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## Liquid Crystals

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Kazuteru Tabayashi

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# Preliminary communication

## Natural abundance $^2\text{H}$ NMR for liquid crystal studies: deuterium isotope effect on microscopic order

KAZUTERU TABAYASHI and KAZUYUKI AKASAKA\*

The Graduate School of Science and Technology, Kobe University,  
1-1 Rokkodai-cho, Nada-ku, Kobe 657-8501, Japan

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Quadrupolar splittings in the  $^2\text{H}$  NMR spectrum obtained from a sample with natural abundance  $^2\text{H}$  isotope are shown to be considerably different from those obtained from specifically deuteriated samples in an example of 4'-propyl-4-(3,4-difluorophenyl)bicyclohexane. The result indicates that the molecular ordering may be altered significantly by selective deuteration, and shows the importance of natural abundance  $^2\text{H}$  measurement in liquid crystal studies.

Deuterium NMR ( $^2\text{H}$  NMR) is a frequently used technique for the study of microscopic order in liquid crystals [1, 2]. Because the abundance of the deuterium in nature is extremely low (0.015%), the procedure of specific deuteration has been followed to measure  $^2\text{H}$  NMR spectra. Here, the isotope effect is usually neglected, and the value of a property obtained from a  $^2\text{H}$ -labelled sample is considered to represent that of the native liquid crystal [1, 2]. Recently, however, it was reported that there is some difference in the dielectric anisotropy between 4'-propyl-4-(3,4-difluorophenyl)bicyclohexane and its deuteriated analogues (see figure 1) [3-6]. The result suggested that there may be some change in molecular ordering induced by the deuterium substitutions. In this report, we wish to examine in the same system, by measurements of deuterium quadrupolar splittings, whether the molecular ordering is indeed affected by specific deuteration.

Recently, we have shown that the measurement of  $^2\text{H}$  NMR spectra is possible on liquid crystals with natural abundance deuterium isotope [7]. In this case, the abundance of the  $^2\text{H}$  isotope is so low that the  $^2\text{H}$  NMR signals monitoring the microscopic ordering may be safely taken to represent the original property of the liquid crystal. The materials 4'-propyl-4-(3,4-difluorophenyl)bicyclohexane (compound 1) and its deuteriated analogues (figure 1) were gifts from Dainippon Ink & Chemicals, Inc. Compound 2 was deuteriated at positions near the side chain, while compound 3 was deuteriated at

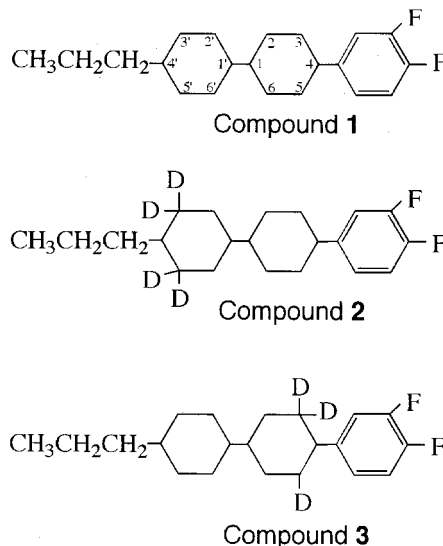


Figure 1. Structure of 4'-propyl-4-(3,4-difluorophenyl)bicyclohexane (compound 1) and its deuteriated analogues, 4'-propyl-4-(3,4-difluorophenyl)-3',3',5',5'-tetra-deuterio-bicyclohexane (compound 2) and 4'-propyl-4-(3,4-difluorophenyl)-3,3,5-trideuterio-bicyclohexane (compound 3).

positions near the benzene ring. Moreover, compound 3 has three deuterons: two at axial positions and the other at the equatorial position in the cyclohexane ring. The non-equivalent deuteration comes from the synthetic path way in which a cyclohexene derivative compound is hydrogenated with  $\text{H}_2$  gas with Pd on carbon as catalyst [4]; hydrogen is then introduced into the equatorial position. Natural abundance  $^2\text{H}$  NMR spectra

\* Author for correspondence.

were recorded on a Bruker DMX-750 spectrometer (115.15 MHz for  $^2\text{H}$ ) under proton decoupling at temperatures below  $80^\circ\text{C}$ . The temperature of the sample was controlled by the temperature control unit supplied by Bruker which was independently calibrated with a thermistor sensor (Takara D641 type 1/100) to a precision of  $\pm 0.2^\circ\text{C}$ . The temperature variation over 24 h was well within  $\pm 1^\circ\text{C}$ . Spectra with acceptable signal-to-noise ratios were obtained by signal accumulation, typically for 20 h for samples with natural abundance deuterium isotope, but for 1 min for deuterium-enriched samples.

Figure 2(a) shows the natural abundance deuterium NMR spectrum of 4'-propyl-4-(3,4-difluorophenyl)bicyclohexane (compound 1) obtained under proton decoupling.

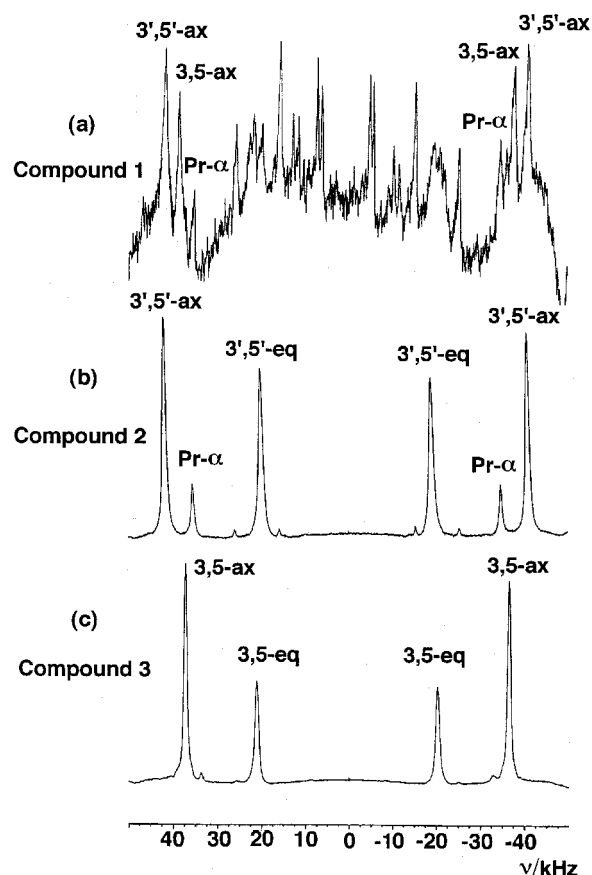


Figure 2. Natural abundance  $^2\text{H}$  NMR spectra of compound 1 (a);  $^2\text{H}$  NMR spectra of compound 2 (b) and compound 3 (c); recorded at 115.15 MHz at  $75^\circ\text{C}$  ( $T_c = 49^\circ\text{C}$ ) under proton decoupling. The spectra were obtained after accumulation of 200 000 scans for compound 1, and only 4 scans for compounds 2 and 3. Marks Pr- $\alpha$ , 3',5'-ax and 3',5'-eq correspond to the propyl  $\alpha$ -methylene, cyclohexyl 3',5'-axial, and cyclohexyl 3',5'-equatorial deuterons of compound 2, respectively. Marks 3,5-ax and 3,5-eq correspond to the cyclohexyl 3,5-axial and 3,5-equatorial deuterons of compound 3, respectively.

We note many pairs of lines split by quadrupolar couplings. Figures 2(b) and 2(c) show  $^2\text{H}$  NMR spectra of compounds 2 and 3, respectively. In figure 2(c), we assigned the highly intense outer doublet to the axial deuterons and the less intense inner doublet to the equatorial deuteron, because compound 3 contains one equatorial deuteron and two axial deuterons. In figure 2(b), we found another low intensity doublet, assignable to the propyl  $\alpha$ -methylene deuterons that were introduced presumably as by-product when the deuterated cyclohexanone was alkylated by a Wittig reaction [4]. Indeed, in figure 2(b) the signal for the equatorial deuteron (3',5'-eq) is slightly lower in intensity than the signal for the axial deuteron (3',5'-ax) due to the transfer of deuteron from the former to the propyl  $\alpha$ -methylene.

The corresponding signals for propyl  $\alpha$ -methylene and cyclohexyl axial deuterons in the natural abundance  $^2\text{H}$  NMR spectrum, figure 2(a), could be identified by comparing their resonance positions with the signals in figures 2(b) and 2(c). Unfortunately, we could not identify the signals of the equatorial deuterons of the cyclohexyl ring in the natural abundance  $^2\text{H}$  NMR spectrum, because of the overlap of the signals in the corresponding region of the spectrum in figure 2(a). As a result, we decided to use the signals of the axial deuterons and propyl  $\alpha$ -methylene deuterons to examine possible isotope effects.

Figure 3 plots the quadrupolar splittings of the axial deuterons of the cyclohexyl ring and the propyl  $\alpha$ -methylene deuterons in compounds 1, 2 and 3 as functions of temperature between  $40$  and  $80^\circ\text{C}$ , well below  $T_c$  ( $124^\circ\text{C}$ ). Although the splittings of 3',5'-ax and Pr- $\alpha$  of compound 2 were almost the same as those of compound 1, the splitting of 3,5-ax of compound 3 became much smaller than that of compound 1. The result indicates that the quadrupole splitting of 3,5-ax in compound 1 is decreased by approximately 5 kHz (or the orientational order decreased by about 4%) at all temperatures by the deuteration in compound 3. The accuracy of measurement of the splittings is determined by the linewidths of the corresponding resonance lines which were on the order of 1 kHz, assuring that the observed change in the splitting, 5 kHz, is well beyond experimental error. The change in the orientational order would explain the decrease in dielectric anisotropy ( $\Delta\epsilon$ ) between compounds 1 ( $\Delta\epsilon = 6.1$ ) and 3 ( $\Delta\epsilon = 5.6$ ) [4, 8]. The results shown in figure 3 further indicate that the deuterium isotope effect is dependent on the position of the deuteration, e.g. in this case the effect is greater at 3,5-positions near the benzene ring than at 3',5'-positions near the side chain.

Although the change in quadrupole splitting by deuteration is shown above only for a single liquid

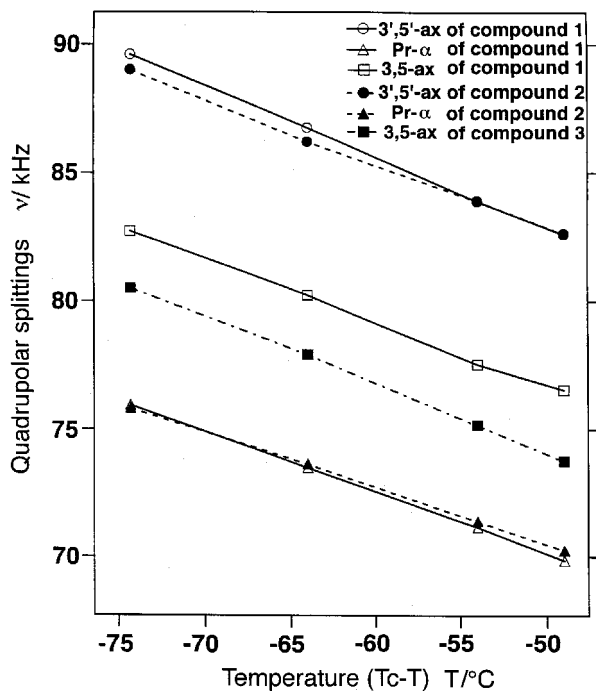


Figure 3. Plot of the observed quadrupolar splittings of the propyl  $\alpha$ -methylene and cyclohexyl axial deuterons against temperature. The open circle, square and triangle correspond to cyclohexyl 3',5'-axial, cyclohexyl 3,5-axial and propyl  $\alpha$ -methylene in compound 1, respectively. The full circle and triangle correspond to cyclohexyl 3',5'-axial and propyl  $\alpha$ -methylene in compound 2, respectively. The full square corresponds to cyclohexyl 3,5-axial in compound 3.

crystal compound and therefore its generalization may not be made at this moment, the result has shown that the microscopic order of a selectively deuterated liquid crystal can be considerably different from that of the

non-deuterated compound. Moreover, the effect is shown to be dependent on the site of deuteration. Thus the result of  $^2\text{H}$  NMR experiments performed on selectively deuterated compounds may not always represent correct ordering properties of the corresponding virgin liquid crystal. This result shows the merit and importance of carrying out natural abundance  $^2\text{H}$  NMR measurements in liquid crystal studies.

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