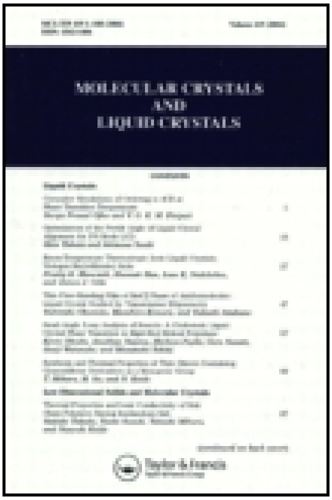

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Design, Synthesis and Physical Properties of New Liquid Crystal Materials for Active Matrix LCD (2)

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Design, Synthesis and Physical Properties of New Liquid Crystal Materials for Active Matrix LCD

(2)

--- New Aromatic Ring Systems Prepared by Regioselective Fluorination as New Mesogens Containing Fluorines ---

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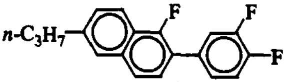
Novel 1-fluoro- and 1,2-difluoronaphthalene derivatives were designed for active matrix LCD and were prepared through the regioselective fluorination of 6-substituted 2-naphthols. These compounds exhibited high nematic-isotropic transition temperatures with very large dielectric anisotropy and large birefringences. These results are useful for design of new liquid crystal mixtures for TFT-displays.

Keywords: fused ring structure; fluorinated naphthalene; dielectiric anisotropy; birefringences; active matrix LCD

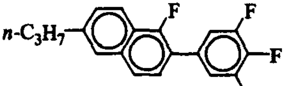
INTRODUCTION

Although a number of liquid crystal materials having a naphthalene moiety have been designed and synthesized to be nematic, ferroelectric or antiferroelectric liquid crystals,[1-5] only a few liquid crystalline containing 1-fluoronaphthalen-2,6-diyl structure.[5] Moreover, the

1-fluoronaphthalene derivatives with the fluoro-substituted aromatics and 1,2-difluoronaphthalene derivatives have not been considered. In order to study the utility of fluorinated naphthalene derivatives for active matrix LCD, we designed 1-fluoronaphthalene derivatives **1a-1e** and 1,2-difluoronaphthalene derivatives **2a-2e**. Herein we report their synthesis and physical properties.



1a Cr 33 I



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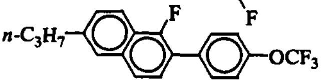
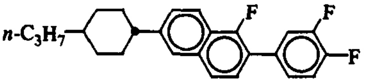
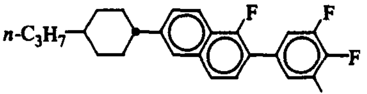


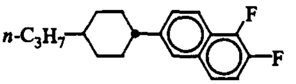
1c Cr 70 S_B 113 S_A 119 I



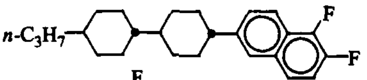
1d Cr 85 N 199 I



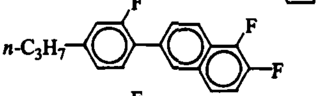
1e Cr 92.5 N 159 I



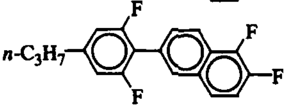
2a Cr 48.5 I



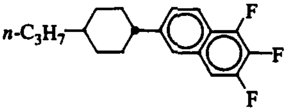
2b Cr 115 N 234 I



2c Cr 60 I



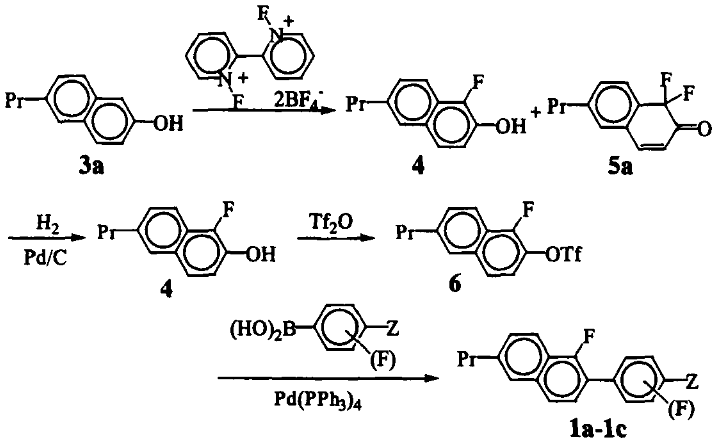
2d Cr 64.7 I



2e Cr 42 I

SYNTHESIS

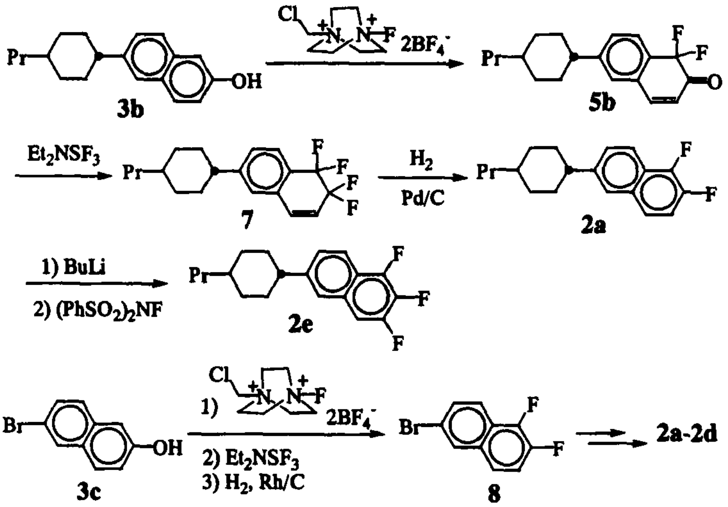
2-Aryl-1-fluoro-6-propylnaphthalenes **1a-1c** were prepared according to the route shown in Scheme 1. 6-Propyl-2-naphtol (**3a**), prepared from 2-naphthol or 6-bromo-2-naphthol, was reacted with *N,N'*-difluoro-2,2'-bipyridinium bis(tetrafluoroborate)[6] in the presence of trifluoromethanesulufonic acid in dichloromethane as a solvent at room temperature to give 9:1 mixtures of **4** and **5a**. Hydrogenation of **5a** of the mixtures and dehydrofluorination afforded **4**. Reaction **4** with trifluoromethanesulfonic anhydride followed by Suzuki coupling of resulting **6** with a substituted phenylboronic acid afforded **1a-1c**. In the similar manner, **1d** and **1e** were synthesized, starting with 6-(*trans*-4-propylcyclohexyl)-2-naphthol (**3b**) in lieu of **3a**.



Scheme 1.

Di- and trifluoronaphthalene derivatives **2a** and **2e** were prepared according to the route shown in Scheme 2. The tetrafluorodihydronaphthalene **7** was prepared by fluorination of difluoroketone **5b** obtained by the reaction of cyohexylnaphthol **3b**

with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis-(tetrafluoroborate)[7] in acetonitrile at room temperature. Hydrogenation of 7 followed by dehydrofluorination afforded 2a. In the similar manner, 2b, 2c and 2d were synthesized. On the other hand, lithiation of 2a followed by fluorination of resulting 1,2-difuluoro-3-naphthyl lithium with *N*-fluorobenzenesulfonimide[8] afforded trifluoronaphthalene 2e.



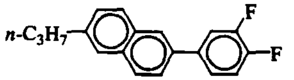
Scheme 2.

6-Bromo-1,2-difluoronaphthalene (8) was easily prepared from 6-bromo-2-naphthol (3c) in 3 steps (Scheme2). Bromonaphthalene 8 was a good intermediate for the syntheses of 1,2-difuruoronaphthalene derivatives 2a-2d.

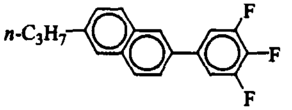
PROPERTIES

2-Aryl-1-fluoro-6-propylnaphthalenes

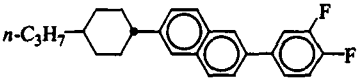
Of the compounds prepared, **1d** and **1e** exhibited stable nematic phase over a wide range of temperatures. The nematic-isotropic transition temperatures (T_{NI}) of **1d** and **1e** were almost same as those of non-substituted naphthalenes **9d** and **9e** (199 °C *vs* 200.5 °C and 159 °C *vs* 153.5 °C). Additionally the melting points of 1-fluorinated series **1a**, **1b**, **1d** and **1e** were usually lower than those of non-fluorinated analogs **9a**, **9b**, **9d** and **9e** (33 °C *vs* 62 °C, 38.5 °C *vs* 50 °C, 85 °C *vs* 99 °C and 92.5 °C *vs* 159 °C), thus 1-fluoronaphthalene derivatives were found to show wider temperature range of nematic phase.



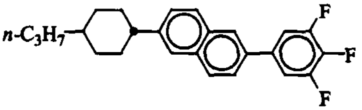
9a Cr 62 I



9b Cr 50 I



9d Cr 99 N 200.5 I



9e Cr 94.5 N 153.5 I

Each of **1a**-**1e** and **9a**-**9e** 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 mixtures containing **1a**-**1e** were larger dielectric anisotropy (Δε) than those of **9a**-**9e** (6.6 *vs* 5.4, 7.9 *vs* 6.4, 6.2 *vs* 5.4 and 7.5 *vs*

6.3). The Δε values of **1a-1e** were extrapolated between 12 and 21. The birefringences (Δn) of the mixtures containing **1a-1e** and **9a-9e** were larger than that of the host mixture (0.105-0.117 *vs* 0.090). The Δn values of **1a-1e** and **9a-9e** were extrapolated about 0.2.

Table 1. The physical properties of 1-fluoronaphthalene derivatives **1a-1e, 9a, 9b, 9d** and **9e** in host LC.

Compound	T_{NI} 1)	Δε 1)	Δn 1)
1a	90.9	6.6	0.110
1b	87.4	7.9	0.105
1c	100.0	6.0	0.111
1d	126.7	6.2	0.113
1e	120.7	7.5	0.112
9a	91.0	5.4	0.112
9b	84.9	6.4	0.107
9d	128.4	5.4	0.117
9e	120.5	6.3	0.113
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'-vinylbicyclohexane and 50% of *trans*-4-(3,4-difluorophenyl)-*trans*-4'-(3-butenyl)bicyclohexane.

In Figure 1 the structures of 2,6-substituted naphthalene and 1-fluoro-2,6-substituted naphthalene are schematically drown. Fluorine atom of 1-position of naphthalene has large dipole moment to the molecular long axis. By the fluorine introduction to 1-position Δε could be enlarged. Although liquid crystal materials having a 2-fluorobiphenyl group exhibited universally low T_{NI} and poor co-solubility, 1-fluoronaphthalene derivatives showed high T_{NI} and good co-solubility. We consider that the fluorine atom is no effective for stabilizing nematic phase and co-solubility because the fluorine atom is sealed by proton of 8-position.

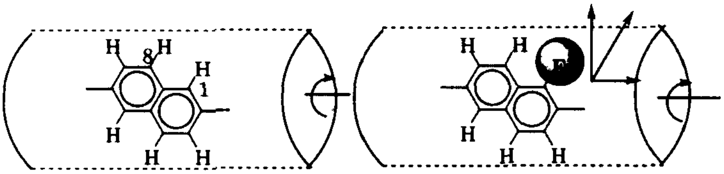


Figure 1

1,2-Difluoronaphthalene derivatives

Of the compounds prepared, **2b** exhibited stable nematic phase over a wide range of temperatures. Each of **2a**-**2e** was added to a host liquid crystal mixture and physical properties of resulting mixtures were measured as summarized in Table 2

Table 2. The physical properties of 1-fluoronaphthalene derivatives **2a**-**2e** in host LC.

Compound	T_{NI} 1)	$\Delta\varepsilon$ 1)	Δn 1)
2a	98.3	5.4	0.095
2b	139.2	5.3	0.105
2c	91.5	6.0	0.111
2d	84.1	6.2	0.113
2e	92.7	6.4	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'-vinylbicyclohexane and 50% of *trans*-4-(3,4-difluorophenyl)-*trans*-4'-(3-butenyl)bicyclohexane.

The mixtures containing **2a-2e** were larger Δε than that of host mixture (5.3-6.4 *vs* 4.8). The Δε values of **2a-2e** were extrapolated between 7 and 13 which were slightly larger than those of corresponding benzene analogs. The Δn of the mixtures containing **2a-2e** were rather larger than that of the host mixture (0.095-0.113 *vs* 0.090). So the wide variation of properties can be attained by the selection of the other structure unit of the molecule.

CONCLUSION

A series of 1-fluoro and 1,2-difluoronaphthalene derivatives were synthesized *via* regioselective fluorination of 6-substisuted 2-naphthols. It was found that these products exhibited relatively wide nematic mesophase ranges, large Δε and large Δn.

References

[1] S.-L. Wu, D.-G. Chen, S.-J. Chen, C.-Y. Wang, J.-T. Shy, and G.-H. Hsiue, *Mol. Cryst. Liq. Cryst.*, 264, 39 (1995); S.-L. Wu and W.-J Hsieh, *Chem. Mater.*, **11**, 852 (1999).

[2] JP 90–166392.

[3] DE-OS 4240041 (1994).

[4] GB 89–00870.

[5] JP 97–52859A.

[6] T. Umemoto, M. Nagayoshi, K. Adachi, and G. Tomizawa, *J. Org. Chem.*, **63**, 3379 (1998).

[7] R. E. Banks, M. K. Besheesh, S. N. Mohialdin-Khaffaf, and I. Sharif, *J. Chem. Soc., Perkin Trans. 1*, **1996**, 2069.

[8] E. Differding and H. Ofner, *Synlett*, **1991**, 187.