FTIR and ^1H -NMR studies of chiral (S)-(-)-2-methylbutyl 4'-(4''-hexyloxy-, (S)-(-)-2-methylbutyl 4'-(4''-(d₁₃)-hexyloxy-, (S)-(-)-2-methylbutyl 4'-(4''-octyloxy- and (S)-(-)-2-methylbutyl 4'-(4''-(d₁₇)-octyloxyphenyl)benzoates

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Abstract. Four organic chiral compounds (S)-(-)-2-methylbutyl 4'-(4''-hexyloxy-, (S)-(-)-2-methylbutyl 4'-(4''-(d₁₃)-hexyloxy-, (S)-(-)-2-methylbutyl 4'-(4''-octyloxy- and (S)-(-)-2-methylbutyl 4'-(4''-(d₁₇)-octyloxy-phenyl)benzoates were synthesized via generalized methods and characterized by elemental analysis, FTIR and ^1H NMR. A noticeable difference between the compounds which possess hydrogenated achiral substituent with the deuterated counterparts as exemplified from the FTIR spectra has been suggested for the first time to result from the affinity of the latter compounds towards hydroxylation induced by potassium bromide.

1. Introduction

Over the last few years, a considerable amount of organic compounds which possess mesogenic properties have been synthesized and studied particularly from the viewpoint of material science. One of these materials has been classified as ferroelectric liquid crystals (FLCs). Ferroelectric liquid crystals are the most recent members of the family of ferroelectric materials, and the first one with fluid properties [1].

Although the physical properties of (S)-(-)-2-methylbutyl 4'-(4''-hexyloxy- and (S)-(-)-2-methylbutyl 4'-(4''-octyloxyphenyl)benzoates have well been studied [2–4] but its' analogous compounds which contain deuterated C₆D₁₃O– or C₈D₁₇O– as the achiral substituent have hitherto not been reported. The importance of having deuterated atoms lies on the possibility to enhance the stability of the mesophase.

As such, we would like to report here the synthesis and characterization of title compounds which encompass, for the first time, the use of deuterated achiral alkoxyl chain in the biphenyl system. The ordinary materials which contain C₆H₁₃O– and C₈H₁₇O–, respectively, are also included in this paper for comparison purpose. Their molecular structures with abbreviations are shown as follows:

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The compounds thus obtained were characterized by elemental analysis, FTIR and ^1H NMR. The purities of all final products were confirmed by thin layer chromatography using a mixture of ethyl acetate : *n*-hexane (1 : 10) as the eluent.

2. Experimental

(S)-(-)-2-methylbutanol, 1-bromohexane, d₁₃-1-bromohexane, 1-bromooctane and d₁₇-1-bromooctane were purchased from TCI Chemical Company in Japan. All reagents were directly used without further purification.

The synthetic methods of compounds with hydrogenated and deuterated substituent have been generalized in two different manners and can be represented by respective preparation as follows:

(a) Preparation of (S)-(-)-2-methylbutyl 4'-(4''-hexyloxyphenyl)benzoate, (S)-MBHOB

A mixture of 2.8 g (10 mmol) of S-(-)-2-methylbutyl 4'-(4''-hydroxyphenyl)benzoate (preparative method has been reported [5]). 1.1 g (10 mmol) of 1-bromohexane, 0.8 g (15 mmol) potassium hydroxide and catalytic amount of potassium iodide in 50 ml of dimethylformamide was heated under reflux for 24 hours. The dilute HCl was added to the resulting solution whereupon the white precipitate formed. The product was filtered and chromatographed over the silica gel (0.040–0.063 mm for column chromatography) with a solvent mixture ethyl acetate : *n*-hexane (1 : 10) as the eluent. Yield: 75%. Anal Calcd for C₂₄H₃₂O₃: C, 78.21; H, 8.77; Found: C, 78.15; H, 8.74; FTIR (cm⁻¹) 2960, 2930, 2860, 2840, 1710; ^1H NMR (δ ppm) 8.1 (d, 2H), 7.6 (d, 2H), 7.5 (d, 2H), 7.0 (d, 2H), 4.2 (m, 2H), 4.0 (t, 2H), 0.9–1.9 (other alkyl chain H).

(b) Preparation of (S)-(-)-2-methylbutyl 4'-(4''-(d₁₃)-hexyloxyphenyl)benzoate, (S)-MB-d₁₃-HOB

A mixture of 2.8 g (10 mmol) of S-(-)-2-methylbutyl 4'-(4''-hydroxyphenyl)benzoate, 1.1 g (10 mmol) of deuterated d₁₃-1-bromohexane and 3.4 g (25 mmol) potassium carbonate was refluxed for 16 hours in acetone. The reaction mixture was cooled down upon completion before filtration. The excess solvent

of the filtrate was evaporated off at room temperature by standing overnight. The white precipitate thus obtained was recrystallized from *n*-hexane and purified via column chromatography (silica gel 60) by using ethyl acetate : *n*-hexane (1 : 10) as the eluent. Yield 63%. Anal Calcd for $\text{C}_{24}\text{H}_{19}\text{D}_{13}\text{O}_3$: C, 75.54; H, 5.03; Found: C, 75.23; H, 5.03; FTIR (cm^{-1}) 2960, 2930, 2860, 2840, 1710; ^1H NMR (δ ppm) 8.1 (d, 2H), 7.6 (d, 2H), 7.5 (d, 2H), 7.0 (d, 2H), 4.2 (m, 2H), 1.0–1.9 (other alkyl chain H).

(c) Preparation of (S)-(-)-2-methylbutyl 4'-(4''-octyloxyphenyl)benzoate, (S)-MBOOB

The experimental procedure is similar to that in 2(a). Yield 65%. Anal Calcd for $\text{C}_{26}\text{H}_{36}\text{O}_3$: C, 78.73; H, 9.17; Found: C, 78.74; H, 9.02; FTIR (cm^{-1}) 2960, 2925, 2870, 2850, 1715; ^1H NMR (δ ppm) 8.1 (d, 2H), 7.6 (d, 2H), 7.5 (d, 2H), 7.0 (d, 2H), 4.2 (m, 2H), 4.0 (t, 2H), 0.9–1.9 (other alkyl chain H).

(d) Preparation of (S)-(-)-2-methylbutyl 4'-(4''-(d_{17})-octyloxyphenyl)benzoate, (S)-MB- d_{17} -OOB

The experimental procedure is similar to that in 2(b). Yield 48%. Anal Calcd for $\text{C}_{26}\text{H}_{19}\text{D}_{17}\text{O}_3$: C, 75.49; H, 4.64; Found: C, 75.22; H, 4.60; FTIR (cm^{-1}) 2950, 2930, 2870, 1705; ^1H NMR (δ ppm) 8.1 (d, 2H), 7.6 (d, 2H), 7.5 (d, 2H), 7.0 (d, 2H), 4.2 (m, 2H), 1.0–1.9 (other alkyl chain H).

Elemental analyses were carried out on Yanaco MT-5 elemental analyzer at Tokyo Institute of Technology.

IR data were recorded using a JASCO 410 FTIR spectrophotometer in the frequency range 4000–450 cm^{-1} . FTIR spectra of both (S)-MBHOB and (S)-MBOOB possessing hydrogenated achiral hexyloxy and octyloxy groups were recorded with sample in KBr discs. However, the spectra of (S)-MB- d_{13} -HOB and (S)-MB- d_{17} -OOB which possess deuterated substituent were measured in thin film sandwiched between two strontium fluoride plates.

^1H NMR spectra were recorded on a JEOL 300 MHz NMR spectrometer with sample dissolved in deuterated CDCl_3 and TMS used as internal standard.

The purities of the compounds were analyzed using 1.0×2.5 cm aluminium plates coated with silicone oxide (silica gel 60) in the presence of ethyl acetate and hexane (1 : 10) as the solvent system and visualized using a UV lamp.

3. Result and discussion

All final products were crystallized out from the filtrate as white precipitates after being extracted by *n*-hexane. Further purification using flash column chromatography was also carried out wherein ethyl acetate and hexane (1 : 10) were used as the eluent.

Microanalytical results are in agreement with the empirical formulas for (S)-MBHOB, (S)-MB- d_{13} -HOB, (S)-MBOOB and (S)-MB- d_{17} -OOB.

In the IR data for (S)-MBHOB, a band at 2930 cm^{-1} is seen to appear with larger intensity as compared to that in the intermediate (S)-(-)-2-methylbutyl 4'-(4''-hydroxyphenyl)benzoate [5]. In addition, a band at 2860 cm^{-1} is shouldered with a new band which lies at slightly lower frequency. These two features strongly suggest that the hydroxyl group in the biphenyl fragment has been alkylated by hexylbromide leading to the formation of a compound which contains hexyloxy group $\text{C}_6\text{H}_{13}\text{O}-$. The disappearance of a strong band assignable to the stretching of O–H as that presents in the IR spectrum of the intermediate [3] has also supported the success of hexyloxylation. Another notable feature as inferred from the IR spectrum of (S)-MBHOB is that the stretching frequency owing to the carbonyl group $\text{C}=\text{O}$ at 1705 cm^{-1} is higher than that in the intermediate (1680 cm^{-1}) [5]. One of the reasons which can attribute to this observation is that the substitution of hydrogen atom from the OH substituent by hexyl group enhances

Fig. 1. IR spectrum of (S)-MB-d₁₇-OOB, wherein the compound was mixed with KBr.

the electron density of biphenyl ring. Hence, the strength of pi bond of C=O group which relies partly on the pi electrons density from the biphenyl ring also increases. The existence of this electronic factor has also been reported as the electronic donor-pi-acceptor system in other compounds including the helical nonchiral molecules [6].

The molecular structure of (S)-MBHOB can also be substantiated from the ^1H NMR wherein a singlet attributable to the aromatic hydroxyl proton as reported for that in the intermediate at $\delta = 5.0$ ppm [5] is found to be absent. This observation strongly suggests the replacement of HO- substituent by achiral $\text{C}_6\text{H}_{13}\text{O}-$. The presence of hexyloxy substituent can be evident from a triplet which occurs at $\delta = 4.0$ ppm indicating the presence of $-\text{OCH}_2-$ group.

Inspection from the IR spectrum of (S)-MB-d₁₃-HOB clearly illustrates that the bands assignable to the alkoxyl C-H are rather weak in comparison with those in (S)-MBHOB. This observation indicates that the achiral hexyloxy chain is fully deuterated. The presence of deuterated chain can also be supported by the appearance of two additional bands at 2210 and 2100 cm^{-1} which can be attributed to the asymmetric and symmetric stretchings of both CD_3 and CD_2 , respectively [7].

The IR and ^1H NMR data for (S)-MBOOB and (S)-MB-d₁₇-OOB were found to be identical with (S)-MBHOB and (S)-MB-d₁₃-HOB wherein the diagnostic bands and peaks characteristic for the functional groups and protons in each molecule are very close.

A significant difference between (S)-MBHOB and (S)-MBOOB with (S)-MB-d₁₃-HOB and (S)-MB-d₁₇-OOB has well been exemplified by FTIR wherein an additional band assignable to the stretching vibration of O-H at 3450 cm^{-1} is observed in the IR spectra of both (S)-MB-d₁₃-HOB and (S)-MB-d₁₇-OOB. A representative IR spectrum of (S)-MB-d₁₇-OOB, as illustrated in Fig. 1, shows a strong and broad band assignable to OH at 3450 cm^{-1} . The presence of OH has initially been ascribed to the presence of water molecules presumably from the moisture in the air wherein these molecules held to the KBr surface via an interaction with one water molecule bonded to two bromines as reported in the literature [8,9]. The presence of these water molecules leads us to further assumptions: (a) the KBr contains substantial amount of water, (b) water molecules were trapped in the layer during the preparation of KBr discs, and (c) (S)-MB-d₁₇-OOB contains water. An observation from the spectrum of (S)-MBOOB (Fig. 2) which shows the absence of OH band has undoubtedly ruled out (a) and (b).

Fig. 2. IR spectrum of (S)-MBOOB, wherein the compound was mixed with KBr.

Fig. 3. IR spectrum of (S)-MB-d₁₇-OOB, wherein the compound was sandwiched between two SrF₂ plates.

In order to clear the doubt owing to (c), an indepth study has been carried out by fabricating a thin film from the partially deuterated compounds by spreading over the strontium fluoride (SrF₂) plates with 2 μm spacers. The target compounds were then inserted between the plates and IR spectra were recorded on the same spectrophotometer. Prior to the measurement upon both MB-d₁₃-HOB and (S)-MB-d₁₇-OOB, the empty cell of SrF₂ was used for calibration purpose.

Observation upon the IR spectrum of (S)-MB-d₁₇-OOB (Fig. 3) which was sandwiched between the SrF₂ plates shows that a band as that appears in the IR spectrum of similar compound in KBr discs has disappeared. This observation has proven that the above assumption (c) is unlikely leading to an indication that the interaction of KBr with water molecules is dependent on the compound mixed with the substrate. Thus, the presence of deuterated achiral side-chain is one of the factors contributing to the enhancement of this interaction. This phenomenon has also been found for (S)-MB-d₁₃-HOB.

Further investigation upon the interaction between KBr and water molecules in the presence of selective compounds, and the potential mesomorphic behaviours of the title compounds particularly the deuterated materials; (S)-MB- d_{13} -HOB and (S)-MB- d_{17} -OOB in liquid crystalline phases would be reported elsewhere.

4. Conclusion

The spectroscopic methods (IR and ^1H -NMR) are shown to be useful for the structure elucidation upon a very wide range of compounds including the (S)-MBHOB, (S)-MBOOB, (S)-MB- d_{13} -HOB and (S)-MB- d_{17} -OOB. Whilst both ordinary (S)-MBHOB and (S)-MBOOB show no indication of the presence of OH band in the IR spectra when mixed with KBr, the other analogous compounds (S)-MB- d_{13} -HOB and (S)-MB- d_{17} -OOB which possess deuterated achiral $\text{C}_n\text{D}_{2n+1}\text{O}$ ($n = 6$ and 8) substituents at the lateral position of the biphenyl ring exhibit a strong band assignable to OH at 3450 cm^{-1} . The use of SrF_2 glass plates as substrates for the IR measurement of these compounds suggests that both (S)-MB- d_{13} -HOB and (S)-MB- d_{17} -OOB are capable of enhancing the interaction between KBr and water molecules.

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