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Synthesis, computational modelling and liquid crystalline properties of some [3]ferrocenophane-containing Schiff's bases and β-aminovinylketone: Molecular geometry–phase behaviour relationship

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Abstract

Rotationally fixed [3]ferrocenophane extends the variety of possible molecular geometries in its derivatives in comparison with unbridged ferrocenes. In this respect molecular geometry–liquid crystalline properties relationship studies in [3]ferrocenophane mesogens are of considerable interest. Different positional isomers of mono- and di-substituted [3]ferrocenophanes which are obtained by incorporating one or two promesogenic building blocks into the cyclopentadienyl rings are reported in this article. A series of mono-substituted [3]ferrocenophane-containing Schiff's bases was synthesized by condensing isomeric *p*-aminophenyl [3]ferrocenophanes with appropriate aldehydes. Isomers of di-substituted [3]ferrocenophane amines gave rise to a series of azomethines with two promesogenic substituents in the cyclopentadienyl rings. Besides, a β-enaminoketone was prepared from 3-(*p*-aminophenyl)[3]ferrocenophane. Nematic and smectic mesophases were observed in the synthesized compounds under a polarizing optical microscope. The [3]ferrocenophane-containing β-enaminoketone showed complex mesomorphic behaviour connected with occurrence of the keto-enamine and imino-enol tautomeric equilibrium in this compound. On the base of computational models obtained by semi-empirical quantum chemistry calculations the molecular geometry–phase behaviour relationships were examined. It was demonstrated that mesomorphism of [3]ferocenophane azomethines depends on the spatial orientation of the substituents with respect to the propanediyl bridge in a case of mono-, and as well as to each other in a case of di-substituted derivatives.

Keywords: Ferrocenophane; Liquid crystals; Metallomesogens; Azomethine; β-Aminovinylketone

1. Introduction

Ferrocene containing liquid crystals attract continuous interest of many researchers in the world. Imrie et al. and Deschenaux et al. have summarized in reviews results obtained in this field to the end of last century [1]. Research efforts on syntheses, structural characterization and properties of new liquid crystalline ferrocene derivatives still persist in recent years [2].

Thus, unbridged ferrocenomesogens are widely explored. The synthesized examples of ferrocene-containing liquid crystals can be classified into three main groups: (i) mono-substituted; (ii) homoannularly di-substituted; (iii) heteroannularly di-substituted (see Fig. 1). Because of the rotational freedom of the cyclopentadienyl rings around the normal axis both S-shaped and U-shaped conformations are possible in a liquid crystalline state for heteroannularly substituted ferrocenes.

There is another less investigated type of ferrocenomesogens such as derivatives of the bridged ferrocenes. For example, the reported liquid crystalline [3]ferrocenophane compound showed broader mesophase in comparison with

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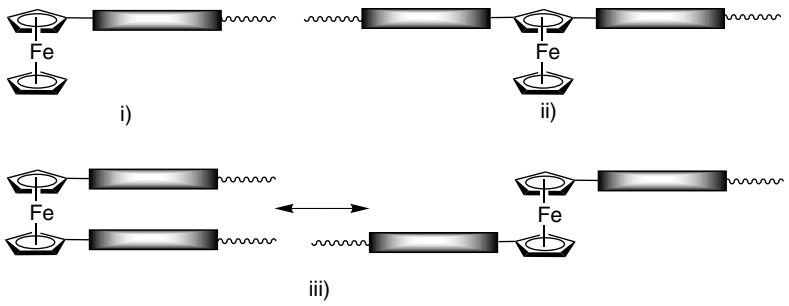


Fig. 1. Molecular shapes occurring in the liquid crystalline ferrocene derivatives.

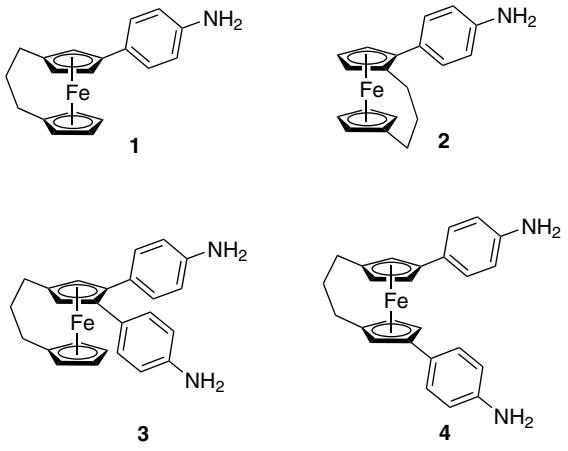
its unbridged analogue [3]. Hence, incorporation of a ferrocenophane unit into the liquid crystalline structures can bring certain advantages over its unbridged ferrocene counterparts. Furthermore, the possibility of various positional isomers in derivatives of rotationally fixed ferrocenophanes results in wide diversity of the molecular geometries that can be realized in the liquid crystalline structures on their base. In this respect molecular geometry–liquid crystalline properties relationship studies in [3]ferrocenophane mesogens are of considerable interest.

Recently, we have reported inclusion of the aryl substituents into a [3]ferrocenophane moiety [4], which gave rise to isolation of several *p*-nitrophenylated isomers. Further efforts to obtain mesogenic materials from these arylated products gave rise to a series of new [3]ferrocenophane-containing liquid crystals which are described in the present article. Some of these synthesized compounds are designed specially for coordinating transition metal ions and obtaining heteronuclear metallomesogenic systems, which are of special interest due to the potential revelation of the unique magnetic and optical properties [5].

2. Results and discussion

2.1. Syntheses and spectral properties

The ferrocenophane-containing amines **1**–**4** were obtained by reduction of the respective *p*-nitrophenyl[3]ferrocenophanes with stannous(II) chloride (see Scheme 1). The imines **5**–**8** were obtained by Schiff's condensation of amines **1**–**4** with corresponding aldehydes **10** and **19** (see Schemes 2 and 3).



Scheme 1. Structures of [3]ferrocenophane-containing amines **1**–**4**.

All of the synthesized alkoxylated products were prepared using the Williamson reaction: 4-dodecyloxybenzaldehyde **10a** and 2-hydroxy-4-dodecyloxybenzaldehyde **10b** were prepared by etherification correspondingly of 4-hydroxybenzaldehyde **9a** and 2,4-dihydroxybenzaldehyde **9b** with dodecyl bromide and potassium carbonate in acetone; similar procedure was used to prepare 4-dodecyloxyacetophenone **12** from 4-hydroxyacetophenon **11**; 4-dodecyloxybenzoic acid **17** was obtained via hydrolysis of ethyl-(4-dodecyloxy)benzoate **16**, where the latter was prepared by an etherification reaction between ethyl-(4-hydroxy)benzoate **15** and 1-bromododecane. An esterification reaction between 4-hydroxybenzaldehyde **9a** and 4-dodecyloxybenzoyl chloride **18** afforded 4-(4′-dodecyloxybenzoyloxy)benzaldehyde **19a**. In the same conditions 2,4-dihydroxybenzaldehyde **9b** reacts yielding 2-hydroxy-4-(4′-dodecyloxybenzoyloxy)benzaldehyde **19b**. Using a reaction of 4-dodecyloxybenzoylacetaldehyde sodium salt **13** with hydrochloride of 3-(4′-aminophenyl)[3]ferrocenophane **1**, β-aminovinylketone **14** was synthesized. Mass-spectroscopic, IR and ^{1}H NMR data of the synthesized compounds are in a full agreement with the proposed structures. Noticeably, compounds **5b**, **5d** and **14** are able to form complexes with various transition metals due to inclusion of the appropriate coordinating groups into their molecules.

The illustrated configurations of the amines **1**–**4** are based on the X-ray structural studies of their nitro-precursors [4]. The propylidene bridge of [3]ferrocenophane appears as three groups of signals in the areas of 1.85–2.00, 2.00–2.10 and 2.30–2.45 ppm in ^{1}H NMR spectrum of the amine **2**, while in the amine **1** all relevant signals appear in the region of 1.85–2.05 ppm. This conforms to a less symmetric structure of the amine **2** in comparison with the amine **1** and consequently more varied distances between a benzene mojety and different protons of an alkylidene bridge. It is remarkable that in a ^{1}H NMR spectrum of the amine **3** two protons assigned to the diarylated cyclopentadiene ring appear as a singlet at 3.24 ppm. The chemical and magnetic equivalency of these protons is a consequence of their equal surrounding in