

^1H Nuclear Magnetic Resonance Study of an Incommensurate-Commensurate Phase Transition in a Dimesogenic Liquid Crystal

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^1H nuclear magnetic resonance (NMR) was employed in order to probe an incommensurate-commensurate phase transition in a dimesogenic liquid crystal, *N*-[4-(6-cholesteryloxycarbonyl) pentyloxy]-4-*n*-butylazobenzene (KI5A). The recrystallization and the isotropic phase transitions exhibited a discontinuous first-order nature in the ^1H NMR spin-lattice (T_1) and in the spin-spin relaxation time (T_{2E}) measurements, and an incommensurate smectic *A* (S_{Ainc}) to commensurate helical smectic *C* (S_C^*) liquid crystalline phase transition was marked by a discontinuity in the NMR line splitting representing the orientational order. Furthermore, T_1 and T_{2E} showed distinct temperature dependencies in the S_{Ainc} phase and in the S_C^* phase.

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Liquid crystals possessing molecular orientational order have been attracting considerable attention for their scientific interest and practical applications. While early liquid crystals consisted of a single rigid core (mesogen) and a flexible chain part, dimesogenic liquid crystals containing two rigid cores have shown peculiar phenomena such as ferroelectricity and incommensurability [1–10]. While various means of investigation have been employed in order to study liquid crystals, nuclear magnetic resonance (NMR) has proven to be very useful for understanding their phase transitions and molecular orientational order.

Thermotropic liquid crystals can have nematic, smectic and cholesteric phases at different temperatures [1–7]. Unlike the nematic phase possessing only orientational order, the smectic phase additionally possesses a minimal positional order. The director is parallel to the planar normal in the smectic *A* (S_A) phase, and it is tilted in the smectic *C* (S_C) phase. The S_C phase in which the molecules possess chirality is dubbed S_C^* .

In this work, we have employed ^1H NMR to investigate peculiar incommensurate-commensurate liquid crystalline phase transitions in a dimesogenic liquid crystal, *N*-[4-(6-cholesteryloxycarbonyl) pentyloxy]-4-*n*-butylazobenzene (KI5A), showing a crystalline in-

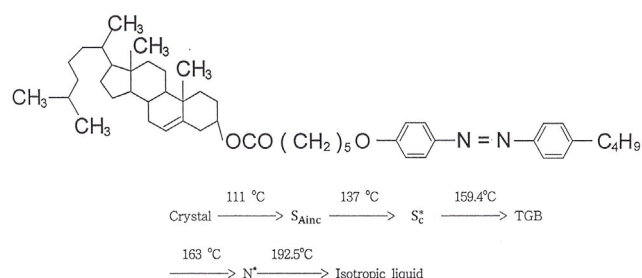


Fig. 1. Structure of the *N*-[4-(6-cholesteryloxycarbonyl) pentyloxy]-4-*n*-butylazobenzene (KI5A) dimesogenic liquid crystal. The phase transition sequence is also shown.

commensurate smectic *A* (S_{Ainc}), commensurate helical smectic *C* (S_C^*), twisted grain boundary (TGB) and cholesteric (N^*) liquid crystalline phases, as well as an isotropic phase [8,9]. The phase transitions in KI5A occur at 111, 137, 159.4, 163 and 192.5 °C, respectively (see Fig. 1) [10].

The dimesogenic liquid crystal KI5A was synthesized as reported in the literature [8–10]. The laboratory-frame ^1H NMR measurements were made at temperatures from room temperature to 210 °C by using a home-built pulsed spectrometer operating at 45 MHz [5–7,11,12]. The spin-lattice relaxation time (T_1) was measured by using the inversion recovery method, and solid echo

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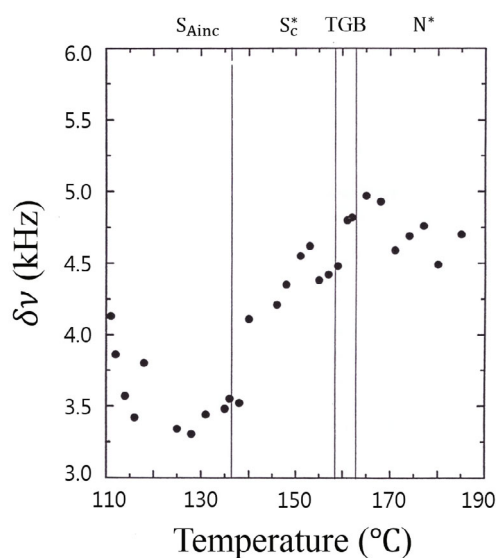


Fig. 2. ¹H NMR line splitting in the liquid crystalline phases of KI5A as a function of temperature.

pulse sequences ($90^\circ_x - \tau - 90^\circ_y$) were employed for the measurement of the spin-spin relaxation time (T_{2E}). The NMR lineshapes were obtained by Fourier-transforming the free-induction decay (FID) signals.

The ¹H NMR lineshape was well fitted by using a single Lorentzian component in the crystalline and the isotropic phases and by using two separate Lorentzian line components in the liquid crystalline phases. The line splitting $\delta\nu$, *i.e.*, the separation between two line components, in the liquid crystalline phases arises from the dipole-dipole interaction of adjacent protons in the benzene rings and is related to the orientational order parameter S as $\delta\nu = 6\mu_H r^{-3}(\frac{3}{2}\cos^2\phi - \frac{1}{2})S$. Here, r is the inter-proton distance and ϕ is the angle between the para axis and the major molecular axis [13]. Figure 2 shows the line splitting in the liquid crystalline phases as a function of temperature. Interestingly, the incommensurate-commensurate ($S_{Ainc} - S_C^*$) phase transition is marked by a discontinuity in the orientational order as sensitively reflected by the NMR line splitting. In other words, the sudden change from the incommensurate phase to the commensurate phase is accompanied by a sudden increase in the orientational order.

The nuclear spin-lattice relaxation in liquid crystals may mostly be understood by using the intramolecular dipole-dipole interaction based on orientational order fluctuation, local molecular reorientation and translational self diffusion [14, 15]. Figure 3 shows the temperature dependence of the ¹H NMR spin-lattice relaxation time, displaying changes associated with the phase transitions. A discontinuity accompanying a first-order transition takes place at the recrystallization and at the isotropic phase transition temperatures, which may be attributed to a sudden change in active molecular mo-

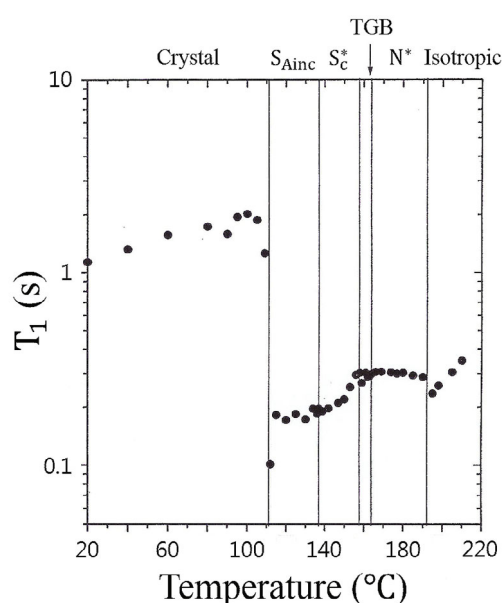


Fig. 3. ¹H NMR spin-lattice relaxation time (T_1) of the dimesogenic liquid crystal KI5A as a function of temperature.

tions such as fast rotational or translational diffusion at the phase transition temperatures. The spin-lattice relaxation shows little temperature dependence in the incommensurate S_{Ainc} phase, apparently indicating little change in the director's fluctuations. On the other hand, T_1 showed a distinct behavior in the commensurate S_C^* phase, increasing with temperature. Thus, quite distinct molecular motions take place in the incommensurate (S_{Ainc}) phase and in the commensurate (S_C^*) phase.

Figure 4 shows the spin-spin relaxation time as a function of temperature, reflecting the slow molecular dynamics [16]. As in the case of the temperature-dependent T_1 , the recrystallization and isotropic phase transitions exhibited a discontinuity. On the other hand, the temperature derivative of T_{2E} changed its sign at the $S_{Ainc} - S_C^*$ liquid crystalline phase transition, increasing with temperature below the transition temperature and decreasing with temperature above it. Thus, quite distinct spin-spin interactions take place in the incommensurate S_{Ainc} phase and in the commensurate S_C^* phase. ¹H magic-angle spinning (MAS) NMR in the rotating frame may be useful in distinguishing between the protons in the cholesterol and alkyl groups and the benzene parts of the liquid crystal system.

In summary, the *N*-[4-(6-cholesteryloxycarbonyl)pentyl]oxy]-4-*n*-butylazobenzene (KI5A) dimesogenic liquid crystal has been studied by using ¹H NMR lineshape and nuclear spin relaxation time measurements. The incommensurate smectic *A* (S_{Ainc}) to commensurate smectic *C* (S_C^*) liquid crystalline phase transition was sensitively reflected by a discontinuity in the NMR line splitting, which is indicative of the orientational

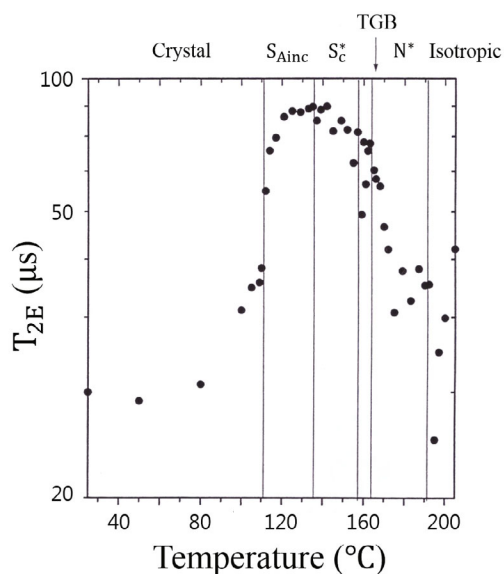


Fig. 4. ^1H NMR spin-spin relaxation time (T_{2E}) of the dimesogenic liquid crystal KI5A as a function of temperature.

order. The spin-lattice and the spin-spin relaxation times, which exhibited a discontinuity at the recrystallization and the isotropic phase transitions, showed distinct temperature dependencies at temperatures below and above the incommensurate-commensurate phase transition temperature.

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