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# Synthesis and Properties of Optically Active α-Trifluoromethylbenzyl Derivatives as New Chiral Dopants for Ferroelectric Liquid Crystals

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Optically active α-trifluoromethylbenzyl derivatives as new chiral dopants for ferroelectric liquid crystals (FLCs) were synthesized utilizing optically active 4,4,4-trifluoro-3-(4-methoxyphenyl)butanoic acid prepared by optical resolution procedures. The magnitudes of spontaneous polarization (Ps) and the response time depended on the type of the linkage between the optically active block and core blocks.

Recently a lot of ferroelectric liquid crystals (FLCs) and chiral dopants for FLCs have been studied with a great interest in connection with their application for fast response display devices.$^{1,2)}$ The response time which is thought to be one of the most important properties depends on the magnitude of spontaneous polarization (Ps) and viscosity of the FLCs. However, the relationship between the molecular structure of a FLC and its properties is not clear. In this paper, we report the synthesis and properties of optically active α-trifluoromethylbenzyl derivatives shown in Fig.1 as new chiral dopants for FLCs. **8a** and **11b** did not have any liquid crystal phase, while **8b** and **11a** had one, but showed no ferroelectric liquid crystal phase. The phase transition temperatures of the chiral dopants were shown in Fig.1.

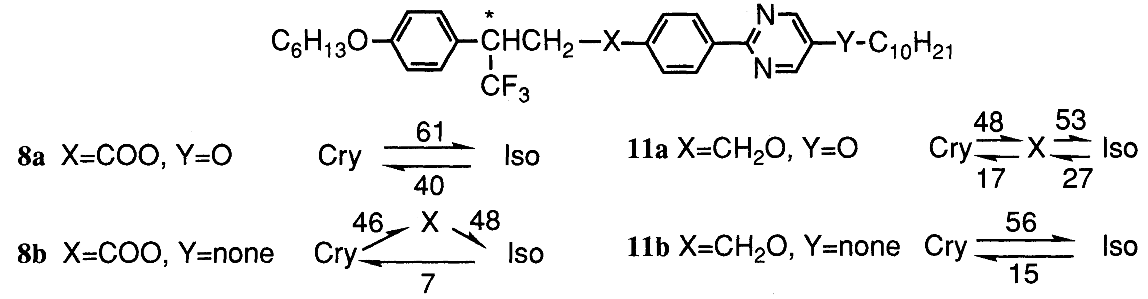
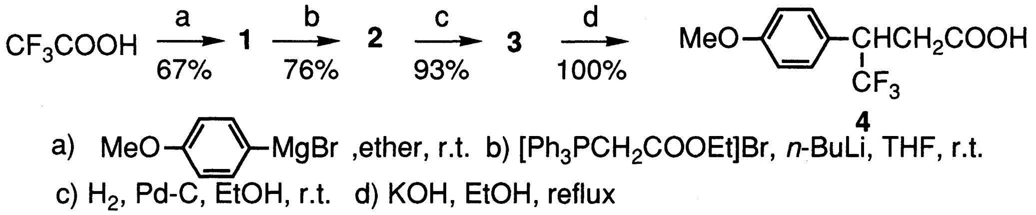


Fig.1. The chiral dopants and their phase transition temperatures [°C].
Cry: crystal, Iso: isotropic liquid, X: unidentified phase.

The racemic 4,4,4-trifluoro-3-(4-methoxyphenyl)butanoic acid (**4**) were prepared, as shown in Scheme 1. Thus, 1,1,1-trifluoro-4-methoxyacetophenone (**1**), prepared from the reaction of trifluoroacetic acid with 4-methoxyphenylmagnesium bromide, was converted to ethyl 4,4,4-trifluoro-3-(4-methoxyphenyl)-2-butenoate (**2**) by the treatment with phosphonium salt (b) in the presence of *n*-BuLi. The hydrogenation of **2** over palladium-carbon afforded ethyl 4,4,4-trifluoro-3-(4-methoxyphenyl)-2-butanate (**3**) which was hydrolyzed to give **4**.$^{3)}$



Scheme 1.

Optically active 4,4,4-trifluoro-3-(4-methoxyphenyl)butanoic acid (**4**) was obtained by the diastereomeric salt formation method in good yield using an optically active amine, such as *cis*-2-benzylaminocyclohexanemethanol (Fig.2) as a resolving agent. The salts of **4** were recrystallized with 95%-ethanol as the resolving solvent. The results and properties of **4**$^*$ are shown in Table 1.

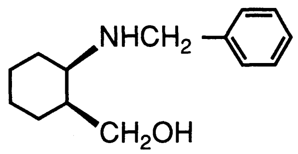


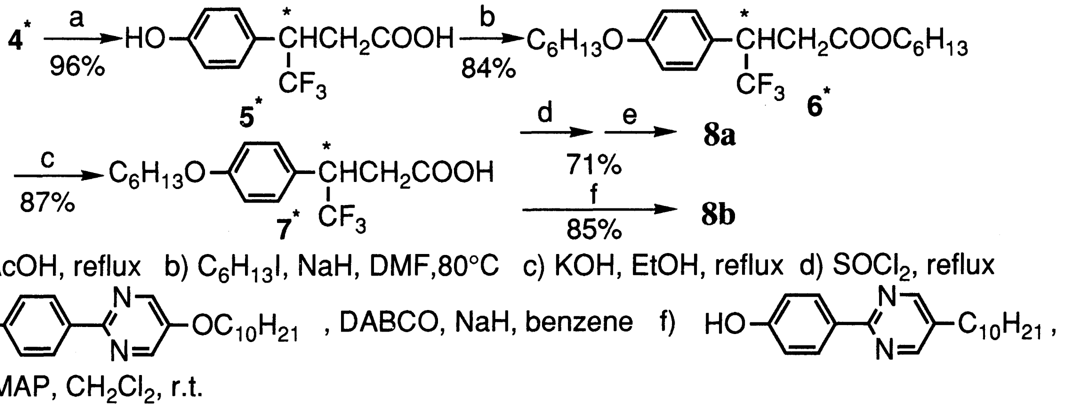
Fig.2. *cis*-2-Benzylaminocyclohexanemethanol. (1S, 2R)-(-)-isomer.

Table 1. Optical resolution of (±)-**4**

| | Salt$^{a)}$ | | | Free acid | | O.P. / %e.e. $^{d)}$ | Yield / % $^{e)}$ |
|---|---|---|---|---|---|---|---|
| | $[\alpha]_D$ / °$^{b)}$ | $[\alpha]_{435}$ / °$^{b)}$ | Mp $\theta_m$ / °C | $[\alpha]_D$ / °$^{c)}$ | $[\alpha]_{435}$ / °$^{c)}$ | | |
| (+)-**4** | +17 | +35 | 179-180 | +45 | +94 | >99 | 69 |
| (-)-**4** | -17 | -34 | 179-180 | -46 | -96 | >99 | 67 |

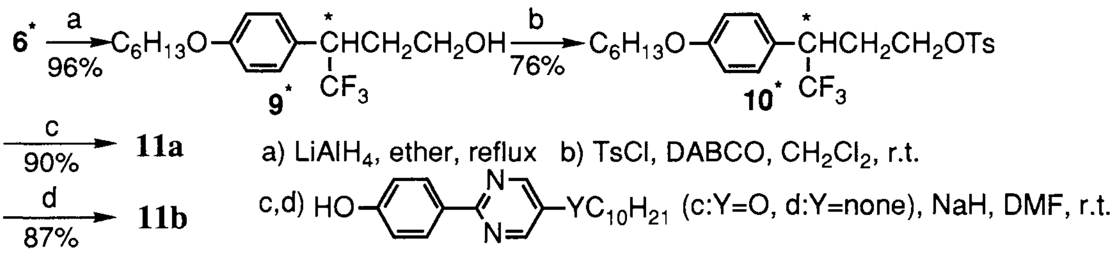
a) (+)-(+)-salt and (-)-(-)-salt. b) Solvent: MeOH. c) Solvent: 99%EtOH. d) The optical purities of **4**$^*$ were determined as its ethyl ester using HPLC equiped with a chiral column,"CHIRALCEL OB"(4.6 mm X 250 mm, carrier solvent hexane:2-propanol=99:1). e) The yields were calculated based on half the amount of racemic **4**.

Demethylation of **4**$^*$ with hydrobromic acid quantitatively afforded a phenol derivative **5**$^*$ which was alkylated with hexyliodide to give **6**$^*$. Following hydrolysis of **6**$^*$ gave **7**$^*$. The chiral dopants **8a** and **8b** were thus obtained by esterification of **7**$^*$ with phenol derivatives (Scheme 2).



Scheme 2.

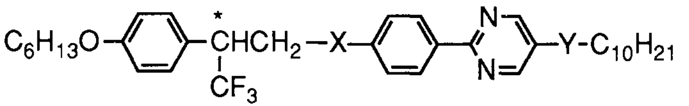
The reduction of $6^*$ with lithium aluminium hydride gave alcohol derivative $9^*$which was converted to $10^*$ by following tosylation. The chiral dopants **11a** and **11b** were yielded by the treatment of $10^*$ with phenol derivatives (Scheme 3).[4)]



Scheme 3.

As the chiral dopants **8a**, **8b**, **11a**,and **11b** showed no chiral smectic C ($Sc^*$) phase, FLC mixtures were prepared by adding 10 wt% of the chiral dopant into an achiral host liquid crystal mixture.[5)] The phase transition temperatures, Ps, response times ($\tau_{10\text{-}90}$) and tilt angle ($\theta$) of the FLC mixtures were shown in Table 2.

Table 2. Electro-optical properties of FLC mixtures[a)] at 25 °C



| Chiral dopant | X | Y | Phase transition temp / °C<br>Cry⇌Sc* | ⇌S$_A$ | ⇌N* | ⇌Iso | Ps[b)]<br>nC cm$^{-2}$ | $\tau_{10\text{-}90}$[c)]<br>μs | θ<br>deg |
|---|---|---|---|---|---|---|---|---|---|
| (-)-**8a** | COO | O | 1<br>-6 | 59<br>56 | 64<br>64 | 74<br>74 | +2.0 | 230 | 21 |
| (-)-**8b** | COO | - | 0<br>-5 | 52<br>51 | 61<br>57 | 74<br>72 | +3.5 | 300 | 20 |
| (+)-**11a** | $CH_2O$ | O | -2<br>-7 | 50<br>49 | 63<br>63 | 73<br>73 | -8.0 | 100 | 18 |
| (+)-**11b** | $CH_2O$ | - | 1<br>-6 | 47<br>47 | 60<br>59 | 72<br>72 | -7.5 | 92 | 22 |

a) FLC mixtures comprised of a chiral dopant (10 wt%) and the host liquid crystal (90 wt%).[5)] b) The magnitudeof Ps was measured by the triangular wave method.[6)] c) The change of transmittance (from 10 to 90 %) of light was observed when a square wave of 10Vpp$\mu m^{-1}$ was applied to the cell.

The phase transition temperatures of **11a** were lower than those of **8a**, while those of **8b** were lower than those of **8a**. Thus the phase transition temperatures of the FLC mixtures depend on the number of oxygen atom in the chiral dopant molecule.

At 25 °C, the values of Ps of the FLC mixtures containing chiral dopants having -$CH_2O$- group at X were about twice as large as those of the FLC mixtures containing chiral dopants having -COO- group at X. On the other hand, the magnitudes of Ps of the FLC mixtures hardly concerned whether the chiral dopant molecule has -O- at Y or not.

The response times of FLCs substantially decreased with the increase of the magnitudes of Ps. Those

$\tau_{10\text{-}90}$ of FLC mixtures containing chiral dopants having -$CH_2O$- group at X was about half as compared with that of the FLC mixtures containing chiral dopants having -COO- group at X.

Finally, the tilt angles of FLC mixtures at 25 °C were about 20 degrees, and hardly concerned with chiral dopants.

Further, detailed studies on new chiral dopants for FLC are actively in progress.

References

1) For example: J. W. Goodby, R. Blinc, N. A. Clark, S. T. Lagerwall, M. A. Osipov, S. A. Pikin, T. Sakurai, K. Yoshino, and B. Zeks, "Ferroelectric Liquid Crystals," Gordon and Breach Science Publishers (1990).

2) The FLCs with a trifluoromethyl group at the chiral center were reported. T. Ishizuka, H. Miura, and H. Nohira, *Nippon Kagaku Kaishi*, **10**, 1121 (1990); A. Sakaigawa, Y. Tashiro, Y. Aoki, and H. Nohira, *Mol. Cryst. Liq. Cryst.*, **206**, 147 (1991).

3) Spectroscopic data for **4** were given as follow: IR ($cm^{-1}$, KBr) 2940, 1711, 1518, 1306, 1244, 1183, 1156, 1106, 1029, 969, 924, 831, 814, 642; MS m/z = 247 ($M^+$-1); $^1H$ NMR (60 MHz, DMSO-$d_6$) $\delta$ 2.9-3.0 (m, 2H, $CH_2$), 3.4-4.2 (m, 4H, $OCH_3$ and $CHCF_3$), 7.0 (d, 2H, Ar), 7.4 (d, 2H, Ar). The absolute configuration of **4** has not been determined yet.

4) Spectroscopic data for **8a** were given as follow: IR ($cm^{-1}$, KBr) 1747, 1517, 1458, 1439, 1380, 1321, 1265, 1199, 1163, 1152, 1110, 1014, 964, 787; MS m/z = 627 ($M^+$-1); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 0.89 (m, 6H, $CH_3$), 1.28 (m, 20H, $CH_2$), 1.78 (m, 4H, $CH_2$), 3.07-3.29 (m, 2H, $CH_2COO$), 3.93-3.97 (m, 3H, $CH_2OAr$ and $CHCF_3$), 4.07 (t, 2H, $CH_2OAr$), 6.90 (d, 2H, Ar), 6.93 (d, 2H, Ar), 7.29 (d, 2H, Ar), 8.30 (d, 2H, Ar), 8.40 (s, 2H, Ar): **8b**; IR ($cm^{-1}$, KBr) 1764, 1616, 1516, 1430, 1302, 1248, 1197, 1162, 1143, 1116; MS m/z = 611 ($M^+$-1); $^1H$ NMR (90 MHz, $CDCl_3$) $\delta$ 0.9 (m, 6H, $CH_3$), 1.2-1.7 (m, 24H, $CH_2$), 2.6 (t, 2H, Ar-$CH_2$), 3.1-3.2 (m, 2H, $CH_2COO$), 3.9-4.0 (m, 3H, $OCH_2$ and $CHCF_3$), 6.90 (d, 2H, Ar), 7.0 (d, 2H, Ar), 7.3 (d, 2H, Ar), 8.4 (d, 2H, Ar), 8.6 (s, 2H, Ar): **11a**; IR ($cm^{-1}$, KBr) 1514, 1427, 1326, 1301, 1242, 1160, 1111, 1067, 1040, 847, 828, 799; MS m/z = 613 ($M^+$-1); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 0.88 (m, 6H, $CH_3$), 1.27-1.44 (m, 20H, $CH_2$), 1.76 (m, 4H, $CH_2$), 2.15-2.54 (m, 2H, $CH_2$), 3.57-3.73 (m, 2H, $CH_2OAr$), 3.88-4.03 (m, 5H, $CH_2OAr$ and $CHCF_3$), 6.84 (d, 2H, Ar), 6.86 (d, 2H, Ar), 7.18 (d, 2H, Ar), 8.24 (d, 2H, Ar), 8.38 (s, 2H, Ar): **11b**; IR ($cm^{-1}$, KBr) 1515, 1434, 1245, 1161, 1112, 1070, 1039, 844, 828, 791; MS m/z = 597 ($M^+$-1); $^1H$ NMR (90 MHz, $CDCl_3$) $\delta$ 0.9 (m, 6H, $CH_3$), 1.2-1.7 (m, 24H, $CH_2$), 2.1-2.7 (m, 4H, Ar-$CH_2$ and $CH_2$), 3.6-4.0 (m, 5H, $CH_2OAr$ and $CHCF_3$), 6.8 (d, 2H, Ar), 6.9 (d, 2H, Ar), 7.3 (d, 2H, Ar), 8.3 (d, 2H, Ar), 8.6 (s, 2H, Ar).

5) The host liquid-crystalline mixture consists of 2-(4-dodecyloxyphenyl)-5-hexylpyrimidine (20 wt%), 2-(4-nonyloxyphenyl)-5-octylpyrimidine (20 wt%), 2-(4-nonyloxyphenyl)-5-nonylpyrimidine (20 wt%), 2-(4-hexyloxyphenyl)-5-decylpyrimidine (20 wt%), 4-(5-undecyl-2-pyrimidinyl)phenyl-4-heptylcyclohexanecarboxylate (10 wt%), 4-(5-dodecyl-2-pyrimidinyl)phenyl-4-butylcyclohexanecarboxylate (10 wt%). In the host liquid-crystalline mixture phenylpyrimidine derivatives were available for stabilization of $Sc^*$ phase, and cyclohexanecarboxylate derivatives were available for the rise of Tc. However this host was not completely optimized. The phase transition temperatures were $\mathrm{Cry} \underset{-2}{\overset{4}{\rightleftharpoons}} \mathrm{Sc} \underset{64}{\overset{66}{\rightleftharpoons}} \mathrm{S_A} \underset{68}{\overset{70}{\rightleftharpoons}} \mathrm{N} \underset{80}{\overset{81}{\rightleftharpoons}} \mathrm{Iso}$.

6) K. Miyasato, S. Abe, H. Takezoe, A. Fukuda, and E. Kuze, *Jpn. J. Appl. Phys.*, **22**, 661 (1983).

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