement of local directors, whilst in the high-temperature non-chiral nematic the tilt must involve a non-chiral arrangement. It is proposed that in both phases the tilting of directors has a common origin in the bent shape of the molecules.

Keywords: liquid crystal, nematic, twist-bend nematic, order parameter, ¹³C NMR.

Introduction

A number of liquid crystals have been synthesized recently which have two nematic phases: the molecules are achiral, and the higher temperature nematic phase is, as expected, nonenantiomorphic, but the lower temperature phase is enantiomorphic [1-4]. Both phases are of uniaxial symmetry and lack any translational order. The unusual enantiomorphic nematic phase was initially labelled "N_X" [1-3,5], but more recently has been described as a twistbend nematic, N_{TB} [4,5-10]. Compounds showing this continue to be studied by a variety of techniques primarily with the aim of understanding why an enantiomorphic phase can be formed by achiral molecules [11-13]. Less attention has been given to the higher temperature nematic phase, which it has been assumed is like all other uniaxial nematic calamitic phases. The temperature dependence of the molecular orientational order parameter, *S*, for "classical" nematic phases composed of rod-like molecules has a characteristic form, which is that of a continuously increasing value throughout the whole range of the phase [14]. The compound studied here, DTC5C9, whose structure is shown in Fig. 1, has two nematic phases, N_U and N_{TB} and unlike almost all other materials reported so far has a negative dielectric anisotropy. This class of materials has very recently attracted interest because of their potential electroptical properties, the ability to form fibres, and the relatively easy control of the LC transition temperatures [15,16] The behaviour of DTC5C9 in the N_{TB} phase has been characterized by freeze fracture TEM studies, X-ray diffraction experiments and electrooptical studies [10], essentially techniques which rely on the preparation of thin films. The properties of this system have not been investigated in the bulk, and for this NMR techniques are uniquely useful. In this report we show the results of the first NMR investigation of a negative dielectric anisotropy material in the isotropic, N_U and N_{TB} phases.



Fig. 1. The structure and atomic labelling used for DTC5C9 in the text.

The sequence of phases is:

Isotropic 161.8 °C \rightarrow nematic \rightarrow 125.2 °C chiral nematic, N_{TB} \rightarrow 81.1 °C S_X \rightarrow 72.2 °C \rightarrow crystal.

Isolated molecules of DTC5C9 are achiral, whilst the second nematic phase formed on cooling is enantiomorphic.

The single most characteristic property of a liquid crystalline phase is the orientational order of their constituent molecules, as measured by second-rank order parameters, $S_{\alpha\beta}$, introduced by Saupe for uniaxial phases:

$$S_{\alpha\beta} = \langle (3\cos\theta_{\alpha}\,\cos\theta_{\beta}\,-\,\delta_{\alpha\beta})/2 \rangle,\tag{1}$$

where $\langle \rangle$ signifies an average, and θ_{α} and θ_{β} are the angles that a unit vector \mathbf{n}_{j} at a point *j* in the phase, known as the director makes with axes α and β fixed in the molecule. Values of the order parameters for molecules in a uniaxial liquid crystal phase may be obtained by measurement of the component along the director, A_{\parallel} , of a second-rank property of the molecules, which for a rigid molecule is related to components, $A_{\alpha\beta}$, by:

$$A_{\parallel} = A_{iso} + \frac{2}{3} \sum_{\alpha\beta} A_{\alpha\beta} S_{\alpha\beta}. \tag{2}$$

 A_{iso} is the magnitude of A averaged over an isotropic distribution of molecular orientations, and can be obtained by a measurement in the isotropic phase. The molecules which form liquid crystal phases are almost invariably flexible because of hindered rotation about bonds. The dependence of order parameters on the conformational distribution of the molecules can be allowed for by introducing order matrices, S(n), for each of *n* conformations, each assumed to be rigid, with probabilities p(n), thus

$$\langle A_{||} \rangle = A_{\rm iso} + \frac{2}{3} \sum_{n} p(n) \sum_{\alpha\beta} A_{\alpha\beta}(n) S_{\alpha\beta}(n).$$
(3)

The physical properties used to obtain values of order parameters include the refractive index, the magnetic susceptibility and the electrical permittivity. The values of $A_{\alpha\beta}$ for these properties are measurable only for the whole molecule, and their relationship to molecular structure, and of how they are averaged over conformational states can be difficult to quantify, and so too are order parameters derived from them. Extracting conformationally-dependent order parameters from experimental values of $(\langle A_{||} \rangle - A_{iso})$ requires experiments which yield sufficiently large sets of data at each temperature. This has been demonstrated for studies using sets of NMR data, such as partially-averaged (also called "residual") deuterium quadrupolar splittings, Δv_i , where *i* labels a nucleus [17]. Such studies have usually required enriching the mesogen with deuterium. Partial deuterium labelling, combined with ${}^{1}H - {}^{2}H$ double-resonance experiments have yielded sets of residual dipolar couplings, $D_{i,j}$, between protons in compounds forming nematic, smectic A, and smectic B phases, and for an example see [18]. These experiments again require isotope labelling. It has also proved possible to obtain sets of residual dipolar couplings between protons and ¹³C nuclei present at natural abundance by two-dimensional, separated local field experiments and for the molecule CB7CB to test models for both the conformational distribution and the orientational order in both N_U and N_{TB} phases [7].

The present study initially aimed to obtain sets of residual dipolar couplings between ^{13}C at all sites in DTC5C9 and directly-bonded protons from SLF experiments, and to use these to test models for the conformational distributions in N_U and N_{TB} phases. The complexity, and size of the structure of this molecule has meant that this aim has been only partially

successful. However, it is relatively easy to obtain order parameters for axes fixed in rigid parts of complex molecules from measurements of ¹³C chemical shifts. Thus, if it is assumed that the difluoroterphenyl groups retain the same structure in all the molecular conformations, then it is possible to define order parameters S_{xx} , S_{yy} , and S_{zz} with respect to axes *x*, *y* and *z* as averages over all the *n* conformations of the molecules:

$$S_{\alpha\alpha} = \sum_{n} p(n) S_{\alpha\alpha}(n), \tag{4}$$

where p(n) is the normalised probability of each conformation.

These order parameters S_{aa} may be obtained from values of $\langle A_{ii}(i) \rangle$, $\langle A_{iso}(i) \rangle$ and $\langle A_{\alpha\beta}(i) \rangle$, where *i* is a nucleus in the rigid fragment, from the relationship:

$$\langle A_{\parallel}(i) \rangle = \langle A_{iso}(i) \rangle + \frac{2}{3} \sum_{\alpha\beta} \langle A_{\alpha\beta}(i) \rangle S_{\alpha\beta}.$$
(5)

These "rigid-fragment" or "local" order parameters are obtained easily from the chemical shifts of ¹³C nuclei even for a molecule as complex as DTC5C9, and they have been used to obtain the temperature dependence of the order parameter S_{zz} throughout both N_U and N_{TB} phases. This temperature dependence is found to be substantially different from that expected of a classical nematic phase, and it is proposed that this reflects an unusual tilted alignment of the directors in both N_U and N_{TB} phases.

Experimental

Proton decoupling is essential in order to obtain simple, well-resolved ¹³C spectra from strongly-ordered liquid crystal samples, and this requires using a NMR spectrometer which has the capability of decoupling proton-¹³C dipolar interactions of ~ 5 kHz. In the present case such ¹³C – {¹H} spectra were obtained at the Centre de RMN à Très Hauts Champs at Lyon, using a spectrometer operating with a magnetic field strength of 11.75 T (500 MHz Larmor frequency for ¹H, and 125 MHz for ¹³C). The spectra obtained of DTC5C9 are

characteristic of uniformly aligned samples. The probe used has a horizontal 5 mm static solenoid coil, and the sample was contained in an "L"-shaped glass tube of 4 mm o.d diameter [6], and ~ 10 mm length. The temperature is controlled by a flow of N₂ gas and monitored by a thermocouple located close to the coil. An essential first step is to calibrate the temperature given by this thermocouple, with the flow rate of the N₂ gas used, for the isotropic – nematic transition by recording ¹H NMR spectra and noting the temperature when the spectrum changes from a set of narrow lines (~ 10 Hz wide) in the isotropic to a very broad resonance (~ 20 kHz wide) in the nematic phase, as shown in Figure 2.



Figure 2. 500 MHz ¹H spectra of pure DTC5C9 obtained in (A) the isotropic phase (B) nematic-isotropic biphasic and (C) the uniaxial nematic phases. The isotropic spectrum is much more intense than the nematic spectrum because resonance linewidths are much narrower, for this reason it is plotted with a scaling factor of 0.04. Each spectrum was acquired with 22492 complex points and 16 scans, over a spectral windows of 150 kHz. The acquisition time was 149.9 ms and the recycle delay was 3.0 s. The ¹H $\pi/2$ pulse was 5.0 µs long. All the spectra were processed with an exponential window function of 2 Hz.

 ${}^{13}C - \{{}^{1}H\}$ spectra were obtained at set temperatures in the range of 166 °C, when the sample is in the isotropic phase, to 87 °C, when the sample froze. An interval of 10 minutes was used between setting the temperature and recording the spectra to allow thermal equilibrium to be maintained.



Fig. 3. The ${}^{13}C - {}^{1}H$ spectra of DTC5C9 at 11.75 T in the isotropic, nematic and twistbend nematic phases. The spectra were obtained with a cross-polarisation step from protons to carbon with 2.0 ms of contact time followed by proton decoupling using SPINAL-64 [19] whist acquiring 256 ${}^{13}C$ free induction decays. A spectral width of 31.25 kHz was used, acquired into 3494 points of computer store, for an acquisition time of 55.9 ms. The proton decoupling was applied only during acquisition, with a strength of 50 kHz. A recycle delay

of 5 s ensured minimal heating by the ¹H decoupling. The chemical shifts are calibrated relative to the transmitter frequency of 125.7661416MHz. The assigned peaks are labelled with the atomic sites given in figure 1.

A 1D ¹³C spectrum was also recorded of a sample dissolved in CDCl₃. It was recorded at 14.1 T and has narrower lines, but is otherwise very similar to that recorded for the pure sample in the isotropic phase above 162 ° C. These two ¹³C – {¹H} spectra are compared in Fig. 4.



Fig. 4. Comparison between the ¹³C spectra of DTC5C9 in CDCl₃ solution at 25 °C and 14.1 T (upper part), and that of pure DTC5C9 in the isotropic phase at 166 °C and 11.75 T (lower part). The spectrum in CDCl₃ solution was obtained by adding 4096 scans, acquired over a spectral window of 59.5 kHz, with an acquisition time of 274.0 ms (16384 complex

points). The $\pi/2$ ¹³C pulse was 14.1 µs and the recycle delay was 10 s. ¹H WALTZ16 decoupling [20] at 3.125 kHz was applied during acquisition. A weaker decoupling of about 0.95 kHz was applied during the recycle delay to increase the ¹³C polarization by ¹H-¹³C cross-relaxation. The spectrum was processed with 65536 complex points and using an exponential window function of 2.0 Hz. The spectrum in the isotropic phase is the result of acquiring 192 scans, each with a spectral window of 50.0 kHz, and an acquisition time of 51.2 ms (2560 complex points). The $\pi/2$ ¹³C pulse was 5.0 µs and the recycle delay was 2.5 s. ¹H SPINAL64 decoupling at 50.0 kHz was applied during acquisition. The spectrum was processed with 65536 complex points and using an exponential window function of 10.0 Hz.

The ¹³C assignments for the sample in the two isotropic phases (the solution in CDCl₃ and the pure sample above 162 °C) were obtained by combining 1D ¹H and ¹³C spectra with a 2D ¹³C-¹³C INADEQUATE spectrum [21] and 2D ¹H-¹³C gradient-HSQC [22], 2D ¹H-¹³C gradient-HMBC [23], and 2D ¹H-¹H COSY spectra [24]. Standard sequences were used for the 2D ¹³C-¹³C INADEQUATE and 2D ¹H-¹³C gradient-HSQC, 2D ¹H-¹³C gradient-HMBC, and 2D ¹H-¹H COSY spectra. The $\pi/2$ hard pulses were 8.25 µs and 14.1 µs for ¹H and ¹³C, respectively. Adiabatic inversion and refocusing pulses of 500 µs and 2000 µs were used for ¹³C in the ¹H-¹³C HSQC and ¹H-¹³C HMBC, respectively. A Garp-4 decoupling [25] of 4.1 kHz was applied on the ¹³C channel during the ¹H acquisition in the ¹H-¹³C HSQC. A matrix of 2048 x 2048 real points were acquired for ¹H-¹³C HSQC and ¹H-¹³C HMBC and of 4096 x 1024 real points for ¹H-¹H COSY. Spectra were processed with 4096 x 2048 matrices using a square cosine windows function for ¹H-¹³C HSQC and ¹H-¹³C HMBC, and a square sine and square cosine window function for ¹H-¹H COSY.

Results and Discussion

The chemical shifts of the ¹³C nuclei in the isotropic phase

The assignment of the ¹³C resonances for the sample as a solution in CDCl₃ relied on the 2D correlation experiments. These methods are not applicable for the pure sample in the isotropic phase mainly because of broader lines in the ¹H spectrum leading to insufficient signal resolution to produce good 2D correlation spectra. In the absence of this spectroscopic information it is necessary to rely on a comparison between the ¹³C – {¹H} spectra taken on the two isotropic samples which are compared in figure 4. The ¹³C chemical shifts, $\delta_{i, methyl}$, measured in each case relative to the resonance from the methyl groups in the n-pentyl chains are given in Table 1.

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Table 1. Chemical shifts,($\delta_{i,methyl}$)/ppm of ¹³C nuclei in DTC5C9 relative to the resonance from the methyl groups, for the CDCl₃ solution compared with the pure compound in the isotropic phase at 166 °C. These values are compared with differences , ($\sigma_{0,methyl} - \sigma_{0,i}$)/ppm of the isotropic components, σ_0 , of the nuclear shielding tensors calculated by the GIAO method using eigenfunctions obtained by the DFT method B3LYP using a 6-31G* basis set as implemented in the Gaussian Program G09 [26].



117.92

118.60

111.72

1 (or 13)

2 (or 5)	115.46	115.96	109.03
3(or 4)	110.50	110.63	102.17
4(or 3)	110.50	110.63	101.95
5(or 2)	115.46	115.96	109.32
6 (or 7)	134.69	135.40	129.18
7(or 6)	134.69	135.40	129.20
8 (=12) or 14 (=18)	114.67	115.02	106.59
9 (=11) or 15 (=17)	114.63	114.80	106.40
10 (or 16)	129.03	129.27	120.42
13 (or 1)	117.92	118.60	111.68
14 (=18) or 8(=12)	114.67	115.02	106.68
15(=17) or 9(=11)	114.63	114.80	106.39
16 (or 10)	129.03	129.27	120.23
31	21.57	22.07	23.49
32	17.29	17.11	21.57
33	15.41	16.03	18.00
34	15.27	15.78	17.18
35	15.41	16.03	17.62
36	21.57	22.07	23.48
37	17.49	18.17	21.64
38	17.01	16.76	19.08
39	8.48	8.65	10.21
40	0.00	0.00	0.00

The ¹³C chemical shifts are a sensitive reflection of the structure of a molecule, and in particular the symmetry of the molecule usually dictates the number of resonances resolved. However, this is not the case for DTC5C9, for which both isotropic samples have chemical shift equivalences for ¹³C nuclei in the difluoroterphenyl groups which are consistent with a higher symmetry than that of the molecule, thus $\delta_1 = \delta_{13}$, $\delta_2 = \delta_5$, $\delta_3 = \delta_4$, $\delta_6 = \delta_7$, $\delta_8 = \delta_{12} =$ $\delta_{14} = \delta_{18}$, $\delta_9 = \delta_{11} = \delta_{15} = \delta_{17}$ and $\delta_{10} = \delta_{16}$. The ¹³C chemical shifts for each nucleus in both the CDCl₃ solution and the pure sample are very similar (within 0.7 ppm), which suggests that intermolecular effects on the isotropic chemical shifts are small. The chemical shifts are related to ¹³C nuclear shielding constants, σ_i , which are secondrank tensorial properties of the nuclei. For the present experiments the spectra are recorded in magnetic fields which are of sufficient strength that only the components along the field, $\sigma_{i,ZZ}$, affect the shielding constants, and these are related to components, $\sigma_{i,\alpha\beta}$, in axes fixed in the rigid part of the molecule containing nucleus *i* by Eq. (5), which becomes:

$$\sigma_{i,ZZ} = \sigma_{i,0} + \frac{2}{3} \sum_{\alpha\beta}^{XYZ} \sigma_{i,\alpha\beta} S_{\alpha\beta} , \qquad (6)$$

where $S_{\alpha\beta}$ is a component of the order matrix defined with respect to the magnetic field direction and for axes fixed in the rigid segment. Only the term $\sigma_{i,0}$ is non-zero in an isotropic phase, so that the chemical shift for the *i*th nucleus relative to a reference nucleus in an isotropic phase is just:

$$\delta_i = \sigma_{\text{ref}} - \sigma_{i,0}. \tag{7}$$

It is possible to calculate the tensor components $\sigma_{i,\alpha\beta}$ for all the magnetic nuclei in a rigid molecule for any set of molecule-fixed axes, and to extract the isotropic components $\sigma_{i,0}$, having first calculated a geometry which minimizes the total energy. For a molecule as large as DTC5C9, containing 119 atoms this proved possible with the computer resources available to us using a *DFT* method (B3LYP) with a basis set 6-31 G*, as implemented in the Gaussian g09 computer program [26].

The conformations generated for DTC5C9 by rotations about bonds

The observed chemical shifts are averages over all the conformations adopted by the molecule by rotations about single bonds and Figure 5 illustrates the conformations that are generated by hindered rotation about various C-C bonds in DTC5C9. In the approximation, known as the rotational isomeric state (RIS) model, in which the only allowed conformations

are between local minimum energy forms, there is still a very large number, N_{conf} , of conformations generated for the whole molecule by bond rotations. The total number is a product of the numbers of conformations generated within molecular sub-groups. Thus,

 $N_{conf} = (N_{alkane})(N_{pentyl})(N_{ring})(N_{ring-chain}).$

(8)



Figure 5. Generation of conformations in DTC5C9 by hindered rotations about C – C bonds.

Rotation about each of the $C_k - C_{k+1}$ bonds in the fragments $C_{k-1} - C_k - C_{k+1} - C_{k+2}$ in the alkyl and alkane chain groups is between three local energy minima: a single *trans* (*t*) form of lowest energy, and two *gauche* (*g*+ and *g*-) forms each with an energy higher than *trans* of E_{tg} . This produces a value for N_{alkane} of $3^8 = 6561$ of which just one, the all-trans, in which each C-C-C fragment is in a *trans* configuration, contributes to the minimum energy form of the whole molecule. There are 3^3 RIS conformers for each pentyl chain, so that $N_{pentyl} = 3^6$ = 729 of which one has both chains in the all-trans form.

The calculated values of E_{tg} vary with the location of the C_k –C_{k+1} bond in the molecule, and are very similar to values calculated previously for 5CB [27] and CB7CB [7], as demonstrated by the data shown in Table 2.

Table 2. Values of E_{tg} calculated for C-C bonds in the end pentyl chains of DTC5C9 compared with similar positions in 5CB. The values of E_{tg} calculated for C-C bonds in the linking alkane fragment are compared with those at similar positions in the C7 linker in CB7CB.





Alkane linker



Rotation about the bond between the phenyl rings and the alkyl chains (ϕ_{rc} in figure 54) are between just two essentially equal energy forms having the ring and chain in perpendicular orientations, with $\phi_{rc} = 90^{\circ}$ or 270°, to give a value for $N_{ring-chain} = 2^4 = 16$. The rotation about each inter-ring bond is through an angle ϕ_{rr} which generates in each case four essentially equal local minimum energy forms at values of $\phi_{rr} = \phi_0^{\circ}$, (180 - ϕ_0)°, (180 + ϕ_0)°, and (360 - ϕ_0)°. The value of $\phi_0 \sim 38^{\circ}$, and $N_{ring} = 4^4 = 256$.

It is a special feature of DTC5C9 that the isolated molecules have groups of equal energy conformations formed by combining the possible values of both ϕ_{rc} and ϕ_{rr} . Although there are 4096 ways of combining these two angles these conformations form smaller groups with distinctly different shapes, as shown in figure <u>65</u>.



Figure 6. Examples of the shapes of conformations of DTC5C9 generated by combining the different values of the rotation angles ϕ_{rc} and ϕ_{rr} .

The optimisation process finds the bond lengths and angles for the molecule in the lowest energy conformation, which for an isolated molecule corresponds to the three alkyl chains each being in an all-trans configuration. The geometry for the molecule in the lowest energy conformation is given in Table S3 of Supplementary Information.

An estimate has been made of the effect on the shielding constants of introducing single *gauche* links at each position of the alkane chain spacer. A set of conformations, *n*, was

generated comprising for the alkane spacer the 16 single gauche forms, plus the all-trans form. The relative energy of a conformation is zero for the all-trans and is just the value of E_{tg} for conformers containing just a single gauche link. The shielding constants, $\sigma_{i,0}(n)$, were calculated for each carbon nucleus in each conformation, and the averages, $\langle \sigma_{i,0} \rangle_n$ calculated as the weighted average

$$\langle \sigma_{i,0} \rangle_n = p(n) \sigma_{i,0}(n), \tag{9}$$

where

$$\mathbf{p}(n) = \frac{\exp[-E_{tg}(n)]/RT}{\sum_{n} \{\exp[-E_{tg}(n)/RT]\}}.$$
(10)

The values calculated for $(\langle \sigma_{0,methyl} \rangle_n - \langle \sigma_{i,0} \rangle_n)$ and p(n) for the alkane and alkyl chain carbons are given in Table 3.

Table 3. The calculated values of $(\langle \sigma_{0,methyl} \rangle_n - \langle \sigma_{i,0} \rangle_n)$ (in ppm) and p(n) for the alkane and alkyl chains in DTC5C9.



k-1	k	k+1	k+2	probability at 439 K
33	34	35	34'	0.097
33'	34'	35	34	0.097
32	33	34	35	0.099
32'	33'	34′	35	0.099
31	32	33	34	0.094
31′	32'	33'	34'	0.094
16	31	32	33	0.139
16′	31'	32'	33'	0.139

Average of calculated shifts $(\langle \sigma_{0,methyl} \rangle_n - \langle \sigma_{i,0} \rangle_n)/ppm$ compared with values $(\sigma_{0,methyl} - \sigma_{i,0})_{min}/ppm$ calculated for DTC5C9 in the minimum energy conformation.

Carbon atom	$(<\sigma_{0,methyl}>_n - <\sigma_{i,0}>_n)$	$(\sigma_{0,methyl} - \sigma_{i,0})_{min}$
31	23.14	23.49
32	20.86	21.57
33	17.08	18.10
34	16.77	17.18
35	16.86	17.16



Probability at 439 K

0.286

all-trans conformer	
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single-gauche conformer for the segment C(k-1)-C(k) - C(k+1) - C(k+2)

k-1	k	k+1	k+2	probability at 439 K
10	36	37	38	0.298
36	37	38	39	0.209
37	38	39	40	0.206

Average of calculated shifts $(\langle \sigma_{0,methyl} \rangle_n - \langle \sigma_{i,0} \rangle_n)/ppm$ compared with values $(\sigma_{0,methyl} - \sigma_{i,0})_{min}/ppm$ calculated for DTC5C9 in the minimum energy conformation.

Carbon atom	$(<\sigma_{0,methyl}>_n$ - $<\sigma_{i,0}>_n)$	$(\sigma_{0,methyl} - \sigma_{i,0})_{min}$
36	22.706	23.477
37	20.133	21.639
38	17.256	19.078
39	9.794	10.207
40	0.000	0.0000

Changing the relative orientations of the six phenyl rings in the two difluoroterphenyl groups has negligible effects (to within ~ 0.2 ppm) on the calculated shielding constants, as also does changing the relative conformations of the two n-pentyl groups. It can be concluded, therefore, that the close similarity of the ¹³C chemical shifts in the spectra of the two isotropic samples is consistent with the molecules having similar conformational distributions in these two isotropic phases. The small differences in the observed chemical shifts are probably caused by differences in temperature and density.

The ¹³C spectra in the liquid crystal phases

The accidental equivalences observed between ¹³C nuclei in the individual difluoroterphenyl groups noted as occurring in the isotropic phase are removed to varying extents when the sample is in the liquid crystalline phases, where each ¹³C resonance, except those from C6 and C7 (which are not resolved, and of low intensity because of weak cross-polarisation) is a triplet with splitting $\Sigma_{\text{CiF}} = \frac{1}{2}(T_{C_iF_{19}} + T_{C_iF_{20}})$ centred on the chemical shift, δ_i (LC). The total coupling, T_{CiF_k} , is,

$$T_{C_i F_k} = J_{C_i F_k} + 2D_{C_i F_k}, (11)$$

where $J_{C_iF_k}$ is the scalar and $D_{C_iF_k}$ the residual dipolar coupling. The values of $T_{C_iF_k}$ are expected to decrease with distance from the two ¹⁹F nuclei and their average values were used to assign the peaks given by the carbons in the difluoroterphenyl groups (other than C6 and C7) when the sample is in the N_U or N_{TB} phases. However, C10 and C16 are equidistant from the fluorine nuclei and so their resonances cannot be differentiated, and similarly the peaks from C1 and C13 also cannot be differentiated in this way. The values of $\Delta_i = \delta_i(LC) - \delta_i(iso)$ are given in Table S1 and those for Σ_{CiF} in Table S2 in Supplementary Information for all the aromatic carbons, and C39 and C40, the only aliphatic carbons which could be assigned unambiguously.

The relationship between ¹³C chemical shifts and molecular orientational order.

A local order parameter, S_{zz} , for the axis z can be obtained from the ¹³C chemical shifts, thus from Eq. (6):

$$\Delta_{i} = \frac{2}{3} S_{zz} [\sigma_{zz} - \frac{1}{2} (\sigma_{xx} + \sigma_{yy})] + \frac{1}{3} (S_{xx} - S_{yy}) (\sigma_{xx} - \sigma_{yy}) + 4 [S_{xy} \sigma_{xy} + S_{xz} \sigma_{xz} + S_{yz} \sigma_{yz}]/3, \quad (12)$$

where $\Delta_i = \delta_i(\text{LC}) - \delta_i(\text{iso})$, the difference in chemical shift for nucleus *i* in the liquid crystal and isotropic phases; σ_{xx} etc. are components of the nuclear shielding tensor for axes *xyz* fixed in a rigid part of the molecule. There is insufficient experimental data to obtain the set $S_{\alpha\beta}$ of local order parameters from just one value of Δ_i at each temperature, and so approximations are introduced in order to simplify Eq. (12). Values of local order parameters can also be obtained from residual dipolar couplings, D_{ij} , which for the nuclei in the centre difluorinated ring are related to order parameters by:

$$D_{ij} = -K_{ij}r_{ij}^{-3}[S_{zz}(3\cos^2\theta_{ijz} - 1) + (S_{xx} - S_{yy})(\cos^2\theta_{ijx} - \cos^2\theta_{ijy})],$$
(13)

with,

$$K_{i,j} = \mu_0 \gamma_i \gamma_j \, h / 32\pi^3 \,. \tag{14}$$

The angles θ_{ijx} etc. are between r_{ij} and axis x. Note that there may also be a contribution to the measured value of D_{ij} from an anisotropic contribution to indirect spin-spin coupling, but this is estimated to be less than ~ 2% for C-F pairs [28,29] and will be neglected. Using Eq.

(13) with geometrical parameters taken from the *DFT* calculation (see table S3 in Supplementary Information) enabled values of the local order parameters to be obtained for axes fixed in the difluorinated rings.

Counsell [30] has compared values of Δ_{CN} obtained for carbon directly bonded to the nitrogen in the nematogen 5CB labelled with ¹⁵N, with the residual dipolar coupling ${}^{1}D_{CN}$. MMeasurements of ${}^{1}D_{CN}$ were combined with an assumed C-N distance to obtain values of S_{zz} at temperatures throughout the nematic range of 5CB, with *z* along the *para* axis. Plotting S_{zz} against Δ_{CN} for 5CB gave a good fit to a straight line showing that Eq (12) for this carbon shift anisotropy simplifies to:

$$\Delta_{i} = \frac{2}{3} S_{zz} [\sigma_{zz} - \frac{1}{2} (\sigma_{xx} + \sigma_{yy})], \tag{15}$$

or simply

$$\Delta_i = A_i \, S_{zz},\tag{16}$$

where A_i is a constant. The same linear relationship will be assumed to hold for the values of Δ_i for the ¹³C nuclei on the *para* axis of the difluoroterphenyl groups in DTC5C9.

The chemical shift anisotropies of ¹³C nuclei in DTC5C9

Figure <u>76</u> shows the temperature dependence of the chemical shift anisotropy for C10 in DTC5C9.



Fig. <u>76</u>. The temperature dependence of the chemical shift anisotropy, Δ_{10} , of C10 in DTC5C9.

Very similar shaped curves are obtained for all the carbons on the *para* axis (see figure S1 in Supplementary Information), with each reaching a maximum in the nematic phase at ~ 134 °C. Note that the rapid increase in values of .4. at the lowest temperatures are attributed to the onset of a new, unidentified phase. The rapid increase in values of *A* at the lowest temperatures are attributed to the onset of another liquid crystal phase termed provisionally SmX. The details of the structure have not yet been identified fully, however comparison with the analogue DTC5C7, containing similar mesogenic and terminal groups, but with a shorter heptyl spacer linking the two mesogens, -suggest that the formation of tilted layers is an important feature of the phase structure [31]. The optical polarizing microscopy observations for this phase, provisionally termed SmX for DTC5C9 are consistent with these results: for an optical polarizing microscope micrograph, see figure S4 in Supplementary Information. However, a full investigation of this phase is outside the scope of this work.

The values obtained for the average residual dipolar coupling, $\langle D_{CiF} \rangle = \frac{1}{2}(D_{CiF19} + D_{CiF20})$, for carbons on the terphenyl *para* axis, i.e carbons 1, 2, 5, 10 and 16, were used to obtain values at 134 °C of the two order parameters $S_{zz} = 0.488 \pm 0.006$ and $S_{xx} - S_{yy} = 0.018 \pm 0.004$ for axes fixed in the central, difluorinated ring from Eqs (13) and (14) using geometrical parameters obtained for this ring by the DFT calculation on DTC5C9 in the all-trans minimum energy form given in Table S3 of Supplementary Information. This value of S_{zz} was used together with the value for the chemical shift anisotropy, Δ_{I0} , measured for C10 of 48.166 ± 0.005 ppm to give the proportionality constant A_{I0} in Eqn (16) as 98.700 ± 0.005 ppm. The biaxial molecular order parameter, $S_{xx} - S_{yy}$ is just 3.7% of S_{zz} and will be neglected, and together with other systematic errors in this method of obtaining the order parameter for the difluoroterphenyl para axes the combined error for S_{zz} is estimated to be ± 5 %.

Figure $\underline{87}$ shows the temperature dependence of S_{zz} obtained from the shift anisotropies of C10 in the N_U and N_{TB} phases.



Figure <u>87</u>. The temperature dependence of the order parameter S_{zz} for the bent-shaped DTC5C9 (o) compared with those for the rod-shaped compound KS7 (•), whose structure is shown in Figure <u>98</u>.

Comparison between the order parameter temperature profiles of DTC5C9 and KS7, which has a classic calamitic N_U phase

It is often assumed for simplicity that the orientational order of the molecules in a uniaxial nematic phase can be described by a single second-rank order parameter, *S*. This is equivalent to assuming that the molecules are rigid and have at least C_{3v} symmetry, with *S* defined as:

$$S = \langle \frac{1}{2}(3\cos^2\beta_s - 1) \rangle, \tag{17}$$

where β_s is the angle that the director makes with the assumed symmetry axis of a molecule at a moment in time, and the angular brackets denote an equilibrium average. This approximate way of measuring the molecular orientational order has the advantage that it can be obtained from experimental values of any second-rank property of the liquid crystal sample, and has been measured for a large number of nematic liquid crystals in each case over the whole range of temperature of the liquid crystal phase. Most temperature profiles of *S* have been found to have a very similar shape, as reported by Simões *et. al.* [14], so that *S*(*T*) is regarded as being a characteristic property of a *N*_U phase. Thus, Haller [3132] has suggested that the temperature dependence *S* for a nematogen should follow the equation:

$$S(\Delta T) = S_0(\Delta T)^{\gamma},\tag{18}$$

where $\Delta T = T_{NI} - T$, and $S_0 = 1/T_{NI}^{\gamma}$.

Geppi *et al.* [332] have measured the order parameter, S_{zz} , for the para axis of the difluoroterphenyl group in the compound KS7 whose structure, shown in figure 98, is that of a fragment of *DTC5C9*, and have shown that it closely follows Eqn (18).



Fig. <u>98</u>. The compound, KS7, studied by Geppi *et al.*[3<u>3</u>2].

The order parameters $S_{zz}(DTC5C9)$ and $S_{zz}(KS7)$ are compared in figure <u>87</u>, where it is seen that they have very different temperature dependencies. The most unusual behaviour of $S_{zz}(DTC5C9)$ with temperature in the N_U phase is that it passes through a maximum at ~ 134 °C which is ~ 10 °C above the transition to the N_{TB} phase. The value of $S_{zz}(DTC5C9)$ then decreases smoothly until the N_{TB} phase is reached when there is a small discontinuity (~2%). This is apparent from the peaks from C10 and C16 in the vicinity of the transition which are shown in Fig. S<u>3</u> in the Supplementary Information.

Possible reasons for the different temperature profiles of $S_{zz}(KS7)$ and $S_{zz}(DTC5C9)$ in the N_U phase

The molecules KS7 molecules are similar to those included by Simões *et. al.* [14] in their comparison of the temperature profiles of the order parameter in being a reasonable approximation to a rigid cylindrical shape, with the assumed symmetry axis , defining the direction of the single order parameter, S(KS7), describing the orientational order of the molecules. A local order parameter, $S_{zz}(KS7)$ is defined for the *para* axis of the

difluoroterphenyl group, for which it is reasonable to assume axial symmetry about *z*, and to also to assume that the cylinder axis makes a fixed angle, θ_s , with *z*. In this simple model for KS7 the two order parameters are related by:

$$S_{zz}(KS7) = S(KS7) \frac{1}{2}(3\cos^2\theta_s - 1).$$
(19)

The value of θ_s is expected to be small (~ 5-10°) so that $S_{zz}(KS7) \sim 0.97S(KS7)$, and if S(KS7)(T), obeys the Haller equation then so too will $S_{zz}(KS7)(T)$, as observed by Geppi *et al.*

The situation is very different for *DTC5C9* which has a pronounced bent shape imposed by the presence of the alkane chain spacer. In a rigid conformation, *n*, of DTC5C9 the relationship between local order parameters, $S_{\alpha\beta}(q,n)$ for axes fixed in fragment *q*, for example, one of the difluoroterphenyl groups, and principal order parameters $S_{\delta\delta}(r,n)$ is:

$$S_{\alpha\beta}(q,n) = \sum_{\delta} \cos \theta_{\alpha\delta}(n) \cos \theta_{\beta\delta}(n) S_{\delta\delta}(r,n), \qquad (20)$$

where $\theta_{\alpha\delta}(n)$ is the angle between axis α fixed in fragment q, and principal axis δ . The principal axes for *DTC5C9* are conveniently centred on C35, which has the advantage that one of these axis will be a 2-fold axis of symmetry for some of the conformations. Note that both $S_{\alpha\beta}(q,n)$ and $S_{\delta\delta}(r,n)$ have averages, $S_{\alpha\beta}(q)$ and $S_{\delta\delta}(r)$, over all conformations given by Eqn (4), but there is not a simple relationship between these averaged, local order matrices, thus:

$$S_{\delta\delta}(r) = \sum_{n} p(n) S_{\delta\delta}(r, n), \qquad (21)$$

and

$$S_{\alpha\beta}(q) = \sum_{n} p(n) \sum_{\delta} \cos \theta_{\alpha\delta}(n) \cos \theta_{\beta\delta}(n) S_{\delta\delta}(r, n).$$
(22)

Furthermore, whilst the averaged local order matrices for the difluoroterphenyl groups are found experimentally to be close to axial symmetry, the order matrix for the whole molecule in principal axes probably has a large biaxiality, as found for the similar shaped mesogen CB7CB [7], which considerably complicates the relationship in Eqn (22). The bent shape and the molecular flexibility, therefore, make it difficult to predict how $S_{zz}(DTC5C9)$ should vary with temperature, but some general guidelines are possible. Thus, in the limit of complete molecular order at 0 K, the molecules will be in just one conformation with an axially-symmetric order matrix with the major principal order parameter of $S_0 = 1$. The bent shape, and the 2-fold symmetry in this dimeric molecule means that the order parameter for both the *z* axes will have a low temperature limit of :

$$S_{zz}(DTC5C9)(0 K) = \frac{1}{2}(3\cos^2\beta_{bend} - 1) = P_2(\cos\beta_{bend}).$$
(23)

The value of β_{bend} for the molecule in the minimum energy conformation, which has the alkane spacer in the all-trans form, is ~ 30°, which corresponds to $P_2(cos\beta_{bend}) = 0.625$. In fitting the observed order parameter $S_{zz}(DTC5C9)$ to values observed in the N_U phase, $S_{zz}(DTC5C9)(0 \text{ K})$ is treated as an adjustable parameter to give:

$$S_{zz}(DTC5C9)(\Delta T) = S_{zz}(DTC5C9)(0 \ K)(1 - T/T_{NI})^{\gamma}.$$
(24)

In this form $S_{zz}(DTC5C9)(T_{NI})$ is zero, as in the function proposed by Haller, whilst in practice it is finite, albeit small, and an improvement is to replace T_{NI} by $T^* = T_{NI} + 0.5$, thus:

$$S_{zz}(DTC5C9)(\Delta T) = S_{zz}(DTC5C9)(0 K) (1 - T/T^{*})^{\gamma}.$$
(25)

Fitting the values of $S_{zz}(DTC5C9)(0 \ K)$ and γ to the experimental values of $S_{zz}(DTC5C9)$ for ΔT between 4 °C and 16 °C gives $S_{zz}(DTC5C9)(0 \ K) = 0.82$ and $\gamma = 0.17$, and a predicted value of $S_{zz}(DTC5C9)$ at T_{NI} of 0.26. The calculated values of $S_{zz}(DTC5C9)(\Delta T)$ for this



modified Haller function are compared with those observed in figure 109.

Fig. <u>109</u>. The observed values of $S_{zz}(DTC5C9)$ (•) compared with values calculated by the modified Haller function of Eqn (25) (×).

If Eqn (25) is assumed to be an approximate representation of the temperature variation of the local order parameter of a rigid fragment in a bent, dimer mesogen, then there has to be an extra temperature-dependent effect which is producing the maximum in the observed variation of $S_{zz}(DTC5C9)$ with temperature. The order parameter $S_{zz}(DTC5C9)$ is defined with respect to the applied magnetic field, B₀, of the NMR spectrometer, which in a normal N_U phase with a positive magnetic susceptibility will align the local directors, **n**_i parallel to **B**₀. If the local directors in the N_U phase of DTC5C9 tilt uniformly through an angle ϕ_B away from the **B**₀ direction, then all the local order parameters, such as $S_{zz}(DTC5C9)$ will be scaled by P₂(cos ϕ_B). In addition, if the tilt increases with decreasing temperature then this could explain the maximum in the temperature dependence of $S_{zz}(DTC5C9)$ measured from experimental data with those calculated to fit the modified Haller equation. Values of ϕ_B obtained in this way are shown in Figure 1<u>1</u>0.



Figure 110. The tilt angle, ϕ_B , obtained by comparing S_{zz} (DTC5C9) calculated by the modified Haller function with observed values.

The presence of a tilt of the directors in the N_U phase is not consistent with this phase being comprised of molecules, bent or otherwise, interacting with each other as single molecular species, and it is proposed that this is a consequence of their bent shape leading to entangled, intercalated arrangements of near neighbours.

The temperature dependence of $S_{zz}(DTC5C9)$ in the N_{TB} phase

The spectra in the temperature interval between $T_{NI} - T = 34^{\circ}$ C and $T_{NI} - T = 38^{\circ}$ C, shown in Figure S₃, when the change from the N_U to N_{TB} takes place are a super-position of spectra from both phases and it is difficult to determine precisely how *S*_{zz}(DTC5C9) is changing, whether continuously or with a small discontinuity. It is clear, however, that *S*_{zz}(DTC5C9) continues to decrease in the N_{TB} phase at a similar rate as in the N_U, and assuming a similar tilting of the phase director away from the magnetic field direction leads to the continued increasing of the values calculated for ϕ_B , reaching ~ 26° at ~ 73 ° C below T_{NI} as shown in Fig. 1<u>1</u>0. Just such a tilting of local directors is proposed to occur in the model for the N_{TB} phase proposed by Dozov [3<u>4</u>3], and to be a consequence of the formation of a helical arrangement of the **n**_i, with ϕ_{cone} being the cone angle, the angle between local directors and the helix axis, as sketched in figure 124. If the helix axis is aligned along the magnetic field in the N_{TB} phase, than the local directors will make an angle $\phi_B = \phi_{cone}$, which will be expected to increase with decreasing temperature.



Figure 124. The heliconical arrangement of local directors, \mathbf{n}_i , (red arrows) in the N_{TB} phase, as proposed by Dozov [343]. The local directors (red) make a constant angle, ϕ_{cone} with respect to the helix axis.

In this model the N_U to N_{TB} phase transition should be accompanied by a change in ϕ_B from zero to a finite value which should then increase with decreasing temperature. This behaviour is consistent with analysis of ²H and ¹²⁹Xe NMR spectra[354], and optical birefringence on CB7CB[365]. The temperature dependence of *S*_{zz}(DTC5C9) and hence of ϕ_B shown in Fig. 110 for the N_{TB} phase is consistent with that expected from the Dozov model in that the order parameter decreases with decreasing temperature and the bend angle increases, however the continuity of the temperature variation of both these parameters as the phase changes from N_U to N_{TB} suggests that the entangled, intercalated arrangements of near neighbours is also continuous across this phase change. The onset of phase chirality in the N_{TB} phase could simply be a consequence of the development of a coherent twist into a helical structure of these entangled molecules.

Conclusion

The chemical shift anisotropies of ¹³C nuclei which are located in difluoroterphenyl groups in DTC5C9 have been used to obtain the temperature dependence of an order parameter $S_{zz}(DTC5C9)$ for the *para* axis in this group. The values of $S_{zz}(DTC5C9)$ reach a maximum ~ 9 °C above the temperature of the transition to the chiral N_{TB}, and then decrease, passing through the N_U to N_{TB} transition with a ~ 2 ° decrease in value and then continue decreasing into the chiral phase. This unusual behaviour has been interpreted as evidence that in both phases the local directors are tilted relative to the applied magnetic field, and that this is a consequence of the bent shape of individual molecules leading to the local directors representing the orientational order of aggregates rather than individual molecules. It is proposed that the difference between the two phases is that the molecular aggregation in the N_{TB} phase leads to a helical structure which produces an enantiomorphic phase, whilst in the N_U phase the molecular aggregates are not chiral.

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Supporting Information Available.

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