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Variable-temperature high-resolution solid-state ^{13}C N.M.R. spectra of chiral smectogenic 4-heptyloxyphenyl 4′-[(s)-2-methylbutyl]biphenyl-4-carboxylate

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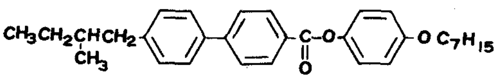
High-resolution solid-state ^{13}C N.M.R. spectra are studied for a chiral smectogenic compound 5*BBCOOBO7 at various temperatures. Below the ambient temperatures two spectral lines of protonated carbons show the existence of a 180° flip of the phenylene ring surrounded by the carboxyl and the alkoxy groups and the activation energy was obtained to be about 17 kJ/mol (4 kcal/mol). The cooperative librational motions are present, which include the exchange between two conformers in the unit cell. The ^{13}C chemical shifts induced in the solid state are also discussed with relation to the crystal structure.

1. Introduction

Because of the ferroelectricity, the chiral smectogens have been actively studied during the last decade, but their precise structures are not yet sufficiently understood. ^{13}C N.M.R. spectroscopy is one of the powerful methods to study molecular structures and dynamic properties. When the measurements of the ^{13}C N.M.R. spectra of liquid crystalline compounds are made by a liquid-state spectrometer under complete ^{1}H decoupling, well separated spectral lines have been observed in the isotropic, the nematic, and the smectic A phases [1]. High-resolution solid-state ^{13}C N.M.R. spectroscopy also gives information on molecular motions and structures in the solid state. The method involves cross polarization (CP), high-power ^{1}H decoupling and magic angle spinning (MAS). The spectral lines of the CP/MAS ^{13}N.M.R. of liquid crystalline compounds are reported to be sharp and well resolved in the solid state [2–6]. But in our preliminary experiments, some of the spectra show unexpected splittings, broadening and/or disappearance of particular signals, for which simple interpretations are difficult [7]. Then it is preferable to study the liquid crystalline compounds whose crystal structures were determined. A chiral smectogen, 4-heptyloxyphenyl 4′-[(s)-2-methylbutyl]biphenyl-4-carboxylate,



which is abbreviated to 5*BBCOOBO7, was studied by X-ray analysis and the results have been reported [8]. The crystal has a layer structure composed of two non-equivalent molecules, which are related by pseudo-inversion except for the chiral parts, and the paraffinic chains take an extended conformation.

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Although the ^{13}C N.M.R. spectrum of 5*BBCOBO7 in the mesophases show broad signals under the high-power ^{1}H decoupling without MAS [7], the CP/MAS spectrum in the solid state consists of well separated lines at ambient temperature, and some lines disappear, which suggests that dynamic processes are present within a molecule. Then we observed the spectra in various temperatures, since the CP/MAS ^{13}C N.M.R. is a useful technique to study the molecular dynamics and offer a useful complement to the information available from the X-ray analysis.

2. Experimental

Variable-temperature high-resolution solid-state ^{13}C N.M.R. spectra were observed at 50·10 MHz by a JEOL FX-200 spectrometer equipped with a CP/MAS and a variable temperature units. The spinning speed for the MAS rotor was about 4·5 kHz. Since the temperature was controlled by air or nitrogen gas of the MAS unit, the real temperature of the sample was obscure. The preliminary result indicated that the temperature of the sample inside the rotor was always higher than the temperature of the gas around rotor. The optimum contact time for CP/MAS spectrum was 3 ms at the ambient temperature (gas temperature: 25°C, and the sample temperature: approximately 45°C, estimated from the temperature of the sample melting), and the same contact time was used at all the temperatures. Typically 100 accumulations were made for each spectrum. To emphasize the non-protonated carbons, the dipole dephasing spectra [9] were observed, where the delay time before data acquisition was set at 40 μs. The chemical shifts were referred to external adamantane, where the ^{13}C shift value of CH peak was set to 29·5 ppm. The solid-state spin–lattice relaxation times, T_1, were measured by the inversion recovery method under the CP condition reported by Torchia [10].

The transition temperatures of 5*BBCOOBO7 have been reported to be crystalline –(80.4°C)–(S_C^*)–(87.3°C)–cholestric–(157.7°C)– isotropic [11]. The synthesized compound used in the present study showed essentially the same transition temperatures [12].

3. Results

3.1. *The assignment of the spectral lines*

The ^{13}C N.M.R. spectra observed at ambient temperature are shown in figure 1 for (*a*) the $CDCl_3$ solution, (*b*) the solid-state CP/MAS, and (*c*) the dipole dephasing spectra of 5*BBCOOBO7. The assignments of the solution spectrum was made by consulting the data in our Spectral Database System (SDBS) constructed by our laboratory [13, 14], as shown in figure 1.

The individual lines of the solid-state spectrum of 5*BBCOOBO7 are generally well separated, and the assignments of the peaks may be made by comparing the solution and the dipole dephasing spectra. In the latter, one can usually observe only the resonances from quaternary carbons and mobile carbons such as methyl groups, whereas the other signals decay during the delay time before the data acquisition due to the strong dipolar coupling with protons. In addition to those of one carbonyl, six aromatic quaternary and three methyl carbons, dipole dephasing spectrum of 5*BBCOOBO7 contains the signals for CH_2(*3**) and CH(*2**) of the chiral side chain which are reasonably expected to be more mobile than the alkoxy methylenes. When the signal positions and the relative intensities in the side chain region are compared with the solution spectrum, the individual lines in the solid state do not always correspond to those in the solution spectrum in figure 1. Among them, some lines are

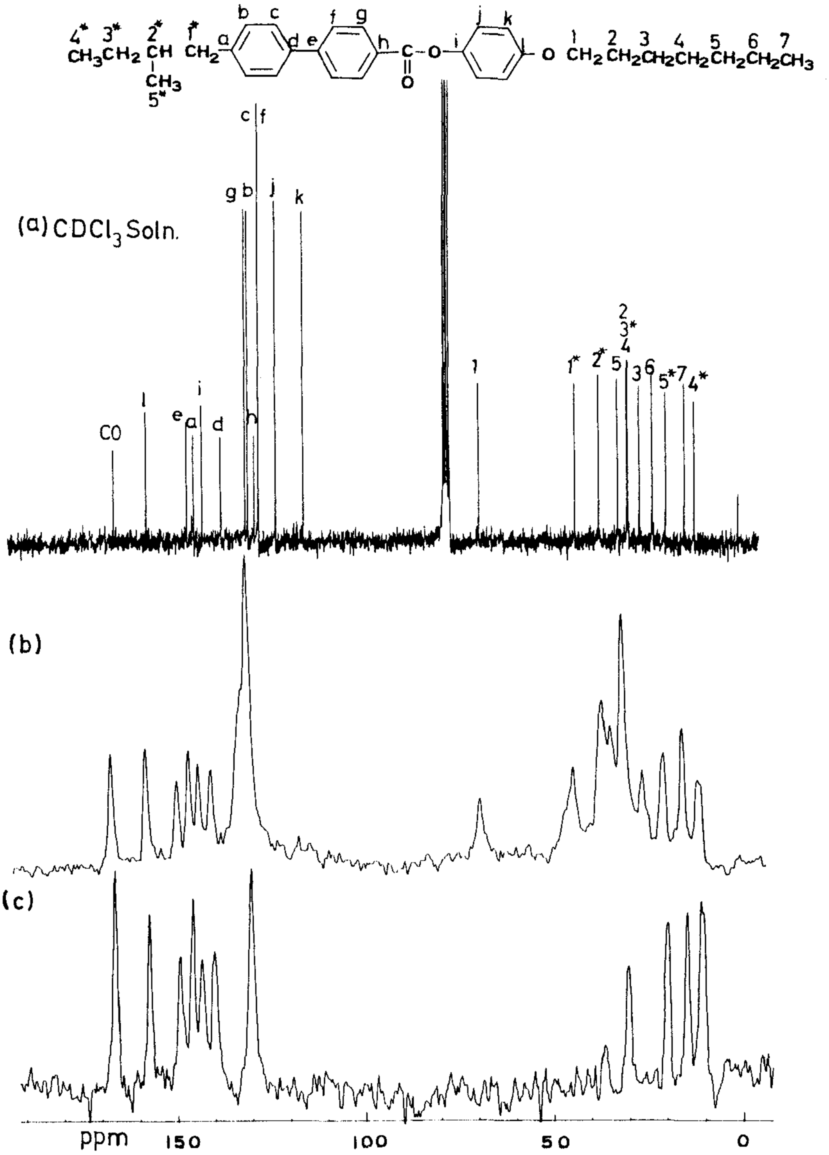

Figure 1. The ^{13}C N.M.R. spectra of 5*BBCOOBO7 for (*a*) the $CDCl_3$ solution, (*b*) the CP/MAS and (*c*) the dipole dephasing measurements at the ambient temperature. The assignments are shown for the $CDCl_3$ solution spectrum.

removed and easily assigned. The residual several peaks which are for the carbons *2*, *3*, *4*, *5* in the alkoxy chain are difficult to make assignment. Here it is assumed that the deviations of the chemical shifts from the solution spectrum are small. Then the assignment for the carbons *3* and *5* can be fixed. Since the solution chemical shifts for the carbons *2* and *4* are similar, the tentative assignment is made by assuming the larger shift for carbon *2* because of the twisted structure around C_lH_2–C_2H_2 axis is given by the X-ray analysis [8].

The shift values for the solution and the solid-state spectra are compared at the ambient temperature and the induced chemical shifts in the solid state are summarized

The induced ^{13}C shifts (ppm) and T_1 (*s*) in the solid state.

Aromatic		Alkoxy chain			Chiral chain		
	shift		shift	T_1		shift	T_1
CO	0·2	1	−0·8	4·3	1*	0·1	1·0
a	1·0	2	2·4	3·0	2*	−0·7	–
b	−0.4	3	3·7	–	3*	0·5	–
c	2·5	4	0·6	–	4*	−0·6	0·8
d	2·3	5	2·6	–	5*	0·4	0·7
e	2·3	6	2·4	3·1			
f	2·5	7	0·2	1·4			
g	1·1						
h	1·3						
i	0·5						
l	−0·3						

in the table. A little larger lower field shifts (about 2·5 ppm) for the aromatic *c*, *d*, *e*, and *f* carbons are observed, which are located at the biphenyl ring adjacent to the inner bond. The temperature dependence of the chemical shifts is small for the aromatic and carbonyl carbons. In the side chain region, the induced ^{13}C shifts for the carbons in the chiral chain is small, while some carbons (*2*, *3*, *5* and *6*) in the alkoxy chain experience larger shifts (2·4–3·7 ppm) to the lower field by changing from the solution to the solid states and also by decreasing the temperature.

3.2. *Temperature dependent spectra*

It is surprising that in solid state spectrum, the number of spectral lines is too small to find the corresponding lines of the solution spectrum in the aromatic region. Especially in 110–125 ppm region, there are no signals. The lack of the signals are for the protonated carbons *k* and *j*, which are located at the ortho- and meta-positions to the alkoxy chain. The two carbons ortho to alkoxy or hydroxyl groups are known to be often non-equivalent and give two separate peaks in the solid state [15], and also the line broadening was observed for the liquid crystalline compounds [7]. The reason that these signals are not observed may arise from the effect of chemical exchange. To confirm this, we observe spectra at lower temperatures, which are shown in figure 2.

Upon decreasing the temperature, two broad signals begin to appear at about 10°C in the 110–125 ppm region. The positions of the peaks correspond to those of carbons *j* and *k* in the solution spectrum. When the temperature decreases, the signal of the carbon *k* becomes a little sharper (0°C), collapsed (−10°C), a broad doublet (−20°C), and a sharper doublet (−30°C), where the temperatures are only approximate. The spacing of the doublet is 5·1 ppm (256 Hz) and the width of each line of the doublet is about 60 Hz at −30°C. Since the spacing of the signal of the carbons *j* is smaller (1·8 ppm, 90 Hz) at −30°C, the change of the pattern is not so large but a similar behaviour can be observed. The spectral patterns depending on the temperature are the typical ones for the chemical exchange of two sites having equivalent population in the liquid state [16]. Thus, a simulation calculation was carried out to extract the correlation times in the temperature range between 10 and −30°C for the signal *k*. The simulated patterns are also shown in figure 2. The correlation times τ for these temperatures are about several ten ms. The Arrenius plot gives the activation energy of about 17 kJ/mol (4 kcal/mol). Since the spacing of the two lines for the carbons *j* is smaller, the simulation was not carried out. At temperatures higher than ambient temperatures the signals for the carbons *j* and *k* disappear.

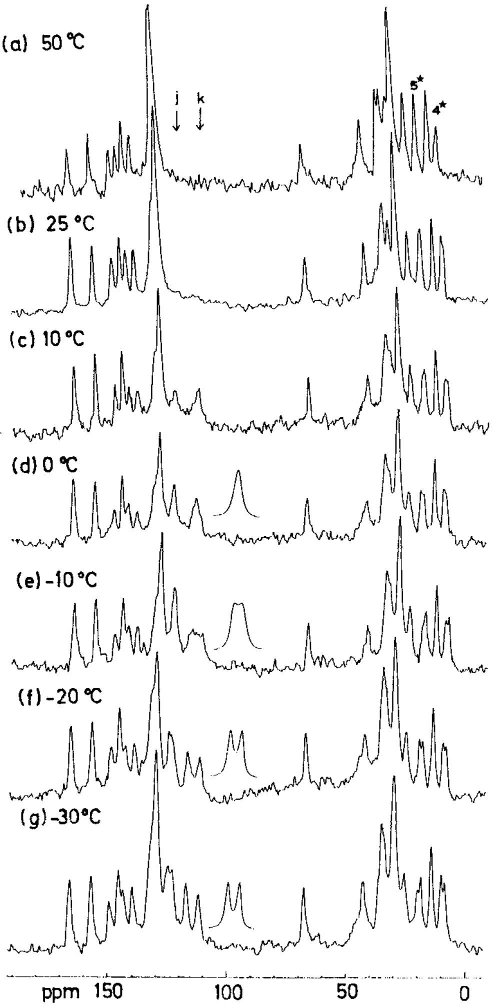

Figure 2. The temperature dependent spectra of 5*BBCOOBO7 observed by the CP/MAS method. The temperatures in the figure are expressed by the setting values, and the real sample temperatures are higher (about 20°C). The simulated patterns are also shown for the signals of the carbons *k*.

Below the ambient temperature, the two signals for the two methyl groups in the chiral chain also split into doublets, and the spacings of the both signals increase gradually, and at $-30°C$ are 1·65 and 1·48 ppm for carbons *5 ** and *4**, respectively. Here again the two-site chemical exchanges were assumed for these signals, and simulation calculations were carried out. The correlation times between 10 and $-30°C$ are also several 10 ms and the apparent activation energy is about 8 kJ/mol (2 kcal/mol) obtained by the Arrenius plot.

3.3. *Spin-lattice relaxation times*

The spin-lattice relaxation time T_1 measured in the solid state at the ambient temperature are also included in the table, where the T_1 values for the separated lines are obtained. The rough estimation of the T_1 of the aromatic carbons gave the values longer than 50 s, except for the carbons *j* and *k*, for which signals disappear.

4. Discussion

The existence of the chemical exchange process for 5*BBCOOBO7 is explicitly shown by the change of the ^{13}C N.M.R. line shapes for the carbons *k* and *j* depending on the temperature. There may be two mechanisms that can explain the process observed in the solid state. The first one is a 180° flip of the benzene ring inversion around $O–C_i–C_l–O$ axis. A second possibility may be the segmental motion of the alkoxy side chain. The flip angle of the oxygen atom in the alkoxy side chain may be less than 180°, but there is not a clear evidence for the segmental motion for the carbon *l* both in the line width and the ^{13}C shift. The similar temperature dependent patterns of the CP/MAS ^{13}C N.M.R. spectra were reported for an epoxy polymer [17], for which the activation energy was obtained to be 50 kJ/mol (12 kcal/mol), and the 180° phenylene ring inversion was assumed for the dynamic process. The line shape analysis of the ^{13}C chemical shift anisotropy was also reported for phenyl carbons of polycarbonates which undergo the 180° flip and the additional rotation [18].

In addition a number of ^{2}H N.M.R. studies have been reported about phenyl ring 180° flips for crystalline phenylalanine derivatives [19, 20], phenylalanines and tyrosines in membranes [21], tyrosine in peptides [22, 23], phenylalanines in proteins [19, 24] and aromatic rings in synthetic polymers [25, 26]. The correction times for the 180° flips obtained by the line shape analysis and the measurement of the relaxation times are between 10^{-4} and 10^{-9} s, and the activation energies are between 6·5 and 20 kcal/mol [23]. These investigations strongly suggest that the 180° flipping motions depend on the cooperative motions of the surrounding groups [18–26]. The activation energy of 5*BBCOOBO7 is 17 kJ/mol, which is a little smaller compared with the other systems hitherto studied. Nevertheless the 180° flipping of the benzene ring may be assumed for the dynamic process to interpret the temperature-dependent ^{13}C spectra observed for the signals *k* and *j*. It is not clear that the obtained value of the activation energy can be attributed to the pure 180° flipping motion. The relatively small values of the activation energy and the long correlation times strongly suggest that the ring flip accompanies with cooperative proesses in 5*BBCOOBO7 in the solid state.

There is another question why both the signals for the carbons *j* and *k* can not be observed at the ambient and the higher temperatures. If the chemical exchange between the two sites, i.e., the 180° flip of the benzene ring, is fast enough, the two sharp singlets should appear [16]. From the measurement of ^{2}H N.M.R. [19–26], two types of motions have been proposed for the phenyl ring dynamics, that is, a rapid, small-amplitude fluctuation and a slower 180° flip. It is possible that the rapid fluctuations may be accelerated for the carbons *k* and *j* before melting. Theoretically, the large line broadening can be assumed for the protonated carbons under the condition $\omega_1\tau \sim 1$, where $\omega_1 = \gamma B_1$ corresponds to the proton decoupling power and τ is the correlation time [27]; experimentally, the broad line was observed for adamantane in some temperature range [28]. In the present experiment, since ν_1 $(=\omega_1/2\pi)$ of the ^{1}H decoupler is about 50 kHz, $\tau \sim 10^{-6}$ s for $\omega_1\tau \sim 1$. The correlation times for the ring inversion are several ten ms between 10 and -30° C. and it may become shorter with increasing temperature. Actually, in the liquid crystalline compound PAA, the self-diffusion and the reorientation of the molecular axis in the solid state have been reported from the measurement of the relaxation timed of the ^{1}H N.M.R.

below the transition temperature [29, 30]. Then in 5*BBCOOBO7, the motions of the benzene ring in the order of 10^{-6} s can be assumed to bring the line broadenings and the disappearance of the signals. It should be remarked that the other signals are definitely observable in the same temperature range, including the quaternary carbons *i* and *l* adjacent to the carbons *j* and *k*. The flipping motion plus the rapid fluctuation about the axis O–C_i–C_l–O before melting may be important to form the mesophases.

We must discuss the possibility of intramolecular motions about the biphenyl ring. The ^{13}C chemical shifts of the internal carbons *c*, *d*, *e*, and *f* move to the lower field in the solid state in 5*BBCOOBO7. While the internal rotation can be assumed in the solution, the two benzene planes are fixed in the solid state with the twisted angles 51·5 and 52·2° for the two conformers [8]. Preliminary experiments for the homologues indicate that the upper field shifts are observed for the coplanar configuration of biphenyl ring [7]. It may be said that the ^{13}C chemical shift values are sensitive to the angels of the two benzene planes. Figure 3 shows that the temperature dependences of the chemical shifts are generally small for the aromatic carbons. If there were an internal rotation about the biphenyl ring, the angle would change, and its effect would appear in the chemical shifts. It may be concluded that intramolecular motions about the biphenyl ring are not so fast as observable in the N.M.R. time scale.

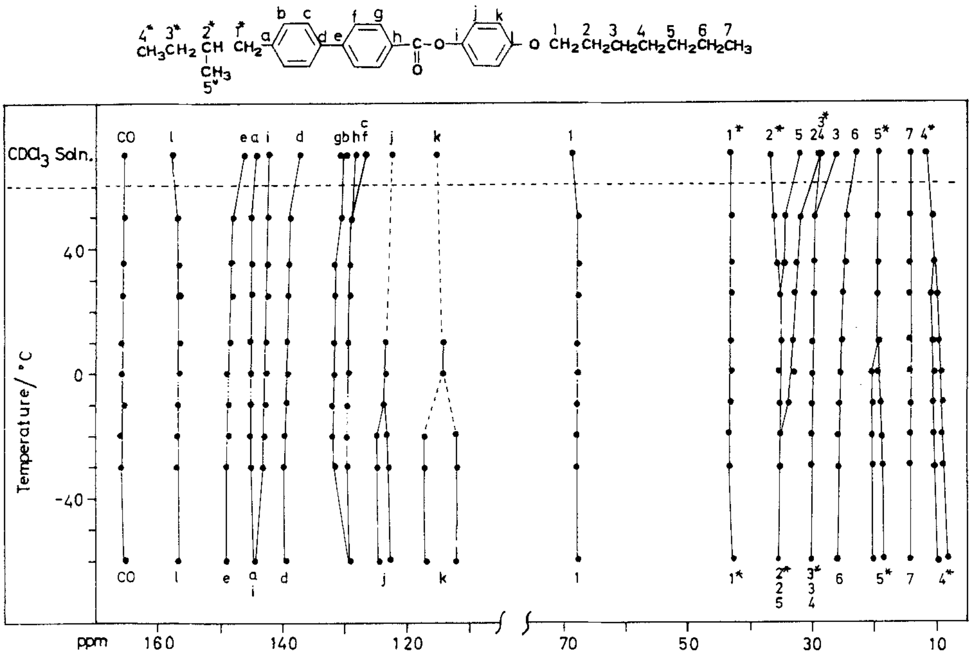

Figure 3. The temperature dependences of the ^{13}C shifts for each signals in the solid state. The shift values in $CDCl_3$ solutions are shown on the top.

These different molecular motions between the benzene ring and the biphenyl moiety are attributable to their different environments in the crystal structure. Biphenyl moieties have a closely stacked zig-zag arrangements along the *c* axis with C · · · C interatomic distances of 3·8 ~ 4·1 Å. On the other hand, although one side of the benzene ring has a close contact with a part of biphenyl moiety with C · · · C distances of 3·7 ~ 4·1 Å, the other side has only a close contact with the ends of the rather flexible aliphatic chains; interatomic relation in space due to the gap of the two molecules and the C · · · C distances of the benzene ring are larger on average rather than those of the biphenyl moiety [31].

From X-ray analysis, two different conformers exist in one unit cell and the most different portion of the two conformers is the spatial structure of the chiral chains. At ambient temperature, the ^{13}C N.M.R. spectrum in the solid state does not show a split pattern corresponding to the two conformers. By decreasing temperature, the splittings appear only in the signals of the methyl carbons in the chiral chain. Here it must be emphasized that these methyl signals can be observed in the dipole dephasing spectrum at −60°C. This fact indicates that there exists a rapid internal rotation of the methyl protons around the three-fold symmetry axis. It should be noted that the chiral chain is attached to the biphenyl ring and not to the benzene ring which underdoes the 180° flip. There are two possibilities to explain the temperature dependence of the signal splittings for the methyl carbons in the chiral chain. One is librational motions of the whole molecules, and the other is that the difference in the circumstances around the chiral chains become larger at the lower temperature and induces the chemical shift differences. The activation energy for the 180° flip of the benzene ring is rather low, which strongly suggests the existence of cooperative librational motions rather than the rigid crystal structure. In general, two types of the librational motions can be assumed; one is the cooperative torsional oscillations within the conformers and the other is the exchange between the conformers. Here the exchange means that one molecule changes a conformation and simultaneously another molecule changes the conformation within the unit cell. Since a definite splitting of the methyl signals can be observed, we may assume that the librational motion is the exchange between the two conformers in the unit cell. The apparent activation energy about 2 kcal/mol obtained from the signals of the methyl carbons which undergo rapid internal rotations would not come from the pure exchange energy between the two conformers. In the present study it is difficult to specify the modes of the molecular motions. Therefore we intend to study the dynamic properties more precisely by selectively deuterated compounds.

Vanderhart studied the influence of the molecular packing effects on the solid-state ^{13}C chemical shifts of *n*-alkanes and found that the lower field shift up to 1·3 ± 0·4 ppm from the solution may arise from the different crystal forms [32]. Similarly no larger shifts induced by the solidification has been found for the other organic molecules [15]. In 5*BBCOOBO7 the shifts induced are small and less than 0·7 ppm for the carbons in the chiral chain, but larger lower-field shifts are induced in the alkoxy carbons. The largest one is about 3·7 ppm for the carbon *3* which is much larger than those in *n*-alkanes. These larger values are consistent with the results of X-ray analysis, since the torsional angles between O–C_1 and C_2–C_3 axis are 62·7 and 64·6° for the two conformers. The large shifts are also observed for the carbons *5* and *6*. The origin of the shifts may be the stretched ordering of the alkoxy chain.

The segmental motions of the side chains in liquid crystals are a well-known phenomenon in the mesophases, and are clearly observed in the side chains of 5*BBCOOBO7 in the solid state from the measurement of T_1 values at the ambient temperature. We can assume that $\tau\omega_0 \gg 1$ and then the T_1 values are proportional to the correlation times. The thermal parameters of the X-ray analysis for the chain carbon atoms are also larger and their magnitudes are approximately related to $1/T_1$. Then the shorter T_1 values for the carbons in the chiral chain indicate faster segmental motions than those in the alkoxy chain in the solid state. The segmental motions, the 180° flip of the benzene ring, and the librational exchange between the two conformers may be highly related to the formation of the mesophases including the S_C^* phase.

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