

SYNTHESIS AND MESOMORPHIC PROPERTIES OF 4,4'-BIS[*F*-ALKYLETHYL-3-THIOPROPOXY]BIPHENYL

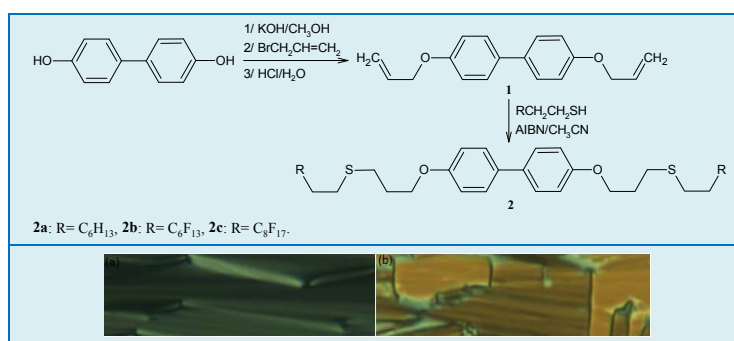
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Received May 13, 2018

The synthesis and characterization of a series of new symmetrical 4,4'-biphenyl derivatives carrying a hydro or perfluoroalkyl chain via, ethyl-3-thiopropoxy linker are described. The mesomorphic properties were studied using differential scanning calorimetry and polarizing optical microscopy techniques. It has been found that compounds having longer fluoroalkyl chain exhibit higher transition temperatures. Only compounds with fluoroalkyl segment exhibit smectic phases.



INTRODUCTION

Compounds containing biphenyl and alkyl chain, show interesting mesomorphic behaviour depending on the length and structure of the linking groups. Perfluorinated groups used to enhance the liquid crystal character of biphenyl molecules were localized in the side chain.^{1,2} The mesomorphic property of *F*-alkylated biphenyl derivatives is strongly influenced by the nature of the spacer separating the perfluorinated tail and the biphenyl rigid core.³ Generally, liquid crystals incorporating perfluoroalkyl chains are known to show smectic properties.⁴⁻⁷ Even very simple molecules, for example di-block molecules combining a hydrocarbon and a fluorocarbon chain, form smectic liquid-crystalline phases.^{8,9}

In previous papers,¹⁰ we have reported the synthesis and mesomorphic behavior of a series of

rod-shaped biphenyl benzoate liquid crystals carrying a perfluorinated segment with three uncommon types of flexible spacer, namely 2-iodopropoxy, (*E*)-2-propenyloxy and ethyl-3-thiopropoxy. The mesomorphic behavior shows low- melting and high-clearing smectic mesophases.

In this paper, we will describe the synthesis and the mesomorphic properties of a new 4,4'-biphenyl derivatives containing hydro or perfluoroalkyl chains linked to biphenyl rigid core by ethyl-3-thiopropoxy.

RESULTS AND DISCUSSION

The synthesis of 4,4'-bis[*F*-alkylethyl-3-thiopropoxy]biphenyl **2** were performed in two steps (Scheme 1). In the first step, the bisallyloxybiphenyl **1** was obtained from the reaction of biphenyl 4,4'-diol with two equivalent of allylbromide in presence

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of potassium hydroxide. In the second step, the *F*-alkyl chain was grafted onto the allelic double bonds of biphenyl derivative prepared **1**, by radical addition reaction of *F*-alkylethane thiol, initiated by azo-bis-isobutyronitrile (AIBN).^{11,12} The resulting compound was exclusively the product of bis-1,2-addition (Scheme 1). All compounds were obtained in good purity according to ¹H, ¹³C and ¹⁹F NMR, FTIR, and mass spectra.

The mesomorphic properties of compounds **2a-c** were studied by polarization microscopy (POM) and differential scanning calorimetry (DSC) with heating and cooling rates of 10 °Cmin⁻¹. The texture of the mesophase was identified by microscopy studies. The phase transition temperatures as well as the phase transition enthalpy changes are compiled in Table 1.

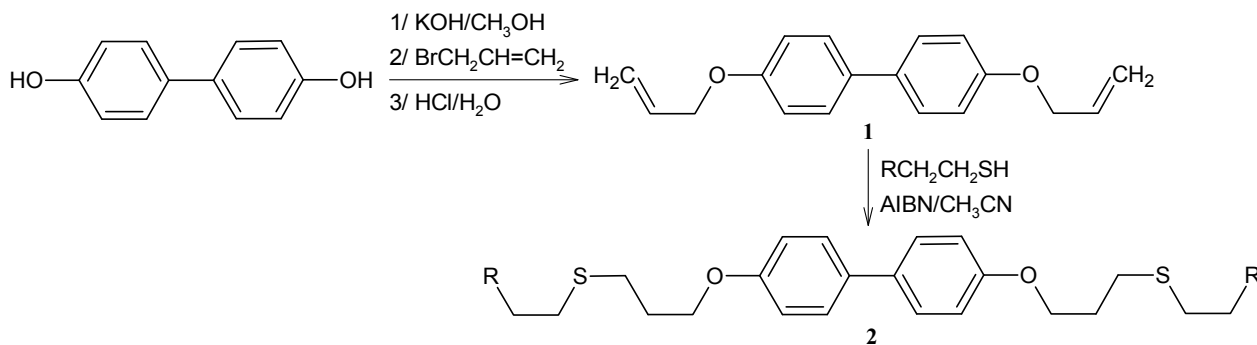
It is noteworthy to mention that the temperature *T_i* leading to the isotropic phase of the fluorinated compound **2b** are higher than those of the hydrocarbon analogues **2a**¹³⁻¹⁵ and increases as fluoroalkyl chain length become longer in both compounds **2b,c**.^{7,14,15} On the other hand, the fluorinated compound **2b** has a significant enhanced stability of the mesophases in comparison to the hydrocarbon analogue **2a**. This increased mesophase stability should mainly be

due to the increased intramolecular polarity contrast on replacing the alkyl chains by the more lipophilic semifluorinated chains.⁷

The DSC thermograms of the synthesized compounds **2a-c** are shown in Figure 1. Three peaks were observed on heating from room temperature to isotropic liquid or on cooling from the isotropic phase to crystalline state.

Compound **2b** shows two distinct mesophases. On cooling from the isotropic liquid state, the first birefringent texture of a smectic A (SmA) mesophase was clearly identified by characteristic focal-conic defects (Figure 2a). On further cooling, the focal-conic fans of the SmA phase organized within the layers. This is characteristic of the smectic E phase (Figure 2b). Compound **2c**, which has a longer fluoroalkyl chain than **2b** has similar textures observed for these compound.

The hydrocarbon derivative **2a** does not have an observable liquid crystal character as compared to the fluorinated homologue **2b**. Nevertheless, it is worth noting that this result is not surprising when we examine the literature on biphenyl derivatives.¹⁶⁻¹⁸ Thermal transitions *T_{i1}*, *T_{i2}* observed by DSC of compound **2a** could be associated with solid–solid transitions or possibly with crystal–crystal transitions.¹⁹



2a: R= C₆H₁₃, **2b**: R= C₆F₁₃, **2c**: R= C₈F₁₇.

Scheme 1 – Synthesis of 4,4'-bis[F-alkylethyl-3-thiopropoxy]biphenyl **2**.

Table 1

Transition temperature and corresponding enthalpy changes of 4,4'-biphenyl derivatives **2**

Compound	Heating (H)		Cooling (C)		<i>T_i^c</i> (°C)
	<i>T_i^a</i> (°C)	ΔH_i^b (kJ.mol ⁻¹)	<i>T_i</i> (°C)	ΔH_i (kJ.mol ⁻¹)	<i>T_{ic}</i> (°C)
2a	69.1	2.36	87.9	-4.08	108.7
-	88.8	4.17	67.9	-2.28	107.8
2b	106.9	3.01	129.9	-10.76	143.1
-	130.8	10.98	105.8	-2.92	142.9
2c	134.9	5.46	157.9	-17.28	171.1
-	159.1	17.54	134.1	-5.32	169.9

a: Transition temperature, b: enthalpy change, c: isotropic temperature.

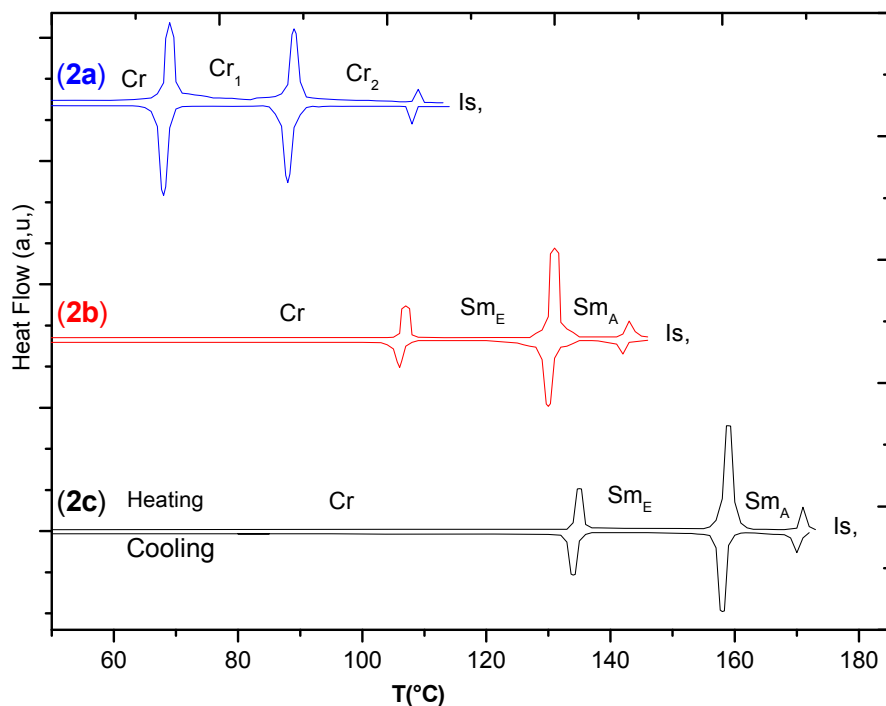


Fig. 1 – DSC thermograms of **2a-2c** during heating and cooling cycles at $10\text{ }^{\circ}\text{Cmin}^{-1}$.

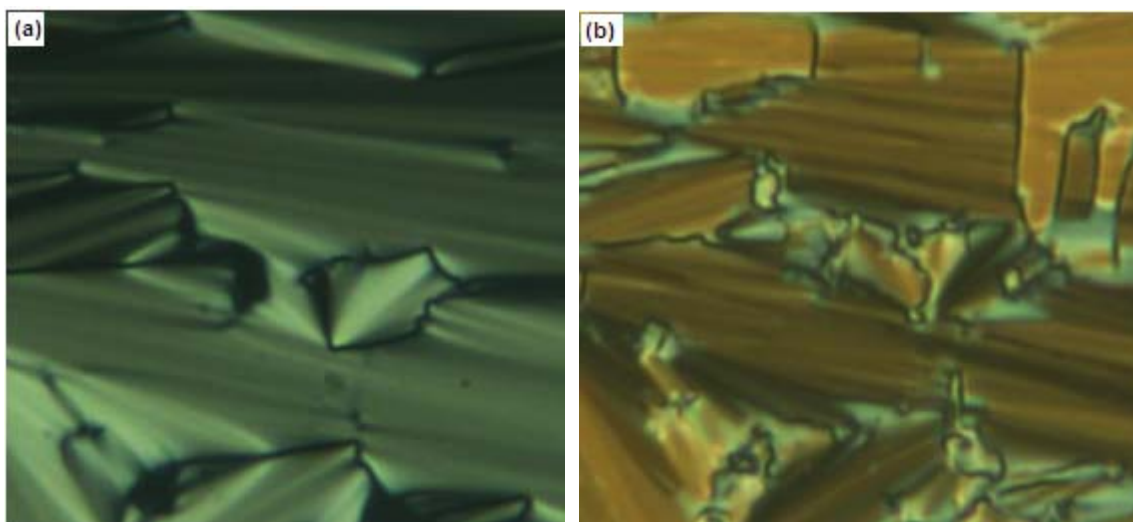


Fig. 2 – Optical polarizing micrograph of **2b**, on cooling from the isotropic phase: (a) SmA phase at $133\text{ }^{\circ}\text{C}$, (b) SmE phase at $105\text{ }^{\circ}\text{C}$.

EXPERIMENTAL

Materials and characterisation

All chemicals were purchased from Aldrich or Acros and used as such unless otherwise specified. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker AC 300 at 300, 75 and 282 MHz spectrometers, respectively. Me_4Si and CFCl_3 were used as internal references, coupling constant are reported in hertz. The IR spectra were recorded on a Bruker IFS 66 V/S spectrometer. HRMS (EI) experiments were performed on Bruker spectrometers at the Mass Spectrometry. Differential scanning calorimetry (DSC) was performed on a Metler DSC-30 instrument. Thermograms were recorded at

$10\text{ }^{\circ}\text{Cmin}^{-1}$ heating/cooling scan rate. Texture observation was performed using a polarizing optical microscope (Olympus BX51) equipped with digital CCD camera.

Synthetic procedures

Synthesis of diallyloxybiphenyl 1

A mixture of 4,4'-dihydroxybiphenyl (7.42 g, 40 mmol) and potassium hydroxide (4.40 g, 80 mmol) in dry methanol (100 mL) was heated at $65\text{ }^{\circ}\text{C}$ and stirred until complete dissolution. Then, allyl bromide (7.15 g, 80 mmol) was slowly added and the mixture was refluxed for 24 h. The resulting suspension containing KBr was filtered and methanol was removed under reduced pressure. Diethyl ether (100 mL) and

an aqueous solution of 5% HCl (100 mL) were added to the crude residue. After phase separation and distillation of diethyl ether, the product was recrystallized from ethanol.

Preparation of compounds 2: general procedure

In a 25 mL round bottomed flask was placed under nitrogen atmosphere a mixture of 4,4'-bis(allyloxy)biphenyl (0.53 g, 2 mmol), *F*-alkylethyl sulfanyl (5 mmol), AIBN (0.13 g, 0.8 mmol) and 2 mL of dry CH₃CN. The mixture was then stirred at 83°C for 12 h. After cooling to room temperature, the solvent was removed under vacuum and the obtained compound was purified on a column chromatography (silicagel, ethyl acetate/hexane: 1/3).

(2a): Yield 87%, IR (cm⁻¹) ν_{C-H} = 2858, ν_{C-Arom} = 2939, ν_{C=C} = 1510, ¹H NMR (CDCl₃) δ(ppm) 0.80 (t, 6H, 2SCH₂CH₂(CH₂)₅CH₃), ³J_{HH} = 5.74 Hz), 1.19 (m, 20H, 2SCH₂CH₂(CH₂)₅CH₃), 1.52 (m, 4H, 2SCH₂CH₂(CH₂)₅CH₃), 2.01 (t, 4H, 2SCH₂CH₂(CH₂)₅CH₃), ³J_{HH} = 5.74 Hz), 1.54 (m, 4H, 2OCH₂CH₂CH₂S), 2.61 (t, 4H, 2 OCH₂CH₂CH₂S, ³J_{HH} = 5.74 Hz), 4.01 (t, 4H, 2OCH₂CH₂CH₂S, ³J_{HH} = 5.74 Hz), 6.98-7.49 (2d, 8H, H_{arom}, ³J_{HH} = 8.61 Hz), ¹³C NMR (CDCl₃) δ(ppm) 14.14 (s, 2C, 2SCH₂CH₂(CH₂)₄CH₂CH₃), 22.68 (s, 2C, 2SCH₂CH₂(CH₂)₄CH₂CH₃), 28.60, 28.89, 29.05, 29.24 (4s, 8C, 2SCH₂CH₂(CH₂)₄CH₂CH₃), 29.28 (s, 2C, 2SCH₂CH₂(CH₂)₄CH₂CH₃), 31.76, 30.06 (2s, 2C, 2OCH₂CH₂CH₂S), 31.57, 31.76 (2s, 2C, 2CH₂CH₂SCH₂CH₂S), 66.20 (s, 2C, 2OCH₂CH₂CH₂S), 114.76, 127.78, 133.48, 158.00 (4s, 12C, C_{arom}), HRMS (ESI) calculated for: (C₃₄H₅₄O₂S₂Na)⁺: 581.9105, found: 581.9108.

(2b): Yield 85%, IR (cm⁻¹) ν_{C-F} = 1143, ν_{C-Arom} = 1513, ¹H NMR (CDCl₃) δ(ppm) 2.51 (m, 4H, 2SCH₂CH₂CF₂), 2.75 (t, 4H, 2SCH₂CH₂CF₂), ³J_{HH} = 2.87 Hz), 1.95 (m, 4H, 2OCH₂CH₂CH₂S), 2.72 (t, 4H, 2 OCH₂CH₂CH₂S, ³J_{HH} = 2.87 Hz), 4.02 (t, 4H, 2OCH₂CH₂CH₂S, ³J_{HH} = 5.74 Hz), 6.88-7.40 (2d, 8H, H_{arom}, ³J_{HH} = 8.61 Hz), ¹³C NMR (CDCl₃) 30.51 (t, 2C, 2SCH₂CH₂CF₂), ³J_{CF} = 22.03 Hz), 30.19 (s, 2C, 2OCH₂CH₂CH₂S), 31.56, 31.74 (2s, 2C, 2CH₂CH₂SCH₂CH₂CF₂), 66.24 (s, 2C, 2OCH₂CH₂CH₂S), 114.71, 127.73, 133.44, 157.96 (4s, 12C, C_{arom}), ¹⁹F NMR (CFCl₃) δ(ppm) -81.69 (m, 6F, 2CF₃), -114.47 (m, 4F, 2CF_{2a}), -122.81 (m, 4F, 2CF_{2β}), -123.80 (m, 4F, 2CF_{2γ}), -124.53 (m, 4F, 2CF_{2δ}), -127.12 (m, 4F, 2CF_{2α}), HRMS (ESI) calculated for: (C₃₄H₂₈F₂₆O₂S₂Na)⁺: 1049.6626, found: 1049.6621.

(2c): Yield 82%, IR (cm⁻¹) ν_{C-F} = 1144, ν_{C-Arom} = 1505, ¹H NMR (CDCl₃) δ(ppm) 2.50 (m, 4H, 2SCH₂CH₂CF₂), 2.74 (t, 4H, 2SCH₂CH₂CF₂), ³J_{HH} = 2.87 Hz), 2.71 (t, 4H, 2OCH₂CH₂CH₂S, ³J_{HH} = 2.87 Hz), 1.94 (m, 4H, 2OCH₂CH₂CH₂S), 4.01 (t, 4H, 2OCH₂CH₂CH₂S, ³J_{HH} = 5.74 Hz), 6.87-7.39 (2d, 8H, H_{arom}, ³J_{HH} = 8.61 Hz), ¹³C NMR (CDCl₃) δ(ppm) 30.02 (s, 2C, 2OCH₂CH₂CH₂S), 31.39 (s, 2C, 2OCH₂CH₂CH₂S), 30.49 (t, 2C, 2SCH₂CH₂CF₂), ³J_{CF} = 22.03 Hz), 31.86 (s, 2C, 2SCH₂CH₂CF₂), 66.22 (s, 2C, 2OCH₂CH₂CH₂S), 114.78, 127.57, 133.63, 157.92 (4s, 12C, C_{arom}), ¹⁹F NMR (CFCl₃) δ(ppm) -81.89 (m, 6F, 2CF₃), -114.47 (m, 4F, 2CF_{2a}), -122.60 (m, 4F, 2CF_{2β}), -122.89 (m, 8F, 4CF_{2γ}), -123.61 (m, 4F, 2CF_{2δ}), -124.47 (m, 4F, 2CF_{2ε}), -

127.02 (m, 4F, 2CF_{2α}), HRMS (ESI) calculated for: (C₃₈H₂₈F₃₄O₂S₂Na)⁺: 1249.6926, found: 1249.6922.

CONCLUSION

A series of 4,4'-biphenyl derivatives carrying a perfluorinated segment via ethyl-3-thiopropoxy linker has been synthesized and characterized. Thermotropic phase behaviors of these compounds have been investigated by DSC and POM. The obtained results show that the transition temperatures increases with the increasing of the fluoroalkyl chain length. Compounds having a perfluoroalkyl chains display a smectic phase.

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