Synthesis and structures of new helical, nanoscale ferrocenylphenyl amides

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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 Pca21. 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. ¹H NMR spectra were recorded on a Bruke-DPX400 spectrometer, using CDCl₃ 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 CH₂Cl₂ 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 CH₂Cl₂. 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 H₂O. The organic layer was separated and dried over anhydrous MgSO₄ and the solvent removed. The crude product was purified on silica gel using petroleum ether-CH₂Cl₂ (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 CH₂Cl₂ and petroleum ether at room temperature.

For compound 3: m.p. 208–209°C; ¹H 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,
Crystal system, space group Triclinic, $P\bar{1}$ Orthorhombic, space group $P2_12_12_1$ (with $a = 10.980 \, \text{Å}$, $b = 13.970 \, \text{Å}$, $c = 15.016 \, \text{Å}$, $\alpha = 91.73 \, (3)^\circ$, $\beta = 92.68 \, (3)^\circ$, $\gamma = 112.84 \, (3)^\circ$). $V = 2.175 \, (7) \, \text{nm}^3$, $Z = 2$, $D_c = 1.420 \, \text{Mg\cdot m}^{-3}$, $\mu = 0.859 \, \text{mm}^{-1}$, $F(000) = 936$. ($\Delta\rho_{\text{max}} = 297 \, \text{e}^{-}\text{nm}^{-3}$, $S = 1.071$, ($\Delta\rho_{\text{min}} = -373 \, \text{e}^{-}\text{nm}^{-3}$). The final $R$ factor was 0.0625, $wR = 0.0986$, $w = 1/[\sigma(Fo)^2 + (0.0446)^2 + 0.2440P]^2$ 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$^{-1}$, 1536 cm$^{-1}$ and 1538 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](image-url)