

Syntheses of Novel Liquid Crystalline Compounds with Partially Fluorinated Side Chains

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A new series of three ring type liquid crystalline compounds containing partially fluorinated alkenyl or alkyl side chains together with fluorine substituted cyclohexylbiphenyls were designed and synthesized in this study. The structures of synthesized compounds were established by ¹H, ¹³C and ¹⁹F NMR spectroscopy. The phase transition temperatures of fluorinated liquid crystalline compounds were determined by cross-polarizing microscopy equipped with hot stage. All compounds were found to have nematic liquid crystalline phase with relatively low phase transition temperature and wide liquid crystalline temperature range. The dependence of phase transition temperatures on the chain length falls into three categories; (a) decreasing transition temperatures for 4-fluoro-4'-[4-fluoro-4-(1-fluoroalkyl)cyclohexyl]biphenyl (**15**) series, (b) higher transition temperatures for odd numbered chains for 4-fluoro-4'-[4-fluoro-4-(1-fluoroalk-1-enyl)cyclohexyl]biphenyl (**14**) series, (c) higher transition temperatures for even numbered chains for 4-[4-(1,2-difluoroalk-1-enyl)-4-fluorocyclohexyl]-4'-fluorobiphenyl (**16**) series.

Introduction

Liquid crystalline materials have been extensively investigated because of their applicability to liquid crystal display (LCD). Especially, partially fluorinated liquid crystals have been extensively studied because of their unique properties such as low viscosity, low birefringence, and low conductivity.¹⁻⁹ Among the various lateral substituents in the liquid crystalline system, fluorine substituent is most commonly used because of its small size, high electronegativity, large C-F bond dissociation energy, and poor leaving group ability.^{1,10,11} Recently, liquid compounds with partially fluorinated alkyl chains are of special interest in fine tuning liquid crystalline properties.^{1-4, 7,8,12} In the case of some liquid crystalline compounds with 3 ring system, it was reported that by the introduction of fluorine atoms at the terminal phenyl group, nematic-isotropic (NI) point decreased, nematic temperature range narrowed, optical anisotropy and elastic constant decreased, and dielectric anisotropy increased.¹³

As a part of an effort to develop novel liquid crystalline compounds which can be used in liquid crystal display (LCD), we designed new three ring type compounds containing partially fluorinated alkenyl or alkyl side chains together with fluorine substituted cyclohexylbiphenyls. These compounds were designed on the following basis. First, the terminal fluorine atom of biphenyl and fluorine atoms in the side chain would increase the dipole moment to the long axis of the molecule. Second, the fluorine atoms in the side chain would increase the dipole moment in the middle portion to

cause the decrease the interactions between molecules. Here, we developed a new and versatile synthetic pathway to synthesize a series of partially fluorinated liquid crystalline compounds.

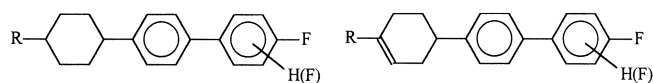
Experimental Section

Caution! Metal-halogen exchange reaction and deprotonation should be carried out at below -100 ~ -110 °C in order to avoid side reaction. Also, it was reported that diethyaminosulfur trifluoride (DAST) can decompose violently upon contact with water or heating above 50 °C. Fluorination should be carried out in a fume hood.

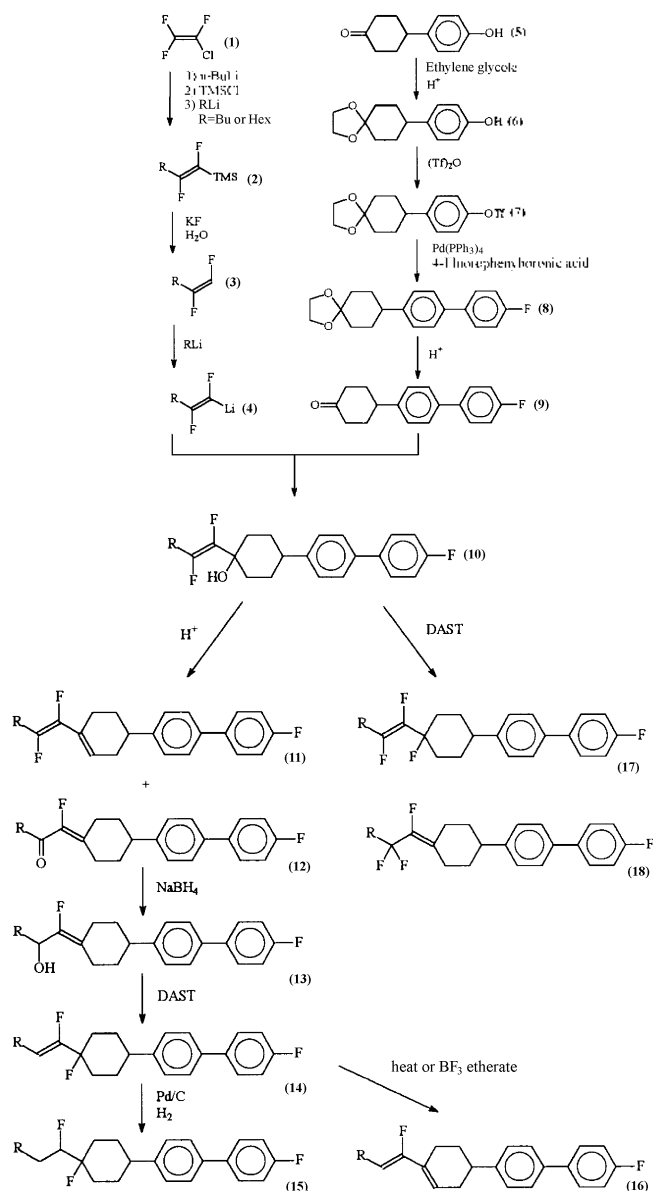
Reagents and Instruments. Alkylolithium compounds were purchased from Aldrich or prepared from corresponding alkyl bromides. ¹H, ¹³C and ¹⁹F NMR spectra were obtained using Bruker Avance 400 spectrometer. The phase transition temperatures and liquid crystalline phases were observed on Mettler FP 90 coupled with Olympus BII-2.

Synthesis. The synthetic route for the preparation of liquid crystal compounds is shown in Scheme 1. One of the key reactions in our synthesis is the coupling of 1,2-difluoroalkenylolithium with 4-(4'-fluorobiphenyl-4-yl)cyclohexanone (**9**) to give 1-(1,2-difluoroalk-1-enyl)-4-(4'-fluorobiphenyl-4-yl)-cyclohexanol (**10**). *trans*-1,2-Difluoroalkene **3** was prepared according to J. Normants work which was lithiated with *n*-alkylolithium at low temperature.¹⁴⁻¹⁶ Compound **9** was prepared from commercially available 4-(4-hydroxyphenyl)cyclohexanone *via* a series of reactions such as protection with ethylene glycol, triflation, Suzuki coupling reaction¹⁷ with 4-fluorophenylboronic acid and deprotection of ketal group.

The typical synthetic procedure for the preparation of liquid crystalline compounds with the alkyl chain length of six is described as follows.



R=partially fluorinated alkyl or alkenyl



Scheme 1. Synthetic Scheme for the Preparation of Liquid Crystalline Compounds.

1-(1,2-Difluorohex-1-enyl)-4-(4'-fluorobiphenyl-4-yl)-cyclohexanol (10). To a solution of *trans*-1,2-difluorohex-1-ene (**3**; 1.73 mL, 10.6 mmol) in THF (10 mL) was added 2.5 M *n*-BuLi (4.26 mL, 10.6 mmol), the rate of addition was adjusted so that the reaction temperature did not rise above $-100\text{ }^{\circ}\text{C}$ using pentane/ N_2 bath. The reaction mixture was maintained for 1 h at $-78\text{ }^{\circ}\text{C}$. To this reaction mixture was added compound **9** (2.596 g, 9.67 mmol) dissolved in THF (35 mL) dropwise. After 1 hour, the temperature was raised to rt. The reaction mixture was quenched with saturated NH_4Cl , extracted with ethyl acetate, dried over Na_2SO_4 . The solvent was evaporated *in vacuo* to give crude **10**, which was chromatographed (hexanes : ethyl acetate – 4 : 1, R_f –0.56, *trans*; R_f –0.30, *cis*) to give a white solid **10a** (*trans*, 0.842 g, 22.4%) and liquid **10b** (*cis*, 2.478 g, 65.9%). **10a**; ^1H NMR (400 MHz, CDCl_3): δ 0.94 (3H, t), 1.35 (2H, m), 2.53

(2H, m), 1.92 (9H, m), 2.36 (2H, m), 2.59 (1H, m), 7.10 (2H, m), 7.31 (2H, m), 7.49 (4H, m); ^{13}C NMR (100 MHz, CDCl_3 , *trans*): δ 14.1, 22.3, 27.2(d), 28.2, 28.9, 35.1, 43.6, 71.4(q), 115.8, 116.0, 127.4, 127.7, 128.9(d), 137.6(d), 138.5, 146.5, 150.9(q), 152.3(q), 162.7(d). **10b**; ^1H NMR (400 MHz, CDCl_3 , *cis*): δ 0.96 (3H, t), 1.42 (2H, m), 1.61 (4H, m), 1.95 (2H, m), 2.23 (1H, bs), 2.45 (4H, m), 2.63 (1H, m), 7.09 (2H, m), 7.24 (2H, m), 7.47 (4H, m); ^{13}C NMR (100 MHz, CDCl_3 , *cis*): δ 14.1, 22.4, 27.3(d), 28.2, 31.8, 36.8(d), 43.2, 73.5(q), 115.9, 116.1, 127.4, 127.7, 128.9(d), 137.5(d), 138.6, 145.8, 150.7(dd), 153.3(dd), 162.8(d); ^{19}F NMR (376.4 MHz, CDCl_3): δ 116.3(m), 146.6(dt), 164.2(d).

Rearrangement of (10). Compound **10** was rearranged to 4-[4-(1,2-difluorohex-1-enyl)cyclohex-3-enyl]-4'-fluorobiphenyl (**11**; 64 mg, 2.7%) and 1-fluoro-1-[4-(4'-fluorobiphenyl-4-yl)cyclohexylidene]hexan-2-one (**12**; 1.20 g, 51.2%) in the presence of catalytic amount of acid which was present in CDCl_3 . **11**; ^1H NMR (400 MHz, CDCl_3): δ 0.94 (3H, t), 1.39 (2H, m), 1.54 (2H, m), 1.81 (1H, m), 2.04 (1H, d), 2.4 (6H, m), 2.86 (1H, m), 6.13 (1H, s), 7.11 (2H, m), 7.3 (2H, d), 7.51 (4H, m); ^{13}C NMR (400 MHz, CDCl_3): δ 14.2, 22.4, 26.0(q), 27.5(d), 28.5, 30.0, 33.7, 39.4, 115.9, 125.2(d), 127.4, 127.7, 128.9(d), 137.5(d), 138.6, 146.1, 149.1(q), 152.0(q), 162.7, 116.1. **12**; ^1H NMR (400 MHz, CDCl_3): δ 0.93 (3H, t), 1.36 (2H, m), 1.6 (4H, m), 2.05 (4H, m), 2.63 (2H, m), 2.78 (1H, m), 3.04 (1H, d), 3.85 (1H, d), 7.08 (2H, m), 7.24 (2H, d), 7.5 (4H, m); ^{13}C NMR (100 MHz, CDCl_3): δ 14.3, 22.8, 25.9(d), 27.5(q), 34.8(q), 40.3(d), 43.9, 116.0(d), 127.5, 127.7, 128.9(d), 132.9(d), 137.5(d), 138.6, 145.5, 148.9(d), 162.8(d), 197.6(d).

1-Fluoro-1-[4-(4'-fluorobiphenyl-4-yl)cyclohexylidene]-hexan-2-ol (13). To the solution of **12** (4.32 g, 11.7 mmol) in THF (70 mL) was added to sodium borohydride (0.11 g, 2.91 mmol). The reaction mixture was stirred for 12 h at rt, quenched with saturated NH_4Cl (50 mL), extracted with ethyl acetate (2 \times 50 mL), washed with water (2 \times 30 mL), and dried over Na_2SO_4 . The solvent was evaporated *in vacuo* to give diastereomeric mixture of **13**, which was chromatographed on silica gel (hexane : ethyl acetate – 6 : 1) to give a white solid **13a** (R_f –0.25, 1.99 g, 45.8%) and a white solid **13b** (R_f –0.15, 1.76 g, 40.5%). **13a**; ^1H NMR (400 MHz, CDCl_3): δ 0.89 (3H, t), 1.29 (8H, m), 1.63 (4H, m), 1.86 (2H, m), 2.00 (3H, m), 2.57 (1H, d), 2.69 (1H, m), 3.01 (1H, d), 4.52 (1H, td), 7.09 (2H, m), 7.25 (2H, d), 7.545 (4H, m); ^{13}C NMR (100 MHz, CDCl_3): δ 14.5, 23.0, 25.8, 25.9(d), 28.0(d), 29.5, 32.2, 34.4, 35.0, 35.1, 44.4, 67.5(d), 115.9, 116.1, 117.2(d), 127.4, 127.7, 128.9(d), 137.5(d), 138.5, 146.1, 151.8(d), 162.8 (d). **13b**; ^1H NMR (400 MHz, CDCl_3): δ 0.90 (3H, t), 1.41 (10H, m), 1.79 (4H, m), 2.06 (3H, m), 2.55 (1H, d), 2.71 (1H, m), 3.01 (1H, d), 4.52 (1H, td), 7.10 (2H, m), 7.25 (2H, d), 7.51 (4H, m); ^{13}C NMR (100 MHz, CDCl_3): δ 14.5, 23.1, 25.8, 26.2 (d), 28.2(d), 29.5, 32.3, 34.7, 34.8, 35.6, 44.3, 67.5(d), 115.9, 116.1, 117.7(d), 127.4, 127.7, 128.8(d), 137.5(d), 138.6, 146.0, 151.5(d), 162.8(d).

4-Fluoro-4'-[4-fluoro-4-(1-fluorohex-1-enyl)cyclohexyl]-biphenyl (14). To the solution of DAST (1.58 L, 11.9 mmol) in CH_2Cl_2 (5 mL) was added compound **13** (3.69 g, 9.96

mmol) in CH_2Cl_2 (20 mL) maintaining below 76°C . After the addition, the temperature was slowly raised to 0°C . The reaction mixture was quenched with ice and water, extracted with ethyl acetate (2×50 mL), dried over Na_2SO_4 . The solvent was evaporated *in vacuo* to give crude **14**, which was chromatographed on silica gel (hexane : ethyl acetate = 10 : 1) to give a white solid **14a** (R_f = 0.45, 1.72 g, 46.4%, assigned to have *trans* configuration) and a colorless liquid **14b** (R_f = 0.45, 1.51 g, 40.7%, assigned to have *cis* configuration). **14a**; ^1H NMR (400 MHz, CDCl_3): δ 0.91 (3H, t), 1.35 (4H, m), 1.84 (6H, m), 2.14 (4H, m), 2.58 (1H, m), 4.98 (1H, dt), 7.09 (2H, m), 7.29 (2H, d), 7.50 (4H, m); ^{13}C NMR (100 MHz, CDCl_3): δ 14.4(d), 22.7(d), 23.4(d), 29.1, 31.8, 33.3, 33.5, 43.0, 92.1(dd), 106.0(q), 115.9, 116.1, 127.5, 127.8, 128.9(d), 137.5 (d), 138.6, 146.1, 159.5(dd), 162.8(d). **14b**; ^1H NMR (400 MHz, CDCl_3): δ 0.93 (3H, t), 1.42 (4H, m), 1.66 (2H, m), 1.1.85 (2H, m), 1.98 (2H, m), 2.22 (2H, m), 2.37 (2H, m), 2.71 (1H, m), 5.14 (1H, dt), 7.10 (2H, m), 7.25 (2H, d), 7.45 (4H, m); ^{13}C NMR (100 MHz, CDCl_3): δ 14.3, 22.7(d), 23.7 (d), 31.6, 33.5(d), 33.7(d), 42.9, 94.4(dd), 111.2(q), 115.9, 116.1, 127.5, 127.7, 128.9(d), 137.4(d), 138.7, 145.0, 157.1 (dd), 162.8(d).

4-Fluoro-4'-[4-fluoro-4-(1-fluorohexyl)cyclohexyl]biphenyl (15). Crude mixture of compound **14** (100 mg, 0.268 mmol) in ethanol (30 mL) was reduced with H_2 (45 psi) and Pd/C (5 mg, 10% Pd). The Pd/C was filtered off and the residue was evaporated *in vacuo* to give a crude compound, which was purified by column chromatography (hexane) to give a white solid **15** (44 mg, 43.8%). ^1H NMR (400 MHz, CDCl_3): δ 0.91 (3H, t), 1.6 (14H, m), 2.0 (1H, m), 2.13 (1H, m), 4.31 (1H, dt), 7.1 (2H, m), 7.3 (2H, d), 7.5 (4H, m); ^{13}C NMR (100 MHz, CDCl_3): δ 14.4, 22.9, 25.8(d), 29.0(d), 29.3(dd), 30.7(dd), 31.8(dd), 32.0, 43.3, 94.8(dd), 97.1(dd), 116.0(d), 127.4, 127.7, 128.9(d), 137.5(d), 138.6, 146.1, 162.8(d).

4-Fluoro-4'-[4-(1-fluorohex-1-enyl)cyclohex-3-enyl]biphenyl (16). To the solution of compound **14b** (500 mg, 1.34 mmol) in THF (10 mL) was added $\text{BF}_3 \cdot \text{OEt}_2$ (0.80 mL, 6.2 mmol) at rt for 1 hr. The reaction mixture was quenched with 5% aq. NaHCO_3 , extracted with ethyl acetate (2×20 mL), dried over MgSO_4 . The solvent was evaporated *in vacuo* to give crude **14**, which was chromatographed on silica gel (hexane : CH_2Cl_2 = 10 : 1) to give a white solid **16** (0.46 g, 97.2%) ^1H NMR (400 MHz, CDCl_3): δ 0.91 (3H, t), 1.35 (4H, m), 1.82 (1H, m), 2.04 (1H, m), 2.19 (2H, m), 2.30 (3H, m), 2.51 (1H, m), 2.85 (1H, m), 4.80 (1H, td), 6.19 (1H, bs), 7.11 (2H, m), 7.29 (2H, d), 7.50 (4H, m); ^{13}C (100 MHz, CDCl_3): δ 14.3, 22.8, 24.1(d), 25.2(d), 30.0, 32.2, 33.6, 39.8, 105.4(d), 115.9, 116.1, 123.4(d), 127.5, 127.7, 128.9(d), 129.1(d), 137.5(d), 138.6, 146.1, 158.0(d), 162.8(d).

Reaction of 1-(1,2-Difluorohex-1-yl)-4-(4'-fluoro-biphenyl-4-yl)cyclohexanol (10) with DAST. DAST (0.233 mL, 1.77 mmol) in CH_2Cl_2 (2 mL) was introduced to a well dried 5 mL 1-neck round bottom flask under Ar and cooled to -76°C . To this solution was added **10** (627 mg, 1.61 mmol) in CH_2Cl_2 (2 mL) maintaining below -76°C . After the addition, the temperature was slowly raised to 0°C . The reaction mixture was quenched with ice and water, extracted with

ethyl acetate (2×20 mL), dried over Na_2SO_4 . The solvent was evaporated *in vacuo* and chromatographed on silica gel (hexane) to 4-[4-(1,2-difluorohex-1-enyl)-4-fluorocyclohexyl]-4'-fluorobiphenyl (**17**; 64 mg, 10.5%) and 4'-fluoro-4-[4-(1,2,2-trifluorohexylidene)cyclohexyl]biphenyl (**18**; 248 mg, 39.0%). **17**; ^1H NMR (400 MHz, CDCl_3): δ 0.94 (3H, t), 1.45 (4H, m), 1.91 (6H, m), 2.41 (4H, m), 2.62 (1H, m), 7.10 (2H, m), 7.30 (2H, m), 7.50 (4H, m); ^{13}C NMR (100 MHz, CDCl_3): δ 13.9, 22.0, 24.0, 26.8, 27.7, 35.2(t), 42.6, 115.6(d), 123.5 (q), 127.1(d), 127.3, 128.5(d), 137.1, 138.2, 145.5(d), 148.5 (q), 152.5(m), 163.6(d). **18**; ^1H NMR (400 MHz, CDCl_3): δ 0.93 (3H, t), 1.50 (6H, m), 2.00 (6H, m), 2.69 (1H, m), 3.00 (2H, m), 7.06 (2H, m), 7.22 (2H, m), 7.48 (4H, m); ^{13}C NMR (100 MHz, CDCl_3): δ 13.9, 22.5, 24.2(t), 26.3(t), 26.6(t), 34.3, 34.7, 35.8(t), 43.8, 115.6(d), 120.5(td), 122.4(d), 127.1, 127.4, 128.6(d), 137.2(d), 138.3, 145.3(dt), 145.4, 162.2(d).

Result and Discussion

In our synthetic scheme compounds **10** were key compounds to a series of liquid crystalline compounds through acid catalyzed rearrangement, fluorination with DAST,¹⁸ catalytic hydrogenation, or reduction of rearranged compounds followed by fluorination. Compounds **10** were obtained as mixture of *cis* and *trans* compounds which were able to be separated easily with silica gel column chromatography. These compounds were labile to acids and rearranged mainly to enones **12**^{19,21} and small amount of dienes **11** even in the presence of trace amount of HCl which was present in CDCl_3 . The rearranged α -fluoro enone compounds **12** were reduced with NaBH_4 to give diastereomeric mixture of compounds **13** which were separated with silica gel column chromatography. The reactions of **10** with catalytic amount of acid and DAST gave interesting results. The reason for the formation of **12** and **18** as major products is explained due to the stability of carbocation at the α position of fluorine is greater than that of tertiary position of cyclohexane ring (Figure 1).

In this study, we designed and prepared novel liquid crys-

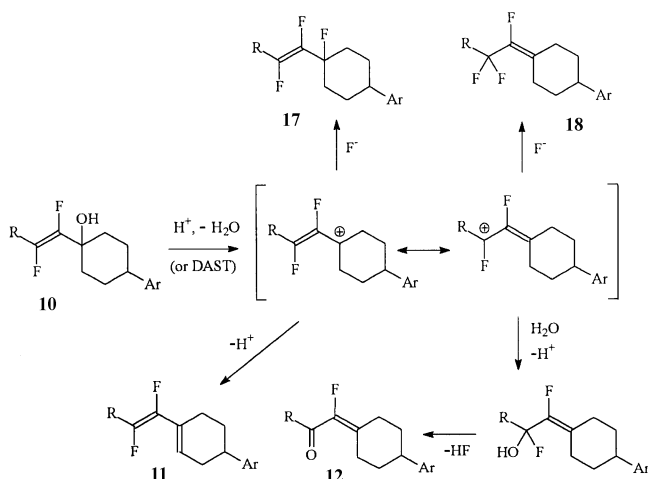


Figure 1. Proposed mechanism for the formation of **12** and **18** as major products from **10**.

Table 1. The phase transition temperature of liquid crystalline compounds

Compound No	$R=C_nH_{2n-1}$		Phase Transition Temperature $^{\circ}C$	
	n		Crystal-Nematic	Nematic-Isotropic
11	4	Heating	67, 124*	132.5
		Cooling	40.2	132.5
14	3	Heating	65	90 dec.
		Cooling	50	
	4	Heating	61	90 dec.
		Cooling	39.7	
	5	Heating	67.6	90 dec.
		Cooling	43.5	
6	Heating	53	90 dec.	
	Cooling	34		
15	3	Heating	119.5	177 dec.
		Cooling	88	
	4	Heating	110.2	172.7 dec.
		Cooling	89.1	
	5	Heating	104	161.4 dec.
		Cooling	81.6	
6	Heating	103.6	163.3 dec.	
	Cooling	93		

talline compounds and developed a synthetic pathways. The phase transition temperatures of the synthesized liquid crystalline compounds were determined by cross-polarizing micro-

Table 1. Continued

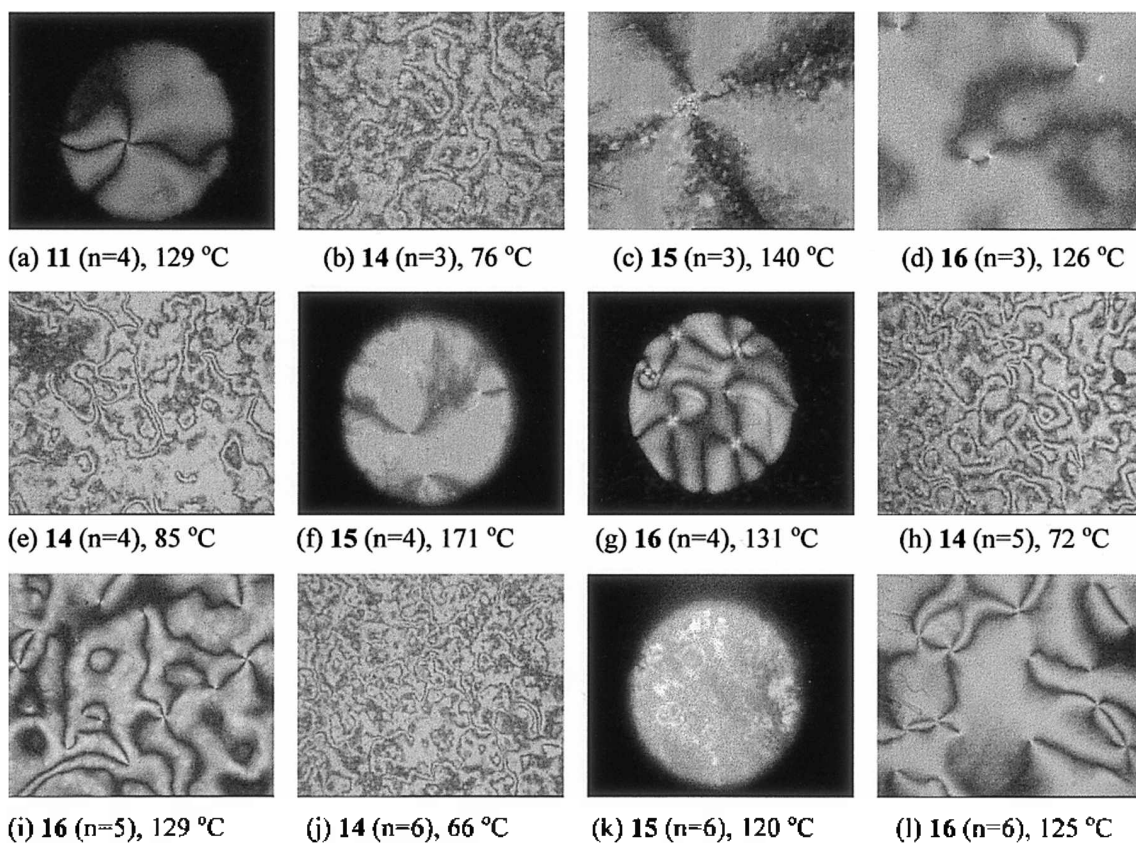
Compound No	$R=C_nH_{2n-1}$		Phase Transition Temperature $^{\circ}C$	
	n		Crystal-Nematic	Nematic-Isotropic
16	3	Heating	62	126
		Cooling	42.8	126
	4	Heating	73.5	132.3
		Cooling	55.6	132.3
	5	Heating	63	130
		Cooling	48	130
6	Heating	67	126	
	Cooling	55	126	
17	4	Heating	34.0	60.5
		Cooling	20.4	52.71

*showed dark area due to vertical orientation between 67 $^{\circ}C$ and 124 $^{\circ}C$. nematic liquid crystalline state between 124 $^{\circ}C$ and 132.5 $^{\circ}C$.

scopy equipped with hot stage (Table 1).

Most of the compounds showed nematic liquid crystalline phase between 60 $^{\circ}C$ ~130 $^{\circ}C$. Nematic phase can be identified due to its characteristic shape under polarizing microscope. Photomicrographs of some of the liquid crystalline compounds are shown in Figure 2.

To our surprise compound **11** has vertical orientation above nematic transition temperature, showing dark area between 67 $^{\circ}C$ and 124 $^{\circ}C$. It showed another liquid crystal-

**Figure 2.** The microscopic images of nematic phase of synthesized liquid crystalline compounds.

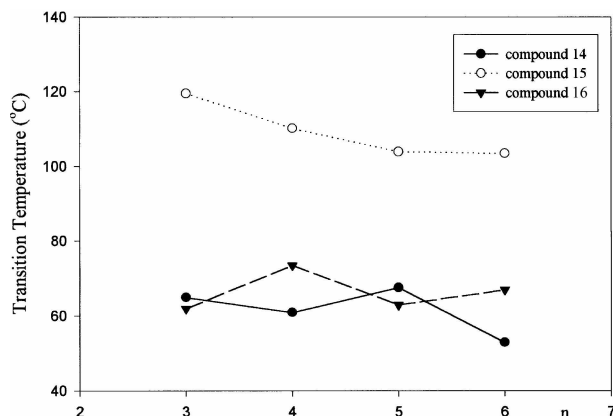


Figure 3. The dependence of transition temperature on the alkyl chain length on heating scan.

line state about 8 degrees below isotropic state to show colorful area. Compounds **11** and **17** showed relatively low phase transition temperature without decomposition. However, they were obtained as minor product in the course of main synthetic scheme. Compounds **14** and **15** decomposed to **16** at high temperature by losing IIF. Compounds **14b** and **18** do not have liquid crystalline properties probably because of their bent structure.

The dependence of transition temperature on the alkyl chain length is different for each series of liquid crystalline compounds. (Figure 3) Compound **14** series show lower transition temperature for even number chain, compound **17** series show lower transition temperature for odd number chain, and compound **15** series show lowering transition temperature as chain length increase.

Conclusion

All the compounds designed and prepared in this work showed nematic liquid crystalline properties. At this stage, the length of fluorine substituted side alkyl chain was limited only to five and eight carbons due to the commercial availability of alkyllithium. Further variation of cyclohexene moiety and side chain will give better physical properties. Other physical properties such as dielectric anisotropy, resistivity, viscosity are under investigation. In order to be used in liquid crystalline mixture for LCD, further blending study will be carried out.

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