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Deuterium NMR analysis of dimer liquid crystals

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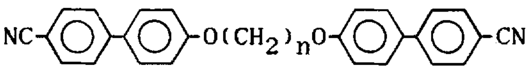
SUMMARY

Deuterium NMR measurements have been performed for dimer liquid crystals (DLC) having structures such as $NC\phi\phi\text{-}O(CH_2)_nO\text{-}\phi\phi CN$ (CBA) with n=9, 10. Fully deuterated CBAs with n=9 and 10 exhibit, respectively, three and four splittings in the D-NMR spectra. By using partially deuterated samples, the signals corresponding to the largest splittings were found to include contributions from the α- and β-CD_2 groups. The origins of the rest of the signals were elucidated by the RIS method previously established. Characteristic properties of the nematic mesophase were estimated for CBA-10. The results were found to be consistent with those of the previous analysis on Griffin et al.'s DLC.

INTRODUCTION

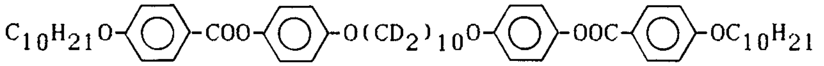
Thermodynamic properties of polymer liquid crystals (PLC) comprising a rigid mesogenic core and a soft-spacer in a repeat unit have been extensively studied. The orientational order parameter of the molecular axis is a primarily important structural criterion in characterizing the mesophase. Deuterium NMR technique has been proved to be useful in monitoring the average orientation of anisotropic molecules when they are properly labeled. In a previous paper,1) we have developed a method to elucidate molecular conformation of main-chain liquid crystals carrying deuterated flexible spacers by utilizing the information provided by the D-NMR method. In this treatment, the molecular axis of a conformer has been defined along the line connecting the centers of the neighboring mesogenic cores. Numerical values of the conformational statistical weight factors assigned to the individual bond rotations are adjusted so as to reproduce the observed profile of the D-NMR spectrum.

In this paper, we wish to report our recent experimental results of the deuterium NMR measurements on dimer liquid crystals (DLC) such as α,ω-bis(4,4'-cyanobiphenyloxy)alkane (CBA):



(I-n)

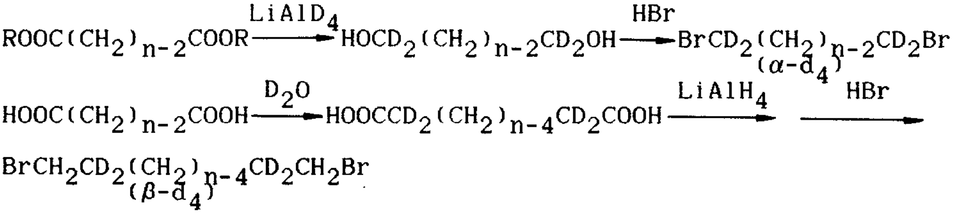
with n = 9 and 10. Physical properties of the CBA liquid crystals have been widely investigated.2-4) These compounds exhibit a thermotropic nematic liquid crystalline region over certain temperature range. Various thermodynamic quantities observed at the nematic-isotropic (NI) transition temperature are known to oscillate alternately with the number n of methylene units incorporated in the spacer. Because of the similarity in the thermodynamic characteristics, DLCs are often regarded as a model of main-chain PLCs. The results on DLC I-10 will be compared with those of Griffin et al.'s data[5] reported for an ether-type DLC such as


(II-10)

These two DLC samples differ with each other only in the chemical structure of the mesogenic core.

EXPERIMENTAL

CBA samples carrying a fully or partially deuterated spacer were synthesized from 4-hydroxy-4'-cyanobiphenyl and deuterated α,ω-dibromoalkanes according to Emsley et al.'s method.[2] The α,ω-dibromoalkanes specifically deuterated either at the α- or β-position were prepared by the following scheme:



$$ROOC(CH_2)_{n-2}COOR \xrightarrow{LiAlD_4} HOCD_2(CH_2)_{n-2}CD_2OH \xrightarrow{HBr} \underset{(\alpha\text{-}d_4)}{BrCD_2(CH_2)_{n-2}CD_2Br}$$

$$HOOC(CH_2)_{n-2}COOH \xrightarrow{D_2O} HOOCCD_2(CH_2)_{n-4}CD_2COOH \xrightarrow{LiAlH_4} \xrightarrow{HBr} \underset{(\beta\text{-}d_4)}{BrCH_2CD_2(CH_2)_{n-4}CD_2CH_2Br}$$

For the β-d_4 sample, the degree of deuteration was kept moderate (ca. 10 %) in order to prevent some undesirable side reactions. The CBA samples thus derived were studied by DSC as well as a polarizing microscope. The observed phase transition behaviors were in agreement with those reported by Emsley et al.[2] and Griffin et al.[4]

The D-NMR spectra were recorded on a JEOL JNM-GX-500 spectrometer. Measurements were carried out under a complete proton decoupling and non-spinning mode. In these measurements, samples initially kept at a temperature above T_{NI} were cooled slowly to turn into the nematic phase.

RESULTS AND DISCUSSION

Shown in Figure 1 are the D-NMR spectra obtained for a series of CBA I-10 just below the NI transition temperature. The fully deuterated sample exhibits three splittings as indicated in the diagram 1a. The ratio of the peak intensities is 2:2:1 starting from the outside signal. For an unambiguous assignment of the peaks, CBA samples deuterated specifically at the α- and β-position were prepared. As illustrated in Figures 1b and 1c, the observed splittings $\Delta\nu_\alpha$ and $\Delta\nu_\beta$ were both found to be identical to $\Delta\nu_1$ of Figure 1a, indicating that this signal comprises contributions from the α- and β-CD bonds: i.e. $\Delta\nu_1 = \Delta\nu_\alpha$ and $\Delta\nu_\beta$. These results support our previous assignment of $\Delta\nu_1$ in the n = 10 ether-DLC system[1] (cf. seq.).

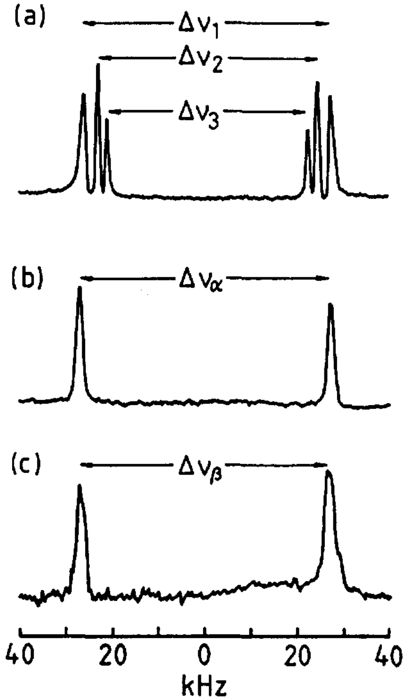


Figure 1. D-NMR spectra of CBA carrying an even number of methylene units (n=10), taken at 184 °C (just below T_{NI}): (a) fully deuterated, (b) α-d_4, and (c) β-d_4.

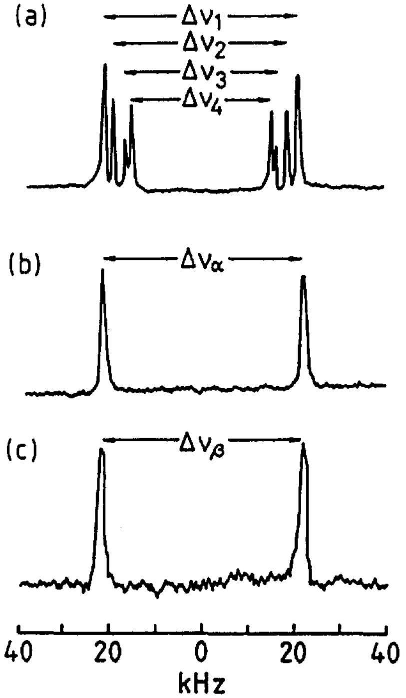


Figure 2. D-NMR spectra of CBA carrying an odd number of methylene units (n=9), taken at 172 °C. See Legends to Figure 1.

The results obtained for CBA samples with n = 9 are shown in Figure 2. The NMR spectrum of the fully deuterated CBA (Figure 2a) consists of four splittings, with the relative intensity ratio of 4:2:1:2. Comparison with the D-NMR spectra of the α- (Figure 2b) and β-deuterated samples (Figure 2c) indicates that the largest splitting $\Delta\nu_1$ includes contribution from the α- and β-CD bonds: i.e. $\Delta\nu_1 = \Delta\nu_\alpha$ and $\Delta\nu_\beta$. The signal of the lowest intensity may be assigned to the ε-CD_2 group located in the middle of the flexible spacer: $\Delta\nu_3 = \Delta\nu_\varepsilon$. The rest of the splittings, $\Delta\nu_2$ and $\Delta\nu_4$, should correspond to either γ- or δ-CD_2. The origin of these signals cannot be determined solely from the experimental observations described above.

Numerical values of the splittings are summarized in Table I, where Griffin et al.'s data on DLC II-10[5] are also included for comparison. Quadrupolar splittings $\Delta\nu_i$ of the i-th CD bond may be expressed as

$$\Delta\nu_i = \text{Const}\ S_{ZZ}\ (3\langle\cos^2\phi\rangle - 1)/2 \qquad (1)$$

where S_{ZZ} denotes the orientational order parameter of the molecular axis (Z-axis) with respect to the director of the nematic domain, ϕ represents the angle between the C-D bond and molecular axis, and the brackets denote an average over all allowed conformations. The ratio between two different $\Delta\nu$ values should be free from the S_{ZZ} value: thus,

$$\Delta\nu_i/\Delta\nu_j = (3\langle\cos^2\phi_i\rangle - 1)/(3\langle\cos^2\phi_j\rangle - 1) \qquad (2)$$

The right-hand-side of this expression includes terms such as $\langle\cos^2\phi\rangle$, the average which solely depends on the spatial configuration of the flexible spacer. The observed ratios expressed relative to the largest splittings $\Delta\nu_1$ are indicated in the last column of Table I. Values of $\Delta\nu^{obs}/\Delta\nu_1^{obs}$ obtained for I-10 are quite similar to those of II-10, immediately suggesting that the nematic configurations of the flexible spacer are nearly identical between these two systems.

The experimental data of I-10 have been analyzed according to the procedure described in our previous paper.[1] In Table II, some preliminary results obtained in this work are compared with those previously reported on Griffin et al.'s DLC (II-10).[5] Here f_N indicates the nematic fraction, and $\Delta\langle E\rangle_{NI}$ and ΔS_{NI} represent, respectively, the latent energy and entropy at the NI phase transition. Included also in the table are the $P_2(\cos\psi)$ term for the orientation of the mesogenic core with respect to the molecular axis, and the order parameter S_{ZZ} of the molecular axis. As indicated by comparison, the molecular alignment is slightly better in the CBA I-10 system, and correspondingly the nematic fraction of I-10 tends to be somewhat smaller. Since the chemical structure of the spacer is identical in these two DLCs, the difference noted above should arise from the dissimilarity in the mesogenic cores. In agreement with the previous assignment, the observed spectrum was satisfactorily interpreted by adopting the identity $\Delta\nu_2 = \Delta\nu_\gamma$ and $\Delta\nu_\delta$, and $\Delta\nu_3 = \Delta\nu_\varepsilon$ in the n = 10 system. Our treatment can be easily extended to polymers which comprise similar repeating units. The D-NMR data reported by Müller et al.[6] on a partially deuterated PLC have been shown to give results consistent with those described above.[7]

In our previous studies,[8,9] distribution curves were derived for the orientational correlation between the neighboring mesogenic groups incorporated in an ether-type main-chain liquid crystals. When n = odd, the major portion (ca. 90 %) of the angle defined by the two successive mesogenic core axes is located in the region 50° to 90°. The distribution profiles are very much different between the n = odd and even series. For DLC I-9, elucidation of the nematic fraction conforming to the observed quadrupolar splittings requires some elaboration: the preliminary analysis leads to the assignment such as $\Delta\nu_2 = \Delta\nu_\delta$ and $\Delta\nu_4 = \Delta\nu_\gamma$. The details of the results will be reported in the forthcoming paper.

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Table I
Summary of Experimental D-NMR Data on DLCs

Compound	Temp/K	$\Delta\nu^{obs}$/kHz	$\Delta\nu^{obs}/\Delta\nu_1^{a}$
I-10	457	53.5	1.0
		47.7	0.89
		43.6	0.81
I-9	445	42.0	1.0
		38.0	0.90
		32.1	0.76
		30.4	0.72
II-10[b]	409	47.4	1.0
		40.7	0.86
		37.4	0.79

[a] Ratio of the splittings expressed relative to $\Delta\nu_1$.
[b] Ref. 5.

Table II
Characteristic Properties of the Nematic Phase
for DLCs with n=10

	I-10	II-10
f_N / %	7.83	10.60
$\Delta\langle E\rangle_{NI,conf}$/kcal mol^{-1}	0.88	0.65
$\Delta S_{NI,conf}$/cal mol^{-1} K^{-1}	6.82	6.04
$P_2(\cos\psi)$	0.92	0.91
S_{ZZ}^{a}	0.56	0.49

[a] Estimated from $\Delta\nu_1^{obs}$ by using the relation given in Eq. 1.

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