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Design, Synthesis and Physical Properties of New Liquid Crystal Materials Having a Fluoro-Substituted Tetrahydronaphthalene Structure for Active Matrix LCD

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DESIGN, SYNTHESIS AND PHYSICAL PROPERTIES OF NEW LIQUID CRYSTAL MATERIALS HAVING A FLUORO-SUBSTITUTED TETRAHYDRONAPHTHALENE STRUCTURE FOR ACTIVE MATRIX LCD

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Liquid crystal materials having a fluoro-substituted tetrahydro-naphthalene structure were designed for active matrix LCD. 6-Aryl-5-fluoro-1,2,3,4-tetrahydronaphthalenes and 5,6-difluoro-1,2,3,4-tetrahydronaphthalenes were prepared by regioselective fluorination and hydrogenation of 2-naphthols. 6-Aryl-5,7-difluoro-1,2,3,4-tetrahydronaphthalenes were synthesized from 5,7-difluoro-1,2,3,4-tetrahydronaphthalene-2-one. The liquid crystal mixture containing these compounds with very good co-solubility exhibits a wide nematic temperature range with low melting point and very large value of dielectric anisotropy. From these results these compounds are useful for design of new liquid crystal mixtures for TFT-displays.

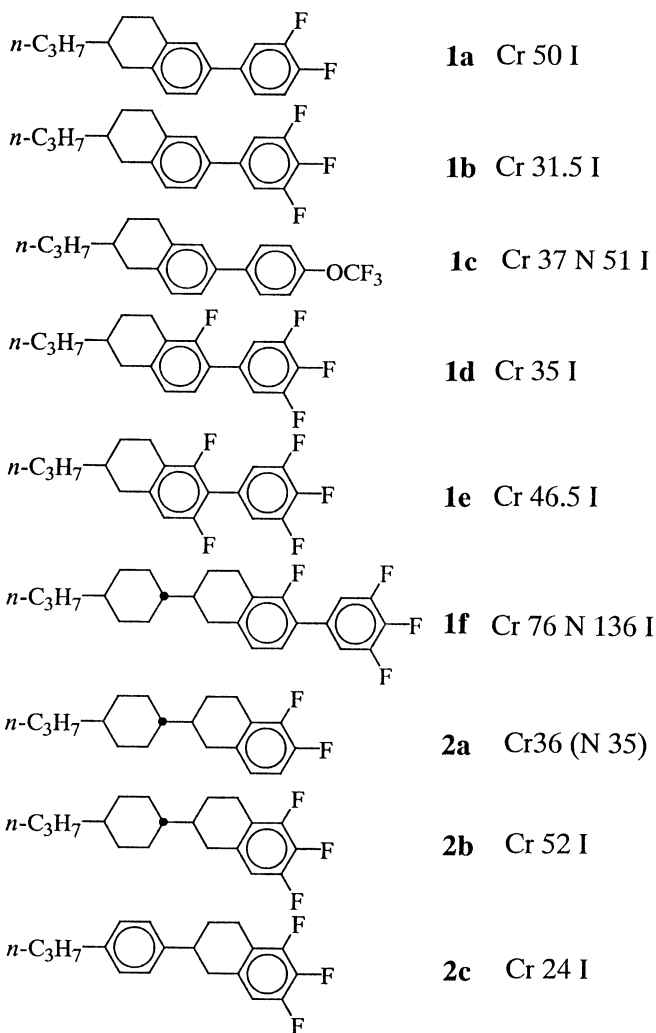
Keywords: active matrix LCD; fused ring structure; low birefringences; tetrahydronaphthalene.

INTRODUCTION

Although a large number of liquid crystalline compounds has been designed and synthesized for liquid crystal display application, it is still necessary to

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improve liquid crystalline materials. Recently we have been reported regarding design, synthesis and properties of naphthalene and decahydronaphthalene derivatives for active matrix LCD [1–4]. But the tetrahydronaphthalene derivatives have not been almost considered. In order to study the utility of tetrahydronaphthalene derivatives for active matrix LCD, we designed **1a–1f** and **2a–2c**. Herein we report their synthesis and physical properties.



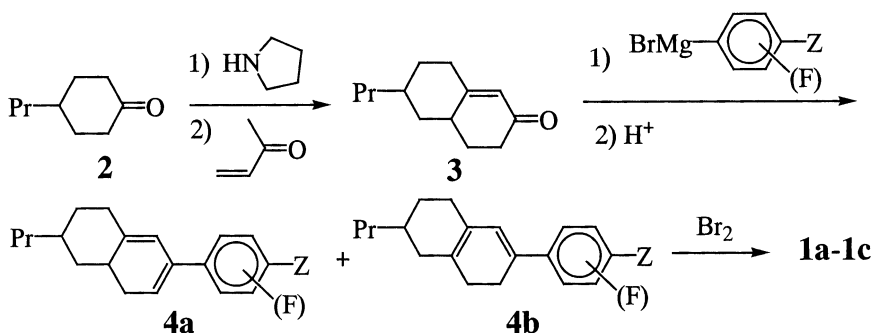
SYNTHESIS

Synthesis of 6-aryl-2-propyl-1,2,3,4-tetrahydronaphthalenes **1a-1c** were carried out according to the route shown in Scheme 1. The octahydronaphthalenone **3**, prepared by Robinson annulation of 4-propylcyclohexanone **2** with methyl vinyl ketone using pyrrolidine, was reacted with fluorinated phenyl magnesium bromide flowed by dehydration of the resulting alcohol using *p*-toluenesulfonic acid afforded the mixture of **4a** with **4b**. Aromatization of the mixture using bromine gave **1a-1c** which were purified by recrystallization.

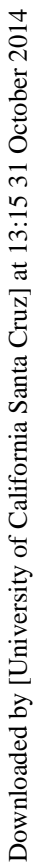
5-Fluoro-1,2,3,4-tetrahydronaphthalene derivatives **1d** and **1e** were prepared according to the route shown in Scheme 2. 1-Fluoronaphthol **5**, prepared from 6-propyl-2-naphthol by the reaction with *N,N'*-difluoro-2,2'-bipyridinium bis(tetrafluoroborate), was reacted with acetyl chloride to give **6**. Regioselective hydrogenation of **6** followed by hydrolysis afforded 5-fluoro-1,2,3,4-tetrahydronaphthalen-2-ol **7**. Reaction of **7** with trifluoromethanesulfonic anhydride followed by Suzuki coupling of resulting **8** with a trifluorophenylboronic acid afforded **1d**. In the similar manner, **1f** was synthesized, starting with 6-(*trans*-4-propylcyclohexyl)-2-naphthol in lieu of 6-propyl-2-naphthol.

Difluorotetralone **9** prepared from difluoropheylacetic acid was reacted with allylmagnesium chloride flowed by hydrogenation, dehydration and hydrogenation of the resulting alcohol afforded difluoro-2-propyltetralone **11**. Iodination of **11** using butyllithium with iodine followed by Suzuki coupling afforded **1e**.

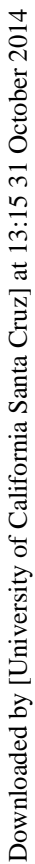
Di- and trifluorotetrahydronaphthalene derivatives **2a** and **2b** were prepared by hydrogenation of corresponding naphthalene (**12a** and **12b**) [4]. On the other hand, **1c** was synthesized from trifluorotetralone (Scheme 3).



SCHEME 1 .



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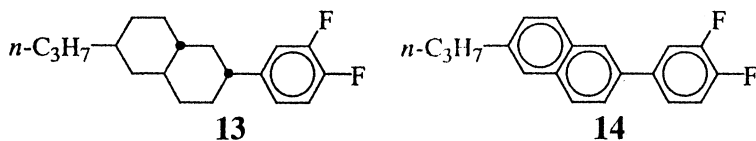


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PROPERTIES

Each of **1a–1f**, **2a–2c**, **12a**, **13** [3] and **14** [3] was added to a host liquid crystal mixture composed of *trans*-4-(3,4-difluorophenyl)-*trans*-4'-vinyl-bicyclohexane and *trans*-4-(3,4-difluorophenyl)-*trans*-4'-(3-butenyl)bicyclohexane and physical properties of resulting mixtures were measured as summarized in Table 1.

The mixture containing phenyltetrahydronaphthalene **1a** exhibited lower nematic-isotropic transition temperature (T_{NI}) than those of phenyl-decahydronaphthalene **13** and phenyl naphthalene **14** (87.1 *vs* 94.3 and 91.0). The dielectric anisotropy ($\Delta\epsilon$) and the birefringences (Δn) of the mixture containing **1a** were larger than those of **13** and smaller than those of **14** (5.1 *vs* 4.9 and 5.7, 0.095 *vs* 0.084 and 0.112).



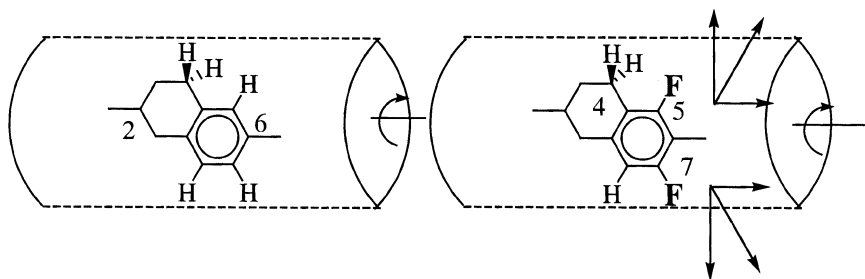
Although the mixture containing 5-fluorotetrahydronaphthalene **1d** exhibited larger $\Delta\epsilon$ (7.3 *vs* 6.3) and smaller Δn (0.090 *vs* 0.092) than those

TABLE 1 The Physical Properties of Decahydronaphthalene Derivatives **1a–1h** in Host LC

Compound	T_{NI}^1 (°C)	$\Delta\epsilon^1$	Δn^1
1a	87.1	5.1	0.095
1b	80.9	6.3	0.092
1c	93.3	4.9	0.099
1d	81.2	7.3	0.090
1e	75.7	8.4	0.088
1f	118.7	7.4	0.100
2a	97.2	5.2	0.085
2b	92.3	5.8	0.084
2c	72.3	5.8	0.085
12a	98.3	5.4	0.095
13	94.3	4.9	0.084
14	91.0	5.4	0.112
host LC ²	116.7	4.8	0.090

¹ These values were measured using a mixture of 20% of each compound and 80% of host LC.

² It consists of 50% of *trans*-4-(3,4-difluorophenyl)-*trans*-4'-vinyl-bicyclohexane and 50% of *trans*-4-(3,4-difluorophenyl)-*trans*-4'-(3-butenyl)bicyclohexane.

**FIGURE 1 .**

of **1b**, T_{NI} of the mixture of **1d** was higher than that of **1b** (81.2 *vs* 80.9). On the other hand, the mixture of 5,7-difluorotetrahydronaphthalene **1e** showed lower T_{NI} (75.7), larger $\Delta\epsilon$ (8.4) and smaller Δn (0.088) than those of **1b** and **1d**. The $\Delta\epsilon$ values of **1d** and **1e** were extrapolated 20 and 24. Fluorotetrahydronaphthalenes **1d** and **1e** were very effective to lower the driving voltage.

In Figure 1 the structures of 2,6-substituted 1,2,3,4-tetrahydronaphthalene and 5,7-difluoro-2,6-substituted 1,2,3,4-tetrahydronaphthalene are schematically drawn. Fluorine atoms of 5- and 7-position of tetrahydronaphthalene has large dipole moment to the molecular long axis. By the fluorine introduction to 5- and 7-position $\Delta\epsilon$ could be enlarged. Although the fluorine atom of 7-position lowers the T_{NI} , that of 5-position raises the T_{NI} . We consider that the fluorine atom is no effective for stabilizing nematic phase and co-solubility because the fluorine atom is sealed by protons of 4-position.

The mixtures containing **2a-2c** were larger $\Delta\epsilon$ than that of host mixture (5.3–5.8 *vs* 4.8). Although T_{NI} and $\Delta\epsilon$ of the mixture of difluorotetrahydronaphthalene **2a** were similar (little lower and smaller) to that of difluoronaphthalene **12a** (97.2 *vs* 98.3, 5.2 *vs* 5.4) the Δn of **2a** was rather smaller than that of **12a** (0.085 *vs* 0.095). On the other hand, **2a** exhibited higher T_{NI} and larger $\Delta\epsilon$ than those of decahydronaphthalene **13** which showed similar Δn of **2a** (97.2 *vs* 94.3, 5.2 *vs* 4.9, 0.085 *vs* 0.084). So fluorotetrahydronaphthalenes **2a-2c** were useful for preparation of LC mixtures with small Δn .

CONCLUSION

A series of 1,2,3,4-tetrahydronaphthalene derivatives were synthesized. It was found that these products exhibited relatively wide nematic mesophase ranges, large $\Delta\epsilon$ and moderate (small) Δn .

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