Journal of Organometallic Chemistry 696 (2011) 2429–2437

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

Phase behavior of some mono-substituted ferrocene- and [3] ferrocenophane-containing nematics with the cyclohexane ring in the rigid core

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ARTICLE INFO

Article history:
Received 28 January 2011
Received in revised form
27 February 2011
Accepted 7 March 2011

Keywords:
Liquid crystals
Metallomesogens
Synthesis design
Phase transitions
Mesophases
Ferrocene

ABSTRACT

Generally, incorporation of the cyclohexane rings into the rigid core of rod-like mesogens leads to improved technological parameters, i.e. low viscosity, ambient transition temperatures and stability of the nematic state. Taking this into consideration, a series of novel cyclohexane-containing derivatives of ferrocene has been synthesized. The effect of various structural factors on liquid crystalline behavior of the synthesized ferrocene-containing nematics has been examined. Ferrocenophane compounds exhibited enhanced liquid crystalline properties in comparison with the derivatives of unbridged ferrocene. Depending on thermal prehistory of the samples, some of the synthesized ferrocenomesogens showed remarkable migration of the phase transition temperatures. In one case such behavior led to stabilization of the initially monotropic nematic mesophase in subsequent heating cycles. In another case, the phase transition shifts caused the lowering of the crystal-to-nematic transition temperature and the broadening of the mesophase range. There was also a case of alteration from the initially enantiotropic to monotropic behavior. The obtained novel metallomesogens are important footsteps toward the development of low-viscous and low-temperature materials for liquid crystal applications possessing a chromophoric, redox-switchable, polarizable and chemically stable superaromatic ferrocene unit.

1. Introduction

The presence of transition metals brings unusual properties to liquid crystals and opens wide possibilities for new applications. This perception stimulated A.M. Giroud-Godquin and others to start systematic studies of metal-containing liquid crystals in 1977 [1,2]. Ferrocene-containing liquid crystals among various types of metallomesogenic systems attracted reasonable interest of researchers during recent decades [3,4]. Certainly, a chemical and thermal stability of superaromatic ferrocene moiety radically exceeds a stability of other metal-containing coordination sites that are traditionally used in the molecular design of metallomesogens. Besides, ferrocene is a good chromophore, redox-switchable and polarizable unit due to the increased electronic density around the metal center. Hence, mesogenic ferrocene derivatives are valuable candidates for potential applications in liquid crystal devices taking into account the above characteristics. Despite of bulky end-groups mono-substituted ferrocenomesogens are able to show liquid crystalline properties. As a rule, they exhibit nematic mesomorphism sometimes preceded by smectogenic behavior [4–14]. Introducing asymmetric fragments into the mesogenic core of mono-substituted ferrocenomesogens leads to chiral organization of the mesophases [15–17]. Besides, chiral mesophases can be achieved in multi-substituted ferrocene derivatives with planar chirality. The latter compounds were characterized as weakly ferroelectric liquid crystals [18,19]. Bridged ferrocenes or ferrocenophanes with a minimal structural variation from mono-substituted ferrocenomesogens show enhanced mesomorphism [20,21]. Hexagonal columnar and bicontinuous cubic mesophases were observed in supramolecularly organized ferrocene-containing liquid crystals [22,23] and hexacatenar 1,1′-bis substituted ferrocene derivatives [24]. Recently, unusual mesophases showing ambidextrous chirality were found in unsymmetrically 1,1′-bis substituted ferrocenomesogens, which are preliminarily assigned to mesophases with tetrahedral symmetry [25]. Finally, ferrocene units can be successfully tailored into various liquid crystalline polymer structures [26–31].

The phase transition temperatures in mono-substituted ferrocenes often far exceed 100 °C. Regarding disubstituted liquid crystalline ferrocene derivatives, they often show even higher

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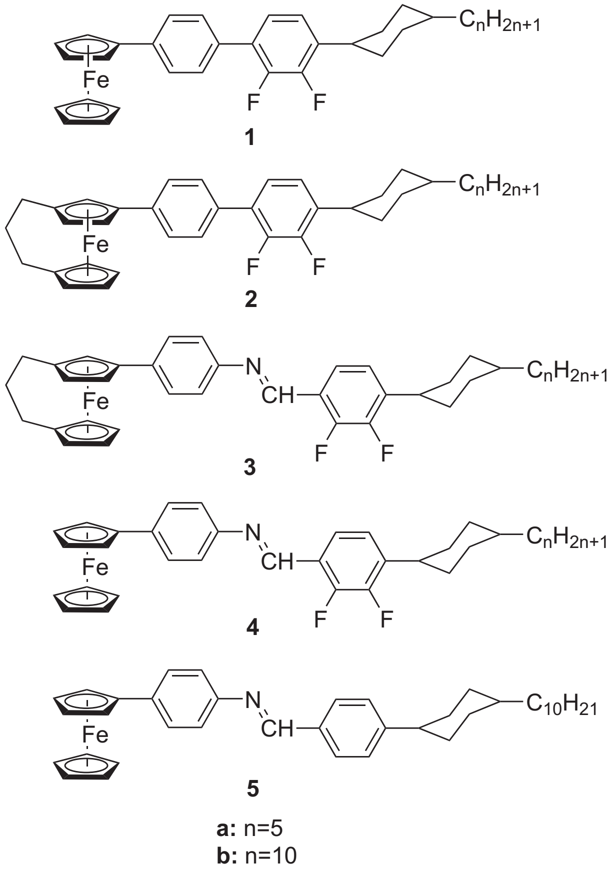
doi:10.1016/j.jorganchem.2011.03.013

temperatures of mesophase transitions. It seems there are two major ways for decreasing the temperatures of phase transitions in ferrocene-containing liquid crystals: 1) incorporation of cyclohexane fragments into the rigid core; 2) lowering symmetry of the substituents in the ferrocene unit. The first approach is applicable to both mono- and bis-substituted ferrocenomesogens. T. Hanasaki et al. successfully applied the second approach in some unsymmetrically bis-substituted ferrocenomesogens with the crystal-to-nematic transition below 100 °C [32]. The purpose of the present studies was preparation of various mono-substituted ferrocene-containing liquid crystals with a cyclohexane ring in the rigid core, and investigation of the effect of some selected structural factors on their liquid crystalline properties. In all cases, pure *trans*- isomers of the disubstituted cyclohexanes were used for replacement of benzene rings in the rigid core. In general, a cyclohexane structural unit reduces viscosity and stabilizes the technologically important nematic state [33,34]. Structural variations in the synthesized ferrocenomesogens comprised a different number of carbon atoms in the terminal alkyl chains, the azomethine linking group, the lateral fluoro-substituents, and the 1,3-propylidene bridge in the ferrocene fragment (Scheme 1).

2. Experimental section

2.1. Materials and instruments

Reagent grade chemicals and solvents were purchased from Aldrich (Yongin, Kyounggi-Do, Korea, Korea Branch). Solvents were dried and freshly distilled just before use. Melting points were determined by capillary method in a Stuart Scientific apparatus SMP3. ^{1}H NMR spectra were measured on a Bruker AM 400 with internal TMS standard. Mass-spectra were obtained on a Bruker microflex MALDI-TOF mass spectrometer. Elemental analyses were performed on a Fisons instrument 2A1108 at Korea Institute of Science and Technology. DSC thermographs were obtained on Perkin Elmer Diamond DSC with various scanning rates. Thermo-optical observations were carried out on a Nicon Eclipse E600 Pol optical polarized microscope equipped with a Mettler Toledo FP82 HT hot stage system and Mettler FP90 central processor. Microphotographs were obtained with a Moticam 2300 digital camera. The syntheses of 4-bromophenylferrocene and 4-(4-*n*-decylcyclohexyl)-2,3-difluorobenzene as a mixture of *cis*- and *trans*- isomers are described in our earlier publication [25].



Scheme 1. Chemical structures of the mesogenic ferrocenes **1**–**5** with a cyclohexane fragment in the rigid core.

2.1.1. 4-Bromophenylferrocenophane (*8*)

A mixture of 4-bromoaniline (2.02 g, 11.7 mmol), concentrated H_2SO_4 (7.3 mL, 133 mmol) and water (15 mL) was cooled down to −5 °C and diazotized with a solution of $NaNO_2$ (0.81 g, 11.7 mmol) in water (5 mL). Addition of $NaNO_2$ solution was carried out in such a way so temperature inside of the reaction mixture was not allowed to rise higher than 0 °C. The cold diazonium salt solution was added portion wise to a cold solution (0 °C) of [3]ferrocenophane (1.50 g, 6.6 mmol) in a mixture of diethyl ether (30 mL) and hexadecyltrimethylammonium bromide (0.15 g, 0.4 mmol). The reaction mixture was stirred at 0 °C for 3 h and then at room temperature for overnight. After that the solution was neutralized by NaOH (aq. 10%) and the ether layer was separated with a separation funnel. The aqueous phase was extracted with diethyl ether (×3) then the combined organic extracts were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The residue after evaporation of diethyl ether was placed on an Al_2O_3 column and eluted with hexane. The first fraction containing a mixture of aromatics together with [3]ferrocenophane traces was rejected. The second fraction was collected and evaporated to dryness. The obtained residue was recrystallized from hexane. Yield 1.39 g (58%). Orange powder, m.p. 98.2–99.0 °C; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.42–7.22$ (m, 5H), 4.47 (d, $J = 1.8$ Hz, 2H), 4.21 (t, $J = 2.1$ Hz, 2H), 4.13 (t, $J = 1.9$ Hz, 1H), 3.96–3.86 (m, 1H), 3.44–3.36 (m, 1H), 2.16–1.83 (m, 6H); MS (EI): 380 (379.99) and Anal. Calcd for $C_{19}H_{17}BrFe$ (%): C 59.88, H 4.50; found: C 59.85, H 4.47.

2.1.2. 4-Aminophenyl ferrocene (*9*)

4-Nitrophenylferrocene (0.40 g, 1.3 mmol) was dissolved in EtOH (5 mL), and 10% Pd/C (0.14 g) was added to the obtained solution. The mixture was reduced in a hydrogenation apparatus under pressure of H_2 (3 atm) for 6 h. The resulting mixture was filtered off through a Celite layer, evaporated to dryness and purified by column chromatography. Yield 0.28 g (78%). Yellowish orange powder, m.p. 152–154 °C (lit. [35] 157–159 °C). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.29$ (d, $J = 8.9$ Hz, 2H), 6.64 (d, $J = 8.5$ Hz, 2H), 4.53 (t, $J = 1.8$ Hz, 2H), 4.23 (t, $J = 1.8$ Hz, 2H), 4.03(s, 5H).

2.1.3. 4-(4-n-Pentylcyclohexyl)-2,3-difluorobenzaldehyde (*10a*)

n-Butyllithium (11.8 mL of 2.5 M in cyclohexane, 30.0 mmol) was added dropwise for 30 min to a cooled (−78 °C) solution of 1,2-difluorobenzene (2.74 g, 24.0 mmol) in dry THF (80 mL) under vigorous stirring in dry argon atmosphere. The mixture was stirred at −78 °C for 2.5 h, and then a solution of 4-pentylcyclohexanone (3.66 g, 21.8 mmol) in dry THF (10 mL) was added dropwise at the same temperature for 30 min. The mixture was allowed to warm up to room temperature overnight and the excess of organometallics was quenched with aqueous saturated ammonium chloride (40 mL). The crude product was extracted into ether (×2), and the combined organic layers were dried over anhydrous $MgSO_4$. The obtained solution was filtered, and solvents were evaporated. The residue was