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Synthesis of new chiral compounds for cholesteric liquid crystal display

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The synthesis and properties of (*S*)-(2-methylbutyl)benzene derivative and (*S*)-2-phenylpropionic acid derivatives were studied with a view to their application on cholesteric liquid crystal devices. Compared with available chiral compounds the new compounds exhibited larger helical twisting power and higher dielectric anisotropy. The relationship between structure and properties of these compounds is discussed.

Keywords: chiral compound; cholesteric liquid crystal display; (*S*)-(2-methylbutyl)benzene derivative; (*S*)-2-phenylpropionic acid derivative; helical twisting power; dielectric anisotropy

1. Introduction

One of the applications of the selective reflection phenomenon of cholesteric liquid crystals is the bright reflection type liquid crystal display (LCD) that has a memory function (*1–7*). If the helical axis of a cholesteric liquid crystal is aligned in a perpendicular direction on a pair of parallel substrates (planar arrangement), the liquid crystal optical element will reflect light of a selective wavelength. On the other hand, when it is aligned in a parallel direction on a pair of parallel substrates (focal conic arrangement), the incident light almost transmits through the liquid crystal cell (Figure 1).

These two arrangements can be changed by the application of a low voltage. Moreover, the application of a high voltage leads to a homeotropic arrangement, which can be easily changed to planar arrangement by turning off the power. The selective reflection wavelength (λ) can be calculated by

$$\lambda = np, \tag{1}$$

where n is the average refractive index and p is the helical pitch of the liquid crystal composition.

Further, the helical pitch can be calculated by (*8*)

$$p = (c \times \mathrm{HTP})^{-1}, \tag{2}$$

where c is the mass fraction of the chiral dopant and HTP is the helical twisting power of the optically active compound.

Thus, the selective reflection colour is determined by the HTP and the added amount of the optically active compound. A chiral nematic liquid crystal can be obtained by mixing a nematic liquid crystal and optically active compound. A reduction of the driving voltage requires a decrease of the threshold voltage of the electro-optical response, which can be most conveniently achieved by using a more polar material, i.e. by increasing the dielectric anisotropy ($\Delta\varepsilon$) of the liquid crystal (*9–11*). Chiral materials can be inherently of a high viscosity owing to their branched structure and will add to the viscosity of a mixture for devices. Hence, a high HTP enables less of the chiral material to be used to generate the required chirality-dependent properties in a mixture. Similarly, highly polar material can be of a high viscosity. Hence, the addition of small quantities of very high dielectric anisotropy materials to a low-viscosity nematic mixture would be beneficial to the overall properties of the liquid crystal mixture. Therefore it could be advantageous to combine, in one material, a high HTP and a high positive dielectric anisotropy, to benefit the overall properties of the final liquid crystal mixture.

Figure 2 shows the structural formulae of commercially available chiral dopants. Recently Nohira and co-workers reported the chiral dopants **1** and **2**, prepared from optically active 2-phenylpropanoic acid (Figure 3) (*12, 13*). But, their performances were not sufficient for cholesteric LCD in low-voltage application.

In this paper, we report on the synthesis of some new chiral compounds, **3–8** (Figure 4), derived from (*S*)-(2-methylbutyl)benzene derivatives or (*S*)-2-phenylpropanoic acid (*14–16*), and discuss the relationship between the molecular structure of the chiral compounds and their performance, such as HTP and

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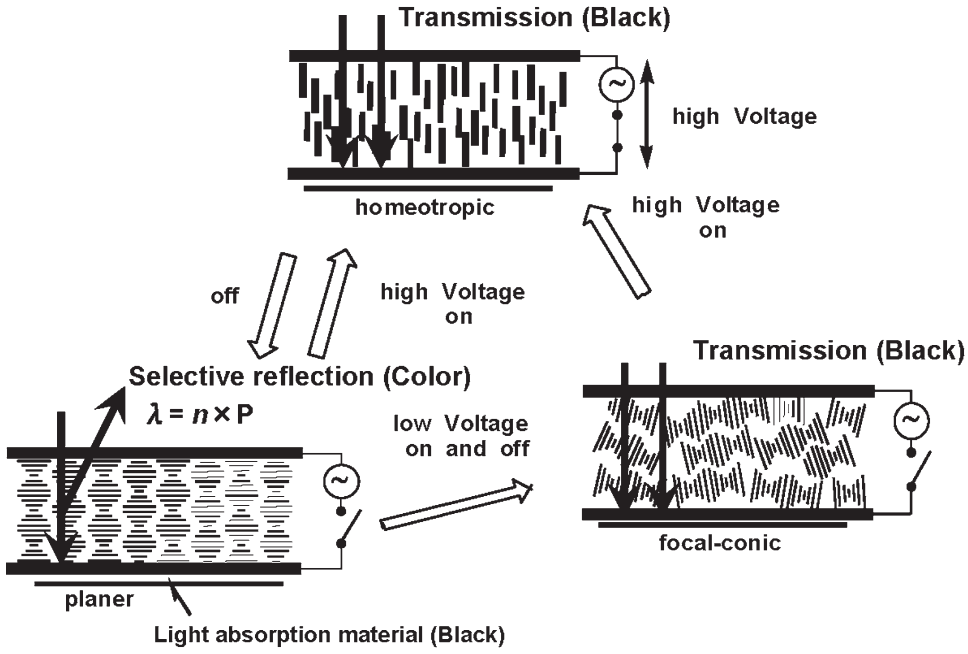


Figure 1. Reflective cholesteric LCDs.

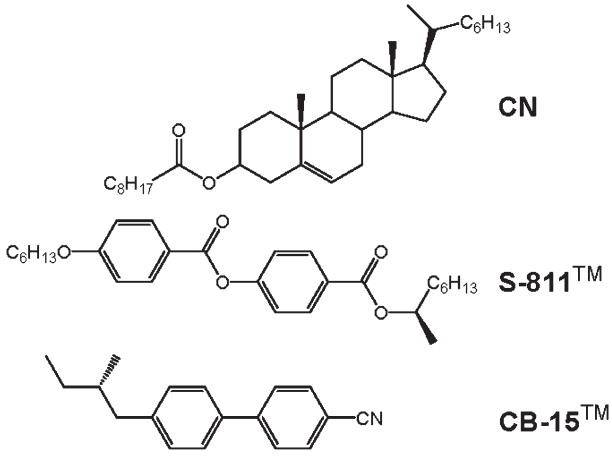


Figure 2. Structures of commercial chiral dopants.

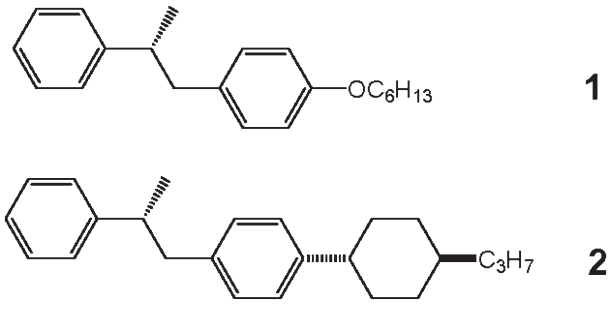


Figure 3. Structures of chiral dopants derived from (*S*)-2-phenylpropanoic acid.

$\Delta\varepsilon$. We have successfully made cholesteric liquid crystal mixtures for cholesteric LCDs by using the novel chiral compounds.

2. Results and discussion

Synthesis of chiral compounds

(S)-(2-Methylbutyl)benzene derivatives.

New chiral compounds **3** and **4** were synthesised (Scheme 1). The reaction of (*S*)-4-(2-methylbutyl)-1-chlorobenzene [AGC Seimi Chemical Co, Ltd, enantiomeric purity not specified, $[\alpha]_D^{20}$ +10.6° (c 1.0, $CHCl_3$)] with magnesium followed by carbon dioxide gave (*S*)-4-(2-methylbutyl)benzoic acid (*17,*

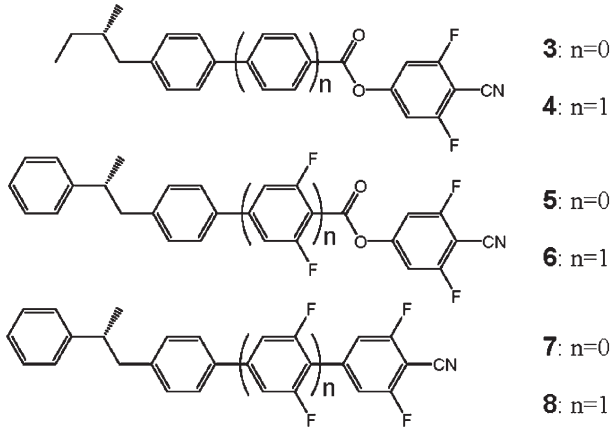
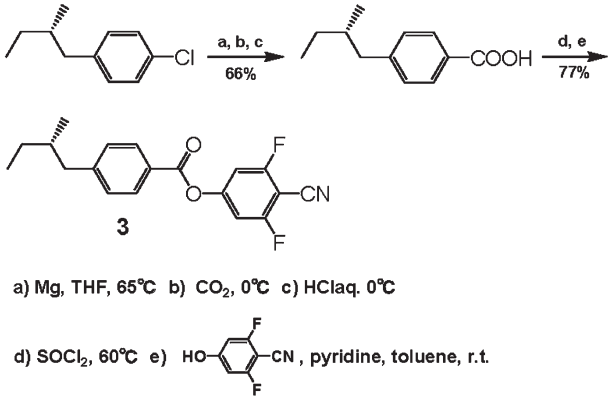


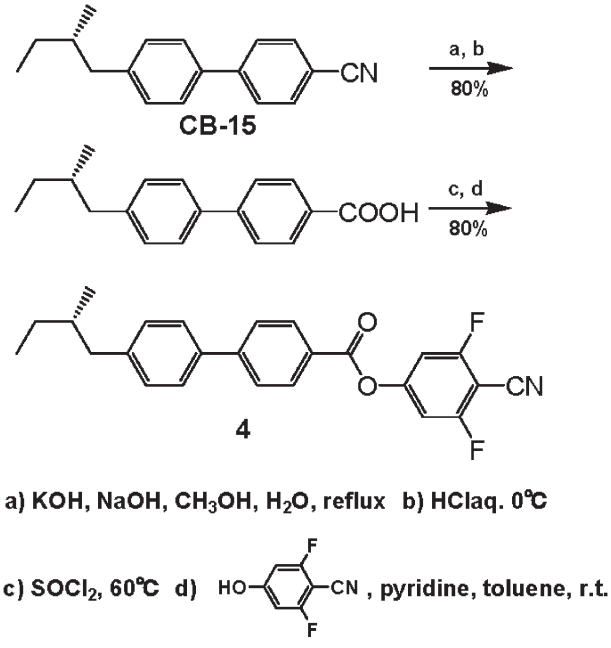
Figure 4. Structures of new chiral compounds with high $\Delta\varepsilon$.

18). Esterification with 4-cyano-3,5-difluorophenol (*19, 20*) gave chiral dopant **3**.



Scheme 1. Synthesis of (*S*)-4-(2-methylbutyl)benzoic acid derivatives.

Hydrolysis of the chiral dopant CB-15 [Merck KGaA, enatiomeric purity not specified, $[\alpha]_D^{20}$ +13.2 (c 1.0, $CHCl_3$)] gave (*S*)-4′-(2-methylbutyl)biphenyl-4-carboxylic acid (*17, 21*) and esterification with 4-cyano-3,5-difluorophenol gave chiral dopant **4** (Scheme 2).



Scheme 2. Synthesis of (*S*)-4′-(2-methylbutyl)biphenyl-4-carboxylic acid derivatives.

(S)-2-Phenylpropanoic acid derivatives.

New chiral compounds **5–8** with high Δε were synthesised by the following routes shown in Scheme 3.

(*R*)-1-(4-Chlorophenyl)-2-phenylpropane **9** was synthesised from (*S*)-2-phenylpropanoic acid by three steps (*12*). Subsequent carboxylation and esterification with 4-cyano-3,5-difluorophenol gave 4-cyano-3,5-difluorophenyl-(*R*)-4-(2-phenylpropyl)benzoate **5**. (*R*)-3,5-difluoro-4′-(2-phenylpropyl)biphenyl **10** was synthesised from compound **9** by three steps. Subsequent introduction of a cyano group gave (*R*)-4-cyano-3,5-difluoro-4′-(2-phenylpropyl)biphenyl **7**. Carboxylation of compound **10** followed by esterification with 4-cyano-3,5-difluorophenol gave 4-cyano-3,5-difluorophenyl-(*R*)-3,5-difluoro-4′-(2-phenylpropyl)biphenyl-4-carboxylate **6**. Moreover, introduction of 3,5-difluoro-4-cyanophenyl group into compound **10**, using Suzuki–Miyaura cross-coupling reaction (*22, 23*), gave (*R*)-4-cyano-3,5,2′,6′-tetrafluoro-4″-(2-phenylpropyl)-*p*-terphenyl **8**.

Performances of chiral compounds

The HTP of each chiral dopant was measured as a 1 wt% mixture in the host liquid crystal ZLI-1565 (Merck KGaA). The nematic–isotropic phase transition temperature (T_{ni}), kinematic viscosity (v) and dielectric anisotropy value (Δε) of each chiral dopant were measured using a 5 wt% mixture in the host liquid crystal ZLI-1565. The extrapolation data for each chiral dopant were calculated by following equations:

$$T_{ni(measured)} = 0.95T_{ni(ZLI-1565)} + 0.05T_{ni(chiral\ dopant)},$$

$$\mathrm{Log}_{10}(v_{measured}) = 0.95\log_{10}(v_{ZLI-1565}) + 0.05\log_{10}(v_{chiral\ dopant}),$$

$$\Delta\varepsilon_{measured} = 0.95\Delta\varepsilon_{ZLI-1565} + 0.05\Delta\varepsilon_{chiral\ dopant}.$$

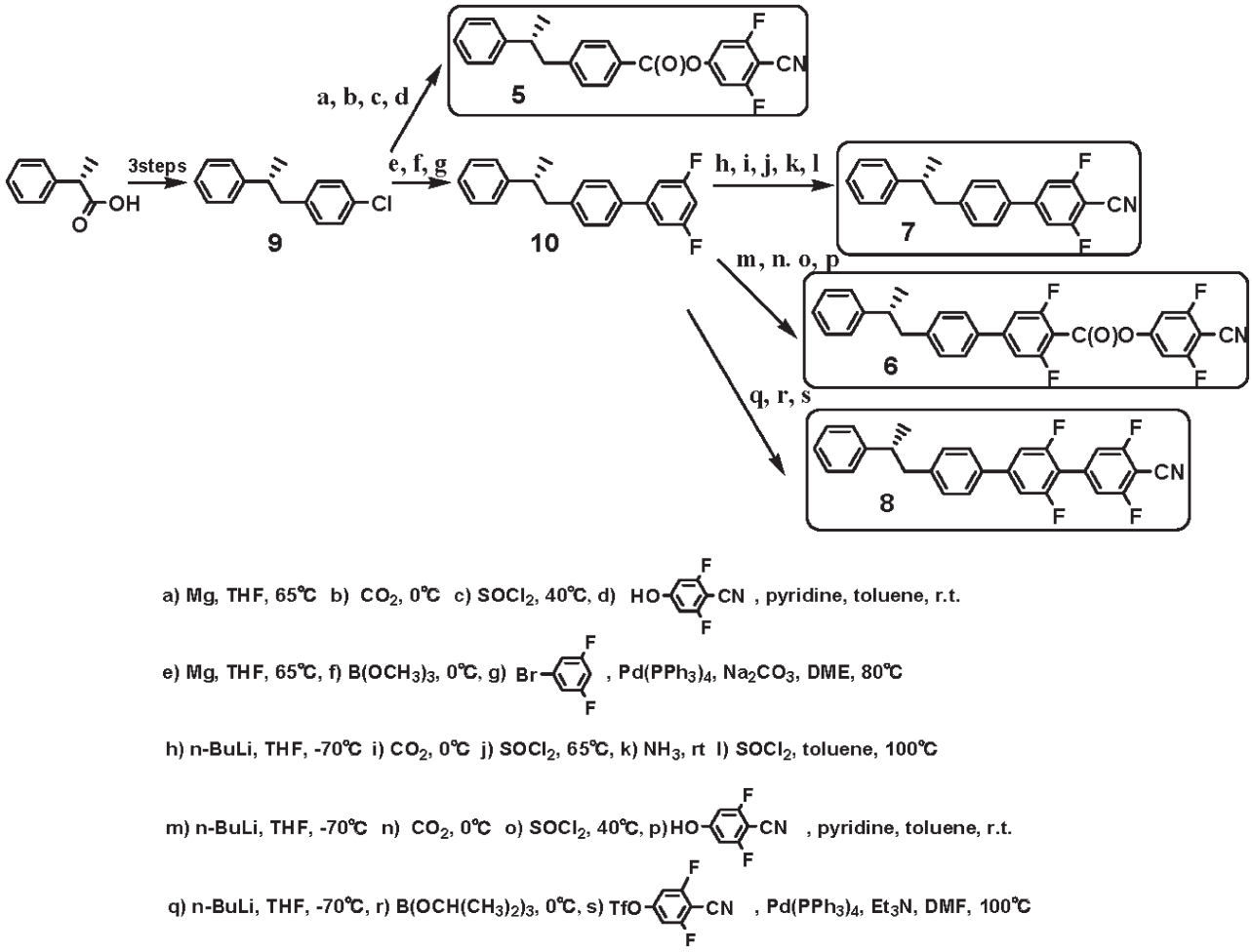
The results and values of some known materials for comparison are summarised in Table 1.

Helical twisting power (HTP).

The dopant **3** and dopant **5** have a similar structure to 4-cyano-3,5-difluorophenyl (*R*)-4-(2-substitutedpropyl)benzoate group (Figure 5). The difference between them is the end group, i.e. dopant **3** has 2-ethylpropyl group and dopant **5** has 2-phenylpropyl group. The HTP value of dopant **5** (12.3 μm^{-1}) is larger than that of dopant **3** (5.2 μm^{-1}).

The molecular geometries of the novel chiral compounds were calculated using the semi-empirical quantum chemical AM1 method (MOPAC 6.0 package) (*24*). The results are shown in Figure 6.

In the case of dopant **5**, as for dopant **7**, the methyl group in the chiral position is almost vertical to the plane of the core structure. On the other hand, in the case of dopant **3**, it is horizontal. Therefore, we assume that the chiral core structure, (*R*)-1,2-diphenylpropane,



Scheme 3. Synthetic routes of new chiral compounds.

Table 1. Physical properties of chiral compounds.

Compound	HTP (μm^{-1})[a]	T_{ni} (°C)[b]	T_{ni} (°C)[c]	v (mm^2s^{-1})[d]	v (mm^2s^{-1})[c]	$\Delta\varepsilon$[d]	$\Delta\varepsilon$[e]
1	14.8	72.3	−188	20.2	1.10×10^4	–	–
2	16.3	79.7	−40	21.5	3.83×10^4	–	–
3	5.2	77.2	−90	20.8	1.97×10^4	11.8	108.7
4	4.9	87.0	106	25.5	1.16×10^6	12.5	122.7
5	12.3	77.8	−78	22.6	1.04×10^5	9.6	64.7
6	10.4	84.4	54	24.5	5.22×10^5	10.3	78.7
7	14.3	77.2	−90	23.1	1.61×10^5	8.2	36.7
8	12.1	82.9	24	23.2	1.75×10^5	9.5	62.7
CN	4.6	85.1	68	20.5	1.48×10^4	–	–
S-811	9.6	79.5	−44	22.2	7.26×10^4	–	–
CB-15	7.6	80.6	−22	20.6	1.63×10^4	6.9	10.7
ZLI-1565[f]	–	86g	–	14.5[g]	–	6.7[g]	–

[a]Measured data at 25°C as 1 wt% mixture to the host liquid crystal ZLI-1565. [b]Measured data as 5 wt% mixture to the host liquid crystal ZLI-1565. [c]Extrapolation data. [d]Measured data at 25°C as 5 wt% mixture to the host liquid crystal ZLI-1565. [e]Extrapolation data at 25°C. [f]Host mixture. [g]Measured data as neat.

is more effective in inducing a helical structure for a mother nematic liquid crystal mixture than (*S*)-4-(2-methylbutyl)phenyl group. In the case of compounds **4** and **6**, the same result was obtained.

As a whole, (*S*)-2-phenylpropionic acid derivatives **5–8** have higher HTP values, as for the known compounds **1** and **2**, than those of chiral dopants cholesteryl nonanoate (CN), S-811 (Merck KGaA)

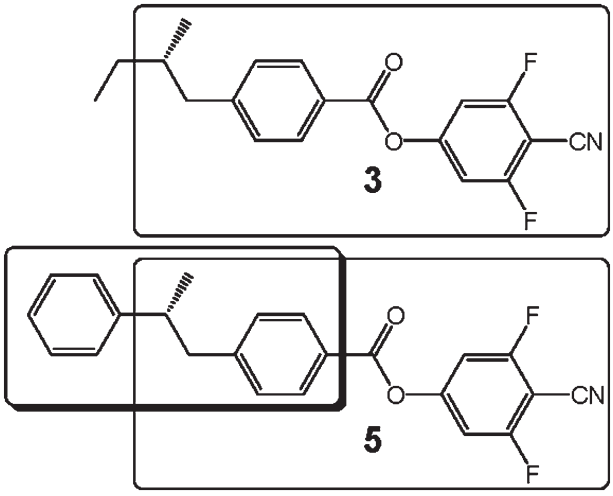


Figure 5. Comparison of structures of new chiral compounds.

and CB-15. These chiral dopants (**3–8**), which induce a right-handed twist, as does CB-15, are suitable for use in chiral nematic liquid crystal mixtures.

*Dielectric anisotropy values (*Δε*).*

For the (*S*)-4-(2-methylbutyl)benzene derivatives **3** and **4**, the Δε values are remarkably high compared with CB-15. In particular, the three-ring compound **4** has the same ability to keep the T_{ni} temperature of the liquid crystal mixture (87°C) as chiral dopant CN. On the other hand, the (*S*)-2-phenylpropionic acid derivatives (**5–8**) also have high Δε values compared with CB-15, but have low Δε values compared with (*S*)-4-(2-methylbutyl)phenyl derivatives **3** and **4**. Moreover, introduction of the 3,5-difluorophenyl group was effective for the increase the Δε values of material, especially, in the case of compound **8**. It was found that the dipole moment of 3,5-difluorophenyl group is equal to that of ester group (C(O)O) since the Δε value of compound **8** is almost equal to that of compound **5**.

The dielectric anisotropy (Δε) of the molecules was calculated according to the Maier–Meier theory

Table 2. Calculated physical constants of novel chiral compounds using MOPAC 6.0 AM1.

Compound	μ /D	α_{av} /a.u.	$\Delta\alpha$ /a.u.	β /°	$\Delta\varepsilon^a$	$\Delta\varepsilon^b$
3	7.8	191.5	188.3	8.9	54.2	108.7
4	8.3	252.9	289.9	7.9	57.9	122.7
5	7.6	229.4	245.7	23.6	35.8	64.7
6	9.7	301.2	345.0	19.6	48.5	78.7
7	5.7	215.4	230.9	6.5	28.8	36.7
8	7.5	285.6	328.9	4.3	38.3	62.7

[a] Calculation data at 25°C. [b] Extrapolation data at 25°C.

(*9*), an extension of the Onsager theory (*25*):

$$\Delta\varepsilon = \varepsilon_{\text{parallel}} - \varepsilon_{\text{vertical}}, \quad (3)$$

$$\Delta\varepsilon = NhF/\varepsilon_0\left[\Delta\alpha - F\mu^2\left(1-3\cos^2\beta\right)/2k_BT\right]S, \quad (4)$$

where k_B is the Boltzmann constant, $\Delta\alpha$ is the anisotropy of the polarisability, μ is the dipole moment and β is the angle between the whole molecular dipole moment and the long axis of the polarisability, $F = 1/(1-\alpha_{av}f)$ with $f=(\varepsilon-1)/[(2\pi\varepsilon_0 a^3)(2\varepsilon+1)]$ and $(4/3)\pi Na^3=1$, $h=3\varepsilon/(2\varepsilon+1)$; α_{av} is the average polarisability. For all calculations, a temperature $T=298$ K was used. An orientational order parameter S of 0.63 was assumed for all molecules under investigation. The results are shown in Table 2.

In the calculated results, although compounds **3** and **5** have similar molecular dipole moment (μ), the calculated dielectric anisotropy (Δε) of compound **3** is higher than that of compound **5**. The β angle of compound **5**, which is larger than that of compound **3**, seems to reduce the polarisability along the long axis of the material. In Figure 6, the 3,5-difluoro-4-cyanophenyl group and ester group (C(O)O) are on the same plane of the core structure in compound **3**. On the other hand, both groups are vertical to each other in compound **5** (Figure 6). We assume that the twisted structure of compound **5** leads to an enhanced β angle. Moreover, compound **7** has smaller Δε values compared with compound **5** since

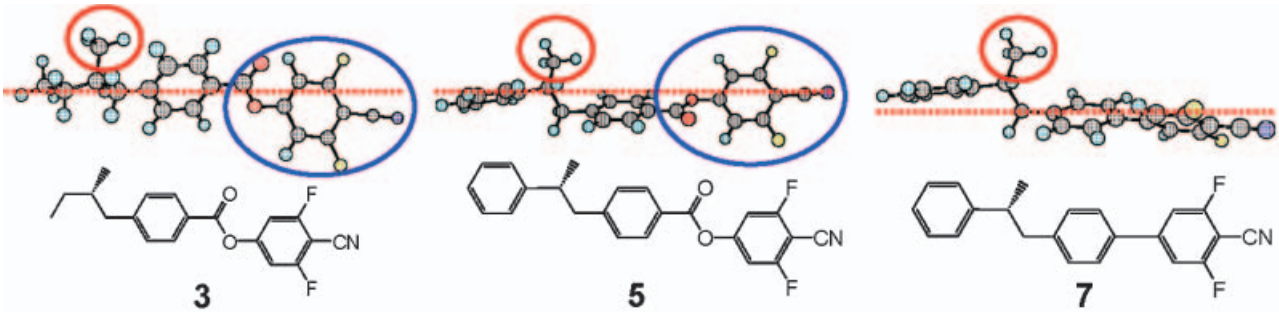


Figure 6. Molecular geometries of novel chiral compounds.

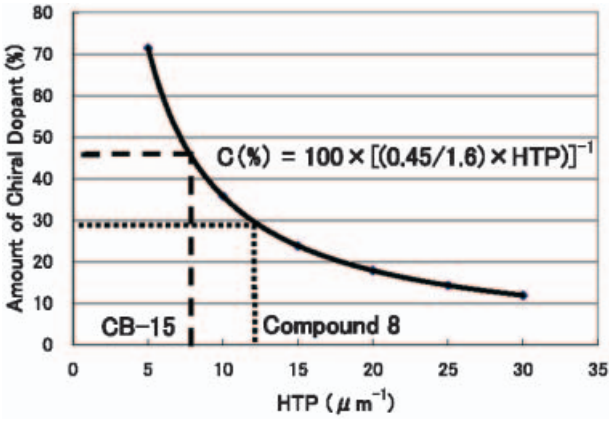


Figure 7. Relationship between HTP and amount of chiral dopant for a selective reflection wavelength of 450 nm.

the former has smaller molecular dipole moment than the latter due to lack of ester group.

*Kinematic viscosity (*ν*).*

Although compound **3** has low viscosity, as for compounds **1**, **2**, CN and CB-15, it has low HTP and it makes T_{ni} of the liquid crystal mixture lower, as for compounds **5** and **7**. Compounds **4** and **6** have higher kinematic viscosity compared with known materials in Table 2. Moreover, in the case of compound **4**, the introduction of a benzene ring to the molecule induced an increase of viscosity. On the other hand, the introduction of 3,5-difluorophenyl group, in case of compounds **6** and **8**, scarcely affected the increase of viscosity. Especially, in the case of dopant **8**, the introduction of 3,5-difluorophenyl group gave high $\Delta\varepsilon$ keeping similar viscosity of dopant **7**. We assumed that the two fluorine atoms on the benzene ring would reduce the intermolecular force since dopant **8** has plane structure like compound **7**.

As a whole, compound **8** has the best performances among the novel compounds (**3–8**) for use in cholesteric liquid crystal mixtures.

Chiral nematic liquid crystal mixture.

The selective reflection wavelength (λ) can be calculated by Equation (1). When the refractive index of liquid crystal composition (n) is 1.6, for the case of obtaining a selective reflection wavelength of 450 nm, i.e. blue, the relationship between HTP and amount of chiral dopant in mother liquid crystal mixture can be calculated by Equation (2). The result is shown in Figure 7.

In using CB-15 and compound **8** as chiral dopant, which has large $\Delta\varepsilon$ value for low driving voltage, extrapolation data for each case are shown in Table 3. The calculated data were obtained using the following equations.

$$(T_{ni})_{calculated} = 0.01 M_{ZLI-1565}(T_{ni})_{ZLI-1565} + 0.01 M_{chiral\ dopant}(T_{ni})_{chiral\ dopant},$$

$$(\Delta\varepsilon)_{calculated} = 0.01 M_{ZLI-1565}(\Delta\varepsilon)_{ZLI-1565} + 0.01 M_{chiral\ dopant}(\Delta\varepsilon)_{chiral\ dopant},$$

$$\log_{10}(v_{calculated}) = 0.01 M_{ZLI-1565}\log_{10}(v_{ZLI-1565}) + 0.01 M_{chiral\ dopant}\log_{10}(v_{chiral\ dopant}),$$

where M_X is the concentration (in wt%) of material X in the liquid crystal mixture.

The new chiral dopants are suitable for chiral nematic liquid crystal mixtures because the additive amount of chiral dopant was small and the performances of the mixture B were better than that of mixture A, such as T_{ni} was higher and kinematic viscosity (v) was lower. Moreover, using compounds that have large $\Delta\varepsilon$ values give a large $\Delta\varepsilon$ mixture for low driving voltage in the cholesteric liquid crystal device.

3. Conclusion

It was shown that the optically active (*S*)-4-(2-methylbutyl)phenyl derivatives (**3, 4**) and (*S*)-2-phenylpropionic acid derivatives with 4-cyano-3,5-difluorophenyl group (**5–8**) have good performances, such as high HTP and large $\Delta\varepsilon$ value, and that the chiral core structure of (*R*)-1,2-diphenylpropane is effective in inducing a helical structure in a host nematic liquid crystal mixture.

Moreover, the introduction of 3,5-difluorophenyl group to the molecule gave high $\Delta\varepsilon$ values without markedly increasing the viscosity. As a result, a good chiral dopant **8** was developed for chiral nematic liquid crystal mixture for application in cholesteric liquid crystal devices.

Table 3. Data extrapolated from mixtures containing chiral dopant in a nematic host mixture (ZLI-1565™)

Mixture	Chiral dopnat	Chiral dopant amount (%)	ZLI-1565 (%)	T_{ni}(°C)	$\Delta\varepsilon$	v (mm^2s^{-1})
A	CB-15	47.0	53.0	35.2[a]	8.6[b]	393[b]
B	**8**	29.5	70.5	67.7[a]	23.2[b]	232[b]
ZLI-1565	–	–	100	86.0[c]	6.7[c]	14.5[c]

[a]Calculation data, [b]Calculation data at 25°C, [c]Measured data as neat.

4. Experimental

Instrumentation and materials

The synthesised compounds were characterised using the following instruments and conditions. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded using a JEOL JSM-AL300 spectrometer (300 MHz) using tetramethylsilane and fluorotrichloromethane as internal standards. The optical purity was determined by high-performance liquid chromatography using a set of JASCO LC 900 series [detector: JASCO CD-1595, chiral column, ''CHIRALCEL OJ'' (Daicel Chem. Ind. Ltd., 4.6 mm × 250 mm)]. Specific rotations were measured with a HORIBA SFPA-200 polarimeter. The helical pitch of a chiral nematic phase was measured using wedge-shaped samples (Cano-wedge cell) by means of the resulting Cano lines (*26*). Dielectric anisotropy ($\Delta\varepsilon$) was measured at 25°C using an Agilent Technologies 4263B LCR meter. Phase transition temperatures were determined using a Perkin Elmer DSC 7 differential scanning calorimeter and Nikon Optiphot polarising optical microscope with a Mettler FP82HT hot stage. Kinematic viscosity (v) was measured at 25°C using a Shibayama Scientific Ostwald's viscometer SS-290S. The physical properties of the host mixture ZLI-1565 are T_{ni}=86°C, $\Delta\varepsilon$=6.7.

Synthesis of (S)-(2-methylbutyl)benzene derivatives

*4-Cyano-3,5-difluorophenyl (S)-4-(2-methylbutyl)-benzoate (**3**).*

To a mixture of (*S*)-4-(2-methylbutyl)-1-chlorobenzene (60 g, 0.328 mmol) and THF (250 ml) was added dropwise a mixture of magnesium (17.6 g, 0.722 mol) and THF (40 ml) at 25°C, and the mixture was refluxed for 11 h. After cooling to −30°C, it was reacted with CO_2, and filtered and the mixture was acidified using dilute hydrochloric acid and extracted with methyl *tert*-butyl ether. The organic layer was dried with anhydrous sodium sulfate. The solvent was evaporated under reduce pressure and the remaining mixture was purified by recrystallisation from toluene to give (*S*)-4-(2-methylbutyl)benzoic acid (41.8 g). Subsequently, (*S*)-4-(2-methylbutyl)benzoic acid (38.2 g, 0.142 mol) was stirred in thionyl chloride (395.5 g, 0.298 mol) for 3 h at 60°C and the mixture was concentrated. To the remaining mixture was added a solution of 4-cyano-3,5-difluorophenol (22 g, 0.142 mol) in toluene (240 ml), and pyridine (13.4 g, 0.170 mol) was added dropwise at 20°C. The mixture was stirred for 18 h at room temperature, poured into water and extracted with toluene. The organic layer was dried with anhydrous sodium sulfate. The solvent was evaporated under reduce pressure and the remaining mixture was purified by column chromatography (silica gel, 50 % toluene in hexane) to give a white solid (46.1 g, yield 77 %). ^{1}H NMR ($CDCl_3$): δ 0.88 (3H, d), 0.93 (3H, t), 1.22–1.70 (3H, m), 2.43 (1H, dd), 2.70 (1H, dd), 7.08–8.19 (10H, m). ^{19}F NMR ($CDCl_3$): δ −102.6 (2F, d). $[\alpha]_D^{20}$ +8.8 (c 1.0, $CHCl_3$).

*4-Cyano-3,5-difluorophenyl (S)-4′-(2-methylbutyl)biphenyl-4-carboxylate (**4**).*

The hydrolysis of (*S*)-4′-(2-methylbutyl)-4-cyanobiphenyl (CB-15) gave (*S*)-4′-(2-methylbutyl)biphenyl-4-carboxylic acid. Subsequently, (*S*)-4′-(2-methylbutyl)-biphenyl-4-carboxylic acid (30 g, 0.156 mol) was stirred in thionyl chloride (39 g, 0.328 mol) for 3 h at 60°C and the mixture was concentrated. To the remaining mixture was added a solution of 4-cyano-3,5-difluorophenol (24.2 g, 0.156 mol) in toluene (240 ml), and pyridine (14.8 g, 0.187 mol) was added dropwise at 20°C. The mixture was stirred for 18 h at room temperature, poured into water and extracted with toluene. The organic layer was dried with anhydrous sodium sulfate. The solvent was evaporated under reduce pressure and the remaining mixture was purified by column chromatography (silica gel: 50 % toluene in hexane) to give a white solid (39.4 g, yield 80%). ^{1}H NMR ($CDCl_3$): δ 0.86 (3H, d), 0.93 (3H, t), 1.22–1.70 (3H, m), 2.47 (1H, dd), 2.75 (1H, dd), 7.05–8.06 (6H, m). ^{19}F NMR ($CDCl_3$): δ −102.6 (2F, d). $[\alpha]_D^{20}$ +8.9 (c 1.0, $CHCl_3$).

Synthesis of (S)-2-phenylpropionic acid derivatives

*(R)-1-(4-Chlorophenyl)-2-phenylpropane (**9**).*

(*S*)-2-Phenylpropanoic acid (100 g, 0.67 mol) was stirred in thionyl chloride (115 g, 0.97 mol) for 2 h at 70°C and the mixture was concentrated. To the remaining mixture was added a solution of chlorobenzene (0.485 mol) and anhydrous aluminium chloride (97 g, 0.73 mol) in CH_2Cl_2 (500 ml) at 0°C. The mixture was stirred for 2 h at room temperature, hydrolysed by ice and dilute hydrochloric acid, and extracted with CH_2Cl_2. The organic layer was dried with anhydrous sodium sulfate. The solvent was evaporated under reduce pressure and the remaining mixture was purified by column chromatography (silica gel: 20 % toluene in hexane) to give (*S*)-1-(4-chlorophenyl)-2-phenylpropane-1-one (53 g). To a solution of (*S*)-1-(4-chlorophenyl)-2-phenylpropane-1-one (48.9 g, 0.2 mol) in trifluoroacetic acid (227 g, 2.0 mol) was added the triethylsilane (58 g, 0.50 mol) for 2 h at 0°C. The mixture was stirred for 3 h at room temperature, hydrolysed by sodium hydroxide solution and extracted with toluene. The organic layer

was dried with anhydrous sodium sulfate. The solvent was evaporated under reduce pressure and the remaining mixture was purified by column chromatography (silica gel: hexane) to give a (*R*)-1-(4-chlorophenyl)-2-phenylpropane **9** (41 g, yield 89 %). The optical purity of compound **9** (99.7%ee) was determined by HPLC analysis (carrier solvent, 1% 2-propanol/hexane; flow rate, 0.3 ml min^{-1}; detection wavelength, 254 nm). ^{1}H NMR ($CDCl_3$): δ 1.18 (3H, d), 2.64–2.71 (1H, q), 2.78–2.96 (2H, m), 6.86–6.91 (2H, m), 7.06–7.24 (7H, m). ^{13}C NMR ($CDCl_3$): δ 21.1, 41.7, 44.2, 126.1, 126.9, 128.1, 128.3, 130.4, 131.5, 139.0, 146.2. $[\alpha]_D^{20}$ −97.7 (c 1.0, $CHCl_3$).

*4-Cyano-3,5-difluorophenyl (R)-4-(2-phenylpropyl)-benzoate (**5**).*

By following the procedure for compound **3** and using (*R*)-1-(4-chlorophenyl)-2-penylpropane **9** (5 g, 0.022 mol) as starting material, 4-cyano-3,5-difluorophenyl (*R*)-4-(2-phenylpropyl)benzoate **5** was obtained as white solid (4.2 g, yield 51%, 99%ee). ^{1}H NMR ($CDCl_3$): δ 1.28 (3H, d), 2.86–3.10 (3H, m), 6.94–6.98 (2H, dd), 7.12–7.26 (7H, m), 7.99 (2H,d). ^{19}F NMR ($CDCl_3$): δ −103.0 (2F, d). ^{13}C NMR ($CDCl_3$): δ 21.2, 41.4, 44.8, 89.5(t), 106.7(dd), 108.6, 125.2, 126.1, 126.8, 128.2, 129.5, 130.0, 145.7, 148.3, 156.0(t), 163.1, 163.2(dd). $[\alpha]_D^{20}$ −91.5 (c 1.0, $CHCl_3$).

*(R)-3,5-Difluoro-4′-(2-phenylpropyl)biphenyl (**10**).*

To a mixture of (*R*)-1-(4-chlorophenyl)-2-penylpropane **9** (30 g, 0.13 mol) and THF (100 ml) was added dropwise a mixture of magnesium (3.5 g, 0.143 mol) and THF (40 ml) at 25°C, and the mixture was refluxed for 8 h. After cooling to −30°C, to the remaining mixture was added a mixture of trimethyl borate (27 g, 0.26 mol) and THF 50 ml. The mixture was stirred for 8 h at room temperature, hydrolysed by dilute hydrochloric acid and extracted with toluene. The organic layer was dried with anhydrous sodium sulfate. The solvent was evaporated under reduced pressure and a solid was obtained. A mixture of remaining solid and 1-bromo-3,5-difluorobenzene (25.1 g, 0.13 mol) and sodium carbonate (40 g, 0.38 mol) in H_2O (180 g) and $Pd(PPh_3)_4$ (3 g, 0.003 mmol) in ethylene glycol dimethyl ether (150 ml) was stirred for 10 h at 80°C, hydrolysed by dilute hydrochloric acid and extracted with toluene. The organic layer was dried with anhydrous sodium sulfate. The solvent was evaporated under reduce pressure and the remaining mixture was purified by column chromatography (silica gel: 50 % toluene in hexane) to give a (*R*)-3,5-difluoro-4′-(2-phenylpropyl)biphenyl **10** (27.6 g, yield 69%, 99%ee). ^{1}H NMR ($CDCl_3$): δ 1.22 (3H, d), 2.71–2.80 (1H, m), 2.88–3.03 (2H, m), 6.61–6.68 (1H, tt), 6.93–7.30 (11H, m). ^{19}F NMR ($CDCl_3$): δ −110.2 (2F, t). ^{13}C NMR ($CDCl_3$)L δ 21.2, 41.7, 44.5, 102.1(t), 109.5(dd), 126.1, 126.6, 127.0, 128.3, 129.7, 136.2(t), 141.2, 144.3, 146.6, 163.2(dd). $[\alpha]_D^{20}$ −102.9 (c 1.0, $CHCl_3$).

*4-Cyano-3,5-difluorophenyl (R)-3,5-difluoro-4′-(2-phenylpropyl)biphenyl-4-carboxylate (**6**).*

To a mixture of (*R*)-3,5-difluoro-4′-(2-phenylpropyl)-biphenyl **10** (20 g, 0.065 mol) and THF (200 ml) was added dropwise a 1.6M *n*-butyllithium/*n*-hexane solution (44.7 ml, 0.075 mol) at −70°C. Subsequently the mixture was stirred for 2 h, was reacted with CO_2, acidified by dilute hydrochloric acid and extracted with toluene. The organic layer was dried with anhydrous sodium sulfate. The solvent was evaporated under reduced pressure and the remaining mixture was purified by recrystallisation from toluene, to give (*R*)-3,5-difluoro-4′-(2-phenylpropyl)biphenyl-4-carboxylic acid (16 g). By following the procedure for compound **4** and using (*R*)-3,5-difluoro-4′-(2-phenylpropyl)biphenyl-4-carboxylic acid (5 g, 0.014 mol) as starting material for esterification, 4-cyano-3,5-difluorophenyl (*R*)-3,5-difluoro-4′-(2-phenylpropyl)-biphenyl-4-carboxylate **6** was obtained as white solid (4.9 g, yield 71%, 96%ee). ^{1}H NMR ($CDCl_3$): δ 1.27 (3H, d), 2.80–2.89 (1H, m), 2.93–3.09 (2H, m), 6.98–7.03 (2H, dd), 7.13–7.28 (9H, m), 7.40 (2H, d). ^{19}F NMR ($CDCl_3$): δ −102.4 (2F, d), −107.6 (2F, d). ^{13}C NMR ($CDCl_3$): δ 21.1, 41.5, 44.4, 90.1(t), 105.8(t), 106.7(dd), 108.4, 110.2(dd), 126.0, 126.5, 126.8, 128.2, 129.9, 134.2(t), 142.8, 146.2, 148.4(t), 155.0(t), 157.7(t), 161.5(dd), 163.2(dd). $[\alpha]_D^{20}$ −87.3 (c 1.0, $CHCl_3$).

*(R)-4-Cyano-3,5-difluoro-4′-(2-phenylpropyl)biphenyl (**7**).*

(*R*)-3,5-Difluoro-4′-(2-phenylpropyl)biphenyl-4-carboxylic acid (10 g, 0.028 mol) was stirred in thionyl chloride (16.9 g, 0.142 mol) for 3 h at 60°C. The mixture was concentrated, reacted with NH_3 in toluene, acidified by dilute hydrochloric acid and extracted with toluene. The organic layer was dried with anhydrous sodium sulfate. The solvent was evaporated under reduced pressure and (*R*)-3,5-difluoro-4′-(2-phenylpropyl)biphenyl-4-carboxamide (9 g) was obtained. A mixture of (*R*)-3,5-difluoro-4′-(2-phenylpropyl)biphenyl-4-carboxamide (9 g) and thionyl chloride (6.7 g, 0.056 mol) in toluene was refluxed for 8 h. The mixture was neutralised by sodium hydroxide solution and extracted with

toluene. The solvent was evaporated under reduced pressure and the remaining mixture was purified by column chromatography (silica gel: 50 % toluene in hexane) to give a (*R*)-4-cyano-3,5-difluoro-4′-(2-phenylpropyl)biphenyl **7** (6.9 g, yield 81%, 98%ee). ^{1}H NMR ($CDCl_3$): δ 1.25 (3H, d), 2.79–2.89 (1H, m), 2.91–3.08 (2H, m), 7.09–7.16 (7H, m), 7.21–7.26 (2H, m), 7.33 (2H, d). ^{19}F NMR ($CDCl_3$): δ −104.5 (2F, d). ^{13}C NMR ($CDCl_3$): δ 21.1, 41.7, 44.3, 89.8(t), 109.2, 109.8(dd), 126.0, 126.5, 126.8, 128.1, 129.9, 134.1(t), 143.0, 146.1, 149.0(t), 163.0(dd). $[\alpha]_D^{20}$ −136.1 (c 1.0, $CHCl_3$).

*(R)-4-Cyano-3,5,2′,6′-tetrafluoro-4″-(2-phenylpropyl)-p-terphenyl (**8**).*

To a mixture of (*R*)-3,5-difluoro-4′-(2-phenylpropyl)-biphenyl **10** (5 g, 0.016 mol) and THF (100 ml) was added dropwise a 1.6M *n*-butyllithium/*n*-hexane solution (10.1 ml, 0.018 mol) at −70°C. Subsequently the mixture was stirred for 2 h. To the remaining mixture was added a mixture of triisopropyl borate (6.1 g, 0.032 mol) and THF 10 ml and the mixture was stirred for 8 h at room temperature, hydrolysed by dilute hydrochloric acid and extracted with toluene. The organic layer was dried with anhydrous sodium sulfate. The solvent was evaporated under reduced pressure and a solid was obtained. A mixture of remaining solid and 4-cyano-3,5-difluorophenyl trifluorometanesulfonate (4.6 g, 0.016 mol), triethylamine (4.9 g, 0.048 mol) and $Pd(PPh_3)_4$ (0.55 g, 0.48 mmol) in DMF (30 ml) was stirred for 10 h at 100°C, hydrolysed by dilute hydrochloric acid and extracted with toluene. The organic layer was dried with anhydrous sodium sulfate. The solvent was evaporated under reduced pressure and the remaining mixture was purified by column chromatography (silica gel: 50 % toluene in hexane) to give a (*R*)-4-cyano-3,5,2′,6′-tetrafluoro-4″-(2-phenylpropyl)-*p*-terphenyl **8** (5.0 g, yield 70%, 98%ee). ^{1}H NMR ($CDCl_3$): δ 1.26 (3H, d), 2.78–2.87 (1H, m), 2.93–3.08 (2H, m), 7.13–7.28 (11H, m), 7.40 (2H, d). ^{19}F NMR ($CDCl_3$): δ −104.6 (2F, d), −114.1 (2F, d). ^{13}C NMR ($CDCl_3$): δ 21.1, 41.6, 44.4, 91.6(t), 108.9, 110.0(ddd), 112.6(t), 114.0(ddd), 126.0, 126.3, 126.9, 128.2, 129.9, 134.9(t), 137.2(t), 142.0, 144.9(t), 146.3, 159.4(dd), 162.7(dd). $[\alpha]_D^{20}$ −90.7 (c 1.0, $CHCl_3$).

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