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# Synthesis of 2,9,23,30-Tetraoxa[2]paracyclo[2](1,1′)ferroceno[2]paracyclo[2](1,1′)ferrocenophane-1,10,22,31-tetraone

Akira Kasahara,* Taeko Izumi, and Katsuo Saito

*Department of Applied Chemistry, Faculty of Engineering, Yamagata University, Yonezawa 992*

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**Synopsis.** Ferrocenophane, in which the two ferrocene rings are linked by ester bonds and *p*-substituted benzene rings, has been synthesized by the reaction of hydroquinone with 1,1′-bis(chloroformyl)ferrocene. The structure of the compound has been studied on the basis of the NMR and electronic spectra.

Although a considerable number of [*m*]ferrocenophanes with one or more bridges joining the two rings of ferrocene nucleus are known, the [*m.n*]ferrocenophane system in which two ferrocene nuclei are joined through two or more bridges has received little attention.1) However, it has recently been reported that the [2.2]-,2) [3.3]-,3) and [5.5]ferrocenophanes3) showed transannular $\pi$-electronic interactions owing to the relative proximity of the two bridging elements. In this report we wish to describe the synthesis of 2,9,23,30-tetraoxa[2]paracyclo[2](1,1′)ferroceno[2]paracyclo[2]-(1,1′)ferrocenophane-1,10,22,31-tetraone (**1**), in which the two ferrocene moieties are linked by ester linkages and *p*-substituted benzene rings.

The reaction of 1,1′-bis(chloroformyl)ferrocene (**2**) with an excess amount of hydroquinone (**3**) led to the formation of 1,1′-bis(*p*-hydroxyphenoxycarbonyl)-ferrocene (**4**), accompanied by a small amount of **1**. The reaction of **2** with **4** afforded **1** in 6% yield. Furthermore, in the presence of trifluoroacetic anhydride, the reaction of ferrocene-1,1′-dicarboxylic acid (**5**) with **3** afforded a mixture of **1** and **4**.

The reference compound, *p*-phenylene bis(ferrocenecarboxylate) (**6**), was prepared by the reaction of (chloroformyl)ferrocene (**7**) with **3**, accompanied by the formation of *p*-hydroxyphenyl ferrocenecarboxylate (**8**).

In the ferrocenophane **1**, the IR spectrum revealed the presence of 1,1′-disubstituted ferrocene and *p*-substituted benzene rings and ester linkage. In ferrocene, the distance between the two cyclopentadienyl rings is 3.32 Å,4) while the van der Waals separation between the parallel $\pi$-systems is 3.345 Å.5) The molecule of **1** probably exists in the conformation with the phenyl rings approximately parallel to each other and approximately coplanar to the plane of the cyclopentadienyl ring. Structural evidence for the structure of **1** mainly came from its $^1$H NMR spectrum, which shows two peaks at $\delta$ 4.62 (m) and 5.01 (m) for the cyclopentadienyl protons and two peaks at $\delta$ 6.70 (d) and 6.99 (d) for the aromatic protons. The aromatic protons in **1** are shifted to higher field than the corresponding protons of the reference compound, *p*-phenylene bis(ferrocenecarboxylate) (**6**) ($\delta$, 7.21 (s)). It has previously been reported that [2]paracyclo[2]-paracyclo[2](1,1′)ferrocenophane-1,9,17-triene, which has the parallel stacked configuration, shows an upfield shift of aromatic protons which lie in close proximity to opposed aromatic moiety.6) So, the remarkable upfield shift of aromatic protons in **1** is probably due to a diamagnetic shielding effect to the opposed aromatic ring and clearly indicates a pallalel stacked configuration (**1**) rather than a cross-stacked one (**1a**).

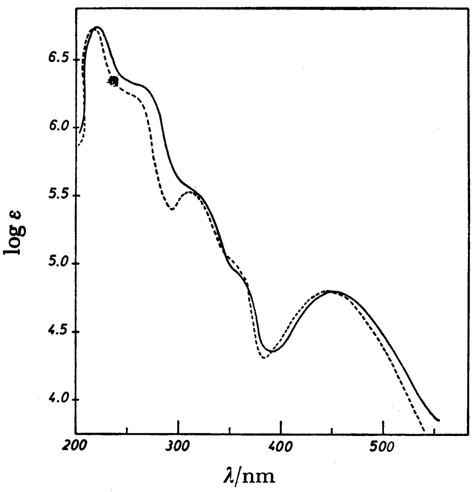
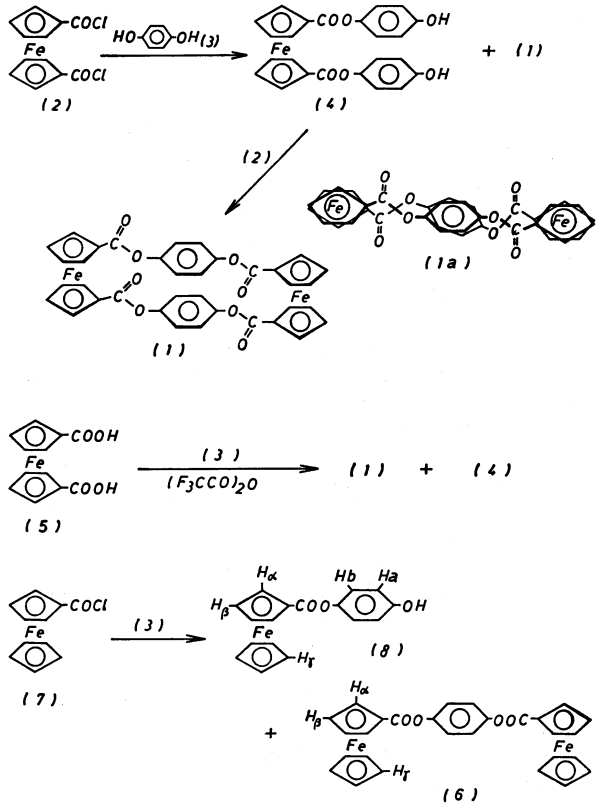


Fig. 1. Electronic spectra of **1** and **6** in tetrahydrofuran.
——: **1**, ----: **6**.



Scheme 1.

The electronic spectra of the ferrocenophane **1** and the reference compound **6** are shown in Fig. 1. It is well known that the transannular electronic interactions in cyclophanes result in the bathochromic and hyperchromic shifts of absorption bands in electronic spectra.[7] The electronic spectrum of **1** showed somewhat bathochromic and hyperchromic shifts and an unambiguous broadening in a range 220—300 nm, compared with those of the reference compound **6**. This result may be due to transannular $\pi$-electronic interactions between the two aromatic chromophores in **1**. On the other hand, the electronic spectrum of ferrocene has two main absorptions at 325 and 440 nm, and it has been found that it is the 440 nm band which is most affected by the ferrocene ring tilt.[8] The electronic spectrum of **1**, in 330—450 nm region, is closely similar to those of open chain model **6**. This suggests that, in **1**, no ferrocene ring tilt distortion occurs.

## Experimental

*Measurements and Materials.* All melting points are uncorrected. All reactions were performed under nitrogen. IR spectra were measured using a Hitachi 260-10 spectrophotometer. $^1$H NMR spectra were obtained at 90 MHz with a Hitachi R-22 spectrometer using TMS as the internal standard. Mass spectra were recorded with a Hitachi RMU-6M spectrometer and electronic spectra with a Hitachi 200-10 spectrophotometer.

1,1′-Bis(chloroformyl)ferrocene (**2**)[9] and chloroformylferrocene (**7**)[10] were prepared by the methods described in the literature.

*The Reaction of 1,1′-Bis(chloroformyl)ferrocene (**2**) with Hydroquinone (**3**).* To a solution of **3** (6.93 g, 63 mmol) in dry acetonitrile (50 cm$^3$) was added dropwise a solution of **2** (6.52 g, 21 mmol) in dry benzene over 24 h under refluxing. After an additional 70 h period of reflux, the mixture was evaporated under reduced pressure. The reddish residue was chromatographed on silica gel.

The first fraction, eluted with chloroform–acetone (5:1) and followed by evaporation and recrystallization from ethanol, afforded orange crystals (3.65 g, 38% yield). These were determined to be **4** (mp 226—228 °C (decomp). IR (KBr): 3370 (–OH), 1690 (ester), 3100, 805 (1,1′-disubstituted ferrocene ring), and 865 cm$^{-1}$ (*p*-substituted benzene ring). $^1$H NMR (acetone-$d_6$): $\delta$=4.68 (t, 4H, $\underline{\mathrm{H}}\beta$), 5.01 (t, 4H, $\underline{\mathrm{H}}\alpha$), 6.83 (d, $J$=9 Hz, 4H, $\underline{\mathrm{H}}$a), 7.05 (d, $J$=9 Hz, 4H, $\underline{\mathrm{H}}$b), and 8.49 (b-s, 2H, –O$\underline{\mathrm{H}}$). Found: C, 62.68; H, 3.81%; M$^+$, 458. Calcd for $C_{24}H_{18}FeO_6$: C, 62.90; H, 3.95%; M, 458.

The second fraction, eluted with chloroform-acetone (5:1) and followed by evaporation and recrystallization from benzene, afforded reddish orange crystals, mp 222—224 °C (decomp) (0.12 g, 0.82% yield). These were determined to be **1**. IR (KBr): 1720 (ester), 3100, 800 (1,1′-disubstiuted ferrocene ring), and 850 cm$^{-1}$ (*p*-substituted benzene ring). $^1$H NMR (tetrahydrofuran-$d_8$): $\delta$=4.62 (m, 8H, $\underline{\mathrm{H}}\beta$), 5.01 (m, 8H, $\underline{\mathrm{H}}\alpha$), 6.70 (d, $J$=9 Hz, 4H, Ar–$\underline{\mathrm{H}}$), and 6.99 (d, $J$=9 Hz, 4H, Ar–H). Found: C, 61.93; H, 3.35%; M$^+$, 696. Calcd for $C_{36}H_{24}Fe_2O_8$: C, 62.09; H, 3.47%; M, 696.

*The Reaction of 1,1′-Bis(chloroformyl)ferrocene (**2**) with 1,1′-Bis(*p*-hydroxyphenoxycarbonyl)ferrocene (**4**).* The reaction of **2** (3.19 g, 10.3 mmol) with **2** (4.39 g, 9.6 mmol) was carried out in the same way as described above, and the ferrocenophane **1** was obtained in 6% yield.

*The Reaction of Hydroquinone (**3**) with Ferrocene-1,1′dicarboxylic Acid (**5**).* At room temperature, the solution of **3** (2.20 g, 20 mmol) in dry acetonitrile (25 cm$^3$) was added to the mixture of **5** (2.75 g, 10 mmol) and trifluoroacetic anhydride (5 cm$^3$) in dry benzene (30 cm$^3$). After an additional 30 h period of stirring, the solution was evaporated *in vacuo* and the residue was extracted with chloroform. The extracts were washed with 5% sodium hydrogencarbonate solution and then with brine, and the solvent was removed. The residue was purified by column chromatography on silica gel (chloroform–acetone (5:1)) to give **2** (25% yield) and **1** (11% yield).

*p-Phenylene Bis(ferrocenecarboxylate) (**6**).* The reaction of chloroformylferrocene (**7**) (9.92 g, 40 mmol) with **3** (1.84 g, 16.7 mmol) was carried out in the same way as has been described for the reaction of **2** with **3**, and the products were separated by chromatography on silica gel.

The first fraction, eluted with chloroform gave *p*-hydroxyphenyl ferrocenecarboxylate (**8**) as orange crystals, mp 179—180 °C, in 20% yield. IR (KBr): 3400 (–OH), 1690 (ester), 3100, 1100, 1000, 800 (monosubstituted ferrocene ring), and 850 cm$^{-1}$ (*p*-substituted benzene ring). $^1$H NMR (acetone-$d_6$): $\delta$=4.30 (s, 5H, $\underline{\mathrm{H}}\gamma$), 4.54 (t, 2H, $\underline{\mathrm{H}}\beta$), 4.92 (t, 2H, $\underline{\mathrm{H}}\alpha$), 6.87 (d, $J$=8 Hz, 2H, $\underline{\mathrm{H}}$a), 7.05 (d, $J$=8 Hz, 2H, $\underline{\mathrm{H}}$b), and 8.48 (b-s, 1H, –O$\underline{\mathrm{H}}$). Found: C, 63.30; H, 4.29%; M$^+$, 322. Calcd for $C_{17}H_{14}FeO_3$: C, 63.38; H, 4.38%; M, 322.

The second fraction, eluted with chloroform gave **6** as reddish orange crystals (mp 183—184 °C (decomp) in 40% yield. IR (KBr): 1725 (ester), 3100, 1100, 1000, and 800 (monosubstituted ferrocene ring). $^1$H NMR (CDCl$_3$): $\delta$=4.29 (s, 10H, $\underline{\mathrm{H}}\gamma$), 4.51 (t, 4H, $\underline{\mathrm{H}}\beta$), 4.97 (t, 4H, $\underline{\mathrm{H}}\alpha$), and 7.21 (s, 4H, Ar–$\underline{\mathrm{H}}$). Found: C, 62.83; H, 2.58%; M$^+$ 534. Calcd for $C_{28}H_{22}Fe_2O_4$: C, 62.95; H, 2.64%; M, 534.

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