

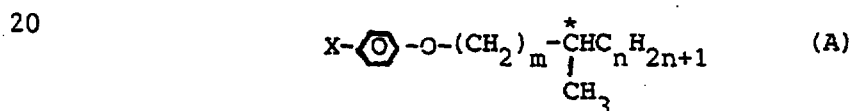
CHIRAL PHENYLETHER INTERMEDIATES FOR FERROELECTRIC
LIQUID CRYSTAL COMPOUNDS

This invention relates to chiral phenylether intermediates for ferroelectric liquid crystal compounds.

5 An alkoxybenzene derivative having asymmetric carbon atoms has recently attracted public attention as an intermediate of a liquid crystal material. Alkoxybiphenyl compounds, alkoxy-phenylpyrimidine compounds, alkoxybenzoic acid derivatives, etc. are known as ferroelectric smectic liquid crystal materials.

10 Generally 6-methyloctoxy groups, 2-methylbutoxy groups, etc. are the alkoxy groups in these liquid crystal materials. However, these compounds are not suitable for practical use because their temperature range is unsuitable for actual use and their stability is far from satisfactory.

15 Therefore, extensive studies on ferroelectric liquid crystal compounds have been carried out. The present inventors have conducted a thorough study of alkoxybenzene compounds and have found that the compounds represented by the following general formula A have excellent optical activity:



where X is a halogen atom, $m = 3$ to 5 , $n = 3$ to 12 and $\star$ is an asymmetric carbon atom.

25 The compounds have a halogen atom which has high reactivity as a nuclear substituting group, and accordingly they are expected to be useful as intermediates of ferroelectric liquid crystal compounds and materials.

X may be chlorine, iodine or fluorine, but preferably is bromine. Further, whilst $n = 3$ to 12 , preferably n is 4 to 10 .

The compounds of the general formula (A) can be easily prepared by known etherification techniques. For example, α
5 4-methylalkanol is sulphonated and thereafter reacted with a 4-halogenated phenol to yield a compound according to the general formula (A).

The present invention is further explained with reference to the following Examples.

10 Example 1

Preparation of 4-methyldecyl 4'-bromophenyl ether

172g (1.0mol) of 4-methyldecanol and 151.5g (1.5mol) of triethylamine were dissolved in 1300ml of dichloromethane and the mixture was cooled down to a temperature of 0 to -10°C .
15 149g (1.3mol) of methanesulphonyl chloride was added dropwise to the mixture and the mixture was stirred at the same temperature for two hours. Then, 1000ml of dichloromethane was added thereto and the mixture was washed with ice-cold water, 10% of hydrochloric acid, saturated aqueous sodium carbonate solution and saturated
20 aqueous salt solution in order, followed by drying with magnesium sulphate. The removal of the solvent gave 4-methyldecyl methane-sulphonate.

A mixture of 125g (0.5mol) of 4-methyldecyl methanesulphonate prepared as above, 95.1g (0.55mol) of 4-bromophenol, 30g (0.75mol)
25 of powdered sodium hydroxide and 800ml of dioxane were mixed and the mixture was stirred under reflux for eight hours. The

absence of sulphonate was confirmed by gas chromatography. The resulting sodium methanesulphonate was filtrated and the solvent was removed. The residue was extracted with 1000ml of toluene and the solution was washed with 5% hydrochloric acid and saturated aqueous salt solution and the solvent was removed.

The residue was distilled under 165°C/1mmHg to obtain 4-methyldecyl 4'-bromophenyl ether. The infrared spectrum analysis of the 4-methyldecyl 4'-bromophenyl ether satisfied the requirements:

1590cm⁻¹ and 820cm⁻¹ (benzene ring)
1380cm⁻¹ (methyl group)
1250cm⁻¹ (ether)

In addition, the specific rotary power was:

$$[\alpha]_D = +2.84^\circ \text{ (chloroform).}$$

Example 2

15 Preparation of 4-methyldodecyl 4'-bromophenyl ether

The method was the same as that of Example 1 but 4-methyldecanol was replaced by 200g (1.0mol) of 4-methyldodecanol. 4-methyldodecanol 4'-bromophenyl ether was the distillate at 175°C/1mmHg. The infrared spectrum analysis of the 4-methyldodecyl 4'-bromophenyl ether satisfied the requirements:

1590cm⁻¹ and 820cm⁻¹ (benzene ring)
1380cm⁻¹ (methyl group)
1250cm⁻¹ (ether)

In addition, the specific rotary power was:

$$[\alpha]_D = +1.99^\circ \text{ (chloroform)}$$

In addition, the specific rotary power was:

$$[\alpha]_d = -0.39^\circ \text{ (at } 26^\circ\text{C, 1.538\% chloroform solution).}$$

Example 4

Preparation of 6-methylnonyl 4'-bromophenyl ether

5 The method was the same as that of Example 3 except that 6-methyl-1-decanol was replaced by 6-methyl-1-nonanol whose specific rotary power was $[\alpha]_d = +1.67^\circ$ (at 28°C , 1.432% chloroform solution). 6-methylnonyl 4'-bromophenyl ether with a boiling point of $165^\circ\text{C}/0.15\text{mmHg}$ was obtained by distillation.

10 The infrared spectrum analysis of the 6-methylnonyl 4'-bromophenyl ether satisfied the following requirements:

1595 cm^{-1} and 820 cm^{-1} (benzene ring)

1380 cm^{-1} (methyl group)

1250 cm^{-1} (ether)

15 In addition, the specific rotary power was:

$$[\alpha]_d = +0.85^\circ \text{ (at } 26^\circ\text{C, 1.412\% chloroform solution).}$$

Example 5

Preparation of 5-methyltridecyl 4'-bromophenyl ether

i) Preparation of 5-methyltridecanol

20 2g of magnesium shavings were dispersed in 8ml of anhydrous ether in a stream of argon. 4g of 4-methyl-1-dodecylbromide which had been dissolved in 4ml of anhydrous ether was added dropwise to the solution to prepare the Grignard reagent. After injection of gaseous formaldehyde into the Grignard reagent

25 for 90 minutes at room temperature, the temperature was reduced to 0°C . 20ml of ice-cold water and 6ml of concentrated sulphuric acid

was added to the solution, and the precipitate was completely dissolved. The organic layer was washed with 5% hydrochloric acid and the solvent was removed.

10ml of ethanol and 0.4ml of concentrated hydrochloric acid
5 were added to the residue and the reflux of the mixture was conducted for 4 hours. Then the solvent was removed and the resulting product was extracted with benzene. The crude product prepared as above was distilled by Kugelrohr, and the distillate was obtained with a boiling point of 112 to 114°C/0.25mmHg. Then the distillate
10 was purified using a silica gel column after it had been diluted with hexane/ethyl acetate (85/15) as a developing solution. As a result, 5-methyltridecanol having the purity of 97.3% was obtained.

ii) Preparation of phenyl ether

The method as in Example 3 was followed except for using
15 5-methyltridecanol obtained as above. The distillate was obtained with a boiling point of 150 to 151°C/0.2mmHg. Then the distillate was diluted with hexane as developing solvent and the solution was purified using a silica gel column to obtain 5-methyltridecyl 4'-bromophenyl ether.

20 The infrared spectrum analysis of 5-methyltridecyl 4'-bromophenyl ether satisfied the following requirements:

1595cm⁻¹ and 820cm⁻¹ (benzene ring)

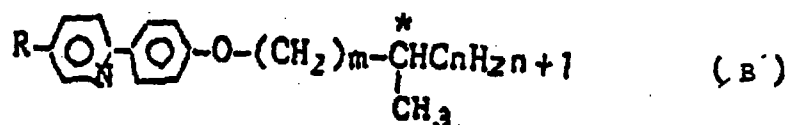
1380cm⁻¹ (methyl group)

1250cm⁻¹ (ether)

25 In addition, the specific rotary power was:

$[\alpha]_D = -0.206^\circ$ (at 29°C, 1.512% chloroform solution)

A compound according to the present invention may be used as an intermediate in the preparation of a compound of the general formula:

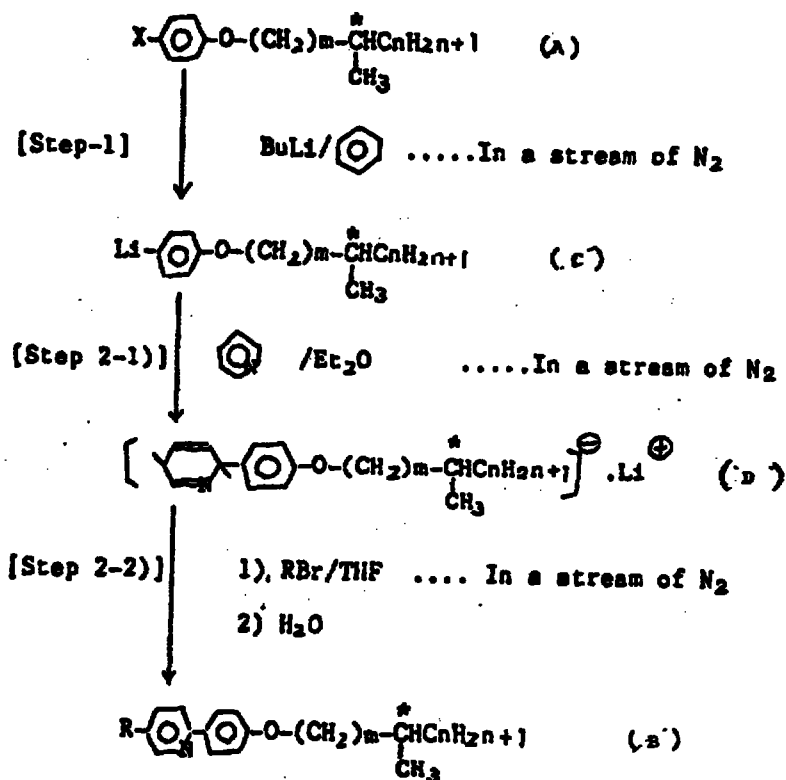


where R is an alkyl group with 7 to 12 carbon atoms. Compounds of the general formula (B) present a chiral smectic phase C (hereinafter referred to as SmC*).

As generally known, SmC* is ferroelectric liquid crystal phase and the electro-optical switching and memory characteristics of ferroelectric liquid crystal compounds is much better than that of other known compounds [N. A. Clark et al. : Appl. Phys. Lett., 36, 899, (1980)].

In practice it is essential for ferroelectric liquid crystal compounds to have a wide liquid crystal temperature range. Compounds according to the general formula (B) are very suitable since they can be used over a range from extremely low temperature to relatively high temperature as shown in Table 1. For example, compounds 6 and 7 present the SmC* phase at extremely low temperature, 36.4 to -2.7°C and 46.8 to 4.1°C, respectively. Compounds 11 and 15 present the SmC* phase at relatively high temperature, 70.6 to 58.5°C and 73.0 to 50.5°C, respectively. The temperature ranges can be arbitrarily selected by changing the position of the asymmetric carbon atom in the compound according to general formula (A). Namely, the temperature characteristics depend on the values of m and n.

Using a compound according to general formula (A), a compound according to general formula (B) can be prepared very easily by the following process:



These steps above are briefly described below:

[Step 1]

The compound (A) is reacted with butyllithium in benzene, in a stream of nitrogen to obtain the compound represented by the formula (C).

[Step 2-1]

The compound (C) is reacted with pyridine in ethyl ether to obtain the compound represented by the formula (D).

[Step 2-2)]

The compound (D) is dissolved in ether solution. Then tetrahydrofuran and 1-bromoalkane are added to the solution and the mixed solution is reacted. Then the reacted solution is hydrolyzed to obtain the compound represented by the general formula (B) (See the Table 1).

In Table 1, K stands for crystalline phase. Smx and Smy stand for unidentified smectic phase. SmC* stands for chiral smectic phase C. SmA stands for smectic phase A. Ch

stands for cholesteric phase. Iso stands for isotropic liquid phase. Figures in the parenthesis means monotropic phase transition. "." means that the compound presents each corresponding phase. "-" means that the compound does not present the isotropic liquid phase.

A ferroelectric liquid crystal composition as shown in Table 2 including a compound according to general formula (B) was thermally sealed into the space between two glass substrates which had a transparent electrode thereon and whose surface had been rubbed. The substrates formed an electric optical element with a thickness of 1 to 2 μm and the element was sandwiched between a polarizer and an analyzer whose directions crossed each other and then an alternating electric field of ± 12 V was applied thereto. As a result, the liquid crystal composition responded according to the direction of electric field.

The transition point from SmA to SmC* was relatively high, i.e. at 58°C . The SmC* temperature range was wide. Around the room temperature (25°C), the operational temperature range was very good, i.e. at about ± 5 degrees. The contrast was also very good, i.e. 1 : 10 in the same temperature range.

In addition, the I_m/I_p ratio, the ratio ^{cf} ~~over~~ the light transmittance I_m when electric field was removed (when memory was operated) / the light transmittance I_p when electric field was applied, was greater than 0.9, i.e. $I_m/I_p > 0.9$ and so the memory characteristic was good.

- 5 As mentioned above, a ferroelectric liquid crystal composition comprising a compound or compounds according to general formula (B) and made using a compound or compounds according to general formula (A) as an intermediate has an extremely wide driving temperature range, good contrast and very
- 10 good memory characteristics even if the optical element thickness is about 1 to 2 μm . Such liquid crystal composition can be applied to light liquid crystal shutters or high multiplex liquid crystal devices etc.

TABLE 1

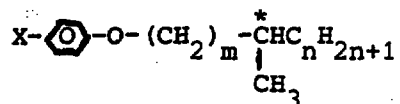
COMPOUND NO.	COMPOUND (A) (B)			PHASE TRANSITION TEMPERATURE (°C)					
	$C_n H_{2n+1}$	R	m	K	$S_{m\alpha}$	$S_{m\gamma}$	$S_{m\alpha^*}$	$S_{m\alpha}$	Ch Iso
1	$C_3 H_7$	$C_9 H_{19}$	3	-42.3 (33.8-)	-58.0 (47.7-)	-64.4 (60.5-)	—	—	.
2	$C_3 H_7$	$C_{11} H_{23}$	3	-36.2 (20.5-)	-55.6 (43.0-)	-58.7 (52.8-)	—	—	.
3	$C_4 H_9$	$C_{10} H_{21}$	3	-62.2 (33.5-)(40.5-)	—	— (57.2-)	—	—	.
4	$C_5 H_{11}$	$C_8 H_{17}$	3	-35.0 (11.8-)(46.5-)	-47.1 (46.5-)	-52.4 (56.9)	—	—	.
5	$C_5 H_{11}$	$C_9 H_{19}$	3	-28.8 (0.4-)(39.0-)	-39.9 (39.0-)	-55.1 (54.6-)	—	—	.
6	$C_5 H_{11}$	$C_{10} H_{21}$	3	-35.3 (-2.7-)	-54.7	— (36.4-)	—	—	.
7	$C_6 H_{13}$	$C_8 H_{17}$	3	-50.0 (-15.4-)(4.1-)	—	— (46.8-)	—	—	.
8	$C_6 H_{13}$	$C_{12} H_{25}$	3	-50.7 (28-)	-54.8 (38.6-)	— (51.7-)	—	—	.
9	$C_8 H_{17}$	$C_8 H_{17}$	3	-48.2 (-8.8-)(27.3-)	—	— (43.3-)	—	—	.
10	$C_8 H_{17}$	$C_9 H_{19}$	3	-42.2 (-1.4-)(34.5-)	-50.1 (34.5-)	— (48.4-)	—	—	.
11	$C_8 H_{17}$	$C_{12} H_{25}$	3	-45.0 (38.0-)(58.5-)	-59.0 (58.5-)	-71.5 (70.8-)	—	—	.
12	$C_3 H_7$	$C_7 H_{15}$	5	-30.5 (0.2-)(36.3-)	-42.5 (36.3-)	-56.0 (53.2-)	—	—	.
13	$C_3 H_7$	$C_9 H_{19}$	5	-33.0 (8.1-)(51.8-)	-52.2 (51.8-)	-58.1	—	—	.
14	$C_3 H_7$	$C_{11} H_{23}$	5	-28.4 (-4.6-)(17.5-)	-55 (17.5-)(36.8-)	-58.7 (47.0-)	—	—	.
15	$C_4 H_9$	$C_7 H_{15}$	5	-43.4 (28.8-)	-59.8 (50.5-)(73.0-)	-73.5 (73.0-)	—	—	.
16	$C_4 H_9$	$C_9 H_{19}$	5	-37.2 (12.0-)(51.4-)	-56.8 (51.4-)(60.4-)	-63.7	—	—	.
17	$C_4 H_9$	$C_{11} H_{23}$	5	-26.6 (11.5-)(32.0-)	-45.1	-58.9 (54.7-)(68.7-)	-71.2	—	.

TABLE 2

COMPOUND		COMPOSITION RATE (wt%)
ferroelectric liquid crystal compound CS-1000 (made by Chisso Corporation)		70
$\text{C}_6\text{H}_{13}^*\text{CH}(\text{CH}_2)_{10}-\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{C}_{12}\text{H}_{25}$ CH_3 (compound No. 8)		20
$\text{C}_6\text{H}_{17}-\text{O}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{CH}_2^*\text{CH}(\text{CH}_3)\text{C}_2\text{H}_5$		10
PHASE TRANSITION POINT (°C)	SmC* SmA Ch Iso 58 71 77	

CLAIMS

1. A chiral phenylether compound represented by the general formula:



5 where X is a halogen atom, m = 3 to 5, n = 3 to 12 and * is an asymmetric carbon atom.

2. A chiral phenylether compound as claimed in claim 1 in which X is a bromine atom.

3. A chiral phenylether compound as claimed in claim 1 or
10 2 in which n is 4 to 10.

4. 4-methyldecyl 4'-bromophenyl ether.

5. 4-methyldodecyl 4'-bromophenyl ether.

6. 6-methyldecyl 4'-bromophenyl ether.

7. 6-methylnonyl 4'-bromophenyl ether.

15 8. 5-methyltridecyl 4'-bromophenyl ether.

9. A method of preparing a chiral phenylether compound as claimed in claim 1 and substantially as herein described with reference to any one of Examples 1 to 5.

