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Journal of Organometallic Chemistry 692 (2007) 5571–5582
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

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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Received 22 June 2007; received in revised form 30 August 2007; accepted 4 September 2007
Available online 21 September 2007

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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doi:10.1016/j.jorganchem.2007.09.010

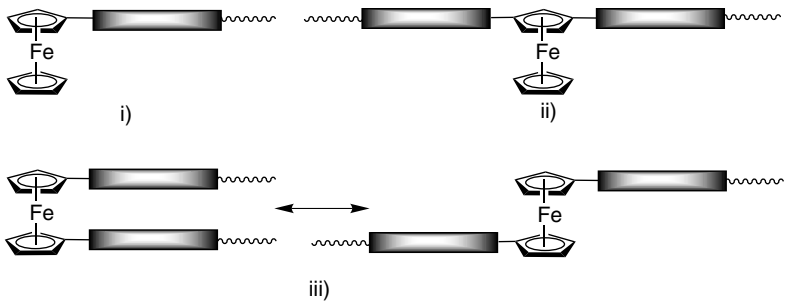


Fig. 1. Molecular shapes occurring in the liquid crystalline ferrocene derivatives.

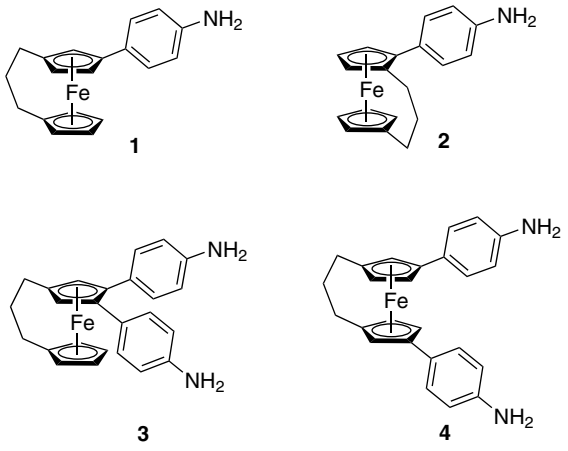
its unbridged analogue [3]. Hence, incorporation of a ferrocenophane unit into the liquid crystalline structures can bring certain advantages over its unbridged ferrocene counterparts. Furthermore, the possibility of various positional isomers in derivatives of rotationally fixed ferrocenophanes results 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

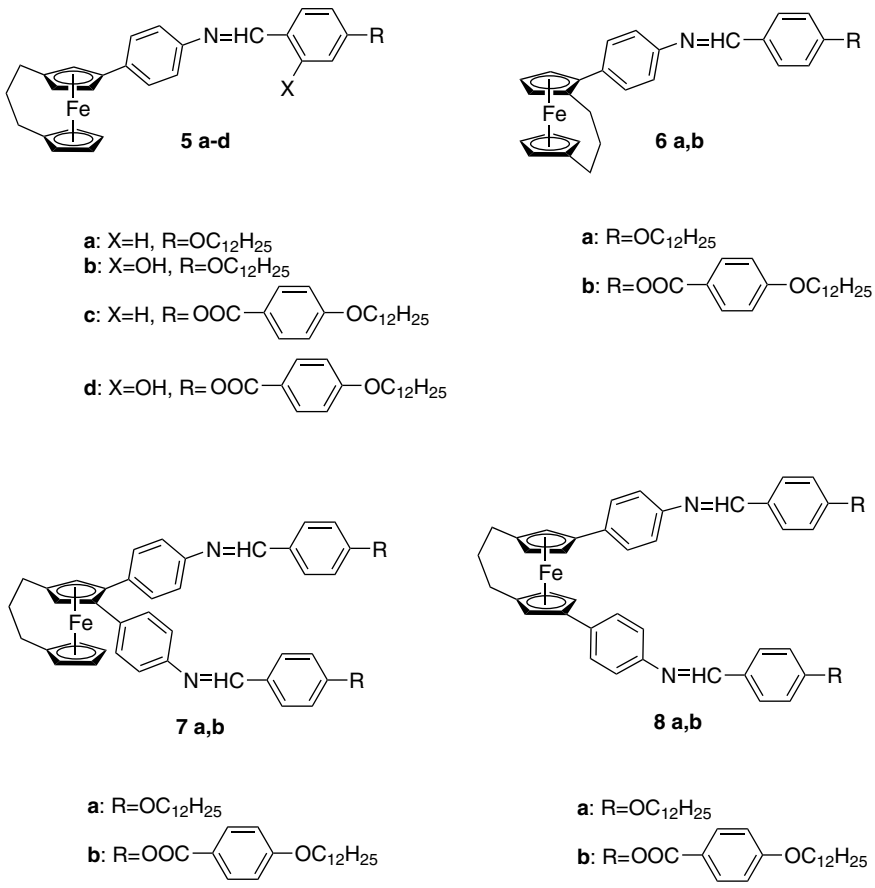
The ferrocenophane-containing amines **1**–**4** were obtained by reduction of the respective *p*-nitrophenyl[3]ferrocenophanes with stannous(II) chloride (see Scheme 1). The imines **5**–**8** were obtained by Schiff's condensation of amines **1**–**4** with corresponding aldehydes **10** and **19**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



Scheme 2. Structures of [3]ferrocenophane-containing Schiff's bases **5**–**8**.

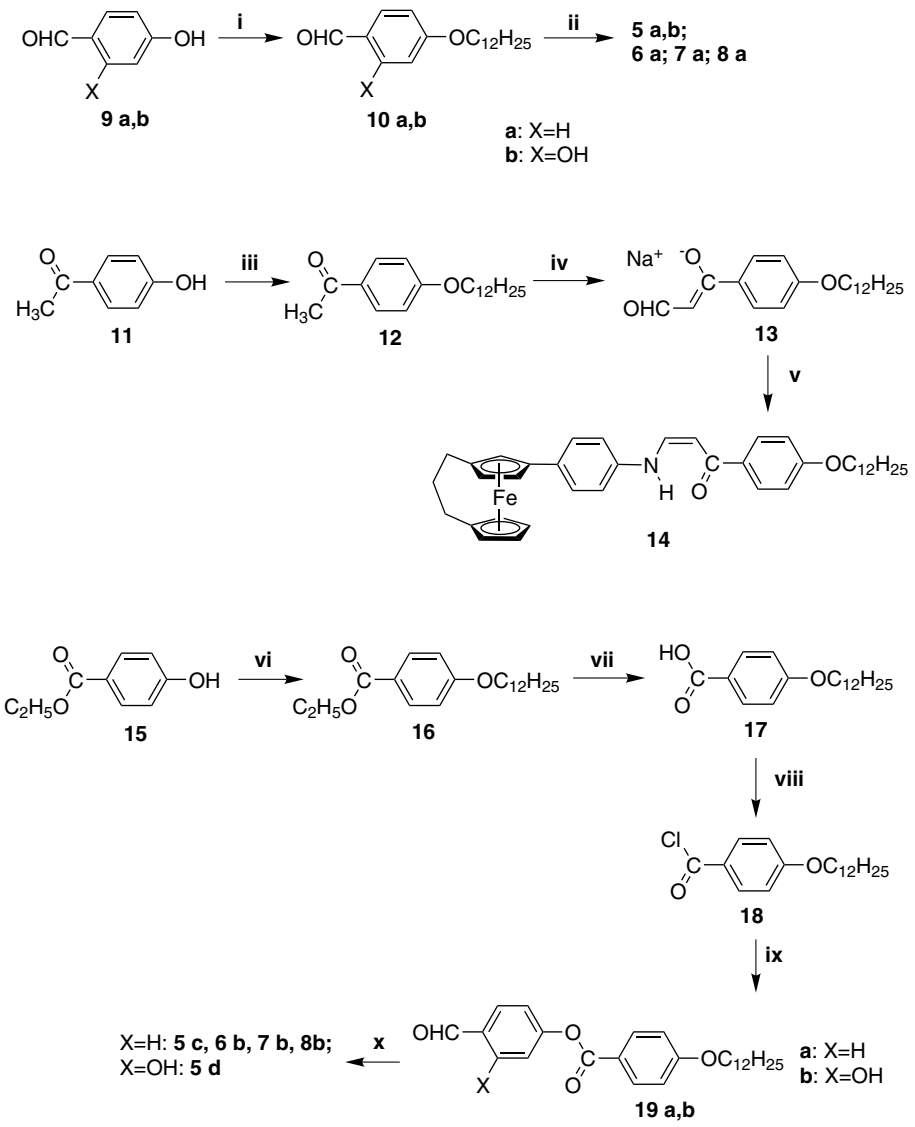
respect to the aromatic substituents and other parts of the [3]ferrocenophane fragment.

A ferrocene moiety is revealed in the UV spectra of all the synthesized compounds (Table 1) by two intensive maxima owing to n–π^* and π–π^* electronic transitions in the regions of 277–297 and 330–339 nm, and non-intensive absorption at 430–450 nm assigned to d-d transitions of the iron atom [6]. The azomethine chromophore appears in the Schiff's bases **5**–**8** and β-aminovinylketone **14** with intensive maxima in the area of 380–390 nm which is absent in the spectra of the amines **1** and **2**. It is noticeable fact that compounds **5b** and **5d** containing a hydroxyl in the *ortho*-position to an azomethine group have an additional intensive maximum at ~350 nm. This additional band connected with the absorption of carbonyl groups emerged as a consequence of the imino-enol–keto-enamine tautomerism in these compounds (see Scheme 4) [7,8]. The intramolecular hydrogen bond provides the necessary stability to the corresponding keto-enamine tautomers.

2.2. Liquid crystalline properties

Thermal behaviour of the synthesized compounds was investigated under a polarizing optical microscope with a heating stage. The transition temperatures and the related mesophases identified by thermal optical microscopy are compiled in Table 2. Unexpectedly, optical textures characteristic for the columnar nematic phase were observed in the super-cooled samples of compound **5a** (Fig. 2). These experimental observations can be rationalized by assumption that at these relatively low temperatures molecules of compound **5a** congregate in bundles due to plane-to-plane interactions of ferrocenophane units with each other, and with the other aromatic rings in rigid core as well. Though the observed mesophase is thermodynamically unstable (monotropic), as a matter of fact [3]ferrocenophane-containing azomethine **5a** is the first example of mono-substituted ferrocenes with two benzene rings showing liquid crystalline properties as there was no reported examples in the earlier literature [1,2]. The mono-substituted [3]ferrocenophane Schiff's base **5b** containing lateral hydroxyl substituent in a rigid core is non-mesomorphic (see Table 2).

The enanthiotropic nematic mesophases were observed under a polarizing optical microscope in **5c** and **5d**, where the aromatic rigid core was extended by the third benzene ring. It is remarkable that compound **6b** which is isomeric to **5c** showed only the monotropic nematic phase in a super-cooled sample (see Fig. 2 for optical textures). There is only a slight difference between these isomers connected with stereochemical position of the propylidene bridge in the ferrocene core towards the aromatic substituent.

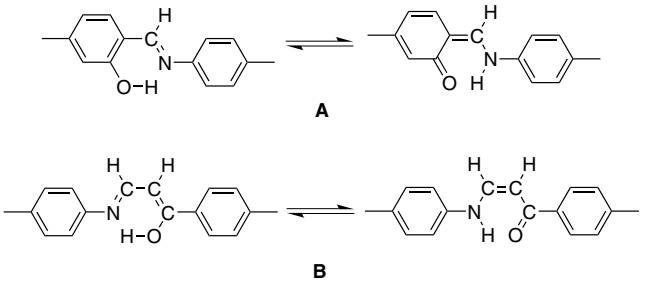


Scheme 3. Synthesis of the [3]ferrocenophane-containing Schiff's bases and β-aminovinylketone. Reagents and conditions: (i, iii, vi) $BrC_{12}H_{25}$, K_2CO_3, in acetone, reflux; (ii, x) relevant amines **1**–**4**, EtOH, reflux; (iv) ethylformiate, Na, abs. benzene, reflux; (v) amine **1**, equimolar HCl, EtOH, reflux; (vii) KOH, water/ethanol, reflux; (viii) $SOCl_2$, reflux; (ix) aldehyde **9a** or **9b**, pyridine/benzene, reflux.

Table 1
UV/Vis (CH_2Cl_2) data of the compounds **1**, **2**, **5a**–**d**, **6a**,**b**, **7b**, **8a**,**b**, and **14**

Compound	λ_{max}, nm ($\log\varepsilon$, $l\,cm^{-1}\,mol^{-1}$)				
1	288 (4.303)	330 (sh) (3.511)	–	–	447 (2.698)
2	285 (4.079)	–[a]	–	–	440 (2.661)
5a	292 (4.461)	330 (4.377)	–	380 (sh) (4.136)	455 (sh) (3.507)
5b	286 (4.169)	326 (sh) (4.169)	347 (4.220)	385 (sh) (4.022)	440 (sh) (3.500)
5c	279 (4.639)	338 (sh) (4.236)	–	389 (sh) (3.909)	450 (sh) (3.483)
5d	277 (4.561)	330 (sh) (4.308)	350 (4.404)	382 (sh) (3.643)	460 (3.722)
6a	293 (4.401)	332 (4.338)	–	380 (sh) (3.968)	430 (sh) (3.293)
6b	277 (4.673)	329 (4.277)	–	385 (sh) (3.845)	425 (sh) (3.355)
7b	276 (5.058)	333 (4.644)	–	390 (sh) (4.228)	446 (sh) (3.820)
8a	297 (4.794)	335 (4.716)	–	387 (sh) (4.356)	455 (sh) (3.886)
8b	278 (4.931)	339 (4.520)	–	390 (sh) (4.165)	455 (3.918)
14	286 (4.224)	–[a]	–	390 (4.499)	450 (sh) (3.983)

[a] The absorption appears as inflexion and can not be defined.



Scheme 4. The imino-enol–keto-enamine tautomeric equilibrium: A for compounds **5b** and **5c**; B for compound **14**.

Obviously, [3]ferrocenophane derivative **5c** has more extended geometry in comparison with the related 2-substituted isomer **6b**. At the same time the cyclopentadien ring of the [3]ferrocenophane fragment in compound **6b** is very likely tilted in respect to the conjugated plane of the adjacent benzene ring because of sterical hindrance from the closely positioned propylidene bridge. The characteristic UV absorption maxima of a ferrocene core at ~430–450 in the compounds **6a** and **6b** are significantly blue-shifted regarding to the related bands for their isomeric counterparts **5a** and **5c** (see Table 1), and this confirms additionally the previously made statement. Thus, the conformational configuration where conjugation planes of the aromatic promesogenic rigid core are tilted from the cyclopentadienyl rings seems unfavorable for appearance of liquid crystalline properties in [3]ferrocenophane-containing systems.

It was interesting to compare liquid crystalline behaviour of the [3]ferrocenophane compounds **5c**, **5d** and their ferrocene analogues [9]. The presence of the propylene bridge in a ferrocene moiety has a significant effect on the temperature range of the nematic phase in a case of compound **5c**, which shows the broader mesophase (138–172 °C, see Table 2) than its corresponding ferrocene counerpart (154–165 °C [9]). The nematic phase in [3]ferrocenophane compound **5d** has almost the same width as in the related ferrocene-containing Schiff's base (130–163 °C, see Table 2, vs. 135–171 °C [9]). In general, addition of the propylidene bridge to a ferrocene fragment in β-position to the promesogenic substituent enhances liquid crystalline properties of mono-substituted ferrocenyl mesogens, while the presence of the propylidene group in α-position drastically reduces mesomorphism.

Homoannularly di-substituted [3]ferrocenophane derivatives **7a** and **7b** did not reveal mesomorphism. Heteroannularly di-substituted compound **8a** exhibited the enanthiotropic nematic mesophase in a short temperature range. Analogous compound **8b** with more extended substituents showed only the monotropic smectic mesophase upon cooling from the isotropic liquid state. Optical texture was not defined clearly in this case, however the observed mesophase can be ascribed to the smectic type on account of its limited fluidity (see Table 2 for phase behaviour, and Fig. 3 for the observed microscopic textures).

In order to compare stereometrical appearance of the isomeric pairs **5c**–**6b** and **7b**–**8b** their conformational models were obtained using HYPERCHEM-7 program for molecular simulation. Initial geometry optimizations of the structures were accomplished by simple molecular mechanics calculations using MM^+ method with a steepest descent calculation algorithm, and then the obtained configurations were optimized further by Fletcher–Reeves algorithm. Finally semi-empirical calculations were performed on the obtained configurations using PM3 method with a conjugate directions algorithm.

The propylidene bridge in mesogenic [3]ferrocenophane compound **5c** extends the long axis of the molecule, while in [3]ferrocenophane compound **6b** it increases overall bulkiness of the ferrocene group in perpendicular direction to the molecular long axis (see Fig. 4). Compound **6b** exhibits poor mesomorphism as result of this unfavourable geometry.

Table 2
Phase behaviour of the compounds **5a**–**d**, **6a**,**b**, **7a**,**b**, **8a**,**b**, and **14**

Compound	Crystal	*T* (°C)	Mesophase type	*T* (°C)	Isotropic liquid
5a	■	[65][a]	•N_{Col}	116	■
5b	■	–	–	52	■
5c	■	138	•N	172	■
5d	■	130	•N	163	■
6a	■	–	–	105	■
6b	■	[66][b]	•N	153	■
7a	■	–	–	60	■
7b	■	–	–	121	■
8a	■	112	•N	116	■
8b	■	[155]	•Sm_X	178	■
14	■	[118]	•Sm_C		
		[124]	•N	152 (192)[c]	■

[a] Monotropic phase transition: anisotropic optical textures observed at fast cooling from isotropic liquid, while at slow cooling crystallization of the sample occured.

[b] Homeotropic texture was observed at fast cooling before crystallization occured.

[c] The monotropic nematic and smectic C mesophases were observed at fast cooling from the isotropic liquid state; at slow cooling and keeping sample between 130 and 140 °C crystallization in the another crystal form occurs, which melted at 192 °C.

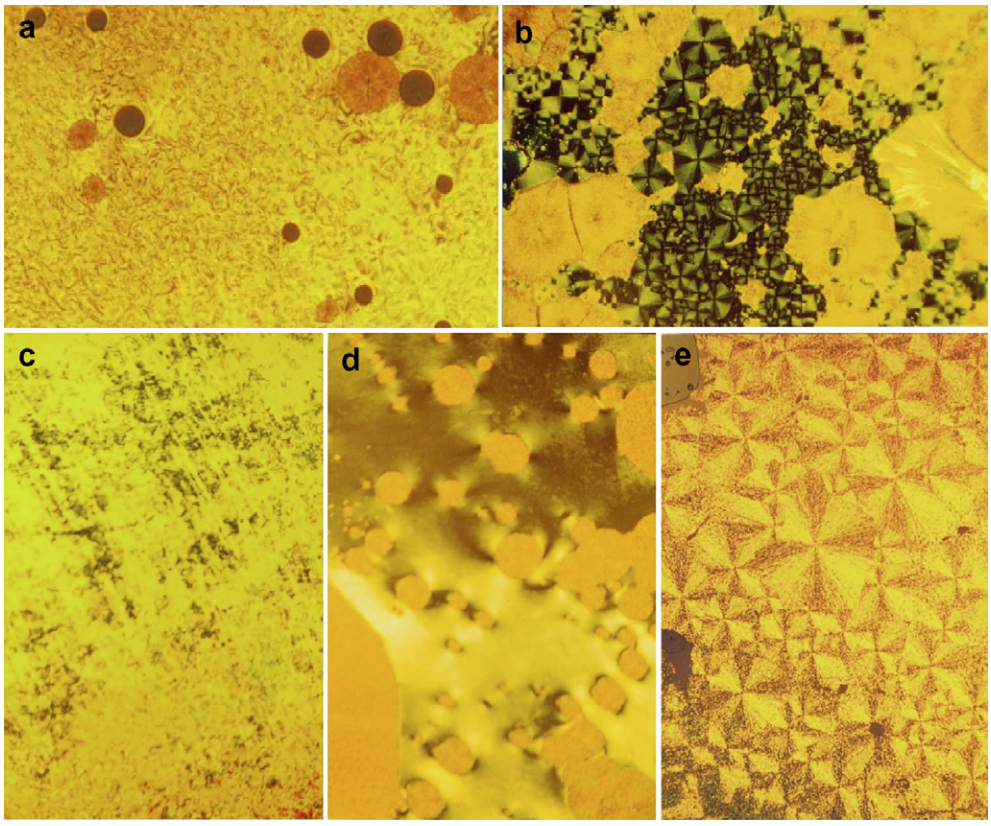


Fig. 2. Photomicrographs of optical textures observed under a polarizing microscope: (a) schlieren texture observed at 60 °C in a super-cooled sample of compound **5a**; (b) focal-conic texture with crystallization areas observed in a super-cooled sample of compound **5a** at 35 °C; (c) marbled texture of the nematic phase in compound **5c** at 156 °C; (d) homeotropic texture with crystallization areas observed at 66 °C in a super-cooled sample of compound **6b**; and (e) crystallization of compound **6b** upon slow cooling from the isotropic liquid phase.

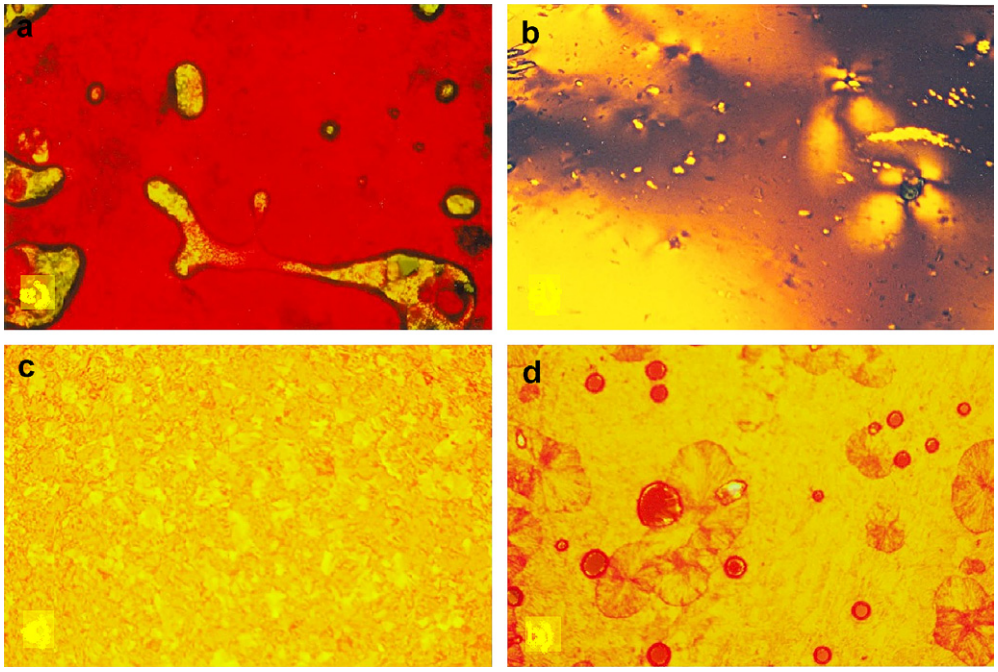


Fig. 3. Photomicrographs under a polarizing microscope: (a) compound **8a** at 115 °C, nematic–isotropic liquid transition; (b) homeotropic texture observed in compound **8a** upon cooling from the isotropic liquid phase; (c) the smectic phase observed in compound **8b** at 156 °C upon cooling from the isotropic liquid; and (d) the smectic phase of compound **8b** with crystallization areas.

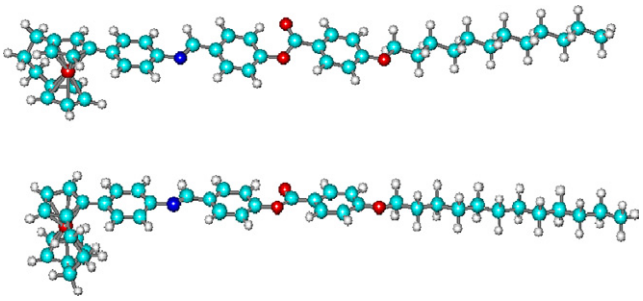


Fig. 4. Computer simulation of the molecules of compounds **5c** and **6b** by HYPERCHEM-7 program (Hypercube Inc.).

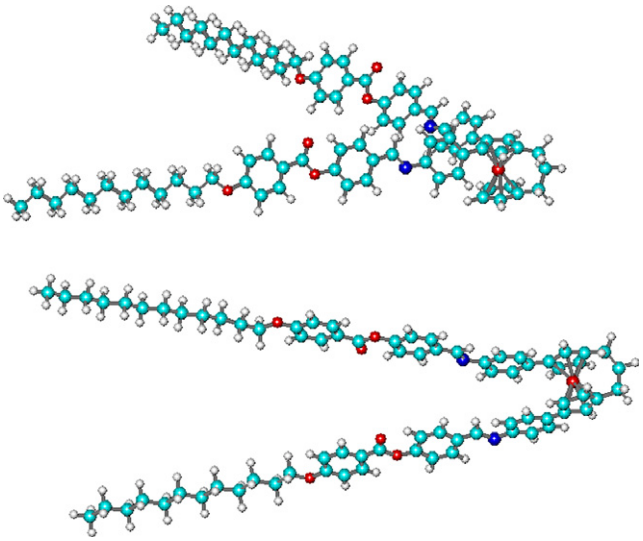


Fig. 5. Computer simulation of the molecules of compounds **7b** and **8b** by HYPERCHEM-7 program (Hypercube Inc.).

Generally, both the di-substituted [3]ferrocenophanes **7b** and **8b** have undesirable stereometrical shapes for appearance of liquid crystalline properties (see Fig. 5). However, the heteroannular di-substituted compound **8b** showed a thermodynamically unstable mesophase (monotropic) (see Table 2). In comparison with the homoannularly di-substituted [3]ferrocenophane **7b** the compound **8b** has no restrictions for effective conjugation of all aromatic rings including cyclopentadiene rings of the ferrocene fragment, while in the former compound two adjacent benzene rings attached to the ferrocene moiety constrain each other, and, as consequence, their alignment in one plane with a cyclopentadien ring is hindered. Over again this confirmed by hypsochromic shift of the UV absorption maximum of the central iron atom at 446 nm in the compound **7b** in comparison with the analogous band for the isomer **8b** (see Table 1). Hence, [3]ferrocenophane derivatives **7a** and **7b** did not exhibit liquid crystalline properties, whereas compounds **8a** and **8b** displayed mesomorphism. Though, mesomorphism of the latter compounds was merely poor due to their still not enough favourable molecular shapes.

The β-aminovinyl ketone **14** showed complex thermal behaviour upon subsequent heating and cooling processes (see Table 2). When a sample of the compound was heated fast, it melted to an isotropic state near 150 °C. On the immediate rapid cooling the monotropic nematic phase was observed at 124 °C, then smectic C at 118 °C which crystallizes upon further cooling below 110 °C (see Fig. 6 for optical textures). This cycle can be repeated if the heating and cooling processes are performed fast enough. When cooling from the isotropic phase is carried out slowly [3]ferrocenophane-containing β-aminovinyl ketone **14** crystallizes in the temperature range of 150–125 °C into another crystal form. This second crystal form is rather high-melting (192 °C) in comparison with the first crystal form. The low-melting crystal form develops only upon fast cooling from the clearing point down to 124 °C, and further cooling from the liquid crystalline state. Generally, a sample of compound **14** after consequent heating-cooling cycles comprises a mixture both of the crystal forms in different ratios depending on its thermal prehistory. It is noticeable that the analogous β-aminovinyl ketone on the base of unbridged ferrocene was non-mesogenic [10]. This confirms above made suggestion that inclusion of the propylidine bridge into a ferrocene unit boost up liquid crystalline properties.

We suggest that the observed phase transformations in the β-aminovinyl ketone **14** are connected with the equilibrium of its keto-enamine and imino-enol tautomers (see Scheme 4). Fig. 7 represents the computer simulated

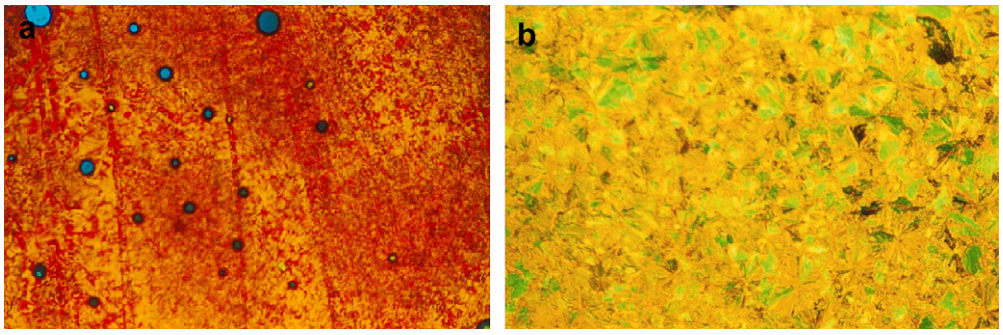


Fig. 6. Photomicrographs of compound **14** under a polarizing microscope: (a) marbled texture of the nematic phase at 124 °C; and (b) broken fan-shaped texture of smectic C phase at 112 °C.

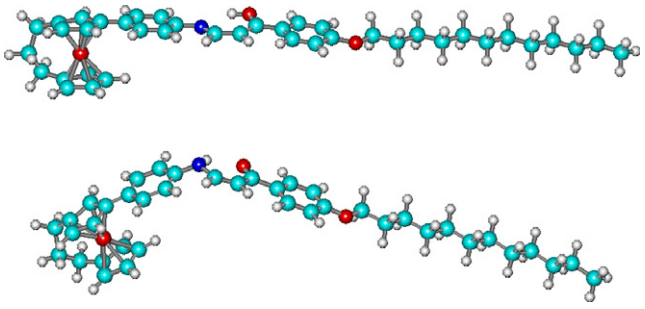


Fig. 7. Computer simulation of imino-enol and keto-enamine tautomeric forms of compound **14** by HYPERCHEM-7 program (Hypercube Inc.).

molecular models of these two tautomers. Molecules of the keto-enamine tautomer are bent as the σ-electronic system of the nitrogen atom has a pyramidal configuration in this case. On the contrary π-electrons of the imine bond in the imino-enol are fully integrated into a conjugational sequence with the aromatic system. As a result molecules of compound **14** in the latter tautomer have less flexible rod-like shape. We believe that the initial low-melting bent keto-enamine tautomer after the first melt transforms into more plane, and, consequently, higher-melting imino-enol tautomer. Separate crystallization of the imino-enol form becomes possible mainly due to the substantial difference in isotropic liquid transition temperatures for two tautomers. If the cooling is performed slowly enough, the imino-enol tautomer starts to crystallize and leaves the liquid phase zone consecutively shifting the tautomeric equilibrium towards imino-enol side. Eventually all the sample crystallizes mainly into the latter form if it was kept long enough at the temperatures 125–140 °C. If the cooling from an isotropic liquid is carried out rapidly down to 125 °C and lower the first tautomer still representes in a mixture of the tautomers by considerable amounts and can be crystallized from the intermediate liquid crystalline phases.

3. Conclusions

Remarkable relationship between liquid crystalline properties and geometrical isomerism in mono- and di-substituted [3]ferrocenophane derivatives was demonstrated. In mono-substituted [3]ferrocenophanes inclusion of the propylidene bridge to a ferrocene fragment in β-position to a promesogenic substituent enhances the liquid crystalline properties, while the propylidene in α-position is less favourable for mesomorphism. It was shown that 3-*p*-aminophenyl[3]ferrocenophane is a superior building block for the syntheses of ferrocenyl liquid crystals.

A series of mesogenic structures were synthesized on the base of an isomeric pair of 3,4-di- and 3,4′-bis-*p*-aminophenyl[3]ferrocenophanes. Generally, the molecular shapes of these isomers are not favourable for revealing mesomorphism. Though heteroannularly bis-substituted [3]ferrocenophane azomethines exhibited some poor liquid crystalline properties.

Interesting phenomenon of complex thermal behaviour was observed in [3]ferrocenophane-containing β-aminovinylketone, when the compound has rather differing isotropic liquid transition temperatures depending on the thermal history of sample. We suggested rationalizing this by taking into consideration keto-enamine – imino-enol tautomeric equilibrium occurring in β-aminovinylketones. Geometric shapes of the respective tautomers have a significant influence on molecular packing of crystals, and, consequently, on their melting points. Separate crystallization of the imino-enol form from a liquid mixture of tautomers can be realized at certain temperatures due to the substantial difference in isotropic liquid transition temperatures for two tautomers.

4. Experimental

4.1. General details

Melting points were determined by the capillary method. Liquid crystalline properties were studied using a polarizing optical microscope "Olympus BH-2" equipped with a heating stage HS1 (INSTEC) and remote temperature controller RTC1 (INSTEC). Photomicrographs were taken with a camera from Nikon. IR spectra were recorded by using a Perkin–Elmer Paragon 1000 instrument. Mass spectra were obtained with a spectrometer MAT 8200 (Finnigan) by electron and chemical ionisation methods at 70 eV. UV and visible spectra in the region of 250–600 nm were recorded on a spectrophotometer Lambda-14 (Perkin–Elmer) in CH_2Cl_2. ^1H NMR spectra were measured on spectrometers ARX 300 and ARX 200 (Bruker) with TMS as an internal standard. All organic and inorganic materials used in the syntheses were purchased from Sigma–Aldrich or FLUKA if it is not stated otherwise. Solvents were dried and distilled before using.

4.1.1. 3-(4-Aminophenyl)[3]ferrocenophane (*1*)

A mixture of 3-(*p*-nitrophenyl)[3]ferrocenophane [4] (1.00 g, 2.880 mmol), $SnCl_2 \cdot 2H_2O$ (2.60 g, 11,522 mmol) and aqueous HCl (conc.) (5 mL) were refluxed for 2 h in a mixture *i*PrOH/H_2O (1:1) (50 mL). A solution changes color from purple to yellow at the end of reaction. The resulting mixture was treated with Na_2CO_3 until obtaining pH 7. Isopropanol was evaporated in a rotary evaporator, and then the obtained yellow suspension was extracted with CH_2Cl_2. An aqueous layer was separated, extracted again with dichloromethane, and the combined organic layers were dried over an anhydrous Na_2SO_4. A sodium sulphate was filtered off, and dichloromethane was evaporated to dryness. The obtained residue was recrystallized from EtOH. Yield 0.86 g (94.1%). Yellowish orange powder, m.p. 95 °C. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.85$–2.05 (m, 6H, C_3H_6 bridge), 3.41 (m, 1H, C_5H_3Fe), 3.20–3.70 (br. s, 2H, NH_2), 3.87 (m, 1H, C_5H_3Fe), 4.03 (m, 1H, C_5H_3Fe), 4.18 (m, 2H, C_5H_4Fe), 4.38 (m, 2H, C_5H_4Fe), 6.57 (m, 2H, C_6H_4), 7.22 (m, 2H,

C_6H_4). IR (KBr tablet): $\tilde{\nu} = 3458.3$ (N–H), 3368.3 (N–H), 2906.1 (C–H), 2835.5 (C–H), 1620.9, 1531.5, 1469.4, 1430.5, 1276.3, 1043.4, 829.0, 801.8 cm^{-1}. Anal. Calc. for $C_{19}H_{19}FeN$: C, 71.94; H, 6.04; N, 4.41. Found: C, 72.03; H, 6.07; N, 4.38%.

4.1.2. 2-(4-Aminophenyl)[3]ferrocenophane (2)

Prepared as described above by reduction of 2-(*p*-nitrophenyl)[3]ferrocenophane [4] (0.15 g, 0.432 mmol) with $SnCl_2 \cdot 2H_2O$ (0.6 g, 2.659 mmol) in a mixture of *i*PrOH/H_2O (1:1) (10 mL) and HCl (conc.) (1 mL). The obtained yellow oil (0.13 g) was purified by column chromatography (Al_2O_3, eluent CH_2Cl_2). Yield 0.07 g (51.1%). Yellow oil. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.85$–2.00 (m, 4H, C_3H_6 bridge), 2.00–2.10 (m, 1H, C_3H_6 bridge) 2.30–2.45 (m, 1H, C_3H_6 bridge), 3.24 (m, 1H, C_5H_3Fe), 3.40–3.80 (br. s, 2H, NH_2), 3.93 (m, 1H, C_5H_3Fe), 4.00 (m, 1H, C_5H_3Fe), 4.06 (m, 2H, C_5H_4Fe), 4.25 (m, 2H, C_5H_4Fe), 6.63 (m, 2H, C_6H_4), 7.23 (m, 2H, C_6H_4). IR (KBr tablet): $\tilde{\nu} = 3451.4$ (N–H), 3369.1 (N–H), 2915.0 (C–H), 2844.3 (C–H), 1620.0, 1524.2, 1437.3, 1277.3, 1044.0, 830.0, 800.8 cm^{-1}. Anal. Calc. for $C_{19}H_{19}FeN$: C, 71.94; H, 6.04; N, 4.41. Found: C, 72.08; H, 6.01; N, 4.45%.

4.1.3. 3,4′-Di(4-aminophenyl)[3]ferrocenophane (3)

Prepared as described above by reduction of 3,4-di-(4-nitrophenyl)[3]ferrocenophane [4] (0.0792 g, 0.169 mmol) with $SnCl_2 \cdot 2H_2O$ (0.2891 g, 1.281 mmol) in a mixture of *i*PrOH/H_2O (2:1) (20 mL) and HCl (conc.) (0.4 mL). The product was crystallized from dichloromethane solution by adding EtOH and evaporating CH_2Cl_2. Yield 0.0681 g (98.6%). Yellowish orange powder, m.p. 112 °C. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.80$–2.15 (m, 6H, C_3H_6 bridge), 2.50–3.50 (br. s, 4H, NH_2), 3.74 (m, 2H, C_5H_4Fe), 4.15 (m, 2H, C_5H_4Fe), 4.29 (s, 2H, C_5H_2Fe), 6.52 (m, 2H, C_6H_4), 7.15 (m, 2H, C_6H_4). IR (KBr tablet): $\tilde{\nu} = 3428.2$ (N–H), 3361.0 (N–H), 1917.3 (C–H), 2845.7 (C–H), 1618.3, 1522.6, 1279.2, 1176.2, 830.6 cm^{-1}. MS (70 eV): *m/z* (%): 408 (100) [M^+]; $C_{25}H_{24}FeN_2$: calc.: 408.3189; found 408.1278. Anal. Calc. for $C_{25}H_{24}FeN_2$: C, 73.54; H, 5.92; N, 6.86. Found: C, 73.78; H, 5.98; N, 6.79%.

4.1.4. 3,4′-Bis-(4-aminophenyl)[3]ferrocenophane (4)

Prepared as described above by reduction of 3,4′-bis-(4-nitrophenyl)[3]ferrocenophane [4] (0.1203 g, 0.257 mmol) with $SnCl_2 \cdot 2H_2O$ (0.4535 g, 2.010 mmol) in a mixture of *i*PrOH/H_2O (2:1) (25 mL) and HCl (conc.) (0.6 mL). The product was crystallized from dichloromethane solution by adding EtOH and evaporating CH_2Cl_2. Yield 0.1001 g (95.4%). Yellowish orange powder, m.p. 91 °C. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.85$–2.10 (m, 6H, C_3H_6 bridge), 2.70–4.10 (br. s, 4H, NH_2), 3.78 (m, 2H, C_5H_3Fe), 4.25 (m, 2H, C_5H_3Fe), 4.32 (m, 2H, C_5H_3Fe), 6.59 (m, 2H, C_6H_4), 7.16 (m, 2H, C_6H_4). IR (KBr tablet): $\tilde{\nu} = 3428.2$ (N–H), 3359.2 (N–H), 2907.3 (C–H), 2837.4 (C–H), 1618.2, 1528.3, 1275.5, 1179.1, 829.0 cm^{-1}. MS (70 eV): *m/z* (%): 408 (100) [M^+]; $C_{25}H_{24}FeN_2$: calc.: 408.3189; found: 408.1449. Anal. Calc. for $C_{25}H_{24}FeN_2$: C, 73.54; H, 5.92; N, 6.86. Found: C, 73.67; H, 5.78; N, 6.81%.

4.1.5. 4-Dodecyloxybenzaldehyde (10a)

A solution of 4-hydroxybenzaldehyde **9a** (6.9783 g, 0.0571 mol) and 1-bromododecane (14.2423 g, 0.0571 mol) in acetone (50 mL) was refluxed for 48 h in the presence of an anhydrous potassium carbonate (15 g). Inorganic salts were filtered off, and acetone was evaporated to dryness. The residue was distilled under vacuum (165–170 °C/0.007 mm Hg). Yield 12.3764 g (74.8%). Light yellow oil, which crystallize upon cooling below 0 °C as paraffin-like solid. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 0.87$ (t, 3H, CH_3), 1.29 (m, 18H, CH_2), 1.77 (m, 2H, $C\underline{H}_2CH_2O$), 4.05 (t, 2H, CH_2O), 6.92 (m, 2H, C_6H_4), 7.77 (m, 2H, C_6H_4), 9.79 (s, 1H, CHO).

4.1.6. 2-Hydroxy-4-dodecyloxybenzaldehyde (10b)

Prepared as described above from 2,4-dihydroxybenzaldehyde **9b** (7.8143 g, 0.0566 mol) and 1-bromododecane (14.1010 g, 0.0566 mol) in a slurry of anhydrous potassium carbonate (40 g) in acetone (100 mL). The residue after evaporation of acetone was crystallized from ethanol. Yield 13.1856 g (76.0%). White powder, m.p. 49–50 °C. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 0.87$ (t, 3H, CH_3), 1.30 (m, 18H, CH_2), 1.75 (m, 2H, $C\underline{H}_2CH_2O$), 4.00 (t, 2H, CH_2O), 6.39 (m, 1H, C_6H_3), 6.51 (m, 1H, C_6H_3), 7.40 (m, 1H, C_6H_3), 9.71 (s, 1H, CHO), 11.45 (s, 1H, OH).

4.1.7. 4-Dodecyloxyacetophenone (12)

Prepared as described above from 4-hydroxyacetophenone **11** (30.20 g, 0.1212 mol) and 1-bromododecane (16.51 g, 0.1212 mol) in a slurry of anhydrous potassium carbonate (35 g) in acetone (100 mL). The product was crystallized from ethanol. Yield 35 g (95%). White crystals, m.p. 58–59 °C. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 0.85$ (t, 3H, CH_3), 1.28 (m, 18H, CH_2), 1.75 (m, 2H, $C\underline{H}_2CH_2O$), 1.49 (s, 3H, CH_3CO), 3.97 (t, 2H, CH_2O), 6.80 (m, 2H, C_6H_4), 7.81 (m, 2H, C_6H_4).

4.1.8. 4-Dodecyloxybenzoic acid (17)

A mixture of ethyl ester of 4-hydroxy benzoic acid **15** (25.0 g, 0.150 mol) and 1-bromododecane (37.5 g, 0.150 mol) was refluxed for 50 h in a slurry of potassium carbonate (130 g) in acetone (250 mL). Inorganic salts were filtered off and the filtrate was evaporated to dryness. A solution of potassium hydroxide (8.4 g, 0.150 mol) in a mixture of water/ethanol (100 mL/100 mL) was added to the residue of crude ester **16**, and the mixture was refluxed for 24 h. Then an aqueous HCl (conc.) (6 mL) was added and refluxing was continued for 2 h. The obtained white precipitate was filtered off and washed several times with water, and two times with ethanol. Yield 44.3 g (96.4%). White powder, Cr–S_A 94 °C, S_A–N 131 °C, N–I 139 °C. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 0.87$ (t, 3H, CH_3), 1.30 (m, 18H, CH_2), 1.76 (m, 2H, $C\underline{H}_2CH_2O$), 3.98

(t, 2H, CH_2O), 6.84 (m, 2H, C_6H_4), 7.90 (m, 2H, C_6H_4), 9–10 (very br. s, 1H, COOH).

4.1.9. 4-(4-Dodecyloxybenzoyloxy)benzaldehyde (**19a**)

A mixture of 4-dodecyloxybenzoic acid **17** (6.21 g, 0.0203 mol) and thionyl chloride (20 mL) was refluxed for 5 h, then $SOCl_2$ excess was distilled off under atmospheric pressure. The remaining $SOCl_2$ was removed at room temperature by applying vacuum for 1 h. This fresh chloridic anhydride **18** was dissolved in dry benzene (20 mL) and added dropwise during 45 min to a stirred solution of 4-hydroxybenzaldehyde **9a** (2.48 g, 0.0203 mol) in a mixture pyridine/benzene (10 mL/10 mL). The reaction mixture was refluxed for 4 h, then cooled down and stirred at room temperature overnight. The obtained products were poured into 100 mL of water. The organic layer was separated in a separating funnel and washed with diluted aqueous HCl, then separated again and dried over a sodium sulphate. Drying agent was filtered off and the filtrate was evaporated to dryness. The residue was recrystallized from ethanol. Yield 7.69 g (92.3 %). White powder, Cr–N 66 °C, N–I 77 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 0.90$ (t, 3H, CH_3), 1.26 (m, 18H, CH_2), 1.79 (m, 2H, $C\underline{H}_2CH_2O$), 3.98 (t, 2H, CH_2O), 6.86 (m, 2H, C_6H_4), 7.27 (m, 2H, C_6H_4), 7.82 (m, 2H, C_6H_4), 8.04 (m, 2H, C_6H_4), 9.83 (s, 1H, CHO).

4.1.10. 2-Hydroxy-4-(4-dodecyloxybenzoyloxy) benzaldehyde (**19b**)

Prepared in a previous manner by esterification reaction between 4-hydroxysalicylaldehyde **9b** (3.5231 g, 0.0255 mol) and 4-dodecyloxybenzoic acid (7.8168 g, 0.0255 mol). Yield 5.5407 g (50.9%). White fibrous crystals, m.p. 73–74 °C.

4.2. General procedure for obtaining Schiff's bases (**5**–**8**)

Ferrocenophane-containing amines **1**–**4** were dissolved in minimal amount of hot ethanol and added to a solution of slightly excess from equimolar quantity of the appropriate aldehydes **10**, **19**. The reaction mixtures were refluxed for 0.5–1 h. The precipitate obtained after cooling of the mixture was filtered, then recrystallized from ethanol, or reprecipitated from a CH_2Cl_2 solution by adding ethanol. Yields varied from 70% to 95%.

4.2.1. 3-[4-(4-Dodecyloxybenzaldimino)phenyl][3] ferrocenophane (**5a**)

Prepared from 3-(4-aminophenyl)[3]ferrocenophane **1** (0.5128 g, 1.618 mmol) and compound **10a** (0.4955 g, 1.706 mmol). Yield 0.8322 g (87.0%). Light orange powder. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.88$ (t, 3H, CH_3), 1.27 (m, 18H, CH_2), 1.81 (m, 2H, $C\underline{H}_2CH_2O$), 1.90–2.15 (m, 6H, C_3H_6 bridge), 3.43 (m, 1H, C_5H_3Fe), 3.90 (m, 1H, C_5H_3Fe), 4.01 (t, 2H, CH_2O), 4.12 (m, 1H, C_5H_3Fe), 4.23 (m, 2H, C_5H_4Fe), 4.50 (m, 2H, C_5H_4Fe), 6.96 (m, 2H, C_6H_4), 7.10 (m, 2H, C_6H_4), 7.42 (m, 2H, C_6H_4), 7.83 (m, 2H, C_6H_4), 8.42 (s, 1H, CH=N). IR (KBr tablet): $\tilde{\nu} = 2919.4$ (C–H), 2846.5 (C–H), 1607.9 (CH=N), 1568.9, 1519.6, 1465.5, 1421.6, 1304.1, 1247.2, 1162.4, 848.2 cm^{-1}; MS (70 eV): *m/z* (%): 589 (100) [M^+], 420 (11.58) [$M^+-C_{12}H_{25}$]; $C_{38}H_{47}FeNO$: calc.: 589.6345; found: 589.3024. Anal. Calc. for $C_{38}H_{47}FeNO$: C, 77.40; H, 8.03; N, 2.37. Found: C, 77.63; H, 7.98; N, 2.34%.

4.2.2. 3-[4-(2-Hydroxy-4-dodecyloxybenzaldimino)phenyl] [3]ferrocenophane (**5b**)

Prepared from 3-(4-aminophenyl)[3]ferrocenophane **1** (0.1424 g, 0.449 mmol) and compound **10b** (0.1534 g, 0.500 mmol). Yield 0.2379 g (87.3%). Yellowish orange powder. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.88$ (t, 3H, CH_3), 1.27 (m, 18H, CH_2), 1.79 (m, 2H, $C\underline{H}_2CH_2O$), 1.90–2.15 (m, 6H, C_3H_6 bridge), 3.44 (m, 1H, C_5H_3Fe), 3.89 (m, 1H, C_5H_3Fe), 4.00 (t, 2H, CH_2O), 4.11 (m, 1H, C_5H_3Fe), 4.22 (m, 2H, C_5H_4Fe), 4.49 (m, 2H, C_5H_4Fe), 6.44 (m, 1H, C_6H_3), 6.55 (m, 1H, C_6H_3), 7.10 (m, 2H, C_6H_4), 7.42 (m, 2H, C_6H_4), 8.08 (m, 1H, C_6H_3), 8.86 (s, 1H, CH=N). IR (KBr tablet): $\tilde{\nu} = 2918.8$ (C–H), 2848.8 (C–H), 1608.1 (CH=N), 1592.5, 1519.2, 1466.9, 1431.7, 1316.2, 1279.4, 1185.6, 1102.0, 816.5 cm^{-1}. MS (70 eV): *m/z* (%): 605 (100) [M^+]. Anal. Calc. for $C_{38}H_{47}FeNO_2$: C, 75.36; H, 7.82; N, 2.31. Found: C, 75.08; H, 7.98; N, 2.27%.

4.2.3. 3-{4-[4-(4-Dodecyloxybenzoyloxy)benzaldimino] phenyl}[3]ferrocenophane (**5c**)

Prepared from 3-(4-aminophenyl)[3]ferrocenophane **1** (0.2503 g, 0.789 mmol) and compound **19a** (0.3255 g, 0.792 mmol). Yield 0.3968 g (70.8%). Yellowish orange powder. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C):$\delta = 0.88$ (t, 3H, CH_3), 1.24–1.35 (m,18H, CH_2), 1.82 (m, 2H, $C\underline{H}_2CH_2O$), 1.90–2.10 (m, 6H, C_3H_6 bridge), 3.44 (m, 1H, C_5H_3Fe), 3.90 (m, 1H, C_5H_3Fe), 4.04 (t, 2H, CH_2O), 4.13 (m, 1H, C_5H_3Fe), 4.23 (m, 2H, C_5H_4Fe), 4.52 (m, 2H, C_5H_4Fe), 6.97 (m, 2H, C_6H_4), 7.14 (m, 2H, C_6H_4), 7.33 (m, 2H, C_6H_4), 7.44 (m, 2H, C_6H_4), 7.96 (m, 2H, C_6H_4), 8.15 (m, 2H, C_6H_4), 8.51 (s, 1H, CH=N). IR (KBr tablet): $\tilde{\nu} = 2920.4$ (C–H), 2849.9 (C–H), 1720.8 (C=O), 1610.0 (CH=N), 1514.5, 1466.1, 1320.2, 1267.6, 1206.9, 1173.7, 1161.0, 1079.9, 845.6 cm^{-1}. MS (70 eV): *m/z* (%): 709 (100) [M^+], 420 (15.04) [$M^+-C_{12}H_{25}$-OC_6H_4CO], 289 (17.66) [$C_{12}H_{25}OC_6H_4CO^+$], 120 (64.02) [$OC_6H_4CO^+$]; $C_{45}H_{51}FeNO_3$: calc.: 709.7406; found: 709.7062. Anal. Calc. for $C_{45}H_{51}FeNO_3$: C, 76.15; H, 7.24; N, 1.97. Found: C, 76.02; H, 7.18; N, 1.92%.

4.2.4. 3-{4-[2-Hydroxy-4-(4-dodecyloxybenzoyloxy) benzaldimino]phenyl}[3]ferrocenophane (**5d**)

Prepared from 3-(4-aminophenyl)[3]ferrocenophane **1** (0.1443 g, 0.455 mmol) and compound **19b** (0.1941 g, 0.455 mmol). Yield 0.2561 g (77.5%). Yellowish orange powder. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.88$ (t, 3H, CH3), 1.24–1.35 (m, 18H, CH_2), 1.82 (m, 2H, $C\underline{H}_2CH_2O$), 1.90–2.10 (m, 6H, C_3H_6 bridge), 3.44 (m,

1H, C_5H_3Fe), 3.90 (m, 1H, C_5H_3Fe), 4.04 (t, 2H, CH_2O), 4.15 (m, 1H, C_5H_3Fe), 4.24 (m, 2H, C_5H_4Fe), 4.52 (m, 2H, C_5H_4Fe), 6.82 (dd, $J_1(H,H) = 2.24$ Hz, $J_2(H,H) = 8.37$ Hz, 1H, C_6H_3), 6.88 (d, $J_1(H,H) = 2.24$ Hz, 1H, C_6H_3), 6.97 (m, 2H, C_6H_4), 7.19 (m, 2H, C_6H_4), 7.42 (d, $J_2(H,H) = 8.37$ Hz, 1H, C_6H_3), 7.46 (m, 2H, C_6H_4), 8.14 (m, 2H, C_6H_4), 8.66 (s, 1H, CH=N). IR (KBr tablet): $\tilde{\nu} = 2918.5$ (C–H), 2848.0 (C–H), 1724.1 (C=O), 1601.9 (CH=N), 1522.2, 1466.8, 1251.9, 1167.4, 1149.3, 1117.9, 1064.2, 837.9 cm^{-1}. MS (70 eV): *m/z* (%): 725 (100) [M^+], 436 (87.53) [$M^+-C_{12}H_{25}OC_6H_4CO$], 289 (7.68) [$C_{12}H_{25}OC_6H_4CO^+$], 120 (50.76) [$OC_6H_4CO^+$]; $C_{45}H_{51}FeNO_4$: calc.: 725.7400; found: 725.5511. Anal. Calc. for $C_{45}H_{51}FeNO_4$: C, 74.47; H, 7.08; N, 1.93. Found: C, 74.62; H, 7.16; N, 1.91%.

4.2.5. 2-[4-(4-Dodecyloxybenzaldimino)phenyl][3]ferrocenophane (6a)

Prepared from 2-(4-aminophenyl)[3]ferrocenophane **2** (0.0247 g, 0.078 mmol) and compound **10a** (0.0236 g, 0.081 mmol). Yield 0.0428 g (93.2%). Yellowish orange powder. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.88$ (t, 3H, CH_3), 1.25–1.35 (m, 18H, CH_2), 1.81 (m, 2H, $C\underline{H}_2CH_2O$), 1.88–2.00 (m, 4H, C_3H_6 bridge), 2.09 (m, 1H, C_3H_6 bridge), 2.44 (m, 1H, C_3H_6 bridge), 3.25 (m, 1H, C_5H_3Fe), 3.95 (m, 1H, C_5H_3Fe), 4.02 (t, 2H, CH_2O), 4.02 (m, 1H, C_5H_3Fe), 4.13 (m, 2H, C_5H_4Fe), 4.31 (m, 1H, C_5H_4Fe), 4.36 (m, 1H, C_5H_4Fe), 6.97 (m, 2H, C_6H_4), 7.14 (m, 2H, C_6H_4), 7.44 (m, 2H, C_6H_4), 7.84 (m, 2H, C_6H_4), 8.44 (s, 1H, CH=N). IR (KBr tablet): $\tilde{\nu} = 2917.7$ (C–H), 2849.2 (C–H), 1602.1 (CH=N), 1584.7, 1510.1, 1466.1, 1248.8, 1160.2, 848.3 cm^{-1}. MS (70 eV): *m/z* (%): 589 (100) [M^+], 420 (7.67) [$M^+-C_{12}H_{25}$]; $C_{38}H_{47}FeNO$: calc.: 589.6345; found: 589.4709. Anal. Calc. for $C_{38}H_{47}FeNO$: C, 77.40; H, 8.03; N, 2.37. Found: C, 77.59; H, 8.09; N, 2.31%.

4.2.6. 2-{4-[4-(4-Dodecyloxybenzoyloxy)benzaldimino]phenyl}[3]ferrocenophane (6b)

Prepared from 2-(4-aminophenyl)[3]ferrocenophane **2** (0.0304 g, 0.096 mmol) and compound **19a** (0.0393 g, 0.096 mmol). Yield 0.0473 g (69.7%). Yellowish orange powder. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.88$ (t, 3H, CH_3), 1.25–1.35 (m, 18H, CH_2), 1.82 (m, 2H, $C\underline{H}_2CH_2O$), 1.88–1.97 (m, 4H, C_3H_6 bridge), 2.10 (m, 1H, C_3H_6 bridge), 2.45 (m, 1H, C_3H_6 bridge), 3.26 (m, 1H, C_5H_3Fe), 3.96 (m, 1H, C_5H_3Fe), 4.03 (m, 1H, C_5H_3Fe), 4.05 (t, 2H, CH_2O), 4.14 (m, 2H, C_5H_4Fe), 4.31 (m, 1H, C_5H_4Fe), 4.37 (m, 1H, C_5H_4Fe), 6.98 (m, 2H, C_6H_4), 7.18 (m, 2H, C_6H_4), 7.33 (m, 2H, C_6H_4), 7.46 (m, 2H, C_6H_4), 7.98 (m, 2H, C_6H_4), 8.15 (m, 2H, C_6H_4), 8.53 (s, 1H, CH=N). IR (KBr tablet): $\tilde{\nu} = 2919.6$ (C–H), 2849.7 (C–H), 1731.2 (C=O), 1602.7 (CH=N), 1510.2, 1254.3, 1198.0, 1160.0, 1063.6, 1007.6, 843.2 cm^{-1}. MS (70 eV): *m/z* (%): 709 (100) [M^+], 420 (7.79) [$M^+-C_{12}H_{25}OC_6H_4CO$], 289 (40.50) [$C_{12}H_{25}OC_6H_4CO^+$]; 120 (65.18) [$OC_6H_4CO^+$]; $C_{45}H_{51}FeNO_3$: calc.: 709.7406; found: 709.6663. Anal. Calc. for $C_{45}H_{51}FeNO_3$: C, 76.15; H, 7.24; N, 1.97. Found: C, 76.32; H, 7.31; N, 1.91%.

4.2.7. 3,4-Di[4-(4-dodecyloxybenzaldimino)phenyl][3]ferrocenophane (7a)

Prepared from 3,4-di(4-aminophenyl)[3]ferrocenophane **3** (0.0320 g, 0.078 mmol) and compound **10a** (0.0455 g, 0.158 mmol). Yield 0.0615 g (82.5%). Yellowish orange amorphous solid. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.88$ (t, 6H, CH_3), 1.24–1.37 (m, 36H, CH_2), 1.80 (m, 4H, $C\underline{H}_2CH_2O$), 1.95–2.10 (m, 6H, C_3H_6 bridge), 3.81 (m, 2H, C_5H_4Fe), 4.01 (t, 4H, CH_2O), 4.22 (m, 2H, C_5H_4Fe), 4.44 (s, 2H, C_5H_2Fe), 6.97 (m, 4H, C_6H_4), 7.05 (m, 4H, C_6H_4), 7.37 (m, 4H, C_6H_4), 7.83 (m, 4H, C_6H_4), 8.42 (s, 2H, CH=N). MS (70 eV): *m/z* (%): 952 (100) [M^+-H]; $C_{63}H_{80}FeN_2O_2$: calc.: 953.1724; found: 953.1212. Anal. Calc. for $C_{63}H_{80}FeN_2O_2$: C, 79.38; H, 8.46; N, 2.94. Found: C, 79.12; H, 8.28; N, 2.90%.

4.2.8. 3,4-Di{4-[4-(4-dodecyloxybenzoyloxy)benzaldimino]phenyl}[3]ferrocenophane (7b)

Prepared from 3,4-di(4-aminophenyl)[3]ferrocenophane **3** (0.0251 g, 0.061 mmol) and compound **19a** (0.0505 g, 0.123 mmol). Yield 0.0650 g (88.0%). Yellowish orange powder. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.88$ (t, 6H, CH_3), 1.25–1.35 (m, 36H, CH_2), 1.82 (m, 4H, $C\underline{H}_2CH_2O$), 1.95–2.10 (m, 6H, C_3H_6 bridge), 3.83 (m, 2H, C_5H_4Fe), 4.05 (t, 4H, CH_2O), 4.23 (m, 2H, C_5H_4Fe), 4.46 (s, 2H, C_5H_2Fe), 6.98 (m, 4H, C_6H_4), 7.08 (m, 4H, C_6H_4), 7.33 (m, 4H, C_6H_4), 7.40 (m, 4H, C_6H_4), 7.97 (m, 4H, C_6H_4), 8.15 (m, 4H, C_6H_4), 8.52 (s, 2H, CH=N). IR (KBr tablet): $\tilde{\nu} = 2921.8$ (C–H), 2850.9 (C–H), 1734.0 (C=O), 1604.0 (CH=N), 1510.9, 1466.5, 1257.3, 1200.9, 1165.6, 1064.5, 843.7 cm^{-1}. MS (70 eV): *m/z* (%): 1192 (88.61) [M^+-H], 903 (15.76) [$M^+-C_{12}H_{25}OC_6H_4CO$], 289 (19.11) [$C_{12}H_{25}OC_6H_4CO^+$], 120 (100) [$OC_6H_4CO^+$]; $C_{77}H_{88}FeN_2O_6$: calc.: 1193.3846; found: 1192.8614. Anal. Calc. for $C_{77}H_{88}FeN_2O_6$: C, 77.50; H, 7.43; N, 2.35. Found: C, 77.73; H, 7.54; N, 2.41%.

4.2.9. 3,4′-Bis-[4-(4-dodecyloxybenzaldimino)phenyl][3]ferrocenophane (8a)

Prepared from 3,4′-bis-(4-aminophenyl)[3]ferrocenophane **4** (0.0245 g, 0.060 mmol) and compound **10a** (0.0365 g, 0.126 mmol). Yield 0.0423 g (73.4%). Yellowish orange powder. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.88$ (t, 6H, CH_3), 1.24–1.50 (m, 36H, CH_2), 1.80 (m, 4H, $C\underline{H}_2CH_2O$), 2.00 (m, 6H, C_3H_6 bridge), 3.91 (m, 2H, C_5H_3Fe), 4.02 (t, 4H, CH_2O), 4.35 (m, 2H, C_5H_3Fe), 4.45 (m, 2H, C_5H_3Fe), 6.98 (m, 4H, C_6H_4), 7.13 (m, 4H, C_6H_4), 7.35 (m, 4H, C_6H_4), 7.85 (m, 4H, C_6H_4), 8.46 (s, 2H, CH=N). IR (KBr tablet): $\tilde{\nu} = 2922.4$ (C–H), 2850.8 (C–H), 1607.5 (CH=N), 1570.0, 1520.8, 1464.5, 1422.1, 1306.0, 1249.3, 1162.8, 844.3 cm^{-1}. MS (70 eV): *m/z* (%): 952 (100) [M^+-H]; $C_{63}H_{80}FeN_2O_2$: calc.: 953.1724; found: 953.1243. Anal. Calc. for $C_{63}H_{80}FeN_2O_2$: C, 79.38; H, 8.46; N, 2.94. Found: C, 79.53; H, 8.35; N, 2.97%.

4.2.10. 3,4′-Bis-{4-[4-(4-dodecyloxybenzoyloxy) benzaldimino]phenyl}[3]ferrocenophane (**8b**)

Prepared from 3,4′-bis-(4-aminophenyl)[3]ferrocenophane **4** (0.0290 g, 0.071 mmol) and compound **19a** (0.0583 g, 0.142 mmol). Yield 0.0663 g (78.1%). Yellowish orange powder. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.88$ (t, 6H, CH_3), 1.25–1.35 (m, 36H, CH_2), 1.83 (m, 4H, $C\underline{H}_2CH_2O$), 1.99–2.05 (m, 6H, C_3H_6 bridge), 3.94 (m, 2H, C_5H_3Fe), 4.05 (t, 4H, CH_2O), 4.23 (m, 2H, C_5H_3Fe), 4.47 (m, 2H, C_5H_3Fe), 6.98 (m, 4H, C_6H_4), 7.17 (m, 4H, C_6H_4), 7.34 (m, 4H, C_6H_4), 7.38 (m, 4H, C_6H_4), 7.99 (m, 4H, C_6H_4), 8.15 (m, 4H, C_6H_4), 8.56 (s, 2H, CH=N). IR (KBr tablet): $\tilde{\nu} = 2920.8$ (C–H), 2850.3 (C–H), 1729.8 (C=O), 1603.0 (CH=N), 1510.1, 1255.0, 1197.9, 1158.1, 1064.4, 843.4 cm^{-1}. MS (70 eV): *m/z* (%): 1192 (69.12) [M^+-H], 903 (15.76) [$M^+-C_{12}H_{25}O$-C_6H_4CO], 289 (26.39) [$C_{12}H_{25}OC_6H_4CO^+$], 120 (100) [$OC_6H_4CO^+$]; $C_{77}H_{88}FeN_2O_6$: calc.: 1193.3846; found: 1193.3039. Anal. Calc. for $C_{77}H_{88}FeN_2O_6$: C, 77.50; H, 7.43; N, 2.35. Found: C, 77.34; H, 7.48; N, 2.39%.

4.3. Preparation of [3]ferrocenophane-containing β-aminovinylketone

4.3.1. 3-{4-[1-(4-Dodecyloxybenzoyl)ethenyl-2-amino] phenyl}[3]ferrocenophane (**14**)

Equimolar amounts of absolute ethanol and formic acid were refluxed over an anhydrous $CaCl_2$ for 30 min, then ethyl ester of formic acid was distilled off from the mixture (b.p. 53–54 °C). A mixture of ethyl formiate (0.4261 g, 0.575 mol) and 4-dodecyloxyacetophenone **12** (1.7501 g, 0.575 mol) in absolute benzene (10 ml) was refluxed for 6 hrs in the presence of Na (0.1322 g, 0.575 mol). The precipitate of sodium enolate **13** was filtered off, recrystallized from benzene, and the obtained white powder used without characterization. Yield 1.3562 g (66.6%). A mixture of sodium enolate **13** (0.3348 g, 0.944 mmol), amine **1** (0.2996 g, 0.944 mmol) and 5 N HCl (0.2 mL) were refluxed in ethanol (10 mL) for 15 min. The precipitate was filtered off, dissolved in CH_2Cl_2 and filtered through Celite 545. Dichloromethane was evaporated from the filtrate, and the residue was recrystallized from *n*-butanol. Yield 0.4670 g (78.3%). Yellowish orange powder. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.88$ (t, 3H, CH_3), 1.15–1.65 (m, 18H, CH_2), 1.80 (m, 2H, $C\underline{H}_2CH_2O$), 1.90–2.15 (m, 6H, C_3H_6 bridge), 3.42 (m, 1H, C_5H_3Fe), 3.90 (m, 1H, C_5H_3Fe), 4.01 (t, 2H, CH_2O), 4.11 (m, 1H, C_5H_3Fe), 4.21 (m, 2H, C_5H_4Fe), 4.46 (m, 2H, C_5H_3Fe), 5.97 (d, J_1(H,H) = 7.88 Hz, 1H, CH–CO), 6.93 (m, 2H, C_6H_4), 6.97 (m, 2H, C_6H_4), 7.37 (m, 2H, C_6H_4), 7.45 (dd, J_1(H,H) = 7.88 Hz, J_2(H,H) = 12.25 Hz, 1H, CH=CH) 7.90 (m, 2H, C_6H_4), 12.14 (d, J_2(H,H) = 12.25 Hz, 1H, N–H). IR (KBr tablet): $\tilde{\nu} = 2920.5$ (C–H), 2850.1 (C–H), 1626.4, 1599.7, 1573.1, 1531.7, 1465.9, 1279.5, 1244.9, 1168.4, 1038.8, 831.2 cm^{-1}. MS (70 eV): *m/z* (%): 631 (100) [M^+], 462 (6.32) [$M^+-C_{12}H_{25}$]; $C_{40}H_{49}FeNO_2$: calc.: 631.6714; found: 631.9114. Anal. Calc. for $C_{40}H_{49}FeNO_2$: C, 76.06; H, 7.82; N, 2.22. Found: C, 76.23; H, 7.69; N, 2.28%.

Acknowledgements

O.N. Kadkin acknowledges the Deutscher Akademischer Austauschdienst (DAAD). Special thanks to Prof. Dr. Willy Friedrichsen for his advising and encouraging this work. We are grateful to Mr. Elmar Schneider and Ms. Utta Oelbermann for mass, IR and UV spectroscopy measurements, and Mr. Dirk Mayer, Ms. Wiebke Delfs and Mr. Holger Franzen for recording ^{1}H NMR spectra. Financial support from Korean government program BK-21 is also gratefully acknowledged.

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