Mesophase behaviour of laterally di-fluoro-substituted four-ring compounds

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(Received 21 June 2015; accepted 20 August 2015)

Four new groups of the di-fluoro-substituted 4-(2′-(or 3′)-fluoro phenylazo)-2-(or 3′-fluoro phenylazo)-biphenyl benzoates (I–IV)n were prepared and investigated for their mesophase behaviour. An alkoxy group of variable chain length (n = 6, 10 and 14 carbons) is attached to the terminal phenylazo benzoate moiety, and two lateral fluoro substituents are attached individually with different orientations to the other two adjacent rings. The molecular structures of the prepared compounds were confirmed by Fourier transform infrared spectroscopy and 1H NMR spectroscopy. The study aims to investigate the steric effect of the spatial orientation and relative positions of the two lateral fluoro atoms on the mesomorphic properties in their pure states. The mesophase behaviour was investigated via differential scanning calorimetry and mesophases were identified by polarised light microscopy. The investigation shows that these compounds exhibit high enantiotropic mesophases (SmC and N) and broad mesophase temperature range. The type and stability of the mesophase depends on the length of the terminal alkoxy chain and the position the two fluoro substituents. A comparison between these investigated compounds with their corresponding three-ring analogues was discussed.

Keywords: lateral fluorine; mesophase behaviour; four-ring; azo/ester compounds

1. Introduction

In order to understand the relationship between molecular structures of mesogens and their mesomorphic properties, several azo/ester homologous series of calamatic liquid crystals have been reported and are often studied from the point of view of their interesting optical properties.[1,2] From these structural investigations, one can mention the ester orientation within the rigid core, the position of azo/ester groups, lateral substitutions, as well as the terminal chain length.[3–12] In a liquid crystal compound, lateral substitution makes molecules broad, thus playing an effective role in the mesogenic properties of the resulting derivatives. Lateral substituent in rigid core can destroy the molecular closed packing, reduce liquid crystal melting point, thereby improving the solubility of liquid crystal effectively.

Due to its smaller size (1.47 Å) compared to the hydrogen atom, lateral fluorine-substitution within the mesogenic core will have but relatively small steric effect, nevertheless, the fluorine atom protruding from the side of the molecules will disrupt the smectic molecular packing.[13,14] On the other hand, a fluoro substituent is of high polarity, bearing the highest electronegativity (3.98). Such a combination, of small size and high polarity, enables the fluoro substituents to play a key role in tailoring the important physical properties of liquid crystals, such as melting point, phase transition temperatures, mesophase morphology, dipole moment, dielectric anisotropy, spontaneous polarisation, tilt angle, pitch length, optical anisotropy, elastic constants and viscosity.[15–25] In addition, the strong C–F bond confers chemical stability onto the resulting fluoro-substituted compound. For instance, a terminal fluoro substitution into a calamatic mesogen tends to induce the formation of smectic phases.[26] A fluoro substituent can be located in many different positions of a liquid crystal molecule, including (1) a lateral position of the mesogenic core [27–31]; (2) a terminal position [32–34]; (3) within a terminal chain inducing a chiral centre [35]; and (4) as part of a linking group.[36,37]

In addition, the fluoro substituent has a low polarisability (5.57 × 10−25 cm2), which confers low intermolecular dispersion interactions. However, in a laterally substituted mesogen, the effect of fluoro substitution is strongly dependent on the location.

Keeping all these in view, we are going to prepare and investigate four new four-ring homologous series (I–IV)n attached via two azo and one ester central linkages. An alkoxy group of variable chain length (n = 6, 10 and 14 carbons) is attached to the terminal phenylazo benzoate moiety, and two lateral fluoro substituents are attached with different orientations to the other two adjacent rings in order to investigate the effect of the orientation and relative positions of the two lateral fluorine atoms on mesomorphism. The prepared derivatives will be compared with those previously investigated three-ring compounds (Vn–VIII)n.
N=N \text{OCO} \text{F} \text{N=N OR F} 

(I)

N=N \text{OCO} \text{F} \text{N=N OR F} 

(II)

N=N \text{OCO} \text{F} \text{N=N OR F} 

(III)

N=N \text{OCO} \text{OCnH}_{2n+1} \text{F} 

(IV)

N=N \text{OCO} \text{OCnH}_{2n+1} \text{F} 

(V)

N=N \text{OCO} \text{OCnH}_{2n+1} \text{F} 

(VI)

N=N \text{OCO} \text{OCnH}_{2n+1} \text{F} 

(VII)

N=N \text{OCO} \text{OCnH}_{2n+1} \text{F} 

(VIII)
2. Experimental
Chemicals were of very pure grades and purchased from the following companies: Buchs (Switzerland), Aldrich (Wisconsin, USA), E. Merck (Darmstadt, Germany), Alfa Aesar (Karlsruhe, Germany) and Acros (New Jersey, USA).

2.1. Preparation of materials
Compounds I<sub>n</sub>–IV<sub>n</sub> were prepared according to the following scheme:

2.1.1. Synthesis of the intermediate compounds (A)
Compounds 4-(2′-(or 3′-) fluoro phenylazo)-2-(or 3-)
fluoro phenol (A) were prepared according to the method described previously.[38] The 2- (or 3-) fluoro aniline (0.05 mole) was dissolved in dilute hydrochloric acid and cooled in ice-salt bath to 0°C. To the resulting solution, a cold aqueous solution of sodium nitrite was added drop-wise with stirring. The cold mixture was then added slowly to a cold 2-(or 3-) fluoro phenol (0.05 mole) in sodium hydroxide solution (1:1). The mixture was further stirred at room temperature for 1 h, acidified with dilute hydrochloric acid, and the solid product obtained was filtered and recrystallised twice from glacial acetic acid to give pure compounds, as indicated by thin-layer chromatography (TLC) analysis.

2.1.2. Synthesis of the intermediate compounds (B<sub>n</sub>)
4-n-Alkoxy phenylazo benzoic acids (B<sub>n</sub>) were prepared by the methods described previously.[39] Ethyl 4-amino benzoate (0.01 mole) was dissolved in concentrated hydrochloric acid (0.04 mole) and cooled in ice-salt bath to 0°C. To the resulting solution, a cold aqueous solution of sodium nitrite (0.03 mole) was added drop-wise with stirring. During the addition, the temperatures did not exceed 2°C. After complete addition, the cold mixture was added drop-wise to an ice-cold solution of 3-(or 2-) phenol (0.01 mole) in sodium hydroxide (0.03 mole). The mixture was further stirred at 0°C for 1 h then acidified with dilute hydrochloric acid. The solid separated was filtered...
and crystallised twice from ethanol. The obtained product of 4-hydroxyphenylazo benzoate (0.005 mole) was dissolved in alcoholic KOH (0.1 mole) and slightly excess amount of 1-bromo-

alkane (0.06 mole) was added drop-wise while stirring. Stirring was continued at room temperature for two days. The solid separated was filtered off, the solution evaporated and the residue crystallised twice from ethanol.

2.1.3. Synthesis of 4-((2′-(or 3′)-fluoro phenylazo)-2-(or 3′)-fluoro phenyl-4′-alkoxyphenylazo benzoates, In-IVn

Molar equivalents of the 4-(2′(or 3′)-fluoro phenylazo)-2-(or 3′)-fluoro phenol (A) and 4-n-alkoxyphenylazo benzoic acid (Bn) (0.01 mole each) were dissolved in 25 ml dry methylene chloride. To the resulting mixture, N, N′-dicyclohexyl carbodiimide (DCC, 0.02 mole) and few crystals of 4-(dimethylamino)-pyridine (DMAP), as catalyst, were added and the solution left to stand for 72 h at room temperature with stirring. The solid separated was then filtered off and the solution evaporated. The solid residue obtained was recrystallised twice from acetic acid and twice from ethanol to give TLC-pure products.

Since almost identical infrared and $1^H$ NMR spectra were observed for all of the members of the four homologous series (In-IVn), Fourier transform infrared spectroscopy (FTIR), $1^H$ NMR spectral data (S1 and S2, supplemental information) and elemental analyses of 4-(3-fluoro phenylazo)-2-(or 3′)-fluoro phenol (A) and S2, supplemental information) and elemental analyses of 4-(3-fluoro phenylazo)-2-(or 3′)-fluoro phenylazo benzoates (IV6), as an example, are given below:

**FTIR (KBr, $v_{\text{max}}$ cm$^{-1}$):** 3101 and 3077 (C–H aromatic), 2850–2924 (C–H alkoxy group), 1750 (–COO–), 1597 (–C=C– aromatic), 1650 (–N=N– group), 1250–1097 (–C–O–C– of alkoxy group), 1139 (–C–O– of ester group), 1068, 1097 (–C–F).

$1^H$ NMR (300 MHz, CDCl$_3$) δ ppm: 0.87–0.92 (t, 3H, –CH$_3$), 1.21–1.56 (m, 6H, –O–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_2$–), 1.85 (m, 2H, –O–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_2$–), 4.08 (t, 2H, –O–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_2$–), 7.03–8.36 (m, 15H, Ar–H).

Elemental analyses: Found (Calc.) C, 68.51 (68.62); H, 5.13 (5.20); N, 10.40 (10.33); F, 6.93 (7.00).

2.2. Measurements

Infrared spectra were recorded using Perkin-Elmer B25 spectrophotometer (Perkin-Elmer, Inc., Shelton, CT USA) by the KBr pellet technique. $1^H$-NMR spectra were performed using a Varian EM 350L 400 MHz spectrometer (Oxford, UK) using tetramethylsilane as internal standard and CDCl$_3$ as solvent; the chemical shift values were recorded as δ (ppm units).

Different scanning calorimetry (DSC) was performed using a Shimadzu, model DSC-60 (Shimadzu, Japan). The instrument was calibrated using the melting temperature and enthalpy of indium and lead standards. DSC investigation was carried out for small samples (2–3 mg) placed in sealed aluminium pans. All measurements were achieved under heating rate of 10°C/min in an inert atmosphere of nitrogen gas (20 ml/min).

Transition temperatures were checked and types of mesophases identified, for all compounds prepared, with a standard polarised light microscope (PLM, Wild, Germany) attached to a home-made hot stage.

The purity of the prepared samples was checked with TLC using TLC sheets coated with silica gel (E Merck), and CH$_2$Cl$_2$/CH$_3$OH (9:1) as eluent, whereby only one spot was detected by a UV lamp.

3. Results and discussion

3.1. Confirmation of molecular structures

Infrared spectra, mass spectra and elemental analyses for compounds investigated were consistent with the structures assigned. $1^H$-NMR data showed the expected integrated aliphatic to aromatic proton ratios in all compounds investigated.

3.2. Mesophase behaviour of compounds

The DSC scans carried out on these compounds show transitions at temperatures which are in agreement with those obtained by optical microscopy. Typical DSC curves of homologues I10–IV10 are depicted in Figure 1. The phase transition temperatures and associated enthalpy (Δ$H$) and entropy change, expressed as the dimensionless quantity, ΔS/R, of the prepared compounds (In-IVn) are given in Table 1. As can be seen from Table 1, within each homologous series, the first three homologous series investigated showed no systematic change in their melting points upon increase of the terminal alkoxy chain length (n). With respect to their mesophase behaviour, all compounds showed enantiotropic SmC and N mesophases accompanied with broad mesophase ranges. The type of phase or phases observed for any individual compound depends mainly upon the location and/or orientation of the two fluoro substituents. Thus, when the two fluorine atoms are located, in separate rings, pointing towards the core of the
molecule (i.e., both in position 2, as in the homologues \( I_n \)), the nematic phase is dominant, covering the whole mesophase range. Conversely, when the two fluoro substituents are located into two separate rings directing away from the core (i.e., both in position 3, as in the homologues \( IV_n \)), all homologues except \( IV_6 \) are dimorphic, exhibiting the nematic and SmC phases. For the homologues \( II_n \), where one of the fluoro substituent is located in the terminal ring pointing towards the core, while the other is located in the inner ring pointing away from the core (i.e., in positions 2 and 3, respectively), the lower homologue \( II_6 \) is purely nematic, while the higher ones, \( II_{10} \) and \( II_{14} \), are dimorphic, exhibiting SmC and nematic mesophases. Similarly, for the homologous series \( III_n \), where the location of the two fluoro substituents is the reverse of series \( II_n \) (i.e., they are located in positions 3 and 2, respectively), the mesophase behaviour parallels that of series \( II_n \).

Representative examples of microscopic images of the mesophases are shown in Figure 2. Compound \( IV_6 \) exhibited a nematic phase with the characteristic Schlieren texture (Figure 2a). While compound \( II_{14} \) exhibits both SmC and nematic phases (Figure 2b and c).

Table 1. Phase transition temperatures (°C), enthalpy of transitions (\( \Delta H \), kJ/mol) and transition entropies (\( \Delta S/R \)), for the homologous series \( I_n–IV_n \).

| System | \( T_{Cr-C} \) | \( \Delta H_{Cr-C} \) | \( T_{Cr-N} \) | \( \Delta H_{Cr-N} \) | \( T_{C-N} \) | \( \Delta H_{C-N} \) | \( \Delta S_{C-N}/R \) | \( T_{N-I} \) | \( \Delta H_{N-I} \) | \( \Delta S_{N-I}/R \) |
|--------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| \( I_6 \) | – | – | 155.2 | 29.1 | – | – | – | 283.6 | 1.1 | 0.24 |
| \( II_6 \) | – | – | 141.5 | 35.7 | – | – | – | 278.5 | 1.3 | 0.29 |
| \( III_6 \) | – | – | 143.7 | 29.9 | – | – | – | 287.8 | 1.4 | 0.30 |
| \( IV_6 \) | – | – | 150.5 | 36.3 | – | – | – | 291.0 | 1.2 | 0.25 |
| \( I_{10} \) | – | – | 121.0 | 49.1 | – | – | – | 246.4 | 2.2 | 0.50 |
| \( II_{10} \) | 119.6 | 44.6 | – | – | 194.9 | 1.9 | 0.49 | 250.7 | 1.5 | 0.36 |
| \( III_{10} \) | 120.0 | 51.2 | – | – | 186.5 | 1.4 | 0.36 | 253.0 | 1.1 | 0.25 |
| \( IV_{10} \) | 130.1 | 43.0 | – | – | 247.0 | 1.9 | 0.44 | 260.1 | 0.8 | 0.18 |
| \( I_{14} \) | – | – | 123.5 | 50.0 | – | – | – | 219.3 | 0.8 | 0.19 |
| \( II_{14} \) | 110.3 | 33.5 | – | – | 192.4 | 0.7 | 0.18 | 224.5 | 0.6 | 0.14 |
| \( III_{14} \) | 118.6 | 59.5 | – | – | 195.9 | 0.9 | 0.23 | 227.3 | 0.7 | 0.17 |
| \( IV_{14} \) | 110.4 | 38.3 | – | – | 238.9 | 3.9 | 0.72 | 257.4 | 1.2 | 0.28 |

Notes: \( Cr-C \) denotes transition from solid to the SmC phase.
\( Cr-N \) denotes transition from solid to the N phase.
\( C-N \) denotes transition from SmC to the N phase.
\( N-I \) denotes transition from nematic to the isotropic phase.

Figure 2. (colour online) Photos, under polarised light microscope, for (a) the N phase of \( IV_6 \) at 209°C, (b) the SmC phase of \( III_{14} \) at 157°C, and (c) the N phase of \( III_{14} \) at 221°C.
The entropies ($\Delta S_{C-N}/R$) of the SmC–nematic and nematic–isotropic ($\Delta S_{N-I}/R$) transitions were determined for all compounds (In–IVn), and the results are appended to Table 1. As seen in Table 1, all entropies of transitions, independent of the length of the alkoxy chain ($n$) or the position of the fluorine atom, showed to have lower $\Delta S_{N-I}/R$ values than those of the corresponding $\Delta S_{C-N}/R$. The lower $\Delta S_{N-I}/R$ values are presumably, in part, a reflection of the increase in biaxiality of the mesogenic group, which resulted in the flexible terminal alkoxy chain being less strongly anchored at its end, resulting in a decrease in the conformational entropy. Similarly, reduced values of $\Delta S_{N-I}/R$ have been observed for liquid crystal dimers either containing A branched terminal chain or for dimers in which the biaxiality of the mesogenic groups has been increased.[40–43]

3.3. Effect of incorporating an extra phenylazo moiety

It may be interesting to investigate the mesophase behaviour, taken as the stability of the mesophase (isotropisation temperature, $T_C$) and the type of mesophase, in the present four-ring series (In–IVn) compared with the previously investigated three-ring homologues (Vn–VIIIn), in which the 4-$n$-alkoxy phenylazo benzoic acid is replaced by the simpler 4-alkoxy benzoic acid.[38] In this way, an extra phenylazo moiety is inserted in the newly prepared homologues (In–IVn). Figure 3 represents the $T_C$–dependencies on the alkoxy chain-length ($n$) of the eight types of molecules (In–VIII).

As can be seen from Figure 3, comparing compounds of series In with their analogously substituted analogues in series Vn revealed that the introduction of an extra phenylazo group in the newly investigated series (In) has led to higher mesophase stability and all their homologues are nematicogenic. Conversely, the previously investigated homologues (Vn) are of lower stability and showed the N phase in the lower homologues ($n < 16$), whereas the SmC phases appear at higher homologues.[38] With respect to series IIln, when compared with their analogues in VIln, it can be shown that the compounds (IIln) are dimorphic, possessing both SmC and N mesophases, except the lowest homologue ($n = 6$) which is purely nematicogenic; whereas the previously investigated homologues (VIIln) are of lower stability and showed the nematic (for $n = 8$ and 10) and the smectic C phases (for $n > 10$). It can also be observed from Figure 3, when comparing compounds IIIln and VIIln, that all homologues are nematicogenic but VIIln homologues are of lower stability than the newly prepared IIIln. Finally, the series VIIln and VIIIln are same as VIIln and VIIIln homologues.

![Figure 3](image-url) (color online) Alkoxy chain length dependency of compounds In–IVn (○, N), and series Vn–VIIIln (□, N and ■, SmC).
4. Conclusion

Four laterally di-flouro-substituted homologous series (Ia–Iv) were prepared having the molecular formula 4-(2′-(or 3′)-fluoro phenylazo)-2-(or 3-) fluoro phenyl-4″-alkoxyphenyazo benzoates. The compounds prepared were investigated for their mesophase behaviour in pure states. The alkoxy chain lengths (n) vary between 6, 10 and 14 carbons. The study revealed that:

1. All compounds showed enantiotropic mesophases (SmC and N) associated with broad mesophase ranges.
2. The type of mesophase observed for any individual compound depends mainly upon the location and/or orientation of the two fluoro substituents.
3. As expected, the entropy associated with the smectic transition (ΔS_C−N/R) is greater than that associated with the nematic transition (ΔS_N−I/R). Both types of entropies vary irregularly, as usual, with the alkoxy chain length n.
4. The stability of the mesophase (T_C) of the four-ring series was found to be higher than that of their corresponding three-ring analogues.

Disclosure statement

No potential conflict of interest was reported by the authors.

Supplemental data

Supplemental data for this article can be accessed here.

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