Research article

Novel ferrocene imide derivatives: synthesis, conformational analysis and X-ray structure

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ABSTRACT

The synthesis and structural characterization of the ferrocene imide derivatives Fe–CO–NH–CO–Me (4), Fe–CO–NH–CO–F (7) and Fe–CO–NH–CO–Fn–CO–NH–CO–F (8) have been reported. The mononuclear, dinuclear and trinuclear ferrocene imides were prepared by the reaction of ferrocenecarboxamide (3), with acetyl chloride, ferrocencarbonyl chloride (2) and ferrocene-1,1′-(dicarbonyl chloride) (6), respectively. IR spectroscopic analysis revealed the absence of intramolecular hydrogen bonds in solutions of imides 4, 7 and 8. The crystal packing of N-acetylferrocencarboxamide (4) is characterized by N–H⋯O hydrogen bonds forming centrosymmetric dimers, while the molecules of its homologue N-methylferrocencarboxamide (5) are self-assembled by intermolecular N–H⋯O bonds into infinite chains. A detailed conformational analysis (DFT study) suggests the cis-trans configuration of ferrocene imide derivative 7 in solution. The effect of different substituents attached to bridged imide nitrogen on conformational properties of bis-ferrocenyl imides was further investigated and results compared to the existing experimental data.

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1. Introduction

Aromatic foldamers are architectures constructed by linking aromatic monomers with various linkers such as urea [1], guanidine [2], or most commonly amide spacers [3, 4]. The folding properties of these molecules depend on noncovalent interactions and the conformational properties of the linker, which are determined by steric and electronic factors [5]. The high stability of the folded structures and the predictability of the folding patterns are remarkable properties of these “abiotic” foldamers [6]. Although several foldamers containing various aromatic subunits and spacers have been prepared, literature data dealing with those containing imide linkers are limited [7, 8, 9, 10, 11]. One of the first examples of a foldamer containing napthalene rings linked by an imido group that forces the aromatic rings to be placed in the positions facing each other and allows stacking interactions was given by Kohmoto and co-workers [11]. The folding of this system into predominantly one helix was achieved by introducing a chiral centre at the nitrogen atom of the imidocarbonyl spacer and confirmed by electronic circular dichroism (ECD) spectroscopy. Our group has reported the synthesis and structural studies of bis- and tris-ferrocenyl imide foldamers Fc–CO–NH–CO–Fc (I) and Fc–CO–NH–CO–F–Fc (II), where the presence of a simple N-methyl substitution of the imido bridges efficiently induces the formation of helical conformations [12]. Due to favourable stacking and C–H⋯π interactions between the ferrocenyl units and steric factors, cis-cis conformations are present both in the solid state and in solution of I and II, rather than an energetically favourable cis-trans conformations found in simple acyclic imides [13, 14]. A twisted imide bond (cis-cis) was also reported in the crystal structure of the novel noncyclic imide derived from 4-chloroniline and 2-furic acid [15]. The nonplanarity of the imide group was related to the steric hindrances of the 2-carbonyl furan rings. Recently, a few papers were focused on a conformational analysis of structurally very similar compounds derived from ureas. N-Acyl urea compounds, R–CO–NH–CO–NH–R, when compared to basic imides, R–CO–NH–CO–R, have an additional NH group [16, 17]. However, this NH group may form six-membered rings via intermolecular hydrogen bond, N–H⋯OC, thus initiating very similar relative orientation of the rest of the fragment as reported in cis-trans stereoisomers of imides.

The ferrocene-containing imide bridged systems are even rarer than similar aromatic counterparts. Among the already mentioned bis-ferrocenyl imide compound with methylated imide group [12], there are only two other similar systems. The first has phenyl group [18], and the second pyridyl group [19, 20] on the imide nitrogen atom. Continuing the study of poorly described aromatic systems with imide linkers, we have synthesized the derivatives Fe–CO–NH–CO–Me (4), Fe–CO–NH–CO–Fc (7), and Fe–CO–NH–CO–F–Fc (8), which are the lowest homologues of ferrocene foldamer sequences. Prior to our study, we had expected that the NH hydrogen bond donor in the imide linker of the trinuclear derivative 8 might initiate hydrogen bond formation and consequently different, presumably helical, conformational outcomes compared to other reported N-substituted imide derivatives.

2. Experimental

The syntheses were carried out under an argon atmosphere. The toluene, dichloromethane and dioxane used for the synthesis were dried (CaH₂) and freshly distilled before use. The products were purified by preparative thin layer chromatography on silica gel (Merck, silica gel 60HF254) using EtOAc, CH₂Cl₂/EtOAc and CH₂Cl₂/EtOH as eluents. Melting points were determined using a Reichert Thermovar HT1 BT 11 melting point apparatus. IR spectra were recorded as KBr pellets using a Bomem MB 100 mid FTIR spectrophotometer. 1H and 13C NMR spectra were recorded using a Varian Gemini 300 spectrometer in CDCl₃ solution with Me₄Si as internal standard. HR-ESI mass spectra (MS) were recorded on a JEOL-JMS-700. Elemental analyses were performed by the analytical laboratory of the department of physical chemistry, Ruđer Bošković Institute. Starting compounds ferrocene-carboxylic acid (1), ferrocenecarbonyl chloride (2) [21], ferrocene-1’-dicarbonyl chloride (6) [22], and N-methylferrocenecarboxamide (5) [23], were prepared according to the previously described procedures.

### Table 1. Crystallographic data, collection, and structure refinement details for 4 and 5.

| Compound | 4 | 5 |
|----------|---|---|
| Empirical formula | C₂₂H₂₀FeNO₂ | C₂₂H₂₀FeNO |
| Formula wt./g mol⁻¹ | 271.09 | 243.08 |
| Crystal dimensions | 0.22 × 0.20 × 0.18 | 0.25 × 0.20 × 0.20 |
| Space group | P 2₁/c | P T |
| a/Å | 7.37810 (10) | 10.1461 (4) |
| b/Å | 6.7572 (10) | 10.1635 (5) |
| c/Å | 20.3958 (4) | 10.9934 (4) |
| α/° | 90 | 103.531 (4) |
| β/° | 90 | 105.935 (4) |
| γ/° | 90 | 90.024 (4) |
| Z | 4 | 4 |
| V/Å³ | 1152.06 (4) | 1057.28 (8) |
| Dcalc/g cm⁻³ | 1.563 | 1.527 |
| μ/mm⁻¹ | 10.402 | 11.185 |
| θ range/° | 4.34-76.05 | 4.31-76.52 |
| T/K | 293 (2) | 293 (2) |
| Diffractometer type | Xcalibur Nova | Xcalibur Nova |
| Range of h, k, l | –9 < h < 8 –9 < k < 9 –12 < k < 12 –17 < l < 25 | –11 < l < 13 |
| Reflections collected | 5384 | 9547 |
| Independent reflections | 2370 | 4375 |
| Observed reflections (I ≥ 2σI) | 2072 | 3672 |
| Absorption correction | Multi-scan | Multi-scan |
| Rσ | 0.0284 | 0.0343 |
| R (F) | 0.0339 | 0.0405 |
| Rw(Fσ)| 0.1056 | 0.1225 |
| Goodness of fit | 1.026 | 1.069 |
| H atom treatment | Constrained | Constrained |
| No. of parameters | 154 | 271 |

IR spectra were recorded as CDCl₃ solutions with Me₄Si as internal standard. 1H NMR (CDCl₃) δ/ppm: 2.59 (s, 3H, CH₃), 4.25 (bs, 5H, H₃/C₄), 4.51 (bs, 5H, H₃/C₄), 4.82 (bs, 2H, H₂/C₅), 5.86 (s, 1H, NH). 13C NMR δ/ppm: 25.5 (CH₃), 69.0 (2C, C₃/C₄), 70.2 (5C, CP₃unub), 72.2 (2C, C₂/C₃), 73.3 (C₁), 169.9.
Scheme 1. Synthesis of mononuclear (4), dinuclear (7) and trinuclear (8) ferrocene imides. More details can be found in the Experimental section. (i) (COCl)$_2$, Py, dry CH$_2$Cl$_2$, reflux 2 h, (ii) NH$_3$, dry toluene, r.t. 2 h, (iii) CH$_3$COCl, NaH, dioxane, r.t. 1½ h, (iv) HOBt/EDC, dry CH$_2$Cl$_2$, 2. CH$_3$NH$_2$ · HCl/Et$_3$N, (v) FeCOCl (2), NaH, dioxane, r.t. 1½ h, (vi) Fc(COCl)$_2$ (6), NaH, dioxane, r.t. overnight.

Figure 1. The NH stretching vibrations in concentration-dependent IR spectra of compounds 4 (a) and 7 (b) in the range from $\epsilon = 5 \times 10^{-2}$ mol dm$^{-3}$ (solid line) to $1 \times 10^{-3}$ mol dm$^{-3}$ (dotted line). More details in Supporting information.
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Table 2. The stretching vibrations, $^1$H NMR signals and $\Delta \delta^o$ values of NH groups of 4, 5 and 7.

| Compound | $\nu$ NHfree (cm$^{-1}$) | $\nu$ NHamb (cm$^{-1}$) | $\delta$ NH | $\Delta \delta^o$ (ppm) |
|----------|---------------------------|--------------------------|------------|------------------------|
| CH$_2$Cl$_2$ | KBr | CH$_2$Cl$_2$ | KBr | (ppm) | (ppm) |
| 4 | 3400 m | - | 3276 vW | 3354 w | 3309 w | 8.56 | 0.04 |
| 5 | 3463 w | - | - | 3298 m | 5.91 |
| 7 | 3450 w | - | 3393 vW | 3349 w | 3307 w | 8.37 | 0.10 |
| 8 | 3412 w | - | - | 3348 vW | 3309 vW | 8.68 | 0.04 |

$^a \Delta \delta$ (ppm) = $\delta$(CDCl$_3$, c = $1 \times 10^{-3}$ mol dm$^{-3}$) - $\delta$(CDCl$_3$, c = $1 \times 10^{-3}$ mol dm$^{-3}$).

N,N'-((Ferrocene-1,1'-dicarbonyl))bisferrocenecarboxamide (8) Compounds 3 (420 mg; 1.833 mmol) was activated with sodium hydride as previously described and after heating at 120 °C for 5 h, the mixture was cooled to 0 °C and a solution of ferrocene-1,1'-dicarbonyl chloride (6) (268 mg; 0.863 mmol) in dry dioxane was added. The mixture was stirred overnight at 64 °C. The solvent was removed, and the residue was dissolved in dichloromethane. After aqueous workup, the organic layer was evaporated to dryness in vacuo, which gave 112.6 mg (19%) orange crystals of 8 after TLC purification with dichloromethane/ethanol (10:1) mixture as eluent. m.p. > 230 °C (decomposition). IR (CH$_2$Cl$_2$) $\nu_{\text{max}}$/cm$^{-1}$: 3412 w (N–Hfree), 1727 s, 1671 m (C=O), $^1$H NMR (CDCl$_3$) $\delta$/ppm: 4.37 (bs, 10H, Cp$_{0}$), 70.2 (10C, Cp$_{0}$unsub.), 70.9 (2C, C$_1$), 168.6 (C$_{CO}$), 72.1 (8C, C$_{N}$/C$_{0}$/C$_{1}$), 72.9 (4C, C$_{N}$/C$_{0}$), 74.3 (2C, C$_{N}$), 168.6 (C=O), 169.0 (C=O). HRMS(EI): calcd for C$_{46}$H$_{32}$Fe$_2$N$_2$O$_4$: 696.0097; found 696.0089. Anal. Calcd for C$_{46}$H$_{32}$Fe$_2$N$_2$O$_4$: C 60.04, H 4.05, N 5.12; found C 60.03, H 4.02, N 5.10.

2.1. X-ray diffraction

Single crystal measurements were performed on an Oxford Diffraction Xcalibur Nova R (CCD detector, microfocus Cu-tube). Program package CrysAlis PRO [24] was used for data collection. The structures were solved using SHELXS97 [25] and refined with SHELXL97 [25]. Models were refined using the full-matrix least squares refinement; all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as constrained entities, using the command AFIX in SHELXL97 [25]. Molecular geometry calculations were performed by PLATON [26], and molecular graphics were prepared by CCDC-Mercury software [27]. Crystallographic and refinement data for the structures reported in this paper are shown in Table 1.

2.2. Computational details

Conformational analysis was performed in three stages for each of the five compounds (4, 5, 7, 9 and 10). This approach was already used in many of our investigations regarding mono- and disubstituted ferrocenes [28, 29, 30, 31, 32, 33, 34, 35, 36, 37]. Low-level optimizations were performed in MacroModel [38, 39] and OPLS2005 force field was used with different search algorithms to obtain the best set of geometries at the molecular mechanics level of theory. A series of the most stable conformers were further optimized in Gaussian16 [40] on the B3LYP-D3/LanL2DZ level of theory. In the last stage, the most stable conformers from a previous step were submitted to full optimizations in chloroform modelled as polarizable continuum (SMD model, chloroform) at the B3LYP-D3/6-311+g (d,p) level of theory while LanL2DZ was used for Fe. Vibrational analysis was performed to verify each structure as a minimum on the potential energy surface. Reported energies refer to standard Gibbs free energies at 298 K calculated relative to the energy of the most stable conformer in chloroform for each series of the investigated compounds.

3. Results and discussion

3.1. Synthesis of ferrocene imides

The synthesis of the target ferrocene imides Fe–CO–NH–CO–Me (4), Fe–CO–NH–CO–Fc (7) and Fe–CO–NH–CO–Fnc–CO–NH–CO–Fe (8) is shown in Scheme 1. Ferrocenecarbonyl chloride (2), obtained from ferrocenecarboxylic acid (1) by a standard procedure described in the literature, was treated with gaseous ammonia to give ferrocenecarboxamide (3) [41]. Addition of 1.5 mol of acetyl chloride or 1 mol of ferrocenecarbonyl chloride (2) or 0.5 mol of ferrocene-1,1'-dicarbonyl chloride (6) to the cooled suspension of ferrocenecarboxamide sodium salt (obtained by heating with a large molar excess of NaNH in mineral oil) gave imides 4 (80%), 7 (52%) and 8 (19%). N-methylferrocenecarboxamide (5) was prepared by a standard HOBt/EDC procedure by reaction of ferrocenecarboxylic acid (1) and methyleneimine [12].

Structural characterization of the novel ferrocene imides 4, 7 and 8 was performed by IR, NMR spectroscopy and mass spectrometry. The NMR and IR spectra of imides 4 (Figures S1–S4), 7 (Figures S5–S8) and 8 (Figures S9–S13) are depicted in the Supporting Information. The IR spectra of all compounds are characterized by bands at ~1700 cm$^{-1}$ attributable to symmetric and the antisymmetric C=O stretching vibrations of imide carbonyls, signals belonging to N–H stretching vibrations at ~3400 cm$^{-1}$ as well as other bands characteristic for acyclic imides [42]. IR spectra of NH-region of imides 4, 7 and 8 recorded in dichloromethane solutions (c = 5 × 10$^{-2}$ mol dm$^{-3}$) contain bands belonging to free (above 3400 cm$^{-1}$) and hydrogen bonded (below 3400 cm$^{-1}$) NH groups (Figure 1 and Table 2). Full IR spectra in Figures S3, S7 and S12. Since the intensity of the former bands is much stronger than that of the latter, it can be assumed that the conformations with free NH groups dominate in the solutions of 4, 7 and 8, especially in the case of 8 in whose spectrum the signal below 3400 cm$^{-1}$ is negligible. Moreover, the weak signals attributed to hydrogen-bonded NH groups of 4 and 7 decrease upon dilution due to dissociation of intermolecular hydrogen.

Figure 2. Molecular structures of 4 and 5A. Thermal ellipsoids are drawn for the probability of 50 % and hydrogen atoms are depicted as spheres of arbitrary radii.

Table 3. Selected torsion angles (in deg) defining the orientation of the substituted amide group in compounds 4 and 5.

| Compound | $\phi$ (deg) |
|----------|--------------|
| 4        | 105          |
| 5A       | 105          |
| 5B       | 105          |
Figure 3. In crystal packing of 4 dimers are formed through centrosymmetric hydrogen bonded ring via a pair of symmetry-related N1–H1⋯O2 hydrogen bonds (crystallographic inversion centres are shown as black circles). Dimers are connected through C8–H8⋯O1 hydrogen bonds along the direction [001] (above specified contacts are shown as turquoise lines), whereas the contact C6–H6⋯O2 completes the network in the plane (100) (shown as black dashed lines). Hydrogen atoms which do not participate in hydrogen bonding were omitted for clarity.

Table 4. Geometric parameters of hydrogen bonds.

|   | D–H/Å | H⋯A/Å | D⋯A/Å | D–H⋯A° | Symm. op. on A |
|---|--------|--------|--------|--------|----------------|
| 4 | N1–H1–O2 | 0.86 | 2.15 | 2.989 (3) | 165 | 1–x, 1–y, 1–z |
|   | C6–H6–O2 | 0.93 | 2.50 | 3.255 (3) | 138 | 1–x, 1–y, 1–z |
|   | C8–H8–O1 | 0.93 | 2.58 | 3.462 (4) | 158 | 1–x, –1/2 + y, 1/2–z |
|   | C13–H13A–O1 | 0.96 | 2.04 | 2.808 (4) | 136 | x, y, z |
| 5 | N1A–H1A–O1B | 0.86 | 2.13 | 2.943 (4) | 157 | 1–x, 1–y, 1–z |
|   | N1B–H1B–O1A | 0.86 | 2.16 | 2.964 (4) | 156 | –x–1, 1–y, 1–z |
|   | C11B–H11B–O1A | 0.93 | 2.71 | 3.488 (6) | 142 | –x–1, 1–y, 1–z |
|   | C9A–H9A–O1B | 0.93 | 2.67 | 3.459 (6) | 143 | 1–x, 1–y, 1–z |
|   | C3A–H3A–O1B | 0.93 | 2.13 | 3.564 (7) | 157 | 1–x, 1–y, 1–z |

Figure 4. Crystal packing of 5 with hydrogen bond N–H⋯O (shown as turquoise lines) connecting crystallographically independent molecules A and B into a chain extending in the direction [100].
and for C7A/C7B conformation with related torsion angles C2 and C7 (the latter comprising two molecules in an asymmetric unit, labelled as A and B, being the same conformer) (Figure 2) were determined by X-ray structure analysis revealing them as π-coordination π-complexes characterised by Fe²⁺–Cp bonds of 2.0242 (2)–2.061 (2) Å in 4; 2.039 (3)–2.055 (4) Å (for molecule A) and 2.036 (5)–2.053 (5) Å (for molecule B) in 5.

In both compounds C–C bonds of cyclopentadienyl rings are conjugated; for 4 bonds values are in the range: C2–C6 [1.416 (3)–1.441 (3) Å] and for C7–C11 [1.394 (4)–1.436 (5) Å]; for 5 C2A/C2B–C6A/C6B bonds values are in the range: [1.415(4)/1.416(5)/1.433(5)/1.439(4) Å] and for C7A/C7B–C11A/C11B [1.405(6)/1.398(6)/1.422(6)/1.421(6) Å]. The cyclopentadienyl rings in both compounds are in an eclipsed conformation with related torsion angles C2–Cp1–Cp2–C7 [8.17°] for 4, and [−12.69°] (molecule A) [−7.01°] (molecule B) in 5.

Selected torsion angles defining the conformation of amide substituents in 4 and 5 relative to Cp rings are listed in Table 3. The conformation of amide substituent in 4 is defined by the two torsional angles: O1–C1–N1–C12 [7.6 (4)°] and O2–C12–N1–C1 [−179.7 (2)°]. The amide groups of 5 (molecules A and B) are planar with the mean value of deviations [0.004 (3) Å] from the best least-squares planes (defined by atoms C1, O1, N1, C12).

In synthesis of 4 and 5 racemic precursors were used and enantiomeric resolution has not occurred neither in syntheses nor for crystallization.

In the crystal packing of 4 the main motif are hydrogen-bonded centrosymmetric dimers generated through a pair of symmetry-related hydrogen bonds N1–H1–O2 (forming an R²₂(8) motif; Figure 3, Table 4). Two C–H–O hydrogen bonds connect the dimers into layers parallel to the plane (100) (Figure 3, Table 4). The layers stack in the direction [001] and are connected by C–H–O interactions (2.78 Å) along [100] direction involving the ferrocene group and van der Waals forces.

Crystal packing of 5 is characterised by N–H–O hydrogen bonds connecting molecules A•••••••A into a chain in the direction [100] (Figure 4, Table 4). The chains are further stabilised by C–H–O hydrogen bonding (2.79 Å) in the direction [001]. In other two directions, [100] and [010], the crystal is held together by van der Waals forces and C–H•••π interactions (Table 5). The hydrophilic chains are embedded into hydrophobic FeCp₂ regions and connected by C–H•••π interactions (Table 5).

3.2. Molecular structures and crystal packing of 4 and 5

The molecular and crystal structures of the compounds 4 and 5 (the latter comprising two molecules in an asymmetric unit, labelled as A and B, being the same conformer) (Figure 2) were determined by X-ray structure analysis revealing them as π-coordination π-complexes characterised by Fe²⁺–Cp bonds of 2.0242 (2)–2.061 (2) Å in 4; 2.039 (3)–2.055 (4) Å (for molecule A) and 2.036 (5)–2.053 (5) Å (for molecule B) in 5.

Table 5. Geometric parameters of the C–H–π interactions.

| Compound | C–H–Cg/Å | C–H–Cg° | C–Cg/Å | Symm. operation on Cg° |
|----------|----------|---------|--------|------------------------|
| 5        |          |         |        |                        |
| C11A–H11A–C2A–C6A | 3.00 | 151 | 3.845 | x, y, 1 + z |
| C7A–H7A–C7B–C11B | 3.48 | 151 | 4.325 | x, y, 1 + z |
| C13–H13–C8–C9–C10 | 3.08 | 161 | 3.969 | −1/2 + x, 3/2, y, z |
| C9B–H9B–C9A–C6A | 3.16 | 143 | 3.946 | x, −1 + y, −1 + z |

a Cg is the centre of gravity of the proton acceptor moiety.

In the theory, three imide groups (R⁰, R⁰⁰ and R⁰°) can adopt four different conformations (Figure 5) differing in positions of the carbonyl groups relative to the substituent attached to nitrogen (R⁰). When two of these groups are the same (R¹ = R⁰) the number of different stereoisomers is reduced to three because cis-trans becomes equal to trans-cis. In previous studies the imide, R–CO–NH–CO–R system was usually considered as an amino group flanked by two carbonyls, and because of the resonance the free imide groups are essentially planar [13, 43]. The relative stability of different stereoisomers was further explained by the steric and electronic effects as follows. While cis-cis has the highest relative energy due to repulsion between two substituents (R¹ and R⁰), the cis-trans isomer is the most stable one and usually observed in solutions. The trans-trans conformer is less stable in comparison to cis-trans due to unfavourable repulsions between imide carbonyl groups.

To better explain the effect of the N-substituted imide nitrogen, in this paper we have focused on three different R⁰ groups (hydrogen in 7, methyl in 9 and phenyl in 10, Figure 6) attached to the imide nitrogen. Other two groups remain the same (Fc = R¹ = R⁰°) in all three computationally

Table 6. List of the most stable conformers of 7, 9 and 10. Energy of each conformer was calculated relative to the energy of the most stable conformer from each series.

| Label | Stereochemical descriptor | E_{cis}/kJ mol⁻¹ |
|-------|--------------------------|-----------------|
| 7–1   | cis-trans                | 0.00            |
| 7–2   | cis-trans                | 1.82            |
| 7–3   | trans-trans              | 3.17            |
| 7–4   | cis-trans                | 4.40            |
| 7–5   | cis-trans                | 5.27            |
| 7–cc² | cis-cis                  | 12.13           |
| 9–1   | cis-cis                  | 0.00            |
| 9–2   | cis-trans                | 9.96            |
| 10–1  | cis-cis                  | 0.00            |
| 10–2  | cis-cis                  | 1.12            |
| 10–3  | trans-trans              | 1.32            |
| 10–4  | trans-trans              | 5.22            |

a some cis-trans conformers between 7-5 and 7-cc were omitted from table.
investigated compounds. A relative distribution of the most contributing conformers in three dinuclear complexes was calculated in solvent (chloroform) modelled as polarizable continuum. Conformers are arranged in Figure 6 according to their relative energies. The conformational search methodology is explained in more details in section Computational details. It is based on three-step approach starting from the lowest level of theory (OPLS2005 force field, Monte Carlo conformational search algorithms) and only the representative sets of conformers were submitted further to full DFT optimizations in chloroform and verified as minima on the potential energy surface. We particularly chose chloroform based on our previous studies where computational data were tested against the NMR experiments to detect the most stable conformers [28, 29, 30, 31, 32, 33, 34, 35, 36, 37].

As expected, as the most stable conformers were found those with cis-trans relative orientation of the carbonyl groups relative to the N-substituted group for derivatives 7 and 10 (Table 6 and Figure 7). While there is preferentially only one such conformer below 5 kJ mol⁻¹ characterized for phenyl substituted compound (e.g., 10-1) there are at least three conformers of cis-trans configuration found for nonsubstituted imide 7, mostly differing in a relative orientation of ferrocene units. In comparison with 10, where phenyl can sterically interfere with nonsubstituted cyclopentadienyl ring, such interference is much weaker in compound 7 with small hydrogen atom on the imide group (e.g., 7-1). Interestingly, cis-cis configuration was confirmed as the most stable for N-methyl substituted 9 while the energy gap between the first (cis-cis) and the second (cis-trans) conformer is about 10 kJ mol⁻¹, what corroborates previously published experimental data that cis-cis conformer of 9 is especially favourable in condensed phase. A very similar cis-cis configurations also exists in 7 with hydrogen, but it is one of the less

![Figure 7. DFT optimized geometries of the most stable conformers of imide N-substituted bis-ferrocene derivatives 7 (R = H), 9 (R = Me) and 10 (R = Ph). Relative energies (in kJ mol⁻¹) are displayed in parenthesis after the labels.](image-url)
Figure 8. Superposition of two geometries, X-ray determined crystal structures are coloured in blue and geometries of the most stable conformers are coloured in orange. The calculated RMSD values are 0.145 Å for 4 and 0.057 Å for 5.

4. Conclusion

In this research, we presented the synthesis and spectroscopic analysis of aromatic imides possessing one (4), two (7) and three (8) ferrocene units connected with iminodiacarbonyl linkers, as well as the crystal structures of N-methylferrocenecarboxamide (5) and N-ace tyferrocenecarboxamide (4). Compounds Fe–CO–NH–CO–Me (4), Fe–N–NH–CO–Fe (7) and Fe–CO–NH–CO–F (8) were prepared by amidation reactions starting from the corresponding ferrocenecarboxyl chloride or acetyl chloride and ferrocenecarboxamide. The NH-region of the IR spectra of imides 4, 7 and 8, taken in diluted solutions of nonpolar solvent, is dominated by signals above carboxamide. The NH-region of the IR spectra of imides are self-assembled by intermolecular N–H···N hydrogen bonds association the molecules of the solid state. In addition, we have investigated the distribution of bis-ferrocenyl imide bridged compounds and confirmed matching with the experimental data.

Declarations

Author contribution statement

Mojca Cakić Semenič, Ivan Kodrin: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Kresimir Molcanov, Monika Kovačević: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Vladimir Rapić: Contributed reagents, materials, analysis tools and data.

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Data availability statement

Data included in article supplementary material/referenced in article.

Declaration of interests statement

The authors declare the following conflict of interest: Ivan Kodrin is a member of the advisory board for Heliyon (section: Heliyon Chemistry).

Additional information

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