Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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Guixiang Sun[a]; Bing Chen[a]; Hong Tang[a]; Shouyi Xu[a]
[a] Department of Chemistry Tsinghua University Beijing 100084 PR China,

To cite this Article Sun, Guixiang , Chen, Bing , Tang, Hong and Xu, Shouyi(2003) 'Synthesis and mesomorphic properties of four-ring liquid crystals containing 2,3-difluorophenyl and 1,3-dioxane units', Liquid Crystals, 30: 8, 921 — 926

To link to this Article: DOI: 10.1080/0267829031000136039

URL: http://dx.doi.org/10.1080/0267829031000136039

Liquid Crystals, Vol. 30, No. 8, August, 2003, 921–926

Synthesis and mesomorphic properties of four-ring liquid crystals containing 2,3-difluorophenyl and 1,3-dioxane units

GUIXIANG SUN*, BING CHEN, HONG TANG and SHOUYI XU
Department of Chemistry, Tsinghua University, Beijing 100084, PR China

(*Received 5 December 2002; in final form 19 February 2003; accepted 15 March 2003*)

Two series of novel liquid crystalline materials were synthesized: 2-(2,3-difluoro-4-alkoxyphenyl)-5-[4-(4-alkylcyclohexyl)phenyl]-1,3-dioxanes ($\mathbf{A}_{m\text{-}n}$) and 2-(2,3-difluoro-4-alkylphenyl)-5-[4-(4-alkylcyclohexyl)phenyl]-1,3-dioxanes ($\mathbf{B}_{m\text{-}n}$). Their mesmorphic properties were characterized by polarizing optical microscopy and differential scanning calorimetry. All these compounds exhibit broad mesomorphic phases, and most of them show wide smectic C phases and the phase sequence Cr–SmC–SmA–N–I. The relationship between properties and chemical structures is discussed in detail.

1. Introduction

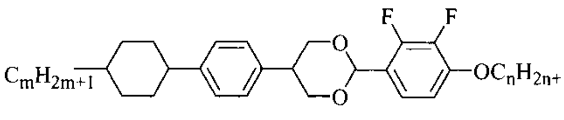
Ferroelectric liquid crystal (FLC) display devices have received increasing attention because of their fast switching times and bistable operation [1, 2]. Several physical properties and requirements are important in formulating SmC* mixtures for use in ferroelectric cells, these include (*a*) low birefringence, (*b*) negative dielectric anisotropy, (*c*) a broad temperature range of chiral smectic C* phase and (*d*) the phase sequence SmC*–SmA*–N*–I, for good alignment [3, 4]. In addition, FLC materials are usually prepared by mixing chiral dopants and achiral host liquid crystal mixtures which have the best possible combination of the desirable properties [3, 5], thus achiral liquid crystals suitable for FLC mixtures have been intensely studied in recent years. Previous research has shown that liquid crystals containing 2,3-difluorophenyl units can exhibit negative dielectric anisotropy and tilted smectic C phases [3, 4, 6–13]. Many such materials have proved to be excellent host materials for ferroelectric mixtures.

It is now well established that lateral fluoro-subsitituents can improve certain characteristics of a material or may completely change its nature [14]. For example, they can reduce the melting point of the parent system and may be well suited for achieving a high negative dielectric anisotropy. Unfortunately, low melting points and high negative dielectric anisotropies are obtained at the expense of a decrease in the clearing temperatures by about 30–40 K per fluorine substituent [15]. In order to obtain liquid crystal materials with a high clearing temperature as well as low birefringence, negative dielectric anisotropy and wide smectic C temperature range, we have introduced *trans*-1,4-substituted cyclohexane, 2,5-substituted 1,3-dioxane and 1,4-substituted 2,3-difluorophenyl units into the LC molecules and synthesized two new types of compound. The general structures of these systems are shown in scheme 1 (**A** and **B**).

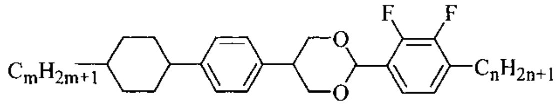
2. Experimental

2.1. *Characterization*

The structures of the final products and intermediates were confirmed by infrared spectroscopy (Nicolet 560 spectrophotometer), ^{1}H NMR spectroscopy (Bruker 300 spectrometer, where the spectra, unless otherwise stated, were recorded using Me_4Si as an internal standard; the *J* values are given in Hz), and mass spectroscopy (AEIMS-50 SD90 spectrometer). The phase transition temperatures of the target compounds were determined by polarizing optical microscopy using a polarizing light microscope (Olympus PM-10AD)



A: m = 2, 3, 4, 5; n = 2, 3, 4, 5, 6, 7, 8, 9, 10.



B: m = 2, 3, 4, 5; n = 5

Scheme 1. The structures of the target compounds.

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*Author for correspondence;
e-mail: sgx01@mails.tsinghua.edu.cn

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2003 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/0267829031000136039

Table 1. Transition temperatures (°C) of the target compounds. Cr = crystal; SmC = smectic C phase; SmA = smectic A phase; N = nematic phase; I = isotropic liquid.

Compound	*m*	*n*	Cr		SmC		SmA		N		I
A	2	5	●	92.9	●	125.4	●	187.8	●	221.5	●
A	3	2	●	146.0			●	179.0	●	273.3	●
A	3	3	●	140.6	●	153.7	●	201.8	●	261.3	●
A	3	4	●	120.9	●	153.0	●	213.4	●	257.0	●
A	3	5	●	109.5	●	153.1	●	213.3	●	243.1	●
A	4	2	●	102.5	●	151.7	●	194.1	●	268.1	●
A	4	3	●	85.1	●	164.5	●	214.4	●	254.2	●
A	4	4	●	69.4	●	164.0	●	226.5	●	242.1	●
A	4	5	●	93.2	●	164.3	●	225.2	●	237.5	●
A	5	3	●	76.1	●	169.3	●	222.2	●	254.3	●
A	5	4	●	79.3	●	171.6	●	231.9	●	252.2	●
A	5	5	●	74.7	●	171.9	●	233.3	●	243.0	●
A	5	6	●	76.2	●	169.1	●	231.7	●	238.0	●
A	5	7	●	79.1	●	165.7	●	227.5			●
A	5	8	●	82.2	●	164.2	●	223.5			●
A	5	9	●	89.7	●	162.5	●	220.5			●
A	5	10	●	93.1	●	159.6	●	216.6			●
B	2	5	●	108.3	●	143.7	●	172.4	●	198.1	●
B	3	5	●	116.1	●	166.5	●	201.1	●	223.3	●
B	4	5	●	108.3	●	174.4	●	209.1	●	219.9	●
B	5	5	●	92.0	●	181.5	●	215.1	●	221.8	●

fitted with a hot stage (Mettler FP-80) and control unit (FP-82), and by differential scanning calorimetry (Mettler DTA TA-2010 DSC). Elemental analysis for carbon and hydrogen were conducted on a Heraeus CHN-O-Rapid elemental analyser. The purity of each final compound listed in table 1 was determined by HPLC (Hypersil OD52 C18 Reverse Phase Column 250 × 4.6 mm); they were found to be >99% pure. Phase identification was made by comparing the observed textures with those reported in the literature [16, 17].

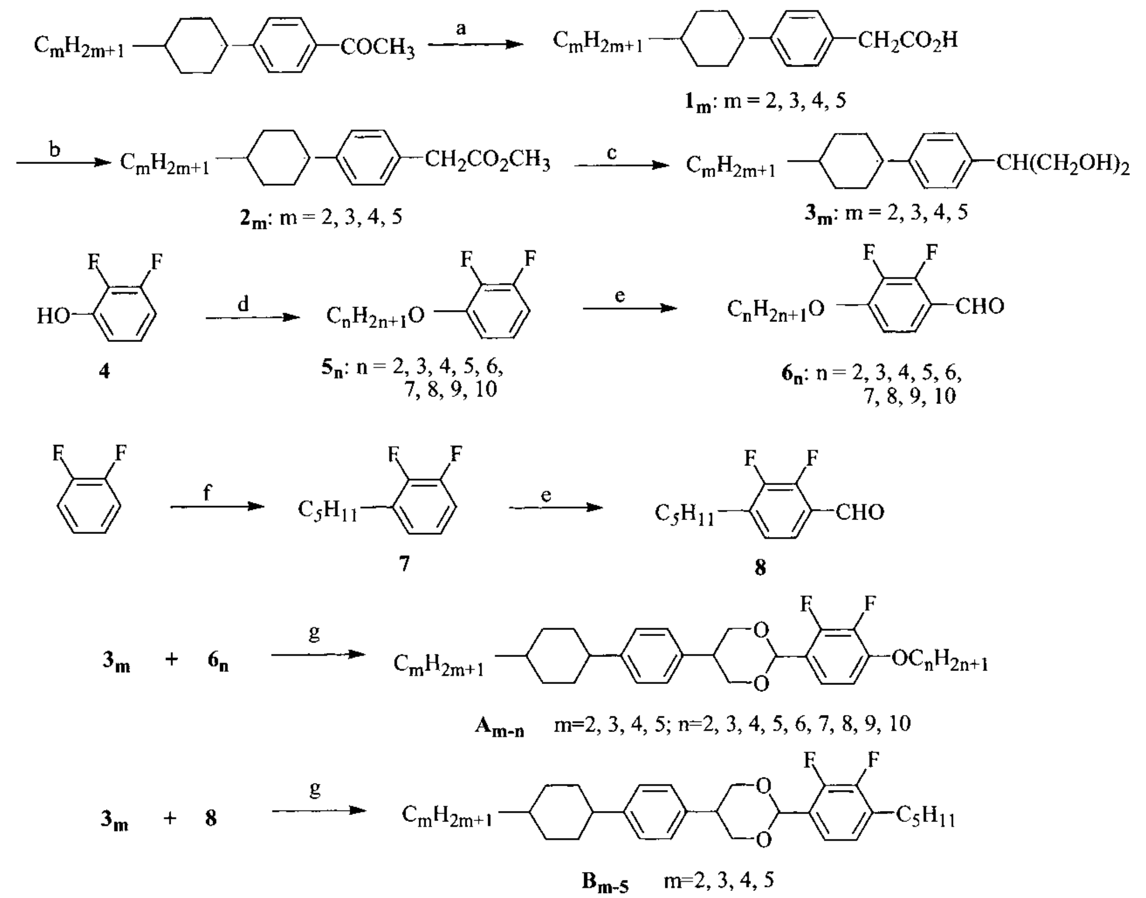
2.2. *Synthesis*

The target compounds were prepared according to the procedures detailed in scheme 2.

Compounds $\mathbf{1}_{m}$, **4** and **7** were prepared by reported methods [6, 18]; compounds $\mathbf{5}_{n}$ were prepared by the etherification of **4** using $Br(CH_2)_nH$. Compounds $\mathbf{2}_{m}$ were synthesized from the esterification of $\mathbf{1}_{m}$ using methanol in the presence of concentrated sulphuric acid. Compounds $\mathbf{3}_{m}$ were obtained by condensation between $\mathbf{2}_{m}$ and methyl formate in the presence of sodium methoxide, followed by reduction with sodium borohydride. Intermediates $\mathbf{6}_{n}$ and **8** were synthesized respectively from compounds $\mathbf{5}_{n}$ and **7** with BuLi/THF and DMF at −78°C. The target compounds $\mathbf{A}_{m\text{-}n}$ and $\mathbf{B}_{m\text{-}5}$ were obtained by the coupling reaction of compounds $\mathbf{3}_{m}$ with $\mathbf{6}_{n}$ and with **8** using *p*-toluenesulphonic acid as catalyst.

2.2.1. *2-[4-(trans-4-n-Pentylcyclohexyl)phenyl]-1,3-propanediol* $\mathbf{3}_{5}$

Methyl formate (6 ml, 91 mmol) was added dropwise to a stirred warm (45°C) mixture of sodium methoxide (9 g, 0.17 mol), compound $\mathbf{2}_{5}$ (25 g, 83 mmol) and toulene (150 ml). The mixture was stirred for 4 h at the same temperature. After cooling to room temperature, the mixture was poured into stirred aqueous sulphuric acid (10%, 70 ml), and the separated organic layer was washed with water (2 × 100 ml) and dried (Na_2SO_4). The solvent was removed *in vacuo* to yield a pale yellow oil. A solution of the pale yellow oil in ethanol (100 ml) was added dropwise to a suspension of sodium borohydride (6 g, 0.16 mol) in ethanol (150 ml) maintained at 15–30°C by external cooling. After heating the reaction mixture at 55°C for 4 h, hydrochloric acid (10%, 100 ml) was added dropwise at a temperature of less than 55°C. Following the addition of hydrochloric acid, the reaction mixture was heated at 55°C for 1 h and vacuum distilled to remove ethanol. The residual product was dissolved in ether (300 ml), washed with water (2 × 150 ml) and dried (Na_2SO_4). The solvent was removed *in vacuo* and the pure product isolated by recrystallization from hexane. Yield 13 g, 52%, m.p. 148–150°C. IR (KBr)ν_{max}: 3327, 2920, 2850, 1516, 1442, 1345, 1062, 1030, 980, 823 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.90 (3H, t, *J* 7.2), 0.91–1.50 (13H, m), 1.88 (4H, d, *J* 10.8), 2.09 (2H, s), 2.44 (1H, t, *J* 8.0), 3.07 (1H, t, *J* 6.6), 3.96 (4H, m, *J* 8.0 and 6.0), 7.15 (4H, m).



Scheme 2. Synthetic pathway to the target materials. Reagents and conditions: (a) 1. sulphur, morpholine, reflux; 2. acetic acid, sulphuric acid, reflux; (b) methanol, sulphuric acid, reflux; (c) 1. sodium methoxide, methyl formate, toluene, 50°C; 2. sodium borohydride, ethanol, 55°C; (d) $C_nH_{2n+1}Br$, K_2CO_3, Me_2CO, reflux; (e) *n*-BuLi, THF, −78°C, then DMF; (f) 1. n-BuLi, THF, −78°C, then $C_{n-1}H_{2n-1}CHO$; 2. P_2O_5, *n*-hexane, r.t; 3. H_2, 5% Pd-C, ethanol, 40°C; (g) TsOH, toluene, reflux.

2.2.2. *2,3-Difluoro-4-pentoxybenzaldehyde* 6_5

n-Butyllithium (100 ml, 2.8M in hexane, 0.28 mol) was added dropwise to a stirred, cooled (−78°C) solution of compound 5_5 (50 g, 0.25 mol) in dry THF (400 ml) under an atmosphere of dry nitrogen. The reaction mixture was stirred (1.5 h), then a previously cooled (−78°C) solution of DMF (22 ml, 0.28 mol) in dry THF (50 ml) was added dropwise at −78°C. The reaction mixture was allowed to warm to room temperature then stirred (1 h) with hydrochloric acid (10%, 350 ml). The product was taken up in ether (2 × 150 ml), and the combined ether extracts were washed with water (2 × 200 ml) and dried (Na_2SO_4). The solvent was removed *in vacuo* and the pure product isolated by recrystallization from hexane. Yield 33 g, 58%, m.p. 39–41°C. IR (KBr)ν_{max}: 2943, 2937, 2853, 1689, 1623, 1510, 1471, 1303, 1080, 817, 777, 731 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.94 (3H, t, *J* 7.0), 1.47 (4H, m, *J* 6.6 and 4.2), 1.87 (2H, m, *J* 7.0), 4.13 (2H, t, *J* 6.6), 6.84 (1H, d), 7.58 (1H, d), 10.19 (1H, s).

2.2.3. *2-(2,3-Difluoro-4-pentoxyphenyl)-5-[4-(trans-4-n-pentylcyclohexyl)phenyl]-1,3-dioxane* $A_{5\text{-}5}$

A mixture of compound 3_5 (1.0 g, 3.3 mmol), 6_5 (0.75 g, 3.3 mmol), dry toulene (50 ml) and *p*-toluenesulphonic acid (10 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%, 50 ml). The separated organic layer was washed with water (2 × 50 ml) and dried (Na_2SO_4). The solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C)/ethyl ether (20/1) as the eluant, to give pale yellow crystals which were recrystallized from petroleum ether (b.p. 60–90°C) twice to yield white needle crystals of compound $A_{5\text{-}5}$. Yield 0.8 g, 48%, m.p. 74.7°C, purity (HPLC) 99.3%. Elemental analysis: calculated (found) for $C_{32}H_{44}F_2O_3$ C 74.68 (74.51), H 8.62 (8.57%). IR (KBr) ν_{max}: 2928, 2870, 1641, 1517, 1487, 1398, 1319, 1294, 1141, 1082, 1030, 984, 824, 793 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.91 (6H, m, *J* 7.0 and 4.0), 0.97–1.90 (23H, m), 2.47 (1H, t, *J* 7.5), 3.35 (1H, m), 4.05 (4H, m, *J* 8.5 and 3.5), 4.35 (2H, t, *J* 6.9), 5.82 (1H, s), 6.79 (1H, m), 7.22 (4H, m), 7.54 (1H, m). MS *m*/*z*: 514 (M^+, 0.5%), 284, 256 (100%), 158, 143, 117, 91.

2.2.4. *2-(2,3-Difluoro-4-pentylphenyl)-5-[4-(trans-4-n-pentylcyclohexyl)phenyl]-1,3-dioxane* $\boldsymbol{B_{5\text{-}5}}$

The experimental procedure was the same as for the preparation of compound $\mathbf{A_{5\text{-}5}}$. The following quantities were used: compound $\mathbf{3_5}$ (0.31 g, 1.0 mmol), **8** (0.21 g, 1.0 mmol), dry toulene (50 ml) and *p*-toluenesulphonic acid (5 mg). Yield 0.2 g, 40%, m.p. 92.0°C, purity (HPLC) 99.1%. Elemental analysis: calculated (found) for $C_{32}H_{44}F_2O_2$ C 77.07 (76.95), H 8.90 (8.83%). IR (KBr) ν_{max}: 2924, 2852, 1641, 1516, 1473, 1404, 1286, 1144, 1113, 1016, 980, 899, 824 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.92 (6H, m, *J* 7.0 and 4.0), 1.01–1.89 (23H, m), 1.92 (2H, t, J 10.8), 2.49 (1H, t, *J* 7.5), 2.69 (2H, t, *J* 7.5), 3.39 (1H, m), 4.08 (2H, t, *J* 10.8), 4.38 (2H, m, *J* 6.6 and 4.5), 5.89 (1H, s), 7.04 (1H, m), 7.22 (4H, m), 7.35 (1H, m). MS *m*/*z*: 497 (M^+–1, 0.4%), 284, 256 (100%), 158, 143, 117, 91.

The other compounds in the **A** and **B** series were prepared following the same general procedures. All of the new target compounds had appropriate ^1H, IR and MS spectral data.

3. Results and discussion

Two series of liquid crystals containing 2,3-difluorophenyl and 1,3-dioxane units were synthesized. All of the compounds exhibit liquid crystalline behaviour. Table 1 and figures 1–5 show the phase sequences and transition temperatures for the novel liquid crystal series **A** and **B**.

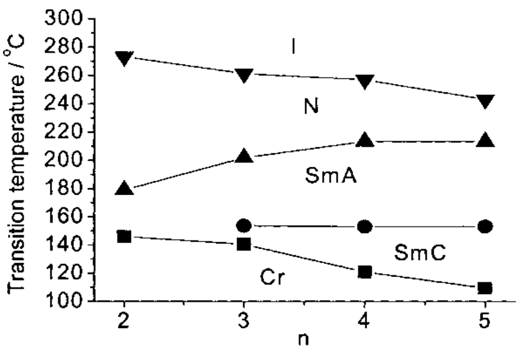


Figure 1. Plots of transition temperatures for series $\mathbf{A_{3-n}}$ ($m=3$).

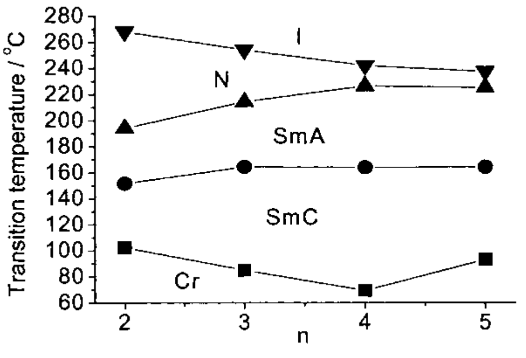


Figure 2. Plots of transition temperatures for series $\mathbf{A_{4-n}}$ ($m=4$).

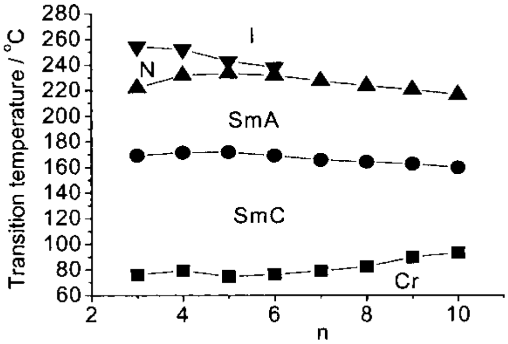


Figure 3. Plots of transition temperatures for series $\mathbf{A_{5-n}}$ ($m=5$).

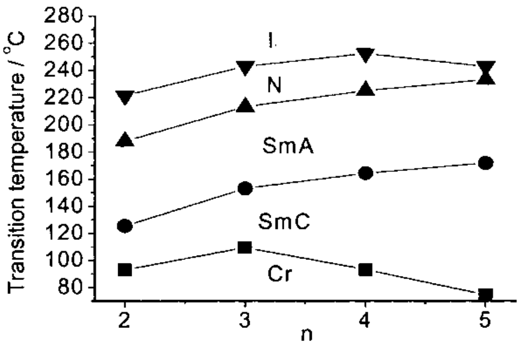


Figure 4. Plots of transition temperatures for series $\mathbf{A_{m-5}}$ ($n=5$).

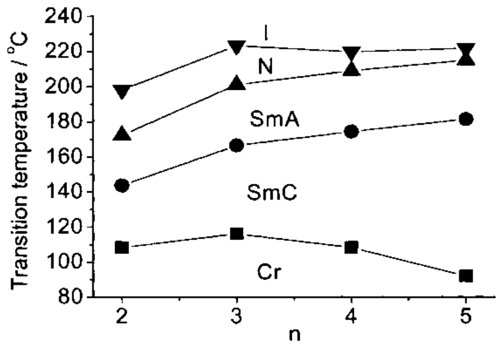


Figure 5. Plots of transition temperatures for series $\mathbf{B_{m-5}}$ ($n=5$).

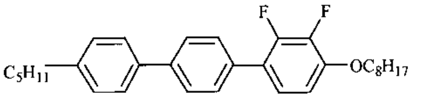
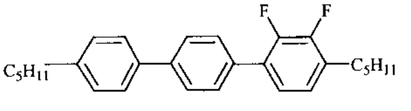
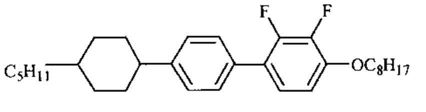
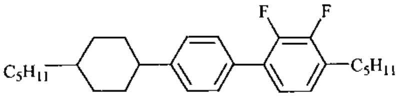
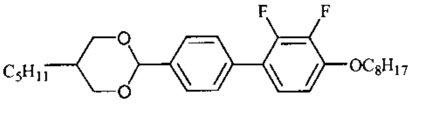
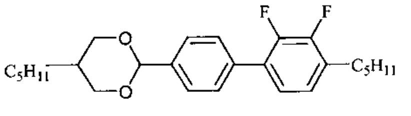
From table 1 and figures 1–5, a general trend is evident, namely, the overall effect of increasing the length of the terminal chain *L* or *R* is generally to decrease the temperature range of the nematic mesophase which, in some cases, is eliminated. This is due to the greater lateral intermolecular attractive forces and the smaller terminal intermolecular cohesive forces [19].

In series **A**, the clearing points decrease steadily as the alkoxy chain length (*n*) increases for each set of compounds. However, the melting point changes on increasing *n* are far more complex than the changes in the clearing point. The temperature range of the smectic A phase increases as *n* increases across each series, but with little variation for series $\mathbf{A}_{m\text{-}5}$. Compound $\mathbf{A}_{3\text{-}2}$ (with the shortest alkyl and alkoxy chains) is the shortest compound and is the exception in that it does not exhibit a smectic C phase; its smectic A phase temperature range is shorter than for any other homologue. Its nematic phase temperature range (94.3°C) is, however, somewhat broader than for any other homologue. These phenomena may be explained by the fact that $\mathbf{A}_{3\text{-}2}$ has the smallest length–breadth ratio in series **A** and therefore shows the smallest lateral intermolecular attractive forces but the largest terminal intermolecular cohesive forces. Compound $\mathbf{A}_{4\text{-}4}$ exhibits the lowest melting point (69.4°C) of these compounds, a very wide smectic C phase (93.6°C) and the phase sequence Cr–SmC–SmA–N–I. Thus it might be an excellent candidate for use in large, flat panel ferroelectric liquid crystal displays.

It is interesting that the phase behaviour of series $\mathbf{A}_{m\text{-}5}$ is very similar to that of $\mathbf{B}_{m\text{-}5}$. On increasing the length of the terminal alkyl chain (*m*) across each series, the temperatures of the melting (Cr–SmC) transition first increase, then decrease; compounds $\mathbf{A}_{3\text{-}5}$ and $\mathbf{B}_{3\text{-}5}$ have the highest melting points in their respective series. The SmC–SmA and SmA–N transition temperatures increase significantly across each series. Thus the temperature ranges of the smectic C phase increase markedly with an increase in the length of the terminal alkyl chain *m*, but the temperature ranges of the smectic A phase show little variation. With the increase of *m* across each series, the N–I transition temperatures first increase, then decrease or show little variation. This may be explained in terms of molecular alignment.

However, more detailed comparison of the transition temperatures of compounds $\mathbf{A}_{m\text{-}5}$ and $\mathbf{B}_{m\text{-}5}$ reveals that the $\mathbf{B}_{m\text{-}5}$ series has higher melting and lower clearing points than corresponding member of the $\mathbf{A}_{m\text{-}5}$ series. It appears that the ether oxygen significantly changes the liquid crystal transition temperatures. This may be the result of the decrease in molecular polarizability on

Table 2. Transition temperatures (°C) of previously studied materials for comparative purposes. Cr = crystal; SmC = smectic C phase; SmA = smectic A phase; N = nematic phase; I = isotropic liquid.

Compound	Structure	Cr		SmC		SmA		N		I	Ref.
9		●	93.5	●	144.0	●	148.0	●	159.0	●	[6]
10		●	81.0	●	115.5	●	131.5	●	142.0	●	[6]
11		●	53.5	●	57	●	125.5	●	142	●	[1]
12		●	33.0		—	●	96.5	●	123.0	●	[14]
13		●	62	●	85.8		—	●	133.9	●	[4]
14		●	65		—		—	●	119.6	●	[4]

reducing the dipole moment at the aromatic end of the molecule.

Four-ring liquid crystals containing 2,3-difluorophenyl and 1,3-dioxane units have not been reported previously. We have compared the transition temperatures and mesophase stability of these two series of compounds with those of similar three-ring liquid crystalline ferroelectric host materials described in the literature (table 2). It is easy to see that the clearing points (Sm/N to I) of series **A** and **B** are much higher as expected than those of the previously studied materials. This may be the result of the increase in the number of core rings in the molecular structure. Series **A** and **B** have much broader smectic C temperature ranges than those of the analogous three-ring compounds. This may be because the molecule possesses two sites of high electronic 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 dioxane ring. These two dipoles have promoted the smectic C phase stability. Moreover, as stated previously, series **A** and **B** compounds have higher clearing points. In conclusion, the mesophase stability of series **A** and **B** compounds is higher than that of the analogous three-ring compounds (table 2).

4. Conclusion

Two series of novel four-ring liquid crystals containing 2,3-difluorophenyl and 1,3-dioxane units were synthesized and characterized. Most of them show wide smectic C phases and the phase sequence Cr–SmC–SmA–N–I. The terminal alkoxy/alkyl groups have profound effects on the phase transition temperatures of these liquid crystals. These liquid crystal materials could find useful application in LC displays.

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