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Journal of Organometallic Chemistry 691 (2006) 3037–3042

Journal of Organo metallic Chemistry

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Formation of intramolecular hydrogen bonds in heterodisubstituted ferrocene diamides with a secondary and a tertiary amido group: X-ray structure of 1′-(*N*′-butyl-carbamoyl)-morpholino ferrocenecarboxamide

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Received 10 January 2006; received in revised form 27 February 2006; accepted 8 March 2006
Available online 14 March 2006

Abstract

Various unsymmetrically substituted ferrocene 1,1′-diamides have been synthesized via homogeneous catalytic carbonylation starting from 1,1′-diiodoferrocene. The unique features observed in the ^{1}H NMR and IR spectra of the compounds bearing a secondary and a tertiary amido group are explained by the formation of an internal hydrogen bond between the substituents. Addition of chloride ions (as a tetrabutylammonium salt) into the solutions of these compounds results in spectroscopic changes due to the formation of intermolecular hydrogen bonds between the ferrocene diamide and the anion. The solid state structure of 1′-(*N*′-butyl-carbamoyl)-morpholino ferrocenecarboxamide (**1a**) has also been determined by X-ray crystallography. A strong intramolecular H-bond between the NH group of the *N*′-butyl-carbamoyl moiety and the CO of the tertiary amido group was observed.

Keywords: Ferrocene; Diamides; Carbonylation; Palladium; Intramolecular hydrogen bond

1. Introduction

In the past few decades numerous new ferrocene derivatives have been synthesized and characterized due to their favorable electrochemical properties which make them excellent candidates for the preparation of chemical sensors and molecular receptors [1–5].

In these applications formation of hydrogen bonds between the host ferrocene derivative and the guest molecule or between two appropriate substituents on the ferrocene itself often plays a crucial role. Various ferrocene amides can be used as anion receptors due to the formation of a hydrogen bond between the amide NH and the anion (e.g. chloride) [6,7]. Strong intramolecular hydrogen bonds between ester CO and amide NH of disubstituted ferrocene amino acid conjugates have been detected [8]. This interaction leads to an ordered conformation even in solution and makes these derivatives good organometallic mimics of peptide β-turn structures [9].

Due to these applications, the formation of hydrogen bonds in ferrocene amide derivatives has been extensively studied. The existence of different types of hydrogen bonds has been observed for a ferrocene 1,1′-bis(phenylalanine) derivative [9]. While in solution the existence of NH…CO(ester) bond was detected in accordance with other amino acid conjugates, in the solid state the formation of an NH…CO(amide) bond has been proved. An unsymmetrical diferrocene diamide derived from 1-aminoferrocene-1′-carboxylic acid was found to possess a dynamic intramolecular hydrogen bond in solution [10]. At the same time, no indication for an intramolecular hydrogen bond in the solution of the 1,1′-diamide produced from (*S*)-1-phenylethylamine was observed according to the infrared and ^{1}H

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0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.03.013

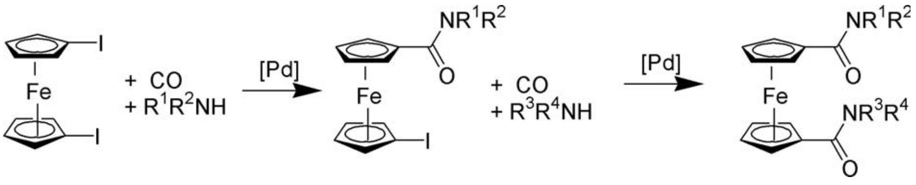
NMR data, although a large negative value for temperature dependence seemed to suggest a hydrogen bond [9].

Recently, we have reported on the homogeneous catalytic synthesis of various ferrocene amides and diamides starting from iodoferrocene and 1,1′-diiodoferrocene, respectively [11–13]. Some of the unsymmetrically substituted 1,1′-ferrocene diamides showed unique spectroscopic properties compared to others.

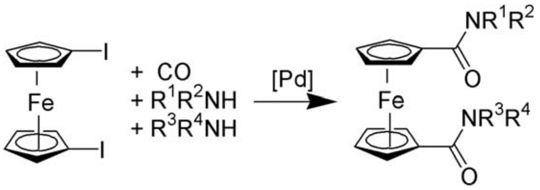
In this paper, the structure of ferrocene diamides with a secondary and tertiary amido group is discussed and the formation of an intramolecular hydrogen bond between the 1-amide CO and 1′-amide NH group of these compounds (both in the solid state and in solution) is reported.

2. Results and discussion

As a part of our series of investigations concerning palladium-catalyzed carbonylation of iodoferrocene and 1,1′-iodoferrocene, two methods for the synthesis of new unsymmetrically substituted 1,1′-ferrocene diamides have been reported. These compounds can be formed either in two separate carbonylation steps (Eq. (1)) [13] or in one pot, using two different amines as nucleophiles simultaneously (Eq. (2)) [12]. In the present work the second method was found to be superior and several heterodisubstituted ferrocene diamides (e.g. **1a**–**e**, Fig. 1) have been prepared in fair yields (36–85%).



(1)



(2)

In these aminocarbonylation reactions the symmetrical ferrocene diamides (**2a**–**d**, Fig. 1), some of them synthesized before starting from *bis*(chlorocarbonyl)-ferrocene [14], were also formed as side products.

During the characterization of the diamides evident differences in the ^{1}H NMR spectra of compounds bearing one secondary and one tertiary amido group (**1a**–**c**) have been observed compared to the other disubstituted derivatives (**1d**,**e** or **2a**–**d**). The signal corresponding to the NH in the secondary amido group of **1a**–**c** appeared at 8.32, 8.42 and 8.53 ppm, respectively, while a chemical shift of 6.68 ppm for the two identical NH of **2a** was observed. This large amide ‘downfield’ NH shift strongly suggested the formation of an intramolecular hydrogen bond in products **1a**–**c**. There were also some remarkable changes in the region of the Cp protons. In the spectra of **1d**,**e**, as it was expected, four broad singlets could be assigned to the 2,5; 3,4; 2′,5′ and 3′,4′ protons, respectively. Besides, the chemical shifts of these singlets corresponded well to the chemical shifts of the two pairs of singlets that were observed in the two symmetrically substituted diamides with the same amido groups. As an example, the Cp protons of **1d** had four chemical shifts of 4.62, 4.58, 4.38 and 4.36 ppm, while Cp protons of **2c** and **2d** were observed at 4.63, 4.36 ppm and 4.58, 4.38 ppm, respectively. At the same time in the spectra of **1a**–**c**, some of the signals of this region merged, which later was also proved to be a sign for the intramolecular hydrogen bond.

Because of the above observations, a more detailed investigation of the structure of **1a** has been carried out both in the solid state and in solution.

2.1. Solid state structure of *1a*

ORTEP plot of the structure **1a** is shown at Fig. 2. The strong intramolecular H-bond can be characterized by H42...O1 distance of 2.18(5) Å, N42...O1 2.933(6) Å and N42–H42...O1 174(4)° angle data. Coordination of iron center is the expected one and the Fe–C bond lengths are in the range of 2.01–2.05 Å which is shorter than 2.080 Å given by earlier database studies [15,16].

However, in our case because of the strong intramolecular hydrogen bond between N42–H and O1 rotation of the Cp ring is prevented. Atoms C41–N42–O1–C1–Fe1 are in a plane with rms deviation of 0.055 Å. For further stabilization of the structure there are weak C–H...O hydrogen bonds between appropriate Cp as well as morfoline ring hydrogen atoms and acceptors O1 or O41. The packing diagram shows orientation of the molecules in that way that there are apolar aliphatic side chain and morfoline ring layers between the polar ferrocenyl layers. This

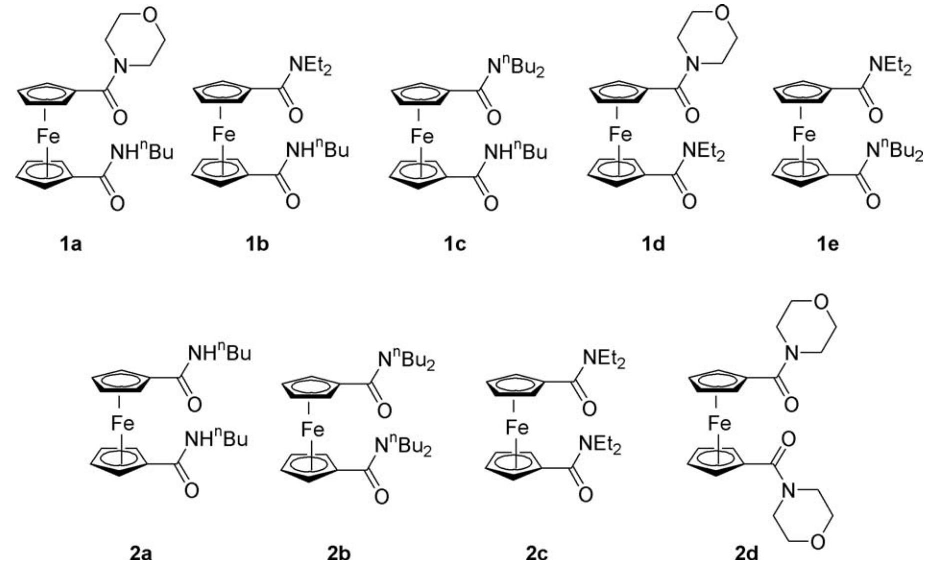


Fig. 1. 1,1′-Ferrocene diamides synthesized by palladium-catalyzed carbonylation.

layered structure is stabilized by van der Waals interaction between the paraffin side chains of neighboring molecules.

The IR spectrum of **1a** (in KBr) showed a ν(NH) band at 3252 cm^{-1}, two carbonyl stretching frequencies (or amide$_{\rm I}$ bands) of equal intensity at 1642 and 1593 cm^{-1} corresponding to non-hydrogen bonded and hydrogen bonded CO, respectively, and an amide$_{\rm II}$ band at 1552 cm^{-1}.

2.2. Solution structure

Although the solid state structure provided a reliable proof for the formation of an intramolecular hydrogen bond between the two substituents of **1a**, molecular conformation in solution remained still to be proved. Two spectroscopic methods, infrared and ^{1}H NMR, were used to clarify this question.

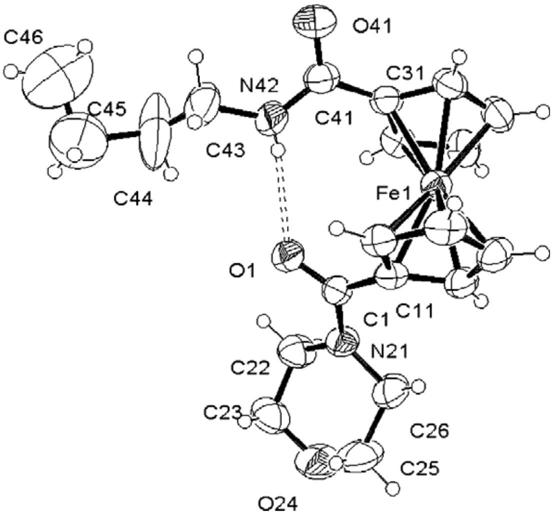


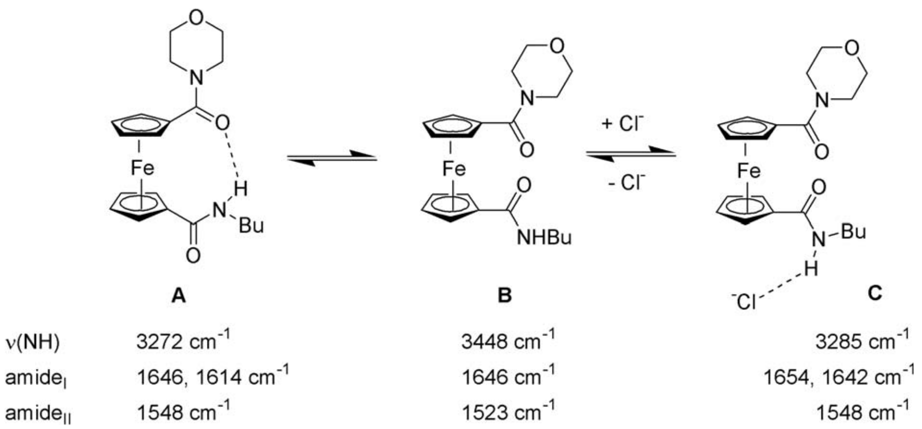
Fig. 2. Thermal ellipsoid plot of **1a** at 50% probability level with partial numbering scheme. Selected bond length (Å) and angles (°): Fe–C 2.013–2.052; C1–O1 1.237(5); C1–C11 1.494(5); C1–N21 1.339(5); C31–C41 1.469(5); C41–O41 1.235(5); C41–N42 1.318(6); N42–C43 1.463(7) O1–N42 2.938(5); N42–H42–O1 174(6).

According to the literature, amide NH atoms that are not hydrogen bonded show νNH stretching vibrations in the infrared spectra at wavenumbers higher than 3400 cm^{-1} and have chemical shifts between 5.5 and 7.0 ppm in the ^{1}H NMR spectra. At the same time hydrogen bonded amide NH display stretching vibrations in the infrared spectra below 3400 cm^{-1} and give proton signals above 7.5 ppm in the ^{1}H NMR spectra. Besides, small values (-2 to -4 ppb K^{-1}) of temperature dependence of $\Delta\delta$H of amide NH in the ^{1}H NMR are characteristic for protons that are not hydrogen bonded or fixed in a very strong hydrogen bond [9]. All these criteria were taken into account in our investigation concerning the structure of **1a**.

The chemical shift of NH of **1a** is 8.32 and 8.47 ppm at 30 °C in CDCl$_3$ and in toluene-d_8, respectively. The change of the latter value is within 0.02 ppm on 15-fold dilution with toluene that supports the presence of an intramolecular interaction. On heating, a -14.3 ppb K^{-1} $\Delta\delta$H (temperature range: 303–353 K) was observed in toluene that shows a moderately strong dynamic hydrogen bond.

The IR spectrum of **1a** in CH$_2$Cl$_2$ shows two bands that can be assigned as NH stretching: one at 3448 cm^{-1} and a stronger one at 3272 cm^{-1}. This can be explained by the presence of both hydrogen bonded (Structure A in Eq. (3)) and non-hydrogen bonded NH (Structure B in Eq. (3)) under these conditions, with the prevail of the hydrogen bonded conformation.

The effect of hydrogen bonding can also be seen on the characteristic stretching frequency of the carbonyl group (amide$_{\rm I}$ band) that is substantially lowered. Accordingly, there are two ν(C=O) (or amide$_{\rm I}$) frequencies in the spectrum: a more intense and somewhat broader band at 1646 cm^{-1}, corresponding to non-hydrogen bonded carbonyls of structures A and B (Eq. (3)) and another one at 1614 cm^{-1} corresponding to hydrogen bonded CO in conformation A. There are also two amide$_{II}$ bands at 1548 and 1523 cm^{-1} corresponding to structures A and B, respectively.



(3)

As ferrocene amides and diamides have been reported to be good anion receptors [17], the behavior of **1a** in the presence of chloride ions has also been investigated. As anions as hydrogen acceptors bind to amide groups, the presence of chloride ions can presumably affect the internal hydrogen bond. The addition of chloride ion as its tetra-*n*-butyl ammonium salt indeed led to a change both in the infrared and ^1H NMR data of **1a** (Table 1). The disappearance of the stretching of free NH groups at 3448 cm^{-1} and a splitting of the amide$_I$ band around 1650 cm^{-1} was observed in the infrared spectra. However, the latter signal cannot be used as a precise indication of the change in the molecular structure because of the broadening of the signal and mergence of the peaks. The stretching of free NH groups around 3440 cm^{-1} disappeared upon adding 4 equivalents of Cl^- per **1a** into the solution. (At higher concentrations of tetra-*n*-butyl ammonium chloride, the NH stretching of the hydrogen bonded derivative was merged into the CH stretching of the salt, but there was no indication of the presence of any free NH group.) The initial downfield shift of the NH signal in the ^1H NMR spectrum also showed that all of the NH protons became hydrogen bonded in the presence of the chloride ions (structures A and/or C, Eq. (3)).

At high chloride concentrations, a change in the Cp region of the ^1H NMR spectrum was also evident, the four singlets characteristic for heterodisubstituted ferrocene derivatives appeared. This may be explained by the break-off of the internal hydrogen bond and the prevail of structure C (Eq. (3)) that resembles to the other heterodisubstituted ferrocene derivatives (e.g. **1d**, **1e**) with no internal hydrogen bonds.

3. Conclusions

It is proved that an internal hydrogen bond connecting the NH and CO groups of secondary and tertiary amido substituents of unsymmetrically substituted ferrocene diamides is formed both in the solid state and in solution. Solution phase ^1H NMR and IR measurements supports the existence of an equilibrium between the hydrogen bonded and non hydrogen bonded forms. The addition of chloride ions results in the disappearance of the non hydrogen bonded form, presumably through

Table 1
Characteristic ^1H NMR and infrared data of **1a** in the presence of chloride ions

Cl^-/**1a**	νNH[a]	Amide$_I$[a]	Amide$_{II}$[a]	δNH[c]	δCp[c]
–	3252[b]	1640, 1593	1552	–	–
–	3448, 3272	1646, 1614	1523, 1548	8.32	4.58; 4.34; 4.31
2	3444, 3280	1654, 1646, 1642, 1617	1525, 1556	8.35	4.55; 4.32; 4.29
4	–, 3285			8.37	4.47; 4.23; 4.19
8				8.34	4.38; 4.12; 4.01
18				8.13	4.09; 3.80; 3.76; 3.71

[a] In CH_2Cl_2, concentration of **1a**: 3×10^{-2} M, at 25 °C.

[b] In the solid state in KBr.

[c] In $CDCl_3$ (the chemical shifts are referred to $CHCl_3$, 7.26 ppm), concentration of **1a**: 5×10^{-2} M, at 30 °C.

the formation of intermolecular hydrogen bond between the NH group of the ferrocene diamide and the chloride.

It should be mentioned that the lack of H-bonds in the solutions of ferrocene diamides with two secondary amido groups was observed by us and others [9].

4. Experimental

4.1. Synthesis of unsymmetrically substituted 1,1′-ferrocene diamides

1,1′-Diiodoferrocene (0.5 mmol), $Pd(OAc)_2$ (0.025 mmol), PPh_3 (0.05 mmol), the amines (1.25 mmol $BuNH_2$ and 3.75 mmol morpholine for **1a**, 1.25 mmol $BuNH_2$ and 3.75 mmol Et_2NH for **1b**, 1.67 mmol $BuNH_2$ and 3.33 mmol Bu_2NH for **1c**, 2.5 mmol morpholine and 2.5 mmol Et_2NH for **1d** and 2.5 mmol Et_2NH and 2.5 mmol Bu_2NH for **1e**), Et_3N (0.5 mL) and toluene (10 mL) were transferred under an inert atmosphere into a stainless steel autoclave. It was charged with carbon monoxide (40 bar at room temperature) and heated with stirring in an oil bath at 100 °C for 8 h. Then the mixture was diluted with 20 mL of toluene, washed with 30 mL of 5% H_3PO_4, 30 mL of saturated aqueous $NaHCO_3$ and 30 mL of brine and dried over Na_2SO_4. The evaporation of the solvent and chromatography (aluminium oxide, toluene/EtOAc = 1/1 to 1/10) resulted in pure products in fair to good isolated yields (**1a**: 62%, **1b**: 44%, **1c**: 36%, **1d**: 85%, **1e**: 77%). Crystals suitable for X-ray analysis of **1a** were grown by hexane diffusion into a CH_2Cl_2 solution at room temperature.

4.2. Physical measurements

The ^1H NMR spectra were recorded on a VARIAN INOVA 400 spectrometer at 400 MHz in $CDCl_3$. IR spectra were made using an Avatar 330 FT-IR instrument. Samples were prepared as KBr pellets or as CH_2Cl_2 solution.

1d [12] and **1e** [13] have been characterized before. Compounds **2a**–**d** were obtained as side products, so for these compounds no yields are indicated here. However, they can be obtained in good yields via aminocarbonylation of 1,1′-diiodoferrocene in the presence of the corresponding amine as it has been shown before for **2c** [18]. Spectroscopic data of **2c** and **2d** corresponded well to the literature report [14].

4.2.1. 1′-(N′-butyl-carbamoyl)-morpholino ferrocenecarboxamide (*1a*)

^1H NMR ($CDCl_3$) δ: 8.32 (brs, 1H); 4.57 (s, 2H); 4.33 (brs, 4H); 4.31 (s, 2H); 3.64 (m, 8H); 3.36 (q, 7.5Hz, 2H); 1.60 (qui, 7.5 Hz, 2H); 1.42 (m, 2H); 0.95 (t, 7.5 Hz, 3H). MS (*m*/*z*/rel. int.): 398 (M^+)/34; 313/8; 285/14; 241/34; 213/14; 185/13; 149/20; 121/100; 56/71. IR (KBr, cm^{-1}):3252; 1642, 1593, 1552. Anal. Calc. for $C_{20}H_{26}FeN_2O_3$ (398.28): C, 60.31; H, 6.58; N, 7.03. Found: C, 60.78; H, 6.79; N, 6.75%. Yield: 62%.

4.2.2. 1′-(N′-butyl-carbamoyl)-N,N-diethyl ferrocenecarboxamide (*1b*)

^1H NMR ($CDCl_3$) δ: 8.42 (brs, 1H); 4.60 (s, 2H); 4.36 (brs, 4H); 4.32 (s, 2H); 3.47 (m, 2H); 3.38 (m, 4H); 1.29–1.65 (m, 4H); 1.19 (m, 6H); 0.95 (t, 7.5 Hz, 3H). MS (*m*/*z*/rel. int.): 384 (M^+)/38; 313/8; 285/17; 241/26; 229/12; 220/22; 213/22; 190/20; 163/20; 149/18; 128/38; 121/86; 72/100; 56/68. IR (KBr, cm^{-1}): 3315; 1646, 1613, 1535. Anal. Calc. for $C_{20}H_{28}FeN_2O_2$ (384.30): C, 62.51; H, 7.34; N, 7.29. Found: C, 62.15; H, 7.61; N, 7.62%. Yield: 44%.

4.2.3. 1′-(N′-butyl-carbamoyl)-N,N-dibutyl ferrocenecarboxamide (*1c*)

^1H NMR ($CDCl_3$) δ: 8.53 (brs, 1H); 4.59 (s, 2H); 4.28 (brs, 6H); 3.10–3.42 (m, 6H); 1.10–1.65 (m, 12H); 0.88–1.00 (m, 9H). MS (*m*/*z*/rel. int.): 440 (M^+)/100; 312/18; 241/44; 128/56; 121/63; 56/19. IR (KBr, cm^{-1}): 3297; 1650, 1610, 1535. Anal. Calc. for $C_{24}H_{36}FeN_2O_2$ (440.41): C, 65.45; H, 8.24; N, 6.36. Found: C, 65.81; H, 8.56; N, 6.12%. Yield: 36%.

4.2.4. 1,1′-bis(N-butyl carboxamido) ferrocene (*2a*)

^1H NMR ($CDCl_3$)δ: 6.67 (brs, 2H); 4.46 (s, 4H); 4.3 (s, 4H); 3.36 (q, 6.8 Hz, 4H); 1.61 (m, 4H); 1.41 (m, 4H); 0.98 (t, 7.2 Hz, 6H). MS (*m*/*z*/rel. int.): 384(M^+)/52; 312/14; 285/15; 241/28; 190/28;146/28; 121/100. IR (KBr, cm^{-1}): 3321; 1630; 1552.

4.2.5. 1,1′-bis(N,N-dibutyl carboxamido) ferrocene (*2b*)

^1H NMR ($CDCl_3$) δ: 4.60 (brs, 4H); 4.35 (brs, 4H); 3.35 (t, 7.7 Hz, 8H); 1.58 (m, 8H); 1.15 (m, 8H); 0.89 (m, 12H). MS (*m*/*z*/rel. int.): 496 (M^+)/82; 241/55; 141/100; 95/75; 91/78; 67/79; 55/85; 43/99. IR (KBr, cm^{-1}): 1617.

4.3. X-ray structure

Orange prism crystals (0.36 × 0.22 × 0.2 mm) of **1a** was fixed on a glass capillary using epoxy glue. Data were collected at 293(1) K, Bruker–Nonius MACH3 diffractometer, Mo Kα radiation $\lambda = 0.71073$ Å, ω motion, $\theta_{max} = 26.05°$ [19]. The structure was solved using the SIR-92 software [20] and refined on F^2 using SHELX-97 [21] program, publication material was prepared with the WINGX-97 suite [22]. Hydrogen atoms were fixed into geometric position except N–H which could be found at the difference electron density map and its coordinate were refined. A few bond length constrains should be applied to regulate C43–C46 side chain.

Acknowledgements

The authors thank the Hungarian National Science Foundation for financial support (OTKA T048391, TS044742, TS044800). R.S-F. thanks the Hungarian Academy of Sciences for the J. Bolyai Fellowship and A.B. for the Hungarian Ministry of Education for Széchenyi István fellowship.

Appendix A. Supplementary data

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 293446 for compound **1a**.

Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK, fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.03.013.

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[19] Crystal data for **1a**: Formula $C_{20}H_{26}FeN_2O_3$, $M = 398.28$, monoclinic, space group $P2_1/n$, $a = 9.835(4)$ Å, $b = 20.165(3)$ Å, $c = 9.863(8)$, $\beta = 104.51(4)°$, $V = 1893.7(17)$ Å^3, $Z = 4$, $\rho_{calc} = 1.397$, 3662 measured, 2597 reflections were unique with $I > 2\sigma(I)$, decay: 3%, $R_1 = 0.0551$ and $wR_2 = 0.1581$ for all data, GOF = 1.067, 3662, 238 parameters. Residual electron density: 0.481/−0.345 e/Å^3.

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