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Fluorinated tolan-type nematic mesogens containing a 1,3-dioxan unit

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Twenty new 2,5-disubstituted 1,3-dioxans were prepared, and their mesomorphic properties were investigated by optical polarizing microscopy and DSC; all of the compounds exhibit the nematic phase only. With fluorination in the mesogenic core, the melting and clearing points were reduced, but their nematic phase range only slightly shortened.

1. Introduction

High performance LCDs require liquid crystals mixtures with low viscosity to reduce the response times [1, 2], large positive dielectric anisotropy to reduce threshold and driver voltage; and adjustable optical properties. During the last 20 years, 2,5-disubstituted 1,3-dioxans have been reported as new types of nematic liquid crystal materials [3–9], and the tolan-type 1,3-dioxans were regarded as especially good viscosity reducing agents for use in the production of fast-response LCD cells [10]. It is also well known that the introduction of fluorine atoms into the mesogenic core can have dramatic effects on mesomorphic behaviour and certain physical properties, such as reducing the viscosity and increasing the dielectric anisotropy. Thousands of liquid crystalline compounds with mono-, di-, and tri-fluorophenyl groups [11–14], or 2,3,5,6-tetrafluorophenylenes [15–17] are reported as useful components of liquid crystal mixtures. Therefore, it was decided to investigate a number of systems based on the very successful tolan-type 1,3-dioxan, but where the aromatic ring has been fluorinated. In this paper, we report the synthesis of some new heteroalicyclic liquid crystalline materials, and their mesomorphic properties.

2. Experimental

2.1. Analysis

The structures of all intermediates and final mesogens were determined by spectroscopic methods. IR spectra were recorded on a PE-983G spectrometer using a KBr disc. ^1H NMR spectra (with TMS as the internal standard) and ^{19}F NMR spectra (with trifluoroacetic acid (TFA) as external standard) in CDCl_3 as the solvent, were recorded on a FX-90Q (90 MHz) or Bruker 300AM

instrument. For ^{19}F NMR spectra, the high field was positive. MS spectra were measured with a Finnigan 4021 spectrometer. The phase transition temperatures of all the target compounds were measured by optical microscopy using a polarizing optical microscope (POM, Olympus PM-6) equipped with a hot stage (Mettler FP-80) and a control unit (FP-82); also by differential scanning calorimetry (DSC, Shimadzu DSC-50 calorimeter with a data system) with heating and cooling rates of 5°C min^{-1} . The transition temperatures shown in this paper are the peak values of the transitions on DSC traces. Phase identification was made by comparing the observed textures with those reported in the literature [18, 19].

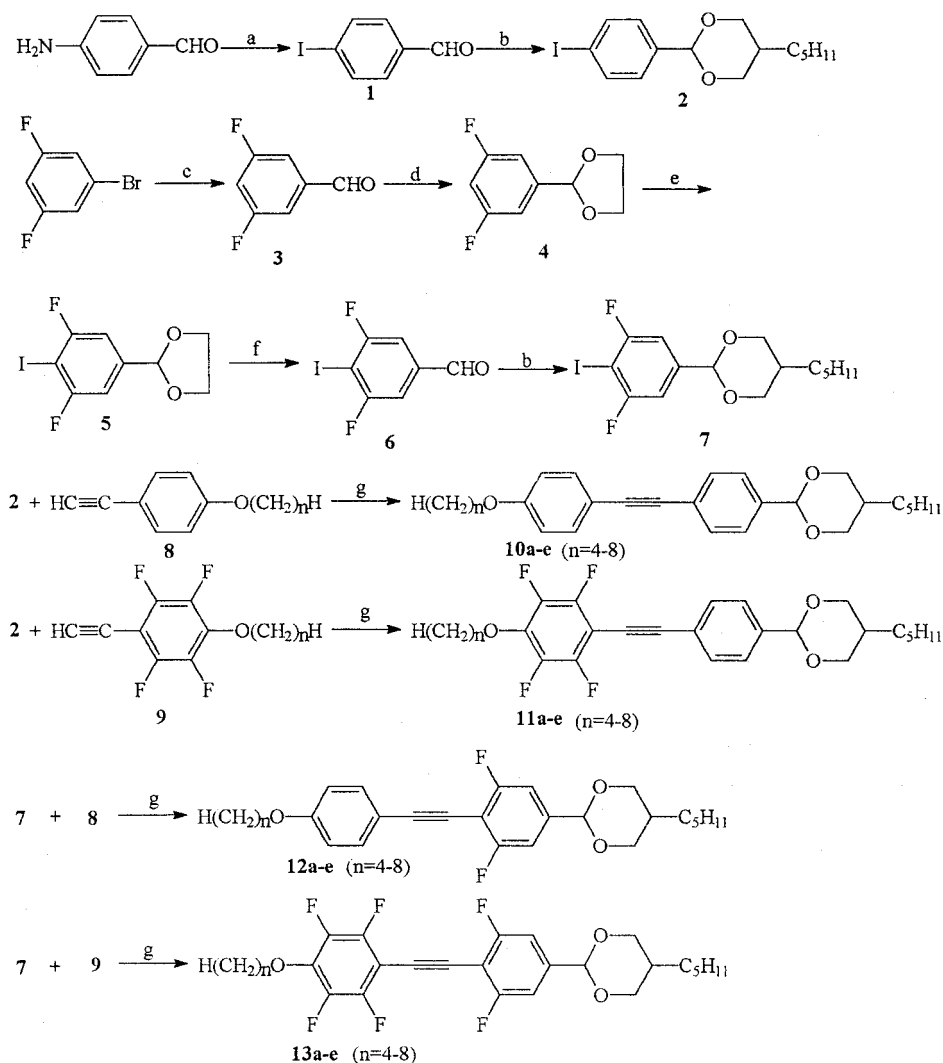
2.2. Synthesis

Twenty novel liquid crystalline compounds were prepared according to the procedures shown in the scheme. The results of thermal analysis are summarized in the table. The intermediates 4-alkyloxyphenylacetylene, 4-alkyloxy-2,3,5,6-tetrafluorophenylacetylene [17, 20] and pentylpropane-1,3-diol [21], were prepared with the procedures reported in the literature.

2.2.1. 4-Iodobenzaldehyde (I)

A mixture of *p*-aminobenzaldehyde (18 g, 0.148 mol), water (300 ml) and concentrated hydrochloric acid (26 ml), was cooled to -5°C , then added dropwise to a solution of NaNO_2 (30 g, 0.434 mol) in H_2O (40 ml). The temperature was kept below 0°C . After stirring for 30 min, a solution of KI (75 g, 0.458 mol) and CuI (85.5 g, 0.449 mol) in H_2O (100 ml) was added, after which the mixture was allowed to warm to room temperature. It was filtered, and the filtrate was extracted with ethyl acetate (2×150 ml). The extracts were washed with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ and dried (MgSO_4).

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Reagents and conditions: (a) NaNO_2 , CuI , KI , 0°C to r.t.; (b) $\text{C}_5\text{H}_{11}\text{CH}(\text{CH}_2\text{OH})_2$, TsOH , toluene, reflux; (c) Mg , THF , then DMF ; (d) $\text{HOCH}_2\text{CH}_2\text{OH}$, TsOH , toluene, reflux; (e) $n\text{BuLi}$, -78°C , then I_2/THF ; (f) dioxan, HCl ; (g) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , PPh_3 , NEt_3 .

Scheme. Synthetic pathway to the target dioxan-containing materials.

The solvent was removed *in vacuo*, and the residue purified by column chromatography on silica gel, eluting with petroleum to give the desired 4-iodobenzaldehyde as a white crystalline solid. Yield = 15.7 g (46%) δ_{H} : 10.18 (s, 1H, $-\text{CHO}$), 7.74–8.17 (dd, 4H, $-\text{C}_6\text{H}_4-$) ppm; m/z : 232 $[\text{M}]^+$, 203.

2.2.2. 2-(4-Iodophenyl)-5-pentyl-1,3-dioxan (2)

A mixture of compound **1** (3.5 g, 0.015 mol), pentylpropane-1,3-diol (2.63 g, 0.018 mol), dry toluene (50 ml) and *p*-toluenesulphonic acid (25 mg) was heated under reflux using a Dean and Stark trap to remove water. On cooling to room temperature, the mixture was poured into aqueous sodium hydrogen carbonate (5%, 50 ml)

and the separated organic layer was washed with more aqueous sodium hydrogen carbonate (5%, 2×50 ml), water (2×50 ml) and dried (Na_2SO_4). The solvent was removed *in vacuo* and the residue purified by crystallization from methanol to remove the *cis*-isomer. Yield = 2.43 g (45%). δ_{H} : 0.89 (t, 3H, $-\text{CH}_3$), 1.28 (m, 8H, $-(\text{CH}_2)_n-$), 2.07 (m, 1H), 3.49 (dd, $J = 11.5$ and 11.5 , 2H, Ha), 4.22 (dd, $J = 11.5$ and 4.5 Hz, 2H, He), 5.31 (s, 1H), 7.34–7.82 (m, 4H, $-\text{C}_6\text{H}_4-$) ppm; m/z : 360 $[\text{M}]^+$, 231.

2.2.3. 3,5-Difluorobenzaldehyde (3)

A solution of the Grignard reagent prepared from 3,5-difluoro-1-bromobenzene (77.2 g, 0.40 mol) and magnesium (10 g, 0.41 mol) in dry THF (300 ml) was

Table. Transition temperatures of the synthesized compounds.

Compounds	<i>n</i>	T_{CrN}	T_{NI}
10a-e	4	104.4	216.3
	5	100.2	205.5
	6	94.9	201.1
	7	98.4	192.9
	8	100.9	188.8
11a-e	4	77.3	176.9
	5	65.2	167.8
	6	58.7	163.0
	7	58.7	155.3
	8	59.2	155.3
12a-e		94.3	
	4		188.5
	5	86.3	177.9
	6	94.4	157.5
	7	97.2	158.5
13-e	8	85.0	165.0
	4	87.2	167.1
	5	74.2	155.7
	6	66.2	153.0
	7	60.3	145.2
	8	63.4	143.6

cooled to -15°C , then added dropwise to DMF (32 ml, 0.40 mol); after addition, the reaction mixture was stirred overnight at room temperature. Hydrochloric acid (10%, 200 ml) was added at the end of the reaction, and the mixture was extracted with diethyl ether ($2 \times 100\text{ ml}$); the combined organic layer was washed with water, then dried (Na_2SO_4). The solvent was removed *in vacuo*, and the pure product isolated by distillation under reduced pressure. Yield = 41 g (73%), b.p. $90^{\circ}\text{C}/10\text{ mm Hg}$. δ_{H} : 7.26 (m, 1H), 7.60 (m, 2H), 10.13 (s, 1H, $-\text{CHO}$) ppm; δ_{F} : 33.2 (s, 2F) ppm; m/z : 142 $[\text{M}]^+$, 113, 63.

2.2.4. 2-(3,5-Difluorophenyl)-1,3-dioxolan (4)

A mixture of compound **3** (40 g, 0.28 mol), ethylene glycol (18.6 g, 0.30 mol), dry toluene (300 ml) and *p*-toluenesulphonic acid (50 mg) was heated under reflux using a Dean and Stark trap to remove water. After cooling to room temperature, the mixture was poured into aqueous sodium dicarbonate (10%, 100 ml). The toluene layer was separated from the aqueous phase which was then shaken with diethyl ether ($2 \times 150\text{ ml}$); the organic phases were combined and dried (Na_2SO_4). The solvent was removed *in vacuo* and the residue purified by distillation under reduced pressure. Yield = 42 g (80%), b.p. $120^{\circ}\text{C}/10\text{ mm Hg}$. δ_{H} : 4.32 (s, 4H), 6.03 (s, 1H), 7.07–7.28 (m, 3H) ppm; δ_{F} : 35.3 (s, 2F) ppm; m/z : 186 $[\text{M}]^+$, 141, 114.

2.2.5. 2-(3,5-Difluoro-4-iodophenyl)-1,3-dioxolan (5)

n-Butyllithium (100 ml, 2.5M in hexane), was added dropwise to a stirred, cooled (-78°C) solution of compound **4** (48 g, 0.258 mol), in dry THF (300 ml) under an atmosphere of dry nitrogen. The reaction mixture was stirred (2 h), then a solution of iodine (63.4 g) in dry THF (80 ml) was added dropwise at -78°C . The reaction mixture was allowed to warm to room temperature overnight then mixed with saturated aqueous ammonium chloride solution (200 ml); the organic layer was separated from the aqueous phase which was shaken with diethyl ether ($2 \times 150\text{ ml}$). The organic phases were washed with saturated aqueous sodium thiosulfate (200 ml) and dried (Na_2SO_4). The solvent was removed *in vacuo* and the residue purified by distillation under reduced pressure. Yield = 34.6 g (43%), b.p. $110\text{--}114^{\circ}\text{C}/0.2\text{ mm Hg}$. δ_{H} : 4.26 (s, 4H), 6.07 (s, 1H), 7.20 (m, 2H) ppm; δ_{F} : 14.0 (s, 2F) ppm; m/z : 312 $[\text{M}]^+$, 267, 185.

2.2.6. 3,5-Difluoro-4-iodobenzaldehyde (6)

Compound **5** (18.5 g, 0.059 mol), concentrated hydrochloric acid (10 ml) and dioxan (150 ml) were heated under reflux for 1 h. The reaction mixture was allowed to cool and then poured into water (150 ml). The product was extracted into diethyl ether ($2 \times 100\text{ ml}$); the extracts were combined and dried (Na_2SO_4). The solvent was removed *in vacuo* and the residue purified by crystallization from hexane to furnish the desired 3,5-difluoro-4-iodobenzaldehyde as a white solid. Yield = 11.7 g (74%). δ_{H} : 7.62 (m, 2H), 10.18 (s, 1H, $-\text{CHO}$) ppm; δ_{F} : 10.1 (s, 2F) ppm; m/z : 268 $[\text{M}]^+$, 239, 112.

2.2.7. 2-(2,5-Difluoro-4-iodophenyl)-5-pentyl-1,3-dioxan (7)

Compound **7** was prepared using a procedure similar to that described for the synthesis of compound **2**. Quantities: 2,3-difluoro-4-iodobenzaldehyde (**6**) (5.4 g, 0.02 mol), pentylpropane-1,3-diol (3.0 g, 0.021 mol). Yield = 3.3 g (43%). δ_{H} : 0.89 (t, 3H, $-\text{CH}_3$), 1.28 (m, 8H, $-(\text{CH}_2)_n-$), 2.07 (m, 1H), 3.49 (dd, $J = 11.5$ and 11.5 , 2H, Ha), 4.22 (dd, $J = 11.5$ and 4.5 Hz , 2H, He), 5.31 (s, 1H), 7.01 (m, 2H, $-\text{C}_6\text{H}_2\text{F}_2-$) ppm; δ_{F} : 15.5 (s, 2F) ppm; m/z : 396 $[\text{M}]^+$, 267, 69.

2.2.8. 2-[(4-Butyloxyphenyl)ethynyl]phenyl-5-pentyl-1,3-dioxan

The preparation of this compound provides an example of the general methods used for all compounds **10**, **11**, **12** and **13**.

A mixture of compound **2** (200 mg, 0.555 mmol), 4-butyloxyphenylacetylene (116 mg, 0.666 mol), bis(triphenylphosphine)palladium dichloride (10 mg), copper(I) iodide (15 mg) and 10 ml of anhydrous triethylamine 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 ether (b.p. 60–90°C)–dichloromethane (3:1) as the eluant, to give pale yellow crystals which were recrystallized from isopropanol to yield white flaky crystals of compound **10a**. Yield = 164.7 g (73%), m.p. 104.4°C. $^1\text{H NMR}$ δ_{H} (300 MHz; CDCl_3 ; TMS): 0.88–1.78 (m, 18H, aliphatic hydrogens); 2.15 (m, 1H); 3.54 (t, 2H, $J = 11.5$ Hz); 3.95–4.01 (m, 2H); 4.22–4.27 (m, 2H); 5.41 (s, 1H); 6.84–6.90 (m, 2H); 7.44–7.53 (m, 6H). MS m/z (rel. int.): 406 (M^+ , 100.0), 222 (43.35). Elemental analysis for $\text{C}_{27}\text{H}_{34}\text{O}_3$: calcd C 79.77, H 8.43; found C 79.91, H 8.53%. ν_{max} (KBr): 2954, 2924, 2853, 2212, 1600, 1564, 1515, 1307, 1251, 1162, 1025, 818 cm^{-1} .

3. Results and discussion

The phase transition temperatures of all the compounds were determined by DSC with heating and cooling rates of 5°C min^{-1} . The mesomorphic textures were observed with the polarizing optical microscope for determining the type of mesophase. The transition temperatures shown in the table are the maxima of transition peaks on each DSC trace.

As mentioned above, our target was to synthesize fluorinated mesogens with a 1,3-dioxane unit; the non-fluorinated analogues (compounds **10a–e**) were therefore synthesized first for comparison. Their phase transition temperatures are summarized in the table and represented graphically in figure 1. It is clear that the compounds **10a–e** show a simple mesophase sequence; their nematic phase ranges are about 100°C . Increasing the length of the terminal alkoxy chain (n) across the series, the temperature of the melting (Cr–N) transition first decreases, then increases; compound **10c** ($n = 6$) has the lowest melting point. The transition temperatures between the

nematic phase and the isotropic liquid decreased with increasing values of n . The overall effect of increasing the value of n is generally to decrease the nematic phase range and stability.

The fluorinated dioxan compounds were synthesized by methods to that for their non-fluorinated analogues. Their phase transition temperatures are summarized in the table and represented graphically in figures 2, 3 and 4. It is clear that their phase behaviour is similar to that of the non-fluorinated analogues; that is, they also show only a nematic phase. The clearing points decreased with increasing length of the terminal alkoxy chain.

We now discuss the effect of fluoro-substitution in the three-ring mesogen on the mesomorphic properties. The fluorine atom combines the properties of large electronegativity and small size, so the fluoro-substituent is ideal for varying the physical properties of liquid crystal molecules. The fluorinated compounds **11a**, **12a**, **13a** exhibit lower melting and clearing points compared with the non-fluorinated analogue compound **10a**. This is because the introduction of a fluorine atom into the

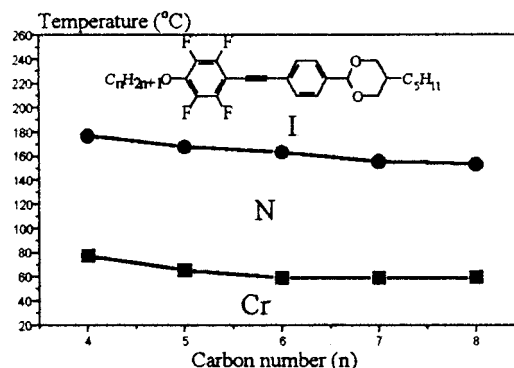


Figure 2. The transition behaviour of compounds **11a–e**: dependence of transition temperatures on the number (n) of the alkoxy chain.

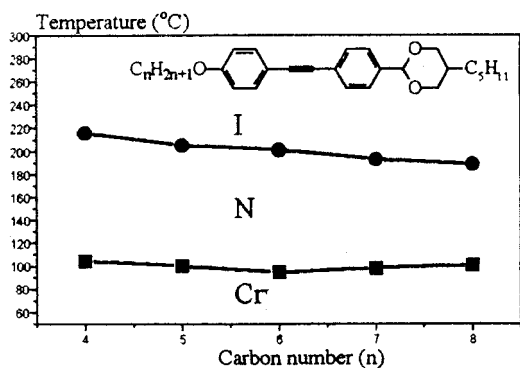


Figure 1. The transition behaviour of compounds **10a–e**: dependence of transition temperatures on the number (n) of the alkoxy chain.

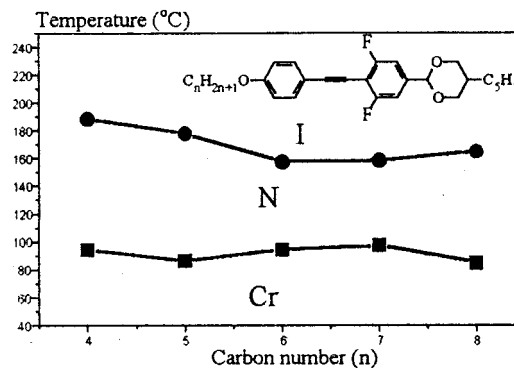


Figure 3. The transition behaviour of compounds **12a–e**: dependence of transition temperatures on the number (n) of the alkoxy chain.

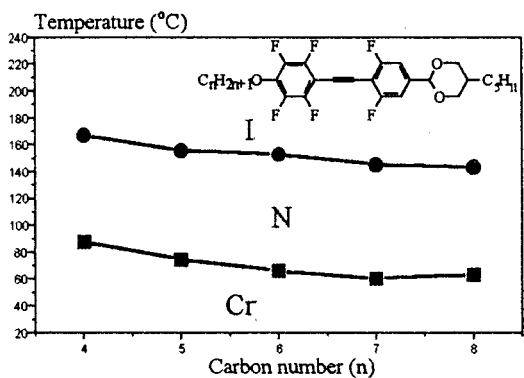


Figure 4. The transition behaviour of compounds **13a–e**: dependence of transition temperatures on the number (n) of the alkoxy chain.

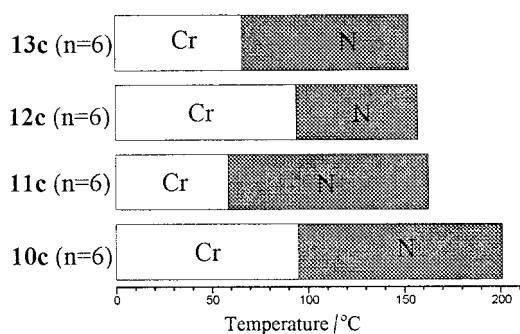


Figure 5.

lateral position reduces the intramolecular forces, and broadens the molecule. Increasing the quantity of lateral fluoro-substituents introduced into the nematogen results in decreasing the clearing temperatures of the liquid crystals. The series **11**, with a tetrafluorophenylene placed in the side ring of the mesogen, has a nematic phase range only slightly shorter than the parent compounds **10**, because the polar effects of the four fluorine atoms are mutually counteracted. But for the series **12**, the difluoro-substitution in the mid-ring of the mesogen leads to a sharp decrease of the nematic phase range. This may be explained in both steric and electronic terms. The two fluorine atoms located on the two sides of the core broaden the molecule, and make its shape unsuitable for good aligning, thus decreasing the nematic stability. In terms of the electronic properties, the molecule possesses two sites of high electron density; one as a consequence of the alkoxy and difluoro substituents located on the aromatic portion of the core, the other

due to the two oxygen heteroatoms in the dioxan ring. Two dipoles have the same direction along the X axis, resulting in the decrease of the nematic phase range.

An interesting phenomenon has been found in the series **12**: the nematic phase range first shortens, then widens with the increasing length of the alkoxy chain, and when $n = 7$ the phase range is minimum. But the other three series show the opposite trend; when $n = 6$, the nematic phase range has its maximum value, as seen in figure 5. This may be explained in terms of molecular alignment.

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