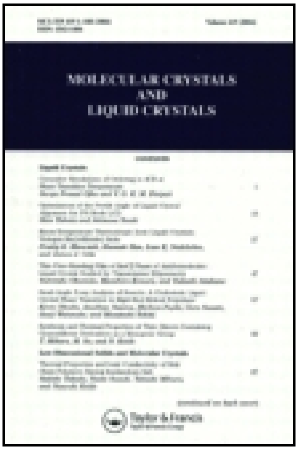

Molecular Crystals and Liquid Crystals

Development and Industrialization of Liquid Crystal Materials

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Development and Industrialization of Liquid Crystal Materials

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The development and industrialization of some liquid crystal materials: the ester with strong positive dielectric anisotropy for TN LCD, the tolan with large birefringence, the alkenyl with large k33/k11 elastic ratio and the azine with large birefringence and high N-I transition temperature for STN LCD, and the fluorinated liquid crystals of fused ring systems for TFT LCD, are reviewed. The work on new fluorinated naphthalene with negative dielectric anisotropy for VA LCD is introduced.

Keywords: alkenyl; azine; fused ring; liquid crystal material; naphthalene; tolan

1. INTRODUCTION

Since the first pocket calculator with a liquid crystal display (LCD) was put on the market in 1973, the market of LCD has been growing. The TN (twisted nematic) LCD replaced the DSM (Dynamic Scattering Mode) and came into wide use for watches, calculators and automobiles. Although the LCD market in 1980 reached 50 billion yen and the digital display of LCD was popularly known, the market failed to increase because of the insufficient performance for information displays in the first half of 1980s. In such circumstances, the STN (super twisted nematic) LCD was developed in 1986 and came into use for a word processor. The LCD market expanded with the new applications and reached 330 billion yen in 1990. Subsequently, the STN LCD was used in a mobile communication tool or a note PC, having some problems to be solved on the viewing angle and the response speed. As a good result of large-scale investment on AM (active matrix) LCD using TFT (thin film transistor) in the latter half of 1990's, the price of TFT

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LCD with high performance was decreased and the note PC market drastically expanded. Afterwards, the monitor with TFT LCD became widespread and the LCD market in 2000 reached 2.6 trillion yen. Recently, the LCD TV has been popular and the mode of TFT LCD is changing from TN to VA (vertical align) or IPS (in-plane switching). In coming several years, the LCD market will increase mainly for TV and is estimated to exceed 8 trillion yen in 2010.

Development of liquid crystal materials also took an important role in such expanding market. In this paper, the cases of the development and the industrialization of liquid crystals, in which the author was involved, are reviewed, and the recent work is described.

2. TN LIQUID CRYSTALS

Liquid Crystalline Ester With Strong Positive $\Delta\varepsilon$

As the multiplexibility of liquid crystal materials for TN LCD was required in the latter half of 1970s, the other advanced liquid crystals beside the liquid crystalline biphenyl were demanded. Dainippon Ink (DIC) was developing the liquid crystal materials with high multiplexibility jointly with Hitachi. Toriyama, who was in charge of a liquid crystal design in Hitachi, achieved an evaluation method of liquid crystal materials for multiplexed TN LCD, and was interested in Demus ester (cyclohexane carboxylic acid ester ***1***) as a non-polar liquid crystal based on the idea that the liquid crystals consisting of strong polar components and non-polar components show high multiplexibility. We were engaged in the establishment of manufacturing process of Demus ester and the development of a strong polar component under the reliable liquid crystal design. We developed the 3-chloro-4-cyanophenyl ester ***2*** having +36 of $\Delta\varepsilon$ as a strong polar component in 1978. Moreover, we developed the 3-fluoro-4-cyanophenyl ester [1] ***3*** replaced the chloro-group for ***2*** by the fluoro-group. ***3*** shows a monotropic nematic phase whereas ***2*** does not show a liquid crystal phase. Then, the drastic improvement was achieved by the liquid crystalline component ***3*** which is still used for TN or STN LCD. And now, ***4*** [2] with high N-I transition temperature and the alkylbenzoyloxy ester [3] ***5***, ***6*** with larger $\Delta\varepsilon$ by further introduction of fluoro-group are used.

3. STN LIQUID CRYSTALS

Liquid Crystalline Tolan

Although STN LCD was used for a word processor in 1986, the display performances such as contrast or response were insufficient.

Especially, in order to improve the response that enables the application to a note PC, the liquid crystal having large birefringence (Δn) with low viscosity was strongly required.

The wide operating temperature range and low viscosity are the characteristics that are always required for liquid crystal materials. The liquid crystal component with high N-I transition temperature is necessary to widen the temperature range. However, the liquid crystal component with high N-I transition temperature has generally high viscosity, and the liquid crystal component with low viscosity has low N-I transition temperature. Moreover, the liquid crystal component with large Δn was considered to have high viscosity. The author *et al.* found a drastic advantage of the liquid crystalline tolan [4] **7** having 0.3 of large Δn, 70 degree C of relatively high N-I transition temperature and 20 mPa·s of low viscosity at 20 degree C.

The tolan prepared by a conventional method such as de-hydrogen bromide method had a problem in heat stability showing the level below $10^{10}\,\Omega$-cm of low specific resistivity and being colored. By using newly developed a coupling method for the synthesis of the tolan as shown in Figure 1, we succeeded in the improvement of specific resistivity to the level more than $10^{13}\,\Omega$-cm even after heating. Passing the stability test in a real LCD panel, we were able to demonstrate that the liquid crystalline tolan can be used as a practical liquid crystal. Then, we developed a series of many useful liquid crystalline tolans **8**, **9**, **10**, and prepared the liquid crystal mixtures having large Δn and low viscosity with high N-I transition temperature such as DON-605: Δn = 0.283, viscosity at 20 degree C = 20.5 mPa·s, N-I metastasis temperature = 100 degree C which can be a useful non-polar host of STN liquid crystal.

The tolan-liquid crystal drastically surpassed the other conventional liquid crystals having large Δn at that time such as a pyrimidine-liquid crystal (Δn = .196, viscosity at 20 degree C = 37.7 mPa·s) or a biphenyl liquid crystal (Δn = 0.195, viscosity at 20 degree C = 52.8 mPa·s) in

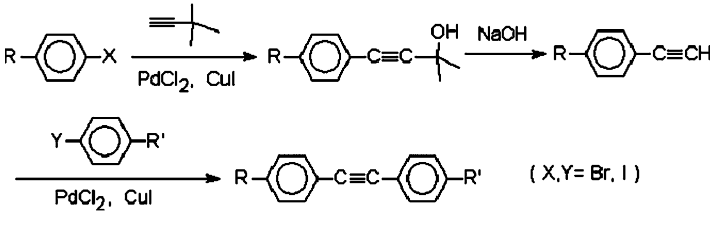


FIGURE 1 Synthesis of tolan by coupling method.

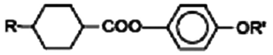
characteristics. By the synergistic effect of the tolan and the alkenyl, the breakthrough of the trade-off relationship between the response and the contrast was achieved [5]. The STN LCD, of which response time was improved from about 300 ms to 120–130 ms, was applied to a note PC, and the market was expanding. Now the liquid crystals including the liquid crystalline tolan is used widely in about 70% of total liquid crystals for STN LCD.

Liquid Crystalline Alkenyl

We were convinced by the evaluation and confirmation of the stability that the liquid crystalline alkenyl with large k33/k11 elastic ratio such as ***11*** developed by Schadt *et al.* [6] has the promising possibility as a STN liquid crystal. Rodic, a joint venture of Roche and DIC, was established in 1988 based on the conviction. We jointly determined each liquid crystalline alkyenyl to be industrialized and focused our efforts on the cost-down. The industrialization was achieved by the optimization of synthetic route, large-scale production of a key intermediate, and production transfer to Japan. In addition to the alkenyl ***11*** with cyano group, the alkenyl ***12*** with fluoro group and the alkenyl of hydorocarbon ***13***, ***14***, ***15*** were used commercially. Then, the alkenyl-liquid crystal joined the mainstream of STN liquid crystals.

Liquid Crystalline Azine

STN LCD and TFT LCD repeated the battles several times for the note PC in the market. In the situation that STN LCD was inferior in the total competitiveness in 1995, the development of the quick response STN liquid crystal being able to compete with the TFT LCD, was required. Because a STN LCD maker has a clear development strategy to use a thinner cell in order to achieve quicker response, we reviewed the liquid crystals with large Δn again, widening the scope of the choices for the practical liquid crystals. And we were interested in the liquid crystalline azine with long conjugated π-electron part in a molecule. The known liquid crystalline azine [7] ***16***, showing a nematic phase in a temperature range between 70 degree C and 103 degree C, has extremely high N-I transition temperature for a liquid crystal component of two ring systems. We finally developed the liquid crystalline dialkenylazine [8] ***17*** combining the azine and the alkenyl after the solution of some problems for a practical liquid crystal material. The liquid crystal azine ***17***, having 0.34 of large Δn and a nematic phase in a temperature range between 57 degree C and 116 degree C, surpassed the liquid crystalline tolan in the characteristics. The



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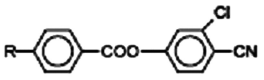

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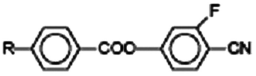

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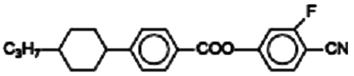

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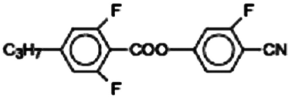

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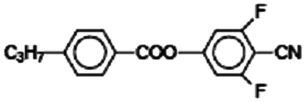

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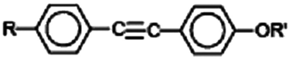

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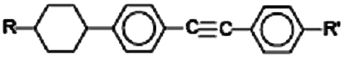

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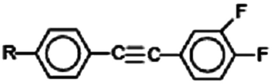

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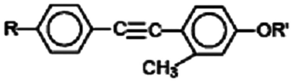

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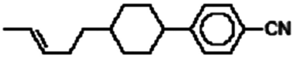

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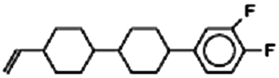

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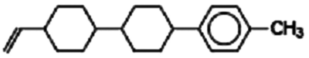

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liquid crystalline azine shows more stable level than the tolan for the sun-test and has a sufficient stability for LCD application in spite of being colored yellow with 400 nm of the absorption edge wavelength.

The liquid crystalline azine **17** improved the trade-off relationship between the response and the contrast of the conventional STN liquid crystals comprising the tolan as shown in Figure 2. By the serial development results for the STN LCD, STN won a great victory over TFT in 1997 in a domain of large-sized LCD. Although all of the large-sized

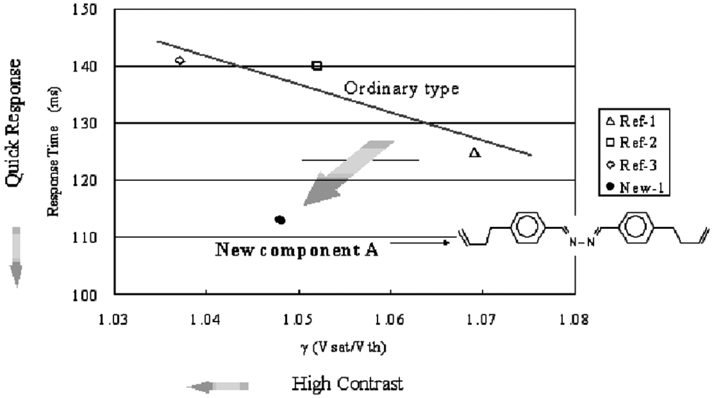


FIGURE 2 Improvement of trade-off relationship between response and contrast by dibutenylazine.

STN panels were replaced by TFT now, the liquid crystalline azine is used as an important component of the STN liquid crystals for a cellular phone, and obtains high evaluation being called golden liquid crystal in Taiwan and China.

4. LIQUID CRYSTALS FOR ACTIVE MATRIX LCD

Fluorinated Liquid Crystals of Fused Ring System

There were a few variations of the characteristics for the conventional TFT liquid crystals with the fluorinated benzene ring. Author *et al.* developed [9] the liquid crystalline decahydronaphthalene ***18***, the 1-fluoronaphthalene 19 and the tetrahydronaphthalene ***20***, paying an attention to the liquid crystals of fused ring systems, and achieved the industrialization by the establishment of production process for the stereoselective catalytic reduction from the naphthalene to the trans-decahydoronaphthalene, the selective fluorination to the 1-position of the naphthalene and regioselective catalytic reduction from the naphthalene to the tetrahydronaphthalene. The decahydronaphthalene ***18*** has 0.059 of small Δn and 5.4 of $\Delta\varepsilon$. The 1-fluoronaphthalene ***19*** has 0.172 of large Δn and 23.6 of large $\Delta\varepsilon$. The tetrahydronaphthalene ***20*** has 0.084 of Δn and 27.9 of extremely large $\Delta\varepsilon$ as a fluorinated liquid crystal component.

It is a problem to prepare a liquid crystal having simultaneously large $\Delta\varepsilon$ to be driven by low voltage and 0.06–0.07 of small Δn for reflective or transflective LCD. In order to meet the requirement for quick response, the cell thickness of TN LCD is getting thinner

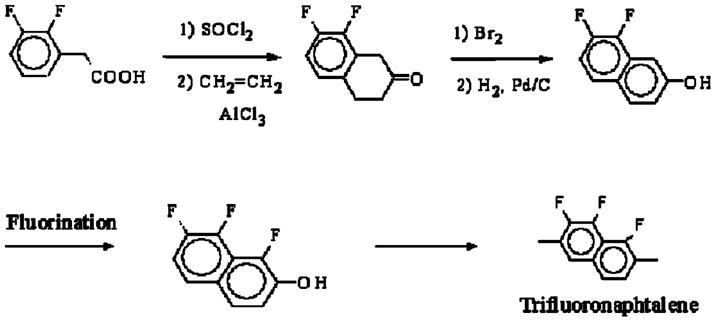


FIGURE 3 Synthetic route of 1,7,8-trifluoronaphthalene.

gradually from about 5 μm to 3–4 μm. With the decrease of cell thickness, the requirement for Δn is changing from 0.09 to 0.12–0.14. Furthermore, liquid crystals with 0.16–0.20 of large Δn are also required for OCB (optically compensated bend) LCD. The liquid crystals of fused ring systems can meet the demand of the variety of Δn by using less than 0.06 of the decahydronaphthalene, 0.08–0.09 of the tetrahydronaphthalene and 0.17–0.20 of the naphthalene.

A liquid crystal compound with large Δε enables low driving voltage or enables low viscosity because large quantity of non-polar components of low viscosity can be used to meet the required Δε. In the case of liquid crystal component for AM LCD, Δε can be increased by the link of benzene rings with fluoro or trifluoromethoxy group. However, it often

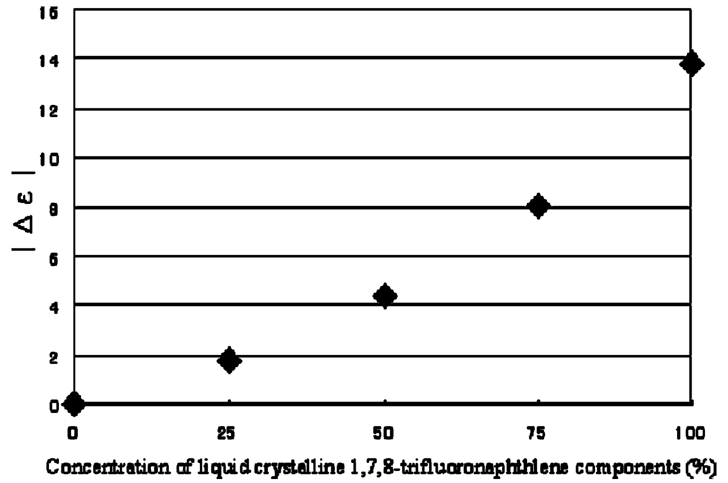
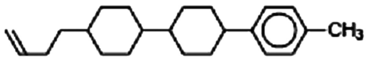


FIGURE 4 Dielectric anisotropy of 1,7,8-trifluoronaphthalene.



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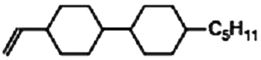

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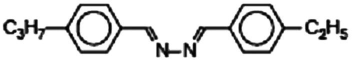

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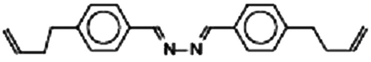

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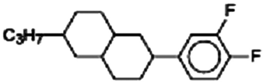

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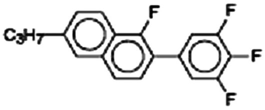

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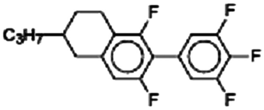

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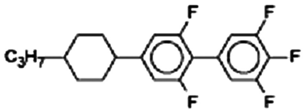

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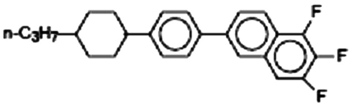

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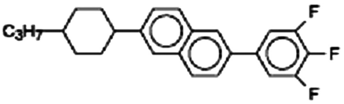

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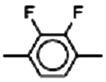

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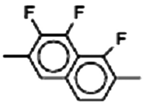

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happens that the co-solubility becomes extremely bad with the increase of the fluoro groups. The liquid crystal ***21*** having five fluoro groups in the biphenyl rings shows bad solubility in a host LC, and cannot be used actually because even 5% of the addition causes the crystallization.

To the contrary, the tetrahydronaphthalene **20** with five fluoro groups can be solved 30% in a host LC without crystallization.

The N-I transition temperatures of the liquid crystals of fused ring systems are about in the middle value of the cyclohexane ring system and the bicyclohexane ring system, and the viscosities are also in the middle. Therefore, the use together with non-polar liquid crystal components with low viscosity is requisite for quick response. The liquid crystalline naphthalene **22** with fluorinated naphthalene ring as a terminal was developed [10] in order to improve the viscosity of the naphthalene **23**. Comparing the physical properties of the two liquid crystalline naphthalenes, the terminal naphthalene **22** has 186 degree C and the naphthalene **23** has 154 degree C of N-I transition temperature, 0.214 and 0.205 of Δn, 15.0 and 12.8 of $\Delta\varepsilon$, and 28.3 mPa.s and 33.8 mPa.s of viscosity at 20 degree C being mixed 20 wt% in a host LC, respectively. The terminal naphthalene has higher N-I transition temperature, larger Δn and $\Delta\varepsilon$, and has remarkably lower viscosity.

Liquid Crystalline 1,7,8-Trifluoronaphthalene

In the case of VA mode, the liquid crystal should be n type having negative $\Delta\varepsilon$. In order to obtain negative $\Delta\varepsilon$, it is necessary to introduce fluoro groups so that an electric dipole moment in perpendicular to a liquid crystal molecule axis increases. The current n type liquid crystal has 2,3-difluorobenzene ring **24** with two lateral fluoro groups in a benzene ring, and a limit for $\Delta\varepsilon$ is about -7 or -8 as the absolute value is not increased by the link of the difluorobenzene rings. A naphthalene ring enables the increase of absolute value of $\Delta\varepsilon$, being able to introduce three lateral fluoro groups in a same plane. We succeeded in the development of a new series of n type liquid crystal components having 1,7,8-trifluoronaphthalene such as **25** by the synthetic route in Figure 3 and achieved the industrialization by the establishment of production procedures. As the liquid crystal component with -14 of $\Delta\varepsilon$ is found as shown in Figure 4, the liquid crystalline trifluoronaphthalene is expected to contribute to the performance improvement of VA LCD.

REFERENCES

[1] Sasaki, M., Takeuchi, K., Sato, H., & Takatsu, H. (1984). *Mol. Cryst. Liq. Cryst.*, *109*, 169.

[2] Sasaki, M., Takatsu, H., & Sato, H. (1984). *Japanese Patent Application*, 1984–80651.

[3] McDonnell, D. G., Raynes, E. P., & Smith, R. A. (1989). *Liq. Cryst.*, *6*, 515.

[4] Malthete, J., Leclercq, M., Dvolaitzky, M., Gabard, J., Billard, J., Pontikis, V., & Jacques, J. (1973). *Mol. Cryst. Liq. Cryst.*, *23*, 233.

[5] Ohnishi, H., Takatsu, H., Takeuchi, K., Moia, F., & Schadt, M. (1992). *SID 92 Digest*, 17.

[6] Buchecker, R. & Schadt, M. (1987). *Mol. Cryst. Liq. Cryst.*, *149*, 359.

[7] Mailer, H. & Laskos, S. (1980). *US Patent*, 4196975.

[8] Negishi, M., Ogawa, S., Osawa, M., Takeuchi, K., Takehara, S., & Takatsu, H. (1998). *Japanese Liq. Cryst. Soc. Conf.*, *3B01*, 418; Negishi, M., Ogawa, S., Osawa, M., Takeuchi, K., Takehara, S., Umezu, Y., Kawakami, S., & Takatsu, H. (1999). *DIC Technical Review*, *5*, 17.

[9] Takatsu, H., Takehara, S., Takeuchi, K., & Iwashita, Y. (2001). *Proc. SPIE*, *4463*, 93; Iwashita, Y., Kaneoya, M., Takeuchi, K., Kusumoto, T., Takehara, S., & Takatsu, H. (2001). *SID 01 Digest*, 959.

[10] Umezu, Y., Iwashita, Y., Kawakami, S., Takeuchi, K., Kusumoto, T., Tani, Y., Kanematsu, T., & Takatsu, H. (2003). *SID 03 Digest*, 1051.