



Solid-state ^{13}C NMR study of banana liquid crystals – 3: Alkyl-tail-group packing environments of an acute-angle bent-core molecule in the hexagonal columnar and cubic phases

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ABSTRACT

Solid-state ^{13}C nuclear magnetic resonance (NMR) measurements were performed on the hexagonal columnar and cubic phases of an acute-angle banana-shaped molecule, N(1,7)-S30. In the hexagonal columnar phase, three peaks appear at the NMR chemical shifts assigned to the internal methylene carbons of alkyl tails, indicating that the two alkyl tails have different packing structures, and one of the tails has two different conformations within a single molecule. Combined cross-polarization/magic-angle spinning and pulse saturation transfer/magic-angle spinning measurements show that one of the alkyl chains is located inside and the other is located outside the columnar structure. In the cubic phase, pulse saturation transfer/magic-angle spinning measurement shows that only one peak appears at the NMR chemical shifts assigned to the internal methylene carbons of alkyl tails, indicating that both of the alkyl chains are located outside the cubic structure.

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1. Introduction

To a great extent, the shape of liquid crystalline molecules determines the types of liquid crystals (LCs) in thermotropic LC systems, such as calamitic phases for rod-like molecules and discotic phases for disc-like molecules. Among them, bent-core (banana-shaped) LCs have attracted considerable attention, leading to the creation of unique banana LC phases as relatively young members of LC species [1,2]. To date, at least seven members of banana phases (B phases), designated B1 to B7, are generally acknowledged [3,4]. Most of the B phases, except for B6, are known to possess layered structures due to their steric effects originating in the bent molecular shape [5,6]. Therefore, the overall molecular shape is thought to be the key factor determining the mesomorphism of banana-shaped LC molecules.

The most effective way to adjust the bent molecular shape is to

vary the bending angle of the central bent-core moiety in the molecular scheme. We have revealed that to obtain banana phases, the central bending angle needs to be controlled to less than 140° [7]. On the other hand, a small bending angle (less than 120°) of central core derivatives was also developed. Based on 1,7-naphthalene diol as a central core, novel bent-core mesogens with a bending angle near 60° were investigated and revealed to form not only the well-known B4 phase but also an antiferroelectric SmAP_A phase [8,9]. More recently, our group indicated that these derivatives can also form switchable hexagonal columnar (Col_h) and cubic (Cub) phases when their carbon numbers in the terminal chains were relatively long [10–12]. Furthermore, the well-known polar banana phases of B2 and B7 were also observed in an acute-angle banana molecular system [13].

In our previous study, the novel Col_h phase of N(1,7)-S16 was investigated, and a typical type of molecular packing into the columns that maintains their smectic layered structure was elucidated on the basis of an analysis of two different environments of two terminal thio-alkyl chains [14].

Thus, in this study, we prepared the compound N(1,7)-S30, which possesses extremely long terminal chains with a carbon

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number (n) of 30 [11]. We performed solid-state ^{13}C NMR measurements to investigate the mesomorphic structures of novel Col_h phases originating from the difference in the length of the terminal chains by extending the carbon numbers to almost twice those in our previous system, N(1,7)-S16.

The material designated as N(1,7)-S30 (1,7-naphthalenebis[4-(4-triacontylthiophenyliminomethyl)]benzoate) is shown in Scheme 1.

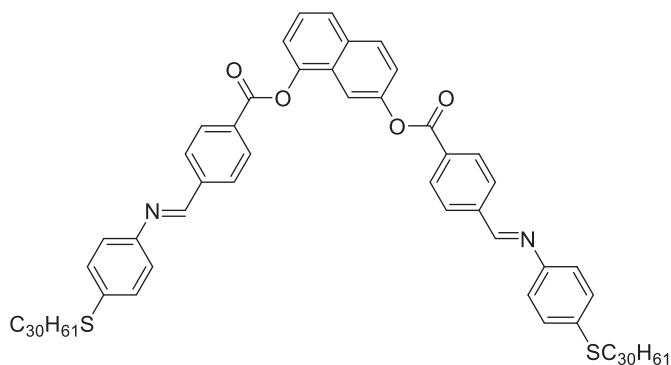
2. Experimental

N(1,7)-S30 was synthesized according to a previously reported method [8]. ^{13}C cross-polarization/magic-angle spinning (CP/MAS) and pulse saturation transfer/MAS (PST/MAS) NMR spectra were measured using a JNM EX-270 NMR spectrometer operating at a frequency of 67.9 MHz and equipped with CP/MAS and variable temperature (VT) accessories. The PST/MAS method uses single-pulse excitation with presaturation of proton spins, and it enhances the intensities of mobile carbons. The sample was placed in a zirconium cylindrical rotor and spun at speeds up to 4.5 kHz. The contact time was 2 ms, and the repetition time was 5 s. The ^1H radio frequency field strength was about 60 kHz for Hartmann–Hahn conditions and proton decoupling. The spectra were obtained by accumulating 10,000–30,000 scans to achieve a reasonable signal-to-noise ratio. The ^{13}C chemical shifts (δ) were indirectly calibrated with adamantane as an external standard (29.5 ppm relative to tetramethylsilane). Solution-state ^{13}C NMR spectra were recorded on a JEOL FT-NMR AL400 (400 MHz) spectrometer using tetramethylsilane as an internal standard. The NMR measurements for Col_h (126 °C) and Cub (140 °C) phases were performed upon heating process.

3. Results and discussion

Fig. 1 shows the differential scanning calorimetry (DSC) thermograms of N(1,7)-S30. Three sharp peaks are observed in both the heating and cooling curves. The sharp peaks at 124.4 °C, 131.0 °C, and 151.2 °C in the heating trace of N(1,7)-S30 correspond to the B4– Col_h , Col_h –Cub, and Cub–Iso phase transitions, respectively [11].

Before the solid-state NMR measurements, N(1,7)-S30 was heated to 170 °C (isotropic melt) and then cooled to room temperature at a rate of 1 °C/min. Fig. 2(b) and (c) show the solid-state VT ^{13}C CP/MAS NMR spectra of N(1,7)-S30 measured at room temperature (25 °C) and at 126 °C (Col_h phase). The solution-state NMR spectrum of N(1,7)-S30 is also shown as a reference in Fig. 2(a). Peaks of the carbonyl carbons of the ester moieties linking the central core and two side wings are observed at around



Scheme 1. N(1,7)-S30.

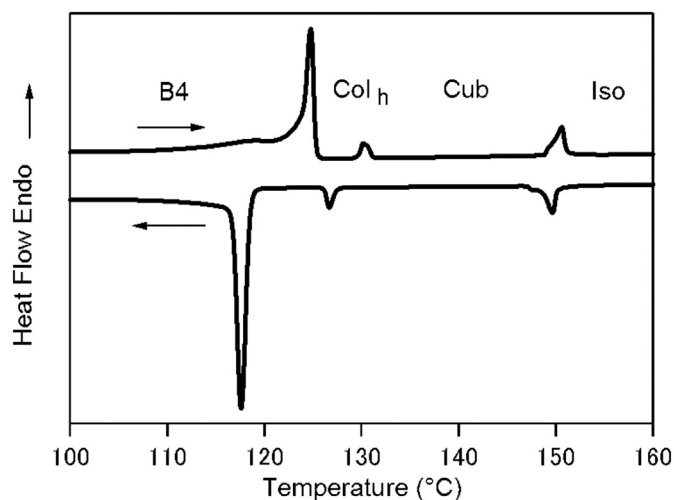


Fig. 1. Differential scanning calorimetry thermograms of N(1,7)-S30.

160 ppm. The peaks at 156, 110–150, and 10–75 ppm are assigned to the carbon atoms of the Schiff base group ($\text{C}=\text{N}$), aromatic rings, and aliphatic chains, respectively [15].

As reported previously [16], the peak splitting of the carbonyl carbons in banana-shaped molecules depends on the higher-order structure because the chemical shifts and molecular mobilities of the carbonyl carbons are sensitive to the packing structure. However, the peak intensities of the carbonyl carbons of N(1,7)-S30 are not high enough to reveal the molecular structure and mobility. Therefore, we focus on the signals at 20–40 ppm attributed to the methylene carbons in the thio-alkyl tails. The ^{13}C chemical shifts of methylene carbons are known to be sensitive not only to the conformation, but also to the packing structure (or interchain interactions) [17,18]. Therefore, the chemical shifts and molecular mobilities of the methylene carbons contain information on the packing structures of the thio-alkyl tails of the banana-shaped molecules.

3.1. Hexagonal columnar phase

Fig. 3 shows the CP/MAS and PST/MAS spectra of the N(1,7)-S30 banana-shaped molecule at 126 °C (Col_h phase). The spectra in the methylene carbon peak region of 20–40 ppm were deconvoluted by computer simulations using a Gaussian function, as shown in Fig. 4. The assignments of the alkyl tail were made according to *ab initio* chemical shift calculations for model molecules, as shown in Fig. 5. The deconvoluted peak intensities, chemical shifts, half-widths, and peak intensity ratios, along with their assignments, are listed in Table 1. As reported [11], the hexagonal columnar phase of N(1,7)-S30 is formed by a hexagonal packing of cylindrical columns composed of enclosed smectic layers [10], as illustrated in Fig. 6. A glance at this structure reveals that the alkyl tails are present in at least two different environments, i.e., in the outer and inner parts of the aromatic column. Three peaks (c, d, and e) in Fig. 4 are observed between 30.5 and 32.4 ppm at 126 °C (Col_h phase) in both the CP/MAS and PST/MAS spectra and are assigned to the internal methylene carbons. The numbering of the methylene and methyl carbons is shown in Fig. 5. A comparison of the CP/MAS and PST/MAS spectra observed at 126 °C shows that the internal methylene carbons exist in three different regions with different mobilities. The relative intensity of the high-field peak (c, 30.7 ppm) in the CP/MAS spectrum is lower than that of the high-field peak (c, 30.5 ppm) in the PST/MAS spectrum, and the relative

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