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New low viscosity liquid crystal compounds containing the 2,3,4-trifluorophenyl moiety for active matrix displays

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The synthetic route and physical properties for new three-ring derivatives, *trans*-4-n-alkyl-4′-(2,3,4-trifluorophenyl)bicyclohexanes (nCCHB3F) with alkyl chain length n from 2 to 5 are presented. They exhibit broad range nematic phases exceeding 40 K, and low viscosity with a low activation enthalpy; they also show low dielectric anisotropies and high birefringence. Their dielectric properties are compared with those of their three-ring homologues with a lateral $^{-}$NCS group. The Maier–Meier theory is used to evaluate the temperature dependence of the value of 'dielectric anisotropy divided by order parameter ($\Delta\varepsilon/S$)'. The temperature dependence of $\Delta\varepsilon/S$ in several phenylbicyclohexane homologues is explained. Furthermore, the viscosity of nematic liquid crystal mixtures containing these materials is significantly reduced. These mixtures are suitable for the improvement of the switching time of liquid crystal displays using TFT Twisted Nematic (TN) modes.

1. Introduction

Liquid crystal displays (LCDs) have been well accepted as flat panel displays, for example, for notebooks, desktop monitors, television screens, cellular phones and personal digital assistants (PDAs). Cathode ray tubes (CRTs) are the dominant technology of monitors; however, advanced new LCD technologies such as the twisted nematic (TN) mode with compensation films, in-plane switching (IPS) mode and vertically aligned (VA) modes, have recently been introduced and the optical performance of these LCD monitors has already achieved a level comparable with that of CRTs for still pictures. But the performance is not yet adequate for full moving pictures. Therefore, the switching speed of these displays has been significantly improved and further improvement of switching speed is one of the most challenging tasks.

The switching speed of LCDs is a relatively complicated function of driving voltages, optical anisotropy, elastic constants, dielectric anisotropies and rotational viscosity [1, 2]. These parameters are related to the optical retardation, the threshold voltages and/or the saturation voltages. Therefore, the only remaining free parameter for optimization of the switching time of LC materials is the rotational viscosity. But generally, if the viscosity of an LC material is lower, its T_{NI} temperature tends to be lower.

In the following, advanced technologies are introduced for the design of LC materials featuring extremely low viscosity with, at the same time, high clearing points, T_{NI}. Furthermore, another class of novel LC substances with the feature of high protection against ionic contamination is introduced; this is applicable to many kinds of AM-LCD.

In this paper, we report the synthesis of new 2,3,4-trifluorinated liquid crystals with low viscosity and high T_{NI}, and characterization of their physical properties. Their physical constants are discussed in relation to molecular parameters calculated using molecular orbital theory, and practical LC mixtures with the 2,3,4-trifluorinated liquid crystals are designed. We have succeeded in identifying LC single materials that improved the switching speed by significant reduction of the viscosity of their LC mixtures.

2. Synthesis

All air-sensitive manipulations were carried out under an atmosphere of dry nitrogen. Stirring was achieved by Teflon-coated magnetic stirring bars. Cold temperature baths (− 78°C) used acetone/dry ice mixtures. Anhydrous diethyl ether was obtained by distillation over sodium and benzophenone; ethanol for recrystallizations was dried over Linde 3 Å molecular sieves. All reaction and extraction solvents were distilled prior to use. Practical grade 1,2,3-trifluorobenzene (98%) was purchased from Aldrich Chemical Company and was not purified before use. Hexane solutions of n-butyllithium were purchased from Aldrich and were standardized by titration against diphenylacetic acid. All other reagents were commercially available and were used without further purification.

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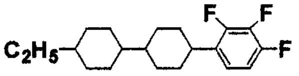
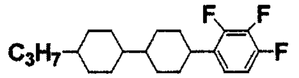
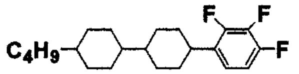
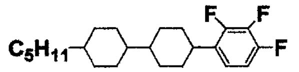
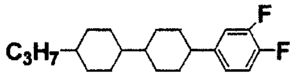
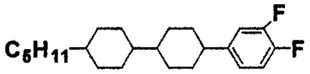
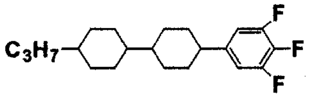
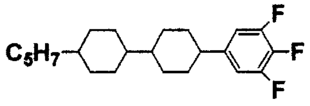
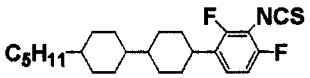
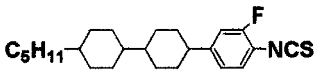
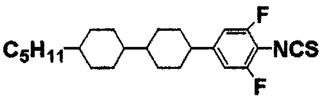
The ^{n}CCHB3F compounds listed in table 1 were prepared by the synthetic route shown in figure 1, employing previously reported synthetic procedures [3, 4]. The introduction of the core structure (phenylbicyclohexyl group) was achieved by a carbon–carbon coupling reaction from the *trans*-alkylbicyclohexanone and the organolithium reagent generated from the corresponding halide derivatives, followed by dehydration and reduction reactions [5–6]. The organolithium exchange couplings of the *trans*-alkylbicyclohexanones with 2,3,4-trifluorobromobenzene were achieved with an overall yield of 90%. As described in figure 1, dehydrogenation of the resulting bicyclohexanol derivative was conveniently achieved with *P*-toluenesulphonic acid-1-hydrate under reflux. The yield from this reaction was 93%. The hydrogenation of the bicyclohexene derivative proceeds at room temperature under H_2 pressure of 4 kg cm^{-2}. Catalytic hydrogenation gave a mixture of *cis* and *trans* compounds. Pure *trans* compounds were obtained after a final stage of successive recrystallization.

Table 1. Chemical structures and abbreviations for the phenylbicyclohexane liquid crystals.

No.	Structure	Abbreviation
1a		2CCHB3F
1b		3CCHB3F
1c		4CCHB3F
1d		5CCHB3F
2a		3CCHBFF
2b		5CCHBFF
3a		3CCHBFFF
3b		5CCHBFFF
4a		5CCHBSFF
5a		5CCHBFS
6a		5CCHBFSF

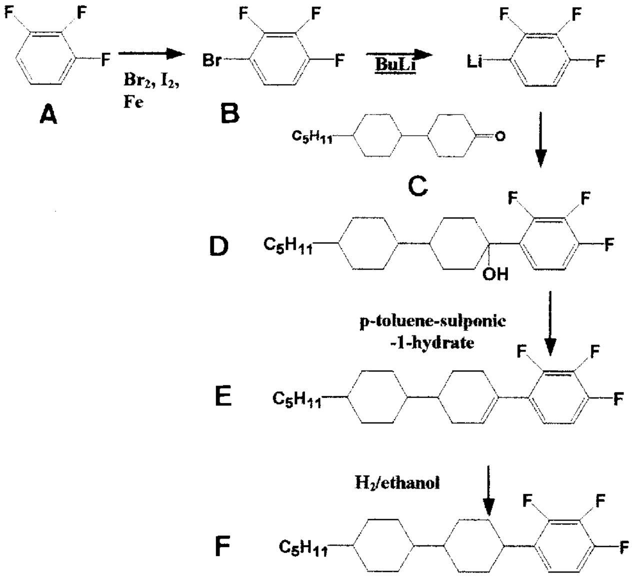


Figure 1. Synthetic route for 2,3,4-trifluorinated phenyl liquid crystals.

3. Characterization

Proton magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker Varian Germini-200 spectrometer at 400 MHz. Unless otherwise specified, samples were dissolved in deuteriochloroform and chemical shifts were determined relative to internal tetramethylsilane. The signals are reported (see § 5) as chemical shifts (δ) in parts per million, followed by multiplicity and relative peak integration in parentheses; s = singlet, d = doublet, t = triplet, m = multiplet. Low and high resolution electron impact mass spectral analyses were performed on a Hewlett Packard 5972 MSD mass spectrometer. The mass to charge ratio (m/z) of the molecular ions (M+) and the base peaks are reported with their relative intensities. The measured exact masses are also compared with calculated values. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} precoated aluminum sheets. Visualization was achieved by irradiation with UV light. Column chromatography was carried out on Merck flash silica, 230–400 mesh, unless otherwise specified. Gas chromatographic (GC) analysis was performed on a Hewlett-Packard 6890 chromatograph with a 30 m column packed with 100% methylsilicon gum.

The transition temperatures were measured and phase identifications made by observing the materials under a polarizing microscope. A mettler FP 82 heating stage, with a temperature accuracy of ± 0.1°C, and an Olympus polarizing microscope were used. The transition enthalpies were determined by differential scanning calorimetry using a Perkin-Elmer DSC-7 calorimeter calibrated against indium standard. Differential thermal analysis was carried out at a rate of 5°C min^{-1}.

An Abbè refractometer (Bellingham and Stanley) was used to measure the refractive indices of homeotropically aligned samples from the critical angle of reflection. A sodium lamp and filter were used to provide the light source at 598 nm. The birefringence values for all of the mixtures for each compound were then extrapolated to give an estimate of the birefringence of the pure compound. The bulk viscosity of mixtures was determined by the capillary method in the temperature range from 20 to 60°C using an Ubberrod viscometer (100E196) from Cannon Instrument Co.

Dielectric anisotropy, $\Delta\varepsilon$, was determined by a capacitive method at a frequency of 1 kHz—$\varepsilon_{\parallel}$ with homeotropically and $\varepsilon_{\perp}$ with planar oriented samples. The measurements were carried out at a fixed temperature $T = 293$ K on 15 wt % solutions of the compound in a standard host mixture (Chisso ZKC5071LA) and extrapolated to 100% concentrations, taking into account the variation of the physical parameters of the mixture under investigation. The molecular geometry was calculated using the semi-empirical quantum chemical AM1 method (MOPAC 5.0 package) [7].

4. Results and discussion

The chemical structures, abbreviations and compound numbers of the synthesized 2,3,4-trifluorinated liquid crystals and their phenylbicyclohexane homologues (for comparison) are listed in table 1. In table 2 phase transition and viscosity data are given. In table 3, calculated molecular parameters such as the molecular dipole moment μ, anisotropy of molecular polarizability $\Delta\alpha$, mean polarizability α and the angle β between the molecular dipole moment and the long molecular axis of the molecule, and selected physical properties are summarized. The 2,3,4-trifluorinated phenyl compounds, **1a**–**1d**, exhibit low dielectric anisotropies $\Delta\varepsilon$ (1.7–2.0), high clearing points T_{NI} ($\sim$120°C) and broad nematic phase ranges ($\sim$60°C), which is particularly important for their use in liquid crystal mixtures with long term stability at low temperatures.

The three-ring systems of six molecular types showed enantiotropic nematic phases except for compound **4a** (5CCHBSFF) (see table 2). The phase transition temperatures were strongly influenced by the number and the position of the substituted fluorine atoms. In the trifluorinated phenyl homologues, introducing fluorine atoms into the 3,4,5 positions of the benzene ring (**3a**, **3b**) diminished the T_{NI} and the nematic ranges decreased and shifted to a lower temperature area; but introducing fluorine atom(s) into the 2,3,4 positions increased the T_{CN} only a little in comparison with the 3,4-difluorinated phenyl compounds **2a** and **2b**.

The length to breadth ratio (l/d) of molecular structures also influenced the phase transition temperatures, as shown in table 2. For the phenylbicyclohexane homologues having a fluorinated or isothiocyanated phenyl ring, the order of the values of the ratio l/d was

Table 2. Phase transition temperatures, transition enthalpies and kinematic viscosities of the phenylbicyclohexane homologues.

Compound	l/d	T_{CN}[a]/°C	T_{NI}[b]/°C	ΔT[c]/°C	ΔH_{CN}[d]/kJ mol^{-1}	ΔH_{NI}[e]/kJ mol^{-1}	$\Delta S_{\mathrm{NI}}/R$[f]/kJ mol^{-1}	$\eta/\mathrm{mm}^2\,\mathrm{s}^{-1}$
2CCHB3F	15.0/4.6	48.6	80.4	31.8	21.95	0.28	0.096	2.2[g]
3CCHB3F	16.5/4.6	37.4	116.8	79.4	24.41	0.45	0.140	2.9[g]
4CCHB3F	17.2/4.6	41.6	118.3	76.7	25.05	0.31	0.096	3.2[g]
5CCHB3F	18.7/4.6	41.7	122.5	80.8	35.79	0.49	0.149	4.5[g]
3CCHBFF	16.6/4.6	44.7	118.5	73.8	27.54	0.31	0.100	20.7[h]
5CCHBFF	18.4/4.6	54.1	125.0	70.9	22.18	0.39	0.126	28.7[h]
3CCHBFFF	17.0/4.8	34.4	95.2	60.8	21.35	0.53	0.162	22.5[h]
5CCHBFFF	18.8/4.8	36	100.0	64	27.17	0.53	0.161	29.4[h]
5CCHBSFF	18.9/5.0	58.9	(52.4)	—	25.70	0.20	0.107	6.5[g]
5CCHBFS[i]	20.5/4.6	56.9	226.8	169.9	31.0	1.00	0.241	31.8
5CCHBFSF[i]	20.6/4.8	62.9	202.4	139.5	29.7	0.87	0.220	30.8

[a] Crystal–nematic transition temperature.

[b] Nematic–isotropic transition temperature. Here, a monotropic transition temperature is denoted by () brackets around the recorded temperature.

[c] $\Delta T = T_{\mathrm{CN}} - T_{\mathrm{NI}} =$ mesorange; a negative sign indicates monotropy.

[d] Enthalpy at T_{CN}.

[e] Enthalpy at T_{NI}.

[f] Entropy divided by gas constant at T_{NI}.

[g] Extrapolated values from 15 wt % solution in ZKC5071LA.

[h] Extrapolated values from 15 wt % solutions in 4-(4-*trans*-pentylcyclohexyl)-1-(3,4-difluorophenyl)cyclohex-1-ene.

[i] For these data see reference [14].

Table 3. Molecular parameters from molecular modelling calculations, and measured physical properties of phenylbicyclohexane homologues.

Compound	α[b]/cm^3	$\Delta\alpha$[c]/cm^3	$\Delta\alpha/M$/cm^3	μ/D	β[d]/°	$\varepsilon_\parallel$	$\varepsilon_\perp$	$\Delta\varepsilon$	Δn
2CCHBF	25.4	12.4	0.0382	3.5	36.3	7.9	5.9	2.0	0.077
3CCHBF	26.6	12.7	0.0375	3.5	36.3	7.6	5.6	2.0	0.077
4CCHBF	27.8	13.3	0.0377	3.5	36.2	7.5	5.8	1.7	0.078
5CCHBF	29.0	13.5	0.0369	3.5	36.2	7.5	5.7	1.8	0.079
3CCHBFF	26.0	12.7	0.0396	3.2	11.4	9.5	3.1	6.4	0.079
5CCHBFF	28.4	13.3	0.0382	3.2	11.2	9.3	3.3	6.4	0.079
3CCHBFFF	26.3	12.5	0.0369	3.8	10.6	13.6	3.9	9.7	0.075
5CCHBFFF	28.7	13.2	0.0360	3.8	10.5	13.4	3.9	9.5	0.078
5CCHBSFF	37.3	32.9	0.0811	3.2	42.8	7.5	4.1	3.5	0.082
5CCHBFS[a]	37.1	27.8	0.0717	3.6	3.6	18.4	2.1	16.3	0.240
5CCHBFSF[a]	37.6	29.8	0.0735	3.7	3.6	20.4	2.8	17.6	0.231

[a] These data are from reference [14].
[b] Mean molecular polarizability.
[c] Polarizability anisotropy calculated by $\Delta\alpha = \alpha_{zz} - 1/2(\alpha_{xx} + \alpha_{yy})$.
[d] Angle between the molecular long axis and the molecular dipole moment.

5CCHBSFF (18.9/5.0) > 5CCHBFF (18.4/4.6) ≒ 5CCHB3F (18.7/4.6) > 5CCHBFFF (18.8/4.8) > 5CCHBFSF 920.6/4.8) > 5CCHBFS (20.5/4.6). The 2,4-difluoro-3-isothiocyanated phenyl compound **4a**, with low l/d, showed a very low T_{NI} of 52.4°C. This means that the size of a lateral substitution group plays a very important role in lowering the melting point. For example, the T_{NI} of compound **1d** is 122.5°C, while the T_{NI} of compound **4a** is as low as 70°C. It can be thought that the lateral isothiocyanato group increases the width of the molecule and so decreases the packing density of the LC molecules. As a result, the temperature required to melt the crystals and to clear the LC phase are much lower.

The corresponding enthalpy and entropy ($\Delta S_{\mathrm{NI}}/R$) values for the nematic–isotropic transition of synthesized compounds **1a**–**6a** are shown in table 2. Generally the $\Delta S_{\mathrm{NI}}/R$ value is 0.09 to 0.22 for low molar mass liquid crystals. The $\Delta S_{\mathrm{NI}}/R$ value of compound **6a** (5CCHBFSF), with the isothiocyanato group as terminal substituent in the benzene ring, is around twice that for compound **4a** (5CCHBSFF), with isothiocyanato as a lateral group. Introducing a fluorine atom as the lateral group in the benzene ring also decreases $\Delta S_{\mathrm{NI}}/R$ values. It is well known that this fluorine substitution affords weaker conformational freedom that could allow the rod-like moieties to align less efficiently with respect to the director, and so pack less efficiently in the mesophase. Therefore, the introduction of a lateral isothiocyanato group causes diminution of molecular ordering in the mesophase, leading to low thermal stability and a monotropic mesophase.

As can be seen in table 3, the dielectric anisotropy values of the polar group-substituted phenylbicyclohexane homologues were in the order 3,(5)-(di)fluoro-4-isothiocyanato > 3,4,5-trifluo > 3,4-difluoro > 2,4-difluoro-4-isothiocyanato > 2,3,4-trifluorinated phenyl compounds. The 3,4,5-trifluorinated phenyl compounds **3a**,**b**, showed larger $\Delta\varepsilon$ (up to 9.7 in table 3) than the 3,4-difluorinated phenyl compounds **2a**,**b**. This is because the dipole moment of the fluorine atom substituted into the benzene ring enhanced the total molecular dipole moment, as shown in the calculated result (see table 3). We also find that the 2,3,4-trifluorinated phenyl compounds **1a**–**d** show a considerably smaller $\Delta\varepsilon$ than the other fluorinated phenyl derivatives, **2a**,**b** and **3a**,**b**, in spite of similar dipole moment μ and anisotropy of molecular polarizability $\Delta\alpha$. This $\Delta\varepsilon$ difference in fluorinated compounds can be explained by the difference in the angle β between the molecular dipole moment and the long molecular axis. In the Maier–Meier formula for dielectric anisotropy, if the angle β is increased to 55°, $\Delta\varepsilon$ is negative see equation (1). That is to say, the smaller β, the greater $\Delta\varepsilon$.

Table 3 also shows that although the angle β for the 2,4-difluoro-3-isothiocyanatophenyl compound **4a** is larger than that for the 2,3,4-trifluorophenyl compounds **1a**–**1d**, the order of $\Delta\varepsilon$ values is 2,4-difluoro-3-isothiocyanato > 2,3,4-trifluorophenyl compound, because compound **4a** has a larger $\Delta\alpha$ (32.9) than compounds **1a**–**d**.

Figures 2(*a*) and 2(*b*), respectively, show the temperature and frequency dependence of the static permittivity of 2,3,4-substituted compounds. In the nematic phase, $\varepsilon_\parallel$ and $\varepsilon_\perp$ of 2,3,4-trifluorinated compounds increases as the reduced temperature, T/T_{NI}, decreases, figure 2(*a*); the static permittivity of all the 2,3,4-substituted phenyl compounds, **1a**–**1d** and **4a** in the isotropic phase, decreased with increase of reduced temperature. Also the dielectric anisotropy values $\Delta\varepsilon$ of 2,3,4-substituted

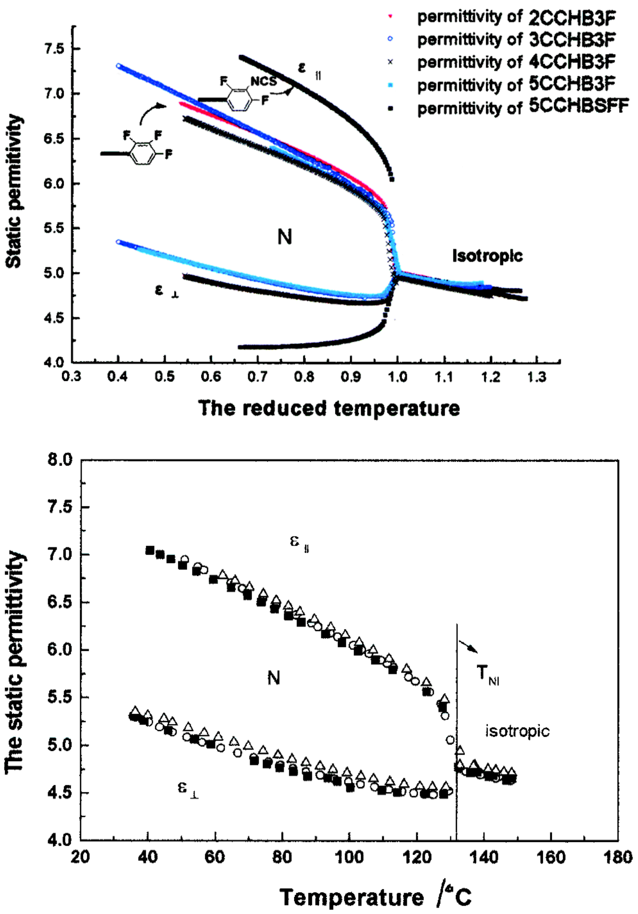


Figure 2. (*a*) The static permittivity of 2,3,4-trifluorinated and 2,3,4-fluoroisothiocyanated compounds vs. T_d (reduced temperature). (*b*) The static permittivity of 4-(4-trans-(4-trans-pentylcyclohexyl)cyclohexyl)-2,3,4-trifluorinated-phenyl, at frequency 1 (○), 10 (■), and 100 kHz (△).

phenyl compounds **1a**–**d** and **4a** increase as the reduced temperature is decreased. As can be seen in figure 2 (*b*), the nematic phase static permittivity, $\varepsilon_\perp$ and $\varepsilon_\parallel$ is independent of frequency in the range between 1–100 kHz.

Fluorinated liquid crystals are known for their modest dielectric anisotropy, larger dipole moment, high stability, high voltage holding ratio, high specific resistance, low threshold voltage and low viscosity. In order to improve these characteristics, an evaluation of the physical constants, especially the order parameter S, is necessary. Recently, Onnagawa *et al.* [8] estimated the temperature dependence of dielectric anisotropy $\Delta\varepsilon$ using the Maier–Meier theory and semiempirical molecular orbital calculation. They have already studied the $\Delta\varepsilon$ of phenylbicyclohexane (PBC) compounds with one or two fluorine substituents in the benzene ring and also reported special fluorinated liquid crystal materials in which the dielectric anisotropy was proportional to the square of the order parameter [9, 10].

We have now studied the temperature dependence of the ratio 'dielectric anisotropy divided by order parameter ($\Delta\varepsilon/S$)'. The dielectric anisotropy, $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$, of the molecules was estimated according to the Maier–Meier theory [11], as an extension to nematic liquid crystals of the Onsager theory [12] of the dielectric polarization of isotropic dipolar fluids, taking into account the anisotropy of the molecular polarizability, the orientation of the permanent dipole moment in the molecular frame and the long range orientational order:

$$\Delta\varepsilon = \frac{NFh}{\varepsilon_0}\left\{\Delta\alpha - \frac{F\mu^2}{2k_B T}(1 - 3\cos^2\beta)\right\}S \qquad (1)$$

Here $\varepsilon_0 = 8.85 \times 10^{-12}$ F m^{-1}, N is the number of molecules per unit volume, k_B is the Boltzmann constant, β is the angle between the molecular dipole moment and the long molecular axis, and h and F are the Onsager local field factors:

$$N = \frac{N_A}{V_m}, \quad h = \frac{3\varepsilon}{2\varepsilon + 1}, \quad F = \frac{1}{1 - \alpha f}, \quad f = \frac{2(\varepsilon - 1)}{2\varepsilon + 1}\frac{N}{3\varepsilon_0}. \qquad (2)$$

N_A is the Avogadro constant, $V_m = \rho/M$ is the molar volume, and ρ is the density assumed as a value of 1000 kg m^{-3} and M is the molecular weight. α and ε are the mean values of the polarizability and the permittivity, respectively, and $\Delta\alpha$ was calculated using $\Delta\alpha = \alpha_{zz} - (\alpha_{xx} + \alpha_{yy})/2$ where zz denotes the axis with the smallest moment of inertia.

According to the above Maier–Meier equations [11], the temperature dependence of the dielectric anisotropy divided by the order parameter ($\Delta\varepsilon/S$) can be given as

$$\Delta\varepsilon/S = \frac{NhF}{\varepsilon_0}\left[\Delta\alpha - F\mu^2\frac{(1 - 3\cos^2\beta)}{2k_B T}\right]. \qquad (3)$$

From the Maier–Meier equations, $\Delta\varepsilon$ is a physical property which depends on the molecular structures of liquid crystals, and the sign of $\Delta\varepsilon$ is related to the directions of β and $\Delta\alpha$. Initially, for calculating the dielectric anisotropy, we have to determine the initial value of ε_{int}. According to the Lorentz–Lorenz formula [13], ε_{int} is given by

$$\varepsilon_{int} = \frac{3\varepsilon_0 + 2\alpha_{av}N}{3\varepsilon_0 - \alpha_{av}N} \qquad (4)$$

Substituting these molecular parameters into the Maier–Meier equations, the temperature dependence of $\Delta\varepsilon/S$ for the various phenylbicyclohexane homologues was calculated (see figure 3). In the Maier–Meier equation (1), temperature dependence is shown only by the second term. In a previous paper [10] special fluorinated liquid crystal materials were reported, with a large dipole moment, in which the dielectric anisotropy was

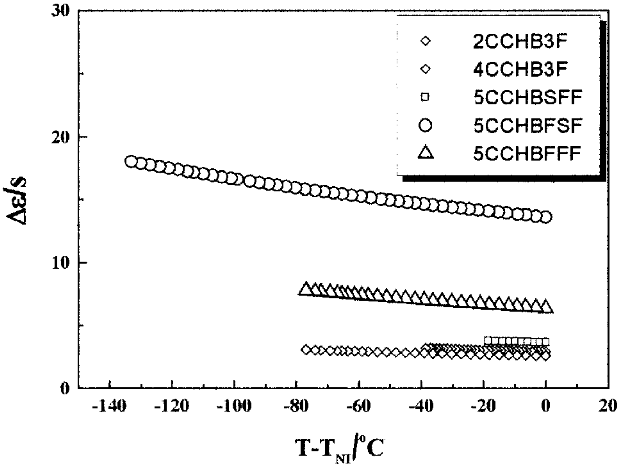


Figure 3. Calculated temperature dependence of $\Delta\varepsilon/S$ by substitution of the molecular parameters into the Maier–Meier equations.

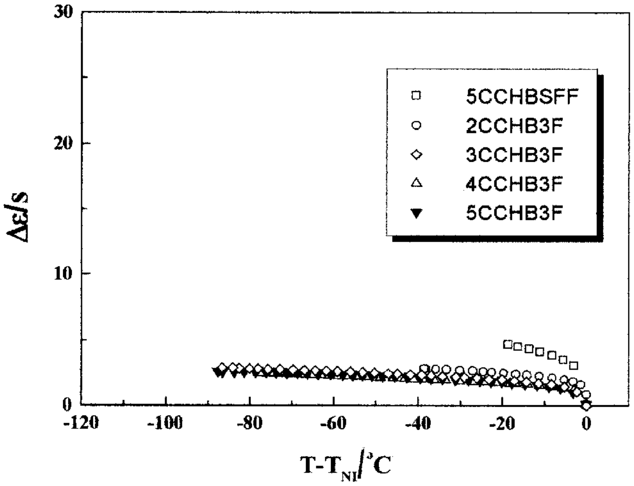


Figure 4. Experimental results of the temperature dependence of $\Delta\varepsilon/S$.

proportional to the square of the order parameter. Therefore, the $\Delta\varepsilon/S$ shows a temperature dependence for special fluorinated liquid crystal materials. For the 2,3,4-trifluorinated phenyl liquid crystal derivatives, the $\Delta\varepsilon/S$ was nearly constant and showed no temperature dependence (see figure 3). The reason is that, although the 2,3,4-trifluorinated phenyl derivatives have a large dipole moment, they have a comparatively large β. This result also appeared in the 2,4-difluoro-3-isothiocyanated phenyl compound **4a** (5CCHBSFF), with a large dipole moment and large β. In the 3,5-difluoro-4-isothiocyanato and 3,4,5-trifluorinated phenyl compounds, **3b** and **6a**, although they have large dipole moments similar to the 2,4-difluoro-3-isothiocyanated phenyl compound **4a**, their $\Delta\varepsilon/S$ values were not constant, and the slope of temperature dependence of $\Delta\varepsilon/S$ was inversely proportional to β. Comparing equation (3) with the related molecular parameter listed in table 3, it can be seen that in the materials with large dipole moment, the angle β affects the temperature dependence of $\Delta\varepsilon/S$. Figure 4 shows the experimental results for the temperature dependence of $\Delta\varepsilon/S$ for 2,3,4-trisubstituted phenyl derivatives. The experimental results obtained were in good agreement with the calculated values.

The optical anisotropies of the phenyl bicyclohexane homologous **1a**–**6a** are listed in table 3. It can be seen that introducing a isothiocyanato group leads to larger Δn. The fluorinated phenyl compounds **1a**–**d**, **2a**,**b** and **3a**,**b**, show Δn values in the range of 0.075–0.079; the Δn value for compounds **5a** and **6a**, with the isothiocyanato group in the terminal position of the benzene ring, is 0.240 and 0.23, respectively—a significantly larger value. The polar isothiocyanato group enhances the mean molecular polarizability of the whole molecule, which is related to optical anisotropy by the Vuks relation [14]. But, the Δn of the 2,4-difluoro-3-isothiocyanated phenyl compound **4a**, with the lateral isothiocyanato group, is 0.082, which is only slightly larger than for the other fluorinated phenyl compounds. Thus although the lateral isothiocyanato group enhanced the mean molecular polarizability of the whole molecule, optical anisotropy was lowered and thermal stability fell because of a reduction in order parameter S.

Of particular significance are the low kinematic viscosities η of the 2,3,4-trifluorinated compounds **1a**–**d**, which are compared with those of other fluorinated phenyl homologues in table 2. The θ values of the 2,3,4-trifluorinated phenyl compounds are drastically reduced by up to 85% in comparison with 3,4,(5)-trifluorinated phenyl compounds **2a**,**b** and **3a**,**b** with the same alkyl chain length.

From figure 5 it is seen that the kinematic viscosity of all phenylbicyclohexane homologue is proportional to their dielectric anisotropy $\Delta\varepsilon$. By introducing the isothiocyanato group as a lateral substituent into the phenyl ring, the viscosity increased little in comparison with compound **1d** with a fluoro-substituent in the same position. As shown in figure 5, the η value of the compound **4a** is so small that it is in the same range as those of **1a**–**d**, but has the disadvantage of much lower T_{NI}. Figure 6 shows the temperature dependence of the viscosity of mixtures containing 15 wt% of the 2,3,4-trifluoro and 2,4-difluoro-3-isothiocyanated phenyl compound in a host mixture (ZKC-5071LA from Chisso Petrochemical Corporation). In figure 6, the η values of nematic mixtures are proportional to the carbon number of the terminal alkyl chain of the added compounds, and are drastically reduced by increased temperature.

Generally the synthesized 2,3,4-trifluorinated phenyl compounds **1a**–**d** show high T_{NI} temperatures, low

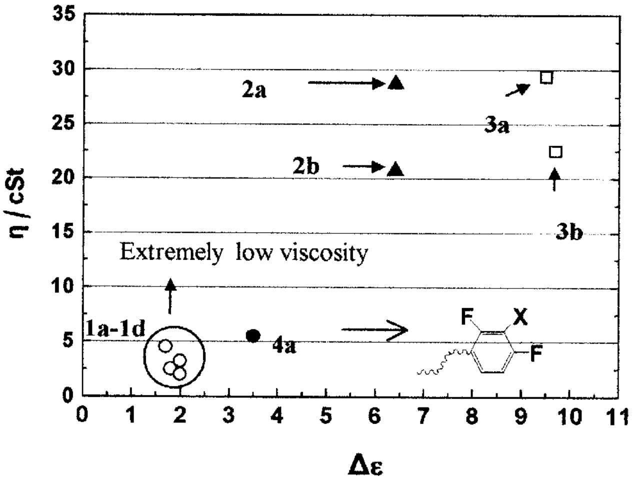


Figure 5. Comparison of the extrapolated viscosity and the dielectric anisotropy of the new compounds **1a**–**1d** and **4a** (○) with those of **2a**,**b** (▲) and **3a**,**b** (□).

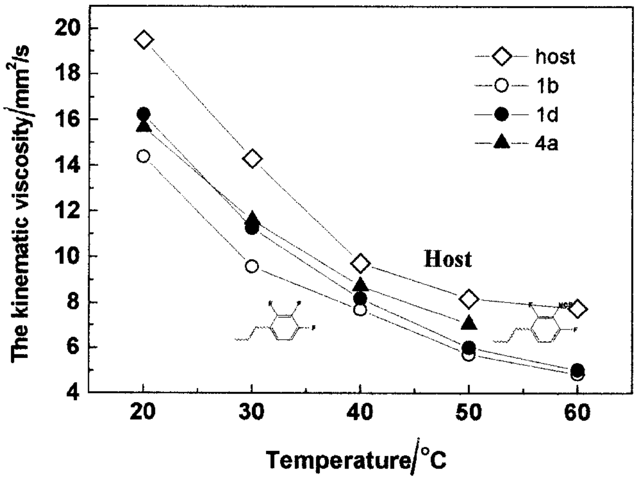


Figure 6. Temperature vs. flow viscosity of the mixtures containing 15 wt % of 2,3,4-trifluoro (**1a**: ○ and **1d**: ●) and 2,4-difluoro-3-isothiocyanated compound (**4a**: ▲), respectively, in host mixture.

viscosity and large $\Delta\varepsilon$. In order to investigate how the liquid crystal mixture for TFT-LCD applications can be improved, particularly in terms of viscosity, 'ELA 18' mixture containing 10 wt % of the synthesized 2,3,4-trifluorinated phenyl compound **1d** (5CCHB3F) in a host mixture with very low flow viscosity and low dielectric anisotropy, were prepared.

In table 4, electro-optic characteristics and physical properties of the ELA mixture and host mixture are listed. The threshold voltage (V_{th}) of the mixture was slightly higher than that of the host mixture. In the TN mode, V_{th} is expressed by equation (5) [15, 16], where ε_0 represents the dielectric constant in a vacuum, and K_{11}, K_{22} and K_{33} represent elastic constant of splay, twist and bend, respectively.

$$V_{th} = \pi(K/\varepsilon_0\Delta\varepsilon)^{1/2} \tag{5}$$

$$K = K_{11} - (K_{33} - 2K_{22})/4. \tag{6}$$

The increment in V_{th} of the ELA mixture is in good agreement with equation (5), in which the value of $\Delta\varepsilon$ is inversely proportional to V_{th}. The switching times, τ_{on} and τ_{off} (if $d \times \Delta n = \text{const.}$, where d is the cell gap) also has an influence on the rotational viscosity γ_1, driving voltage V, elastic constant K, the value of $\Delta\varepsilon$, V_{th} and so on, according to equations (7) and (8) [17, 18]. As shown in table 4, the kinematic viscosity of 'ELA 18' mixture is decreased, and τ_{on} is slightly increased due to the smaller $\Delta\varepsilon$ value in comparison with the host mixture. But, the fall time τ_{off} in the ELA mixture is faster than that of the host mixture because of lower viscosity and increased V_{th}. Therefore the fast switching time of the prepared mixtures, especially ELA 18, was induced mainly by viscosity and partially by V_{th}.

$$\tau_{on} \sim \frac{\gamma_1 d^2}{\varepsilon_0\Delta\varepsilon(V^2 - V_{th}^2)} \tag{7}$$

$$\tau_{off} \sim \frac{\gamma_1 d^2}{\varepsilon_0\Delta\varepsilon V_{th}^2}. \tag{8}$$

It is well known that liquid crystal compounds for AM-LCDs must be completely stable when heated and irradiated by UV and should have high VHR to avoid decrease in contrast and image sticking. From this point of view we also characterized the new LC mixtures in respect of the temperature dependence of VHR. The voltage holding properties were measured at 60 Hz, which is a typical frame frequency of conventional addressing

Table 4. The electro-optic and physical properties of practical LC mixtures of AM-LCDs.

	T_{CN}/°C	T_{NI}/°C	η/mm^2 s^{-1} (20°C)	Δn (25°C)	$\Delta\varepsilon$ (25°C)	V_{th}^{a}/V	τ_{on}^{a,b}/ms	τ_{off}^{a,b}/ms	τ_{all}^{a,b}/ms	VHR^c (25°C)
Host	< −30	60.1	19.5	0.077	3.7	1.61	2.1	18.0	20.1	99.0
ELA18	< −30	70.2	16.3	0.077	3.6	1.82	2.4	13.0	15.4	99.1

[a] Measurement in TN cell with 4.0 μm cell gap.
[b] Measured by applying a square-wave a.c. voltage of $V_1/V_s = 5$ V/1 V at frequency 60 Hz.
[c] Measured at 60 Hz.

schemes. Figure 7 shows the VHR of new ELA mixtures compared with those of the host mixture as reference. ELA 18 mixtures containing the 2,3,4-trifluorophenyl compounds **1a–d** showed a remarkably high VHR at temperatures up to 80°C, which indicates an acceptable stability for AM-LCD applications.

Using the new 2,3,4-trifluorinated materials, a significant improvement of switching time is clearly achieved and improvements up to 25% were achieved for mixture ELA 18, with similar Δn (= 0.077) and $\Delta\varepsilon$ (= 3.6) and higher T_{NI} temperature (= 70.2°C) in comparison with the host mixture, which showed high stability and high VHR (98% at 80°C).

5. Experimental

The *trans*-4-n-alkylbicyclohexyl-2,3,4-trifluorophenyl derivatives were prepared according to the synthetic route in figure 1; representative procedures are described below for the pentyl derivative.

5.1. *2,3,4-Trifluoro-1-bromobenzene (**B**)*

1,2,3-Trifluorobenzene (**A**) (13.2 g, 0.1 mol) and iron powder (0.4 g) were heated to 65°C in 3-neck flask; bromine (5.6 ml) was then added dropwise over 1.5 h to the stirred suspension. This reaction mixture was stirred at 70°C for 1 h, poured into cold 10% aqueous NaOH and extracted with ether. The organic phase was washed with 3 × 200 ml of water and dried over $MgSO_4$. The solvent was removed under reduced pressure to yield 20 g (95%) of crude yellow product. Recrystallization from 250 ml of methanol gave 18.9 g (90%) of white crystals. ^{1}H NMR ($CDCl_3$): δ 6.9–7.1 (d, 1H) 7.1–7.3 (d, 1H). Mass data: 212(M + 2), 210(M+), 131, 95, 61, 36.

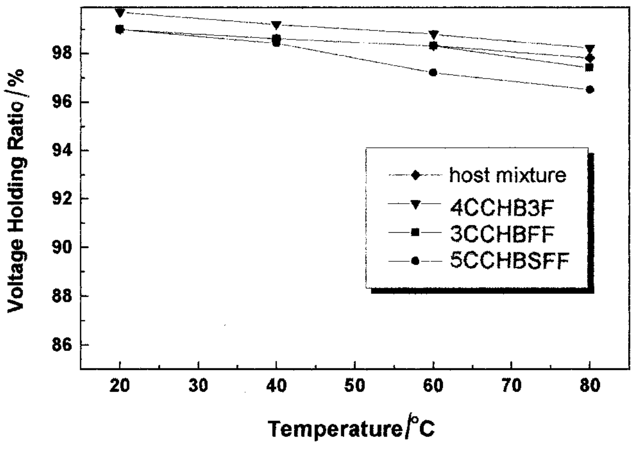


Figure 7. Temperature dependence of voltage holding ratio of the mixtures containing 15 wt% of 2,3,4-trifluoro (4CCHB3F: ▲), 3,4-difluoro (3CCHBFF: ■) and 2,4-difluoro-3-isothiocyanated phenyl compound (5CCHBSFF: ●), respectively, in host mixture.

5.2. *4-Pentyl-4′-(2,3,4-trifluorophenyl)bicyclohexane-4-ol (**D**)*

Under an atmosphere of dry N_2 gas, a solution of compound **B** (8.40 g, 0.0290 mol) in dried diethyl ether (100 ml) was cooled to −80°C using an acetone/dry ice bath. n-Butyllithium (19.7 ml, 1.6M in hexanes, 0.032 mol) diluted with hexane was carefully added dropwise at −80°C over a 20 min period to the stirred reaction mixture. Stirring was continued at −80°C for 20 min and then a solution of *trans*-pentylbicyclohexanone (**c**) (5.00 g, 0.020 mol) in ether (20 ml) was added dropwise, keeping the temperature at −78°C. The mixture was then allowed to warm to room temperature; it was acidified with a 0.1N hydrochloric acid and extracted with ether (50 ml). The organic layer was washed with H_2O (3 × 50 ml), dried, filtered, and the solvent removed in a rotary evaporator to give a crude product **D** as a yellowish solid; yield 90%. This material was used without further purification. Mass data: 382(M+), 364, 206, 174, 55.

5.3. *4-(4-Pentyl)-1-(2,3,4-trifluorophenyl)-cyclohexene (**E**)*

A mixture of the alcohol compound **D** (6.84 g, 0.0186 mol) and p-toluenesulphonic acid 1-hydrate (0.353 g, 0.00186 mol) in toluene (100 ml) was heated under reflux for 3 h until TLC analysis revealed complete reaction. The reaction mixture was extracted into toluene 2 × 200 ml, which was washed with saturated $NaHCO_3$ aqueous solution and water, and then dried ($MgSO_4$). The solvent was removed *in vacuo* and the product obtained as a brownish solid (6.41 g, 0.0175 mol); yield 94%. ^{1}H NMR ($CDCl_3$): $\delta = 0.8$–1.8 (m, 21H), 1.8–2.0 (m, 8H), 7.0–7.1 (m, 2H). Mass data: 364(M+), 179, 166, 127 (RT = 20.47).

5.4. *trans-4-n-Pentyl-4′-(2,3,4-trifluorophenyl)-bicyclohexane (**F**)*

Compound **E** (6.45 g, 0.0176 mol) was dissolved in a mixture of ethanol (100 ml) and toluene (40 ml); 10% palladium on activated charcoal (1.2 g) was then added to the reaction mixture, followed by hydrogenation at r.t., under a hydrogen pressure of 2 kg cm^{-2} for 4 h in an autoclave. The reaction was traced by gas chromatography, and stopped when the raw material was exhausted. The catalyst was filtered off from the hydrogenation product, and the solvent distilled off under reduced pressure. Isolation of *cis* and *trans* forms of the crude product was achieved by the crystallization from solution in ethanol and hexane; yield 40%. ^{1}H NMR ($CDCl_3$): $\delta = 0.7$–1.9 (m, 23H), 0.8–2.0 (m, 8H), 2.8–2.9 (t, 1H), 6.8–7.1 (m, 2H). Mass data: 366(M+), 158, 145, 97 (RT = 19.95).

6. Conclusion

Currently the most important goal for LCD manufactures is reduction in the switching time for moving picture liquid crystal displays. We have succeeded in verifying new 2,3,4-trifluorinated phenyl liquid crystals with small dielectric anisotropies, high clearing temperatures and extremely low viscosities; the flow viscosities of the nematic LC mixtures developed from these materials were significantly reduced. Numerical approaches to the physical characteristics of the 2,3,4-trifluorinated phenyl liquid crystals have also been investigated. In study of the temperature dependence of the ratio $\Delta\varepsilon/S$, values were evaluated from the MOPAC calculation and the Maier–Meier equation; even if the materials had large dipole moments, their $\Delta\varepsilon/S$ showed no temperature dependence. It was found that the new 2,3,4-trifluorinated phenyl LC materials, with the features of extremely low viscosity and small dielectric anisotropy may be introduced into LC mixtures that are applicable to many kinds of AM-LCDs such as VA and TN modes. We are now investigating whether the new 2,3,4-trifluorinated phenyl compounds can be applied to LC mixtures for VA-TFT LCDs.

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