

# Synthesis and Structure of Geometric Isomers of 1-[(methoxyimino)ethyl]ferrocene and Methyl 1'-[(methoxyimino)ethyl]ferrocene-1-carboxylate

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RECEIVED DECEMBER 16, 2009, REVISED MARCH 7, 2010, ACCEPTED MARCH 12, 2010

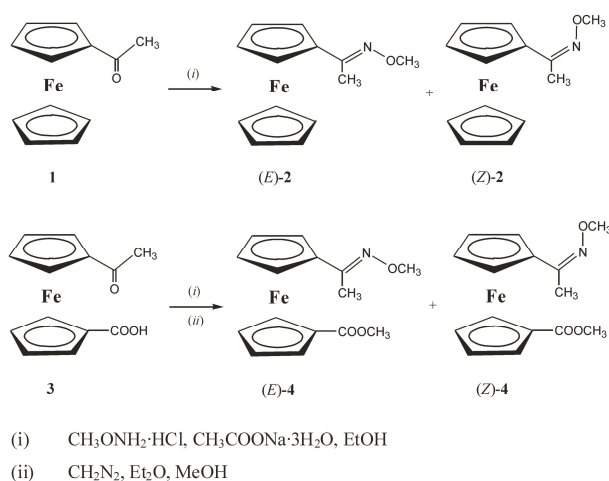
**Abstract.** Here we report synthesis, spectral data and single-crystal X-ray molecular and crystal structures of (*E*)-1-[(methoxyimino)ethyl] ferrocene (**2**) and (*E*)-methyl 1'-[(methoxyimino)ethyl]ferrocene-1-carboxylate (**4**). These organometallics are recognized as precursors for optically pure (1-ferrocenylethyl)amine (**Fea**) and 1'-(1-aminoethyl)ferrocene-1-carboxylic acid (**Fcca**) derivatives. The (*E/Z*)-mixtures of the title compounds **2** and **4** were obtained in ~90 % yield by the action of methoxyamine hydrochloride on acetylferrocene (**1**) and 1'-acetylferrocene-1-carboxylic acid (**3**). By means of preparative thin layer chromatography the synthesized compounds were separated into 75 % of (*E*)-**2** and 15 % of (*Z*)-**2**, as well as into 68 % of (*E*)-**4** and 22 % of (*Z*)-**4**.

Crystal structures of the dominant isomers of **2** (two molecules within asymmetric unit) and **4** confirm that both compounds exist in (*E*)-forms. The ferrocenyl moieties deviate slightly from eclipsed conformation in **2** and **4**. The intramolecular C–H···O contact in the C(CH<sub>3</sub>)–N–OCH<sub>3</sub> group (2.670(7) Å in the second molecule of **2** and 2.644(6) Å in **4**) can be regarded as a weak intramolecular hydrogen bond. The crystal packings of **2** and **4** are characterized only by van der Waals forces.

**Keywords:** [(methoxyimino)ethyl]ferrocene derivatives, *E/Z* isomerism, synthesis, crystal structure

## 1. INTRODUCTION

It is well known that  $\alpha$ -ferrocenylalkylamines are highly efficient ligands in asymmetric catalysis<sup>1–3</sup> and appropriate chiral auxiliaries due to their high chiral induction ability and easy cleavage from the newly generated chiral compounds.<sup>4</sup> In our several previous papers<sup>5–8</sup> we have described synthesis, structural analysis and conformational preferences of chiral 1'-(1-aminoethyl)ferrocene-1-carboxylic acid (**Fcca**) which can be considered as derivative of (1-ferrocenylethyl)amine (**Fea**). Asymmetric reduction of C=N bond of oxime ethers with chiral oxazaborolidines is a convenient method for preparation of the optically pure amines.<sup>9</sup> For further reduction it is essential to synthesize pure oxime geometric isomers, as they can be transformed into the corresponding amine enantiomers. In this context we decided to prepare 1-[(methoxyimino)ethyl] ferrocene (**2**) and methyl 1'-[(methoxyimino)ethyl]ferrocene-1-carboxylate (**4**) as potential precursors for optically pure **Fea** and **Fcca** derivatives (Scheme 1).



**Scheme 1.** Synthesis of (*E/Z*)-1-[(methoxyimino)ethyl]ferrocene (**2**) and (*E/Z*)-methyl 1'-[(methoxyimino)ethyl]ferrocene-1-carboxylate (**4**).

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## 2. EXPERIMENTAL SECTION

### 2.1. General techniques

All chemicals and solvents were used as purchased. CH<sub>2</sub>Cl<sub>2</sub> used for FT-IR was dried (P<sub>2</sub>O<sub>5</sub>), distilled over CaH<sub>2</sub> and stored over molecular sieves (4 Å). Products were separated and purified by preparative thin layer chromatography on silica gel (Merck, Kieselgel 60 HF<sub>254</sub>) using CH<sub>2</sub>Cl<sub>2</sub> or CH<sub>2</sub>Cl<sub>2</sub>/EtOAc mixture. The IR spectra were recorded as CH<sub>2</sub>Cl<sub>2</sub> solutions with a Bomem MB 100 mid FTIR spectrophotometer. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 300 or Bruker Avance 600 MHz spectrometer in CDCl<sub>3</sub> solution with Me<sub>4</sub>Si as internal standard. 1'-Acetylferrocene-1-carboxylic acid (**3**) was prepared according to the previously described procedure.<sup>5</sup>

### 2.2. 1-[(Methoxyimino)ethyl]ferrocene (**2**)

To a stirred suspension of acetylferrocene (**1**, 1 mmol) in 96 % EtOH (10 mL) sodium acetate (1.5 mmol) and methoxyamine hydrochloride (1.5 mmol) were added. After refluxing for 2 hours reaction mixture was poured into water, extracted three times with dichloromethane, dried and evaporated to dryness. The isomeric oxime ethers were separated using TLC-plates with dichloromethane as eluent, the first band contained (*E*)- and second (*Z*)-isomer.

(*E*)-**2**, yield: 75 %. M. p. = 67.3–58.6 °C. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{\max}/\text{cm}^{-1}$ : 2938, 2989, 2817, 1604, 1366, 1302, 1105, 1052, 1035, 1002, 870. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 4.52 (t, 2H, H-2, H-5, F<sub>n</sub>, *J* = 3.5 Hz), 4.28 (t, 2H, H-3, H-4, F<sub>n</sub>, *J* = 3.5 Hz), 4.16 (s, 5H, C<sub>p</sub>unsubst.), 3.89 (s, 3H, OCH<sub>3</sub>), 2.18 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR, APT (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 154.89 (C=N), 81.82 (C-1, F<sub>n</sub>), 69.52 (C-3, C-4, F<sub>n</sub>), 69.17 (C<sub>p</sub>unsubst.), 66.51 (C-2, C-5, F<sub>n</sub>), 61.56 (OCH<sub>3</sub>), 13.47 (CH<sub>3</sub>).

(*Z*)-**2**, yield: 15 %. M. p. = 50.6–51.9 °C. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{\max}/\text{cm}^{-1}$ : 2937, 2816, 1609, 1374, 1106, 1060, 1028, 1002, 824. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 4.81 (t, 2H, H-2, H-5, F<sub>n</sub>, *J* = 3 Hz), 4.33 (t, 2H, H-3, H-4, F<sub>n</sub>, *J* = 3 Hz), 4.15 (s, 5H, C<sub>p</sub>unsubst.), 3.91 (s, 3H, OCH<sub>3</sub>), 2.17 (s, 3H, CH<sub>3</sub>).

### 2.3. Methyl 1'-[(methoxyimino)ethyl]ferrocene-1-carboxylate (**4**)

To a stirred suspension of **3** (1 mmol) in 96 % EtOH (10 mL) sodium acetate (1.5 mmol) and methoxyamine hydrochloride (1.5 mmol) were added. Reaction mixture was refluxed for 4 hours, cooled, poured into CH<sub>2</sub>Cl<sub>2</sub> and extracted with 5 % NaHCO<sub>3</sub>. Aqueous layer was acidified with HCl/H<sub>2</sub>O (1:1), extracted with dichloromethane, washed with saturated aqueous solution of NaCl, dried and evaporated to dryness. Crude carbo-

xylic acid was treated with excess of CH<sub>2</sub>N<sub>2</sub> to afford (*E*)- and (*Z*)-**4**. Resulting isomeric esters were separated using TLC-plates with dichloromethane/ethyl acetate (10:1) as eluent, the first band contained (*E*)- and second (*Z*)-isomer.

(*E*)-**4**, yield: 68.4 %. M. p. = 46.1–47.6 °C. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{\max}/\text{cm}^{-1}$ : 2953, 2939, 2901, 2818, 1712, 1604, 1467, 1143, 1052, 1035, 871. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 4.78 (s, 2H, H-2, H-5, Fc), 4.55 (s, 2H, H-2', H-5', Fc), 4.37 (s, 2H, H-3, H-4, Fc), 4.31 (s, 2H, H-3', H-4', Fc), 3.90 (s, 3H, NOCH<sub>3</sub>), 3.78 (s, 3H, OCH<sub>3</sub>), 2.08 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR, APT (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 171.2 (C=O), 153.41 (C=N), 83.51 (C-1', Fc), 72.42 (C-1, Fc), 72.18 (C-2, C-5, Fc), 71.07 (C-3, C-4, Fc), 70.86 (C-3', C-4', Fc), 67.82 (C-2', C-5', Fc), 61.64 (NOCH<sub>3</sub>), 51.56 (OCH<sub>3</sub>), 13.05 (CH<sub>3</sub>).

(*Z*)-**4**, yield: 22 %. M. p. 42.1–43.2 °C. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{\max}/\text{cm}^{-1}$ : 2953, 2936, 2900, 2817, 1713, 1610, 1467, 1143, 1061. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 4.84 (s, 2H, H-2, H-5, Fc), 4.76 (s, 2H, H-2', H-5', Fc), 4.36 (m, 4H, H-3, H-4, H-3', H-4', Fc), 3.92 (s, 3H, NOCH<sub>3</sub>), 3.82 (s, 3H, OCH<sub>3</sub>), 2.14 (s, 3H, CH<sub>3</sub>).

### 2.4. X-ray diffraction experiment

Single crystals suitable for X-ray diffraction experiment for both compounds **2** and **4** were obtained by slow evaporation from dichloromethane mother liquid at ambient temperature. The single-crystal X-ray and general data for structures **2** and **4** are reported in Table 1. The data collection were collected on Oxford Xcalibur PX for **2** and Xcalibur Nova for **4** with CCD detector with graphite-monochromated MoK $\alpha$  (**2**) and CuK $\alpha$  (**4**) radiation at ambient temperature using  $\omega$ -scans.

Programs CrysAlis CCD and CrysAlis RED were employed for data collection, cell refinement and data reduction.<sup>10</sup>

The Lorentz-polarization effect was corrected and the diffraction data have been scaled for absorption effects by the multi-scanning method.

The structure was solved by direct methods and refined on  $F^2$  by weighted full-matrix least-squares. All non-hydrogen atoms were refined anisotropically.

Hydrogen atoms were placed in geometrically idealized positions [Csp<sup>3</sup>-H 0.96 Å, Csp<sup>2</sup>-H 0.93 Å with  $U_{\text{iso}}(\text{H}) = 1.5$  or  $1.2 U_{\text{eq}}(\text{C})$ ] and were constrained to ride on their parent atoms by using the appropriate SHELXL97 HFIX instructions.

The absolute structure of 1-[(methoxyimino)ethyl]ferrocene, **2**, which crystallizes in a non-centrosymmetric space group, is properly determined by refinement of Flack parameter (Table 1).

Calculations were performed with programs SHELXS97<sup>11</sup> and SHELXL97<sup>11</sup> both integrated in the WinGX program package.<sup>12</sup>

**Table 1.** General and crystal data and summary of intensity data collection and structure refinement for compounds **2** and **4**

Crystal Parameters		
Compound name	<b>2</b>	<b>4</b>
Chemical formula	C <sub>13</sub> H <sub>15</sub> FeNO	C <sub>15</sub> H <sub>17</sub> FeNO <sub>3</sub>
Formula Mass/ <i>u</i>	257.11	315.15
Crystal system, colour and habit	Orthorhombic, orange, needle	Monoclinic, orange, prism
Crystal dimensions (mm <sup>3</sup> )	0.45 × 0.15 × 0.15	0.45 × 0.36 × 0.21
Space group	<i>P n a 2</i> <sub>1</sub>	<i>C 2/c</i>
No. of formula units per unit cell, <i>Z</i>	8	8
Unit cell parameters:		
<i>a</i> /Å	19.3472(18)	15.9682(2)
<i>b</i> /Å	16.7658(17)	9.7022(2)
<i>c</i> /Å	7.4164(6)	18.4085(3)
$\beta$ /°	–	93.5521(14)
Unit cell volume/Å <sup>3</sup>	2405.7(4)	2846.49(8)
Temperature/K	296(2)	296(2)
$\mu$ (mm <sup>-1</sup> )	1.231	8.556
<i>F</i> (000)	1072	1312
Data Collection		
Radiation type, 1/Å	MoK $\alpha$ , 0.71073	CuK $\alpha$ , 1.54184
$\theta$ range for data collection (°)	3.8–27.0	5.5–73
<i>h, k, l</i> range	–24 to 24, –21 to 21, –9 to 9	–19 to 19, –11 to 11, –12 to 12
No. refined parameters, <i>N</i> <sub>p</sub> /restraints	293/1	184/0
Reflections collected, unique, <i>R</i> <sub>int.</sub> , observed [ <i>I</i> > 2.0 $\sigma$ ( <i>I</i> )]	15542, 5034, 0.105, 2130	6151, 2740, 0.037, 2608
Scan type	$\omega$	$\omega$
Refinement		
<i>R</i> <sup>(a)</sup> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0417	0.0599
<i>g</i> <sub>1</sub> , <i>g</i> <sub>2</sub> in <i>w</i> <sup>(b)</sup>	0.0100, 0	0.0574, 8.8122
<i>wR</i> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0564	0.1444
<i>R</i> ( <i>F</i> <sup>2</sup> ) <sup>(c)</sup> (all data)	0.1488	0.0638
<i>wR</i> ( <i>F</i> <sup>2</sup> ) <sup>(d)</sup> (all data)	0.0684	0.1468
Goodness of fit on <i>F</i> <sup>2</sup> , <i>S</i> <sup>(e)</sup>	0.82	1.129
Max., min. electron density (e Å <sup>-3</sup> )	0.32, –0.37	0.62, –0.34
Maximum $\Delta$ /σ	0.001	0.001
Flack parameter	–0.001(18)	–

<sup>(a)</sup>  $R = \sum | |F_o| - |F_c| | / \sum |F_o|$ ; <sup>(b)</sup>  $w = 1 / [\sigma^2(F_o^2) + [g_1P + g_2P]]$  where  $P = (F_o^2 + 2F_c^2)/3$ ;

<sup>(c)</sup>  $R(F^2) = \sum |F_o^2 - F_c^2| / \sum F_o^2$ ; <sup>(d)</sup>  $wR = \sum [w(F_o^2 - F_c^2)^2 / \sum wF_o^2]^{1/2}$ ;

<sup>(e)</sup>  $S = \sum [w(F_o^2 - F_c^2)^2 / (N_r - N_p)]^{1/2}$  where *N*<sub>r</sub> = number of independent reflections, *N*<sub>p</sub> = number of refined parameters.

The molecular geometry calculations were done by using PLATON<sup>13</sup> and the molecular graphics were done with PovRay programme<sup>14</sup> and Mercury.<sup>15</sup>

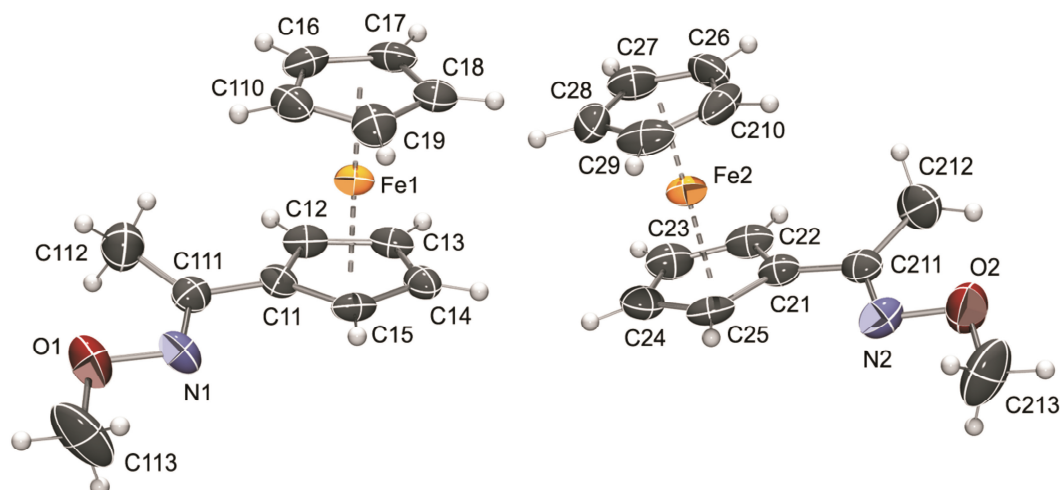
The main geometrical features are given in Tables 2 (for **2**) and 3 (for **4**).

### 3. RESULTS AND DISCUSSION

#### 3.1. Synthesis

Refluxing a solution of acetylferrocene (**1**), methoxyamine hydrochloride and sodium acetate<sup>16</sup> in ethanol

gave 90 % of mixture (*E/Z*)-**2**. The difference in *R*<sub>f</sub> values of these geometric isomers allowed their separation using preparative thin layer chromatography with dichloromethane as eluent. (*E*)-**2** (75 %) was eluted first followed by the smaller amount of (*Z*)-**2** (15 %). Under the similar conditions, 1'-acetylferrocene-1-carboxylic acid (**3**) gave the corresponding (*E/Z*)-methoxyimino-acids which were converted into 90.4 % of (*E/Z*)-methyl 1'-[(methoxyimino)ethyl]ferrocene-1-carboxylates (**4**) by the action of ethereal diazomethane. This isomeric mixture was separated by TLC, using dichloromethane/ethyl acetate (10:1) as eluent, to afford



**Figure 1.** PovRay drawing of **2** with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50 % probability level at 296 K.

68.4 % of (*E*)-**4** and 22 % of (*Z*)-**4**, respectively. It is worth to mention that although the conversions **1**→**2** and **3**→**4** were performed under the same conditions (boiling ethanol solution) the selectivity towards (*E*)-isomer was found to be enhanced in the case of monosubstituted derivative **1** (ratio 5:1) in comparison with heteroannularly substituted and more sterically demanding **3** (ratio 3.1:1).

### 3.2. Spectroscopic analysis

The structure of compounds **2** and **4** was confirmed by spectroscopical methods. The IR spectra of both compounds are characterized with bands at  $\approx 1600\text{ cm}^{-1}$  corresponding to  $\nu(\text{C}=\text{N})$ . Additional signals belonging to C–H and N–O vibrations were found at  $\approx 2900$  and  $\approx 1050\text{ cm}^{-1}$ , respectively. Ester group of compound **4** was registered as  $\nu(\text{C}=\text{O})$  at  $1712\text{ cm}^{-1}$ . In the  $^1\text{H}$  NMR spectra of (*E*)- and (*Z*)-**2** two methyl groups were registered as two singlets at  $\approx 3.9$  and  $\approx 2.17$  ppm. The downfield signal was assigned to  $\text{OCH}_3$  due to deshielding effect of oxygen. The positions of the triplets of the substituted ferrocene rings were significantly different for (*E*)- and (*Z*)-isomers ( $\delta$ ppm: 4.52 and 4.28 for (*E*)-**2**,  $\delta$  4.81 and 4.33 for (*Z*)-**2**). In the  $^1\text{H}$  NMR spectra of (*E*)- and (*Z*)-**4** additional signal belonging to the methyl protons of ester group is observed at  $\approx 3.80$  ppm. Absorptions at  $\delta$  154.89 and 153.41 ppm in  $^{13}\text{C}$  NMR spectra of **2** and **4** were assigned to oxime carbon. Signal at  $\delta$  171.20 ppm belonged to carbonyl C-atom and at  $\delta$  51.56 ppm to methyl carbon of ester group of compound **4**. Two additional methyl groups (C– $\text{CH}_3$  and O– $\text{CH}_3$ ) of derivatives **2** and **4** were found at  $\delta$  13.47/13.05 and  $\delta$  61.56/61.64 ppm, respectively.

### 3.3. X-ray structure description of (*E*)-1-[(methoxyimino)ethyl]ferrocene (**2**)

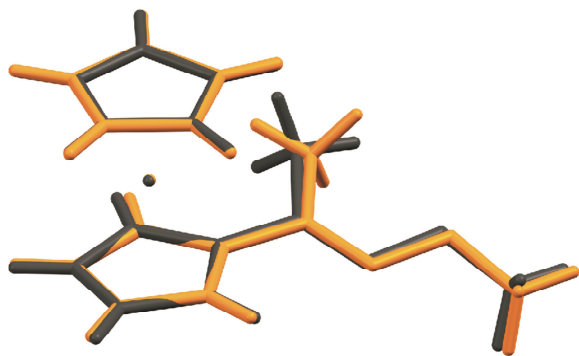
The crystallographic asymmetric unit of monosubstituted compound **2** contains two symmetrically independent, but chemically almost identical molecules labelled as 1 and 2 (the molecular structure is illustrated in Figure 1).

A slight variation of molecular bond distances and angles is observed comparing geometries of the two molecules (Table 2), while the biggest difference arises in the orientation of (methoxyimino)ethyl substituents at the C11 atom of the first molecule and the C21 atom of the second molecule (Figure 2). The substituents are spatially oriented almost identically in relation to the single C111–C112 bond (and C211–C212 bond in the second molecule), but in the opposite directions (torsion angles C15–C11–C111–C112 ( $165.2(5)^\circ$ ) and C25–C21–C211–C212 ( $-165.9(5)^\circ$ ).

Both molecules are in *E* form considering substituent (–Fn; –Fn = ferrocenyl, and – $\text{OCH}_3$ ) positions around the imino C=N bond.

The  $\text{C}(\text{CH}_3)=\text{N}(\text{O}-\text{CH}_3)$  residues are not coplanar with the respective cyclopentadienyl ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) rings. The dihedral angles between Cp rings and the  $\text{C}(\text{CH}_3)=\text{N}(\text{O}-\text{CH}_3)$  residues are  $17.3(4)^\circ$  and  $18.0(4)^\circ$  for the first and second molecule.

In both molecules Cp rings are nearly coplanar (the tilt angles are  $2.4(4)$  and  $1.2(4)^\circ$ , for the first and second molecule, respectively). The ferrocenyl conformation requires  $144^\circ$  and  $180^\circ$  for torsion angle C (substituted C atom of Cp ring), Cg1, Cg2, C (the opposite C atom of another Cp ring) in the case of fully eclipsed and staggered conformation, respectively. The torsion angle C11, Cg1, Cg2, C17 and C21, Cg3, Cg4, C27 amounts  $136.34(4)^\circ$  and  $131.23(4)^\circ$ , respectively.



**Figure 2.** Mercury overlapping diagram of two crystallographically independent molecules of **2** (molecule 1 in orange colour and molecule 2 in dark gray). The atoms of unsubstituted cyclopentadienyl rings and Fe atoms in the first and second molecules, respectively, are taken for overlapping.

The Fe-to-centroid distances are 1.643(2) and 1.650(3) Å for Fe-Cg1 and Fe-Cg2 distances in the first molecule and 1.635(3) and 1.649(4) Å for Fe-Cg3 and Fe-Cg4 distances in the second molecule.

The angles Cg1-Fe1-Cg2 and Cg3-Fe2-Cg4 amount 178.4(1)° and 178.6(2)°, respectively. The shortest and the longest Fe-C bond distances in the first molecule are 2.023(5) Å (Fe1-C15) and 2.057(5) Å (Fe1-C13).

The shortest and the longest Fe-C bond distances in the second molecule are 2.008(6) Å (Fe1-C210) and 2.046(6) Å (Fe1-C24).

The exocyclic  $C_{ar}-C_{sp^2}$  bond distances (C11-C111 and C21-C211; Table 2) as well as the imino C111-N1 bond (1.296(6) Å) and C211-N2 (1.282(6) Å) exhibit common bond distances.<sup>17</sup> The average N-O bond distance in oximes amounts 1.408 Å (Ref. 18) and in the disordered structure of ferrocenecarboxaldoxime containing a mixture of (*E*)/(*Z*) isomers<sup>19</sup> 1.438(10) Å in the (*E*)-isomeric part and 1.478(14) Å in the structure of (*Z*)-isomeric part, while in **2** the values are 1.426(6) Å (O1-N1) and 1.429(6) Å (O2-N2).

The weak intramolecular C212-H21B...O2 hydrogen bond (2.670(7) Å; H21B...O2 distance of 2.20 Å;  $\angle$  C212-H21B...O2 of 107°) in the C(CH<sub>3</sub>)-N-OCH<sub>3</sub> moiety in the second molecule of **2** is found.

The analogous contact in the first molecule is not detected *i.e.* the distance O1...H11A of 2.480 Å is significantly longer than H21B...O2. Along with the other geometrical parameters (C112-H11A...O1 2.662(7) Å;  $\angle$  C212-H21B...O2 90.03°) the contact C112...O1 in the first molecule of **2** can not be regarded as an intramolecular hydrogen bond. This consideration is in agreement with significantly different spatial orientation of methyl groups C112 and C212 in the structure of **2** as it is shown at overlapping diagram (Figure 2).

No contacts shorter than the sum of the van der

**Table 2.** Selected interatomic distances (Å) and valence angles (°) for compound **2**

Molecule 1		Molecule 2	
Bond distances			
Fe1-C110	2.032(5)	Fe2-C210	2.008(6)
Fe1-C11	2.040(5)	Fe2-C21	2.025(5)
Fe1-C12	2.029(5)	Fe2-C22	2.018(5)
Fe1-C13	2.057(5)	Fe2-C23	2.030(6)
Fe1-C14	2.027(5)	Fe2-C24	2.046(6)
Fe1-C15	2.023(5)	Fe2-C25	2.033(5)
Fe1-C16	2.024(5)	Fe2-C26	2.020(6)
Fe1-C17	2.052(5)	Fe2-C27	2.012(6)
Fe1-C18	2.047(5)	Fe2-C28	2.013(6)
Fe1-C19	2.024(5)	Fe2-C29	2.009(6)
C11-C111	1.459(7)	C21-C211	1.446(7)
C111-N1	1.296(6)	C211-N2	1.282(6)
O1-N1	1.426(6)	O2-N2	1.429(6)
Bond angles			
C111-N1-O1	111.0(5)	C211-N2-O2	111.0(5)
N1-C111-C11	115.2(5)	N2-C211-C21	115.7(5)
N1-C111-C112	125.0(5)	N2-C211-C212	125.7(6)
C11-C111-C112	119.7(5)	C21-C211-C212	118.6(6)
N1-O1-C113	106.7(6)	C213-O2-N2	107.1(5)

Waals radii are found between molecules in the crystal.

### 3.4. X-ray structure description of (*E*)-methyl 1'-[(methoxyimino)ethyl]ferrocene-1-carboxylate (**4**)

The compound **4** (the molecular structure is illustrated in Figure 3.) exists in the crystalline state as *E*-isomer considering the spatial arrangement of ferrocene-1-carboxylate and methoxy groups around the imino C=N bond.

The ferrocenyl moiety exhibits eclipsed conformation. The Cp rings, which are parallel to each other within 2.0(3)°, are twisted from the fully eclipsed conformation by 2.2(3)° (maximum).

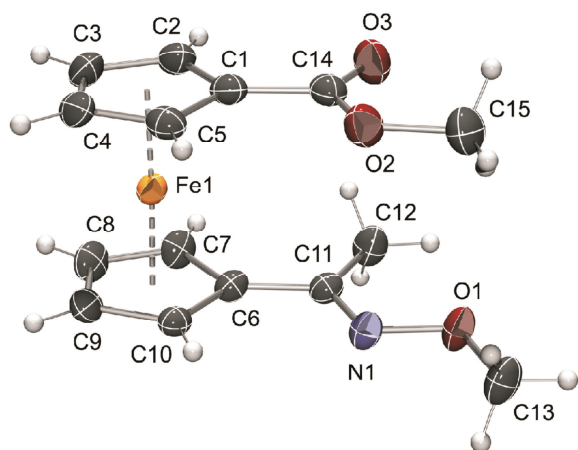
This misalignment is calculated *via* dihedral angle between planes defined by the atom C1 and centroids Cg1 and Cg2 (Cg1 and Cg2 are the centroids of the C1-C5 and C6-C10 rings, respectively) and the atom C8 and centroids Cg1, Cg2. This angle amounts -146.2(3)° in comparison with 144° for fully eclipsed and 180° for staggered conformation.

The Fe-to-centroid distances are 1.653(2) and 1.652(2) Å for Fe-Cg1 and Fe-Cg2 distances, respectively and the Cg1-Fe-Cg2 angle amounts 177.8(1)°. The Fe-C bond distance range for the unsubstituted cyclopentadienyl C atoms is 2.039(4)–2.055(4) Å. The bonds to the substituted C atoms amount 2.039(4) Å (Fe1-C1) and 2.066(4) Å (Fe1-C6).

The exocyclic C1-C14 [C-C(O)] and C6-C11 [C-C(CH<sub>3</sub>)] bond distances of 1.467(6) Å and 1.460(5) Å, respectively, are in agreement with C<sub>ar</sub>-Csp<sup>2</sup> average bond distance values of 1.470 Å.<sup>17</sup> They are also comparable with the distance of 1.460 Å found to be the theoretical value for C-C(O) distance in ferrocene carboxylic acids.<sup>19</sup>

The imino C11-N1 bond (1.286(5) Å) exhibits common bond distance.

The O1-N1 bond of 1.406(4) Å is analogous with



**Figure 3.** PovRay drawing of **4** with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50 % probability level at 296 K.

the average N–O distance in oximes of 1.408 Å,<sup>18</sup> on the contrary to the lengthen values in (*E*)-**2**. The influence of intramolecular hydrogen bond of the C–H...O type within (methoxyimino)ethyl group in one molecule of (*E*)-**2** and in the structure of (*E*)-**4** is negligible on the N–O distance.

The methoxycarbonyl group (–COOCH<sub>3</sub>) is coplanar with the cyclopentadienyl group (C1–C5) to which it belongs within 1.1(3)°, while the (methoxyimino)ethyl group (–C(CH<sub>3</sub>)=N–OCH<sub>3</sub>); (the greatest deviation from the plane calculated through group atoms is 0.014(3) Å for O1 atom) is coplanar with the cyclopentadienyl group (C6–C10) to which it belongs within 3.8(3)°. A coplanar arrangement allows for efficient overlap of the corresponding π-systems.

The C12–C11...O1 (2.644(6) Å) weak intramolecular hydrogen bond is found within the (methoxyimino)ethyl group.

The molecules are joined only by van der Waal's interactions; no intermolecular hydrogen bonds are

**Table 3.** Selected interatomic distances (Å) and valence angles (°) for compound **4**

Bond distances	
Fe1-C1	2.039(4)
Fe1-C2	2.040(4)
Fe1-C3	2.055(4)
Fe1-C4	2.049(4)
Fe1-C5	2.045(4)
Fe1-C6	2.066(4)
Fe1-C7	2.042(4)
Fe1-C8	2.044(4)
Fe1-C9	2.039(4)
Fe1-C10	2.043(4)
C1-C14	1.467(6)
C6-C11	1.460(5)
C11-N1	1.286(5)
O1-N1	1.406(4)
Bond angles	
N1-O1-C13	108.5(3)
C14-O2-C15	116.3(4)
C11-N1-O1	111.4(3)
O3-C14-O2	124.2(4)
O3-C14-C1	124.1(4)
O2-C14-C1	111.7(4)
N1-C11-C6	115.4(3)
N1-C11-C12	124.4(4)
C6-C11-C12	120.2(3)

found.

#### 4. CONCLUSION

In this work we present the synthesis and spectroscopic analysis of 1-[(methoxyimino)ethyl] ferrocene (**2**) and methyl 1'-[(methoxyimino)ethyl]ferrocene-1-carboxylate (**4**), as well as the crystal structures of their (*E*)-isomers revealed by X-ray single crystal diffractometry. (*E/Z*)-**2** and **4** were prepared by conventional methods starting from the corresponding ferrocene ketones and methoxyamine hydrochloride.

No intermolecular hydrogen bonds are found in the solid state. The C–H···O contacts within (methoxyimino)ethyl group of 2.670(7) Å in (*E*)-**2** and of 2.644(6) Å in (*E*)-**4** are found and can be characterized as a weak intramolecular hydrogen bonds. Interestingly, in the one of the molecules of (*E*)-**2** no such contact is found.

The crystal packings are characterized only by van der Waals forces.

*Supplementary Materials.* – Crystallographic data for the structures in this paper has been deposited at Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) and can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers CCDC 755855 (for **2**) & 755856 (for **4**). Structure factors table is available from the authors.

*Acknowledgements.* The research was supported by the Ministry of Science, Education and Sport of the Republic of Croatia (Grants No. 058-1191344-3122 and 098-1191344-2943). The financial support is gratefully acknowledged.

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## SAŽETAK

**Sinteza i struktura geometrijskih izomera  
1-[(metoksiimino)etil]ferocena i  
metil 1'-[(metoksiimino)etil]ferocen-1-karboksilata****Mojca Čakić Semenčić,<sup>a</sup> Gordana Pavlović,<sup>b</sup> Dubravka Šišak<sup>c</sup> i Vladimir Rapić<sup>a</sup>**<sup>a</sup>*Zavod za kemiju i biokemiju, Prehrambeno-biotehnološki fakultet, Sveučilište u Zagrebu,  
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U ovom radu prikazana je sinteza, spektralna analiza i molekulska i kristalna struktura dobivena metodom rentgenske difrakcije na jediničnom kristalu *E*-izomera monosupstituiranog 1-[(metoksiimino)etil]ferocena (**2**) i heteroanularno supstituiranog metil 1'-[(metoksiimino)etil]ferocen-1-karboksilata (**4**), poznatih kao potencijalnih prekursora u dobivanju optički čistih Fea i Fcca derivata. (*E/Z*)-smjese navedenih spojeva **2** i **4** dobivene su u 90/90.4 % iskorištenju reakcijom metoksiamin hidroklorida i acetilferocena odnosno 1'-acetilferocen-1-karboksilne kiseline.

Kristalne strukture spoja **2** (dvije molekule u asimetričnoj jedinki) i spoja **4** pokazuju da spojevi u kristalnom stanju postoje kao (*E*)-izomeri uzimajući u obzir prostorni raspored ciklopentadienilnih supstituenata oko imino veze. Ferocenični fragmenti u **2** i **4** neznatno odstupaju od zasjenjene konformacije. Intramolekulski dodir C–H...O u C(CH<sub>3</sub>)–N–OCH<sub>3</sub> fragmentu (2.670(7) Å u drugoj molekuli spoja **2** i 2.644(6) Å u **4**) može se smatrati slabom vodikovom vezom. Kristalna struktura spoja **2** i **4** karakterizirana je samo van der Waalsovima silama.