## The effect of molecular structure on molecular dynamics and ordering in a chiral smectic liquid crystal

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# The effect of molecular structure on molecular dynamics and ordering in a chiral smectic liquid crystal

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The effect of a branched alkyl chain on molecular dynamics and ordering in a chiral smectic liquid crystal has been investigated by means of DSC, optical microscopy, powder X-ray diffraction, and solid state C-13 NMR. The introduction of a second branched alkyl chain into a $S_C^*$ molecule increases the molecular tilt angle, the value of the spontaneous polarization in the $S_C^*$ phase, and the $S_A$–$S_C^*$ transition enthalpy. The long-range order observed by X-ray measurements and the molecular motion detected by C-13 spin relaxation are not influenced by the branched group. On the other hand, marked NMR line broadenings for the core carbons occur in the oriented $S_C^*$ phase. The results obtained suggest that the branched group affects the dynamics and ordering of the molecular core in the $S_C^*$ phase through the interlayer interaction.

## 1. Introduction

To control the physical properties of a smectic liquid crystal via its molecular structure is a most attractive problem from basic interest and in view of possible applications. A smectic liquid crystal molecule is known to be far from a rigid rod. The phase transition temperatures and the other physical properties of a smectic liquid crystal are strongly influenced by its molecular structure. Since the discovery of a ferroelectric liquid crystal [1], much work has been carried out to establish correlations between physical properties and molecular structure in the $S_C^*$ materials [2–4].

We have reported the effects of dipole moment, alkyl chain length, lateral substitution, and core structure on phase transitions and spontaneous polarization [5–8]. The introduction of a second branched alkyl chain into a $S_C^*$ molecule enhances the ferroelectric properties in the $S_C^*$ phase [9]. We also reported C-13 NMR and X-ray investigations of phase transitions in ferroelectric [10, 11] and antiferroelectric liquid crystals [12], providing useful information concerning molecular ordering and dynamics. Recently, we prepared a thermally stable $S_C^*$ molecule with two branched alkyl chains. In this study, the effect of the second branched alkyl chain on molecular motions and ordering in the $S_C^*$ phase has been investigated by means of optical microscopy, DSC, solid-state C-13 NMR, and powder X-ray diffraction. The present study makes it possible to discuss the relationship between molecular structure and intermolecular interaction in the smectic phases.

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## 2. Experimental

### 2.1. *Materials*

The material under investigation is 4′-(*S*)-2-methyloctanoylbiphenyl-4-yl (*S*)-4-methylhexyloxybenzoate (compound 1). Commercially available (*S*)-2-methyloctanoic acid (Nippon Mining Co., Ltd.) and 4-(*S*)-4-methylhexyloxybenzoic acid (Teikoku Chemical Industry Co., Ltd.) were used as the starting materials. The preparation of the compound was carried out according to our reported method [9]. The route for the preparation is presented in the scheme. 4′-(±)-2-methyloctanoylbiphenyl-4-yl 4-(*S*)-4-methylhexyloxybenzoate (compound 2) was also prepared from racemic (±)-2-methyloctanoic acid. 4-(*S*)-2-methyloctanoylbiphenyl-4-yl 4-octyloxybenzoate (compound 3) was prepared by the esterification of 4-octyloxybenzoic acid with 4′-hydroxy-4-(2-methyloctanoyl)biphenyl. The structures of the final compounds were confirmed by IR and NMR spectral analysis.
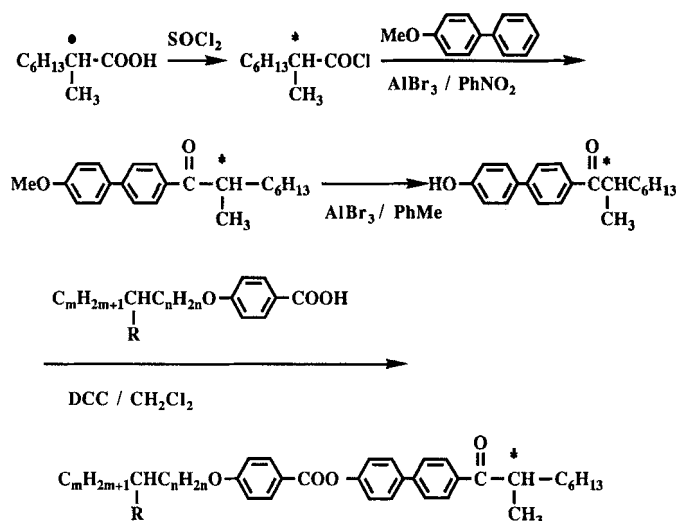
Scheme. Synthetic route to the 4′-(2-methyloctanoyl)biphenyl-4-yl 4-alkyloxybenzoates.

### 2.2. *Measurements*

The liquid crystal transition temperatures and enthalpies were determined by differential scanning calorimetry using a Seiko DSC-200 calorimeter. The liquid crystal transition temperatures were also observed by polarizing optical microscopy using a Mettler FP82 heating stage.

Cell (purchased from EHC Co., Ltd.) of 2·5 μm thickness aligned by rubbing, after coating the ITO deposited glass plates with a polyimide film, were used for measurements of the spontaneous polarization and tilt angle. The spontaneous polarization was measured by the triangular wave method and the tilt angle was derived from the optical switching angle of the sample.

Powder X-ray diffraction patterns were obtained using Rigaku RAD-IIB with a CuKα radiation. All C-13 NMR measurements, both with rapid sample spinning and without sample spinning, were made using a JEOL GSX-270 spectrometer at 67·9 MHz with proton dipolar decoupling. The NMR spectra with magic angle spinning (MAS) were observed at the spinning speed of 4·5 kHz. The temperature under
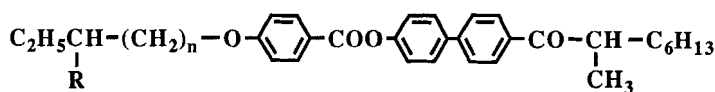
the MAS condition was calibrated from the I–$S_A$ phase transition of the sample. The measurements of C-13 spin–lattice relaxation time in the laboratory frame $(T_1)$ were performed using a 180°–τ–90° pulse sequence. The measurements of C-13 spin–lattice relaxation time in the rotating frame $(T_{1\rho})$ were performed using the spin locking method at the spin locking frequency of 56 kHz. Static C-13 NMR spectra were obtained without MAS. The sample was oriented by slow cooling from the I to the $S_A$ phase in the superconducting magnet at 6·34 T. The cooling rate was about 1°C/15 min.

## 3. Results and discussion

### 3.1. *Transition temperatures and spontaneous polarization*

The structural formulae of the compounds under investigation are shown in figure 1. The transition temperatures measured for the compounds are listed in table 1 and a DSC cooling thermogram for compound **1** is shown in figure 2. The large transition enthalpies at the $S_A$–$S_C^*$ transition were observed both for compounds **1** and **2**.

The temperature dependence of the spontaneous polarization and that of the tilt angle observed for compounds **1** and **3** are shown in figure 3. The spontaneous polarization of compound **2** was $-0.9$ nC cm$^{-2}$ at 89°C. The maximum value of the spontaneous polarization of compound **1** is $-683$ nC cm$^{-2}$ at 32°C. Compound **1** gives higher values of the spontaneous polarization and tilt angle compared to those of compound **3** in the temperature range of the $S_C^*$ phase. The ratios $P_S/\sin\theta$ obtained at 10° below the $S_A$–$S_C^*$ transition for compounds **1** and **3** are $-599$ nC cm$^{-2}$ and $-397$ nC cm$^{-2}$, respectively. The large transition enthalpies at the $S_A$–$S_C^*$ transition observed for compounds **1** and **2** are not attributed to the magnitude of the spontaneous polarization. Intermolecular interactions in the $S_C^*$ phase are affected by the introduction of the branched alkyl chain (4-methylhexyloxy group) located far from the molecular core.

$$C_2H_5\underset{\underset{R}{|}}{C}H-(CH_2)_n-O-\bigcirc\!\!\!-\!\!\!\bigcirc-COO-\bigcirc\!\!\!-\!\!\!\bigcirc\bigcirc\!\!\!-\!\!\!\bigcirc-CO-\underset{\underset{CH_3}{|}}{C}H-C_6H_{13}$$

**1, 2: R = CH₃, n = 3,    3: R = H, n = 5**

Figure 1.    The structure formulae of the compounds 1–3.

Table 1.    Transition temperatures (°C) and enthalpies (kJ mol$^{-1}$) determined† for compounds 1, 2, and 3.

| Compound | C | $S_5$‡ | | $S_4$‡ | | $S_3$‡ | | $S_C^*$ | | $S_A$ | | I |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 64 | (● | 27 | ● | 28 | ● | 34) | ● | 101 | ● | 121 | ● |
| Δ$H$ | 17·5 | | | | | | 0·8 | | 0·8 | | 3·5 | |
| **2** | 75 | | | (● | 17 | ● | 25) | ● | 95 | ● | 119 | ● |
| Δ$H$ | 30·0 | | | | 4·1 | | 0·8 | | 0·5 | | 3·3 | |
| **3** | 81 | (● | 40 | ● | 51 | ● | 65) | ● | 109 | ● | 142 | ● |
| Δ$H$§ | 28·2 | | | | 3·4 | | | | — | | 5·9 | |

† The transition temperatures and enthalpies were determined from cooling cycles by DSC at a cooling rate of 2·0°C min$^{-1}$, except for those of crystal to smectic transitions.

‡ Higher ordered smectic phases are not yet identified.

§ The transition enthalpy of the $S_A$–$S_C^*$ transition for compound **3** was too small to be evaluated.
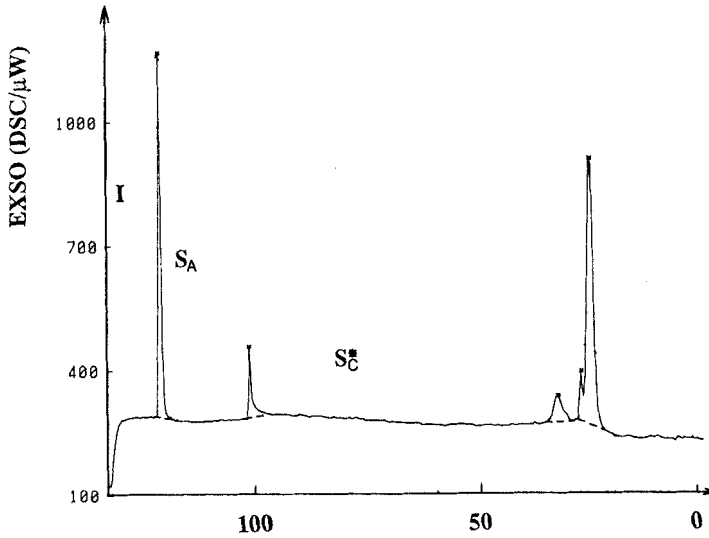
Figure 2.    DSC cooling curve for compound **1**. Cooling rate $2°C\,min^{-1}$.
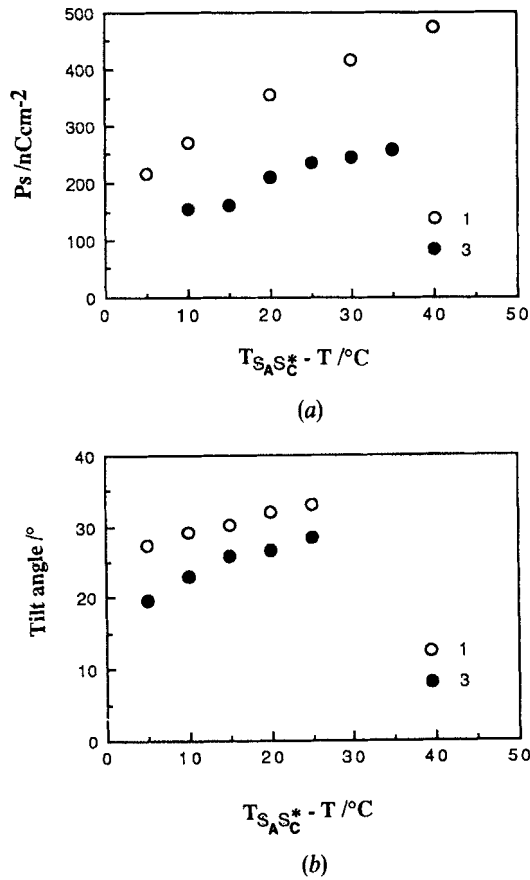


(a)



(b)

Figure 3.    The temperature dependence of (a) the spontaneous polarization and (b) the tilt angle for compounds **1** and **3** in the $S_C^*$ phase.

## 3.2. *Powder X-ray diffraction*

Figure 4 shows the temperature dependent powder X-ray diffraction of compound 1 on heating. The X-ray patterns at small angles display a Bragg reflection from the smectic layers. The patterns at higher angles reflect the order inside the layer. During the phase transition from $S_C^*$ to $S_A$, there is no marked change in the diffraction patterns except for the increase in the layer thickness. The long range order observed by X-ray diffraction is not influenced by the introduction of the branched alkyl group. The tilt angles of compounds 1 and 3 determined by X-ray measurements are shown in figure 5. The tilt angle by X-ray measurements was estimated assuming that the ratio of the $S_C^*$ to $S_A$ layer spacing is proportional to the cosine of the $S_C^*$ tilt angle. In the case of X-ray measurements, compound 1 also gives higher values of the tilt angle compared to that of compound 3.

## 3.3. *C-13 NMR*

Figure 6 shows C-13 NMR spectra of compound 1 in the non-oriented $S_A$ and $S_C^*$ phases with MAS; assignments for the spectrum are given in the figure. During the phase transition from $S_A$ to $S_C^*$, the lines for the core and aliphatic carbons of compound 1 become broad, and the chemical shifts of the core carbons increase [11]. Measurements of $T_1$ for individual carbon atoms of compound 1 were carried out. Molecular motions in the range of $10^{-12}$ to $10^{-8}$ s are effective in C-13 $T_1$ relaxation. The angle between the C–H vector and the molecular long axis also affects the C-13 $T_1$ values. Figure 7 shows the temperature dependence of C-13 $T_1$ for compound 1 in the $S_A$ and $S_C^*$ phases. The upward deviation of unprotonated C-13 $T_1$ was observed in the $S_C^*$ phase near the $S_A$—$S_C^*$ transition or at the transition. The phase transition was
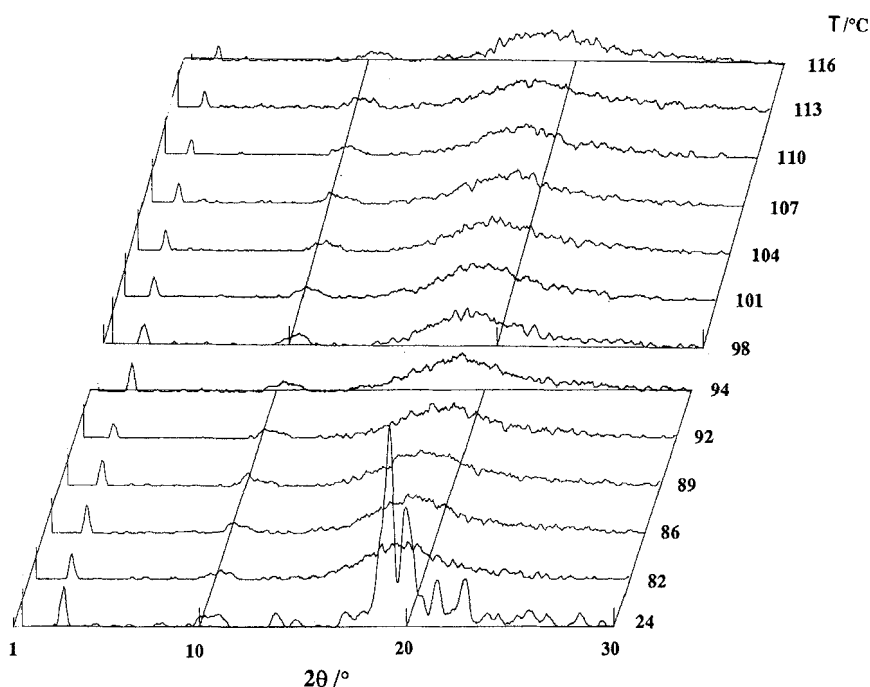


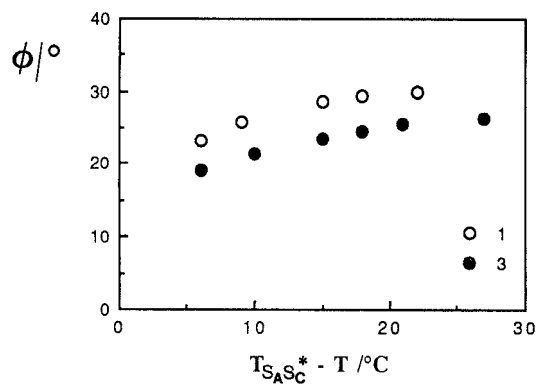Figure 4. Temperature dependent powder X-ray diffraction patterns of compound 1 on heating.

Figure 5.   The temperature dependence of the tilt angle ($\phi$) determined by X-ray measurements
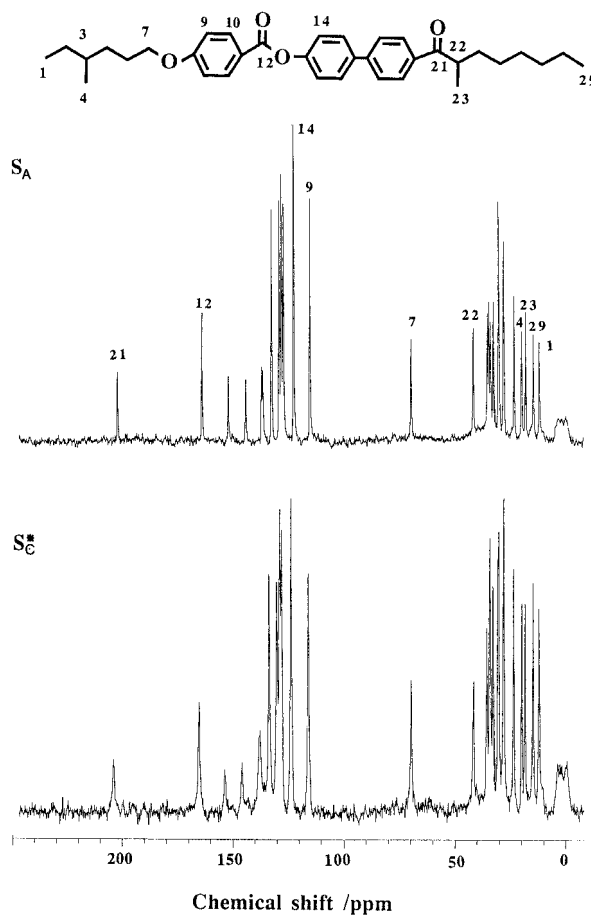for compounds **1** and **3**.



Figure 6.   The C-13 NMR spectra of compound **1** with MAS in the $S_A$ (120°C) and $S_C^*$ (90°)
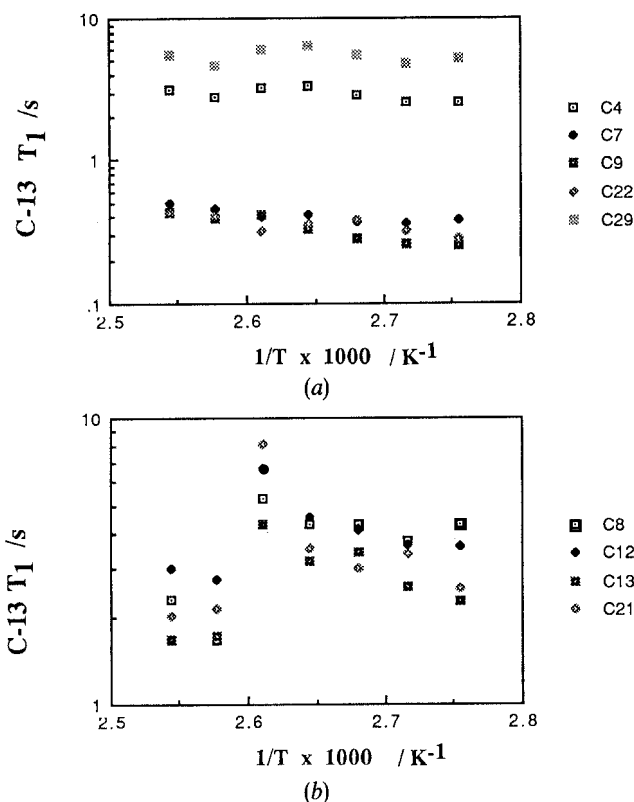phases.

Figure 7. The temperature dependence of C-13 spin–lattice relaxation times with MAS of (a) protonated carbons and (b) unprotonated carbons of compound 1 in the $S_A$ and $S_C^*$ phases. The temperatures in the figure are estimated values.

Table 2. C-13 $T_{1\rho}$ (ms) for the core carbons of compound 1 in the $S_A$ and $S_C^*$ phases.

| $T/^\circ C$ | C10 | C13 | C17 | C21 |
|---|---|---|---|---|
| 110 ($S_A$) | 0·68 | 0·21 | 0·24 | 0·40 |
| 90 ($S_C^*$) | 0·54 | 0·10 | 0·12 | 0·18 |

observed by the change of the C-13 NMR spectrum from $S_A$ to $S_C^*$. The upward deviation of C-13 $T_1$ observed for compound 1 is similar to that for 4-(S)-2-methyloctanoylphenyl-4'-nonylbiphenyl 4-carboxylate (MONBIC) [11]. This increase of C-13 $T_1$ may reflect the fact that the time average of the molecular conformation changes reversibly at the transition [11]. The results obtained suggest that the branched group does not affect the dynamics of an individual molecule detected by C-13 $T_1$ measurements.

C-13 $T_{1\rho}$ measurements with MAS were performed for non-oriented compound 1 in the $S_A$ and $S_C^*$ phases. $T_{1\rho}$ reflects the molecular motion in the range $10^{-6}$ to $10^{-4}$ s. The results obtained for compound 1 are listed in table 2. $T_{1\rho}$ of protonated aliphatic carbons of compound 1 could not be detected in the smectic phases. The C-13 $T_{1\rho}$ values for compound 1 are similar to those for MONBIC [11]. The molecular motion of the core part detected by $T_{1\rho}$ measurements is not influenced by the branched alkyl group located far from the molecular core.
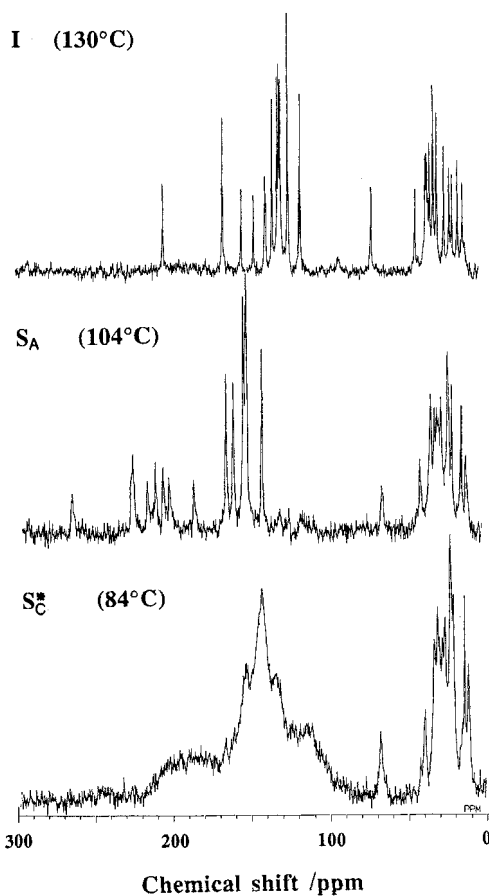
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I    (130°C)

S$_A$    (104°C)

S$_C^*$    (84°C)

|     |     |     |     |
| 300 | 200 | 100 | 0 |

Chemical shift /ppm

Figure 8.   The C-13 NMR spectra of compound 1 without MAS in the I, S$_A$, and S$_C^*$ phases.

Table 3.   Observed chemical shifts† for compound 1 in the I, S$_A$, and S$_C^*$ phases.

|          | Alkyl |      |      | Core |       |       |       |
|----------|-------|------|------|------|-------|-------|-------|
| T/°C     | C1    | C22  | C7   | C9   | C14   | C12   | C21   |
| 130 (I)  | 12·2  | 42·0 | 70·1 | 115·8 | 123·2 | 164·2 | 203·2 |
| 104 (S$_A$) | 11·5 | 40·5 | 65·0 | 141·2 | 150·9 | 223·4 | 262·4 |
| 84 (S$_C^*$) | 11·7 | 39·0 | 67·8 | —     | —     | —     | —     |

† Chemical shifts in ppm referenced to TMS.

In order to investigate the microscopic environment of compound 1 in the oriented sample, static C-13 NMR spectra were measured. Figure 8 shows C-13 NMR spectra of compound 1 in the I, S$_A$, and S$_C^*$ phases without MAS. Table 3 shows observed chemical shifts of the chain carbons (C1, C7, and C22) and the core carbons (C9, C12, C14, and C21) of compound 1 in the I, S$_A$, and S$_C^*$ phases. During the phase transition from I to S$_A$, there are large down field shifts of the keto, ester, and aromatic carbons and slight upfield shifts of the other aliphatic carbons. The molecules orient in such a way that the

director is parallel to the direction of the external magnetic field [10]. During the phase transition from I to $S_A$, the change in the C-13 NMR spectrum observed for compound **1** is similar to that for MONBIC [10, 11]. In the $S_C^*$ phase, the NMR lines of the alkyl chain remain sharp peaks, whilst the lines of the core carbons are broadened remarkably. The NMR lines of the core carbons of compound **1** in the $S_C^*$ phase are broadened considerably compared with those of MONBIC in the $S_C^*$ phase [10, 11]. From $S_A$ to $S_C^*$, down field shifts of C1 and C7 reflect the change in the ordering of the branched alkyl chain.

We estimate the order parameters at the typical nuclear sites of compound **1** in the $S_A$ phase. The chemical shift $\sigma$ in an ordered liquid-crystalline phase is related to the isotropic chemical shift $\sigma_i$, the components of the chemical shift tensor $\sigma_{jk}$, and the order parameters $S_{jk}$ as given by equation (1) [13],

$$\sigma = \sigma_i + (2/3)S_{zz}\{\sigma_{zz} - (1/2)(\sigma_{xx} + \sigma_{yy})\} + (1/3)(\sigma_{xx} - \sigma_{yy})(S_{xx} - S_{yy})$$
$$+ (2/3)S_{yz}\sigma_{yz} + (2/3)S_{xz}\sigma_{xz} + (2/3)S_{xy}\sigma_{xy}. \tag{1}$$

Because of rapid motions, $S_{xy}$, $S_{yz}$, and $S_{zx}$ are zero. $S_{xx} - S_{yy}$ is usually small in uniaxial phases of small molecule liquid crystals. In the $S_A$ phase, equation (1) is reduced to

$$\sigma = \sigma_i + (2/3)S(\sigma_\| - \sigma_\perp), \tag{2}$$

where $\sigma_\| = \sigma_{zz}$ is the chemical shift component along the direction of the long molecular axis and $\sigma_\perp = (1/2)(\sigma_{xx} + \sigma_{yy})$ is the average of the components of the chemical shift tensor in the $xy$ plane, and $S = S_{zz}$ is the order parameter associated with the molecular long axis. $S$ is defined as

$$S = \langle 3\cos^2 \Theta - 1 \rangle / 2, \tag{3}$$

where $\Theta$ describes the orientation of the molecular long axis with respect to the applied static magnetic field, and $\langle \ \rangle$ is a thermal average.

In the simple case of a rapid rotation about the molecular axis, $\sigma_\|$ and $\sigma_\perp$ are given by equation (4) [14],

$$\left.\begin{array}{l} \sigma_\| = \sin^2 \beta(\cos^2 \alpha)\sigma_{11} + \sin^2 \beta(\sin^2 \alpha)\sigma_{22} + (\cos^2 \beta)\sigma_{33}, \\[2mm] \sigma_\perp = (\sigma_{11} + \sigma_{22} + \sigma_{33} - \sigma_\|)/2, \end{array}\right\} \tag{4}$$

where $\alpha$ and $\beta$ are the two first Euler angles. For aromatic carbons, the magnetic equivalence of *ortho* aromatic carbon pairs indicates that the phenyl rings of the mesogenic core perform at least 180° flips. The chemical shifts of the aromatic carbons can be written for *ortho* and *meta* as [15]

$$\left.\begin{array}{l} \sigma_\| = (1/4)(1 + 2\sin^2 \Phi)\sigma_{11} + (1/4)(1 + 2\cos^2 \Phi)\sigma_{22}, \\[2mm] \sigma_\perp = (1/2)[(1/4)(1 + 2\cos^2 \Phi)\sigma_{11} + (1/4)(1 + 2\sin^2 \Phi)\sigma_{22} + \sigma_{33}], \end{array}\right\} \tag{5}$$

where $\Phi$ is the angle between the phenyl *para* axis and the molecular long axis.

We calculate values of $S$ of the chain carbons (C1 and C7) and the core carbons (C9 and C14) from the reported values of principal chemical shifts listed in table 4. Assuming that the alkyl chain bonds are in a *trans*-conformation, we take $\alpha = 60°$ and $\beta = 17·4°$ to calculate values of $\sigma_\| - \sigma_\perp$ for the chain carbons [19]. We calculate values of $\sigma_\| - \sigma_\perp$ for the aromatic carbons with $\Phi = 9°$ [15]. The calculated order parameters of C1, C7, C9, and C14 at 104°C in the $S_A$ phase are 0·06, 0·91, 0·75, and 0·76, respectively. Although the calculations of $S$ are affected by the values of the principal chemical shift

Table 4.   Shielding tensor elements used for the calculation of order parameter.

| Carbon | $\sigma_{11}$ | $\sigma_{22}$ | $\sigma_{33}$ | Ref. |
|--------|--------|--------|--------|------|
| C1  | $-26$    | $-22$    | $-3$    | [16] |
| C7  | $-91$    | $-78$    | $-38$   | [17] |
| C9  | $-184{\cdot}7$ | $-131{\cdot}7$ | $-18{\cdot}7$ | [17] |
| C14 | $-193$   | $-134$   | $-12$   | [18] |

and $\Phi$ used [20], the order parameters obtained give useful information concerning the molecular ordering. In the $S_A$ phase, the order parameters for compound 1 are in relatively good agreement with those for MONBIC [11]. This means that the second branched alkyl chain does not affect the molecular ordering of compound 1 in the oriented $S_A$ phase. The marked line broadenings for the core carbons in the $S_C^*$ phase suggest that the branched group affects the dynamics and ordering of the molecular core in the oriented $S_C^*$ phase. Although the NMR linewidth is well known to be proportional to $1/T_2$ ($T_2$: the spin–spin relaxation time), the NMR spectra of solids are broadened by other factors, for example, chemical shift anisotropy [21]. To our knowledge, there is not a clear theory for the observed effect, and so we interpret the broadened linewidth of the core carbons of compound 1 in the oriented $S_C^*$ phase in the following way. During the phase transition from $S_A$ to $S_C^*$, cooperative slow fluctuation of the long axis around the cone (Goldstone mode) occurs. This motion is affected by interlayer and intralayer interactions, and causes the chemical shift anisotropy which depends on the smectic helicoidal layer structure. In this study, there is no significant difference in C-13 $T_1$ and $T_{1\rho}$ measurements between compound 1 and MONBIC in the non-oriented smectic phases. This indicates that the intralayer/intermolecular interaction is slightly influenced by the second branched alkyl chain located far from the core. The branched group may contribute to the interlayer/intermolecular interaction, which decreases the mobility of the cooperative fluctuations of the long axis around the cone in the $S_C^*$ phase. This marked decrease of the cooperative mobility of the molecular core may be related to the large $S_A$–$S_C^*$ transition enthalpy for compound 1. The sharp NMR lines of the alkyl chain of compound 1 in the oriented $S_C^*$ phase show that the mobility of the alkyl chain of compound 1 changes slightly from $S_A$ to $S_C^*$. The increase in the tilt angle caused by the branched group also suggests that the interlayer/intermolecular interaction through a flexible alkyl chain plays an important role in the molecular tilt in the $S_C^*$ phase.

## 4.  Conclusions

In summary, we prepared a thermally stable $S_C^*$ material, with two branched alkyl chains, which shows a high spontaneous polarization and a large $S_A$–$S_C^*$ transition enthalpy. We have investigated the effect of the second branched alkyl chain on molecular motions and ordering in the $S_A$ and $S_C^*$ phases by means of optical microscopy, DSC, powder X-ray diffraction, and solid state C-13 NMR. The results obtained indicate that the second branched alkyl group located far from the molecular core decreases the cooperative mobility of the core part in the $S_C^*$ phase. It is concluded that the interlayer/intermolecular interaction, affected by the branched group contributes to the mobility of the molecular core and the molecular tilt in the $S_C^*$ phase.

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