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PRELIMINARY COMMUNICATION

5,6-Difluoro-1*H*-indene derivatives: novel core structure of liquid crystals with high Δn and $\Delta\varepsilon$

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We have designed and synthesised the novel liquid crystal core structure, 2-phenyl-5,6-difluoro-1*H*-indene, based on preliminary calculation of the theoretical values of birefringence (Δn) and dielectric anisotropy ($\Delta\varepsilon$). These compounds have been proved to have high nematic–isotropic transition temperature, and high optical anisotropy values with long molecular conjugation length. The introduction of lateral fluorine atoms into the 2-phenyl group of 5,6-difluoro-1*H*-indene derivatives leads to low viscosity and high dielectric anisotropy.

Keywords: liquid crystal; 5,6-difluoro-1*H*-indene derivatives; high nematic–isotropic liquid crystals; high optical anisotropy liquid crystals; high dielectric anisotropy liquid crystals

1. Introduction

High birefringence (Δn) and high dielectric anisotropy ($\Delta\varepsilon$) liquid crystals (LCs) are needed in reflective liquid crystal displays (R-LCDs) (*1*), cholesteric liquid crystal displays (Ch-LCDs) (*2–4*) and so on. In particular, a Ch-LCD is a low-power display that is environmentally friendly as it can still display an image while the power is off. Moreover, the fluorinated LCs are known for their moderate dielectric anisotropy, larger dipole moment, high stability, high voltage holding ratio and low viscosity (*5*). A high Δn value can be achieved by increasing the molecular conjugation length (*6*). A considerable number of π-conjugated compounds have been developed as high Δn LCs (*7*). The tolane-based LCs exhibit reasonably high Δn values, comparatively low viscosity and good chemical, photo and thermal stability (*8*). Molecules that contain highly polarisable groups with high electron density, such as benzene rings or acetylene linking groups, will therefore have large optical anisotropies.

On the other hand, we have discovered the (*E*)-α,β-difluorostilbene (DFS) compounds (Figure 1) that exhibit excellent properties such as high Δn values and extremely low viscosity (*9, 10*). However, it is difficult to use DFS compounds in LCD applications since these compounds tend to isomerise easily under UV light in part to (*Z*)-structures that have no LC properties. We considered that the central double bond would be fixed in the structure of 1*H*-indene, which had previously scarcely been used as a core structure (Figure 1).

Therefore, we focused on the 5,6-difluoro-1*H*-indene derivatives and 5,6-difluoroindan derivatives for the novel LC core structure, because the presence of two fluorine atoms on the terminal benzene ring was expected to induce very high $\Delta\varepsilon$. Although Bremer and Lietzau reported 1,1,6,7-tetrafluoroindan derivatives recently (*11*), those compounds have high dielectric anisotropy ($\Delta\varepsilon$) oriented perpendicular to the long molecular axis. Before the design and synthesis of the target materials, we calculated the LC properties such as the theoretical values of birefringence (Δn) and dielectric anisotropy ($\Delta\varepsilon$) of 2-phenyl-5,6-difluoro-1*H*-indene derivatives expected to have high Δn and $\Delta\varepsilon$. The calculation was carried out using the theories of Vuks and Maier–Meiyer.

The optical anisotropy (Δn) was calculated using the equations proposed by Vuks (*12*), as a generalisation of the relation between the refractive index n and the mean molecular polarisability α in isotropic systems given by the Lorenz–Lorentz expression (*13*) to anisotropic systems

$$\Delta n = n_e - n_o \tag{1}$$

$$(n_e^2 - 1)/(n^2 + 2) = N/3\varepsilon_0 \times (\alpha + 2\Delta\alpha S/3) \tag{2}$$

$$(n_o^2 - 1)/(n^2 + 2) = N/3\varepsilon_0 \times (\alpha + \Delta\alpha S/3) \tag{3}$$

$$n^2 = (n_e^2 + 2n_o^2)/3 \tag{4}$$

where n_e and n_o are the principal refractive indices related to the extraordinary and the ordinary ray,

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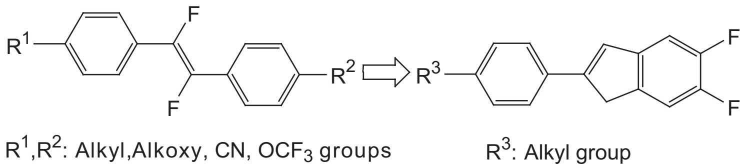


Figure 1. (*E*)-α,β-Difluorostilbene derivatives and 5,6-difluoro-1*H*-indene derivatives.

respectively, $\Delta\alpha$ denotes the anisotropy of the molecular polarisability α, S is the Saupe orientational order parameter, ε_0 is the static dielectric constant and N is the number of molecules per unit volume.

On the other hand, the dielectric anisotropy ($\Delta\varepsilon$) was calculated according to the Maier–Meier theory (*14*), an extension of the Onsager theory (*13*),

$$\Delta\varepsilon = \varepsilon_{\text{parallel}} - \varepsilon_{\text{vertical}} \tag{5}$$

$$\Delta\varepsilon = NhF/\varepsilon_0 \times (\Delta\alpha - F\mu^2 \times (1 - 3\cos^2\beta)/2k_BT) \times S \tag{6}$$

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 molecule, $F = 1/(1-\alpha_{av}f)$ 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 $T = 293$ K was used and an orientational order parameter S of 0.62 was assumed for all molecules under investigation. The molecular geometry was calculated using the semiempirical quantum chemical AM1 method (MOPAC 6.0 package) (*15*).

We have selected four fundamental structures, that is, 2-phenyl-5,6-difluoro-1*H*-indene (**1**), 2-cyclohexyl-5,6-difluoro-1*H*-indene (**2**), 2-phenyl-5,6-difluoroindan (**3**) and 2-cyclohexyl-5,6-difluoroindan (**4**), for the theoretical calculation of Δn and $\Delta\varepsilon$. The results are shown in Figure 2.

It was found that compound **1** had a planar and linear structure as the most stable conformer, and would have excellent performance with regards to high birefringence and high dielectric anisotropy. Compound **4** also had a planar and linear structure although it had quite a low calculated value of Δn. On the other hand, compound **2** was expected to have low Δn for its twisted structure, and compound **3** would have low Δn and moderate $\Delta\varepsilon$ for its bending structure. Among the above four structures, compound **1** looks to be the most suitable for cholesteric LCDs although compound **4** could be applicable as a thin-film transistor (TFT) LCD material.

Therefore, we investigated the synthesis and properties of novel 2-phenyl-5,6-difluoro-1*H*-indene derivatives derived from 5,6-difluoro-1*H*-indene or 5,6-difluoroindan-2-one. We selected the *trans*-4-propylcyclohexyl group for a substituent on the 2-phenyl group of 5,6-difluoro-1*H*-indene. Compound **1a** was expected to show high nematic–isotropic phase transition temperature (T_{ni}), and compound **1b** was expected to have high T_{ni} and $\Delta\varepsilon$ owing to the introduction of two lateral fluorine atoms into benzene ring has been shown to be quite effective for increasing the $\Delta\varepsilon$ in a similar manner to the introduction of an ester group (Figure 3) (*16*).

2. Experimental details

The synthesised compounds were characterised using the following conditions and instruments. ^{1}H nuclear magnetic resonance (NMR), ^{19}F NMR and ^{13}C NMR spectroscopy: JEOL JSM-AL300 spectrometer (300 MHz). Tetramethylsilane and fluorotrichloromethane were used as internal standards. Mass spectroscopy (MS) data were obtained with EI (70 eV) on a Shimadzu GCMS-2010 spectrometer. The purity of compounds was measured using gas chromatography (GC) with an Agilent Technologies Agilent 6850. Phase transition temperatures were measured using a Perkin Elmer DSC 7 differential scanning calorimeter and Nikon Optiphot polarising microscope with a Mettler FP82HT hot stage. Dynamic viscosity (η) was measured at 25°C with a Toki Sangyo E type Viscometer RE-80L. Optical anisotropy (Δn) was measured at 25°C using an Atago 1T Abbe refractometer. Dielectric anisotropy ($\Delta\varepsilon$) was measured at 25°C using an Agilent Technologies 4263B LCR meter.

The intermediate, 5,6-difluoroindan-1-one, was synthesised according to the known procedures (*17*), and 5,6-difluoroindan-2-one was synthesised using the route shown in Scheme 1.

For the synthesis of 5,6-difluoro-2-(4-(*trans*-4-propylcyclohexyl)phenyl)-1*H*-indene (**1a**), a solution of 4-(*trans*-4-propylcyclohexyl)phenylmagnesium bromide (34 mmol) in tetrahydrofuran (THF) was added dropwise to a mixture of cerium (III) chloride (8.38 g, 34 mmol) and THF (50 ml) at 0°C, and the mixture was stirred for 2 hours at 0°C. To the solution was added dropwise 5,6-difluoroindan-2-one (2.86 g, 17

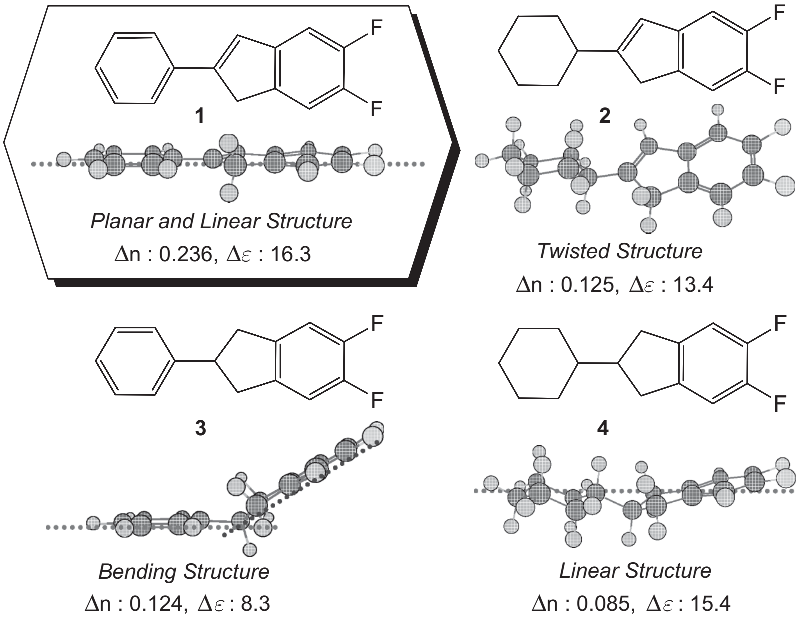


Figure 2. The molecular geometry and calculated Δn and $\Delta\varepsilon$ in novel LC core structures.

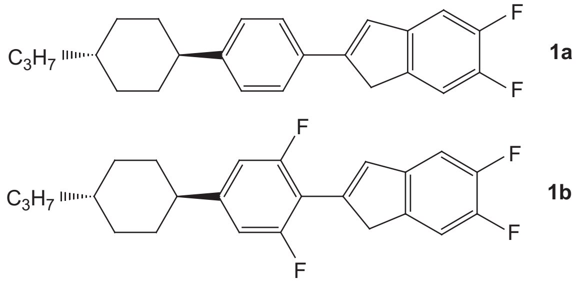
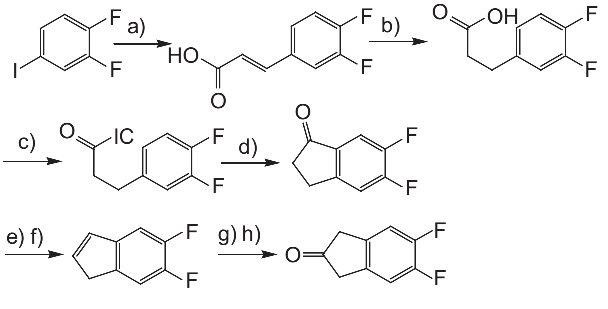


Figure 3. 2-Phenyl-5,6-difluoro-1*H*-indene derivatives.



Scheme 1. Synthetic route for the production of 5,6-difluoroindan-2-one.

mmol) in THF (10 ml), and the mixture was stirred for 2 hours at 0°C. The mixture was acidified with dilute acetic acid and extracted with methyl *t*-butyl ether. The solvent was evaporated under reduced pressure. To the mixture was added *p*-toluenesulfonic acid monohydrate and toluene, and the mixture was stirred at 100°C for 1 hour. After the organic layer was dried over anhydrous sodium sulphate, the solvent was evaporated under reduced pressure and the remaining mixture was purified by column chromatography (silica gel, toluene/hexane: 1:5) to give compound **1a** (0.8 g, 13%, purity 99.2% by GC). MS (EI, 70 eV) *m/z* 352 (M^+, 100), 309 (<1), 267 (30), 254 (17), 241 (14), 228 (4), 151 (11). ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 7.1 Hz, 3H, CH_3), 0.98–1.12 (m, 2H, $-\underline{CH_2}CH_3$), 1.17–1.53 (m, 7H, $>\underline{CHCH_2}CH_2CH_3$ and CH_{ax} in cyclohexane), 1.86–1.91 (m, 4H, CH_{eq} in cyclohexane), 2.42–2.52 (m, 1H, $>\underline{CH}$–Ar), 3.72 (s, 2H, CH_2 in indene), 7.04 (s, 1H, =CH– in indene), 7.11 (dd, J = 7.4, 10.3 Hz, 1H, CH in indene), 7.23 (m, 3H, Ar–H and CH in indene), 7.50 (d, J = 8.3 Hz, 2H, Ar–H). ^{19}F NMR ($CDCl_3$) δ –141.7 (m, 1F), –143.6 (m, 1F). ^{13}C NMR ($CDCl_3$) δ 14.4, 20.0, 33.5, 34.2, 37.0, 38.9, 39.7, 44.4, 109.0 (d, J = 18.5 Hz), 112.7 (d, J = 18.8 Hz), 124.3 (t, J = 2.4 Hz), 125.6, 127.2, 133.0, 138.6 (dd, J = 3.4, 6.5 Hz), 141.6 (dd, J = 3.8, 7.3 Hz), 147.6 (dd, J = 14.3, 105.4 Hz), 148.0, 148.2, 150.8 (dd, J = 13.7, 104.3 Hz).

For the synthesis of 5,6-difluoro-2-(2,6-difluoro-4-(*trans*-4-propylcyclohexyl)phenyl)-1*H*-indene (**1b**), a mixture of 2,6-difluoro-4-(*trans*-4-propylcyclohexyl)iodobenzene (12.0 g, 32.9 mmol), 5,6-difluoro-1*H*-indene (10.0 g, 65.7 mmol), tributylamine (12.2 g, 65.7 mmol), tri-*o*-tolylphospine (0.4 g, 1.3 mmol) and palladium (II) acetate (0.15 g, 0.66 mmol) was stirred for 12 hours at 125°C under nitrogen atmosphere. After cooling to room temperature, toluene (100 ml) was added to the mixture and the mixture was washed with 10% hydrochloric acid solution and water. The organic layer was dried over anhydrous sodium sulphate. The solvent was evaporated under reduced pressure and the remaining mixture was purified by column chromatography (silica gel, toluene/hexane; 1:1) and then by recrystallisation from hexane/ethanol (1:1) to give compound **1b** (9.6 g, 75 %, purity 99.4% by GC). MS (EI, 70 eV) *m/z* 388 (M^+, 100), 345 (<1), 303 (11), 290 (22), 277 (12), 264 (4), 151 (6). ^{1}H NMR ($CDCl_3$) δ 0.80 (t, J = 6.9 Hz, 3H, –CH_3), 0.87–0.98 (m, 2H, –$\underline{CH_2}CH_3$), 1.09–1.13 (m, 2H, –$\underline{CH_2}CH_2CH_3$), 1.19–1.34 (m, 5H, CH_{ax} in cyclohexane), 1.77 (d, J_{gem} = 9.1 Hz, 4H, CH_{eq} in cyclohexane), 2.33 (t, $J_{ax,ax}$ = 11.7 Hz, 1H, >CH–Ar), 3.73 (s, 2H, CH_2 in indene), 6.68 (d, J_{HF} = 10.9 Hz, 2H, –$C_6H_2F_2$–), 7.03–7.17 (m, 3H, =CH– in indene). ^{19}F NMR ($CDCl_3$) δ –110.6 (d, J_{FH} = 10.9 Hz, 2F), –141.7 (m, 1F), –142.6 (m, 1F). ^{13}C NMR ($CDCl_3$) δ 14.0, 19.6, 32.7, 33.3, 36.4, 39.1, 41.4, 43.6, 108.9 (d, J = 18.5 Hz), 109.9 (d, J = 25.8 Hz), 110.0 (m), 111.9 (d, J = 19.0 Hz), 131.1 (t, J = 7.7 Hz), 136.3, 138.7, 140.1, 147.3 (dd, J = 13.0, 71.3 Hz), 149.4 (t, J = 9.6 Hz), 150.5 (dd, J = 13.4, 70.0 Hz), 161.6 (d, J = 8.8 Hz).

3. Results and discussion

We studied the coupling reaction of 5,6-difluoroindan-2-one with 4-(*trans*-4-propylcyclohexyl)bromobenzene via organometallic compounds. The reaction mixture was acidified by dilute hydrochloric acid and was checked using GC. The dehydration reaction proceeded in the GC column at high temperature. The results are shown in Table 1.

It was found that, by using magnesium, the metal reagent was consumed by the side reaction with 5,6-difluoroindan-2-one to form enolate of the indan-2-one and by-product **6**, and further reaction of this enolate with 5,6-difluoroindan gave by-product **5**. On the other hand, in the case of using cerium compound which has lower basicity, this side reaction was suppressed compared with using the Grignard compound (*18*) since only 7% of the by-product **5** was obtained and the amount of compound **6** was smaller. After the dehydration with *p*-toluenesulfonic acid monohydrate, the purification of column chromatography gave the target compound **1a** in low isolated yield (13%).

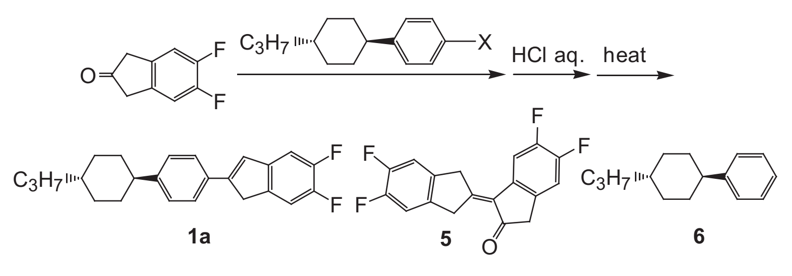
Next, we tried to synthesise the target compound **1b** using the same method as for **1a**. However, we could not obtain **1b**, probably because the metal compounds with two fluorine atoms had little nucleophilicity toward 5,6-difluoroindan-2-one (Scheme 2).

Therefore, we investigated the Mizoroki–Heck reaction (*19–23*). It was found that the reaction of 5,6-difluoro-1*H*-indene with 4-(*trans*-4-propylcyclohexyl)-2,6-difluoroiodobenzene proceeded in high yield (75%) at a much more elevated temperature than the usual Heck reaction condition (*24*) (Scheme 2).

The melting point (T_m) and nematic–isotropic phase transition temperature (T_{ni}) were measured directly using a polarising microscope. The dynamic viscosity (η) was measured as 5 wt% mixtures to the host ester mixture and to the host LC ZLI-1565^{TM} (Merck KGaA). Optical anisotropy values (Δn) and dielectric anisotropies ($\Delta\varepsilon$) of each compound were measured as a 5 wt% mixture to the host LC ZLI-1565^{TM}. The results are summarised in Table 2.

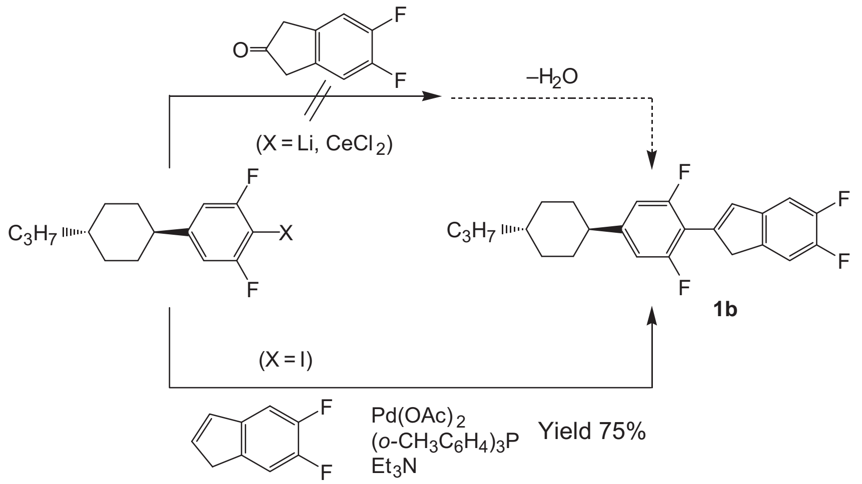
The compounds **1a** and **1b** had excellent performances such as high T_{ni} and high Δn. Although **1a** has high viscosity, it could be applied to LCDs in

Table 1. Cross-coupling reaction of 5,6-difluoroindan-2-one.



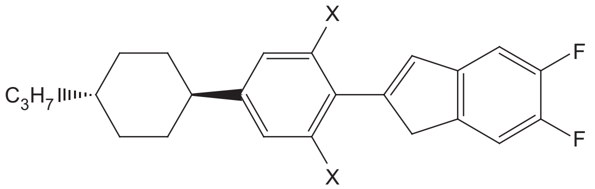
Entry	*X*	**1a** (GC%)	**5** (GC%)	**6** (GC%)[a]
1	MgBr	27	13	56
2	$CeCl_2$	39	7	43

[a] The metal reagent was used at double the molar quantities of the 5,6-difluoro-1*H*-indene.



Scheme 2. Synthetic routes for the production of 5,6-difluoro-2-(2,6-difluoro-4-(*trans*-4-propylcyclohexyl)phenyl)-1*H*-indene.

Table 2. Physical properties of 5,6-difluoro-1*H*-indene derivatives.



Compound	X	T_m (°C)	T_{ni} (°C)	η^a (mPa·s)	η^b (mPa·s)	Δn^c	$\Delta\varepsilon^c$
1a	H	182.3	247.6	19.1	18.0	0.244	5.8
1b	F	109.9	199.6	17.6	16.0	0.235	18.0

[a] Measured data at 25°C as a 5 wt% mixture to the ester mixture (4-butoxyphenyl *trans*-4-propylcyclohexanecarboxylate, 4-ethoxyphenyl *trans*-4-butylcyclohexanecarboxylate, 4-methoxyphenyl *trans*-4-pentylcyclohexanecarboxylate in molar ratio 1:1:1; η = 16.5 mPa·s at 25°C).

[b] Measured data at 25°C as a 5 wt% mixture to the host LC ZLI-1565.

[c] Extrapolation data measured as 5 wt% mixture to ZLI-1565 at 25°C, the extrapolation data of each compound was calculated using the following equations: $\Delta n_{\text{measured}} = 0.95*\Delta n_{\text{ZLI-1565}} + 0.05*\Delta n_{\text{compound}}$, $\Delta\varepsilon_{\text{measured}} = 0.95*\Delta\varepsilon_{\text{ZLI-1565}} + 0.05*\Delta\varepsilon_{\text{compound}}$.

[d] Host mixture ZLI-1565: T_{ni} = 86°C, η = 15.4 mPa·s, Δn = 0.124, $\Delta\varepsilon$ = 6.7.

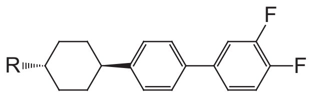
high-temperature drive such as the LCD projector. The introduction of lateral fluorine (**1b**: X = F) lead to low viscosity and high $\Delta\varepsilon$ compared with compound **1a** (X = H). Usually, the increase in the number of fluorine atoms in the compound increases the viscosity. However, Takatsu and co-workers reported that the introduction of fluorine atom into the naphthalene ring lead to low viscosity in some cases (*25*). We think compound **1b** has smaller intermolecular forces in LCs than compound **1a** because of electron repulsion of fluorine atoms.

For the comparison of known core structures, the physical properties of LC materials having other fluorinated core structures, 3,4-difluorobenzene **7a** (*26*), 5,6-difluoronaphthalene **8a** (*26*) and 5,6,7-trifluoronaphthalene **8b** (*27*), are shown in Table 3.

Among the difluoro materials, novel compound **1a** had higher T_{ni} and Δn compared with **7a** and **8a**. Moreover among tetrafluoro materials, novel compound **1b** also had higher T_{ni} and Δn compared with **8b**, although having nearly equal $\Delta\varepsilon$.

It was found that novel core structure, 2-phenyl-5,6-difluoro-1*H*-indene, had suitable performances for using high Δn application. In particular, compound **1b** had a combination of excellent properties such as high T_{ni}, high Δn, high $\Delta\varepsilon$ and low viscosity.

Table 3. Physical properties of some derivatives having different fluorinated core structures.



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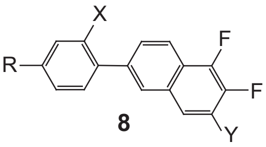

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Compound	*R*	*X*	*Y*	T_{ni} (°C)	Δ*n*	Δε
7a	C_5H_{11}	–	–	105.4	–	6.3
8a	C_3H_7	H	H	14.0	0.212	10.0
8b	A[a]	F	F	130.0	0.195	18.9

[a] Denotes *trans*-4-propylcyclohexyl group.

4. Conclusion

We have designed and synthesised the novel LC core structure, 2-phenyl-5,6-difluoro-1*H*-indene, based on preliminary calculations of the theoretical values of birefringence (Δ*n*) and dielectric anisotropy (Δε). These compounds have been proved to have high nematic–isotropic transition temperature, and high optical anisotropy values with long molecular conjugation length. It was found that 5,6-difluoro-2-(2,6-difluoro-4-(*trans*-4-propylcyclohexyl)phenyl)-1*H*-indene (**1b**), which was obtained by the introduction of lateral fluorine atoms into the 2-phenyl group of 5,6-difuruoro-1*H*-indene derivatives, led to low viscosity and high dielectric anisotropy. Moreover, this compound has high solubility to the host mixture. These facts indicate that these compounds should be useful as components of LC mixtures for high Δ*n* applications.

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