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Syntheses and structural characterization of some mono- and di-*p*-nitrophenyl[3]ferrocenophanes: X-ray structure of [3]ferrocenophane, 3-*p*-nitrophenyl[3]ferrocenophane, and 3,4′-bis-(*p*-nitrophenyl)[3]ferrocenophane; DFT calculations on ferrocene derivatives

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Abstract

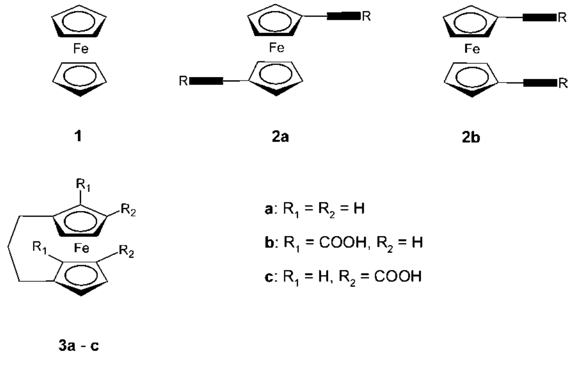
[3]Ferrocenophane (**3a**) reacts in a Gomberg reaction with diazotized *p*-nitroaniline to give a mixture of mono- and di-substituted products. The isomeric pairs of 3- and 2-(*p*-nitrophenyl)[3]ferrocenophanes (**4** and **5**), as well as 3,4′- and 3,4-*bis*-(*p*-nitrophenyl)[3]ferrocenophanes (**6** and **7**) were separated from the mixture by column chromatography on Al_2O_3 and characterized by means of mass, IR, UV, ^1H-NMR spectroscopy, and by X-ray analysis (**4** and **6**). PM3/tm and density functional theoretical calculations on ferrocene (**1**) and ferrocenophane derivatives are reported. A refined X-ray structure determination of [3]ferrocenophane (**3a**) is given. © 2002 Published by Elsevier Science B.V.

Keywords: Bridged ferrocenes; [3]Ferrocenophane; Gomberg arylation reaction; DFT calculations

1. Introduction

Since the discovery of ferrocene (**1**) in 1951 [1], this molecule and a great variety of its derivatives have been used for many different purposes, e.g. as redox active materials, as catalysts for stereoselective syntheses and recently for the preparation of a new class of liquid crystalline compounds [2,3]. Deschenaux and coworkers reported many interesting examples of ferrocene derivatives with LC properties [4–7], especially 1,1′-disubstituted derivatives. The conformation of these molecules in the LC phase is not always known with certainty. Because of the rotational freedom of the cyclopentadienyl rings in ferrocene [8] both S-shape (**2a**) and U-shape (**2b**) conformations [9] are possible (Scheme 1).

It seemed to us that a rotationally fixed ferrocene, e.g. [3]ferrocenophane (**3a**) [10–13] may be a superior building block for LC ferrocene compounds. This presumption has been confirmed since then. LCs derived from 2,2′- and 3,3′-[3]ferrocenophanedicarboxylic acid



Scheme 1.

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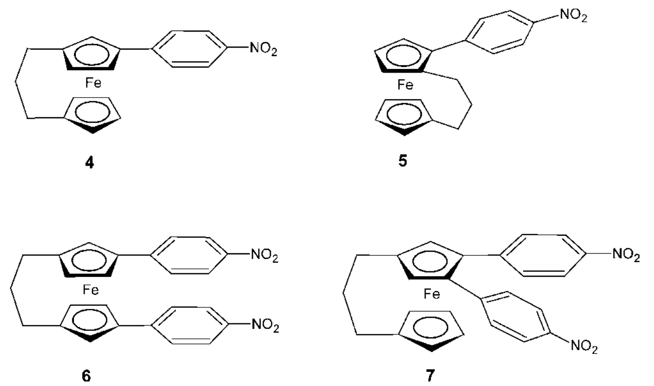


Scheme 2.

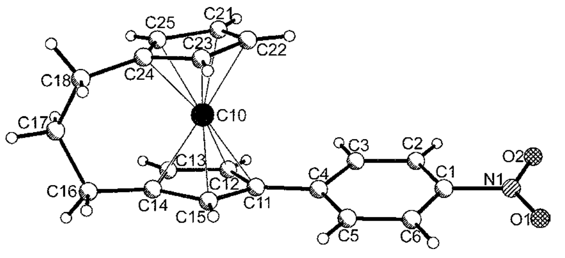


Fig. 1. Crystal structure of compound **4**.

(**3b** and **3c**) have been shown to establish broader LC phases than the corresponding unbridged ferrocene derivatives [14–16]. Therefore there is a certain interest in [3]ferrocenophane derivatives which can be used as starting materials for the preparation of new LCs of this type. In this paper the introduction of aryl substituents in [3]ferrocenophane by a modified [17] Gomberg arylation reaction is reported, as it is known that ferrocene undergoes a arylation reaction of this type to give mono- and 1,1′-bisarylated products [2a,17,18,19,21]. Compounds of this type have also been used as building blocks for ferrocene-containing LCs [22]. In this paper our first results are reported. Additionally some density functional theoretical (DFT) calculations on ferrocene and [3]ferrocenophane derivatives are presented.

2. Results and discussion

The starting material (**3a**) was obtained by the reduction of [3]ferrocenophane-2-one [23], which was in turn available by a one-step annulation procedure from ferrocene [24]. Reaction of **3a** with diazotized *p*-nitraniline in diethylether resulted in the formation of a complex mixture of reaction products. At least six nitrophenylated [3]ferrocenophanes were detected by TLC, which appear as spots with a characteristic purple colour. Finally, four arylated products (**4**–**7**) could be separated by column chromatography (Scheme 2).

Monosubstitution of **3a** can give rise to two isomers (**4** and **5**). Both compounds have been isolated. The structure of **4** has been clarified by an X-ray structure determination (Fig. 1).

In the ^{1}H-NMR spectrum of **4** (Fig. 2) there is an interesting high-field shift of H-5 (3.40 ppm), probably caused by the diamagnetic field of the benzene ring positioned above this proton [25].

Whereas **4** is isolated in 33% yield the second monoarylated product (**5**) is obtained in only 3.9% yield. This result is in line with expectations. Obviously the trimethylene bridge exerts a steric hindrance upon the attack of the aryl moiety. Interestingly, the ^{1}H-NMR spectrum of **5** (Fig. 3) shows a high-field signal at 3.19 ppm, probably resulting from H-4, which is in the diamagnetic region of an aryl group.

In addition to **4** and **5** two bisarylated [3]ferrocenophanes (**6** and **7**) could be isolated, albeit in low yields (**6**: 8.1; **7**: 4.0%). The structure of **6** has again been clarified by an X-ray structure determination (Fig. 4). The torsional angles between the aryl groups and the cyclopentadienyl moieties are small (ω(C1–C6–C7–C8) = 4.11°; ω(C17–C18–C20–C21) = 3.47°, numbering as in Fig. 4), which is in good agreement with DFT calculations (see Section 3).

The cyclopentadienyl part of the ^{1}H-NMR spectrum of **6** represents a classic case of a three nuclear spin system, which can be analyzed as AMX system (Fig. 5).

Protons H1 and H6, H2 and H5, H3 and H4 experience an equal chemical surrounding. The X part of the spectrum (H1 and H6) appears at 4.00 ppm as an almost symmetric doublet of doublets arising from 1–2 coupling with $J = 2.55$ Hz, and an 1–3 coupling with $J = 1.41$ Hz. Protons H2 and H5 generate another doublet of doublets at 4.52 ppm with $J = 2.55$ and 1.46 Hz. As J_{ab} and J_{ax} cross-coupling constants are almost equal and one observes an asymmetric pseudotriplet at 4.55 ppm instead of an (expected) doublet of doublets for H3 and H4. It is remarkable that the central methylene protons of the trimethylene bridge appear as symmetric complex spin system, which is degenerated to a broad singlet at 2.04 ppm, obviously due to the high molecular symmetry **6** (flipping of the trimethylene bridge).

The second bisarylated compound (**7**) could not be obtained as suitable crystals for an X-ray crystal structure determination. Therefore the structure given in this paper rests upon the ^{1}H-NMR spectrum (Fig. 6).

The cyclopentadienyl part of **7** can be explained satisfactorily by making the assumption that both substituents are symmetrically bonded with the same cyclopentadienyl ring. Otherwise the appearance of a singlet at 4.59 ppm and of two pseudotriplets at 4.26 and 3.81 ppm is difficult to understand. A singlet at 4.59 ppm arises from chemically and magnetically equivalent protons H1 and H2 of the substituted cy-

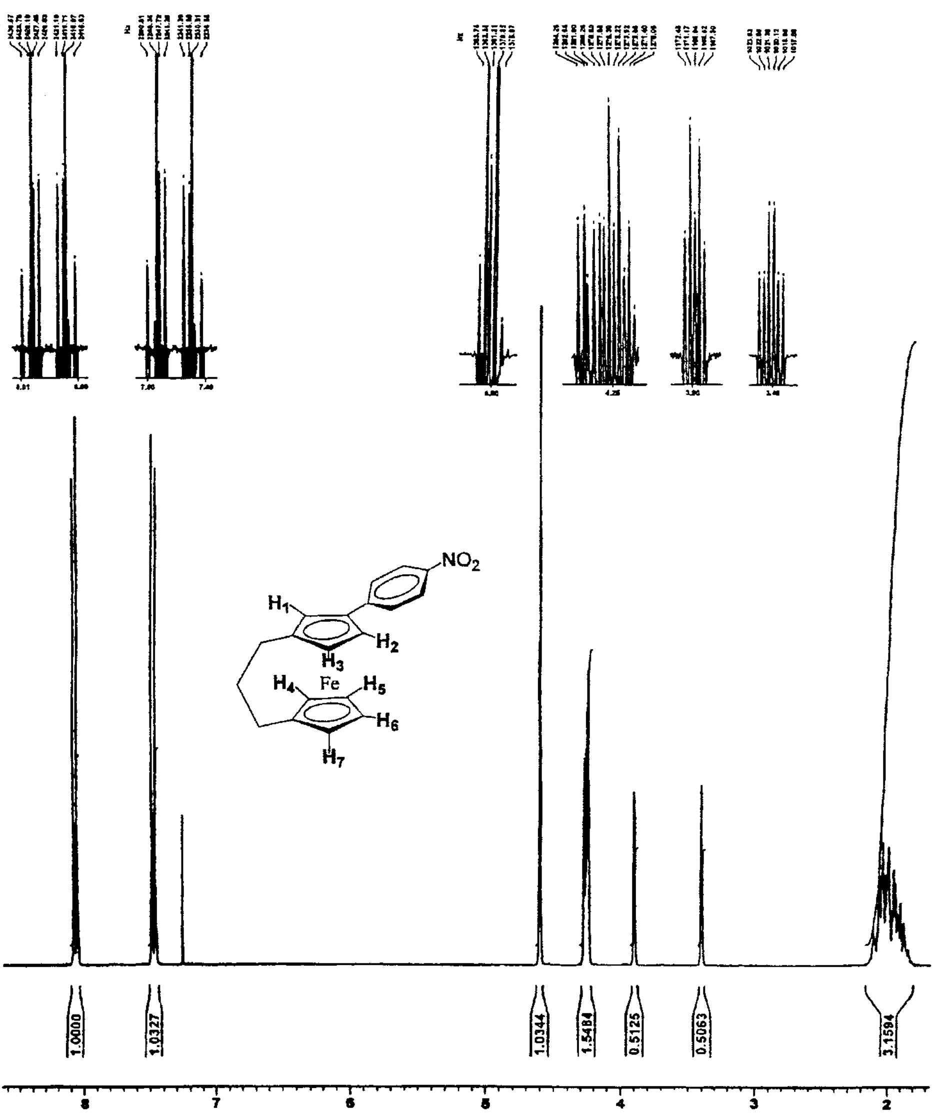


Fig. 2. ^{1}H-NMR spectrum of compound **4**.

clopentadienyl ring. The equivalence of these protons is possible only in the case of a symmetrical alignment of the benzene rings. Otherwise the aromatic protons should experience different chemical surroundings and should show different spectral patterns. The protons in the non-substituted cyclopentadienyl ring can be analyzed as an AA′XX′ system, where the central lines of the subspectra are degenerated into one line. The protons H4 and H5 are shifted downfield due to diamagnetic influence of the benzene ring, contrary to H3 and H6, which are shifted upfield. The protons of the trimethylene bridge appear as two groups of multiplets at 2.10 and 1.95 ppm. A complex multiplicity arises from the magnetic non-equivalency of the proton pairs of each methylene group.

The electronic spectra of compounds **4**–**7** are summarized in Table 1. All compounds show a very strong absorption at 320–330 nm. It is of interest to note that going from **4** to **5** the band is shifted hypsochromically. This is in accord with the assumption that the *p*-nitrophenyl group in **4** is more twisted against the cyclopentadienyl moiety than it is in **5** [31]. ZINDO/S calculations [32] with PM3/tm geometries are in accord with the observed hypsochromic shifts. A similar observation was made for **6** and **7**. Again the hypsochromic shift in **7** (compared with **6**) is in agreement with ZINDO/S results [32,33].

3. Computational results

The structures of ferrocene and other metallocenes have been the subject of numerous theoretical studies [34,35]. Recently it has been shown that DFT calculations [36–38] give a good description of the geometry and other properties of these systems and it seemed to

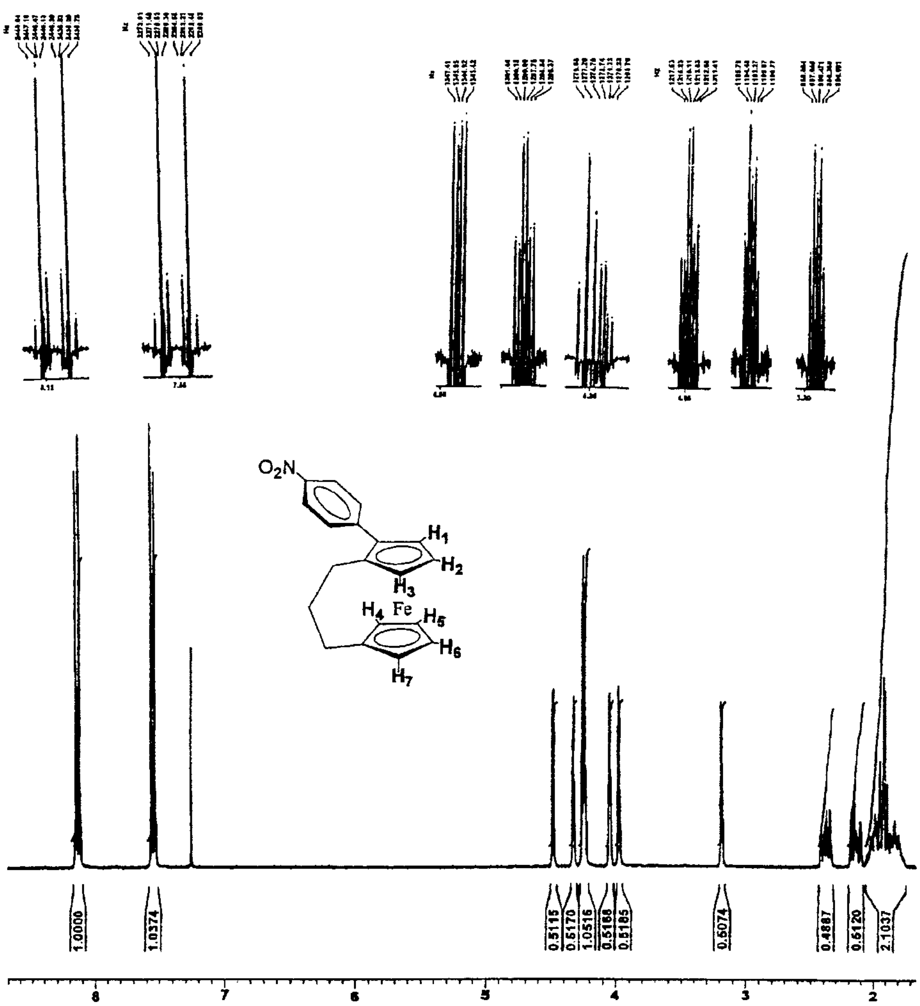


Fig. 3. ^{1}H-NMR spectrum of compound **5**.

be of interest whether DFT methods give reliable results for ferrocenophanes, too. Because of these computationally demanding tasks it is also of interest whether simple semi-empirical methods are also suitable, at least for geometric predictions. In this section a brief overview of our results is given. Ferrocene (**1**) is known to crystallize in a D_{5d} conformation [39]. A PM3/tm optimization results in a D_{5h} geometry, although the energy difference between D_{5d} ($\Delta H_f = -166.98$ kcal mol^{-1}) and D_{5h} ($\Delta H_f = -166.47$ kcal mol^{-1}) is extremely small ($\Delta\Delta H_f = 0.51$ kcal mol^{-1}). The Fe–Cp distance is obtained as $\Delta = 1.676$ Å (D_{5h}) and $\Delta = 1.674$ Å (D_{5d}) in good agreement with experimental data ($\Delta = 1.66$ Å) [39]. Satisfactory values are also obtained for ferrocenophanes (**3a**, **8**, and **9**) (Table 2). It was found experimentally that in these compounds the Cp rings are tilted. PM3/tm calculations are in agreement with these observations, although the agreement is only qualitative, but it should be kept in mind that the variation of ΔH_f with r(C1–C1′) ($3.00 \leq r \leq 3.60$ Å) is only small ($\Delta\Delta H_f \cong 6$ kcal mol^{-1}, PM3/tm values). Th Cp rings in **3a** and **8** were found to be eclipsed, again in agreement with experimental data. An imide-bridged [3]ferrocenophane [12] differs insofar as both experimental data as well as PM3/tm results reveal a staggered arrangement of the Cp rings. In conclusion it can be stated that geometrical predictions with PM3/tm

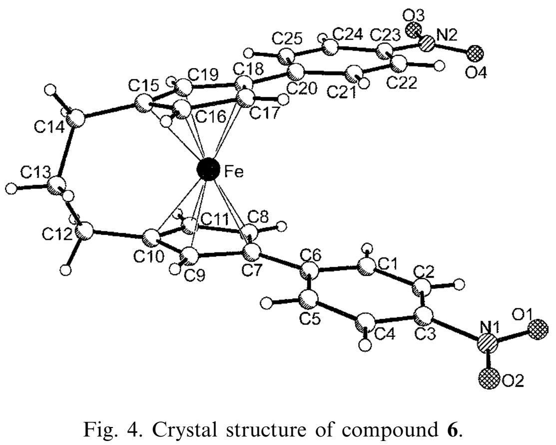


Fig. 4. Crystal structure of compound **6**.

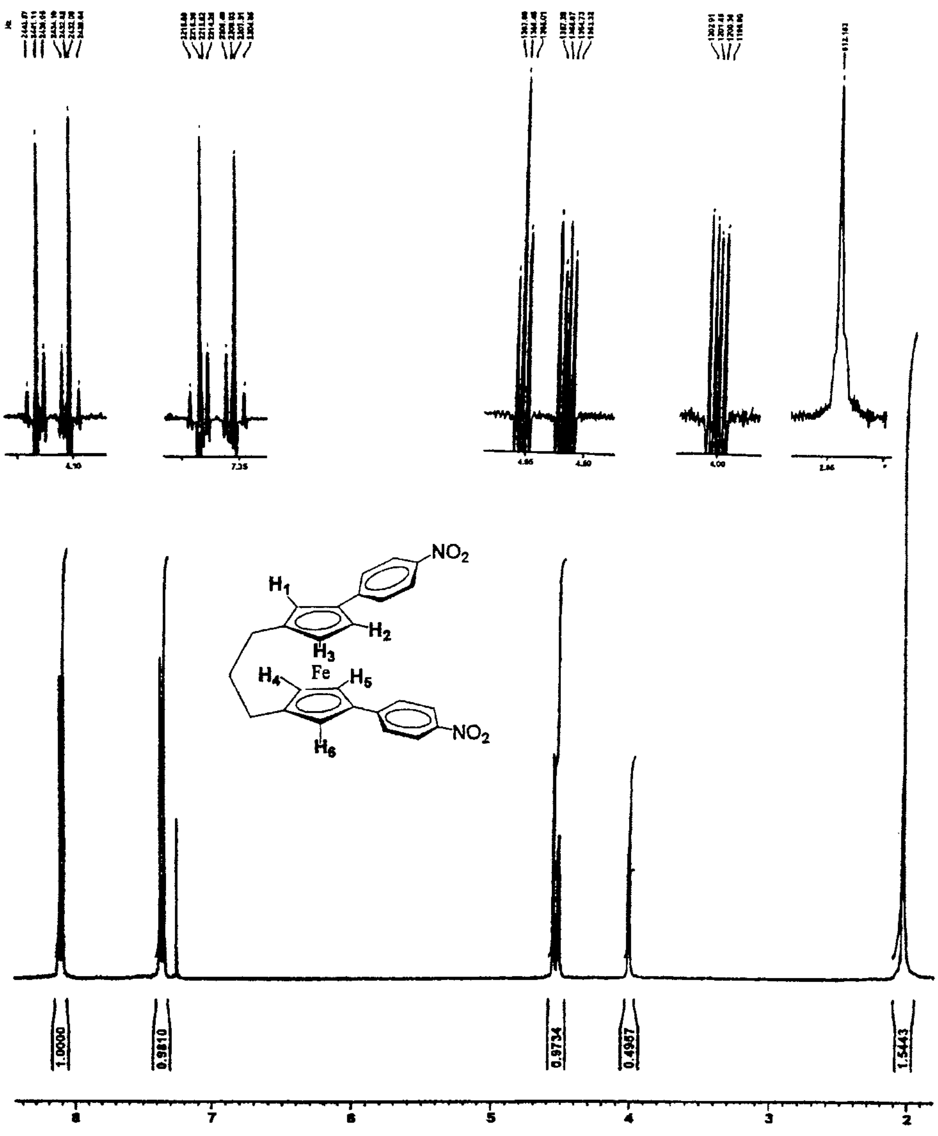


Fig. 5. ^{1}H-NMR spectrum of compound **6**.

for ferrocene and ferrocenophanes seem to be suitable for semi-quantitative purposes [40].

Several ab-initio computational studies have been reported for ferrocene (and other metallocenes as well). Second-order Møller–Plesset calculations and configuration interaction studies fail to predict the experimental Cp–Fe distance. Better agreements have been obtained by complete active space second-order perturbation theory (CASPT2) and coupled cluster calculations. The introduction of electron correlation (together with large one-electron basis sets) increases the computational efforts dramatically. DFT studies have been shown to describe various properties of these molecules satisfactorily with a fraction of computational cost. On the B3LYP/6-31G* level the D_{5h} conformation of ferrocene is slightly more stable than the D_{5d} conformation, although the barrier of rotation is extremely small ($\Delta E \cong 0.12$ kcal mol^{-1}, Fig. 7) [41].

Results for ferrocenophanes **3a**, **8** and **9** using different functionals/basis sets are also given in Table 2. For **3a**, **8** and **9** an eclipsed conformation was found, whereas for an imide-bridged [3]ferrocenophane [12] a staggered conformation was obtained. Generally it can be stated that the agreement with experimental values are good and that there are no remarkable differences between the different methodologies as given in Table 2 with the exception of B3LYP/LANL2DZ. In contrast to PM3/tm results tilt angles are generally found in the experimental region. Computational results for compounds **4**–**7** are given in Table 3.

In conclusion it can be stated that on the DFT level B3LYP/6-31G* and/or B3LYP/LACVP* are entirely sufficient for semi-quantitative purposes.

Whereas DFT results for **1**, **8**, **9** and other ferrocenes generally agree quite well with experimental data, there

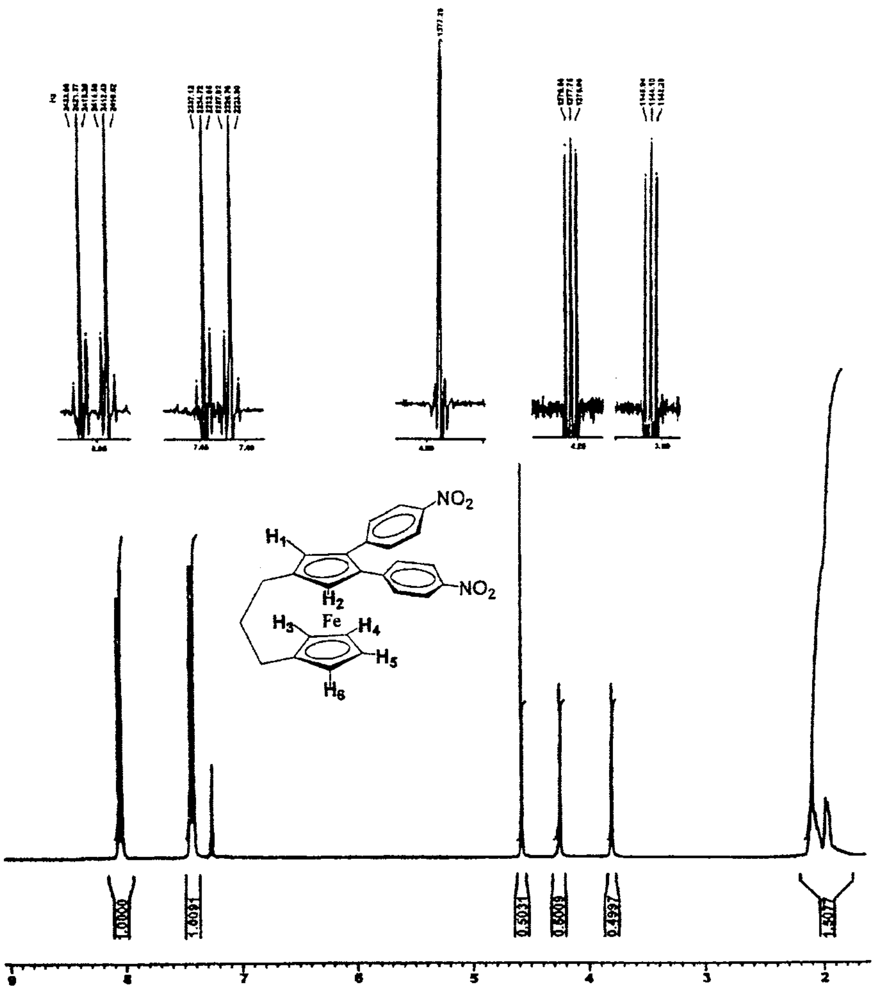


Fig. 6. ^{1}H-NMR spectrum of compound **7**.

was a significant deviation between the calculated values and the X-ray results published for **3a** [11]. Therefore the X-ray structure determination for **3a** was repeated (Fig. 8). The experimental results obtained by this refined measurement now agree substantially better with DFT calculations (Table 2). See also Tables 4 and 5.

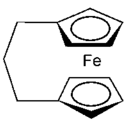
4. Experimental

Melting points were determined by the capillary method. IR spectra were measured by using a Perkin–Elmer Paragon 1000 instrument. Mass spectra were obtained with a spectrometer MAT 8200 (Finnigan) by electron ionization at 70 eV. UV and visible spectra in the region of 250–600 nm were recorded with a spectrophotometer Lambda-14 (Perkin–Elmer) in CH_2Cl_2. ^{1}H-NMR spectra were measured with a spectrometer ARX 300 (Bruker) with Me_4Si as an internal standard. Single crystals for X-ray structure determinations were obtained from saturated benzene solutions which was slowly mixed with hexane vapor in a closed container (**4** and **6**) or from methanol–water (**3a**) [11]. Column chromatographic separations were carried out using neutral Al_2O_3. Thin layer chromatography on Al_2O_3 was used for selecting of the eluents and controlling the separation process. Dried and distilled solvents were used in all cases. [3]Ferrocenophane (**3a**) was synthesized by reduction of [3]ferrocenophane-2-one with $LiAlH_4$, according to literature procedures [23a,42]. [3]Ferrocenophane-2-one was obtained by Turbitt–

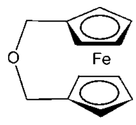
Table 1
UV–vis spectra of compounds **4**–**7** (CH_2Cl_2)

Compound	λ_{max} (nm) (log ε, l cm^{-1} M^{-1})			
4	305 (sh, 3.87)	332 (4.05)	407 (3.39)	516 (3.59)
5		319 (4.21)	407 (3.38)	493 (3.52)
6	305 (sh, 4.31)	324 (4.40)	400 (sh, 3.79)	502 (3.92)
7	305 (sh, 4.24)	315 (4.28)	407 (3.52)	495 (3.67)

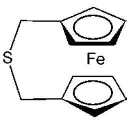
Table 2
Computational results for compounds **3a**, **8**, and **9** (PM3, DFT)



3a



8



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Method	C–C [a]	C1–C1′	C3–C3′	δ(Cp–Cpp) [b]	C–C [a]	C1–C1′	C3–C3′	δ(Cp–Cpp) [b]	C–C [a]	C1–C1′	C3–C3′	δ(Cp-Cp) [b]
PM3	1.461	3.301	3.402	2.5	1.461	3.281	3.372	2.2	1.461	3.347	3.354	0.2
DFT [c]	1.462	3.020	3.350	8.2	–	–	–	–	1.425	3.080	3.340	6.5
DFT [d]	1.424	3.050	3.390	8.4	–	–	–	–	–	–	–	–
DFT [e]	1.430	3.060	3.440	9.4	–	–	–	–	–	–	–	–
DFT [f]	1.424	3-060	3.420	8.9	1.425	3.010	3.470	11.4	1.424	3.130	3.420	7.2
DFT [g]	1.430	3.113	3.505	9.7	1.431	3.068	3.505	10.8	1.430	3.182	3.476	7.3
DFT [h]	1.450	3.150	3.600	11.0	1.440	3.116	3.650	13.1	1.440	3.250	3.574	7.9
Exp. [i]	1.424 [j]	3.038	3.425	9.6	1.425			11.9 [k]	1.410			6.0 [k]

[a] Averaged C–C distance in Cp rings.

[b] Defined as $\delta = 2\arcsin[(\mathrm{C3–C3'}) - (\mathrm{C1–C1'})]/[2(\mathrm{C1–C3})]$.

[c] B3PW91/6-31G*.

[d] B3PW91/6-311G**.

[e] B3LYP/6-311+G(2d,p).

[f] B3LYP/6-31G*.

[g] B3LYP/LACVP*.

[h] B3LYP/LANL2DZ.

[i] As recorded in this paper.

[j] In Ref. [11] an averaged C–C distance of 1.38 Å and a tilt angle of 7.4° was given.

[k] Tilt angle of Cp rings (best plains).

Watts one-step annulation sequence [24] using ferrocene from Aldrich.

4.1. Crystal structure determinations

All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and were refined with isotropic displacement parameters using a riding model. The crystal of compound **4** was non-merohedrically twinned. The reflections of both individuals were indexed and integrated separately. The absolute structure for compound **4** was determined and is in agreement with the selected setting (Flack-x-parameter: -0.03 (4)). In addition, inversion of the structure leads to significant poorer reliability factors (R_1 for all $F_o > 4\sigma(F_o) = 0.0581$; wR_2 for all reflections $= 0.1571$) [42].

4.2. Arylation of [3]ferrocenophane

To a solution of 3.3 g (0.024 mol) of 4-nitroaniline in a mixture of 20 ml of glacial AcOH and 50 ml of absolute ether 1.5 ml (0.024 mol) of concentrated H_2SO_4 was added. To the mixture a solution of 4.00 g (0.034 mole) of n-butyl nitrite in 20 ml of absolute ether was added dropwise during 15–20 min at 0 °C under stirring. The yellow suspension was allowed to react under strong stirring with 5.4 g (0.024 mol) of [3]ferrocenophane (**3a**) in 100 ml of absolute ether for 2 h at 0–5 °C. The intermediate products were destroyed adding portionwise 4 g of anhydrous Na_2CO_3 during 1 h. The reaction mixture was stirred at 0–5 °C for

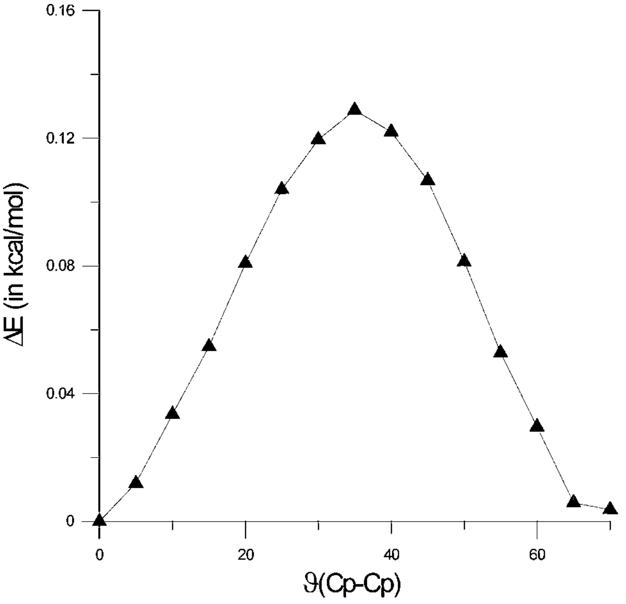

Fig. 7. $D_{5h} \rightarrow D_{5d}$ rotational barrier for ferrocene (**1**) (B3LYP/6-31G*).

Table 3
Computational results for compounds **4**–**7** (values in parenthesis: exp. data)

Method	Atoms	**4**	**5**	**6**	**7**
PM3	C–C (ar1)	1.460 (1.434)	1.462	1.456 (1.428)	1.459
	C–C (ar2)	1.458 (1.423)	1.459	1.456 (1.428)	1.455
	C1–C1′	3.247 (3.043)	3.315	3.231 (3.047)	3.212
	C3–C3′	3.507 (3.424)	3.386	3.610 (3.434)	3.513
	δ(Cp–Cp)	5.2 (9.5) [a]	1.7	9.3 (9.6)	7.4
	δ(Cp–ar1)	42.1 (14.8)	59.4	−48.1 (4.1, 0.93)	45.5
	δ(Cp–ar2)	–	–	43.0 (3.5, 6.4)	62.2
B3LYP/LACVP*	C–C (ar1)	1.433 (1.434)	1.434	1.433 (1.428)	1.436
	C–C (ar2)	1.431 (1.423)	1.431	1.433 (1.428)	1.436
	C1–C1′	3.114 (3.043)	3.105	3.114 (3.047)	3.116
	C3–C3′	3.493 (3.424)	3.521	3.497 (3.434)	3.510
	δ(Cp–Cp)	9.3 (9.5)	10.5	9.4 (9.6)	9.9
	δ(Cp–ar1)	22.3 (14.8)	39.2	15.2 (4.1, 0.93)	44.0
	δ8Cp–ar2)	–	–	18.7 (3.5, 6.4)	39.9

[a] Defined as $\delta = 2$ arc sin [(C3–C3′)–(C1–C1′)]/[2 (C1–C3)].

additional 2 h, then the temperature was allowed to rise to 25 °C overnight. The mixture obtained was filtered, and the filtrate was evaporated to dryness. The filter cake was extracted several times with CH_2Cl_2, the extract was combined with the residue from the ether solution and washed two times with water, which contained 0.2–0.3 g of ascorbic acid. The CH_2Cl_2 layer was dried over Na_2SO_4 and evaporated to dryness with a rotary evaporator. The deep-purple residue was thoroughly freed under vacuum from *n*-butylacetate and placed on a Al_2O_3 column. The unreacted ferrocenophane (**3a**) was eluted by *n*-hexane in a yield 2.60 g (48%). The reaction products were fractionated with a toluene–hexane mixture (1:5), toluene, toluene–benzene (1:1) and finally with benzene. In total seven fractions were obtained. The more strongly adsorbing products were not eluted. The band following ferrocenophane contained minor amounts of a yellow oil, which was rejected. The following six purple bands were purified by a second chromatography and the residues recrystallized from absolute EtOH. According to ^{1}H-NMR spectra two of these fractions were complicated mixtures, although they appeared as single spots on the TLC plate. Four pure isomers (**4**–**7**) were obtained. The pure isomers isolated are given in course as they were removed from the column. In a series of syntheses these isomers were obtained approximately in the same ratio, although the yields depend on the accuracy of the chromatographic separations and the recrystallization procedures.

*4.3. (±)2-(p-Nitrophenyl)[3]ferrocenophane (**5**)*

Yield: 0.21 g (4.9% from recovered **3a**). Purple crystals, m.p. 148 °C. Mass spectrum; *m*/*e*: 347 ([M$^+$], 100), 301 ([M − NO_2]$^+$, 28). IR (KBr, cm^{-1}): 1592.1, 1507.7, 1346.4, 1109.7, 1044.8, 1035.9. ^{1}H-NMR ($CDCl_3$, ppm): 1.75–2.05 (4H, m, $CH_2CH_2CH_2$), 2.08–2.22 (1H, m, $CH_2CH_2CH_2$), 2.30–2.45 (1H, m, $CH_2CH_2CH_2$), 3.19[2] (1H, m, Cp), 3.98 (1H, m, Cp), 4.05 (1H, m, Cp), 4.25 (2H, m, Cp), 4.33 (1H, m, Cp), 4.48 (1H, m, Cp), 7.56 (2H, m, C_6H_4), 8.14 (2H, m, C_6H_4). $C_{19}H_{17}FeNO_2$: Calc.: 347.0609. Found: 347.0606.

*4.4. (±)3-(p-Nitrophenyl)[3]ferrocenophane (**4**)*

Yield: 1.42 g (33.0% from recovered **3a**). Black crystals, m.p. 124 °C. Mass spectrum; *m*/*e*: 347 ([M$^+$], 100), 301 ([M − NO_2]$^+$, 36). IR (KBr, cm^{-1}): 1589.7, 1501.3, 1330.6, 1108.4, 1041.0. ^{1}H-NMR ($CDCl_3$, ppm): 1.85–2.13 (6H, m, $CH_2CH_2CH_2$), 3.40 (1H, m, Cp), 3.90 (1H, m, Cp), 4.25 (3H, m, Cp), 4.60 (2H, m, Cp), 7.48 (2H, m, C_6H_4), 8.08 (2H, m, C_6H_4).

*4.5. 3,4-Bis(p-nitrophenyl)[3]ferrocenophane (**7**)*

Yield: 0.23 g (4.0% from recovered **3a**). Dark-purple crystals, m.p. 206 °C. Mass spectrum; *m*/*e*: 468 ([M$^+$], 100), 422 ([M − NO_2]$^+$, 24), 376 ([M − $2NO_2$]$^+$, 9). IR

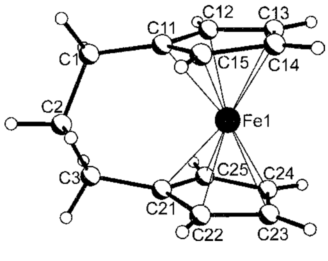

Fig. 8. Crystal structure of [3]ferrocenophane (**3a**).

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[2] Here and in other cases chemical shifts were assigned as centers of multiplets.

Table 4
Crystal data and structure refinement parameters for compounds **3a**, **4** and **6**

Compound	**6**	**4**	**3a**
Empirical formula	$C_{25}H_{20}N_2O_4Fe$	$C_{19}H_{17}NO_2Fe$	$C_{13}H_{14}Fe$
Formula weight (g mol^{-1})	468.28	347.19	226.09
Crystal colour	Red	Red	Dark orange
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1$	$P2_1/n$
Unit cell dimensions			
a (Å)	11.895 (3)	8.334 (1)	7.387 (1)
b (Å)	26.084 (4)	8.328 (1)	9.868 (1)
c (Å)	6.491 (2)	11.320 (1)	13.825 (2)
β (°)	93.15 (2)	98.15 (1)	100.37 (1)
V (Å^3)	2010.9 (9)	777.7 (1)	991.2 (2)
Temperature (K)	293	293	130
Z	4	2	4
D_{calc} (g cm^{-3})	1.547	1.483	1.515
F (000)	968	360	472
2θ Range (°)	3–45	3–52	3–56
Index ranges	$-12 = h = 12$, $-1 = k = 28$, $-0 = l = 6$	$-9 = h = 9$, $-10 = k = 10$, $-12 = l = 13$	$-9 = h = 9$, $-13 = k = 12$, $-18 = l = 18$
Diffractometer	STOE AED-II	STOE IPDS	STOE IPDS
μ (Mo–K$_\alpha$) (mm^{-1})	0.79	0.98	1.47
Measured reflections	3115	2113	9539
R_{int}	0.0407	0.0501	0.0309
Independent reflections	2614	1514	2372
Reflections with $I>2\sigma(I)$	1513	1094	2092
Structure solution	SHELXS-86	SHELXS-86	SHELXS-97
Structure refinement	SHELXL-93	SHELXL-97	SHELXL-97
Refined parameters	289	208	128
R_1 [$I>2\sigma(I)$]	0.0496	0.0488	0.0318
wR_2 [all data]	0.1539	0.1233	0.0881
Goodness-of-fit	1.075	1.030	1.044
Min and max residual density (e Å^{-3})	0.45 and −0.32	0.34 and −0.23	1.10 and −0.24

(KBr, cm^{-1}): 1592.0, 1508.8, 1340.7, 1108.0. ^{1}H-NMR ($CDCl_3$, ppm): 1.90–2.15 (6H, m, $CH_2CH_2CH_2$), 3.81 (2H, m, Cp), 4.25 (2H, m, Cp), 4.59 (2H, s, Cp), 7.43 (2H, m, C_6H_4), 8.05 (2H, m, C_6H_4). $C_{25}H_{20}FeN_2O_2$: Calc.: 468.0772. Found: 468.0772.

Table 5
Selected bond lengths for compounds **3a**, **4** and **6**

Compound **3a**			
Fe1–C11	2.012 (2)	Fe1–C21	2.019 (2)
Fe1–C15	2.025 (2)	Fe1–C25	2.029 (2)
Fe1–C22	2.033 (2)	Fe1–C12	2.035 (2)
Fe1–C23	2.047 (2)	Fe1–C24	2.051 (2)
Fe1–C14	2.054 (2)	Fe1–C13	2.059 (2)
Compound **4**			
Fe1–C13	2.002 (8)	Fe1–C14	2.009 (10)
Fe1–C24	2.015 (9)	Fe1–C23	2.027 (8)
Fe1–C25	2.029 (11)	Fe1–C12	2.038 (11)
Fe1–C15	2.039 (10)	Fe1–C11	2.050 (10)
Fe1–C21	2.050 (9)	Fe1–C22	2.054 (8)
Compound **6**			
Fe–C7	2.050 (6)	Fe–C8	2.056 (7)
Fe–C9	2.034 (7)	Fe–C10	2.018 (7)
Fe–C11	2.031 (6)	Fe–C15	2.027 (7)
Fe–C16	2.018 (7)	Fe–C18	2.043 (6)

4.6. (±)3,4′-Bis(p-nitrophenyl)[3]ferrocenophane (**6**)

Yield: 0.47 g (8.1% from recovered **3a**). Dark-purple crystals, m.p. 235 °C. Mass spectrum; m/e: 468 ([M$^+$], 100), 422 ([M − NO$_2$]$^+$, 21), 376 ([M − 2NO$_2$]$^+$, 6). IR (KBr, cm^{-1}): 1592.6, 1507.9, 1338.1, 1107.2. ^{1}H-NMR ($CDCl_3$, ppm): 2.04 (6H, s, $CH_2CH_2CH_2$), 4.00 (2H, m, Cp), 4.51 (2H, m, Cp), 4.55 (2H, m, Cp), 7.37 (2H, d, m, C_6H_4), 8.12 (2H, m, C_6H_4). $C_{25}H_{20}FeN_2O_2$: Calc.: 468.0772. Found: 468.0772.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 175711–175713 for compounds **6**, **4**, and **3a**, respectively. 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).

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