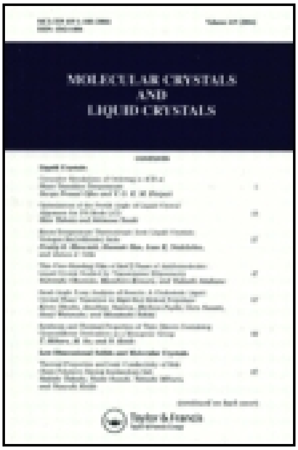

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Design, Synthesis and Physical Properties of New Liquid Crystal Materials for Active Matrix LCD (1)

Yutaka Nagashima [a], Makoto Negishi [a], Tetsuo Kusumoto [a], Kiyofumi Takeuchi [a], Sadao Takehara [a], Haruyoshi Takatsu [a], Corneria Pithart [b], Rainer B. Frings [b], Artur Lachowicz [b] & Gerwald F. Grahe [b]

[a] Liquid Crystal Materials Division, Dainippon Ink & Chemicals, Inc., 4472-1 Komuro, Ina-Machi, Kitaadachi-Gun, Saitama, 362-8577, Japan

[b] R & D Laboratory, Department of Polymer Synthesis, DIC Berlin GmbH, Otisstraße 39, D-13403, Berlin, Germany

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Design, Synthesis and Physical Properties of New Liquid Crystal Materials for Active Matrix LCD (1)

--- New Saturated Ring Systems Prepared by Stereoselective Hydrogenation as New Mesogens Containing Fluorines ---

YUTAKA NAGASHIMA[a], MAKOTO NEGISHI[a],
TETSUO KUSUMOTO[a], KIYOFUMI TAKEUCHI[a],
SADAO TAKEHARA[a], HARUYOSHI TAKATSU[a],
CORNERIA PITHART[b], RAINER B. FRINGS[b],
ARTUR LACHOWICZ[b] and GERWALD F. GRAHE[b]

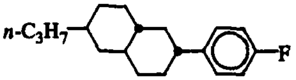
[a]*Liquid Crystal Materials Division, Dainippon Ink & Chemicals, Inc., 4472-1 Komuro, Ina-Machi, Kitaadachi-Gun, Saitama 362–8577, Japan and* [b]*R & D Laboratory, Department of Polymer Synthesis, DIC Berlin GmbH, Otisstraße 39, D-13403 Berlin, Germany*

Liquid crystal materials having a decahydronaphthalene ring structure were designed for active matrix LCD and were prepared by hydrogenation of the ocatahydronaphthalenes obtained through the reaction of a fluorinated phenyl magnesium bromide with the 6-alkyl-decahydronaphthalen-2-ones and followed by dehydration. These compounds exhibit wide nematic temperature ranges with low melting points and very low birefringences. These results are useful for design of new liquid crystal mixtures for TFT-displays.

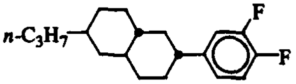
Keywords: fused ring structure; decahydronaphthalene; low birefringences; active matrix LCD

INTRODUCTION

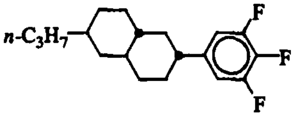
A large number of liquid crystalline materials has been designed and synthesized because of improving the performance of liquid crystal display applications which require a wide range of temperature, low power, wide view-angle, fast switching and so on. Hence, in spite of the synthesis and the investigation of numerous materials possessing specifications such as a wide range of temperature of mesophases, large dielectric anisotropy, low birefringence and low viscosity, it is still necessary to improve liquid crystalline materials.



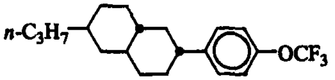
1a Cr 52 (N 46) I



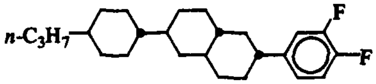
1b Cr 29 I



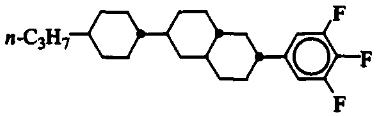
1c Cr 45 I



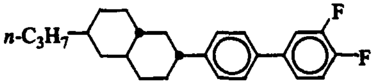
1d Cr 47 I



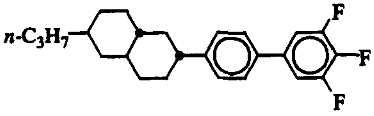
1e Cr 67 N 188.5 I



1f Cr 77.5 N 140.5 I



1g Cr 94 N 175.5 I

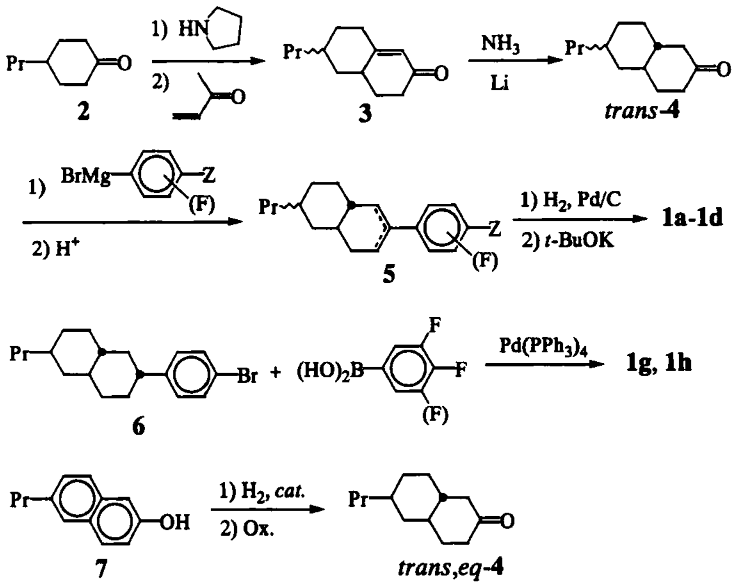


1h Cr 67 N 129 I

Aothough nematic liquid crystal materials having a decahydronaphthalene ring structure has been reported[1,2] and shown to have a wide range of temperature of mesophases, they have not been found to exhibit their physical properties. Moreover, the decahydronaphthalene derivatives with the fluoro-substituted aromatics have not been considered. In order to study the utility of decahydronaphthalene derivatives for active matrix LCD, we designed **1a-1h**. Herein we report their synthesis and physical properties.

SYNTHESIS

Synthesis of 2-aryl-6-propyldecahydronaphthalenes **1a-1d** were carried out according to the route shown in Scheme 1.



Scheme 1

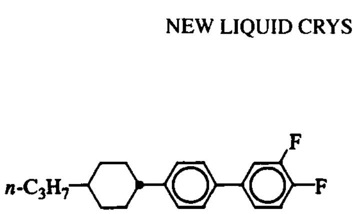
The decahydronaphthalenone *trans*-**4** was prepared by Birch reduction of octahydronaphthalenone **3** obtained by Robinson annulation of 4-propylcyclohexanone **2** with methyl vinyl ketone using pyrrolidine. Reaction of *trans*-**4** with fluorinated phenyl magnesium bromide flowed by dehydration of the resulting alcohol using *p*-toluenesulfonic acid afforded 2-aryl-6-propyoloctahydronaphthalene **5**. Hydrogenation of **5** followed by isomerization of the 2-posision using *t*-BuOK gave **1a**-**1d** which were purified by recrystallization. In the similar manner, **1e** and **1f** were synthesized, starting with 4-(*trans*-4-propylcyclohexyl)cyclohexanone in lieu of **2**.

Biphenyldecahydronaphthalene derivatives **1g** and **1h** were prepared by Suzuki coupling of **6** with di- or trifluorophenylboronic acid (Scheme 1).

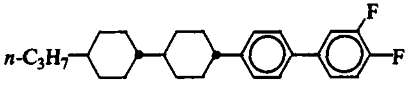
Although *trans*-**4** was stereoselectively prepared by Birch reduction of **3**, stereo-chemistry of the 6-position can not be controlled. In order to solve these synthetic problems, we developed stereoselective hydrogenation of 6-substitued-2-naphtols (Scheme 1). Hydrogenetion of 6-propyl-2-naphthol **7** followed by oxidation of the resulting 6-propyldecahydronaphthalen-2-ol gave over 70% yield of *trans,eq*-**4** with little amounts of the stereo-isomers and 6-propyldecahydronaphthalenes.

PROPERTIES

Of the compounds prepared, **1e**-**1h** exhibited stable nematic phase over a wide range of temperatures. The phase transition temperature from nematic phase to isotropic liquid phase (T_{NI}) of **1g** was higher than that of cyclohexane derivative **8a** and lower than that of bicyclohenane derivative **8b** (175.5 °C *vs* 98.5 °C and 291 °C). Thus it was conformed that the contribution of the decahydronaphthalene moiety to the temperature range of the nematic phase was just between the cyclohexylene and bicyclohexylene group.



8a Cr 67 N 98.5 I



8b Cr 90 (S 88) N 291 I

Each of **1a**-**1h** was added to a host liquid crystal mixture composed of *trans*-4-(3,4-difluorophenyl)-*trans*-4'-vinylbicyclohexane and *trans*-4-(3,4-difluorophenyl)-*trans*-4'-(3-butenyl)bicyclohexane and physical properties of resulting mixtures were measured as summarized in Table 1.

Table 1. The physical properties of decahydronaphthalene derivatives **1a**-**1h** in host LC.

Compound	T_{NI} 1)(°C)	Δε 1)	Δn 1)
1a	97.3	4.3	0.085
1b	94.3	4.9	0.084
1c	87.2	5.5	0.083
1d	96.6	4.8	0.085
1e	131.8	4.7	0.089
1f	122.0	5.4	0.088
1g	126.4	5.2	0.102
1h	120.2	6.2	0.099
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 birefringences of the mixtures containing **1a-1d** were smaller than that of the host mixture (0.083-0.085 *vs* 0.090). The birefringences values of **1a-1d** were extrapolated between 0.04-0.06, which were similar as those of phenylcyclohexane derivatives. The $\Delta\varepsilon$ value of **1b** was similar to the host mixture (4.9 *vs* 4.8). The mixtures containing **1e-1h** showed higher T_{NI} than that of host mixture (120-130 *vs* 116.7). The mixtures containing **1e** or **1f** exhibited similar values of birefringences as that of host mixture.

Furthermore obviously from the perfectly saturated structure, decahydronaphthalene ring was very stable against heat, UV irradiation and humidity, so high holding ratio of the pressure might easily be attained of the decahydronaphthalene derivatives. Due to the higher T_{NI}, the small birefringence and good solubility, liquid crystal mixtures containing decahydronaphthalene derivatives are valuable for AM-LCD especially of 1st minimum system or reflective mode.

CONCLUSION

A series of decahydronaphthalene derivatives incorporating a fluoro-substituted aromatic were synthesized *via* 6-alkyl-*trans*-decahydronaphthalen-2-one intermediates. It was found that these products exhibited relatively wide nematic mesophase ranges, medium $\Delta\varepsilon$ and considerably low Δn.

References

[1] M. Petrzilka and K. Schleich, *Helvetica*, **65**, 1242 (1982).
[2] Ger. Pat. 3150312; G. B. Pat. 2090593; Japan Pat. 57130929; US Pat. 4432885.