Bull. Chem. Soc. Jpn., 61, 2569—2571 (1988)

Solid-State ^{2}H NMR Study of Discotic Benzenehexayl Hexaheptanoate. Conformational Transition of Alkyl Side Chains

Hirokazu Toriumi,* Toru Shimmura, Hiroshi Watanabe, and Hazime Saitô†
Department of Chemistry, College of Arts and Sciences, University of Tokyo,
Komaba, Meguro-ku, Tokyo 153
†Biophysics Division, National Cancer Center Research Institute,
Tsukiji 5-chome, Chuo-ku, Tokyo 104
(Received January 21, 1988)

A ^{2}H NMR study of discotic benzenehexayl hexaheptanoate carrying perdeuterated alkyl side chains (BH7-d_{78}) is reported. Solid-state ^{2}H NMR measurements reveal that the conformational transition of the heptanoate chains takes place at 230 K from nearly static to mobile state. The chains above 230 K undergo flip-flop type reorientational motion, with the degree increasing upon heating. This temperature coincides with the solid-to-solid phase transition temperature, indicating that the phase transition takes place accompanied by the conformational melting of the flexible alkyl side chains. A spectrum measured in the discotic mesophase is also reported.

Extensive efforts have been devoted to characterize the conformational properties of alkyl chains appended to liquid crystalline molecules. In particular, their effects on the structure and stability of liquid crystals have been of both theoretical and practical interest. It is now generally recognized that the chain flexibility has a major contribution to the entropy of melting, hence it exerts significant influence on the phase transition behavior of liquid crystals. The deuterium NMR (^{2}H NMR) has emerged during the course of these studies as a powerful technique for investigating the conformational and dynamic properties of molecules in the mesomorphic state.[1,2] Yet, so far, only little is known about the alkyl chain conformation in the solid state and therefore its effect on the solid to liquid crystal phase transition is still open to debate.

For a homologous series of disc-like liquid crystals, benzenehexayl hexaalkanoates (BHn), $C_6(OCOC_{n-1}H_{2n-1})_6$, Sorai et al.[3–5] have carried out heat capacity measurements and shown that these compounds undergo a series of solid-state phase transitions before forming the discotic mesophase. These transitions are ascribed to the conformational melting of pendent alkyl chains, and the formation of the discotic mesophase of BHn is suggested to be a phenomenon appearing as one stage of successive phase transition driven by the side-chain conformational changes. In this communication, we report a solid-state ^{2}H NMR study of benzenehexayl hexaheptanoate (BH7) and show how the conformational melting of flexible alkyl chains proceeds in the solid phases.

Experimental

The sample of BH7-d_{78}, carrying perdeuterated heptanoate chains, was synthesized from tetrahydroxy-*p*-benzoquinone and heptanoic-d_{13} acid (MSD isotopes) according to the published method.[6,7] The reaction product was purified by repeated recrystallization from absolute ethanol and dried under vacuum to give white needle crystals of BH7-d_{78}. Solid-state ^{2}H NMR spectra were recorded on a Bruker CXP-300 spectrometer at 46.07 MHz using the quadrupole echo pulse sequence ($90^\circ_{\pm x}$-τ-90°_y-τ-echo) with a 90° pulse duration of 4.0 μs and a delay time τ=50 μs. Typically 100—200 spectra were accumulated with a repetition time of 0.2—0.5 s. The ^{2}H NMR spectrum of BH7-d_{78} in the mesomorphic state was measured by a JEOL GSX-270 spectrometer at 41.27 MHz using the single pulse sequence with a 90° pulse length of 5.0 μs. In both experiments, the temperature of the sample was controlled within ±1 °C with nitrogen gas flow.

Results and Discussion

Figure 1 shows the temperature dependence of the ^{2}H NMR spectrum of BH7-d_{78} in the solid state. The spectra at low temperatures consist of superposition of two axially symmetric quadrupolar powder patterns. The outer component is assigned to the methylene deuterons of pendent heptanoate chains and the inner component is assigned to the methyl deuterons. Although the parallel shoulders of the outer powder component (arising from methylene deuterons with C–D bond vectors oriented parallel to the field direction; θ=0° orientation) are lost outside of the spectrum, the perpendicular peaks (corresponding to θ=90° orientation) are clearly resolved with a peak separation of 123 kHz. Since a rigid-limit axially-symmetric powder spectrum of polycrystalline sample appears as superposition of properly weighted quadrupolar doublets, each of which has a spacing[8]

$$\Delta\nu = \frac{3}{2}\,\frac{e^2qQ}{h}\,P_2(\cos\theta) \tag{1}$$

(e^2qQ/h is the quadrupolar coupling constant), the separation between perpendicular peaks (θ=90°) measures a value $(3/4)(e^2qQ/h)$. The observed peak separation $\Delta\nu$=123 kHz yields e^2qQ/h=164 kHz, which is in good agreement with the literature value of the quadrupolar coupling constant of methylene deuterons.[8] The separation between parallel edges of the

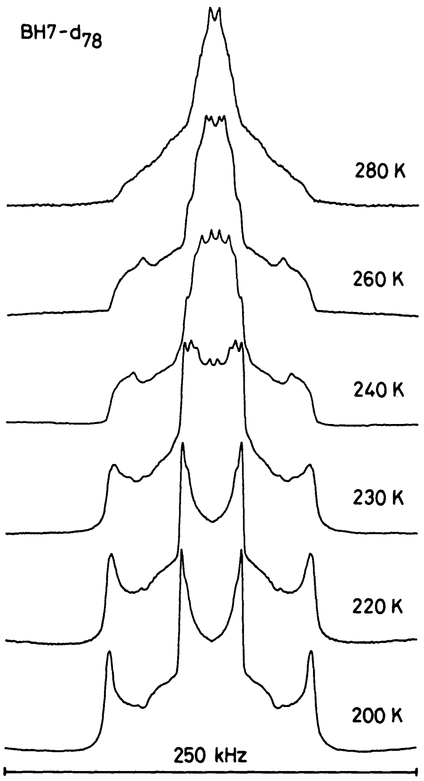

Fig. 1. Temperature dependence of solid-state ^{2}H NMR spectrum of BH7-d_{78} carrying perdeuterated heptanoate side chains.

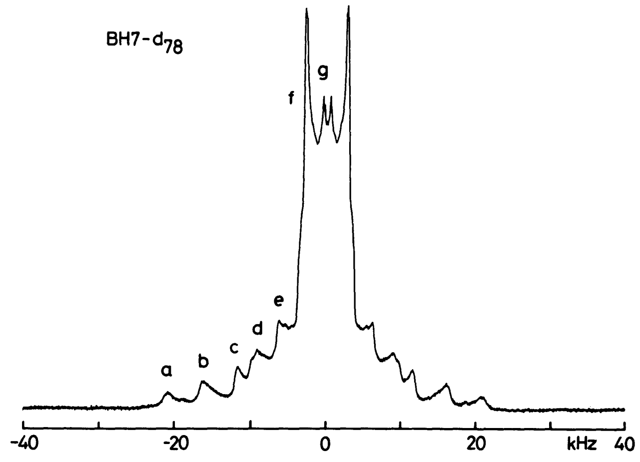

Fig. 2. ^{2}H NMR spectrum of BH7-d_{78} in the discotic mesophase at 354 K.

methyl powder pattern ($\Delta\nu$=71.8 kHz) is just twice as large as its perpendicular peak separation ($\Delta\nu$= 35.8 kHz) in accord with the prediction of Eq 1. If the terminal methyl group, having the tetrahedral geometry (with the C–C–D bond angle β=109.47°), undergoes rapid rotation about its C_3 symmetry axis, separation of peaks is scaled down by a factor $|(1/2)(3\cos^2\beta-1)|=1/3$. The observed peak separation (35.8 kHz) is however slightly smaller than the expected value (41.0 kHz). This additional reduction in $\Delta\nu$ is indicative of either a departure of the methyl group structure from the ideal tetrahedral geometry or the presence of librational motions of the methyl symmetry axis.[9,10] Nevertheless, for the heptanoate chain as a whole, the degree of reorientational motion should be quite low (or the rate is slow on the ^{2}H NMR frequency scale), since the quadrupolar coupling constant observed for the inner methylene deuterons is large and reproduces its rigid-limit value.

Above 230 K the spectral shape changes substantially. A sizable build-up of intensity occurs in the central part of the spectrum, while the intensity of the outermost peaks is decreased and the linewidth is broadened. The 230 K spectrum shows several pairs of powder-pattern peaks in the central pattern indicating that the inner methylene segments aquire the reorientational freedom at this temperature. The narrowing of the central spectral component proceeds continuously with increasing temperature, and eventually results in the line shape such as that observed at 280 K. This pattern, i.e., the biaxial powder pattern which would arise when the C–D bond axis jumps rapidly between discrete sites, suggests the flip–flop type motion of the heptanoate chain. In this connection, it is noteworthy that the 280 K spectrum still preserves a broad component with a separation between extreme edges of ca. 110 kHz. The coexistence of spectral components with widely varying quadrupolar coupling constants is consistent with the flip–flop motion of the chain suggested above; namely, the methylene segment undergoes an increasing degree of motion as it approaches to the chain terminal.

The onset of the aforementioned changes in the ^{2}H NMR line shape was observed at 230 K. This temperature coincides with the first-order solid-to-solid phase transition temperature (230.81 K) determined calorimetrically by Sorai and Suga.[4] They have also reported the results of infrared measurements and pointed out that the molecular and crystal structures are different between these two solid phases. Our present ^{2}H NMR studies clearly demonstrate that the melting of the alkyl chain conformation takes place at this temperature from nearly static state (the chain being in the lowest energy all-trans conformation) to mobile state (undergoing the flip–flop motion). The spectral shape remains essentially unchanged above room temperature (except for the occurrence of continuous narrowing) until the transition to the discotic mesophase at 353.79 K.

Shown in Fig. 2 is the ^{2}H NMR spectrum of BH7-d_{78} recorded in the discotic mesophase. For the measurement the sample was first heated to the isotropic liquid phase (T_{iso}=359.28 K), then cooled down slowly to turn into the mesophase. The spectrum shows five discrete quadrupolar doublets (a—e) with $\Delta\nu$ values ranging from 42 to 12 kHz, which are attributable to the five methylene groups. The innermost doublet (g) with $\Delta\nu=0.96$ kHz is then assigned to the terminal methyl group by taking account of the signal intensity. These discrete quadrupolar doublets arise from BH7-d_{78} molecules oriented uniaxially in the field. Elucidation of the average alkyl chain conformation from the $\Delta\nu$ pattern is possible in terms of the theories described previously.[11,12] However, these doublet patterns are dominated by an intense powder-like component (f). Its peak separation $\Delta\nu=5.6$ kHz is comparable to a value $\Delta\nu=6.6$ kHz observed for peaks in the solid-state spectrum at 280 K in Fig. 1. Obviously, there should coexist unoriented molecules. Corresponding ^{2}H NMR spectra reported for triphenylene-type discotic liquid crystals exhibit only discrete quadrupolar doublets.[13,14] The coexistence of "oriented" and "unoriented" components in our spectrum suggests that the diamagnetic anisotropy of the central benzene core of BH7-d_{78} is not larger than that of the triphenylene core and thereby cannot suffice to cause homogeneous orientation.

In summary, we have demonstrated that the solid-state deuterium NMR is successful in analyzing the conformational properties of flexible alkyl chains appended to liquid crystalline molecules. The observed ^{2}H NMR line shape shows marked differences between phases, reflecting the changes in the mode and degree of reorientational motions of alkyl side chains. Lifshitz, et al.[15] have recently carried out ^{2}H NMR measurements of BH6 (a hexanoate homologue of BH7) and shown that the hexanoate side chains undergo very similar solid-state conformational transitions. Thus, the sequential melting of side-chain conformation at the phase transition appears to be a general characteristic of this class of disc-like liquid-crystalline molecules.

We thank Professor M. Sorai of Osaka University for directing our attention to this problem and for valuable informations concerning the sample synthesis. We are also grateful to JEOL for measuring the spectrum in Fig. 2.

References

1) "Nuclear Magnetic Resonance of Liquid Crystals," ed by J. W. Emsley, D. Reidel, Dordrecht (1985).

2) J. W. Doane, "Magnetic Resonance of Phase Transition," ed by F. J. Owens, C. P. Poole, and H. A. Farach, Academic Press, New York (1979).

3) M. Sorai, K. Tsuji, H. Suga, and S. Seki, *Mol. Cryst. Liq. Cryst.*, **59**, 33 (1980).

4) M. Sorai and H. Suga, *Mol. Cryst. Liq. Cryst.*, **73**, 47 (1981).

5) M. Sorai, H. Yoshioka, and H. Suga, *Mol. Cryst. Liq. Cryst.*, **84**, 39 (1982).

6) I. E. Neifert and E. Bartow, *J. Am. Chem. Soc.*, **65**, 1770 (1943).

7) A. J. Fatiadi and W. F. Sager, *Org. Synth.*, Coll. Vol. 5, 595 (1973).

8) H. H. Mantsch, H. Saitô, and I. C. P. Smith, *Prog. Nucl. Magn. Reson. Spectrosc.*, **11**, 211 (1977).

9) L. S. Batchelder, C. H. Niu, and D. A. Torchia, *J. Am. Chem. Soc.*, **105**, 2228 (1983).

10) H. Saitô, R. Tabeta, A. Kuzuhara, and T. Asakura, *Bull. Chem. Soc. Jpn.*, **59**, 3383 (1986).

11) E. T. Samulski and H. Toriumi, *J. Chem. Phys.*, **79**, 5194 (1983).

12) B. Janik, E. T. Samulski, and H. Toriumi, *J. Phys. Chem.*, **91**, 1842 (1987).

13) D. Goldfarb, Z. Luz, and H. Zimmermann, *J. Chem. Phys.*, **78**, 7065 (1983).

14) D. Goldfarb, E. Lifshitz, H. Zimmermann, and Z. Luz, *J. Chem. Phys.*, **82**, 5155 (1985).

15) E. Lifshitz, D. Goldfarb, S. Vega, Z. Luz, and H. Zimmermann, *J. Am. Chem. Soc.*, **109**, 7280 (1987).