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Synthesis of [3.3](1,3)Ferrocenophane and Its Derivatives

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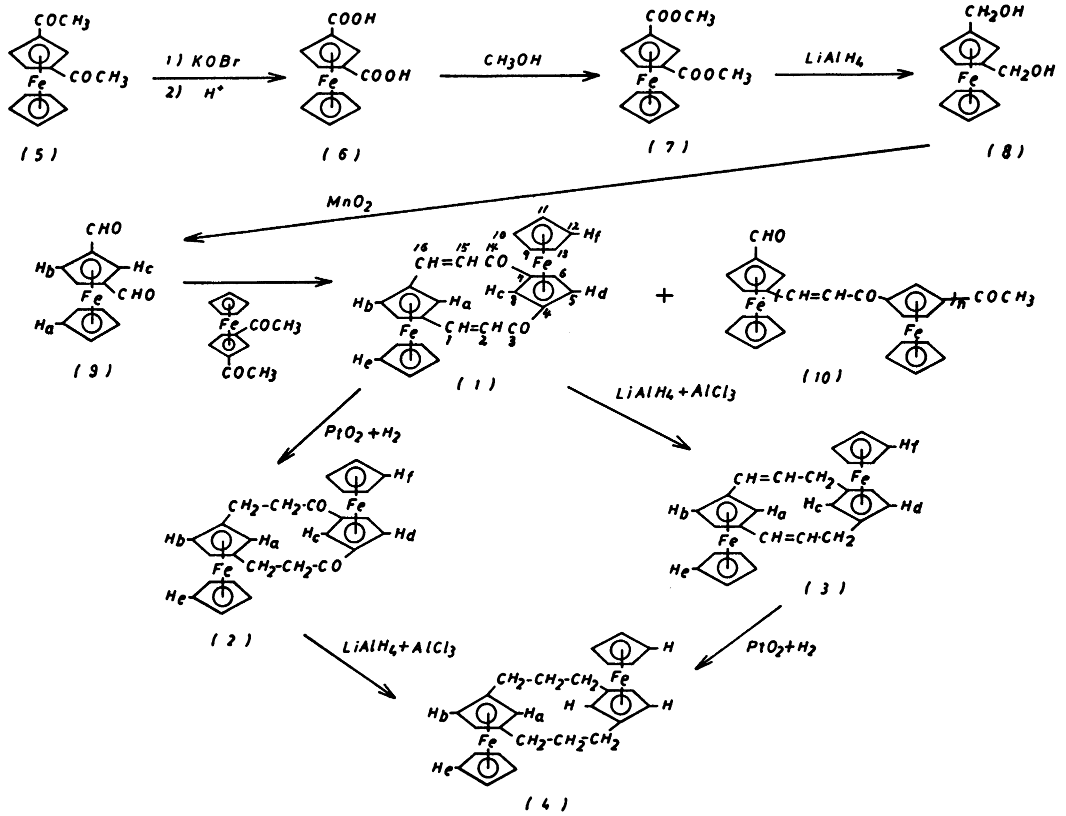
[3.3](1,3)Ferrocenophane-1,15-diene-3,14-dione was synthesized *via* the base-catalyzed condensation of 1,3-ferrocenedicarbaldehyde with 1,3-diacetylferrocene utilizing the high dilution technique. The reduction of the compound with $LiAlH_4$–$AlCl_3$ and the subsequent catalytic hydrogenation led to the formation of [3.3](1,3)-ferrocenophane. The transannular π-electronic interactions between the two ferrocene moieties in these compounds were examined on the basis of NMR and electronic spectra.

Recently, cyclophane compounds in which two or more aromatic rings are mutually stratified have been investigated, with emphasis on transannular π-electronic interactions.[1] However, there are only a few investigations of ferrocenophane having transannular π-electronic interactions: [2.2]Ferrocenophane-1,13-diyne,[2] [2.2]-ferrocenophane-1,13-diene,[3] [2]paracyclo[2]paracyclo-[2](1,1′)ferrocenophane derivatives,[4] [3.3](1,1′)-ferrocenophane-1,15-diene-3,14-dione,[5] [5.5](1,1′)ferrocenophane derivatives,[5] and [0]metacyclo[2]-metacyclo[0](1,1′)ferrocenophan-7-ene.[6] Benedikt and Schlögl[7] have recently reported on the synthesis of [2.2](1,2)ferrocenophane and Yamakawa *et al.*[8] have described the synthesis of [2.2.2](1,3)ferrocenophanetriene.

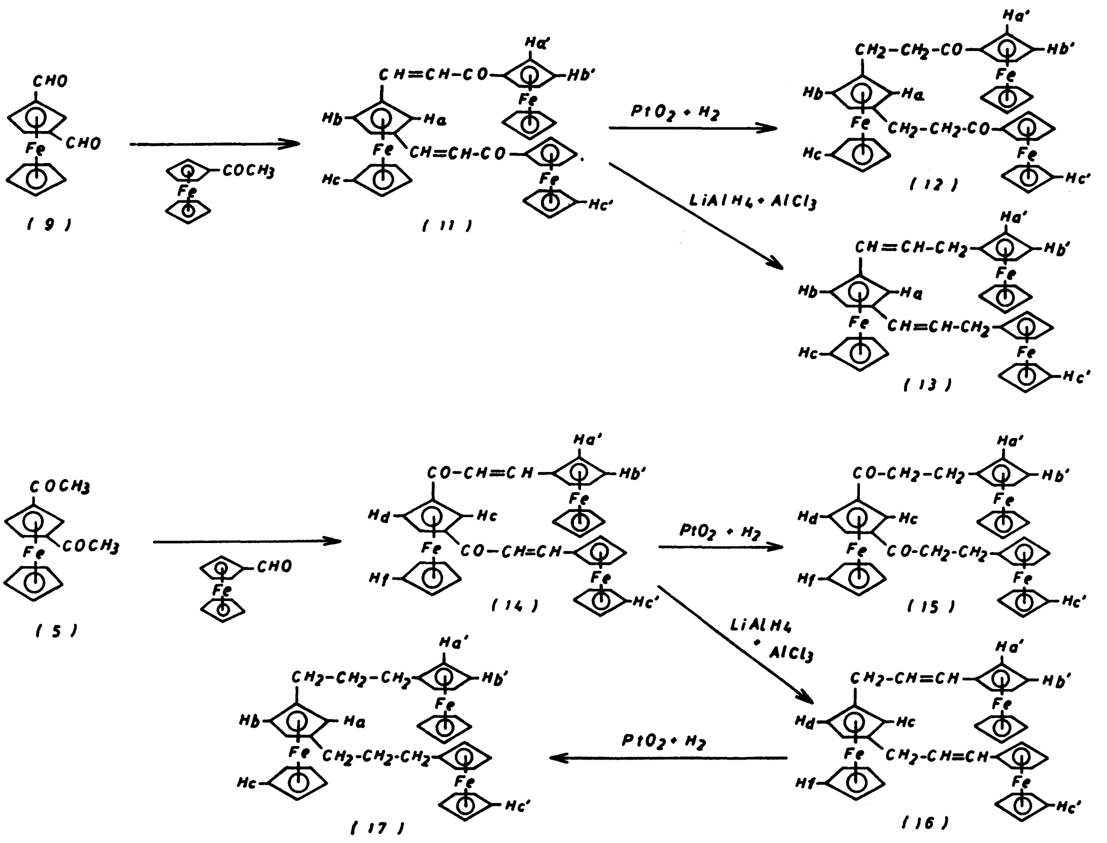
The synthetic methods and structures as well as chemical and physical properties of [2.2]metacyclophanes[9] and [3.3]metacyclophanes[10] have been widely investigated: Based on this and similar experiences in the metallocene field it seemed of considerable interest to prepare and study related metallocenophanes, especially in the ferrocenophane series. According to its molecular geometry, ferrocene cannot accommodate two ethylene bridges between two ferrocene units in the 1,3-positions such as in [2.2]metacyclophane; however, [3.3](1,3)ferrocenophane seemed to be —according to molecular models—a promising target for synthetic and structural investigations. This paper deals with the preparations of four [3.3](1,3)ferrocenophane derivatives (**1**, **2**, **3**, and **4**) having transannular π-electronic interactions.

Experimental

Materials and Measurement. Melting points were not corrected. All the reactions were performed under nitrogen. 1,3-Diacetylferrocene (**5**) was prepared according to the method described by Nesmeyanov *et al.*[11] The IR, NMR, mass, and electronic spectra were recorded with a Hitachi 215, a Hitachi R-22, a Hitachi RMU-6M, and a Hitachi EPS-



Scheme 1. Synthesis of [3.3]ferrocenophane derivatives.



Scheme 2. Synthesis of the refernce compounds.

3T spectrometer, respectively.

Dimethyl 1,3-Ferrocenedicarboxylate (7). To a solution of 23 g (0.58 mol) of sodium hydroxide in 140 ml of water was dropwise added 26 g (0.16 mol) of bromine at 0—10 °C with stirring. Then 70 ml of dioxane was added in portions. At a temperature of 0—5°C, 7.0 g (0.026 mol) of **5** was added in small portions to the vigorously stirred solution. After the addition was over, stirring was continued for one additional hour at 0—5 °C. The reaction mixture was filtered, the filtrate was washed with CH_2Cl_2, and the aqueous layer was heated up to 80 °C. After cooling, acidification with 10% HCl gave orange red crystals, 1,3-ferrocenedicarboxylic acid (**6**) (3.6 g, 50% yield), mp 228 °C (decomp) (lit,[8] mp 227. 5 °C (decomp)). IR (KBr): 3100, 1675 (-C=O), 1100, 1000 cm^{-1}. MS: *m*/*e* 274 (M$^+$).

A suspension of 7.0 g of crude **6** in 150 ml of methanol containing 1 ml of concd H_2SO_4 was heated under reflux for 28 h. After removal of the solvent, the residue was taken up with $CHCl_3$ and chromatographed on silica gel with benzene. The crude product was recrystallized from benzene–hexane to give 6.9 g (90% yield) of **7**, mp 155—157 °C (lit,[8] mp 155—156 °C). IR (KBr): 3100, 1710 (ester), 1100, 1000 cm^{-1}. MS: *m*/*e* 302 (M$^+$).

1,3-Bis(hydroxymethyl)ferrocene (8). To a solution of 2.2 g (0.053 mol) of $LiAlH_4$ in 150 ml of dry diethyl ether was added dropwise a solution of 4.5 g (0.015 mol) of **7** in 50 ml of dry diethyl ether at room temperature with stirring. After the solution was heated under reflux for an additional 4 h, the reaction mixture was decomposed with a small amount of cold water. Yellow crystalline **8**, mp 115—116 °C (lit,[8] mp 115—117.5 °C), was obtained in 95% yield (3.5 g). IR (KBr): 3400, 3200, 3100, 1100, 1000, 905 cm^{-1}. MS: *m*/*e* 246 (M$^+$).

1,3-Ferrocenedicarbaldehyde (9). Active manganese(IV) dioxide (30 g) was added to a solution of **8** (3.0 g, 0.012 mol) in $CHCl_3$ (200 ml) and the resulting mixture was stirred in the dark for 12 h. After filtration, the red solution was evaporated and the dry residue was chromatographed on silica gel with benzene. Bright red crystals, mp 69—70 °C (lit,[8] yellow oil), were obtained in 91% yield (2.7 g). IR (KBr): 3100, 1670 (-C=O), 1100, 995, 920, 905 cm^{-1}. NMR ($CDCl_3$): δ=4.34 (5H, s, H_a), 5.13 (2H, m, H_b), 5.40 (1H, m, H_c), 10.03 (2H, s, -CHO). Found: C, 59.58; H, 4.25%; M$^+$, 242. Calcd for $C_{12}H_{10}O_2Fe$: C, 59.54; H, 4.16%; M, 242.

[3.3](1,3)Ferrocenophane-1,15-diene-3,14-dione (1). To a solution of **9** (2.4 g, 0.01 mol) in ethanol (150 ml) containing 15 g of potassium hydroxide was dropwise added a solution of 2.7 g (0.01 mol) of **5** in ethanol (160 ml) by a motor driven syringe pump over 4 h at room temperature. The resulting mixture was stirred at 55 °C for an additional 2 h, and then evaporated *in vacuo*. The residue was extracted with $CHCl_3$ (300 ml) to isolate the desired product from the polycondensation products (**10**). The $CHCl_3$ extracts were washed with brine to neutralize them and then dried over anhydrous $MgSO_4$. After removal of the solvents, the residue was chromatographed on silica gel with benzene–ether to give 0.6 g 10% yield of **1**, deep red crystals, mp 230—232 °C (decomp). IR (KBr): 3100, 1650 (-C=O), 1100, 995, 920, 905, 815 cm^{-1}. MS: *m*/*e* 476 (M$^+$), 238 (*m*/2*e*), 56 (Fe$^+$). Found: C, 65.51; H, 4.18%. Calcd for $C_{26}H_{20}O_2Fe_2$: C, 65.58; H, 4.23%; M, 476.

[3.3](1,3)Ferrocenophane-1,16-dione (2). An ethanol (100 ml) solution of **1** (0.5 g) was hydrogenated with PtO_2 at room temperature under ordinary pressure. The reaction mixture was filtered to remove the catalyst and the filtrate was evaporated. The residue was chromatographed over silica gel with benzene-hexane to give 0.45 g (90% yield) of **2**, orange red needles,mp 183—184 °C(decomp). IR(KBr): 3100,

1670 (-C=O), 1100, 1000, 920, 905 cm^{-1}. MS: *m/e* 480 (M$^+$), 240 (*m/2e*), 56 (Fe$^+$). Calcd for $C_{26}H_{24}O_2Fe_2$: C, 65.03; H, 5.03%; M, 480.

[3.3](1,3)Ferrocenophane-1,15-diene (3). A dry diethyl ether solution (100 ml) of **1** (0.40 g) was added to a suspension of $LiAlH_4$ (0.2 g) and $AlCl_3$ (0.8 g) in dry diethyl ether (50 ml). After refluxing for 4 h, the excess reagent was decomposed with moist ether and then with water. After the resulting reaction mixture was extracted with ether, the ether extracts were washed with water, saturated sodium hydrogencarbonate solution, and finally brine, and then dried over anhydrous $MgSO_4$. The removal of the solvent left 0.25 g (65% yield) of **3**, orange yellow crystals, mp 196—197 °C (decomp). IR (KBr): 3100, 1100, 1000, 925, 905, 800 cm^{-1}. MS: *m/e* 448 (M$^+$), 224 (*m/2e*), 56 (Fe$^+$). Found: C, 69.55; H, 5.23%. Calcd for $C_{26}H_{24}Fe$: C, 69.67; H, 5.38%: M, 448.

[3.3](1,3)Ferrocenophane (4). Reduction of **2** (0.20 g) with $LiAlH_4$–$AlCl_3$ in anhydrous diethyl ether was carried out in the same way as described for **3**, and 0.11 g of **4** (60% yield), yellow crystals, mp 202—203 °C (decomp), was obtained. Catalytic hydrogenation of **3** with PtO_2 in ethanol also led to the formation of **4** in 75% yield. IR (KBr): 3100, 1100, 995, 925, 905 cm^{-1}. MS: *m/e* 452 (M$^+$), 226 (*m/2e*), 56 (Fe$^+$). Found: C, 68.91; H, 6.08%. Calcd for $C_{26}H_{28}Fe_2$: C, 69.05; H, 6.24%; M, 452.

1,3-Bis[2-(ferrocenylcarbonyl)vinyl]ferrocene (11). To a solution of **9** (2.4 g, 0.01 mol) in ethanol (150 ml) containing 15 g of potassium hydroxide was dropwise added a solution of acetylferrocene (4.6 g, 0.02 mol) in ethanol (150 ml). The resulting mixture was stirred at 55 °C for an additional 2 h, and then evaporated *in vacuo*. The extracts with $CHCl_3$ were washed with an aqueous solution of HCl, saturated sodium hydrogencarbonate solution, and brine, then dried and evaporated. The residue was chromatographed over silica gel with benzene–chloroform to afford **11**, red crystals, mp 220—221 °C (3.5 g, 53% yield). IR (KBr): 3100, 1650 (-C=O), 1590, 970 (*trans* -CH=CH-), 1100, 1000, 920, 905 cm^{-1}. Found: C, 65.21; H, 4.48%; M$^+$, 662. Calcd for $C_{36}H_{30}O_2Fe_3$: C, 65.29; H, 4.56%, M, 662.

1,3-Bis[2-(ferrocenylcarbonyl)ethyl]ferrocene (12). An ethanol–dioxane (200 ml, 1 : 1) solution of **11** (0.9 g) was hydrogenated with PtO_2 at room temperature. The reaction mixture was filtered to remove the catalyst, and the filtrate was evaporated. The residue was chromatographed over silica gel to give 0.8 g of **12** (92% yield), orange red crystals, mp 128—130 °C. IR (KBr): 3100, 1660 (-C=O), 1100, 1000, 920, 905 cm^{-1}. Found: C, 64.73; H, 5.05%; M$^+$, 666. Calcd for $C_{36}H_{34}O_2Fe_3$: C, 64.86; H, 5.14%; M, 666.

1,3-Bis(3-ferrocenyl-1-propenyl)ferrocene (13). The reduction of **11** with $LiAlH_4$–$AlCl_3$ was carried out in the same way as described for **3**, and orange yellow crystals of **13**, mp 113—115 °C, were obtained in 57% yield. IR (KBr): 3100, 1620, 960 (*trans* -CH=CH-), 1100, 1000, 925, 900 cm^{-1}. Found: C, 68.23; H, 5.48%; M$^+$, 634. Calcd for $C_{36}H_{34}Fe_3$: C, 68.11; H, 5.40; M, 634.

1,3-Bis(3-ferrocenylacryloyl)ferrocene (14). The base-catalyzed condensation reaction of ferrocenecarbaldehyde (4.3 g, 0.02 mol) with **5** (2.7 g, 0.01 mol) was carried out in the same way as described for **11**, and red crystals of **14**, mp 237—238 °C (decomp), were obtained in 60% yield. IR(KBr): 3100, 1645 (-C=O), 1600, 980 (*trans* -CH=CH-), 1100, 1000, 920, 905 cm^{-1}. Found: C, 65.17; H, 4.41%; M$^+$, 662. Calcd for $C_{36}H_{30}O_2Fe_3$: C, 65.29; H, 4.56%; M, 662.

1,3-Bis(3-ferrocenylpropionyl)ferrocene (15). The catalytic hydrogenation of **14** with PtO_2 in ethanol–dioxane was carried out in the same way as described for **12**, and orange yellow crystals of **15**, mp 188—190 °C, were obtained in 90% yield. IR (KBr): 3100, 1665 (-C=O), 1100, 1000, 920, 905 cm^{-1}. Found: C, 64.80; H, 5.02%; M$^+$, 666. Calcd for $C_{36}H_{34}O_2Fe$: C, 64.86; H, 5.14%; M, 666.

1,3-Bis(3-ferrocenylallyl)ferrocene (16). The reaction of **14** with $LiAlH_4$–$AlCl_3$ was carried out in the same way as described for **3**, and an orange yellow oil of **16** was obtained in 48% yield. IR (oil film): 3100, 1615, 955 (*trans* -CH=CH-), 1100, 1000, 925, 900 cm^{-1}. Found: C, 68.17; H, 5.45%; M$^+$, 634. Calcd for $C_{36}H_{34}Fe_3$: C, 68.11; H, 5.45%; M, 634.

1,3-Bis(3-ferrocenylpropyl)ferrocene (17). The catalytic hydrogenation of **16** was carried out in the same way as described for **3**, and a yellow oil of **17** was obtained in 94% yield. IR (oil film): 3100, 2950, 1100, 1000, 925,905 cm^{-1}. Found: C, 67.86; H, 6.11%; M$^+$, 638. Calcd for $C_{36}H_{38}Fe_3$: C, 67.74; H, 6.00%; M, 638.

Results and Discussion

Synthesis. All of the [3.3](1,3)ferrocenophanes (**1**, **2**, **3**, and **4**) were prepared by the synthetic sequence shown in Scheme 1. As spectral reference compounds, 1,3-disubstituted ferrocene derivatives (**11**—**17**) were synthesized (see Scheme 2).

In connection with the synthesis of the ferrocenophanes (**1**—**4**), it became desirable to synthesize 1,3-ferrocenedicarbaldehyde (**9**)[12] in quantity. A treatment of 1,3-diacetylferrocene (**5**) with sodium hypobromite in dioxane–H_2O below 10 °C, led to the formation of 1,3-ferrocenedicarboxylic acid (**6**) in 50% yield. Then, 1,3-bis(hydroxymethyl)ferrocene (**8**) was synthesized in 95% yield by the usual $LiAlH_4$ reduction of dimethyl ester (**7**), which was prepared by acid-catalyzed esterification of **6**. The oxidation reaction of **8** in chloroform with active manganese dioxide led to the formation of **9** in good yield.

Under high dilution conditions, a base-catalyzed (ethanolic KOH) condensation of **5** with **9** gave the desired [3.3](1.3)ferrocenophane-1,15-diene-3,14-dione (**1**), accompanied by polycondensation products (**10**). On the other hand, using potassium *t*-butoxide or potassium ethoxide as a base catalyst, the reaction led only to the formation of **10**. The catalytic hydrogenation of **1** afforded [3.3](1,3)ferrocenophane-1,16-dione (**2**) and the reduction of **1** with $LiAlH_4$–$AlCl_3$ gave [3.3](1,3)ferrocenophane-1,15-diene (**3**). Furthermore, both the reduction of **2** with $LiAlH_4$–$AlCl_3$ and the catalytic hydrogenation of **3** afforded the same product: [3.3](1,3)ferrocenophane (**4**).

Structures and Spectra. The NMR spectral data of **1**—**4** and the reference compounds (**11**—**17**) are summarized in Table 1. The structural assignment for **1** is based on spectral evidence and the elemental analyses. The mass spectrum shows two prominent peaks; a molecular ion at *m/e* 476 and a doubly charged ion at *m/2e* 238. This fragmentation pattern is normally observed in [2.2]- and [3.3](1,1')ferrocenophane.[2,3,5] The IR spectrum in **1** exhibits the characteristic absorptions of the carbonyl (1650 cm^{-1}) and *cis* olefinic groups (815cm^{-1}), and of the 1,3-disubstituted ferrocene ring (925 and 905 cm^{-1}).[13] The NMR spectrum of **1** is also consistent with a cyclophane structure and the *anti* orientation of the cyclopentadienyl rings. The chemical

TABLE 1. NMR DATA OF [3.3](1,3) FERROCENOPHANE DERIVATIVES (**1**—**4**) AND REFERENCE COMPOUNDS (**11**—**17**) IN $CDCl_3$ (δ)

Compound	Cyclopentadieny ring protons	Other protons
1	$\underline{H}_a$ 4.30(s,1H)	7.11(d,2H,J=10 Hz,–C=C$\underline{H}$–CO–)
	$\underline{H}_b$ 4.83(b-s,2H)	7.81(d,2H,J=10 Hz,–C$\underline{H}$=C–CO–)
	$\underline{H}_c$ 4.39(s,1H)	
	$\underline{H}_d$ 5.44(b-s,2H)	
	$\underline{H}_e$ 4.27(s,5H)	
	$\underline{H}_f$ 4.33(s,5H)	
2	$\underline{H}_a$ 3.87(s,1H)	2.67—2.75(m,8H,–C$\underline{H}_2$C$\underline{H}_2$CO–)
	$\underline{H}_b$ 4.08(s,2H)	
	$\underline{H}_c$ 3.91(s,1H)	
	$\underline{H}_d$ 4.93(b-s,2H)	
	$\underline{H}_e+H_f$ 4.12(s,10H)	
3	$\underline{H}_a$ 3.90(b-s,1H)	3.02(m,4H,–C=C–C$\underline{H}_2$–Fc)
	$\underline{H}_b$ 4.33(b-s,2H)	5.75(m,2H,–C=C$\underline{H}$–CH$_2$–)
	$\underline{H}_c$ 3.85(b-s,1H)	6.18(b-s,2H,–C$\underline{H}$=C–CH$_2$–)
	$\underline{H}_d$ 4.08(b-s,2H)	
	$\underline{H}_e+\underline{H}_f$ 4.02(s,10H)	
4	$\underline{H}_a$ 3.86(s,2H)	1.46—1.75(m,4H,–C–C$\underline{H}_2$–C–)
	H_b 4.06(s,4H)	2.22(m,8H,–C$\underline{H}_2$–Fc)
	$\underline{H}_e$ 4.00(s,10H)	
11	$\underline{H}_a$ 5.00(s,1H)	6.80(d,2H,J=16 Hz,–C=C$\underline{H}$–CO–)
	$\underline{H}_b$ 4.89(b-s,2H)	7.69(d,2H,J=16 Hz,Fc–C$\underline{H}$=C–CO–)
	$H_c+H_{c'}$ 4.18(b-s,15H)	
	$\underline{H}_{a'}$ 4.84(t,4H)	
	$\underline{H}_{b'}$ 4.57(t,4H)	
12	$\underline{H}_a$ 4.05(b-s,1H)	2.56—2.93(m,8H,–C$\underline{H}_2$C$\underline{H}_2$CO–)
	$\underline{H}_b$ 4.07(s,1H)	
	$\underline{H}_{a'}$ 4.71(t,4H)	
	$\underline{H}_{b'}$ 4.43(t,4H)	
	$\underline{H}_c+H_{c'}$ 4.10(s,15H)	
13	$\underline{H}_a+\underline{H}_b$ 4.15(m,3H)	3.01(d-d,4H,–C$\underline{H}_2$–)
	$\underline{H}_{a'}+\underline{H}_{b'}$ 4.07(m,8H)	6.01(m,2H,–C=C$\underline{H}$–C–)
	$\underline{H}_c+H_{c'}$ 4.00(s,15H)	7.31(d,2H,–C$\underline{H}$=C–C–)
14	$\underline{H}_c$ 5.56(s,1H)	6.81(d,2H,J=16 Hz,–C=C$\underline{H}$–CO–)
	$\underline{H}_d$ 5.19(s,2H)	7.78(d,2H,J=16 Hz,–C$\underline{H}$=C–CO–)
	$\underline{H}_f+\underline{H}_{c'}$ 4.18(s,15H)	
	$H_{a'}$ 4.64(t,4H)	
	$\underline{H}_{b'}$ 4.51(t,4H)	
15	$\underline{H}_c$ 5.03(s,1H)	2.64—2.93(m,8H,–C$\underline{H}_2$C$\underline{H}_2$CO–)
	$\underline{H}_d$ 5.00(s,2H)	
	$\underline{H}_f+\underline{H}_{c'}$ 4.11(s,15H)	
	$\underline{H}_{a'}+\underline{H}_{b'}$ 4.07(s,8H)	
16	$\underline{H}_c+\underline{H}_d$ 4.07(s,3H)	3.01(d-d),4H,–C$\underline{H}_2$–)
	$\underline{H}_f+\underline{H}_d$ 4.00(s,15H)	5.98(m,2H,–C=C$\underline{H}$–C–)
	$\underline{H}_{a'}$ 4.17(m,4H)	7.28(d,2H,–C$\underline{H}$=C–C–)
	$H_{b'}$ 4.12(m,4H)	
17	$\underline{H}_a+\underline{H}_b$ 4.08(m,3H)	1.66(m,4H,–C–C$\underline{H}_2$–C–)
	$\underline{H}_c+\underline{H}_{a'}+\underline{H}_{b'}$ 4.02(b-s,13H)	2.20—2.34(m,8H,Fc–C$\underline{H}_2$–)
	$\underline{H}_{c'}$ 3.96(s,10H)	

shifts for H_a and H_c protons of the cyclopentadienyl rings are found respectively at 0.70 and 1.17 ppm upfield relative to those (H_a and H_c) of the reference compounds, 1,3-bis(2-ferrocenylcarbonylvinyl)ferrocene (**11**) and 1,3-bis(3-ferrocenylacryloyl)ferrocene (**14**). These upfield shifts are expected due to the position of protons (H_a and H_c in **1**) relative to the shielding cone of the nearby cyclopentadienyl ring. On the other hand, the shifts of H_b (Δ, 0.06 ppm) and H_d (Δ, −0.25 ppm) in **1** are negligible, compared with those (H_b and H_d) in **11** or **14**. The smaller upfield shift of the H_b and H_d relative to the H_a and H_c protons is consistent with the *anti* structure for **1** (see Fig. 1). Figure 2 shows the electronic spectra of **1**, **11**, and **14**. In the spectrum of ferrocene itself, the long wavelength bands at 325 and 440 nm can be assigned with some certainty to (d-d)type transitions within the ligand field formalism.[14] The electronic spectrum of **1** is consistent with a cyclophane structure and exhibits three broadened maxima at λ_{max}(dioxane) 308, 422, and 504 nm. Similar to the

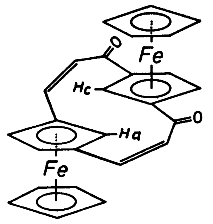


Fig. 1. Conformation of [3.3](1,3)-ferrocenophane (**1**).

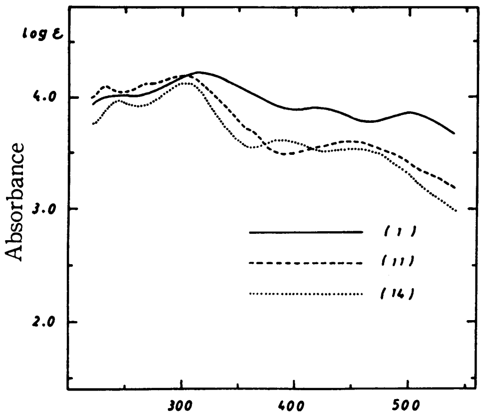


Fig. 2. Electronic spectra of **1**, **11**, and **14** in dioxane.

electronic spectra of other cyclophanes there are observed a general broadening of all bands in the spectrum and hyperchromic and bathochromic shifts of the long wavelength band relative to **11** or **14**. This is probably due to some transannular interaction between the two ferrocene moieties.

The structure of **2** can be assigned to *anti*-conformation by a comparison of its NMR data with those of the reference compounds: 1,3-Bis(2-ferrocenylcarbonylethyl)ferrocene (**12**) and 1,3-bis(3-ferrocenylpropionyl)ferrocene (**15**). Similar to the case of **1**, the upfield shifts of H_b (Δ, -0.01 ppm) and H_d protons (Δ, 0.07 ppm) in **2**, compared with those in **12** and **15**, are explained by the *anti*-structure, in which the internal cyclopentadienyl protons (H_a and H_c) lie in close proximity to the π-cloud (and the cone of shielding) of the opposed cyclopentadienyl moiety. Furthermore, the NMR spectrum of **2** contained H_a at δ 3.87 ppm, indicating an upfield shift (0.53 ppm) with respect to the diene **1** which is characteristic of such pairs of cyclophanes (with saturated and unsaturated bridges).[14] The IR spectrum of **2** also exhibits bands due to the carbonyl group (1670 cm^{-1}) and the 1,3-disubstituted ferrocene rings (920 and 905 cm^{-1}), and the mass spectrum shows two prominent peaks: one due to a molecular ion (m/e 480) and the other to a doubly-charged ion (m/e 240). In the electronic spectra of **2**, compared with those of **12** and **15**, all the absorption curves exhibit common features of cyclophane, *viz.*, broarding, bathochromic, and hyperchromic shifts, caused by the transannular electronic interaction (see Fig. 3).

In compound **3**, the IR spectrum reveals the presence of *cis* olefinic bonds (800 cm^{-1}) and 1,3-disubstituted ferrocene ring (925 and 905 cm^{-1}), and in the mass spectrum, the most intense peaks is that due to the parent ion of m/e 448; the remaining two prominent peaks are m/e 224 and 56, corresponding to a doubly-charged ion and Fe^+. In the NMR spectrum of **3**, the upfield shifts of H_a (Δ, 0.25 ppm) and H_c protons (Δ, 0.22 ppm) and the downfield shifts of H_b (Δ, -0.18 ppm) and H_d protons (Δ, -0.01 ppm), compared with the corresponding ones in the reference compounds: 1,3-bis(3-ferrocenyl-1-propenyl)ferrocene (**13**) and 1,3-bis(3-ferrocenyl-2-propenyl)ferrocene (**16**), are also explained by the *anti*-structure. The upfield shifts of H_a and H_c protons in **3** are not marked, compared with those of compounds **1** and **2**. In Fig. 4, however, the electronic absorption curve becomes relatively structureless, with bathochromic shifts and increased intensity of the bands near 340 and 450 nm, compared with those of the reference compounds **13** and **16**. This indicates that the two ferrocene moieties in **3** interact strongly with each other.

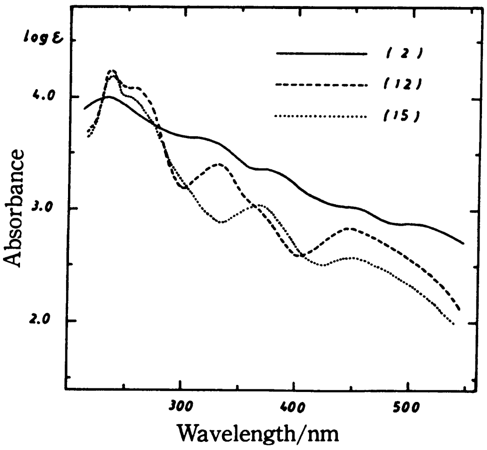


Fig. 3 Electronic spectra of **2**, **12**, and **15** in dioxane.

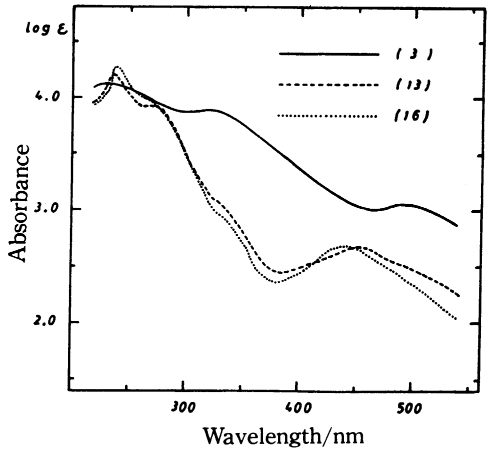


Fig. 4. Electronic spectra of **3**, **13**, and **16** in dioxane.

The spectrum of **4** exhibits bands at 925 and 905 cm^{-1}, which are characteristic of the 1,3-disubstituted ferrocene ring. By comparison with the NMR spectrum of the reference compound, 1,3-bis(3-ferrocenylpropyl)-ferrocene (**17**), the upfield shifts of H_a protons (Δ, 0.22 ppm) and the small upfield shifts of H_b protons (Δ, 0.02 ppm) are consistent with the *anti*-structure for **4**, similarly to the cases of **1**, **2**, and **3**. The electronic spectrum of **4** (Fig. 5) exhibits two broadened maxima in the visible region, at λ_{max}(dioxane) 320 and 488 nm, and there is observed a general broadening and a bathochromic shift (48 nm) of the long wavelength band relative to **17**. These are probably due to some transannular π-electronic interactions between the two ferrocene moieties.

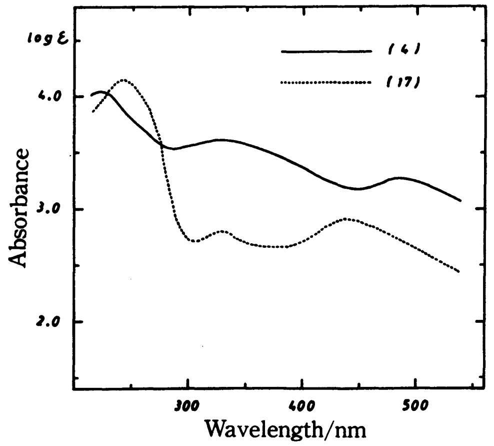


Fig. 5. Electronic spectra of **4** and **17** in dioxane.

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