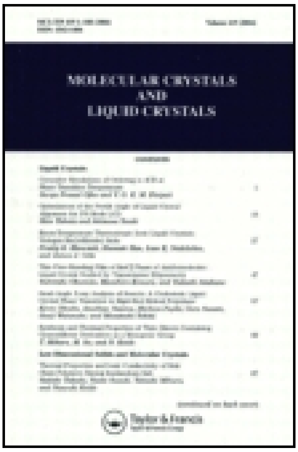


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Liquid Crystalline Compounds Having 1,2,3-Trifluorophenyl Substituent for AM-LCDs with Low-Voltage IC Driver

H. Yamamoto [a], F. Takeshita [a], K. Terashima [a], Y. Kubo [b], Y. Goto [b], S. Sawada [b] & S. Yano [c]

[a] Moriyama TS Center, Chisso Corporation, 230, Kawada-cho, Moriyama, Shiga, 524

[b] Research Center, Chisso Petrochemical Corporation, 51, Goi Kaigan, Ichihara, Chiba, 290

[c] Department of Chemistry, Faculty of Engineering, Gifu University, 1-1, Yanagido, Gifu, 501-11

Version of record first published: 23 Sep 2006.

To cite this article: H. Yamamoto, F. Takeshita, K. Terashima, Y. Kubo, Y. Goto, S. Sawada & S. Yano (1995): Liquid Crystalline Compounds Having 1,2,3-Trifluorophenyl Substituent for AM-LCDs with Low-Voltage IC Driver, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 264:1, 57-65

To link to this article: http://dx.doi.org/10.1080/10587259508037302

Mol. Cryst. Liq. Cryst., 1995, Vol. 264, pp. 57–65
Reprints available directly from the publisher
Photocopying permitted by license only

Liquid Crystalline Compounds Having 1,2,3-Trifluorophenyl Substituent for AM-LCDs with Low-Voltage IC Driver

H. YAMAMOTO, F. TAKESHITA and K. TERASHIMA

Moriyama TS Center, Chisso Corporation, 230, Kawada-cho, Moriyama, Shiga, 524

Y. KUBO, Y. GOTO and S. SAWADA

Research Center, Chisso Petrochemical Corporation, 5–1, Goi Kaigan, Ichihara, Chiba, 290

S. YANO

Department of Chemistry, Faculty of Engineering, Gifu University, 1–1, Yanagido, Gifu, Gifu, 501–11

(Received May 6, 1994; in final form July 11, 1994)

Two- or three-ring compounds having 1,2,3-trifluorophenyl substituent (3F-compounds) were synthesized and their physical properties were measured to evaluate the applications to active matrix liquid crystal displays (AM-LCDs). The 3F-compounds gave good physical properties for AM-LCDs and, in particular, an excellent voltage-holding ratio (VHR), comparable to the compounds having 1,2-difluorophenyl substituents (2F-compound) which are currently used for AM-LCDs. The important point is that 3F-compounds showed much lower threshold voltage (V_{10}) than 2F-compounds. It was demonstrated that one mixture of 3F-compounds with 2F-compounds gave V_{10} of about 1.30 V at 5.5 μm-cell gap. From these results, it was concluded that the 3F-compounds are excellent liquid crystalline materials for AM-LCDs with a low-voltage IC driver, for example the 3V IC driver.

Keywords: Fluorinated liquid crystals, active matrix displays, low-voltage IC driver

INTRODUCTION

Recently, industrial and scientific interest in liquid crystal displays (LCDs) has increased a great deal, with their commercial applications to large-sized displays such as word processers, personal computers and portable color TVs. In particular, active matrix-twisted nematic displays (AM-LCDs) have been in the limelight as an excellent display system to prepare the color and super fine thin-film-transistor LCDs (TFT-LCDs) with high contrast sensitivity, excluding cross talk.[1,2] For these high performance AM-LCD applications, the developments of new liquid crystalline mixtures have been attempted by many researchers.[1–3] In the early stage, cyanophenyl-cyclohexane and cyanobiphenyl derivatives were used as the main component, but their low VHR decreased the contrast of the picture and then a compensated circuit was equipped to avoid this decrease. Therefore, it is one of the most important problems to develop new liquid crystal compounds having a high VHR. Very recently, Sugimori *et al.*[4–9] discovered that the two- or three-ring compounds having 1,2-difluorophenyl (2F-compounds) have high VHR with excellent properties for AM-LCDs such as high dielectric anisotropy, low bulk viscosity, wide mesophase ranges, and extremely high thermal and optical stability.

In this paper we report a new type of liquid crystal compound having 1,2,3-trifluorophenyl substituents (3F-compounds) for AM-LCDs. These trifluorinated compounds and their mixtures had low threshold voltage and high VHR.

EXPERIMENTS

Two- or three-rings compound having 1,2,3-trifluorophenyl substituents were synthesized by almost the same preparation procedure as that reported previously and purified by the column chromatography and recrystallization method.[4–9] The compounds obtained were identified by NMR and MS, and the purity was confirmed to be better than 99.5% by HPLC and GC.

Phase transition temperatures and liquid crystalline textures were determined by a polarizing microscope, Nikon Optiphotopol, equipped with a Mettler hot stage FP32 and control unit FP5, and their enthalpy changes were obtained by a Rigaku-8230 differential scanning calorimeter at the heating rate of about 5 K/min. Optical birefringence (Δn) at 589 nm was measured by an Abbe refractometer (Atago Co. Type 2T) at 25°C. The dielectric measurements were carried out for a TN(90°) cell by use of a precision LCR meter (YHP, Type 4274A). The TN cell was prepared by rubbing the surface of polyimide film coated on an ITO electrode, where the area of ITO electrode was 0.5 cm^2 and the distance between the electrodes was 9.0 μm. The dielectric constant in parallel direction to the molecular axes ($\varepsilon_{\parallel}$) and that in the perpendicular ($\varepsilon_{\perp}$) were estimated from capacitances under the applied voltages of 10 V and 0.5 V, respectively, where the dielectric anisotropy ($\Delta\varepsilon$) is $\varepsilon_{\parallel} - \varepsilon_{\perp}$. The threshold voltage (V_{10}) was determined by monitoring the transmitted intensity of the normal white light in the perpendicular direction under the applied 32 Hz-rectangular electric wave, where the light intensity was measured by use of a LCD evaluation system (Ohtsuka Electric Co. LCD-7000), adjusting $\Delta n \cdot d$ to 550 nm at 25°C. V_{10} is defined as the voltage for the 90% transmitted light intensity. Frank's elastic constant (k_{ii}) was determined by use of an LCR meter (YHP, 4274A) for an anti-parallel rubbing cell and/or a TN rubbing cell, according toFeredericz's method.[10–12] The voltage-holding ratio (VHR) was measured according to the method of Sasaki *et al.*[13]; the electric circuit for VHR is illustrated in Figure 1 and VHR was calculated by the area method. Viscosity was measured by use of a rotational viscometer (Tokimek Type E).

RESULTS AND DISCUSSION

Table 1 shows lists of 3F-compounds and their phase transition parameters. Most homologues of 3F-compounds show the nematic phase and its nematic temperature range is wide enough to use as a component of nematic mixtures for LCDs.

Figure 2 shows the temperature dependence of VHR for ZLI-1132, FB-01 and 20 wt% 1,2,3-trifuluoro-5-[trans-4-(trans-4-propylcyclohexyl) cyclohexyl] benzene ($I(n = 3)$ in Table 1) in FB-01. Here, ZL1-1132 is the mixture from Merck whose main components are compounds having cyanophenyl group, and FB-01 is 1,2-difluoro-4-[trans-4-(trans-4-alkylcyclohexyl) cyclohexyl] benzene from Chisso Co.[15] In ZL1-1132, cyanophenyl derivatives, VHR rapidly decreases with approaching $T-T_c$ (T_c: the clearing point) from -60 to 0°C, but VHR for FB-01 retains almost 100% in $T-T_c$ from 0 to -80°C, as Saito previously reported[14], and so is widely recognized as an excellent compound for AM-LCDs. The 20 wt% $I(n = 3)$ in FB-01 exhibits an excellent VHR-temperature property; VHR is 99 ~ 100% near -60°C of $T-T_c$ and this value is almost retained to -10°C. We examined the temperature dependence of VHR for various 3F-compounds and found that these compounds also show excellent VHR. It is concluded that nematic 3F-compounds have excellent VHR, compared to those of 2F-compounds such as FB-01.

Figure 3 shows the dependence of the threshold voltage (V_{10}) on $T-T_c$ for the mixtures containing fluorinated compounds at $\Delta n \cdot d = 500$ nm. Clearly, the value of V_{10} decreases almost proportional to the number of the substituted fluorine atoms; the decrease of V_{10} was estimated at about 0.15 V per one substituted fluorine atom. The value of V_{10} for 20 wt% 1,2,-difuluoro-4-[trans-4-(trans-4-propylcyclohexyl) cyclohexyl] benzene in FB-01 was almost the same as that for FB-01.

Figure 4 shows the temperature dependence of dielectric anisotropy ($\Delta\varepsilon$): the value of $\Delta\varepsilon$ increases with increasing the number of substituted fluorine atoms and the slope is almost unchanged with the F number. $\varepsilon_{\parallel}$ increased by the substitution of F but $\varepsilon_{\perp}$ is scarcely changed, resulting in the increase of $\Delta\varepsilon$. In Figure 5, the Frank elastic constant (k_{ii}) is plotted against $T-T_c$. The value of k_{11} is independent of the F number but the values of k_{22} and k_{33} decrease with increasing the F number. The value of V_{10} is expressed

$$V_{10} = (\pi/d)\cdot[\{k_{11} + (1/4)\cdot(k_{33} - 2k_{22})\}/\varepsilon_0\cdot\Delta\varepsilon]^{(1/2)} \quad (1)$$

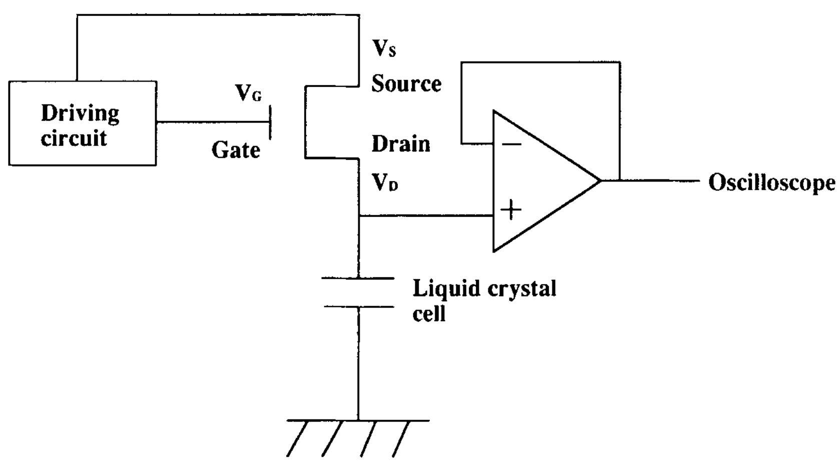
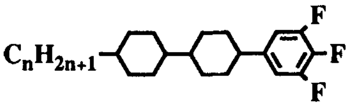
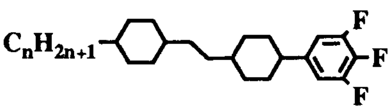
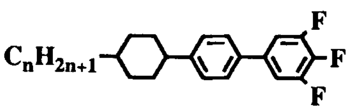
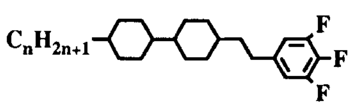


FIGURE 1 The electric circuit for voltage holding ratio (VHR).

TABLE I

Phase transitions of compounds having 1,2,3-trifluorophenyl substituent. Phase Transition (°C)/enthalpy change (kJ·mol⁻¹)

compounds	C1	C2	S	N	I
 (I)					
$n=2$	· 72.4/26.0			(· 48.9/14.1)	·
3	· 64.2/25.3			· 93.4/0.4	·
4	· 63.7/9.8	· 66.2/19.4		· 91.1/0.3	·
5	· 86.4/26.5			· 101.1/0.6	·
7	· 68.5/23.3			· 97.8/0.6	·
 (II)					
$n=2$	· 63.5/30.8			(· 49.6/21.3)	·
3	· 49.5/24.9			· 83.4/0.9	·
4	· 60.8/38.1			· 83.2/0.7	·
5	· 45.7/19.6			· 91.0/0.8	·
 (III)					
$n=3$	· 40.4/20.3			(· 33.1/0.1)	·
4	· 31.4 36.0/			(· 33.0/—)	·
5	· 29.2/18.0			· 57.6/0.2	·
 (IV)					
$n=2$	· 64.3/0.5			· 65.5/—	·
3	· 41.0/14.1			· 97.0/1.0	·
4	· 57.0/6.2 ·			· 96.4/0.9	·
5	· 52.8/4.6	· 56.1/—		· 103.3/1.0	·

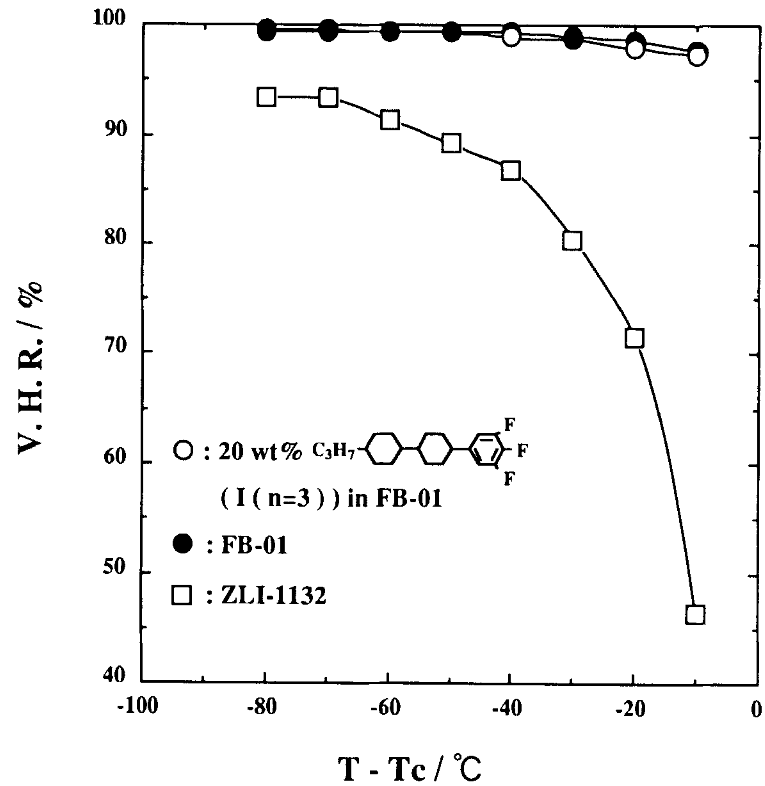


FIGURE 2 Temperature dependence of voltage holding ratio (VHR) for three mixtures.

where d is a cell gap and ε_0 is dielectric constant in vacuum.[16] Therefore, the variation of V_{10} with the F number is closely connected with the variations of $\Delta\varepsilon$ and $k_{33} - 2k_{22}$. In the equation (1), V_{10} decreases as $\Delta\varepsilon$ increases and $k_{33} - 2k_{22}$ decreases. For example, V_{10} is almost 1.80 V and 1.97 V for 20 wt% $I(n = 3)$ in FB—01 and FB—01, respectively, near $-80°$C of $T - T_c$, while $\Delta\varepsilon$ is 5.5 and 4.8, and $k_{11} + (1/4) \cdot (k_{33} - 2k_{22})$ is 11.24 and 11.22, respectively. Therefore, the increase of $\Delta\varepsilon$ may mainly contribute to the decrease of V_{10}. It is emphasized that V_{10} for 3F-compounds is fairly much smaller than that of 2F-compounds.

As mentioned in Introduction, it is well known that cyanobiphenyl and cyanophenyl-cyclohexane derivatives have been low V_{10} but low VHR; The low V_{10} may be due to a large $\Delta\varepsilon$ value induced by the polar CN group but the low VHR may originate in an increase of electric conduction which may be caused by an increase in solubility of ionic impurities to the nematic solvent by the presence of polar CN group (usually the specific resistivity the order of $\sim 10^{11}\,\Omega$cm). In the 3F-compounds, the polar C-F bond outstandingly increases the value of $\Delta\varepsilon$, leading to the decrease of V_{10}, but retained the high VHR, because the F-substituted

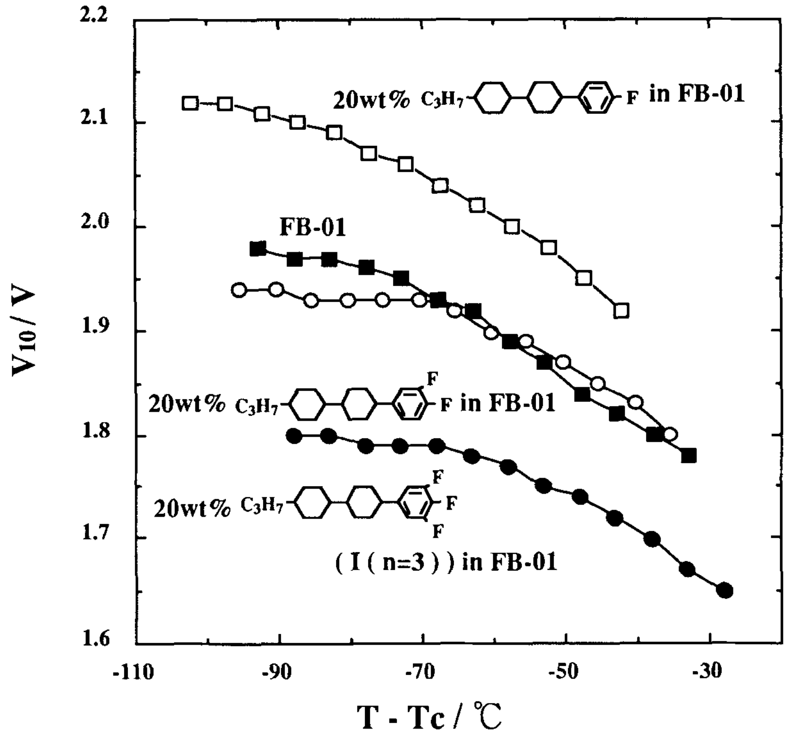


FIGURE 3 Temperature dependence of threshold voltage (V_{10}) at $\Delta n \cdot d = 500$ nm for mixtures.

phenylcyclohexane or biphenylcyclohexane rings may be chemically stable and may dissolve ionic impurities much less, compared with the cianobiphenyl or biphenylcyclohexane derivatives, resulting in keeping a low electric conductivity (usually the specific resistivity the order of $\sim 10^{14}\,\Omega$cm). In conclusion, we found that the 3F-compounds have excellent VHR and V_{10}: VHR for 3F-compounds was comparable to that for 2F-compounds and V_{10} for 3F-compounds was lower than that for 2F-compounds. This fact suggests that the 3F-compounds are applicable for the AM-LCDs using a low-voltage IC driver which is currently being investigated as the next LCD.

We prepared two mixtures A (65 wt% 3F-compounds and 35 wt% 2F-compounds) and B (94 wt% 3F-compounds and 6 wt% 2F-compounds). The physical parameters for mixtures A and B are listed in Table 2, with those for LIXON-5044XX whose compounds consist of 2F-compounds. The V_{10} values of mixtures A and B are 1.43V at $d = 5.7\,\mu$m and 1.30 V at $d = 5.5\,\mu$m, which are considered to be low enough to use for AM-LCDs with a 3V IC driver.

The temperature dependence of VHR is shown in Figure 6. VHR is about 98.3% at room temperature and is scarcely changed by temperature. Consequently these parameters indicated that mixture A and B are applicable for AM-LCDs.

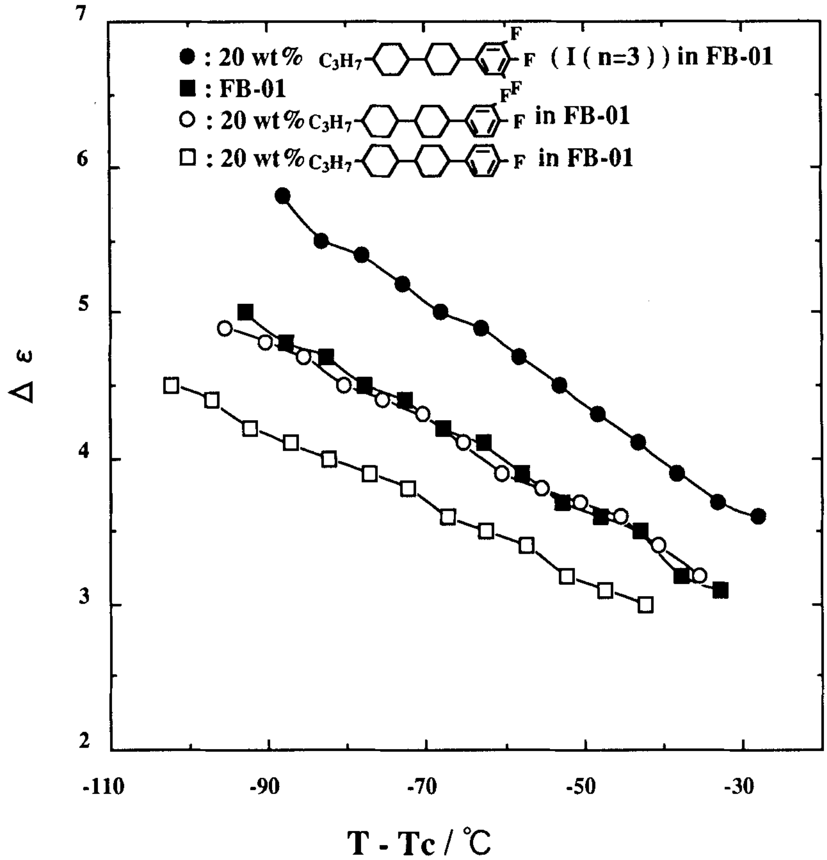


FIGURE 4 Temperature dependence of dielectric anisotropy (Δε) for four mixtures.

TABLE II

Electro-optical parameters for mixture A, B and LIXON 5044XX

Mixture	A	B	LIXON 5044XX
T_{S-N}/°C	< −40	< −30	< −30
T_{N-I}/°C	80.0	80.1	81.0
$\eta/mPa\cdot s$	26.4	27.9	24.4
Δn	0.088	0.087	0.090
$\Delta\varepsilon$	7.2	8.5	4.9
V_{th}/V	1.43	1.30	1.73
$d/\mu m$	5.7	5.5	5.6
V. H. R./%	98.3	98.3	98.2
composition/%	2F-compounds: 35 3F-compounds: 65	2F-compounds: 6 3F-compounds: 94	2F-compounds: 100

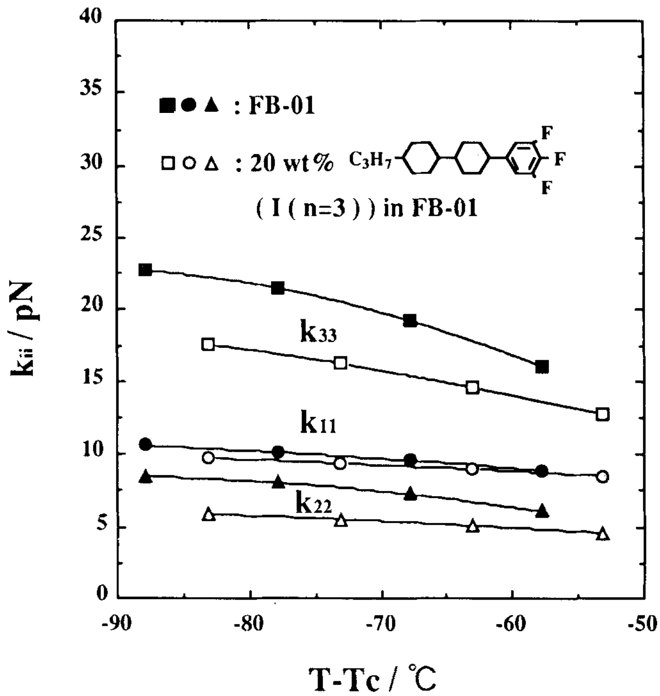


FIGURE 5 Temperature dependence of elastic constants (k_{ii}).

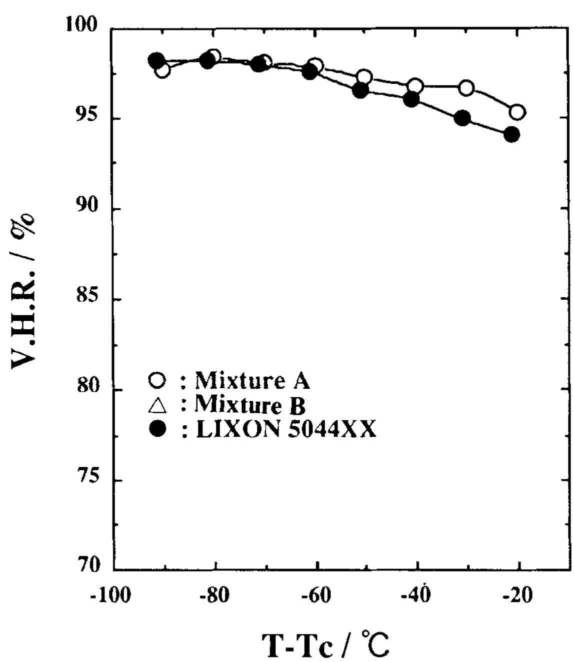


FIGURE 6 Temperature dependence of voltage holding ratio (VHR) for Mixture A, B and LIXON 5044XX.

CONCLUSION

Several two- or three-ring compounds having 1,2,3-trifluorophenyl substituents (3F-compounds) were prepared and their physical properties were measured. The 3F-compounds showed excellent VHR, compared to compounds having 1,2-difluorophenyl substituents (2F-compounds), which are currently used for AM-LCDs and it is emphasized that 3F-compounds gave much lower threshold voltage than 2F-compounds. In fact, a mixture of 94 wt% 3F-compounds and 6 wt% 2F-compounds showed a low threshold voltage of 1.30 V at 5.5 μm cell gap. These results indicated that 3F-compounds are very useful LC materials for AM-LCDs with a low-voltage IC driver.

References

1. E. Kaneko "Liquid Crystal TV Display, Principles and Application of LCDs" Reidel, Dordrecht (1987).
2. Japan Display '89 at Kyoto, Oct. 16–18 (1989).
3. L. Pohl and U. Finkenzeller, "*Liquid Crystals, Applications and Uses*" Vol. 1, Ed. B. Bahadur, World Scientific, NJ, (1990) Chap. 4.
4. Y. Goto, EP 0194879B, US 4695398.
5. Y. Goto, EP 0205998B, US 4797228.
6. S. Sugimori, DE 3139130c, US4405488.
7. Y. Goto, JP applications 01265131.
8. S. Sugimori, JP 89004496B.
9. Y. Goto, T. Ogawa, S. Sawada and S. Sugimori, *Mol. Cryst. Liq. Cryst.*, **209**, 1 (1991).
10. A. Saupe, *Z. Naturforsch.*, **15A**, 815 (1960).
11. H. J. Deuling, *Mol. Cryst. Liq. Cryst.*, **19**, 123 (1972).
12. T. Uchida and Y. Takahashi, *Mol. Cryst. Liq. Cryst. Lett.*, **72**, 137 (1981).
13. K. Sasaki, M. Okada, S. Kohzaki and F. Funada, *Sharp Tech. Report*, **52**, 31 (1992).
14. LIXON Information (1990).
15. H. Saito, Proc. Semicon/Kansai-Kyoto Technology Seminar, '91, 145 (1991).
16. M. Leslie, *Mol. Cryst. Liq. Cryst.*, **12**, 57 (1970).
17. H. J. Deuling, *Mol. Cryst. Liq. Cryst.*, **27**, 81 (1975).