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Optically Active Sulfoxides as Ferroelectric Liquid Crystals and Chiral Dopants for Them

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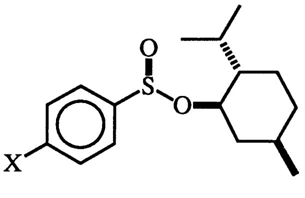
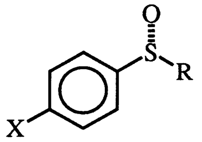
Chiral alkylsulfinylbenzenes having an ester functional group at C-4 were prepared and shown for the first time to be ferroelectric liquid crystals and excellent chiral dopants for them.

Ferroelectric liquid crystal (FLC) materials1) have attracted much attention recently owing to the rapid development of liquid crystal displays. The FLC's have been searched for extensively which have chiral smectic C phase (S_C*) along with high spontaneous polarization (Ps) and short response time (τ). We envisioned that the FLC's having dipolar chiral centers connected directly to aromatic core portions should exhibit much improved Ps and τ. On the basis of this working hypothesis, we planned the synthesis of various chiral molecules within this category. Reported herein are the synthesis of chiral alkyl 4-substituted phenyl sulfoxides **3-7** and some thermotropic and electro-optical properties of the FLC's derived from them.



1: X = MeO
2: X = Br



3: X = MeO, **4**: X = HO, **5**: X = Br
6: X = MeOCO, **7**: X = HOCO

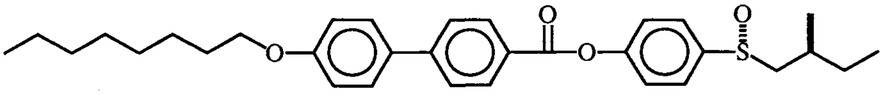
a: R = n-C_5H_{11}, **b**: R = n-C_8H_{17},
c: R = (S)-$CH_2CHMeEt$,
d: R = (S)-CHMe(n-C_7H_{15})
e: R = (R)-CHMe(n-C_7H_{15})
f: R = (S)-CHMe(n-Pr)
g: R = (R)-CHMe(n-Pr)

Chiral 4-substituted alkylsulfinylbenzenes **3a-c** and **5a-c** were prepared from l-menthyl (S)-4-methoxyphenylsulfinate (**1**)2) and (S)-4-bromophenylsulfinate (**2**)3,4) respectively by the reaction with the corresponding alkylmagnesium bromides in benzene.5) Since the sulfinyl group is extremely sensitive to acidic conditions,6) the conversion of the methoxyl group of **3a-c**4) into the hydroxyl functional group was best carried out with sodium ethanethiolate in *N,N*-dimethylformamide (DMF) at 100 °C.[7,8] Under these conditions the racemization of the sulfinyl group was within the error of analysis.[9] The transformation of the bromide **5a-c**[4] to the corresponding carboxylic acids **7a-c**[4] through the metalation using any kinds of alkyllithiums or magnesium metal was unsuccessful.[10] This transformation could, however, be carried out using CO (50-80 kg/cm^2) and $PdCl_2(PPh_3)_2$ (5 mol%) in methanol-triethylamine at 100 °C for 2 d to give the methyl esters **6a-c**,[4,11] which were then hydrolyzed with NaOH in MeOH-H_2O to the corresponding acids **7a-c**.[4,12] Epimerization of the chiral sulfinyl moiety of **7a-c** was estimated to be less than 2%.

In order to effect the conformational change of the alkyl side chain and hopefully to enhance the Ps, we introduced an α-methyl group into the alkyl side chain. Deprotonation of **5b** with 1.2 mol eq of lithium diisopropylamide at -78 °C for 2.5 h followed by the treatment with 1.2 mol eq of methyl iodide at -78 °C afforded a 1 : 1 mixture of **5d**[4] and **5e**[4] in 90% yield.[13] Each diastereomer was separated by silica gel column chromatography. The palladium catalyzed methoxycarbonylation of each resulted in the formation of a complex mixture of products. Probably the thermal [2,3]-sigmatropic reaction took place to give an olefin and a sulfenic acid which in turn might have deactivated the catalyst. The obstacle was cleared to some extent by using an excess amount of triphenylphosphine. Thus the methyl ester **6d**,[4] $[\alpha]_D^{20}$ 123° (*c* 1.38, MeOH), was obtained in 20% yield from **5d** [$PdCl_2(PPh_3)_2$ (5 mol%), PPh_3 (10 mol%), CO (80 kg/cm^2), MeOH, Et_3N, 100 °C, 4 d]. Alkaline hydrolysis of **6d** gave **7d**,[4] mp 115-117 °C, $[\alpha]_D^{20}$ 128° (*c* 1.38, MeOH), in 94% yield. With double amounts of the Pd catalyst and the phosphine ligand, **5e** was converted into **6e** in 45% yield which was hydrolyzed to **7e**,[4] mp 134-135 °C, $[\alpha]_D^{20}$ 122° (*c* 1.38, MeOH), in 99% yield.

The methylation applied to **3b** resulted in the formation of an inseparable mixture of **3d** and **3e**. Thus, the sulfoxides **3f**[4,13] and **3g**[4,13] which have a shorter branched side chain were prepared by the reaction of **1** with 1-methylbutylmagnesium bromide in benzene. Each diastereomer was separated readily and converted into the phenol derivative **4f**[4,14] or **4g** respectively with EtSNa-DMF at 100 °C.

The chiral (4-alkylsulfinyl)benzenols **4** and (4-alkylsulfinyl)benzoic acids **7** were condensed with various core aromatic carboxylic acids and phenols respectively. The procedure through acid chlorides failed to give the expected products. However N,N'-dicyclohexylcarbodiimide or its water-soluble derivative was proved to be the reagent of choice. Among many esters synthesized, only the 4'-octyloxybiphenyl-4-carboxylate esters of **4f** and **4g** exhibited clear S_C* phase. Their thermotropic data[15] were Cr 109 S_C* 141 S_A 153 N* 167 I and Cr 155 S_C* 158 N* 169 I, respectively. Unfortunately, the Ps's of these could not be measured. However, the chiral sulfinyl substituted esters were found to be good chiral dopants for achiral smectic liquid crystals. Each sulfoxide was added by 5% to the host liquid crystal: Cr 13 S_C 68 S_A 73.5 N 83.5 I.[15,16] The electro-optic data of typical examples **8-11** are given in the order of a chiral dopant: its thermotropic data,[15] thermotropic profile of the mixture,[15] Ps (nC/cm^2)[17] at 25 °C, $\tau_{10\text{-}90}$ (μs)[18] at 25 °C, tilt angle (°), and the direction of the helical pitch. **8**: Cr 161 (S_C* 146) S_A 176 I, S_C* 65 S_A 81 N* 86 I, (+) 3.9, 108, 23.0, left; **9**: Cr 158 I, S_C* 68 S_A 73 N* 82 I, (+) 10.9, 58, 16.9, left; **10a**: Cr 66 I, S_C* 59 S_A 71 N* 78 I, (+) 4.6, 100, 22.7, left; **10b**: Cr 73 I, S_C* 60 S_A 71 N* 79 I, (+) 6.5, 90, 24.3, right; **11a**: Cr 98 S_A 120 I, S_C* 67 S_A 73 N* 84 I, (+) 5.2, 112, 22.2, left; **11b**: Cr 127 S_A 138 I, S_C* 69 S_A 76 N* 86 I, (+) 5.4, 90, 23.9, right. In general, linear alkyl sulfoxides induced fairly large Ps's, but the methyl substituted ones **8-11** much higher Ps's. The branching of the alkyl side chain might have restricted the free rotation of the side chain, as expected, to fix the dipole of the S-O moiety and reduce the probability of unfavorable conformers. It should be noted that the sign of Ps[17] is determined by the chirality of the sulfogenous chiral center and the sign of helical pitch by the chirality of the carbogenous chiral center of the side chain (cf. **10a** vs. **10b** and **11a** vs. **11b**).



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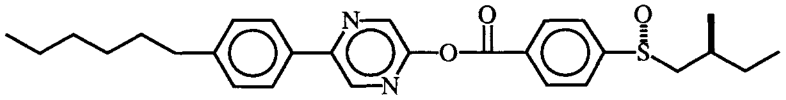

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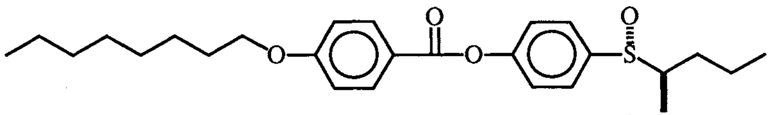
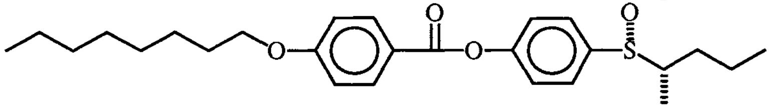
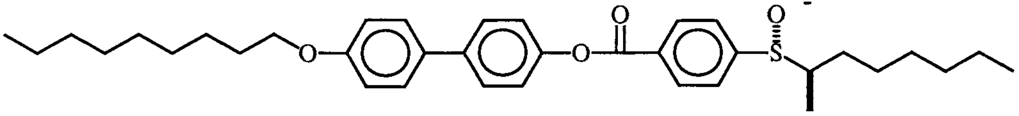


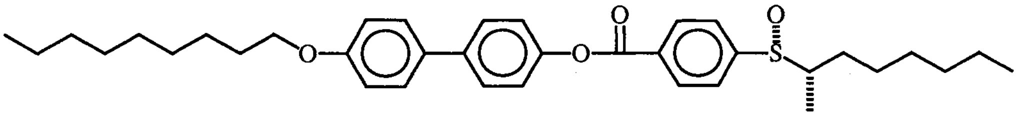
10a



10b



11a



11b

We have introduced chiral sulfoxides for the first time to FLC's.[19] The Ps and $\tau_{10\text{-}90}$ values observed for **9**, in particular, are remarkable,[20] and thus our guiding principle discussed at the beginning should be helpful in developing versatile FLC's applicable to liquid crystal displays. Synthesis and design of pertinent chiral molecules along this line are being studied extensively in our Laboratories.

References

1) R. B. Meyer, *Mol. Cryst. Liq. Cryst.*, **40**, 33 (1977); N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.*, **36**, 899 (1980).

2) H. F. Herbrandson and R. T. Dickerson, Jr., *J. Am. Chem. Soc.*, **81**, 4102 (1959).

3) The sulfinate ester **2**, colorless prisms, mp 117-118 °C (acetone), $[\alpha]_D^{20}$ -158° (*c* 1.11, MeOH), was prepared by the procedure employed for the preparation of **1**. 4-Bromobenzenesulfinic acid was prepared by the reduction of the corresponding sulfonyl chloride with sodium sulfite: M. Kulka, *J. Am. Chem. Soc.*, **72**, 1215 (1950).

4) All the new compounds are characterized spectrometrically and analytically.

5) J. Drabowicz, B. Bujnicki, and M. Mikolajczyk, *J. Org. Chem.*, **47**, 3325 (1982). Thus, **3a** ($[\alpha]_D^{20}$ 147° (*c* 1.30, MeOH), 90% yield, 90% ee by the reaction carried out in the presence of ether), **3b** ($[\alpha]_D^{20}$ 142° (*c* 1.34, MeOH), 99% yield, 98% ee), **3c** (mp 42-43 °C (hexane), $[\alpha]_D^{20}$ 224° (*c* 1.05, MeOH), 99% yield, 99% de, 99% ee), **5a** (mp 44-45 °C, $[\alpha]_D^{20}$ 148° (*c* 1.01, MeOH), 94% yield, 98% ee), **5b** (mp 49 °C (hexane), $[\alpha]_D^{20}$ 130° (*c* 1.08, MeOH), 94% yield, 99% ee), and **5c** ($[\alpha]_D^{20}$ 202° (*c* 1.24, MeOH), 65% yield or 99% yield based on the consumed **2**, 99% de, 99% ee) were obtained. The optical purity of **3a-c** and **5a-c** were determined by HPLC using Chiralcel OB available from Daicel Chemical Industries, Ltd.

6) The demethylation reaction of **3a**, for example, with BBr_3 in CH_2Cl_2 induced deoxygenation to give 4-methoxyphenyl pentyl sulfide in 60% yield.

7) G. I. Feutrill and R. N. Mirrington, *Tetrahedron Lett.*, **1970**, 1327.

8) Accordingly, **4a** (mp 79-81 °C, $[\alpha]_D^{20}$ 152° (*c* 1.16, MeOH), 86% yield), **4b** ($[\alpha]_D^{20}$ 134° (*c* 1.33, MeOH), 96% yield), and **4c** (mp 93-94 °C, $[\alpha]_D^{20}$ 236° (*c* 1.06, MeOH), 85% yield, 99% de, 99% ee) were isolated.

9) The 400 MHz ^1H NMR of **4c** as well as **3c** showed one diastereomer only.

10) Similar observation was reported with respect to *p*-bromophenyl methyl sulfone: W. E. Truce and M. F. Amos, *J. Am. Chem. Soc.*, **73**, 3013 (1951).

11) J. K. Stille and P. K. Wong, *J. Org. Chem.*, **40**, 532 (1975); M. Hidai, T. Hikita, Y. Wada, Y. Fujikura, and Y. Uchida, *Bull. Chem. Soc. Jpn.*, **48**, 2075 (1975). Thus **6a** (94% yield), **6b** (86% yield), and **6c** (90% yield) were obtained.

12) The acids **7a** (mp 164-165 °C, $[\alpha]_D^{20}$ 177° (*c* 0.99, MeOH), 93% yield), **7b** (mp 144-145 °C (AcOEt), $[\alpha]_D^{20}$ 148° (*c* 1.08, MeOH), 94% yield), and **7c** (mp 165-166 °C, $[\alpha]_D^{20}$ 458° (*c* 1.06, MeOH), 94% yield, 96% de, 99% ee) were isolated.

13) We determined the configuration of **3f** (less polar, viscous oil, $[\alpha]_D^{20}$ 178° (*c* 1.28, MeOH),) as (R_S, S_C) and that of **3g** (polar, viscous oil, $[\alpha]_D^{20}$ 167° (*c* 1.35, MeOH),) as (R_S, R_C), since $[\alpha]_D^{20}$ -14° (MeOH) of the sulfide obtained by the reduction of **3g** with $NaBH_4$ and $TiCl_4$ (S. Kano, Y. Tanaka, E. Sugino, and S. Hibino, *Synthesis*, **1980**, 695) was identical with that of the authentic sulfide $[\alpha]_D^{20}$ -13° (MeOH) prepared from 4-bromobenzenethiol and the tosylate of (*S*)-2-pentanol. The same reduction of **5d** (less polar) gave a sulfide which showed $[\alpha]_D^{20}$ -3° ($CHCl_3$) consistent with (*S*)-2-(4-bromophenyl)thiooctane: Chisso Corp., Japan Kokai Tokkyo Koho, JP 63-313768 (1988).

14) The yields of **4f** (mp 110-111 °C (EtOAc), $[\alpha]_D^{20}$ 185° (*c* 0.91, MeOH)) and **4g** (mp 104-105 °C (EtOAc), $[\alpha]_D^{20}$ 187° (*c* 1.02, MeOH)) were 70% and 96% respectively.

15) Given in °C. Cr: crystalline phase, S_C*: chiral smectic C phase, S_A: smectic A phase, I: isotropic liquid phase, N*: chiral nematic phase. Those in the parenthesis refer to that observed under cooling.

16) This is composed of three 5-alkyl-2-(4-alkyloxyphenyl)pyrimidine derivatives and a 2-(4-alkoxyphenyl)-5-(4-alkylphenyl)pyrimidine derivative.

17) The Ps of (*S*)-2-methylbutyl 3-[4-(4-decyloxybenzylideneamino)phenyl]-2-propenoate is defined to be (-), and thus the sign of Ps of **8-11** was determined accordingly.

18) The mixture was sealed in a polyimide rubbing cell of 2 μm thick. Square wave of 10 $V_{p\text{-}p}/\mu m$ was applied to the cell, and the change of transmittance (10%→90%) of light was observed.

19) Although alkyl aryl sulfoxides undergo racemization and/or decomposition at high temperatures (D. R. Rayner, A. J. Gordon, and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4854 (1968)) or under UV irradiation (K. Mislow, M. Axelrod, D. R. Rayner, H. Gotthardt, L. M. Coyne, and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 4958 (1965)), the compounds we prepared were stable under the conditions of measurements (ambient temperatures and visible light).

20) The Ps's of **8-11** may be estimated to be more than 420 nC/cm^2, one of the highest data reported so far: Dainippon Ink and Chemicals, Inc., Japan Kokai Tokkyo Koho, JP 64-47737 (1989).

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