Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Orientational ordering of ferroelectric thiobenzoate liquid crystals

Wolfgang Richter[a]; Dirk Reimer[a]; B. M. Fung[a]; R. J. Twieg[b]; K. Betterton[b]
[a] Department of Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma, U.S.A. [b] IBM Almaden Research Center, San Jose, California, U.S.A.

To cite this Article Richter, Wolfgang , Reimer, Dirk , Fung, B. M. , Twieg, R. J. and Betterton, K.(1990) 'Orientational ordering of ferroelectric thiobenzoate liquid crystals', Liquid Crystals, 8: 5, 687 — 699

To link to this Article: DOI: 10.1080/02678299008047380

URL: http://dx.doi.org/10.1080/02678299008047380

LIQUID CRYSTALS, 1990, VOL. 8, NO. 5, 687–699

Orientational ordering of ferroelectric thiobenzoate liquid crystals

by WOLFGANG RICHTER†, DIRK REIMER and B. M. FUNG
University of Oklahoma, Department of Chemistry and Biochemistry, Norman, Oklahoma 73019, U.S.A.

R. J. TWIEG and K. BETTERTON
IBM Almaden Research Center, San Jose, California 95120-6099, U.S.A.

(*Received 9 February 1990; accepted 9 May 1990*)

The orientational ordering of a series of ferroelectric thiobenzoate liquid crystals was studied by natural abundance ^{13}C NMR spectroscopy. The technique used was a combination of variable angle spinning (VAS) and separated local field spectroscopy (SLF). With rapid sample spinning about an axis forming an angle of *c.* 45° with respect to the magnetic field, the smectic director aligns parallel to the spinning axis, leading to narrow peaks in the ^{13}C NMR spectrum. The two-dimensional NMR spectroscopic method SLF allows the observation of decoupled ^{13}C signals in the $\omega 2$ dimension and first-order C–H splitting patterns in the $\omega 1$ dimension, from which the dipolar C–H coupling constants for individual bonds can be obtained. The order parameters for different molecular segments of eight different compounds, all containing two phenyl rings linked by a thioester group, were obtained this way. A considerable influence of length, branching and chirality of the aliphatic chain on the order parameters was observed.

1. Introduction

The most prominent feature of liquid-crystalline phases is the orientational ordering of molecules in the absence of long-range three-dimensional positional order. This leads to remarkable electrical and optical properties that make liquid-crystalline materials suitable for numerous applications. For the design of new liquid crystals it is desirable to establish correlations between molecular structure and physical properties.

The orientational ordering of the molecules in liquid crystals is quantified by a spatial distribution of the molecular orientations around a unique axis which is called the director. The distribution function can be simplified by considering the symmetry elements of the phase. An expansion of the director on to the axes of the molecular coordinate system could lead to an infinite number of order parameters. The lowest-order terms of this expansion are described by a second-rank tensor called the ordering matrix [1], the elements of which can be determined experimentally.

Several methods have been developed to measure the orientational ordering in liquid-crystalline phases. Among those are IR spectroscopy, Raman spectroscopy, NMR spectroscopy, X-ray diffraction, and dielectric relaxation. NMR spectroscopy has the advantage over the other methods that different parts of the molecule can be observed separately. In the past, proton and deuterium magnetic resonance spectroscopy have been applied almost exclusively [2,3], but the resolution in ^{1}H NMR spectroscopy is rather poor, and the use of ^{2}H NMR spectroscopy involves a considerable amount of synthetic effort due to the low natural abundance of ^{2}H for special isotope substitution.

---

† Exchange student from Technische Universität Berlin.

Recently a method involving ^{13}C natural abundance NMR spectroscopy has been developed in our group [4–13]. The essence of this technique is a combination of the two-dimensional NMR method of separated local field spectroscopy (SLF) [14–17] and variable angle spinning (VAS) [18–23]. The orientational ordering of several classes of nematic and smectic liquid crystals has been investigated by the SLF/VAS technique, including 4-*n*-alkyl-4′-cyanobiphenyls (kCBs) [5, 6, 8], their alkoxy analogues (kOCBs) [7], a series of 1-(4′-cyanophenyl)-*trans*-4-alkylcyclohexanes and 1-(4′-cyanophenyl)-*trans*-4-alkenylcyclohexanes [9, 10], their bicyclohexyl analogues [13], and ferroelectric liquid crystals [11, 12].

The materials studied in this work contain two phenyl rings bridged by a thioester group [24, 25], which are of special interest because they exhibit a chiral smectic C (S_C^*) phase and therefore ferroelectricity [26]. These thioesters have fairly large spontaneous polarization (P_s), in the order of about 100 nC/cm^2 [25]. The importance of ferroelectric liquid crystals for fast switching displays has been well established. In our previous study on the orientational ordering of 4-alkyl-4′-hydroxybiphenyl esters of α-chlorocarboxylic acids, it was found that the order parameter of the C–H bond at the chiral centre containing the chlorine atom has unusually large negative values, which may be an indication of hindered rotation at the chiral centre. Since the motional-averaged lateral dipole moment in the S_C^* phase is responsible for the spontaneous polarization of ferroelectric liquid crystals, the correlation between restricted rotation and P_s is important in understanding factors contributing to the ferroelectricity of S_C^* liquid crystals. In this paper we present the results of the orientational ordering of a class of ferroelectric liquid crystals containing a thioester linkage and compare them with those containing a biphenyl core [11, 12].

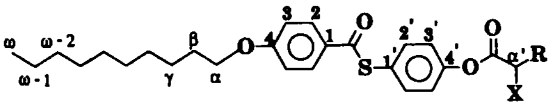
2. Experimental and data treatment

The liquid crystal materials were synthesized at the IBM Almaden Research Center, San Jose, California [25]. These compounds were chosen for study since they possess reasonably broad and stable ferroelectric phases at accessible temperature and smectic A (S_A) phases for alignment. Their structural formulae and transition temperatures are given in table 1. The configuration at atom α′ is S for the optically pure compounds. Two of the racemic mixtures were also investigated in this work; that of compound **2** (R and S) is designated as **2M**, and that of compound **3** (RR, SS, RS and SR) is designated as **3M**. **2M** was prepared by mixing equal quantities of **2**(S) and **2**(R), and **3M** was prepared from the racemic chloroester obtained by diazotitation of DL-isoleucine (FLUKA, perum) in the presence of HCl [27, 28].

All ^{13}C NMR spectra were obtained using a Varian XL-300 spectrometer with a VXR data system and a variable angle probe manufactured by Doty Scientific. We used a single window version [5] of the SLF pulse sequence with a ^{13}C spin echo and the BLEW-48 proton–proton dipolar decoupling sequence [29] in the evolution period.

Details of experimental procedure and data processing have been described previously [5, 9, 12], except for the calibration of the angle β between the spinning axis and the magnetic induction, $\mathbf{B}_0$. In this paper we measure the ^{19}F splitting of a sample of 10 per cent CF_2Cl–CCl_3 in the liquid-crystalline solvent ZLI 1291 [13]. The ratio between the splittings of a spinning sample and a non-spinning sample gives the value of $(3\cos^2\beta - 1)/2$ for $\beta < 54{\cdot}74°$.

Table 1. Structure and phase transition temperatures (°C) of the compounds under investigation. The transition temperatures of the racemic mixture **2M** are the same as **2**, and those of the diastereomeric mixture **3M** are about 3° lower than those of **3**.



	R	X	Transition temperatures								
1	$-CH_3$	Cl	K	85	S_A	98	I				
2	$-CH(CH_3)_2$	Cl	K	72	S_C^*	75	S_A	84	I		
3	$-CH(CH_3)CH_2CH_3$	Cl	K	55	S_C^*	66	S_A	74	I		
4	$-CH_2CH(CH_3)_2$	Cl	K	58	S_C^*	63	S_A	71	I		
5	$-CH_2CH_3$	Cl	K	68	S_C^*	78	S_A	92	I		
6	$-CH_2CH_3$	CH_3	K	60	S_C^*	73	S_A	74	N	76	I
7	$-CH_2CH_2CH_3$	Cl	K	61	S_C^*	71	S_A	81	I		
8	$-CH_2CH_2CH_2CH_3$	Cl	K	55	S_C^*	68	S_A	80	I		

3. Spectral analysis

3.1. *General*

The SLF/VAS method allows the measurement of individual C–H splittings in nematic and smectic liquid-crystalline phases. For nematic and certain smectic liquid crystals with a positive anisotropy of the magnetic susceptibility ($\Delta\chi > 0$), as it is the case here, the director of a static sample aligns along $\mathbf{B}_0$. When the sample is spun rapidly about an axis forming an angle β with respect to $\mathbf{B}_0$, the director would align along the spinning axis provided that the spinning torque is large enough to overcome the magnetic torque and β is less then the magic angle (54·74°) [18–20]. Then, the dipolar coupling constants are reduced by a factor of $(3\cos^2\beta - 1)/2$, and the ^{13}C NMR peaks are much sharper than those of static samples.

To align the smectic samples in a VAS experiment, we found that the following procedure is most effective [12]. The sample is first heated up to the isotropic phase. Then, it is cooled rapidly to the S_A phase while the sample is being spun at a moderate speed (200–300 Hz). After about 30 min, the spinning rate is increased to about 1 kHz. Good macroscopic alignment can then be obtained, as indicated by sharp peaks in the ^{13}C spectrum. It is possible that the slow spinning allows the smectic director to align well along $\mathbf{B}_0$, and the fast spinning tilts the director to make it align along the spinning axis [18–20]. Depending on the length of the pitch and the strength of the magnetic field, the helical structure of the S_C^* phase may be preserved or unwound in the field [12]. For the thioesters studied in this work, we found that slow cooling of aligned smectic A samples to the S_C^* phase would keep the alignment of the directors along the spinning axis. In other words, the helices unwind in a magnetic field of 7·05 T. If the helical structure were preserved, the ^{13}C spectra would show a partial powder pattern rather than sharp peaks [12].

In the SLF method, ^{1}H–^{1}H dipolar decoupling is applied during the evolution period to afford first-order C–H couplings, and broadband decoupling is applied during the acquisition period. Thus, the result of the SLF/VAS experiment is spectra with sharp, broadband decoupled ^{13}C signals in the $\omega2$ dimension, and a set of ^{13}C–^{1}H coupled spectra in the $\omega1$ dimension. As an example, the SLF/VAS spectra of **7** is

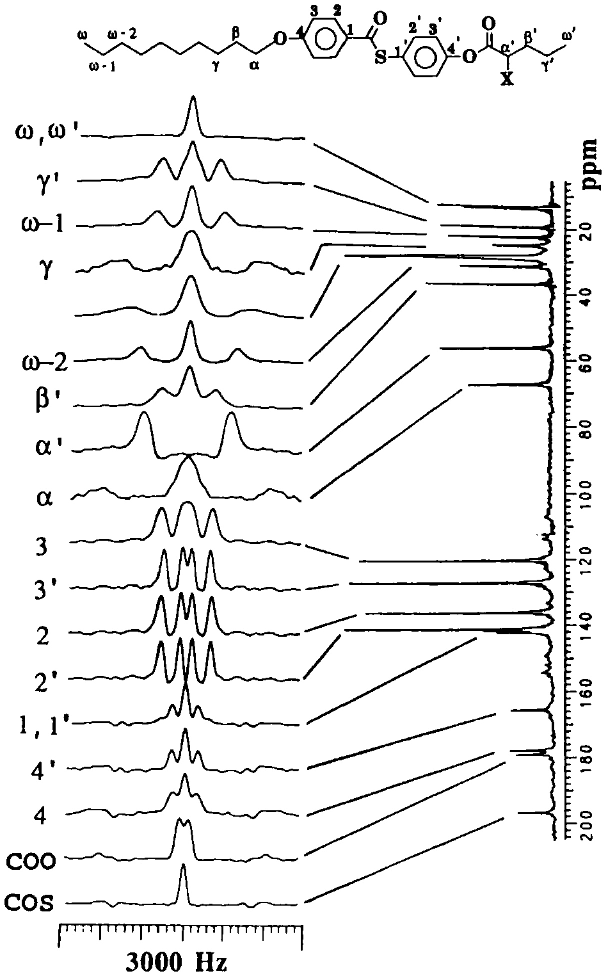


Figure 1. Carbon-13 NMR spectra of 7 at 75·4 MHz and 78°C. The spectra were obtained using the VAS/SLF method as described in the text. The angle β was 46·6°, and the spinning rate was 1·0 kHz. The first spectrum in the ω_2 dimension is displayed on the right-hand side, and shows proton-decoupled ^{13}C peaks. Spectra in the ω_1 dimension are displayed on the left-hand side, and show first-order C–H splittings.

shown in figure 1. Spectra of other compounds studied in this work and the chemical shifts of the peaks are given elsewhere [30, 31]. The peaks were assigned by using 2D-INADEQUATE experiments [32] of isotropic solutions.

In the $\omega 2$ dimension, the splitting of a multiplet is given by [5–7]

$$\Delta\nu = f[(3\cos^2\beta - 1)D + J], \qquad (1)$$

where f is a scaling factor for the dipolar decoupling sequence, D is the C–H dipolar coupling constant, and J is the C–H scalar coupling constant. It was shown that the scaling factor for BLEW-48 is 0·42 [33], which is an empirical value only slightly different from the theoretical value of 0·424 [29]. Due to imperfection in the BLEW-48 sequence, complete proton–proton dipolar decoupling could not be achieved. This is the major contribution to the experimental error; it has been discussed recently [13] and will not be repeated here. Scalar coupling constants have been obtained from measurements in isotropic solution and the literature [34], and it is assumed that anisotropic contributions to J and their temperature dependence are negligible. This is entirely justified because the values of J are from 120 to 170 Hz, and the observed splittings are in the kHz range.

3.2. *Aromatic carbon atoms*

Each signal of the protonated aromatic carbon atoms appears as a doublet of doublets due to splittings by the *ipso* and the *ortho* protons (figure 1, carbons 2, 2′, 3, and 3′; the splittings are not completely resolved for carbon 3). For the quaternary carbons, the signals appear as triplets due to splittings by the two *ortho* protons (figure 1, carbons 1, 1′, 4, and 4′). These ortho protons are magnetically equivalent because the phenyl rings undergo rapid jumps between four equilibrium positions [35, 36]. Since the components of all the multiplets overlap to various extents, the observed signals were fitted to the sum of the appropriate number of gaussian functions, using the non-linear least squares program called SPIRAL [37]. It is a very powerful algorithm; the standard errors in the calculated splittings are usually less than 0·5 per cent and do not contribute significantly to the resulting dipolar coupling constants, which are compiled in tables 2 and 3. Since the signals for C_1 and $C_{1'}$ could not be clearly resolved, their dipolar coupling constants are taken to be the same.

Table 2. Dipolar coupling constants (kHz) for the non-primed ring. The experimental uncertainty is about 5 per cent.

Compound	Phase	T/T_C	C_1–H_2	C_2–H_2	C_2–H_3	C_3–H_3	C_3–H_2	C_4–H_3
1	S_A	0·99	1·0	2·1	−1·6	2·0	−1·5	1·0
2	S_A	0·98	0·83	1·7	−1·3	1·6	−1·3	0·87
	S_C^*	0·97	—	1·7	−1·3	1·7	−1·3	—
2M	S_A	0·98	0·90	1·7	−1·4	1·7	−1·4	0·77
	S_C^*	0·97	—	1·7	−1·3	1·6	−1·3	—
3	S_A	0·99	0·79	1·5	−1·2	1·6	−1·2	0·48
	S_C^*	0·97	—	1·7	−1·1	1·5	−1·3	—
3M	S_A	0·98	0·88	1·8	−1·4	1·7	−1·5	0·92
	S_C^*	0·95	0·99	2·0	−1·6	1·9	−1·7	—
4	S_A	0·98	0·86	1·7	−1·4	1·7	−1·3	0·71
	S_C^*	0·97	—	1·5	−1·4	1·7	−1·4	—
5	S_A	0·97	0·91	1·7	−1·4	1·7	−1·4	0·67
	S_C^*	0·95	—	2·1	−1·2	1·8	−1·5	—
6	S_A	0·99	0·94	1·9	−1·5	1·9	−1·5	1·0
	S_C^*	0·97	1·0	2·0	−1·6	2·0	−1·7	1·0
7	S_A	0·99	0·94	1·8	−1·4	1·7	−1·4	0·91
	S_C^*	0·95	—	1·9	−1·5	1·5	−1·4	—
8	S_A	0·99	0·98	1·9	−1·4	1·8	−1·5	0·91
	S_C^*	0·93	—	—	—	—	—	—

Table 3. Dipolar coupling constants (kHz) for the primed ring. The experimental uncertainty is about 5 per cent.

Compound	Phase	T/T_C	$C_{1'}$–$H_{2'}$	$C_{2'}$–$H_{2'}$	$C_{2'}$–$H_{3'}$	$C_{3'}$–$H_{3'}$	$C_{3'}$–$H_{2'}$	$C_{4'}$–$H_{3'}$
1	S_A	0·99	1·0	2·1	−1·5	1·8	−1·4	1·0
2	S_A	0·98	0.83	1·7	−1·2	1·5	−1·2	0·80
	S_C^*	0·97	—	1·7	−1·2	1·5	−1·2	—
2M	S_A	0·97	0·90	1·8	−1·3	1·6	−1·3	0·96
	S_C^*	0·97	—	1·7	−1·3	1·6	−1·2	—
3	S_A	0·99	0·78	1·5	−1·2	1·4	−1·2	0·81
	S_C^*	0·97	—	1·6	−1·2	1·4	−1·1	—
3M	S_A	0·98	0·88	1·8	−1·4	1·5	−1·3	0·91
	S_C^*	0·95	0·99	2·0	−1·4	1·7	−1·5	1·2
4	S_A	0·98	0·86	1·8	−1·3	1·6	−1·3	0·90
	S_C^*	0·97	—	1·7	−1·3	1·7	−1·3	—
5	S_A	0·97	0·85	1·7	−1·3	1·6	−1·3	0·69
	S_C^*	0·95	—	1·9	−1·2	1·7	−1·4	—
6	S_A	0·99	0·94	1·9	−1·4	1·7	−1·4	1·0
	S_C^*	0·97	1·0	2·0	−1·5	1·8	−1·5	1·1
7	S_A	0·99	0·94	1·8	−1·3	1·6	−1·3	0·95
	S_C^*	0·95	—	1·8	−1·3	1·5	−1·3	—
8	S_A	0·99	0·91	1·8	−1·3	1·6	−1·3	0·93
	S_C^*	0·93	—	1·8	−1·3	1·4	−1·3	—

3.3. *Aliphatic carbon atoms*

Some of the aliphatic carbon atoms (α, β, ω, $\omega - 1$, $\omega - 2$, and α') are well resolved in the $\omega 2$ dimension, and their splitting can be directly measured from the multiplets in the $\omega 1$ dimension (figure 1). The resulting dipolar coupling constants are given in table 4. The ^{13}C signals of the carbon atoms in the middle of the *n*-decyloxy chain could not be resolved.

4. Calculation of the order parameters

4.1. *Aromatic carbon atoms*

The orientational ordering of the mesogenic core can often be described by an ordering matrix for each rigid segment in the molecule. Since the two-fold axes of the two phenyl rings in the thioesters do not coincide, the two rings have different order parameters. In the case of lowest possible symmetry, the ordering matrix can be defined by five independent order parameters. Since the phenyl rings undergo rapid jumps between four equilibrium positions about an axis defined by C_1 and C_4 ($C_{1'}$ and $C_{4'}$), their effective symmetry is D_2 [35, 36]. In this case, the ordering matrix is defined by only two independent quantities, $S_{\zeta\zeta}$ and $S_{\xi\xi} - S_{\nu\nu}$. We choose a molecular axis system for each ring independently as follows: the ζ axis is the two-fold axis of the phenyl ring, and the ν axis is perpendicular to the plane of the ring. The dipolar coupling constant for each C–H pair is then given by

$$\begin{aligned} D_{CH} = & -(\gamma_C \gamma_H h/8\pi^2 r^3)[3\cos^2\Theta_{CH\zeta} - 1)S_{\zeta\zeta} \\ & + (\cos^2\Theta_{CH\xi} - \cos^2\Theta_{CH\nu})(S_{\xi\xi} - S_{\nu\nu})], \end{aligned} \tag{2}$$

Table 4. Dipolar coupling constants (kHz) for the aliphatic C–H bonds. The experimental uncertainty is about 5 per cent. The assignment for ω' and ω'' may be interchangeable. The coupling constants for α are about the same as those for α', and the coupling constants for γ are about 80 per cent of those for α'; however, their accuracies are not very high because of broadening of the wings (see figure 1).

Compound	Phase	T/T_C	α'	β'	γ'	ω'	γ	$\omega - 2$	$\omega - 1$	ω
1	S_A	0·99	6·4	—	—	—	—	2·9	—	0·84
2	S_A	0·98	5·5	1·8	—	0·7	—	3·0	1·9	0·91
	S_C^*	0·97	5·4	1·7	—	0·6	—	2·9	2·0	0·84
2M	S_A	0·98	5·8	1·8	—	0·7	—	3·1	1·9	0·84
	S_C^*	0·97	5·8	1·6	—	0·7	—	3·0	2·0	0·94
3	S_A	0·99	5·1	1·8	2·1, 0·6	—	—	2·9	2·0	0·91
	S_C^*	0·97	5·0	1·7	1·7, 0·5	—	—	—	2·0	0·85
3M	S_A	0·98	5·5	—	2·1, 0·6	—	—	3·4	1·9	1·0
	S_C^*	0·95	5·9	—	2·5, 1·0	—	—	3·0	—	0·80
4	S_A	0·98	5·1	—	1·1	—	—	2·9	2·0	0·92
	S_C^*	0·97	5·0	—	—	—	—	2·8	—	0·92
5	S_A	0·97	5·5	—	—	0·8	—	2·9	2·0	0·85
	S_C^*	0·95	5·6	—	—	0·7	—	3·1	2·0	0·92
6	S_A	0·99	6·5	—	0·4	0·4	4·7	3·1	2·1	0·76
	S_C^*	0·97	5·9	—	0·5	0·5	—	3·6	2·4	0·99
7	S_A	0·99	6·0	1·7	1·8	—	4·5	3·1	2·2	—
	S_C^*	0·95	5·9	1·8	1·9	—	—	3·3	2·3	—
8	S_A	0·99	5·8	2·0	—	—	—	3·1	2·2	0·87
	S_C^*	0·93	6·0	—	—	—	—	—	—	1·1

where r_{CH} is the distance between two nuclei, and Θ_{CHi} is the angle between $\mathbf{r}_{CH}$ and the molecular axis i. Using the experimental C–H dipolar coupling constants, the order parameters for each ring were calculated using a non-linear least squares program. In the initial step of the calculation, all order parameters and C–C–H bond angles were varied simultaneously. To refine the calculation, the average value of each C–C–H bond angle for all the compounds (119·9 ± 0·3° for $\angle C_2\text{–}C_3\text{–}H_3$, $\angle C_3\text{–}C_2\text{–}H_2$, and $\angle C_{3'}\text{–}C_{2'}\text{–}H_{2'}$, and 120·3 ± 0·3° for $\angle C_{2'}\text{–}C_{3'}\text{–}H_{3'}$) were taken and treated as a constant in the least squares calculations. These average values of the bond angles are essentially the same as the undistorted angle of 120°. The averaged values of bond angles were used because experimentally they should be independent of the R and X groups in the chain. Treating them as variables rather than constants actually caused the values of $S_{\zeta\zeta}$ and $S_{\xi\xi} - S_{\nu\nu}$ to vary by only a few per cent in the least squares calculations, and the deviations introduced are well within the experimental errors.

4.2. *Aliphatic carbon atoms*

The complete description of the orientational order of a flexible part of a molecule is very complicated. Instead, we can calculate an order parameter of the C–H bonds in each segment of the aliphatic chains by the relation [3]

$$S_{CH} = -(4\pi^2 r^3/\gamma_C\gamma_H h)D_{CH}. \qquad (3)$$

Table 5. Order parameters for the aromatic rings, $T/T_C = 0{\cdot}98$ for the S_A phase, and $T/T_C = 0{\cdot}96$ for the S_C^* phase. The S_A range of **6** is too narrow to reach $T/T_C = 0{\cdot}98$. The experimental uncertainty is about 10 per cent for $S_{\zeta\zeta}$ and $S_{\zeta\zeta'}$, and 50 per cent for $S_{\xi\xi} - S_{\nu\nu}$ and $S_{\xi\xi'} - S_{\nu\nu'}$.

Compound	Phase	$S_{\zeta\zeta}$	$S_{\xi\xi} - S_{\nu\nu}$	$S_{\zeta\zeta'}$	$S_{\xi\xi'} - S_{\nu\nu'}$
1	S_A	0·70	0·01	0·67	0·003
2	S_A	0·59	0·02	0·56	0·01
	S_C^*	0·59	0·01	0·56	0·007
2M	S_A	0·61	0·02	0·60	0·01
	S_C^*	0·56	0·01	0·56	0·00
3	S_A	0·54	0·01	0·53	0·01
	S_C^*	0·53	0·005	0·52	0·00
3M	S_A	0·65	0·03	0·62	0·02
	S_C^*	0·70	0·04	0·65	0·01
4	S_A	0·60	0·02	0·59	0·007
	S_C^*	0·62	0·03	0·58	0·00
5	S_A	0·61	0·02	0·57	0·01
	S_C^*	0·62	0·00	0·60	0·00
6	S_C^*	0·77	0·03	0·72	0·01
7	S_A	0·64	0·03	0·63	0·02
	S_C^*	0·65	0·03	0·59	0·01
8	S_A	0·66	0·02	0·62	0·080
	S_C^*	—	—	0·61	0·02

Using the value 0·110 nm for the C–H distance, an order parameter for each C–H bond was calculated. The results at reduced temperatures (T/T_C) of 0·98 and 0·96 are given in table 6.

4.3. *Temperature dependence of order parameters*

The 2D VAS/SLF experiments are rather time consuming. Because of limitations in spectrometer time, we could not carry out the 2D experiment at a large number of temperatures for all of the compounds. As an alternative, we obtained the temperature dependence of the order parameters indirectly by measuring the chemical shifts of all peaks as functions of temperature in a series of 1D experiments. Since $S_{\xi\xi} - S_{\nu\nu}$ is small compared to $S_{\zeta\zeta}$ for the rings, it can be shown [12, 13] that

$$\delta_{\text{obs}} \approx \delta_{\text{iso}} + (3/2)S_{\zeta\zeta}\Delta\delta, \qquad (4)$$

where δ_{obs} is the observed chemical shift, δ_{iso} is the isotropic chemical shift, and $\Delta\delta$ is the chemical shift anisotropy. A similar relation holds for S_{CH}. By fitting the order parameters directly obtained from the VAS/SLF experiment at one temperature into equation (4), values of $\Delta\delta$ for each carbon can be obtained. Since the values of $\Delta\delta$ are essentially independent of temperature, they can in turn be used to calculate the order parameter at other temperatures. Although the values of $\Delta\delta$ obtained from equation (4) may not be very accurate because of the omission of the term containing $S_{\xi\xi} - S_{\nu\nu}$, the error introduced would largely cancel out when the same equation is used to obtain $S_{\zeta\zeta}$ (or S_{CH}) for other temperatures. This procedure gives more reliable results

Table 6. Order parameters for the aliphatic C–H bonds. T/T_C = 0·98 for the S_A phase, and T/T_C = 0·96 for the S_C^* phase. The S_A range of **6** is too narrow to reach T/T_C = 0·98. The experimental uncertainty is about 10 per cent. The order parameters for α are about the same as those for α', and the order parameters for γ are about 80 per cent of those for α'; however, their accuracies are not very high because of broadening of the wings (see figure 1).

Compound	Phase	α'	β'	γ'	ω'	γ	$\omega - 2$	$\omega - 1$	ω
1	S_A	−0·28	—	—	—	—	−0·13	—	−0·04
2	S_A	−0·24	−0·08	—	−0·03	—	−0·13	−0·08	−0·04
	S_C^*	−0·24	−0·07	—	−0·02	—	−0·13	−0·09	−0·03
2M	S_A	−0·26	−0·08	—	−0·03	−0·14	−0·09	−0·04	
	S_C^*	−0·26	−0·07	—	−0·03	—	−0·12	−0·09	−0·04
3	S_A	−0·22	−0·08	−0·09, −0·002	—	—	−0·13	−0·09	−0·04
	S_C^*	−0·21	−0·07	−0·07, −0·002	—	—	—	−0·09	−0·03
3M	S_A	−0·24	—	−0·09, −0·003	—	—	—	−0·09	−0·05
	S_C^*	−0·25	—	−0·10, −0·004	—	—	—	—	−0·04
4	S_A	−0·23	—	−0·01	–	–	−0·13	−0·09	−0·04
	S_C^*	−0·22	—	—	—	—	−0·11	—	−0·04
5	S_A	−0·23	—	—	−0·03	—	−0·12	−0·09	−0·04
	S_C^*	−0·23	—	—	−0·03	—	−0·13	−0·09	−0·04
6	S_C^*	−0·30	—	−0·02	—	−0·25	−0·15	−0·11	−0·04
7	S_A	−0·28	−0·07	−0·08	—	−0·20	−0·14	−0·10	—
	S_C^*	−0·27	−0·08	−0·08	—	—	−0·14	−0·10	—
8	S_A	−0·24	−0·09	—	—	—	−0·14	−0·10	−0·04
	S_C^*	−0·25	—	—	—	—	—	—	−0·05

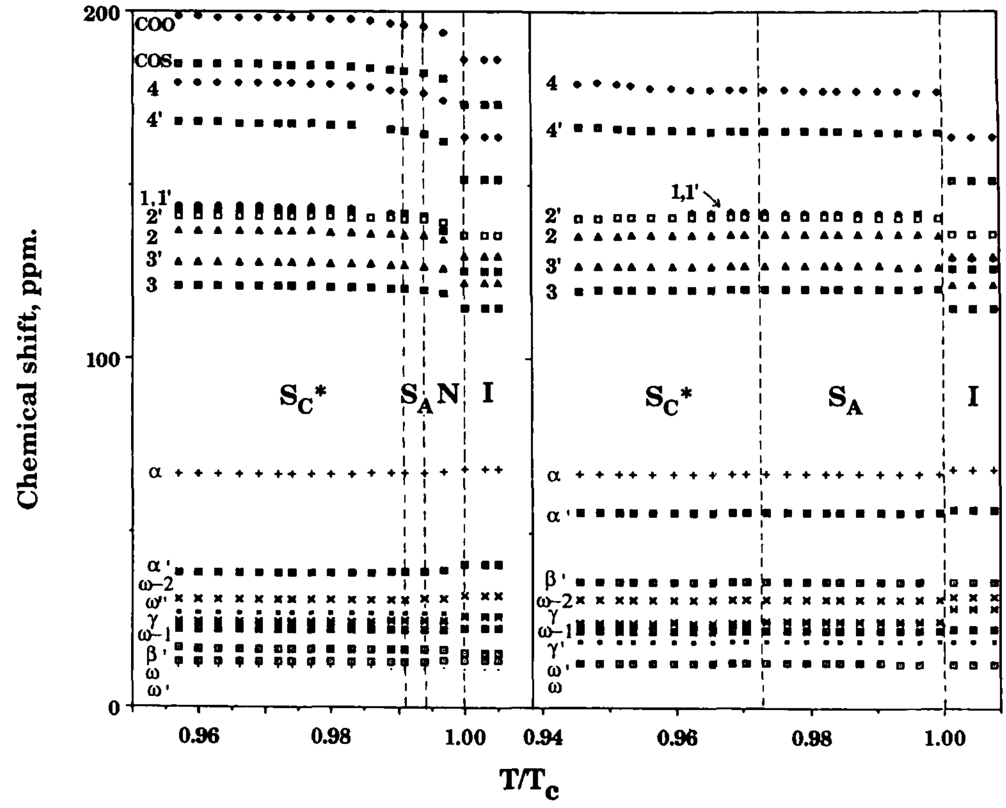


Figure 2. Temperature dependence of ^{13}C chemical shifts of **6** (left) and **7** (right) with VAS at β = 46·6°. Only three data points for each carbon are shown for $T/T_C > 1$ because the chemical shifts did not change with temperature in the isotropic phase.

for the aromatic carbons, because they have much larger chemical shift anisotropy and their observed chemical shifts show considerably larger temperature dependence than the aliphatic carbons (figure 2). It must be cautioned that the use of $\Delta\delta$ values *estimated* from other compounds to calculate order parameters [20, 38, 39] would not give reliable results. As an example of the method used here, the chemical shifts of **6** and **7** as functions of temperature are plotted in figure 2, and their order parameters are plotted in figure 3. The temperature dependence of other compounds with X = Cl is similar to that of **7** [30]. The fluctuations of some of the data with temperature (e.g. $\omega - 1$ for both **6** and **7** and α' for **7** in figure 3) reflect the lack of accuracy in using the chemical shifts to determine the order parameters, as discussed above.

5. Discussion

From the results given in tables 5 and 6 and figure 3, several interesting conclusions can be drawn. First, although the mesogenic core itself does not have uniaxial symmetry, both $S_{\xi\xi} - S_{vv}$ and $S_{\xi'\xi'} - S_{v'v'}$ are very small and close to zero. This indicates that each ring has an essential biaxial symmetry with respect to the corresponding two-fold axes. Second, $S_{\zeta\zeta}$ for the non-primed ring is always slightly higher than that of the primed ring ($S_{\zeta'\zeta'}$). Since the C_2 axis of the non-primed ring and the $C_{2'}$ axis of the primed ring are not collinear, this implies that the director is closer to the C_2 axis

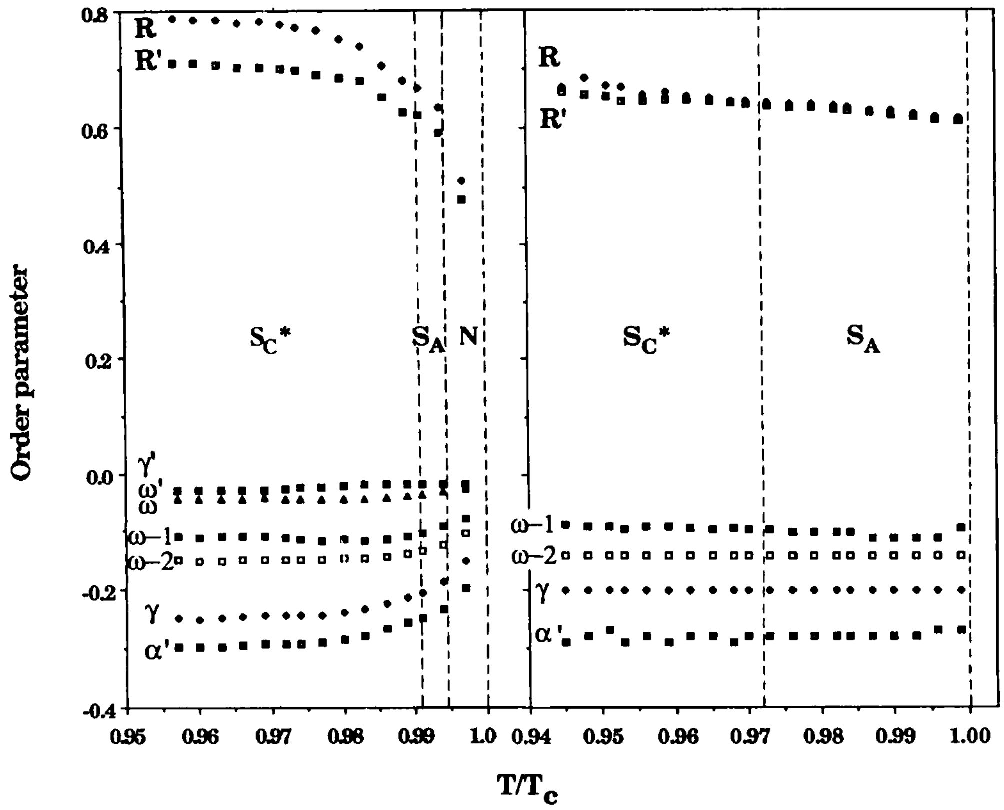


Figure 3. Temperature dependence of the order parameters of **6** (left) and **7** (right). The symbol R refers to $S_{\zeta\zeta}$ of the non-primed ring, and R' refers to $S'_{\zeta\zeta}$ of the primed ring.

than the $C_{2'}$ axis. This may be attributed to the nature of the substituents: the non-primed ring has a long, unbranched *n*-decyloxy chain at the 4-position, while the primed ring has a shorter and branched chain at the 4′-position. In general, the order parameters of both rings are somewhat higher than those of nematic liquid crystals [4–10, 13] but are comparable to other smectic compounds [11, 12].

Unlike the biphenyl analogues of **3** [11, 12], the thioesters show no significant discontinuity in the ordering parameters at the phase transition from S_A to S_C^* (figure 3). This is a rather unexpected result and may be related to the bent configuration of the rigid core. However, we do not have sufficient information to give a satisfactory explanation. Another interesting observation is the following: although the core order parameters of the racemic mixture **2M** are about the same as those of the optically pure compound **2** (table 5), **3M** has significantly higher core order parameters than its optically pure analogue **3** (table 5). In contrast, no systematic difference between the optically pure compounds and their racemic mixtures was observed for the corresponding biphenyl compounds [12]. The reason for this is not clear to us.

A comparison between the different compounds is now appropriate. We only consider the optically pure substances for this. The ordering of the mesogenic core increases in the order of **3** < **2** < **4**, **5** < **7**, **8** < **6**, **1**, with a sufficient correlation between both rings in both phases (table 5). These results indicate that (1) the molecules with unbranched R chains have a higher ordering than those with branched

R chains because of preferable intermolecular alignment; (2) the closer a branching is to the core, the lower is the ordering, but its influence decreases when it is in the more flexible part of the tail; (3) the ordering of **3** is lowest because there are two branches in the chain; (4) the methyl group imparts a larger temperature dependence to the order parameters of both the chains and the rings (figure 3), and increases the ordering compared to the chloro group at lower temperatures; (5) the compound with the shortest chain (**1**) has the highest ordering. We do not have ready explanations for the last two observations, but note that **1** has no S_C phase and is therefore not strictly comparable to the other compounds.

In the decyloxy chain, the C–H order parameters decrease (having less negative values) along the chain for the carbon atoms which give resolvable peaks in the NMR spectra (table 6). This is a common feature for most liquid crystals, and is due to an increasing flexibility when the segment is farther away from the rigid core. Unfortunately, the order parameters can only be obtained for a few segments in this chain because the large number of aliphatic carbon atoms causes the overlap of many of the corresponding signals.

For the branched chain attached to the primed ring, the C–H bond order parameters are obviously dependent on the structure of the chain. The most striking common feature is the rather large negative S_{CH} values of the α' segment and the precipitous decrease in the corresponding values for the β' segment. This may indicate hindered rotation about the chiral centre, which could be caused by the presence of the substituent X, which is bulkier than hydrogen. However, more experimental data are needed to confirm this hypothesis. In the cases of **5** and **6**, they have the same R group but different X groups, and **6** has a more negative S_{CH} value for the α' carbon (table 6). It is not clear whether this is due to the higher core order parameter of **6** (table 5), or if it is an indication of more hindered rotation.

The spontaneous polarization (P_S) of S_C^* liquid crystals depends on the simultaneous existence of a tilted laminar structure, a transverse dipole moment, and a chiral molecular structure [26, 40]. If there is indeed hindered rotation about the chiral centre, the average transverse dipole moment in the carboxyl group could be increased, which may be related to the unusually large spontaneous polarization of the α'-choloroesters [25, 27, 28]. In connection with this, we note that the biphenyl compounds having the same R and X as **3** have more negative S_{CH} values at the α'-position (about $-0{\cdot}30$) [12] than those of the thiobenzoates studied here. Interestingly, the corresponding values of P_S are about 250 and 100 nC/cm^2 [27, 28], respectively. For both types of compounds, P_S as well as $|S_{CH}|$ at the α' position increase with the decrease of temperature. Unfortunately, the accuracy of the S_{CH} values is not high enough to warrant quantitative comparison of different compounds in each homologous series. We must also note that the values of P_s are strongly dependent on the tilt angle. Although the tilt angle is itself temperature-dependent, it is not directly related to the order parameters.

In conclusion, we have performed 2D ^{13}C NMR experiments to determine the core and chain order parameters of a homologous series of thiobenzoate ferroelectric liquid crystals. The order parameters for the two rings are different, and they are dependent on the substituents in the chain attached to the second benzene ring. The C–H order parameters in that chain show a precipitous drop from the α' to the β' position, which may be an indication of hindered rotation about the chiral centre. In general, both the spontaneous polarization and the order parameters of the thiobenzoates are somewhat smaller than those of the corresponding biphenyl compounds.

Financial support from the National Science Foundation (grant number DMR-8704223) and the IBM Almaden Research Center to B.M.F. is gratefully acknowledged.

References

[1] SAUPE, A., 1964, *Z. Naturf.* (*a*), **19**, 161.
[2] EMSLEY, J. W. (editor), 1985, *NMR of Liquid Crystals* (Reidel).
[3] EMSLEY, J. W., and LINDON, J. C., 1975, *NMR Spectroscopy Using Liquid Crystal Solvents* (Pergamon Press).
[4] FUNG, B. M., and AFZAL, J., 1986, *J. Am. chem. Soc.*, **108**, 1107.
[5] FUNG, B. M., AFZAL, J., FOSS, T., and CHAU, M.-H., 1986, *J. chem. Phys.*, **85**, 4808.
[6] FUNG, B. M., POON, C.-D., GANGODA, M., ENWALL, E. L., E. L., DIEP, T. A., and BUI, C. D., 1986, *Molec. Crystals liq. Crystals*, **141**, 267.
[7] POON, C. D., WOOLDRIDGE, C. M., and FUNG, B. M., 1988, *Molec. Crystals liq. Crystals*, **157**, 303.
[8] FORSTER, P., and FUNG, B. M., 1988, *J. chem. Soc. Faraday Trans. II*, **84**, 1083.
[9] FRECH, C. B., FUNG, B. M., and SCHADT, M., 1988, *Liq. Crystals*, **3**, 713.
[10] FRECH, C. B., FUNG, B. M., and SCHADT, M., 1989, *SPIE Proc.*, **1080**, 215.
[11] POON, C.-D., and FUNG, B. M., 1989, *Liq. Crystals*, **5**, 1159.
[12] POON, C. D., and FUNG, B. M., 1989, *J. chem. Phys.*, **91**, 7392.
[13] RICHTER, W., FUNG, B. M., and SCHADT, M., 1990, *Liq. Crystals*, **8**, 63.
[14] WAUGH, J. S., 1986, *Proc. natn. Acad. Sci. U.S.A.*, **73**, 1394.
[15] HESTER, R. K., ACKERMAN, J. L., NEFF, B. L., and WAUGH, J. S., 1976, *Phys. Rev. Lett.*, **36**, 1081.
[16] WAUGH, J. S., and OPELLA, S., 1977, *J. chem. Phys.*, **66**, 4919.
[17] RYBACZEWSKI, E. F., NEFF, B. L., WAUGH, J. S., and SHERFINSKI, J. S., 1977, *J. chem. Phys.*, **67**, 1231.
[18] COURTIEU, J., ALDERMAN, D. W., and GRANT, D. M., 1981, *J. Am. chem. Soc.*, **103**, 6784.
[19] COURTIEU, J., ALDERMAN, D. W., GRANT, D. M., and BAYLES, J. P., 1982, *J. chem. Phys.*, **77**, 723.
[20] TEEÄÄR, R., ALLA, M., and LIPPMAA, E., 1982, *Org. magn. Reson.*, **19**, 134.
[21] HEESCHEN, W. A., ALDERMAN, D. W., and GRANT, D. M., 1984, *J. magn. Reson.*, **59**, 318.
[22] BAYLE, J. P., KHANDAR-SHAHABAD, A., and COURTIEU, J., 1986, *Liq. Crystals*, **1**, 189.
[23] FUNG, B. M., and GANGODA, M., 1985, *J. chem. Phys.*, **83**, 3285.
[24] NGUYEN, H. T., SALLENEUVE, C., BABEAU, A., ROUBINEAU, A., and DESTRADE, C., 1987, *Molec. Crystals liq. Crystals*, **157**, 93.
[25] TWIEG, R. J., BETTERTON, K., NGUYEN, H. T., TANG, W., and HINSBERG, W., 1989, *Ferroelectrics*, **91**, 243.
[26] MEYER, R. B., LIEBERT, L., STRZELECKI, L., and KELLER, P., 1975, *J. Phys., Paris*, **36**, L69.
[27] BAHR, CH., HEPPKE, G., and SABASCHUS, B., 1986, *Molec. Crystals liq. Crystals Lett.*, **4**, 31.
[28] SAKURAI, T., MIKAMI, N., HIGUCHI, R., HONMA, M., OZAKI, M., and YOSHINO, K., 1986, *J. chem. Soc. chem. Commun.*, p. 978.
[29] BURUM, D. P., LINDER, N., and ERNST, R. R., 1981, *J. magn. Reson.*, **44**, 173.
[30] REIMER, D., 1989, M.S. Thesis, University of Oklahoma.
[31] RICHTER, W., 1989, M.S. Thesis, University of Oklahoma.
[32] MARECI, T. H., and FREEMAN, R., 1982, *J. magn. Reson.*, **48**, 158.
[33] FUNG, B. M., 1986, *J. magn. Reson.*, **66**, 525.
[34] KALINOWSKI, H.-O., BERGER, S., and BRAUN, S., 1984, *^{13}C-NMR-Spektroskopie* (Georg Thieme Verlag).
[35] EMSLEY, J. W., LUCKHURST, G. R., and STOCKLEY, C. P., 1981, *Molec. Phys.*, **44**, 565.
[36] SINTON, S. W., ZAX, D. B., MURDOCH, J. B., and PINES, A., 1984, *Molec. Phys.*, **53**, 333.
[37] JONES, A., 1970, *J. Comput.*, **13**, 201.
[38] LUZAR, M., RUTAR, V., SELIGER, J., and BLINC, R., 1984, *Ferroelectrics*, **58**, 115.
[39] BLINC, R., DOLINSEK, J., LUZAR, M., and SELIGER, J., 1988, *Liq. Crystals*, **3**, 663.
[40] LAGERWALL, S. T., and DAHL, T., 1984, *Molec. Crystals liq. Crystals*, **114**, 151.