

액정 디스플레이를 위한 트랜스, 트랜스-4-(2-플루로로-3-아이소싸이오싸이 아네이토-4-프로필페닐)-4'-알킬바이사이클로헥실의 합성

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Synthesis of *trans, trans*-4-(2-Fluoro-3-isothiocyanato-4-propylphenyl)- 4-alkylbicyclohexyl for Liquid Crystal Display

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요 약. 수직배향(VA) 모드 액정디스플레이에 사용될 수 있는 음의 유전율 상수를 갖고 있는 화합물들을 고안·합성하였다. 이들은 분자의 단축방향으로 큰 쌍극자 모멘트와 큰 분극성을 갖고 있어 N 형태의 액정으로 사용될 수 있다. 중심의 바이사이클로헥신벤젠에 플루오린과 NCS기를 말단부분에 알킬기를 도입하였다. 합성된 화합물들은 예상대로 음의 유전율 이방성을 보여 주었다.

주제어: 수직배향, LCD, 음의 유전율 이방성, 액정, NCS

ABSTRACT. We designed and synthesized compounds which have negative dielectric anisotropy (N type) for VA-LCD mode. Due to the large dipole moments toward the minor axis of molecule and anisotropy of polarizability, they can be used as N type LC. F atom and NCS group and propyl group were introduced as substituents on bicyclohexylbenzene core unit and alkyl chains (propyl~heptyl) were introduced on terminal part. All of the synthesized compounds showed negative dielectric anisotropy as expected.

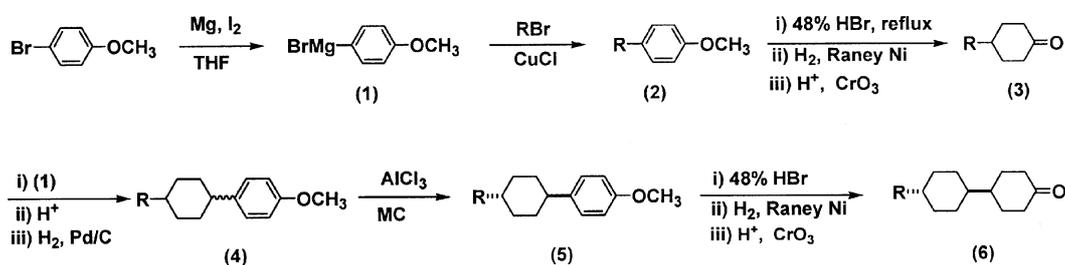
Keywords: Negative Dielectric Anisotropy, VA Mode, LCD, Liquid Crystal

INTRODUCTION

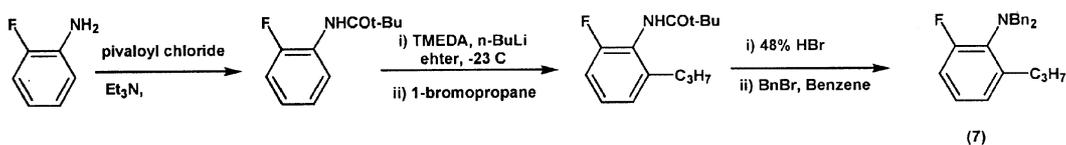
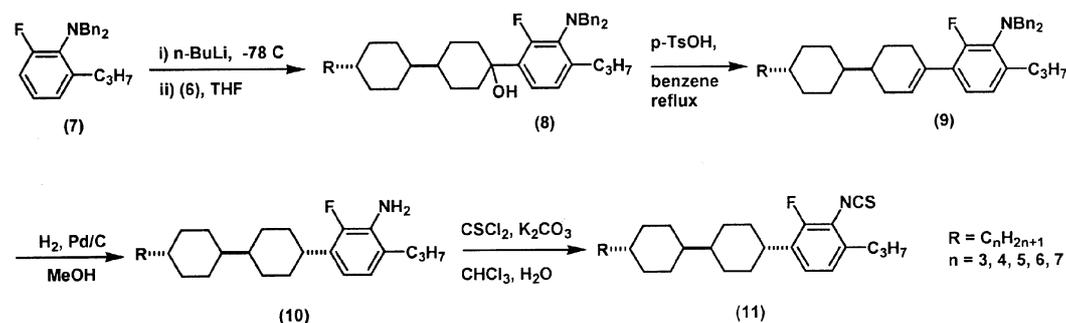
For the latest LCD techniques, it is necessary to enhance the screen quality, viewing angle of broad width and high speed switching time and so on. The VA (vertical alignment) mode is one of the solutions to satisfy these conditions. Compounds with negative dielectric constant ($\Delta\epsilon < 0$) is suitable for VA display mode.¹⁻⁴ In order to develop a nematic mesophase material which has a negative dielectric anisotropy, we designed and synthesized compounds with NCS group and F atom on bicyclohexylbenzene core unit and arrange those substituents toward

the vertical to long axis of molecule. It is reported that liquid crystals with NCS group have low viscosity, nematic phase of wider range and the high stability to heat,⁵⁻¹⁰ therefore, NCS group is regarded as an ideal substituent for nematic mesophase compound. Also, adjacent F atom increases the dipole moment and chemical stability of NCS group,¹¹ and decrease the viscosity. With this background, *trans, trans*-4-(2-fluoro-3-isothiocyanato-4-propylphenyl)-4'-alkylbicyclohexyls are designed and prepared as target materials for LCD. Alkyl groups (C3~C7) were introduced as alkyl chain of terminal group.

Synthetic procedures for intermediates and target



Scheme 1. Synthetic scheme for 4-alkylbicyclohexyl-4-one (6).

Scheme 2. Synthetic scheme for *N,N*-dibenzyl-2-fluoro-6-propylaniline (7).Scheme 3. Synthetic scheme for *trans,trans*-4-(2-fluoro-3-isothiocyanato-4-propylphenyl)-4-alkylbicyclohexyls (11).

compounds are described in Scheme 1, 2, 3.

RESULT AND DISCUSSION

Dielectric anisotropy ($\Delta\epsilon$) depends on the structure of the molecules and can be calculated according to the equation of Maier & Meier.¹²

$$\Delta\epsilon = \frac{N_V F h S}{\epsilon_0} \left\{ \Delta\alpha - F \cdot \frac{\mu^2}{2kT} (1 - 3\cos^2\beta) \right\}$$

$$\epsilon_0 = 8.85 \times 10^{-12}$$

N_V = number of molecules per unit volume

F, h = constants of the internal field

S = degree of order parameter

$\Delta\alpha$ = anisotropy of polarizability, $\Delta\alpha > 0$

k = Boltzmann constant

β = angle between the molecular long axis and the dipole moment μ

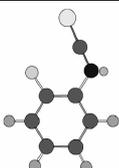
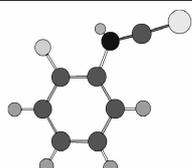
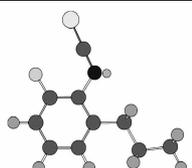
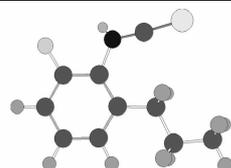
In order for the designed molecules to have negative dielectric anisotropies, β values have to be more than 55°. So we calculated the β value with PM3 force field in MOPAC 2002 before synthesis. (Table 1) Because β values are calculated to be much larger than 55°, it is expected that they will have negative dielectric anisotropy.

Also, we predicted the propyl group effect¹³ which was based on the energy difference between *cis* and *trans* isomers. We optimized the each structure at

Table 1. Calculated β values of designed compounds

	β
C3CCPFNCSC3	78
C4CCPFNCSC3	75
C5CCPFNCSC3	76
C6CCPFNCSC3	74
C7CCPFNCSC3	75

Table 2. Calculation of the heat of formations in 2-fluoroisothiocyanatobenzene conformers

<i>cis</i>	<i>trans</i>	R <i>cis</i>	R <i>trans</i>
			
-822.08207882 II	-822.08112530 II	-935.89828181 II	-935.89661012 II
$\Delta H_f = -0.6$ kcal/mol		$\Delta H_f = -1.05$ kcal/mol	

(1 Hartree=627.5095 kcal/mol)

B3LYP/6-311G-(2d, p) level using in Gaussian 03W.¹⁴ The results are shown in the following Table 2.

The ΔH_f value of the structure with a propyl group is larger than the structure without propyl group. It means that propyl group has large effect on negative dielectric anisotropy. So, the designed molecules are expected to have negative dielectric anisotropy and liquid crystal mesophase.

We measured the physical properties of synthesized compounds and the results are shown in the Table 3 and 4. All of the synthesized compounds exhibited phase transition directly to isotropic state at low temperature without showing liquid crystal mesophase, probably because two possible conformers from interaction of -NCS and adjacent fluorine atoms reduce the vertical dipole moment at molecular long axis. Although the compounds did not exhibit the liquid crystal mesophase, have negative dielectric anisotropy as predicted.

The $V_{90}(V_{90})$ value of the synthesized compounds bring about to larger than host liquid crys-

Table 4. V_{90} values

	$V_{90}(V_{90})$	$V_{90}(V_{90})$
C3CCPFNCSC3	2.35 V	4.95 V
C4CCPFNCSC3	2.30 V	4.85 V
C5CCPFNCSC3	2.35 V	4.85 V
C6CCPFNCSC3	2.20 V	5.00 V
C7CCPFNCSC3	2.20 V	5.20 V
MJ961213	2.50 V	4.40 V

tals value but $V_{90}(V_{90})$ value has improved about 0.2V~0.3V. The synthesized compounds they did not exhibit LC mesophase, however, they exhibited sufficient negative dielectric anisotropy. Also $V_{90}(V_{90})$ for the mixture of synthesized compounds are enhanced a little in comparison with host LC.

In conclusion, the synthesized compounds are expected to be used as mixing LC with other liquid crystal. The usage of these compounds are under investigation.

Table 3. Dielectric anisotropy

Type	Contents	β (degree) cal.	$\Delta\alpha$ (cm ²) cal.	$\Delta\epsilon$ exp.	Phase transition temp.(°C) (C-I)
C3CCPFNCSC3		78	93	-1.85	35
C4CCPFNCSC3		75	97	-1.70	18
C5CCPFNCSC3		76	101	-2.21	49
C6CCPFNCSC3		74	104	-1.67	53
C7CCPFNCSC3		75	108	-1.80	47
MJ961213				-3.018	

(C3-C7: propyl-heptyl)

 $\Delta\epsilon$ was measured by mixing with Merck's MJ961213

EXPERIMENTAL

¹H NMR, ¹³C NMR and ¹⁹F NMR spectra are obtained using Bruker Avance 400 spectrometer and are reported in ppm from TMS on the δ scale. We used commercially available bromoanisole and 2-fluoroaniline as starting material.

trans-4-(3-Dibenzylamino-2-fluoro-4-propylphenyl)-4'-hexylbicyclohexyl-4-ol (8). A solution of *n*-BuLi in hexane 2.5 M (14.4 mL, 36 mmol) was added to a stirred mixture of compound (7) (10 g, 30 mmol) and TMEDA (6 mL, 36 mmol) in THF (60 mL) at -78°C under argon. The mixture was stirred at -60°C for 12 h and then the solution of compound (6) (7.9 g, 30 mmol) in THF (25 mL) was slowly added to it at -78°C . After addition, the mixture was allowed to rt and quenching with NH_4Cl and extracted into ethyl acetate, washed with water and satd NaCl solution, dried over anhydrous MgSO_4 . The solvent was evaporated *in vacuo*, purified by a short column chromatography (hexane: ethyl acetate=10:1) then used for dehydration.

trans-Dibenzyl-[2-fluoro-3-(4-hexylbicyclohexyl-3-en-4-yl)-6-propylphenyl]amine (9). A solution of compound (8) in benzene (30 mL) and a little *p*-TsOH was refluxed for 12 h. The reaction mixture was extracted into ethyl acetate, washed with water and dried over anhydrous MgSO_4 . The solvent was evaporated *in vacuo* to give crude (9), it purified by column chromatography (hexane: ethyl acetate: 10:1) to give a solid (9) (9.8 g, 17 mmol). ¹H NMR (400 MHz, CDCl_3): δ 0.87 (9H, m), 0.97 (1H, m), 1.17 (2H, m), 1.27 (15H, m), 1.81 (6H, m), 2.49 (4H, m), 4.11 (4H, m), 4.11 (4H, s), 5.87 (1H, s), 6.75 (1H, d), 6.90 (1H, t), 7.21 (10H, m); ¹³C NMR (100 MHz, CDCl_3): δ 14.56, 14.72, 22.90, 23.14, 27.11, 27.42, 30.14 (d), 30.20, 30.39, 30.65, 32.02, 32.40, 33.16, 34.00, 37.97, 38.38, 39.23, 43.09, 58.27 (d), 120.88, 124.21, 126.31 (d), 127.29, 127.81 (d), 128.43, 129.59, 134.10, 136.41 (d), 139.77, 142.77 (d), 160.50 (d).

trans,trans-2-Fluoro-3-(4-hexylbicyclohexyl-4-yl)-6-propylphenylamine (10). The reaction mixture of compound (9) (9.8 g, 17 mmol) and palladium on activated carbon (0.01 g) in methanol/THF (20 ml/10 ml) was maintained for 6 h under H_2

stream of 60 psi. After confirmate of complete reaction by ¹H NMR the Pd/C was filtered off and the residue was evaporated *in vacuo* to give (10) (6.5 g, 16.2 mmol). The pure white solid trans-(10) (3.1 g, 7.7 mmol) was obtained by reverse column chromatography (methanol). ¹H NMR (400 MHz, CDCl_3): δ 0.84 (6H, m), 0.90 (5H, m), 1.03 (6H, m), 1.15 (8H, m), 1.31 (1H, m), 1.64 (1H, m), 1.80 (10H, m), 2.44 (2H, t), 2.74 (1H, td), 3.61 (2H, s), 6.54 (1H, t), 6.75 (1H, d); ¹³C NMR (100 MHz, CDCl_3): δ 14.34, 14.35, 22.08, 22.95, 26.92, 30.33, 30.57, 32.50, 33.08, 33.10, 33.90, 37.73, 38.18, 42.21, 43.70, 115.89 (d), 124.13 (d), 126.46 (d), 131.82 (d), 132.27 (d), 149.96 (d).

trans,trans-4-(2-Fluoro-3-isothiocyanato-4-propylphenyl)-4-hexylbicyclohexyl (11). To a solution of trans-(10) (3.1 g, 7.7 mmol) in chloroform (20 mL) cooled at 0°C were added a solution of K_2CO_3 (1.6 g, 11.6 mmol), in water (15 ml). The mixture was treated dropwise with thiophosgene (0.7 ml, 9.2 mmol). The reaction mixture was allowed to stir at room temperature for 4 h. The mixture was extracted into chloroform, washed with water and dried over anhydrous MgSO_4 . The solvent was evaporated *in vacuo* to give crude (11). Then the crude (11) was purified by column chromatography (hexane) to give a white solid (11) (3.2 g, 7.2 mmol). ¹H (400 MHz, CDCl_3): δ 0.88 (6H, m), 0.97 (4H, m), 0.98 (2H, m), 1.15 (6H, m), 1.27 (7H, m), 1.46 (2H, m), 1.62 (2H, m), 1.80 (8H, m), 2.62 (2H, t), 2.75 (1H, td), 6.88 (1H, d), 7.02 (1H, t); ¹³C NMR (100 MHz, CDCl_3): δ 14.13, 14.50, 23.11, 23.74, 27.07, 30.48, 30.56, 32.35, 32.64, 33.42, 34.01, 34.26, 37.70, 37.86, 38.31, 43.26, 43.76, 102.99, 119.25 (d), 124.84 (d), 125.86 (d), 133.12 (d), 137.91, 156.89 (d).

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