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SYNTHESIS OF MHPOBC-d_3 AND MHPOBC-d_{43} AND BEHAVIOR OF METHYL GROUP ATTACHED TO CHIRAL CARBON AS OBSERVED BY FT-IR, RAMAN AND NMR SPECTROSCOPY

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Abstract we have synthesized two deuterated MHPOBCs -MHPOBC-d_3 with the methyl group connecting to the chiral center deuterated, and MHPOBC-d_{43}, all deuterated but the methyl group near the chiral part. The polarization angle dependence of FT-IR shows that the symmetric and asymmetric stretchings of methyl group are in-phase with those of phenyl rings in SA and electrically unwound SC* phases, and the peak of CH_3 of MHPOBC-d_{43} splits into triplet in ^1H NMR and CD_3 of MHPOBC -d_3 into doublet in ^2D NMR.

INTRODUCTION

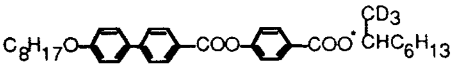
The antiferroelectric liquid crystals have attracted an increasing research interest since the discovery of antiferroelectric phenomena in liquid crystals by Chandani et al.[1] The relationship of the chemical structure and emergence of antiferroelectricity have been extensively studied. It is more and more obvious that the transverse dipoles near the chiral center of liquid crystal molecules play an essential role in the exhibition of antiferroelectricity.[2] Our recent results show that the chiral alkyl chain of the antiferroelectric liquid crystal MHPOBC (4-(1-methylheptyloxycarbonyl)phenyl 4'-octyl oxybiphenyl carboxylate) is actually projecting obliquely from the long core axes with an angle more than so-called magic angle 54.7° even in the SA phase.[3] Combining with the X ray results of Hori and Endo[4] in a crystal phase, such a bent molecular structure may permit the permanent dipoles in adjacent layers interact adequately through the Coumlomb force, which results in stablizing the antiferroelectric phase, according to the pairing model proposed by Takanish et al,[5] or Px model by Miyachi et al.[6]

The FT-IR and NMR spectroscopy have been widely employed to investigate the behavior of specific segment of a molecule if the corresponding peaks can be unambiguously identified. In this paper, we have designed and synthesized two deuterated MHPOBCs: MHPOBC-d_3 with a deuterated methyl group connecting to the chiral center and MHPOBC-d_{43} with all deuterated but the methyl group connecting to the chiral center, which are usuful to investigate the behavior of the methyl group by polarized FT-IR, Raman and NMR spectroscopy. The former, MHPOBC-d_3, used for FT-IR and Raman measurement, has the absorption of C-D stretching of CD_3, which can be distinguished from the absorbtion of the other part of the molecule. And the latter, MHPOBC-d_{43}, has only the peaks of CH_3 on ^1H NMR spectroscopy by proton decoupling of other parts of the molecule with deuteration.

SYNTHESIS AND FT-IR, RAMAN AND ^{1}H NMR MEASUREMENT

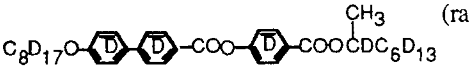
Synthesis

The deuterated target compounds with the following structures shown in Figure 1, were synthesized through the routes summarized in Figure 2 and Figure 3, respectively.



((R)-MHPOBC-d_3)

Iso 148℃ SmA 116℃ SmC* 111℃ SmC_A* <60℃ Cryst



(racemic-MHPOBC-d_{43})

Iso 149℃ SmA 116℃ SmC 101℃ SmC_A <60℃ Cryst

FIGURE 1 Molecular structural fomulas and phase sequences of MHPOBC-d_3 and MHPOBC-d_{43}

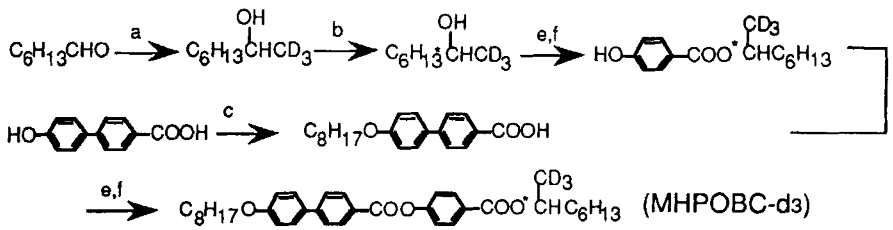
Although the reactions involved in the synthetic process are very common, two problems should be taken into account: The first problem is the synthesis of optical active intermediates. In order to prepare the special deuterated chiral intermediates, we employed the enzyme catalysed biochemical method in the synthesis of 1,1,1-d_3-methyl-1-octanol (Figure 2). In this reaction, we used Lipase QL (Meito Co., Ltd) with acetyl vinyl as a catalyst and proved to be an efficient way toward the desired R isomer with 85%ee. Another problem encountered is the back-exchange of deuteriums of deuterad materials by normal hydrogens.[7] The deutered solvents was used for the reactions involving deuterated reagents. The chemical structures of all the intermediates were identified by ^1H NMR, IR and those of the desired final products, MHPOBC-d_3 and MHPOBC-d_{43}, were elucidated by ^1H NMR, ^{13}C NMR, IR, MS, and elemental analysis.

Measurements of polarized FT-IR, Raman and ^{1}H, ^{2}D NMR

Polarized FT-IR spectra were measured using a JEOL 6000 system equipped with a microattachment and a MCT dector, as a function of polarizer rotation angle. A wire gird polarizer (Cambridge Physical Science IGP227), was employed to obtain polarized ir radiation. For homogeneously aligned thick cells, the cell thickness was considered as a thickness of spacer. Alignment was made under a magnetic field of 5 T.

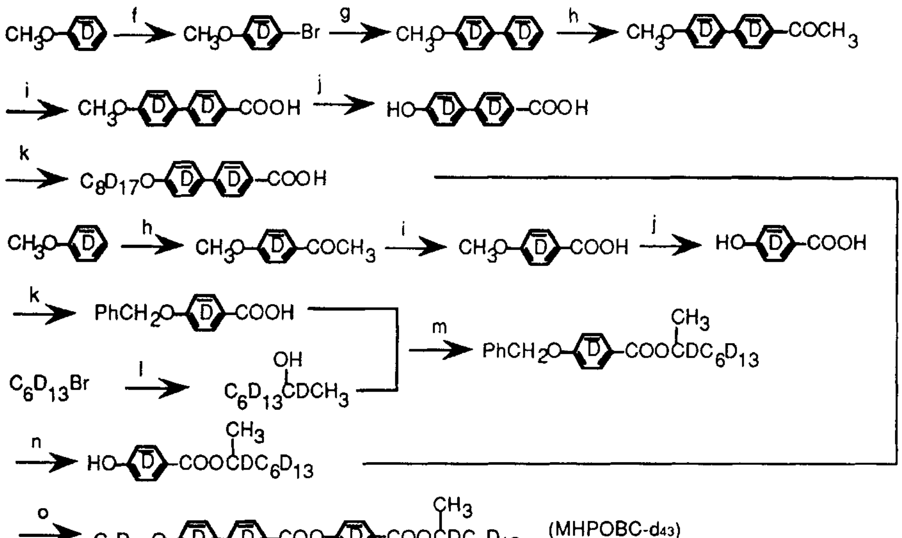
Raman scattering spectra were obtained in the backward scattering, using a JASCO NR-1800 system. The polarized exciting radiation of 514.5 nm from an Ar^+

laser (Coherent, Innova 70) was focused on a powder sample. The measurements were done at room temperature.



a: CD_3MgI/Et_2O b: Lipase QL c: Benzylbromide/KOH
d: Pd-C/H_2 e:Thionyl f: pyridine

FIGURE 2 The synthetic route of MHPOBC-d_3



f: DBMH g:Mg/THF,B(O-i-Pr), 4-bromoanisole-d_5/ $Pd(Ph_3P)_4$ h:acetylchloride i :$NaBrO$/1,2-dioxane j: $AlBr_3$ k:KOH l:Mg/ether, CH_3CDO m:4-benzyloxy benzoic acid/$SOCl_2$, pyridine n: H_2/Pd-C o:DCC/DMAP

FIGURE 3 The synthetic route of MHPOBC-d_{43}.

MHPOBC-d_{43} and MHPOBC-d_3 were used in ^1H and ^2D NMR measurements, respectively. About 200 mg of sample was placed into a zirconia tube and aligned under a magnetic field of 7 T. After the sample was kept at 5℃ higher than clearing point for 10 minutes, it was cooled slowly at a rate of 1℃/min in the magnetic field to ensure a well alignment. The NMR was recorded in cooling process using CMX-300WB solid

NMR spectrometer (300MHz,U.S.A Chemagnetics Co., Ltd).

RESULTS AND DISCUSSION

The ir and Raman spectra of MHPOBC-d_{43} between 2800-3200cm^{-1}, the range of asymmetric and symmetric stretchings of CH_3, were demonstrated in Figure.4. Symmetric stretching should show a relatively strong peak in the Raman spectrum, while asymmetric stretching should exhibit a large peak in the ir spectrum. Therefore, the peaks of 2976 and 2980cm^{-1} are assigned to asymmetric stretching, and 2933 and 2938cm^{-1} to the symmetric stretchings of chiral methyl group. In a similar manner, as shown in Figure 5, the asymmetric (2227, 2234cm^{-1}) and symmetric (2123, 2130cm^{-1}) stretchings of CD_3 were assigned.

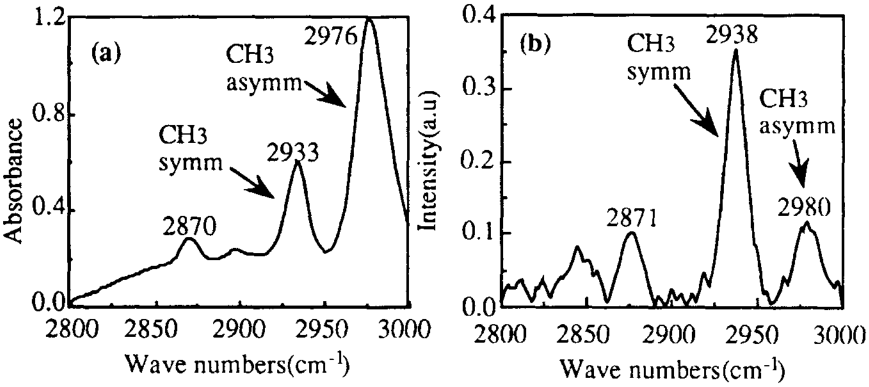


FIGURE 4 (a) Absorption spectra of 100μ m homogeneously aligned sample (130 ℃,SA phase) and (b) Raman scattering spectra of MHPOBC-d_{43} powder together with the assignment of asymmetric and symmetric stretching of CH_3 group.

Figures 6(a) and 6(b) show the absorbance vs polarizer rotation angle observed in the SA phase of MHPOBC-d_{43} and electrically unwound SC* phase of MHPOBC-d_3, respectvely. In a thin cell (5-10μ m), the stretchings of phenyl rings, both for MHPOBC-d_{43} and MHPOBC-d_3, can be observed, whereas those of chiral methyl are weak to be detected. Therefore, the phenyl ring stretchings are studied by using a homogeneously aligned thin cell (5μ m for MHPOBC-d_3 and 10μ m for MHPOBC-d_{43}). However, the asymmetric and symmetric stretchings of chiral CH_3 and CD_3 were measured using a thick cell (100μ m for MHPOBC-d_{43} and 50μ m for MHPOBC-d_3). As shown in Figure 6, the symmetric and asymmetric stretchings of chiral CH_3 and CD_3 are in-phase with that of the phenyl ring, which is considered to be parallel to the molecular long axis,[8] both in the SA (a) and the electrically unwound SC* phases (b). Asreported previously,[3] the chiral alkyl chain is obliquely projecting to the molecular long axis. Both of methyl and chiral alkyl chain are connected with chiral carbon, so there must be some correlations among chiral methyl, hexyl and carbonyl groups. The vibrational directions of symmetric and asymmetric stretchings of chiral CH_3 and CD_3 are perpendicular to each other, therefore, the symmetric and asymmetric stretchings of chiral CH_3 and CD_3 cannot be in-phase unless the angle between C-CH_3 bond and molecular long axis is equal to the magic angle(54.7°). However, it is not the case. The details are not clear at present.

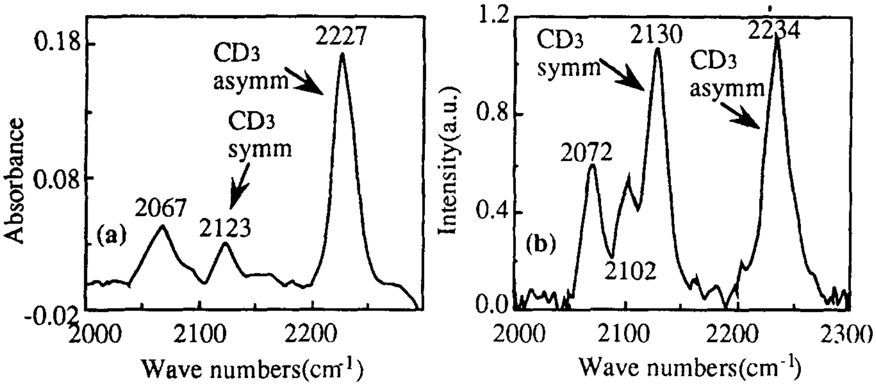


FIGURE 5 (a)Absorption spectra of 50 μ m homogeneously aligned sample and (b) Raman scattering spectra of MHPOBC-d_3 powder together with the assignment of asymmetric and symmetric stretching of CD_3 group.

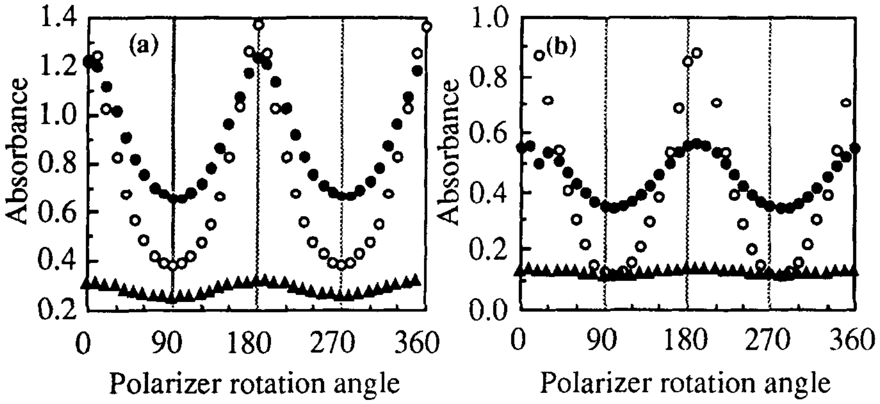


FIGURE 6 Absorbance vs polarizer rotation angle for (a) phenyl ring stretching (○), asymmetric (●) and symmetric (▲) stretching of CH_3 in SA phase, (b) phenylring stretching (○), asymmetric (●) and symmetric (▲) stretching of CD_3 in unwound SC* phaseunder 1V/μ m field.

Figures 7 (a) and 7(b) show the ^{1}H NMR spectra of MHPOBC-d_{43} and ^{2}D NMR spectra of MHPOBC-d_3, respectively. Because of decoupling by deuteration, the ^{1}H NMR spectrum of MHPOBC-d_{43} was much simplified, giving only a triplet with 1:2:1 and the ^{2}D NMR spectrum of MHPOBC-d_3 gave a doublet with 1:1. The detailed studies are under progress.

In conclusion, we have synthesized deuterated MHPOBCs. It is shown that the signals arising from the methyl group connecting to the chiral carbon can be observed by ir, Raman and NMR spectroscopy in spite of the low density of the methyl group.

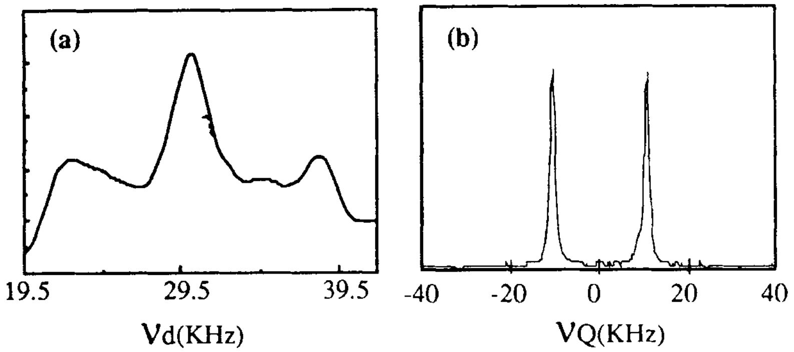


FIGURE 7 (a) ^{1}H NMR spectrum of MHPOBC-d_{43} and (b) ^{2}D NMR spectrum of MHPOBC-d_3

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REFERENCES

1. A. D. L. Chandani, E. Gorecka, Y. Ouchi, H. Takezoe, and A. Fukuda, Jpn. J. Appl. Phys., 28, L1265 (1989).
2. A. Fukuda, Y. Takanishi, T. Isozaki, K. Ishikawa, and H. Takezoe, J. Mater. Chem., 4, 997 (1995).
3. B. Jin, Z. Ling, Y. Takanishi, K. Ishikawa, H. Takezoe, A. Fukuda, M. Kakimoto, and T. Kitazume, Phys. Rev. E., 53, R4295 (1996).
4. K. Hori and K. Endo, Bull. Chem. Soc. Jpn., 66, 46 (1993).
5. Y. Takanishi, K. Hiraoka, V. K. Agrawal, H. Takezoe, A. Fukuda, and M. Matsushita, Jpn. J. Appl. Phys., 30, 2023 (1991).
6. K. Miyachi, J. Matsushima, Y. Takanishi, K. Ishikawa, H. Takezoe, and A. Fukuda, Phys. Rev. E., 52, R2153 (1995).
7. H. Zimmermann, Liq. Cryst., 4, 591 (1989).
8. K. H. Kim, K. Ishikawa, H. Takezoe, and A. Fukuda, Phys. Rev. E., 51, 2166 (1995).