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Liquid Crystals

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Synthesis and mesomorphic properties of fluoro-containing azobenzene liquid crystals

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Four series of azobenzene liquid crystal compounds containing a fluorinated tolan unit have been synthesized. The mesomorphic behaviours of these compounds were characterized by differential scanning calorimetry and optical polarizing microscopy. The compounds of these series exhibit a nematic, a smectic C or a smectic B phase. This investigation revealed that the alkoxy chain at the side of the azobenzene moiety plays a more important role in the formation of smectic phases than the one at the side of the tolan moiety.

1. Introduction

Guest–host liquid crystal displays have for some time been used in digital clocks and instrument panels in cars. Recently, reflection-type guest–host liquid crystal display have attracted much attention due to their brightness [1–12]. Dichroic dyes used in guest–host LCDs are required to have good solubility and dichroism in the liquid crystals. The introduction of tetrafluoro-*p*-phenylene moieties into the molecules of diazo dyes was reported as very effective in increasing the solubility [13, 14]. They are of potential interest as readily soluble dyes with their own liquid crystalline properties (high optical anisotropy, photoinduced *cis–trans*-isomerization) [15]. It is therefore very important to synthesize new kinds of azo compounds containing tetrafluoro-*p*-phenylene. On the other hand, molecules with a little less fluoro-substitution may also be attractive; they were also synthesized in this work, and their mesomorphic properties are discussed in detail.

2. Experimental

The structures of the intermediates and the final products were elucidated by a variety of spectral methods. IR spectra were recorded on a PE-983G spectrophotometer, using KBr pellets of the solids, or films of liquids. ^{1}H NMR spectra, with TMS as internal NMR standard were recorded on a Varian EM 360L spectrometer (60 MHz) or a Fx-90Q (90 MHz); ^{19}F NMR spectra with trifluoroacetic acid (TFA) as external standard were recorded on a Varian EM 360L spectrometer (60 MHz). For ^{19}F NMR spectra the high field was positive. MS spectra were measured with a Finnigan-4021 spectroscope. The phase transition temperatures of the target compounds were measured by optical microscopy using a polarizing microscope (Olympus PM-6) fitted with a heating stage (Mettler FP-80) and a control unit (FT-82), and by differential scanning calorimetry (Shimadzu DSC-50 calorimeter with a data system, heating and cooling rate 5°C min^{-1}). The transition temperatures reported in this paper were the peak values of the transition on DSC traces.

The compounds were synthesized according to the following scheme. The compounds **2**, **3**, **4** were easily obtained by literature methods [5, 16, 17]; **5** was prepared from etherification between **4** and Br(CH$_2$)$_m$H. Then **6** was obtained by the iodization of **5** [18]. The target compound was synthesized by basic detrimethylsilylation of **7** followed by coupling with **2**.

All the twenty compounds were prepared by the coupling reaction of compound **2** and the substituted phenylacetylene in the presence of palladium catalyst. A typical example of this procedure for the synthesis of **4NT4F8** is given as follows:

Under dry nitrogen, to a mixture of compound **2** (200 mg, 0.459 mmol), 4-octyloxy-2,3,5,6-tetrafluorophenylacetylene (166 mg, 0.55 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (10 mg), and CuI (15 mg) was added 10 ml of anhydrous THF and 2 ml of Et$_3$N. The resulting mixture was stirred at 50°C for 24 h. The precipitate formed was filtered off and washed with ether; the filtrate was washed with water and dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel using petroleum

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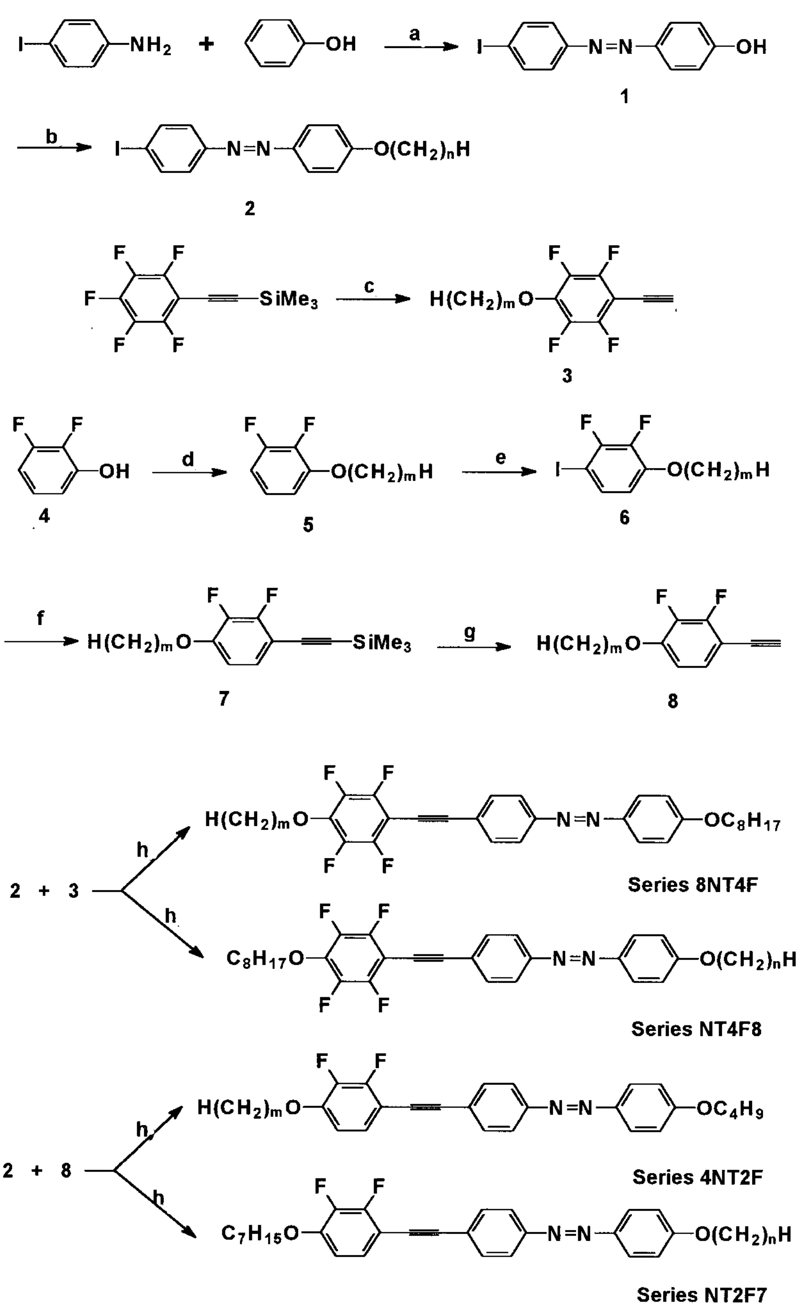


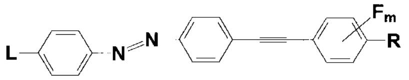
Scheme. a: (1) $NaNO_2$, HCl, (2) Na_2CO_3, NaOH; b: $H(CH_2)_nBr$, KOH, $EtOH/H_2O$; c: K_2CO_3, DMF; d: $H(CH_2)_mBr$, K_2CO_3, acetone; e: BuLi, I_2, − 78°C; f: $Pd(PPh_3)_2Cl_2$, CuI, NEt_3/THF, trimethylsilylacetylene; g: NaOH, MeOH; h: $Pd(PPh_3)_2Cl_2$, CuI, NEt_3/THF.

ether (b.p. 60–90°C)–dichloromethane (3 : 1) as the eluent to give a red solid which was recrystallized from petroleum ether (b.p. 60–90°C) to give red crystals of compound **4NT4F8**. Yield 73%, m.p. 98.7°C. IR(KBr) ν_{max}: 2924, 2866, 1600, 1496, 1247, 1153, 987, 854 cm^{-1}. ^1H NMR δ_H (90 MHz, $CDCl_3$; TMS): 0.89–1.98 (m, 22H, aliphatic hydrogens), 4.03 (t, $J = 6$ Hz, 2H, RCH_2O), 4.25 (t, $J = 6$ Hz, 2H, RCH_2O), 6.97 (d, $J = 9$ Hz, 2H, ArH), 7.61–7.95 (m, 6H, ArH) ppm. ^{19}F NMR (60 MHz, $CDCl_3$, TFA): 61.0 (d, $J = 18.8$ Hz, 2F), 80.3 (d, $J = 18.8$ Hz, 2F) ppm. MS m/z (rel. int.): 554 (M^+, 57.20), 265 (24.16), 149 (100.0). Anal. for $C_{32}H_{34}F_4N_2O_2$: calcd, C 69.30, H 6.18, N 5.08, F 13.70; found, C 69.58, H 6.35, N 4.76, F 13.38%.

All of the final compounds were purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C)–ethyl acetate (20 : 1) as eluent and then recrystallized from petroleum ether (b.p. 60–90°C) and acetone–methanol. All of the new target compounds have satisfactory elemental analysis and appropriate ^{1}H and ^{19}F NMR, IR and MS spectral data.

3. Results and discussion

Four series of liquid crystals containing –N=N– and –C≡C– units were synthesized. All of the compounds exhibit liquid crystalline behaviour. Tables 1 and 2, and figures 1, 2, 3 and 4 show the phase sequences and transition temperatures for the new series **NT4F8**, **8NT4F**, **4NT2F** and **NT2F7**. The structure of the molecules of the four series can be shown as one general structure below.



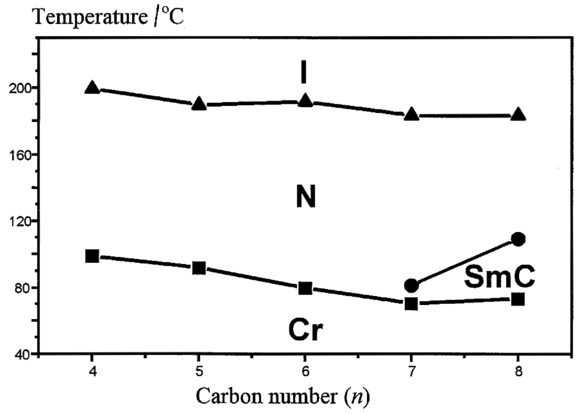


Figure 1. Plots of transition temperatures of series **NT4F8** versus n, the length of alkoxy chain L.

For the series **8NT4F**, with the increasing length of the alkoxy chain R, the clearing point progressively decreases; the nematic and smectic C phase temperature ranges change very little. But for the series **NT4F8**, with the increasing length of the alkoxy chain L the clearing points show an odd–even effect, and when $n \geqslant 7$ the temperature range of the nematic phase quickly narrows; in contrast, the range of the smectic C phase broadens quickly. As with the series **NT4F8** and **8NT4F**, the alkoxy chain in the series **NT2F7** and **4NT2F** plays an important role in the formation of mesophases.

In general, in all these four series, with the increasing length of alkoxy chains L or R, smectic phase are enhanced; in all these compounds the alkoxy chain L enhances the thermal stability of the smectic phase much than does the alkoxy chain R.

Table 1. Phase transition temperatures of the series **NT4F8** and **8NT4F**. Cr = crystal; SmC = smectic C phase; N = nematic phase; I = isotropic liquid; Recr = recrystallization.

Compounds	n	m	Phase transition temperature/°C
4NT4F8	4	8	Cr 98.7 N 199.0 I 197.0 N 92.3 Recr
5NT4F8	5	8	Cr 91.7 N 189.4 I 187.3 N 83.3 Recr
6NT4F8	6	8	Cr 79.5 N 191.3 I 189.2 N 69.2 Recr
7NT4F8	7	8	Cr 70.2 SmC 81.2 N 183.2 I 181.4 N 80.1 SmC 60.1 Recr
8NT4F5	8	5	Cr 85.4 SmC 113.1 N 194.8 I 192.8 N 111.7 SmC 72.0 Recr
8NT4F6	8	6	Cr 78.7 SmC 105.2 N 189.0 I 186.6 N 103.0 SmC 65.1 Recr
8NT4F7	8	7	Cr 75.8 SmC 111.7 N 188.3 I 186.7 N 109.9 SmC 64.9 Recr
8NT4F8	8	8	Cr 72.9 SmC 109.0 N 184.8 I 183.0 N 107.8 SmC 60.1 Recr
8NT4F9	8	9	Cr 68.4 SmC 105.2 N 171.2 I 169.0 N 102.6 SmC 59.9 Recr

Table 2. Phase transition temperatures of the series **4NT2F** and **NT2F7**. Cr = crystal; SmB = smectic B phase; N = nematic phase; I = isotropic liquid; Recr = recrystallization.

Compounds	n	m	Phase transition temperature/°C
4NT2F3	4	3	Cr 156.1 N 269.0 I 263.9 N 136.5 Recr
4NT2F4	4	4	Cr 156.3 N 262.5 I 258.7 N 135.3 Recr
4NT2F5	4	5	Cr 141.5 N 252.9 I 249.0 N 125.6 Recr
4NT2F6	4	6	Cr 120.0 N 244.8 I 241.5 N 112.4 SmB 107.8 Recr
4NT2F7	4	7	Cr 118.3 SmB 121.4 N 229.6 I 226.1 N 118.3 SmB 102.4 Recr
4NT2F8	4	8	Cr 110.6 SmB 119.7 N 223.1 I 221.2 N 117.6 SmB 98.2 Recr
4NT2F10	4	10	Cr 115.8 SmB 126.4 N 218.8 I 217.4 N 124.6 SmB 89.8 Recr
5NT2F7	5	7	Cr 111.7 SmB 136.7 N 227.4 I 225.3 N 134.6 SmB 99.6 Recr
6NT2F7	6	7	Cr 102.8 SmB 143.2 N 217.6 I 215.9 N 142.7 SmB 99.8 Recr
7NT2F7	7	7	Cr 102.6 SmB 155.2 N 215.3 I 213.8 N 153.5 SmB 100.7 Recr
8NT2F7	8	7	Cr 87.9 $\mathrm{SmX_1}$ 101.2 SmB 162.3 N 213.8 I 212.6 N 160.6 SmB 99.1 $\mathrm{SmX_1}$ 80.8 $\mathrm{SmX_2}$ 77.3 Recr

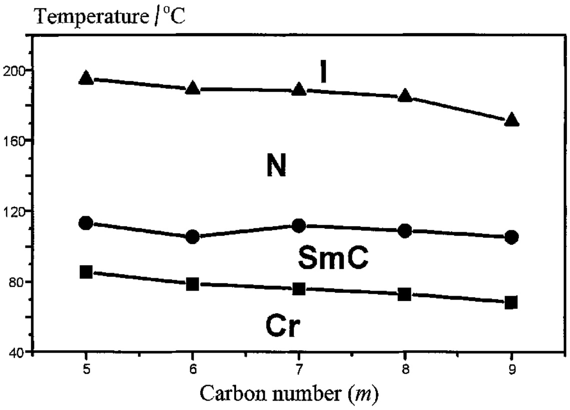


Figure 2. Plots of transition temperatures of series **8NT4F** versus *m*, the length of alkoxy chain *R*.

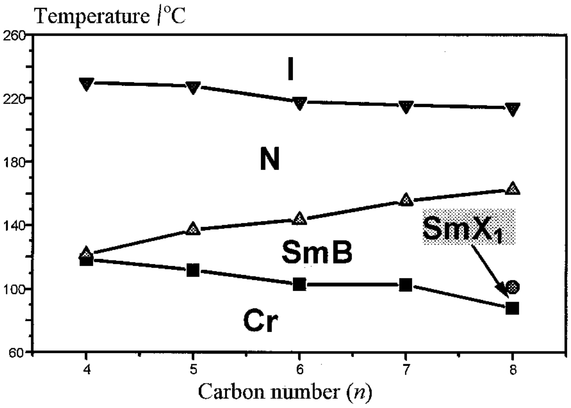


Figure 3. Plots of transition temperatures of series **NT2F7** versus *n*, the length of alkoxy chain *L*.

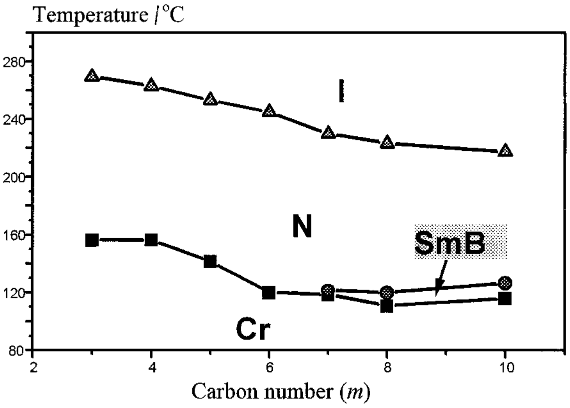


Figure 4. Plots of transition temperatures of series **4NT2F** versus *m*, the length of alkoxy chain *R*.

It is well known that when more than two benzene rings are linked through more than one central group, the liquid crystalline properties are enhanced most when all the rings are conjugated, i.e. the liquid crystal transition temperatures are highest when the entire system is linked through central groups involving multiple bonds [19]. The –N=N– unit is also favourable in regard to mesophase thermal stability, because it can extend a region of conjugation, particularly when placed between two aromatic units, and because it confers a measure of rigidity to the molecule.

The –C≡C– unit, however, conjugates with two phenylene groups which are not in the same plane; so the –C≡C– unit cannot increase the conjugation of the core as much as the –N=N– unit. In addition, the tolan part is perfectly linear; the increasing length of the alkoxy chain cannot change the lateral polarity as much as the azo-linked part can, due to the bent nature of the azo unit. The alkoxy *L* plays an important role in the formation of smectic phases.

It is also well known that lateral fluoro-substitution not only depresses the clearing points but also supresses the formation of more ordered mesophases [17]. The clearing points of the compounds **4NT2F8** and **8NT2F7** are therefore higher than those of the compounds **4NT4F8** and **8NT4F7**, respectively.

It has been found that in the phase transition of normal chain molecular crystals, the greater the density of the unit cell, the more stable is the crystal. And when the molecules tend to be tilted, the density of the unit cell tends to increase [20]. The more we introduce larger fluorine atoms into the same phenylene group of the core, the more useless space is created in an orthogonal packing, owing to steric and polar effects. Thus, the tilted smectic phase is favoured [21].

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