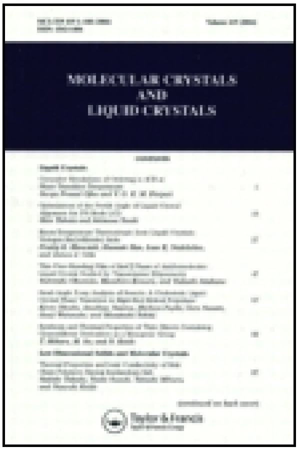

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Fluorinated Liquid Crystals for Active Matrix Displays

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Fluorinated Liquid Crystals for Active Matrix Displays

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Eight types of two- and three-ring liquid-crystalline compounds each possessing a 3,4-difluorophenyl substituent were synthesized. Their liquid-crystalline mixtures were such as to make them useful for active matrix displays, such as TFT (thin-film-transistor) and MIM (metal-insulator-metal) systems. They have high stability and low viscosity, very important properties so far not possible with conventional substances.

Keywords: fluorinated liquid crystals, active matrix displays

INTRODUCTION

Recently, many studies on liquid crystal display (LCDs) with large information contents have been reported.[1,2] Commercial interest in the use of display application has paid attention to the two important systems, such as super-twisted nematic (STN)[3] and active matrix displays (AMDs).[1] The picture elements of the latter system are integrated by a diode for non-linear switching, MIM two-terminal element and TFT three-terminal element. Today, AMDs is spot lighted as the most important display system. It is characterized by a matrix type, full-color display with high contrast sensitivity excluding cross-talk, and are used extensively in portable color TV and computer terminals.[1,2,4]

For the above application, liquid-crystalline mixtures must have greater precision and meet more rigid specification than conventional passive TN systems. For high performance of AMDs, the liquid-crystalline mixtures must have features such as high bulk resistivity and low current consumption, to ensure high reliability. Below, experimental results on eight types of two- and three-ring compounds each possessing a 3,4-difluorophenyl substituent are presented. Liquid-crystalline mixtures were prepared using these compounds. The mixtures were found to have so far unattainable, excellent properties for AMDs such as (1) reasonable high values of dielectric anisotropy, (2) low bulk viscosity, (3) wide mesophase ranges and (4) extremely high stability.

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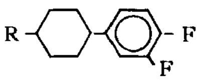
RESULT

(1) Fluorinated Materials

Tables I–VIII show the transition temperatures and enthalpies of the 8 types of liquid-crystalline compounds having a 3,4-difluorophenyl substituent. The transition temperatures were determined with a polarizing microscope, Nikon optiphotopol, equipped with a Mettler hot stage FP52 and control unit FP5, the enthalpies with a differential-scanning calorimeter, Rigaku-8230. The compounds were syn-

TABLE I

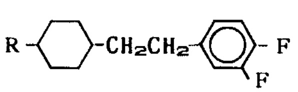
Transition temperatures, transition enthalpies for the series trans-4-alkyl-(3,4-difluorophenyl)cyclohexane[5]



No	R	C		I	ΔH_{melt} KJ/mol
1	C_3H_7	·	-22.3	·	16.90
2	C_5H_{11}	·	-6.1	·	23.60
3	C_7H_{15}	·	8.1	·	29.17

TABLE II

Transition temperatures, transition enthalpies for the series 2-(trans-4-alkylcyclohexyl)-1-(3,4-difluorophenyl)ethane[6]

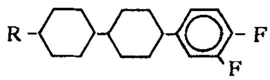


No	R	C		N	I	ΔH_{melt} KJ/mol
4	C_2H_5	·	-35.0		·	15.86
5	C_3H_7	·	-0.2		·	18.03
6	C_4H_9	·	0.5		·	23.34
7	C_5H_{11}	·	2.8	(· -30.1)	·	26.86

( ) denotes a monotropic transition temperature

TABLE III

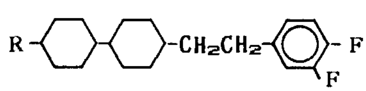
Transition temperatures, transition enthalpies for the series 1,2-difluoro-4-[trans-4-(trans-4-alkylcyclohexyl)cyclohexyl]benzene[7]



No	R	C		N		I	ΔH_{melt} KJ/mol
8	C_2H_5	·	51.8	·	85.4	·	15.31
9	C_3H_7	·	44.2	·	118.0	·	20.96
10	C_4H_9	·	40.5	·	118.3	·	29.25
11	C_5H_{11}	·	45.2	·	125.0	·	25.98

TABLE IV

Transition temperatures, transition enthalpies for the series 2-[trans-4-(trans-4-alkylcyclohexyl)cyclohexyl]-1-(3,4-difluorophenyl)ethane[6]



No	R	C		S_B		N		I	ΔH_{melt} KJ/mol
12	C_2H_5	·	39.8			·	87.9	·	28.49
13	C_3H_7	·	18.4	·	49.7	·	118.0	·	12.76
14	C_4H_9	·	23.3	·	69.1	·	115.2	·	22.84
15	C_5H_{11}	·	50.8	·	74.1	·	121.5	·	24.47

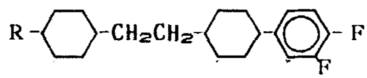
thesized by a well known method and purified by column chromatography, followed by crystallization until constant liquid-crystal transition temperatures were obtained. Their chemical structures were identified by N. M. R. and M. S. Purity was confirmed by H. P. L. C. and G. L. C.

(2) Reliability Test

Seven types of useful liquid-crystalline mixtures, TA-5001 ~ TA-5007 were prepared using the 8 types of liquid-crystalline compounds. In Table IX are shown

TABLE V

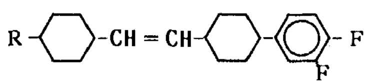
Transition temperatures, transition enthalpies for the series 2-(trans-4-alkylcyclohexyl)-1-[trans-4-(3,4-difluorophenyl)cyclohexyl]ethane[7]



No	R	C		N		I	ΔH$_{melt}$ KJ/mol
16	C_2H_5	·	28.3	·	74.2	·	14.10
17	C_3H_7	·	36.1	·	105.2	·	25.89
18	C_4H_9	·	31.5	·	103.4	·	23.38
19	C_5H_{11}	·	37.6	·	110.6	·	12.84

TABLE VI

Transition temperatures, transition enthalpies for the series trans-2-[trans-4-(3,4-difluorophenyl)cyclohexyl]-1-(trans-4-alkylcyclohexyl)ethane[8]

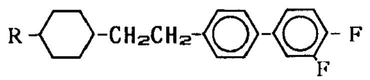


No	R	C		N		I	ΔH$_{melt}$ KJ/mol
20	C_2H_5	·	36.9	·	95.8	·	16.65
21	C_3H_7	·	41.1	·	133.3	·	23.27
22	C_4H_9	·	24.2	·	131.6	·	26.91
23	C_5H_{11}	·	31.0	·	136.2	·	13.64

the properties and reliability assessment results of the 7 liquid crystalline mixtures. For AMD performance, liquid-crystalline mixtures should require low current consumption and have high resistivity. If the liquid crystal layer of a LCD panel has low electric resistance, operating electric charges for the display picture are attenuated within the frame time, resulting in high current consumption. To measure the resistances of the liquid-crystalline mixtures, 1 ml of each mixture was introduced into a cell (Model LE-21) manufactured by Ando Electric Co., Ltd. The

TABLE VII

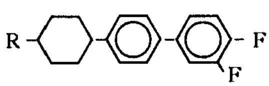
Transition temperatures, transition enthalpies for the series 2-(trans-4-alkylcyclohexyl)-1-(3,4-difluorobiphenyl-4′-yl)ethane[6]



No	R	C		N		I	ΔH_{melt} KJ/mol
24	C_2H_5	·	35.2	·	61.6	·	14.14
25	C_3H_7	·	64.1	·	88.7	·	24.18
26	C_4H_9	·	50.6	·	87.0	·	30.83
27	C_5H_{11}	·	74.8	·	95.9	·	32.38

TABLE VIII

Transition temperatures, transition enthalpies for the series trans-4-alkyl-(3,4-difluorobiphenyl-4′-yl)cyclohexane[9]



No	R	C		N		I	ΔH_{melt} KJ/mol
28	C_2H_5	·	69.0	(·	60.9	) ·	24.74
29	C_3H_7	·	67.9	·	98.6	·	24.41
30	C_5H_{11}	·	55.1	·	108.2	·	18.05

cell was placed in a pA (picoampere) meter (Model 4140B) manufactured by Hewlett Packard Co., Ltd., followed by application of a direct current voltage of 10 V. The initial value was designated as P_0 ($\Omega \cdot$ cm) and resistivity as P_H ($\Omega \cdot$ cm) after heating at 80°C for 1000 hrs. For the heating test, each mixture was placed in an N_2 gas atmosphere in a Pyrex glass container at 80°C. To measure current consumption, each mixture was introduced in a glass cell rubbing-treated and coated with polyimide, and provided with transparent electrodes of 1 cm^2 in area and 9 μm in electrode distance. The current flowing through the electrodes at rectangular pulses of 3 V, 32 Hz and 25°C was measured and taken as current consumption. The initial value was designated as I_0 ($\mu A/cm^2$), and current consumption after

TABLE IX

Reliability test results for and properties of fluoro-type liquid-crystalline mixtures

Mixtures	S-1132	TA-5001	TA-5002	TA-5003	TA-5004	TA-5005	TA-5006	TA-5007
Clearing point, T_{NI}/°C	72.4	78.8	76.2	74.3	83.3	66.0	98.9	75.5
Optical anisotropy, Δn	0.137	0.081	0.071	0.082	0.072	0.065	0.099	0.107
Bulk viscosity, η_{20} cP	27.0	26.0	23.0	23.8	22.0	19.8	23.5	24.4
Dielectric anisotropy, $\Delta\varepsilon$	11.0	6.6	4.5	4.5	4.6	4.1	5.3	4.8
Threshold, V_{10}/V	1.80	1.95	2.10	2.16	2.06	1.96	2.55	2.22
Initial current, $I_{\square}$ (μA/cm²)	0.59	0.30	0.29	0.23	0.26	0.27	0.28	0.30
Current after heating, I_H (μA/cm)	1.04	0.34	0.39	0.26	0.30	0.36	0.30	0.31
Initial resistivity, $\rho_{\square}$ ($\Omega\cdot$cm)	5.0×10^{11}	1.6×10^{14}	4.6×10^{13}	2.1×10^{13}	2.3×10^{14}	3.8×10^{13}	3.5×10^{13}	3.1×10^{13}
Resistivity after heating, ρ_H ($\Omega\cdot$cm)	2.0×10^{11}	4.1×10^{14}	2.0×10^{12}	5.1×10^{12}	4.0×10^{12}	1.5×10^{12}	1.4×10^{12}	1.4×10^{12}

heating at 80°C as I_H ($\mu A/cm^2$). The heating test required 1000 hrs, a period that would permit adequate saturation. This test did not provide UV resistance evaluation, since the light degradation of liquid-crystalline mixtures was adequately dissolved using recently developed UV ray shielding filters.

For comparison, high reliability S-1132 (E. MERCK) having terminal cyano group whose dielectric anisotropy is positive, was used in the above test. The results are shown in Table IX.

DISCUSSION

As evident from Table IX, current consumption of mixtures prepared with the fluoro-type liquid-crystalline compounds, compared with mixtures of cyano group-terminated compounds, is half as much while initial resistivity is higher by as much as $10^2 \sim 10^3$, and that after heating, 10^1. The resistivity of the liquid-crystalline mixtures, of course, depends on the purification of the single compounds after synthesis and on the optimized purification of the liquid crystal after mixing. That fluoro-compounds have lower interaction with ionic impurities in a display element, and undergo less decomposition thus preventing the generation of conductive impurities.

TA-5001 ~ TA-5007, prepared only for illustration, are not restrictive. With the present fluoro-type liquid-crystalline compounds, various mixtures with high stability can be produced.

CONCLUSIONS

Mixtures of liquid-crystalline compounds having a 3,4-difluorophenyl substituent, compared with those containing conventional cyano group-terminated compounds, have much higher stability for AMDs. Fluorinated liquid-crystalline materials, with very high stability, should find application for LCDs.

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