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RESEARCH ARTICLE

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Synthesis and structures of new helical, nanoscale ferrocenylphenyl amides

Abstract Two novel ferrocenylphenyl-containing amides have been synthesized by reaction of ferrocenylbencarboxylchloride and 1, 2-di-(*o*-aminophenoxy)ethane. A single crystal X-ray analysis shows that compound **3** crystallizes in the triclinic system, space group *P*-1, and compound **4** crystallizes in orthorhombic system, space group $P\mathrm{ca}2_1$. There are intramolecular H-bonds in both the compounds, two H-bonds in compound **3** and one in compound **4**. The dihedral angels of Cp-ring and phenyl ring range from 3.8° to 20.8°.

Keywords ferrocenylphenyl, synthesis, crystal structure, hydrogen bond, amide

1 Introduction

In recent years, a considerable amount of research has been devoted to ferrocene-based compounds, as ferrocene could act as a one-electron donor undergoing oxidation to a ferrocenium ion [1]. Such kind of compounds can effectively be used in catalysis [1], medicine [2], electrochemical research [3], and nonlinear optical material [4]. In 1976, Edwards E. I. and Epton R. synthesized ferrocenyl-penicillins and cephalosporins, of which the antibacterial activity was largely enhanced [5]. Amides derivatives were a class of compounds with high biological activity, and a variety of pharmacological activity [6–8]. Ferrocenyl amides and its Schiff-base compounds had some antitumor activity [9]. For getting a good electron-transmission of ferrocene we incorporate the low toxic and reversible redox phenylferrocene into organic molecule amide and, expect to extend π interaction to the ligand and coordination. Therefore, the electron transfer ability and also the biological activity will be improved. In this paper, we report the synthesis of two new helical compounds containing phenylferrocene and amide, and these compounds might have new chemical and physicochemical properties that are absent or little manifested in the parent substance [10]. In addition, the molecular crystal structures are discussed.

2 Experimental

2.1 Reagents and measurements

Infrared (IR) spectra were recorded on a Brucke-VECTOR22 spectrophotometer as KBr pellets in the 400–4000 cm^{-1} regions. ^{1}H NMR spectra were recorded on a Bruke-DPX400 spectrometer, using $CDCl_3$ as solvent and tetramethylsilane as an internal standard. Elemental analyses were determined with a Carlo Erba 1106 elemental analyzer. The melting point was measured on an X4 instrument and uncorrected. All chemicals were of reagent-grade quality obtained from commercial sources, and solvents were purified by standard method.

2.2 Synthesis

Ferrocenylbencarboxylchloride **1** (1 mmol) was dissolved in dry CH_2Cl_2 and slowly added dropwise to a stirred solution of 1, 2-di-(*o*-aminophenoxy) ethane **2** (0.5 mmol) in dry pyridine (0.79 mL) and anhydrous CH_2Cl_2. Compounds **1** and **2** were prepared according to the literature [11,12]. The resulting mixture was stirred at room temperature for 5 h then washed three times with H_2O. The organic layer was separated and dried over anhydrous $MgSO_4$ and the solvent removed. The crude product was purified on silica gel using petroleum ether-CH_2Cl_2 (1:5) as the eluent. The second crop in silica plate is pure compound **3** in 49% yield and the third crop is pure compound **4** in 23% yield.

Single crystals suitable for X-ray analysis were obtained by slow evaporation of solution of the compounds in CH_2Cl_2 and petroleum ether at room temperature.

For compound **3**: m.p. 208–209°C; ^{1}H NMR (δ): 8.67 (s, 1H), 7.61 (d, $J = 8.28$ Hz, 2H), 7.32 (d, $J = 8.32$ Hz, 2H), 7.16–7.08 (m, 4H), 4.64 (s, 2H), 4.58(s, 2H), 4.36 (d,

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$J = 1.48$ Hz, 2H), 4.01 (s, 5H), IR (cm^{-1}): 3426 (ν_{NH}), 3411 (ν_{NH}), 1670 ($\nu_{C=O}$), 1536 (δ_{NH}), 1254 ($\nu_{C\text{–}N}$), 1104 and 1005 (Fc); Anal. Calc. for $C_{48}H_{40}Fe_2N_2O_4$ (%): C 70.26, H 4.91, N 3.41. Found (%): C, 69.97, H, 5.05, N, 3.47. CCDC: 260846.

Compound **4**: m.p. 179−180°C; ^{1}H NMR (δ): 8.77 (s, 1H), 8.55 (s, 1H), 7.7 (d, $J = 8.24$, 2H), 7.3 (d, $J = 8.28$ Hz, 2H), 7.3−6.9 (m, 8H), 5.30 (s, 1H), 4.65 (t, $J = 1.54$ Hz, 2H), 4.4 (d, $J = 5.08$ Hz, 2H), 4.38 (t, $J = 1.64$ Hz, 2H), 4.03 (s, 5H), IR (cm^{-1}): 3483 (ν_{NH}), 3413 (ν_{NH}), 3386 (ν_{NH}), 1667 ($\nu_{C=O}$), 1538 (δ_{NH}), 1258 ($\nu_{C\text{–}N}$), 1105 and 1005 (Fc). Anal. Calc. for $C_{31}H_{28}FeN_2O_3$ (%): C 69.93, H 5.30, N 5.26. Found (%): C 69.75, H 5.45, N 5.39. CCDC: 260844.

2.3 X-ray structure determination

Single crystals of compounds **3** and **4** suitable for X-ray analysis were obtained in mixture solvents of dichloromethane and petroleum ether at room temperature. All data were collected on a Rigaku-Raxis-IV area detector, equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.071073$ nm) at 291 K. The data were corrected for Lorentz and polarization effects. The structure was resolved by direct methods and expanded with difference Fourier synthesis. All nonhydrogen atoms were subjected to refine anisotropically. Hydrogen atoms were included but not refined. All calculations were performed with the SHELX-97 crystallographic software package [13].

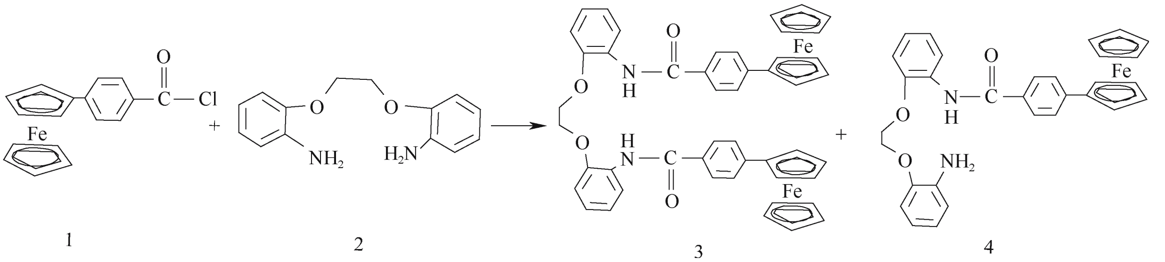
Compound **3** features a helical shape structure, belongs to triclinic system, P-1 space group, with $a = 10.980$ (2) Å, $\alpha = 91.73$ (3)°, $b = 13.970$ (3) Å, $\beta = 92.68$ (3)°, $c = 15.016$ (3) Å, $\gamma = 112.84$ (3)°. $V = 2.1175$ (7) nm^3, $Z = 2$, $Dc = 1.420$ Mg·m^{-3}, $\mu = 0.859$ mm^{-1}, F (000) = 936. $(\Delta/\rho)_{max} = 297$ e·nm^{-3}, $S = 1.071$, $(\Delta/\rho)_{min} = -373$ e·nm^{-3}, The final R factor was 0.0625, $wR = 0.0986$, $w = 1/[\sigma^2(Fo^2) + (0.0446P)^2 + 0.2440P]$ for $P = (Fo^2 + 2Fc^2)/3$.

Compound **4** belongs to orthorhombic system, $Pca2_1$ space group, with $a = 1.7615$ (4) nm, $b = 1.9554$ (4) nm, $c = 0.75269$ (15) nm, $V = 2.5927$ (9) nm^3, $Z = 4$, $Dc = 1.364$ Mg·m^{-3}, $\mu = 0.617$ mm^{-1}, F (000) = 1112. $(\Delta/\rho)_{max} = 581$ e.nm^{-3}, $S = 1.043$, $(\Delta/\rho)_{min} = -228$ e·nm^{-3}, the final R factor was 0.0674, $wR = 0.0821$, $w = 1/[\sigma^2(Fo^2) + (0.0274P)^2 + 0.0000P]$ for $P = (Fo^2 + 2Fc^2)/3$.

3 Results and discussion

3.1 IR spectra

Compounds **3** and **4** have two character peaks of carbonyl and carboxyl at 1670 cm^{-1} and 1666 cm^{-1} of amide I band, respectively; at 3426 cm^{-1}, 3411 cm^{-1} and 3483 cm^{-1}, 3413 cm^{-1}, have stretching vibration peaks of N—H; and at 1536 cm^{-1} and 1538 cm^{-1} have weak peaks of amide II spectra. Both compounds have weak absorption peak at 820 cm^{-1}, which indicated that there was a replacement of *p*-phenyl. The sharp absorption peak of 746 cm^{-1} shows that there was a



Scheme 1

Table 1 Crystal data and structure refinement for compounds **3** and **4**

	Compound **3**	Compound **4**
Empirical formula	C49 H42 Cl2 Fe2 N2 O4	C31 H28 Fe N2 O3
Formula weight	905.45	532.40
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Triclinic, P-1	Orthorhombic, *P*ca2(1)
Absorption coefficient/mm^{-1}	0.859	0.617
F(000)	936	1112
Crystal size/mm^3	0.20 × 0.18 × 0.18	0.20 × 0.18 × 0.18
Theta range for data collection	1.36–25.00°	1.04–23.50°
Index ranges	$-13 \leqslant h \leqslant 11, 0 \leqslant k \leqslant 16, -17 \leqslant l \leqslant 17$	$0 \leqslant h \leqslant 19, -21 \leqslant k \leqslant 21, -8 \leqslant l \leqslant 8$
Reflections collected / unique	5540 / 5540 [*R*(int) = 0.0000]	5713 / 3448 [*R*(int) = 0.0623]
Max. and min. transmission	0.8607 and 0.8470	0.8970 and 0.8865
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5540/0/541	3448/2/346
Goodness-of-fit on F^2	1.071	1.043
Final *R* indices [$I > 2$sigma(I)]	$R1 = 0.0652$, $wR2 = 0.0986$	$R1 = 0.0674$, $wR2 = 0.0821$
R indices (all data)	$R1 = 0.1117$, $wR2 = 0.1105$	$R1 = 0.1173$, $wR2 = 0.0914$

replacement of *o*-phenyl in molecule. The single replacement of ferrocenyl was confirmed by the peaks at 1105 cm^{-1} and 1005 cm^{-1}, similar to those reported in the literature [14,15].

3.2 The crystal structure of the compounds

Crystal data and refinement parameters of compounds **3** and **4** are shown in Table 1. Bond lengths and angles of compound **3** and compound **4** are listed in Table 2 and in Table 3, respectively.

Table 2 Bond lengths [Å] and angles [°] for compound **3**

N(1)-C(17)	1.365(6)	C(23)-O(2)-C(24)	119.2(4)
N(1)-C(18)	1.413(6)	C(26)-O(3)-C(25)	118.5(4)
N(2)-C(32)	1.368(6)	C(6)-C(10)-C(11)	127.2(5)
N(2)-C(31)	1.417(6)	O(1)-C(17)-N(1)	122.1(5)
O(1)-C(17)	1.222(6)	O(1)-C(17)-C(14)	122.5(5)
O(2)-C(23)	1.383(6)	N(1)-C(17)-C(14)	115.4(5)
O(2)-C(24)	1.426(6)	C(19)-C(18)-N(1)	124.8(5)
O(3)-C(26)	1.378(5)	C(22)-C(23)-O(2)	124.6(5)
O(3)-C(25)	1.438(5)	O(2)-C(23)-C(18)	114.0(5)
O(4)-C(32)	1.230(5)	O(2)-C(24)-C(25)	106.7(4)
C(10)-C(11)	1.484(7)	O(3)-C(25)-C(24)	106.1(4)
C(24)-C(25)	1.501(6)	O(3)-C(26)-C(27)	125.5(5)
C(14)-C(17)	1.493(6)	O(3)-C(26)-C(31)	113.8(5)
C(32)-C(33)	1.493(6)	C(30)-C(31)-N(2)	124.2(5)
C(36)-C(39)	1.471(7)	O(4)-C(32)-N(2)	122.8(5)
C(24)-C(25)	1.501(6)	N(2)-C(32)-C(33)	114.4(4)
C(17)-N(1)-C(18)	130.4(5)	C(37)-C(36)-C(39)	120.2(4)
C(32)-N(2)-C(31)	131.2(5)	C(34)-C(33)-C(32)	121.3(4)

Table 3 Bond lengths [Å] and angles [°] for compound **4**

N(1)-C(17)	1.352(9)	C(12)-C(11)-C(10)	122.3(6)
N(1)-C(18)	1.409(8)	C(15)-C(14)-C(17)	122.9(6)
N(2)-C(27)	1.381(13)	O(1)-C(17)-N(1)	122.7(7)
O(1)-C(17)	1.221(7)	O(1)-C(17)-C(14)	123.4(7)
O(2)-C(23)	1.353(8)	N(1)-C(17)-C(14)	113.9(6)
O(2)-C(24)	1.408(8)	C(19)-C(18)-N(1)	124.6(8)
O(3)-C(26)	1.381(9)	N(1)-C(18)-C(23)	115.7(7)
O(3)-C(25)	1.407(7)	O(2)-C(23)-C(22)	127.5(8)
C(10)-C(11)	1.465(8)	O(2)-C(23)-C(18)	113.8(7)
C(14)-C(17)	1.480(9)	O(2)-C(24)-C(25)	107.9(6)
C(24)-C(25)	1.488(9)	O(3)-C(25)-C(24)	109.0(7)
C(17)-N(1)-C(18)	131.4(7)	O(3)-C(26)-C(31)	124.3(8)
C(23)-O(2)-C(24)	118.6(6)	N(2)-C(27)-C(28)	123.9(10)
C(26)-O(3)-C(25)	119.3(6)		

From Fig. 1, we can see that the compound **3** has a helical molecular structure, two phenylferrocene with different configurations suited on the fringe of the molecule. The dihedral angle of Cp-ring C6−C10 and phenyl ring C11−C16 is 3.8° and Cp-ring C39−C43 and phenyl ring C33−C38 is 20.8°. The dihedral angle of two phenyl rings C11−C16, C18−C23 and C26−C31, C33−C38 are 13.9°, 28.3°, respectively. The cyclopentadienyl rings in ferrocenyl fragments are planar and nearly parallel with a dihedral angles of 1.5° (C1−C5 and C6−C10) and 3.6° (C39−C43 and C44−C49). Fe-C$_{ring}$ distances and intracyclo- pentadienyl C—C bond lengths are all similar to those reported in the literature [16]. The torsion angles are −169.0(4)° for C18-N1-C17-C14, −167.2(5)° for C31-N2-C32-C33, 166.2(4)° for C23-O2-C24-C25, and 175.5(4)° for C26-O3-C25-C24. For these torsion angles, the molecule became peculiar helical structure. The distance of the hydrogen atoms located with C46 and C8 is 1.62 nm, which made the molecule gains into a nanoscale [17]. There is a solvent molecule CH_2Cl_2 in the crystal gap that must increase the stability of crystalline structure.

There is one ferrocenylphenyl group in compound **4** that belongs to orthorhombic system, $Pca2_1$ space group, with a = 17.615 (4) Å, b = 19.554 (4) Å, c = 7.5269 (15) Å. The cyclopentadienyl rings in ferrocenyl fragments are planar

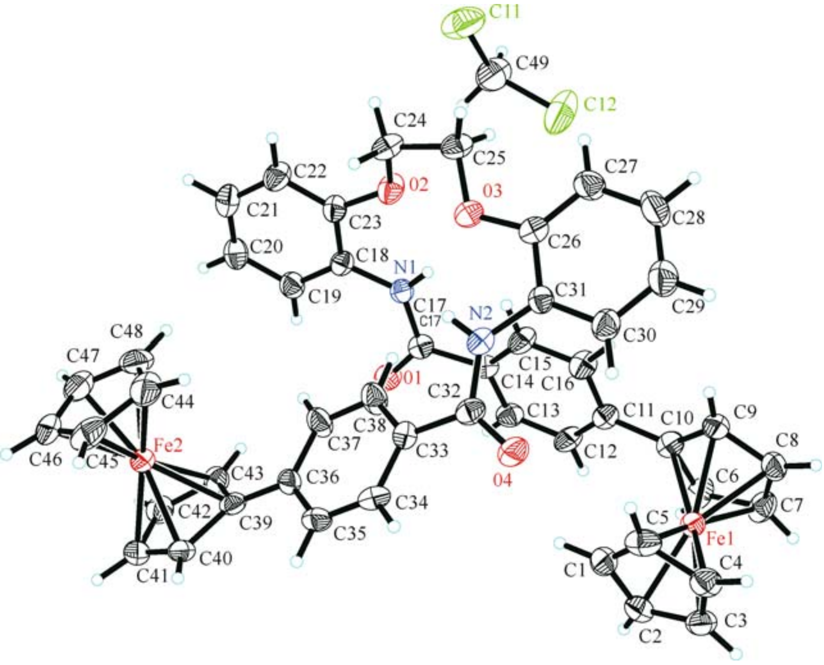


Fig. 1 The molecular structure of compound **3**

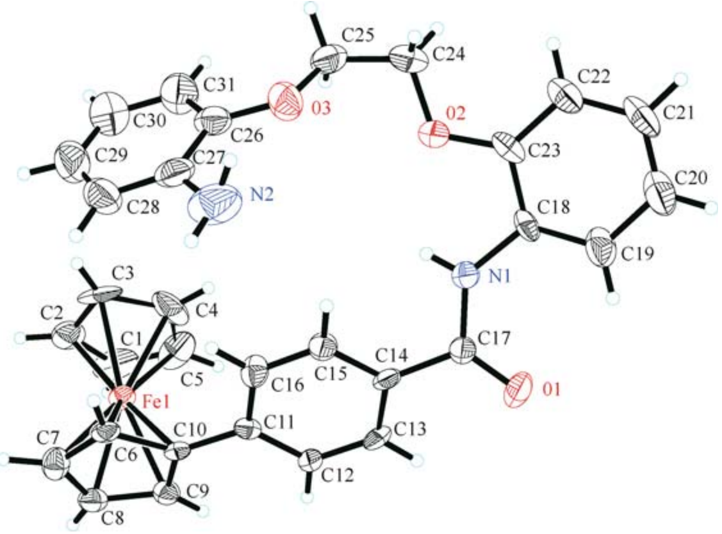


Fig. 2 The molecular structure of compound **4**

and nearly parallel with a dihedral angle of 2.0°. The dihedral angle of Cp-ring C6−C10 and phenyl ring C11−C16 is 13.4° and of the two phenyl rings C11−C16 and C18−C23 is 32.4°. The torsion angles are −179.3 (7)° for C18-N1-C17-C14, −2.2 (8)° for N1-C18-C23-O2, −0.8 (12)° for C18-N1-C17-O1, and −3.3 (12)° for O3-C26-C27-N2. Compound **4** also exhibited helical structure features.

There are intramolecular H-bonds in those two compounds. In compound **3**, the hydrogen bonds originate from N1-H1E with O2 [N1···O2 = 2.570 Å, H1E···O1 = 2.157 Å, N1-H1E···O1 = 113.78°], and N2-H2E with O1 [N2···O1 = 2.574 Å, H2E···O2 = 2.099 Å, N2-H2E···O1 = 117.55°].

In compound **4**, the hydrogen bond originates from N1-H1E with O2 [N1···O2 = 2.578 Å, H1E···O1 = 2.147 Å, N1-H1E···O1 = 113.62°]. Obviously, the N-H···OC interactions are all strong.

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