Journal of Fluorine Chemistry 197 (2017) 15–23

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Synthesis and mesomorphic properties of liquid crystals containing a perfluorinated segment via different linkers

Samir Marzouk[a,b,c], Ali Khalfallah[b], Benoît Heinrich[a], Jamel Eddine Khiari[c], Abdelkader Kriaa[b], Stéphane Méry[a,*]

[a] Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504, 23 Rue de Loess, BP43, 67034 Strasbourg Cedex, France
[b] Laboratoire de Chimie Organique Moléculaire, 5 avenue Taha Hussien, 1008, ENSIT, Tunis, Tunisia
[c] Laboratoire de Chimie organique et Analytique, Institut Supérieur de Formation Continue, 2000 Bardo, Tunis, Tunisia

ARTICLE INFO

Article history:
Received 1 December 2016
Received in revised form 1 February 2017
Accepted 20 February 2017
Available online 22 February 2017

Keywords:
Liquid crystal
Mesomorphe
Mesophase
Smectic
Dehydrohalogenation
Dehydroiodination
Hemi-fluorinated
Perfluorinated
Linker
Spacer
Isomer

ABSTRACT

This study presents the synthesis and mesomorphic properties of a series of biphenyl benzoate liquid crystals carrying a perfluorinated segment, via three uncommon flexible linkers. In particular, a (*E*)-2-propenyloxy linker was used which was issued from an elegant regioselective dehydrohalogenation reaction. The remarkable microsegregation effect of the perfluorinated segment, led to the formation of highly stable untilted smectic mesophases. For all mesophases, the molecular packing corresponds to a monolayer arrangement of the mesogenic parts and a partial intercalation of the perfluorinated chains, measured by a intercalation ratio parameter τ_F. Geometrical calculations based on Xrays data led to τ_F comprised between 1.48 and 1.68 depending of the mesophase and temperature.

Introduction

Fluorinated liquid crystals have been intensively studied as early as in the 60's, because of their interest in liquid crystal displays, in particular [1–4]. Indeed, the presence of fluorine substituent in mesogenic structures has considerable influence on many properties such as phase transitions temperatures, phase structures, dipole moment, dielectric anisotropy, optical anisotropy, elastic constant and viscosity [2–9]. Fluorination can be located in various ways in the rigid aromatic moiety, the lateral chains or else, in the linking groups [6,9]. When present as perfluorinated or semiperfluorinated alkyl chains, specific organization properties take place that essentially arise from a combination of microphase separation and steric effects [8,9]. Actually, perfluorinated alkane segments are strongly not miscible with both aromatic and aliphatics, and easily tend to microsegregate from them [10]. Also, perfluorinated segments have larger molecular volume and reduced flexibility as compared to linear alkyl chains, that impact on molecular organization. For these reasons, fascinating liquid crystal organizations could be obtained on various and unusual types of molecular structures by simple insertion/substitution of perfluorinated segment(s) [9–15].

A number of liquid crystals carrying a perfluoroalkane segment have already been investigated and some general trends could be drawn and reviewed [8,9]. With rod-like mesogens for instance, F. Guittard evidenced the importance to decouple the perfluorinated segment to the rigid core by a short flexible spacer to allow molecular organization [8]. Pushing the limits of segregation on sterically hindered swallow-tailed calamitic systems, Lose et al. observed frustrated smectic phase ultimately leading to the formation of columnar mesophase [16]. Tschierske et al. also reported the stabilization of columnar phases on ("bolaamphiphilic") rod-shaped mesogens with laterally attached perfluorinated chain [13]. Finally, playing with block sequence of aromatic moieties, aliphatic chains and perfluorinated segments, Tournilhac et al. could obtain ferroelectric liquid crystals from achiral

* Corresponding author.
E-mail address: stephane.mery@ipcms.unistra.fr (S. Méry).

http://dx.doi.org/10.1016/j.jfluchem.2017.02.006
0022-1139/

molecules [17]. The presence of partially fluorinated chain in the molecules enables to obtain also high tilted and orthoconic antiferroelectrics [18,19].

In this work, we aim at finely studying the mesomorphic properties of a series of rod-shaped biphenyl benzoate liquid crystals carrying a perfluorinated segment. This series was chosen for it allows a comparison with its fully hydrogenated counterparts, which are poorly mesogenic and only exhibit a nematic phase on a very narrow temperature range [20]. More specifically, the perfluorinated segments were of two different lengths (C_6F_{13}— and C_8F_{17}—) were connected to the rigid core via three uncommon types of flexible spacer, namely 2-iodopropyloxy, (*E*)-2-propenyloxy and ethyl-3-thiopropoxy. Note that the spacer (*E*)-2-propenyloxy was prepared essentially in its *E* isomer from a highly regioselective dehalogenation reaction (Fig. 1).

2. Results and discussions

2.1. Synthesis

The synthetic procedure for the preparation of biphenyl benzoate series carrying a perfluorinated chain (**3a,b**, **4a,b** and **5a,b**) are depicted in Scheme 1. The starting compound, *i.e.* 4-allyloxy-4′-hydroxybiphenyl **1** was prepared from the reaction of biphenyl 4,4′-diol with allylbromide in presence of K_2CO_3. This compound was reacted with benzoyl chloride in triethylamine to afford the key compound 4′-allyloxybiphenyl-4-yl benzoate **2**. The latter was then used for the preparation of the three series of liquid crystals. The first series having a perfluorinated chain connected to the 2-iodopropyloxy spacer (**3a**,**b**) was prepared by radical addition (AIBN) of perfluoro 1-iodohexane and perfluoro 1-iodooctane in 1,2-dichloroethane, giving respectively the compounds **3a** and **3b** [21–23]. Subsequent dehydroiodination of compounds **3a**,**b** with sterically hindered DBU base furnished the olefins **4a,b** as the second series, essentially as the *E* isomer [22–24]. Regioisomers *E* and *Z* were expected from this dehydroiodination reaction of compound **3a**,**b** [25–27], however, only the *E* isomer was obtained, as confirmed by ^{1}H-, ^{13}C- and ^{19}F NMR (see Supporting information). This selectivity can be interpreted by the *anti* process of this elimination (the proton and halogens should be in anti-conformation) and by the fact that this reaction preferably takes place when compounds **3a**,**b** adopt the most stable conformation, *i.e.* where the perfluoroalkyl chain and the biphenyl moiety are *anti* to each other, to minimize the repulsive interactions and steric hindrance when B base attacks, according to E2 elimination mechanism (see Scheme 2).

Finally, the last series of liquid crystalline compounds was prepared by radical addition reaction of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorodecane thiol and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorononane thiol on compounds **2** in presence of AIBN in 1,2-dichloroethane [28–30], to afford compounds **5a** and **5b**, respectively. All compounds were obtained in good purity as deduced ^{1}H and ^{13}C NMR, FTIR, mass spectra and elemental analyses.

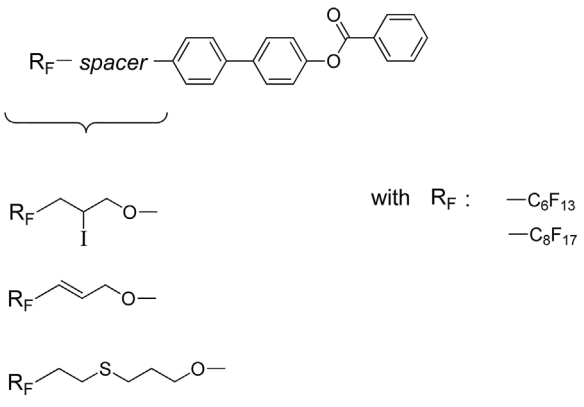

Fig. 1. Molecular structure of the biphenyl benzoate liquid crystal series carrying a semiperfluorinated chain investigated herein.

2.2. Liquid crystal properties

The mesomorphic properties of the final compounds **3a**,**b**, **4a**,**b** and **5a**,**b** have been investigated by means of polarized optical microscopy (POM), differential calorimetry (DSC) and powder small-angle Xray diffraction (XRD). All materials are liquid crystalline and exhibit lamellar mesophases.

The transitions temperatures of the fluorinated liquid crystals determined by POM and DSC, show a remarkable stabilization of the mesophases in respect to their non-fluorinated counterparts (compare Figs. 2 and 3 [20]). In particular, while the fully hydrogenated molecules show a relatively high melting point (around 130 °C) and only a short nematic range (less than 10 °C), the presence of the fluorinated chain reduces the melting temperature down to 60 °C and induce smectic mesophases up to 240 °C (see DSC thermograms in Fig. 4). POM investigation unambiguously shows that all smectic phases are untilted in nature, meaning that the molecular orientation director is normal to the smectic layers (see Fig. 5 and Supporting information). The textural defects and their changes at the transitions strongly indicate the presence of SmA, SmB and SmE phase types (Figs. 2–5).

All compounds have been investigated by X-ray scattering at different temperatures and show, after melting from crystalline state (see Supporting information), typical patterns of SmA, SmB (of hexatic-type) and SmE mesophases, confirming the previous phase assignment. As a common feature, all X-ray patterns exhibit the well-known diffuse bands $h_H \approx 4.6$ Å and $h_F \approx 5.6$ Å, corresponding to the average distance between disordered alkyl segments (spacer) and perfluorinated chains, respectively. All mesophases are lamellar in nature and their symmetry is determined by the molecular organization within the mesogenic sub-layer. Below are described the common characteristics of the four mesophases the present in the fluorinated compounds (see typical patterns in Fig. 6 and in Supporting information).

2.2.1. SmA

In this mesophase, the lateral molecular arrangement is of liquid-like, leading to a merging of the diffuse bands h_{mes} and h_H (average distance between closest mesogens and alkyl chains, respectively)

2.2.2. Hexatic SmB

The lateral organization of the mesogens (assimilated to cylinders) gives a two-dimensional hexagonal array ($Z = 1$ molecule per lattice) which develops to moderate distances. The main reflection (100) is the only one observed, and its broadening corresponds to correlation length of about 200 Å.

2.2.3. SmE

The mesogens are organized at long-range within the layers, into an array of rectangular symmetry *p2gg* ($Z = 2$), with a ratio of the lattice parameters $a/b \neq 3^{1/2}$ (see Fig. 6). The main reflections (200) and (110) are distinct and narrow, while the higher order reflection (210) indicates an alternated chevron packing of mesogen rows.

The fine molecular packing of the fluorinated liquid crystal series could further be characterized. In particular, it was possible to determine how the different parts of the molecules were