

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Orientational ordering of a ferroelectric liquid crystal with high spontaneous polarization

C-D. Poon^a; B. M. Fung^a

^a Department of Chemistry, University of Oklahoma, Norman, Oklahoma, U.S.A.

To cite this Article Poon, C-D. and Fung, B. M.(1989) 'Orientational ordering of a ferroelectric liquid crystal with high spontaneous polarization', *Liquid Crystals*, 5: 4, 1159 – 1169

To link to this Article: DOI: 10.1080/02678298908026420

URL: <http://dx.doi.org/10.1080/02678298908026420>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Orientational ordering of a ferroelectric liquid crystal with high spontaneous polarization

by C.-D. POON and B. M. FUNG

Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73019, U.S.A.

The orientational ordering of the liquid crystal, 3M2CPHOB ((2*S*, 3*S*)-3-methyl-2-chloropentanoic acid-4',4''-hexyloxybiphenyl ester) in its smectic A and chiral smectic C phases has been studied by carbon-13 2D N.M.R. The technique used is separated local-field spectroscopy, which produces a first-order splitting for each carbon signal, from which carbon-proton dipolar constants can be determined. The order parameters for different molecular segments of the liquid crystal can then be calculated. The C-H bond order parameter at the chiral centre with a chlorine atom is unusually large, which is a strong indication of hindered rotation of the molecular segment at the chiral centre. The carbon-13 chemical shifts of 3M2CPHOB were also measured as a function of temperature, and the relation between the chemical shifts and the order parameters is discussed.

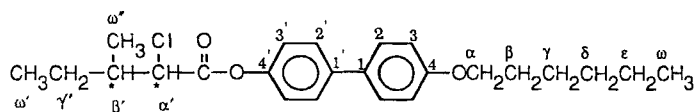
1. Introduction

Ferroelectric liquid crystals have attracted considerable attention since their discovery in 1975 by Meyer and co-workers [1]. These materials can undergo spontaneous polarization in an electric field so that the dipole moments of the molecules align along the same direction macroscopically. The properties of bistability and fast switching make these materials very promising in display and switching devices.

A new type of ferroelectric liquid crystal, prepared by esterification of 4-alkyloxy-4'-hydroxybiphenyls with optically active α -halocarboxylic acids, has been reported independently by two research groups recently [2-10]. These materials exhibit chiral smectic C (S_C^*) phases in a suitable temperature range and show extremely high spontaneous polarization P_s (exceeding $3 \times 10^{-7} \text{ C cm}^{-2}$) and dielectric constants (larger than 7000). The optically active α -chloro and α -bromocarboxylic acids are synthesized from the α -amino acids L-valine, L-leucine and L-isoleucine [2-5]. The liquid crystals made from the chloro derivative of L-isoleucine were found to have the highest spontaneous polarization.

Orientational ordering is one of the most important physical properties of a liquid crystal. We have developed a powerful technique which combines separated local-field spectroscopy (S.L.F., [11-14]) and variable-angle spinning (V.A.S., [15-20]) to study the orientational ordering of nematic liquid crystals by carbon-13 N.M.R. [21-25]. The behaviour of the smectic A (S_A) and smectic C (S_C) phases with rapid sample spinning in a magnetic field is more complicated [26]. In this work, we report the use of S.L.F. without sample spinning to study the orientational ordering of 3M2CPHOB ((2*S*, 3*S*)-3-methyl-2-chloropentanoic acid-4',4''-hexyloxybiphenyl ester). Similar investigations with rapid sample spinning are being conducted and the results will be

reported separately. The molecular formula of 3M2CPHOB is



To the best of our knowledge, there have been only three reports on the use of N.M.R. to study S_C^* liquid crystals [27–29]. Luzar, Rutar, Seliger and Blinc have investigated the carbon-13 N.M.R. of 4-*n*-decyloxybenzylidene-4'-amino-2-methylbutyl cinnamate (DOBAMBC) in its isotropic, S_A and S_C^* phases, and used the chemical-shift data to calculate the order parameters and the tilt angle [27, 28]. Wu and Doane studied the deuterium N.M.R. of a S_C mixture with a chiral dopant, and obtained the tilt angle [29]. Here we report for the first time the determination of order parameters of a ferroelectric liquid crystal from dipolar coupling constants.

2. Experimental

3M2CPHOB was synthesized by the esterification of 4-hexyloxy-4'-hydroxybiphenyl and (2*S*, 3*S*)-3-methyl-2-chloropentanoic acid according to the literature procedure using *N,N'*-dicyclohexylcarbodiimide as reagent and 4-pyrrolidinopyridine as catalyst [30]. The crude product was purified by passing it through a chromatographic column of silica gel and by recrystallization from hexane. The transition temperatures of the purified 3M2CPHOB are 47.5°C from solid to S_C^* , 51.8°C from S_C^* to S_A and 62.1°C from S_A to isotropic liquid, as determined from D.S.C. measurement by using a Perkin–Elmer D.S.C.-2 instrument. Its P_s value and tilt angle are comparable to those reported in the literature [5].

All carbon-13 N.M.R. spectra were obtained by using a Varian XL-300 spectrometer at $B_0 = 7.05$ T with a VXR-4000 data station and a variable-angle probe manufactured by Doty Scientific (Columbia, South Carolina). The sample rotor was allowed to be static and form an angle of about 90° with the magnetic field, so that the effective decoupling field (B_2) was the largest for a fixed input wattage. Since the Doty probe has a double-tuned solenoid coil for both observation and decoupling, the applied B_2 has a larger projection on the axis perpendicular to B_0 when the angle is closer to 90°. In principle, the experiment can also be performed with slow sample spinning along the B_0 axis to align the sample macroscopically. However, we should have to use a probe with saddle coils for this kind of geometry. For a fixed wattage, the B_2 field of saddle coils is usually much smaller than that of a solenoid, and it would be difficult to achieve complete proton–proton dipolar decoupling in the S.L.F. experiment. Therefore, probes with saddle coils were not used in our work. With a static sample in the Doty probe, the compound 3M2CPHOB was aligned macroscopically by slow cooling from the isotropic into the smectic A phase in the magnet. The cooling rate was about 2°C per hour. With an r.f. power of 22 W, $\gamma B_0/2\pi = 28$ kHz. Higher r.f. power was not used in order to avoid excessive r.f. heating. For the same reason, the experiments were carried out with a 0.5–1.0 per cent r.f. duty cycle (percentage on-time of the proton decoupler). The S.L.F. technique implemented with the BLEW-48 dipolar decoupling sequence [31], the setting of the 90° pulse width of the proton decoupler, and the method of data processing have been described in detail elsewhere [21–25].

3. Determination of order parameters from dipolar coupling constants

In the 2D S.L.F. technique, a proton-proton dipolar decoupling sequence is applied in the evolution period so that spectra in the ω_1 dimension show first-order carbon-proton splittings for individual carbons, while spectra in the ω_2 dimension show normal proton-decoupled carbon-13 peaks [11–14]. For 3M2CPHOB, macroscopic alignment of the molecules in the magnetic field results in resolvable peaks in the S_A and S_C^* phases in the ω_2 dimension. As an illustration, the spectra of this compound in its S_C^* phase are shown in figure 1. Although the peaks in the ω_2 dimension are reasonably well resolved, the resolution is not as good as that with fast sample spinning, and some of the signals of the carbon atoms in the aliphatic chains overlap with each other.

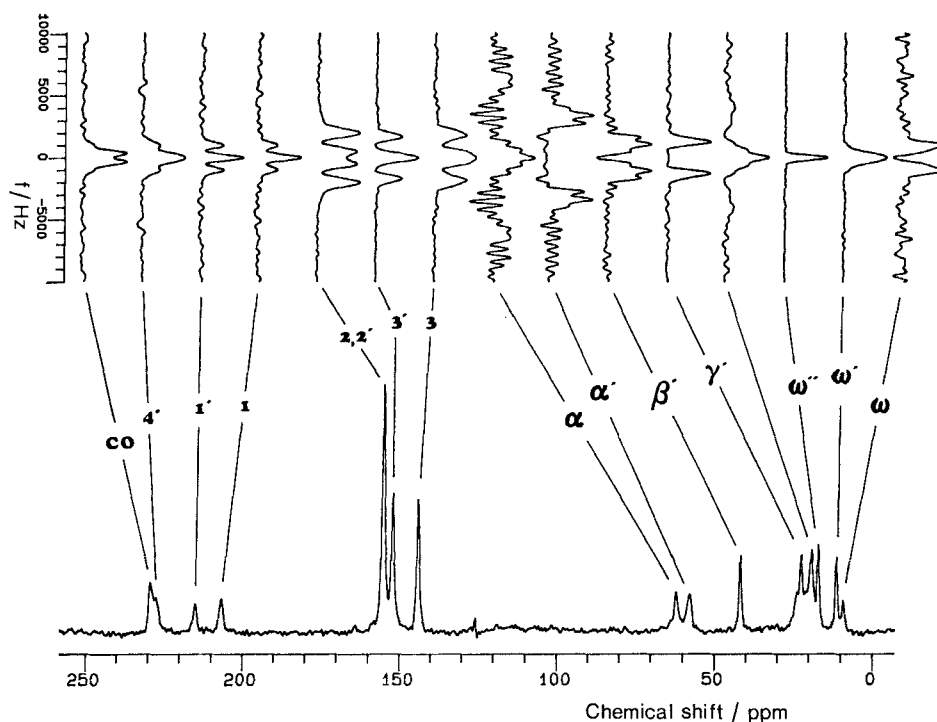


Figure 1. Carbon-13 S.L.F. spectra of a static sample of 3M2CPHOB in the S_C^* phase. The frequency was 75 MHz and the temperature was 12.6 K below the clearing point. Spectra in the ω_1 dimension are shown on the left and the first spectrum in the ω_2 dimension is shown on the right.

When a liquid crystalline material is cooled slowly from its isotropic or nematic phase to the smectic A phase in a magnetic field of sufficient strength, the director (the unit vector describing the average direction of the long molecular axis) orients parallel to B_0 . The behaviour is similar for most S_C compounds. For the compound DOBAMBC studied at 6.34 T, Luzar *et al.* showed that the ordering in the S_C^* phase is such that the helical axis, which is normal to the smectic layers, is parallel to B_0 [27, 28]. In contrast with DOBAMBC, we found that 3M2CPHOB at 7.05 T behaves like normal S_C compounds, and the director is oriented parallel to B_0 whereas the normals to the layers are tilted. This was determined by considering changes in the order parameters and chemical shifts during the phase transition from S_A to S_C^* , as discussed subsequently.

For liquid crystals with the director oriented along B_0 , the proton-carbon splitting in the ω_1 dimension in an S.L.F. experiment is related to the carbon-proton coupling constants by [21-25]

$$\Delta\nu = f(2D + J), \quad (1)$$

where f is a scaling factor for the particular dipolar decoupling sequence, D is the carbon-proton dipolar coupling constant, and J is the carbon-proton scalar coupling constant. In this work the efficient BLEW-48 proton-proton dipolar decoupling pulse sequence [31] is used, and it has a scaling factor of 0.420 [32]. Scalar coupling constants for carbon directly coupled with proton were obtained from proton-coupled carbon-13 spectra of 3M2CPHOB in CDCl_3 and heteronuclear two-dimensional J -resolved spectroscopy. J_{CH} values for two-bond couplings in the aromatic ring are assumed to be +1 Hz. In some cases the ω_1 spectra showed overlapping peaks (e.g. peaks 2, 2', 3, and 3' in figure 1); then they were deconvoluted by fitting each carbon spectrum to the sum of the appropriate number of gaussian functions to obtain $\Delta\nu$ [24, 25]. Once the values of $\Delta\nu$ and J for each C-H pair were determined, the C-H dipolar coupling constant D was readily calculated using equation (1), D_{CH} values at different temperatures for the phenyl rings and the resolvable aliphatic carbons are listed in table 1.

Table 1. D_{CH} values (kHz) of 3M2CPHOB at different temperatures; the experimental errors are about 10 per cent.

Carbon number	$(T_c - T)/\text{K}$						
	3.2	5.1	7.0	9.0	11.5	12.6	13.3
1	1.00	0.95	0.98	1.06	1.17	1.18	1.09
2, 2'	2.39 -1.56	2.42 -1.54	2.41 -1.48	2.49 -1.60	2.81 -1.76	2.86 -1.83	2.80 -1.74
3	2.12 -1.62	2.09 -1.54	2.09 -1.55	2.19 -1.62	2.53 -1.83	2.52 -1.81	2.43 -1.73
1'	1.01	0.96	1.00	1.06	1.23	1.20	1.22
3'	1.78 -1.59	1.65 -1.73	1.70 -1.59	1.86 -1.62	2.11 -1.78	2.16 -1.84	2.11 -1.80
α'	6.23	6.29	6.40	6.44	7.16	7.04	6.95
β'	1.95	2.04	2.03	2.12	2.42	2.45	2.55
γ'	2.38	2.57	2.52	2.46	2.89	2.90	2.98
ω	1.95	1.85	1.76	1.80	2.06	2.08	2.15

For the phenyl ring with the hexyloxy group, S_{zz} and $S_{xx} - S_{yy}$ are the order parameters required to describe the orientational ordering. Splittings by the directly bonded protons were observed for the protonated carbons and splittings by the *ortho* protons were observed for all carbon atoms. The situation for the other phenyl ring (with primes) is similar. The dipolar coupling constants are related to the H-C-C bond angles in the phenyl ring and the order parameters S_{zz} and $S_{xx} - S_{yy}$ by [33]

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

where r_{ij} is the internuclear separation and $\Theta_{ij\alpha}$ is the angle between r_{ij} and a molecular axis (α). In the calculation it was assumed that the benzene rings have hexagonal symmetry, $r_{\text{C-C}}$ is 0.140 nm, and $r_{\text{C-H}}$ is 0.108 nm. Furthermore, since the dipolar

coupling constants for C2 and C2' are not extremely accurate due to overlapping of their peaks (see figure 1), the bond angles were not used as variable parameters in the least squares calculations. Instead, the bond angles determined for the alkyloxycyanobiphenyls were used: H3-C3-C2 and H3'-C3'-C2' have the normal value of 120°, and H2-C2-C3 and H2'-C2'-C3' have the value of 119° because of steric hindrance [24]. The order parameters thus calculated are listed in table 2.

Table 2. Order parameters of 3M2CPHOB at different temperatures; the uncertainties are about 10 per cent

	$(T_c - T)/K$						
	3.2	5.1	7.0	9.0	11.5	12.6	13.3
For the phenyl ring with hexyloxy group							
S_{zz}	0.728	0.705	0.697	0.737	0.823	0.833	0.796
$S_{xx} - S_{yy}$	0.014	0.005	0.002	0.008	0.002	0.004	-0.001
For the phenyl ring with carboxylate group							
S'_{zz}	0.726	0.753	0.710	0.743	0.819	0.846	0.817
$S'_{xx} - S'_{yy}$	0.031	0.047	0.029	0.028	0.024	0.030	0.024
For the aliphatic carbons							
S_{CH}							
α'	-0.275	-0.277	-0.282	-0.283	-0.316	-0.310	-0.306
β'	-0.086	-0.090	-0.089	-0.094	-0.107	-0.108	-0.113
γ'	-0.105	-0.113	-0.111	-0.108	-0.127	-0.128	-0.132
ω	-0.086	-0.082	-0.078	-0.079	-0.091	-0.092	-0.095

For the flexible aliphatic chain, the order parameter of the C-H bond in individual C-H segments is considered. It is calculated from

$$\begin{aligned}
 S_{CH} &= - \frac{4\pi^2 r^3 D_{CH}}{\gamma_C \gamma_H h} \\
 &= -4.407 \times 10^{-5} D_{CH}/\text{Hz},
 \end{aligned}
 \tag{3}$$

in which $r = 0.110$ nm was used. Table 2 includes the order parameters at different temperatures for the aliphatic chain segments that showed resolvable peaks.

On going from the S_A to the S_C^* phase, it is expected that there should be an increase in the order parameters. This behaviour has been observed in achiral S_C systems in which the director is oriented parallel to the external field and the layer normals are tilted. However, for the chiral compound DOBAMBC, it was found that the director forms a tilt angle with respect to the external field, and the layer normals are parallel to the field [27, 28]. In our experiment the core order parameters of 3M2CPHOB do show an abrupt increase at the transition from S_A to S_C^* , and the values of S_{zz} and S'_{zz} are about 0.82 in the S_C^* phase (see table 2). If the layer normal were oriented parallel to the magnetic field and the tilt angle were ϕ then the order parameter of the director would be close to $2S_{zz}/(3\cos^2\phi - 1)$, since the z axis of the phenyl ring is expected to be very close to the long molecular axis. The tilt angle for 3M2CPHOB at the lowest temperature that we studied is about 22° [5]. This would yield an order parameter of about 1.04 for the director, which is unlikely. We therefore conclude that in the S_C^* phase the director of 3M2CPHOB is oriented parallel to the magnetic field whereas the normals of the layers are tilted, a situation similar to that of achiral S_C compounds rather than DOBAMBC. On the other hand,

we have found that homologous compounds of 3M2CPHOB with longer side chains (C_7H_{15} and C_8H_{17} instead of C_6H_{13}) and several S_C^* thioesters containing a $C_{10}H_{21}$ side chain behave like DOBAMBC rather than being like 3M2CPHOB [26]. In other words, for most S_C^* compounds studied, the helices do not unwind at $B_0 \leq 7$ T, and the layer normals align parallel to the magnetic field. Apparently 3M2CPHOB is an exception because of its short C_6H_{13} side chain.

The data in table 2 show that for each phase the values of S_{zz} and S'_{zz} are the same within experimental error, indicating that the C_2 axes of the two phenyl rings are collinear, which is not surprising. The average value is 0.72 in the S_A phase and 0.82 in the S_C^* phase, which are considerably higher than those of the cyanobiphenyls [22–24, 33, 34] in a similar temperature range below the clearing point. The data in table 2 also indicate that $S_{xx} - S_{yy}$ and $S'_{xx} - S'_{yy}$ are close to zero, making the biphenyl core essentially uniaxial. This is in contrast with the situation of the cyanobiphenyls, which have somewhat larger values of $S_{xx} - S_{yy}$ and $S'_{xx} - S'_{yy}$ [22–24, 34, 35].

In comparison with the V.A.S. experiments [21–25], the static sample used in the present work gave lower spectral resolution in the ω_2 dimension and more peak broadening due to unresolved long-range coupling in the ω_1 dimension. Therefore only a few order parameters for the aliphatic chains could be determined (see table 2). The D_{CH} values are negative because on the average the C–H axis is more or less normal to the director. The values for the ω methyl group are almost twice that of 6OCB (-0.050 at 10 K below the clearing point, [24, 35]), indicating that the hexyloxy chain, similarly to the biphenyl core, is more ordered in 3M2CPHOB than that in 6OCB.

The situation of the ester chain is quite interesting. Both the ω' and the ω'' methyl groups did not show any appreciable C–H dipolar splittings (see figure 1). On the other hand, the splittings for the CH and the CH_2 carbons were resolvable (see figure 1), and the corresponding D_{CH} values could be determined (see table 2). Considering that the optimal negative value for the order parameters is -0.5 , the C–H bond order parameter for the α' carbon is quite large. In fact, it is much larger than those for any aliphatic segment in all the nematic liquid crystals reported as far. Furthermore, the sudden decrease in the bond order parameter from the α' to the β' carbon (by a factor of three) is rather unusual, and has only been observed for some of the liquid crystals containing alkenyl chains [25]. This may indicate that the rotation of the α' C–H group, which is at one of the chiral centres and next to the polar carboxy group, could be rather restricted, which may be the cause [3] of the unusually large spontaneous polarization for 3M2CPHOB and its analogues [2–10]. It is also interesting to note that the γ' carbon shows only a doublet (see figure 1), even though it has two directly bonded protons. This is because the neighbouring chiral centre at the β' position makes the two protons inequivalent, and one of the C–H splittings is too small to be resolved.

In addition to splittings by the directly bonded protons splittings of the carboxy carbon by the α' proton and splittings of the α' carbon by the β' proton were also observed (see figure 1). The corresponding D_{CH} values are about 0.80 and 0.49 kHz in the S_A phase, and about 0.90 kHz and 0.66 kHz in the S_C^* phase respectively. These unusually large vicinal C–H couplings may also be due to the presence of restricted rotations at the chiral centres.

Finally, the data in table 2 show that there seem to be no obvious changes in the order parameters with respect to temperature within each phase. However, they may actually increase slightly when the temperature is decreased, as discussed in the next

section. The reason that these changes were not observed in the S.L.F. experiments is due to limitations on the experimental accuracy, especially for the static sample used in the present work.

4. Relation between chemical shifts and order parameters

Because of limited available spectrometer time, our carbon-13 2D N.M.R. study was restricted to a few temperatures. Fortunately, the measurement of 1D spectra is much less time-consuming, and a larger number of 1D spectra were recorded in order to study the chemical shifts as function of temperature. Results for the carbon-13 chemical shifts of the resolvable peaks of 3M2CPHOB in the isotropic, smectic A and chiral smectic C phases are plotted in figure 2.

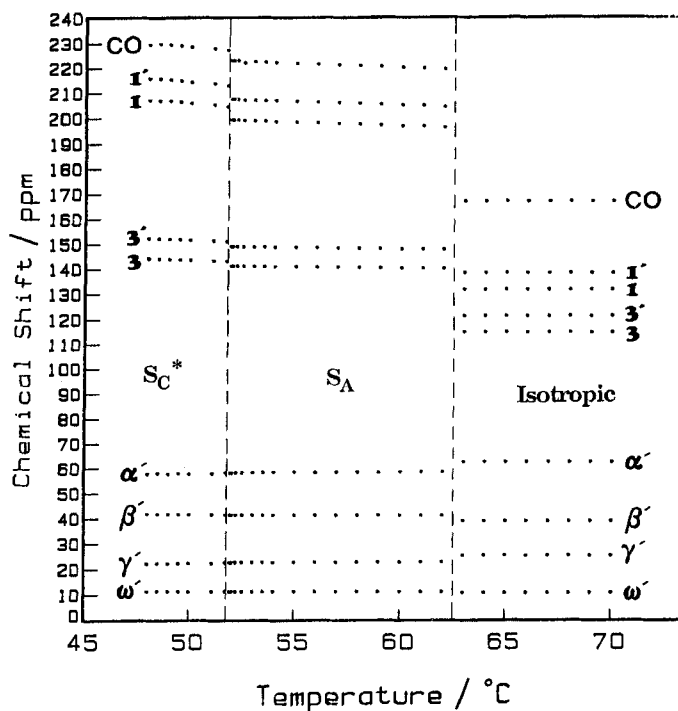


Figure 2. Carbon-13 chemical shifts of 3M2CPHOB at 75 MHz as a function of temperature.

For DOBAMBC, the carbon-13 chemical shifts of the aromatic carbons increase when the phase changes from isotropic to S_A , but decrease when the phase changes from S_A to S_C^* , because the director is oriented parallel to B_0 in the S_A phase but tilted with respect to B_0 in the S_C phase [26, 27]. For 3M2CPHOB, abrupt increases were observed for the phase transitions from isotropic to S_A as well as from S_A to S_C (see figure 2), because in both smectic phases the director is oriented along B_0 .

The chemical shift σ in a macroscopically ordered liquid-crystalline phase is related to the isotropic chemical shift σ_i , the components of the chemical shift tensor σ_{jk} , and the order parameters S_{jk} by [31]

$$\begin{aligned} \sigma = & \sigma_i + \frac{2}{3}S_{aa}\{\sigma_{aa} - \frac{1}{2}(\sigma_{bb} + \sigma_{cc})\} + \frac{1}{3}(S_{bb} - S_{cc})(\sigma_{bb} - \sigma_{cc}) \\ & + \frac{2}{3}S_{ab}\sigma_{ab} + \frac{2}{3}S_{ac}\sigma_{ac} + \frac{2}{3}S_{bc}\sigma_{bc}, \end{aligned} \quad (4)$$

where a , b and c are orthogonal axes set in the molecule. Using equation (4), it is possible to calculate components of the chemical-shift tensor by measuring the anisotropic chemical shifts and order parameters in the molecular axes system [32, 36–39]. On the other hand, if we wish to determine the order parameters from the chemical shifts of an oriented liquid crystal, precise values of the chemical-shift tensor and the angles between the principal axes of the tensor and the molecular axes must be known. However, both sets of data are difficult to measure, and calculations of order parameters from chemical shifts alone [17, 26, 27] may not be accurate. The assumption that carbon-13 chemical-shift tensors can be ‘transferred from one compound to another’ is often invalid because each component of the chemical-shift tensors of benzene derivatives can have very large variations, sometimes as much as 100 ppm [38, 40]. Therefore, even though the order parameter S of the benzene rings of DOBAMBC obtained by Luzar *et al.* [26] is quite reasonable and close to the values of S_{zz} for 3M2CPHOB obtained from dipolar coupling constants (see table 2), the calculation of the tilt angle as a function of temperature based upon the estimated values of chemical-shift tensors is not justified.

Although the order parameters cannot be calculated from carbon-13 chemical shifts without precise knowledge of the chemical-shift tensors, their *changes* as a function of temperature can be related to the corresponding changes in chemical shifts by the following reasons. For substituted benzenes, the direction of the least shielded component of the chemical-shift tensor often nearly coincides with the C–H or C–X bond axis [40–42]. Therefore the a , b and c axes in equation (4) can be substituted by the z , x and y axes respectively without appreciable error. Because of rapid motions, S_{xy} , S_{xz} and S_{yz} are zero for the phenyl rings in 3M2CPHOB. The experimental data show that $S_{xx} - S_{yy}$ is much smaller than S_{zz} (see table 2). Therefore equation (4) is reduced to

$$\sigma = \sigma_i + \frac{2}{3}S(\sigma_{\parallel} - \sigma_{\perp}), \quad (5)$$

where $\sigma_{\parallel} = \sigma_{zz}$ is the chemical-shift component along the direction of the long molecular axis and $\sigma_{\perp} = \frac{1}{2}(\sigma_{xx} + \sigma_{yy})$ is the average of the components of the chemical-shift tensor in the xy plane. In other words, $\sigma - \sigma_i$ for the quaternary carbons in the benzene rings should be proportional to S_{zz} . The situation for the aliphatic carbons is less simple, because we can only determine S_{CH} along the C–H axis, which does not coincide with any principle axis of the chemical-shift tensor. However, the chemical-shift anisotropy of aliphatic carbons is usually quite small [40–42]. If we further assume that all of the order parameters for each molecular segment in the flexible aliphatic chain have the same temperature dependence, we can expect S_{CH} to be a linear function of $\sigma - \sigma_i$. Therefore the *relative* change in the order parameters as a function of temperature may be derived from the corresponding change in the chemical-shift differences, $\sigma - \sigma_i$.

Using this approach, the order parameters S_{zz} of the two phenyl rings and S_{CH} for three of the resolvable aliphatic carbon peaks were calculated as functions of temperature, and the results are presented in figure 3. The circles and diamonds in the figure are data obtained directly from the dipolar coupling constants (see table 2). The dots are indirect values obtained from chemical-shift data by scaling the values of $\sigma - \sigma_i$ to correspond to the medium values of these directly determined order parameters. For the phenyl rings, the chemical shifts of the 1 and 1' carbons were used because the z axis coincides with the C–C bond axis. However, when the chemical-shift data for the 3 and 3' carbons were used in the indirect

calculation of S_{zz} and S'_{zz} , values virtually identical with those represented by the dots in figure 3 were obtained. These indirectly determined order parameters change with temperature more smoothly than the direct values, because the chemical shifts can be measured more accurately than the dipolar coupling constants.

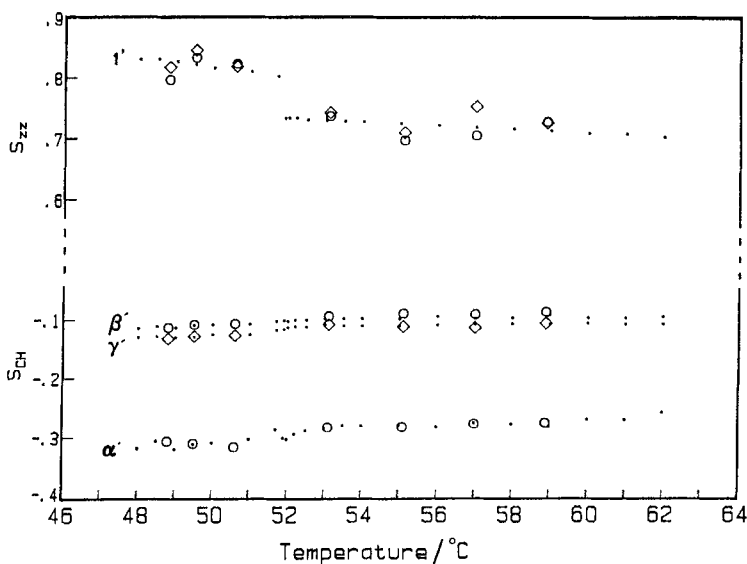


Figure 3. Order parameters of 3M2CPHOB from the S.L.F. results and chemical shift data. The circles and diamonds are data obtained from the S.L.F. results. The dots are indirect values obtained from chemical-shift data.

The results in figure 3 show that for each phase there is a steady and slow increase in the absolute values of the order parameters as the temperature decreases. The values of S_{CH} for the aliphatic carbons are negative because on average the C-H bonds are more or less orthogonal to the long axis of the molecule. At the phase changes from S_A to S_C^* , there is a discontinuity in the order parameters, with the S_C^* phase being more ordered. The percentage changes in the order parameters are about the same for the phenyl rings and for the side chain that contains the chiral centres. This indicates that there is no additional reduction in the chain motion relative to the motions of the mesogenic core when 3M2CPHOB changes from S_A to S_C^* . The carbon-13 peaks in the hexyloxy chain are not sufficiently resolved to offer accurate information.

5. Summary

The orientational ordering of the ferroelectric liquid crystal 3M2CPHOB, which has a very large spontaneous polarization, has been studied by 1D and 2D carbon-13 N.M.R. The results indicate that the director is oriented parallel to B_0 in both the S_A and the S_C^* phases, and there is an abrupt increase in the order parameters of all parts of the molecule at the phase transition. The large P_s of the compound is probably related to the restricted rotation of the molecular segments near the chiral centres. However, we must caution that the H-H dipolar couplings for a static liquid crystal sample are quite large, and the decoupling power used in our experiment (28 kHz)

may not be sufficient for complete H-H dipolar decoupling. Higher decoupler power would cause undesirable RF heating. Therefore, the results may be less accurate than those obtained with rapid off-magic-angle sample spinning [20-25]. Investigations on 3M2CPHOB, its homologous compounds and other S_6^* liquid crystals with rapid sample spinning are in progress.

This material is based upon work supported by the National Science Foundation under Grant No. CHE 8704223. The authors acknowledge Dr W. Tang at the IBM Almaden Research Center for measuring P_s and the tilt angle of 3M2CPHOB.

References

- [1] MEYER, R. B., LIEBERT, L., STRZELECKI, L., and KELLER, P., 1975, *J. Phys. Lett. Paris*, **36**, 69.
- [2] SAKURAI, T., MIKAMI, N., HIGUCHI, R., HONMA, M., OZAKI, M., and YOSHINO, K., 1986, *J. chem. Soc. Chem. Commun.*, p. 978.
- [3] YOSHINO, K., OZAKI, M., KISHIO, S., SAKURAI, T., MIKAMI, N., HIGUCHI, R., and HONMA, M., 1987, *Molec. Crystals liq. Crystals*, **144**, 87.
- [4] BAHR, CH., and HEPPKE, G., 1986, *Molec. Crystals liq. Crystals Lett.*, **4**, 31.
- [5] BAHR, CH., and HEPPKE, G., 1987, *Molec. Crystals liq. Crystals*, **148**, 29.
- [6] BAHR, CH., and HEPPKE, G., 1987, *Molec. Crystals liq. Crystals*, **150b**, 313.
- [7] BAHR, CH., and HEPPKE, G., 1987, *Molec. Crystals liq. Crystals*, **151**, 69.
- [8] BAHR, CH., and HEPPKE, G., 1987, *Liq. Crystals*, **2**, 825.
- [9] BAHR, CH., and HEPPKE, G., and SHARMA, N. K., 1987, *Ferroelectrics*, **76**, 151.
- [10] BAHR, CH., and HEPPKE, G., 1987, *Ber. Bunsenges. phys. Chem.*, **91**, 925.
- [11] WAUGH, J. S., 1976, *Proc. natn. Acad. Sci. U.S.A.*, **73**, 1394.
- [12] HESTER, R. K., ACKERMAN, J. L., NEFF, B. L., and WAUGH, J. S., 1976, *Phys. Rev. Lett.*, **36**, 1081.
- [13] WAUGH, J. S., and OPELLA, S., 1977, *J. chem. Phys.*, **66**, 4919.
- [14] RYBACZEWSKI, E. F., NEFF, B. L., WAUGH, J. S., and SHERFINSKI, J. S., 1977, *J. chem. Phys.*, **67**, 1231.
- [15] CORTIEU, J., ALDERMAN, D. W., and GRANT, D. M., 1981, *J. Am. chem. Soc.*, **103**, 6784.
- [16] CORTIEU, J., ALDERMAN, D. W., GRANT, D. M., and BAYLES, J. P., 1982, *J. chem. Phys.*, **77**, 723.
- [17] TEEÄÄR, R., ALLA, M., and LIPPMAA, E., 1982, *Org. magn. Reson.*, **19**, 134.
- [18] HEESCHEN, W. A., ALDERMAN, D. W., and GRANT, D. M., 1984, *J. magn. Reson.*, **58**, 318.
- [19] BAYLES, J. P., KHANDAR-SHAHABAD, A., and CORTIEU, J., 1986, *Liq. Crystals*, **1**, 189.
- [20] FUNG, B. M., and GANGODA, M., 1985, *J. chem. Phys.*, **83**, 3285.
- [21] FUNG, B. M., and AFZAL, J., 1986, *J. Am. chem. Soc.*, **108**, 1107.
- [22] FUNG, B. M., AFZAL, J., FOSS, T. L., and CHAU, M. H., 1986, *J. chem. Phys.*, **85**, 4808.
- [23] FUNG, B. M., POON, C.-D., GANGODA, M., ENWALL, E. L., DIEP, T. A., and BUI, C. D., 1986, *Molec. Crystals liq. Crystals*, **141**, 267.
- [24] POON, C.-D., WOOLDRIDGE, C. M., and FUNG, B. M., 1988, *Molec. Crystals liq. Crystals*, **157**, 303.
- [25] FRECH, C. B., and FUNG, B. M., 1988, *Liq. Crystals*, **3**, 713.
- [26] POON, C.-D., REIMER, D., and FUNG, B. M. (to be published).
- [27] LUZAR, M., RUTAR, V., SELIGER, J., and BLINC, R., 1984, *Ferroelectrics*, **58**, 115.
- [28] BLINC, R., DOLINSEK, J., LUZAR, M., and SELIGER, J., 1988, *Liq. Crystals*, **3**, 663.
- [29] WU, B.-G., and DOANE, J. W., 1987, *J. magn. Reson.*, **75**, 39.
- [30] HASSNER, A., and ALEXANIAN, V., 1978, *Tetrahedron Lett.*, 4475.
- [31] BURUM, D. P., LINDER, N., and ERNST, R. R., 1981, *J. magn. Reson.*, **44**, 173.
- [32] FUNG, B. M., 1986, *J. magn. Reson.*, **66**, 525.
- [33] EMSLEY, J. W., and LINDON, L. C., 1975, *NMR Spectroscopy Using Liquid Crystal Solvents* (Pergamon).
- [34] EMSLEY, J. W., LUCKHURST, G. R., and STOCKLEY, C. P., 1981, *Molec. Phys.*, **44**, 565.

- [35] EMSLEY, J. W., LUCKHURST, G. R., PARSONS, P. J., and TIMIMI, B. A., 1985, *Molec. Phys.*, **56**, 767.
- [36] APPLEMAN, B. R., and DAILY, B. P., 1974, *Advances in Magnetic Resonance*, Vol. 7, edited by J. S. Waugh (Academic Press), p. 231.
- [37] FUNG, B. M., 1983, *J. Am. chem. Soc.*, **105**, 5713.
- [38] FUNG, B. M., and KONG, C. F., 1984, *J. Am. chem. Soc.*, **106**, 6193.
- [39] PARHAMI, P., and FUNG, B. M., 1985, *J. Am. chem. Soc.*, **107**, 7304.
- [40] VEEMAN, W. S., 1984, *Prog. NMR Spectrosc.*, **16**, 193.
- [41] TORMAN, J. VAN D., and VEEMAN, W. S., 1978, *J. chem. Phys.*, **68**, 3233.
- [42] MARICQ, M. M., and WAUGH, J. S., 1979, *J. chem. Phys.*, **70**, 3300.
- [43] BAX, A., SZEVEHENYI, N. M., and MACIEL, G. E., 1983, *J. magn. Reson.*, **55**, 494.