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Synthesis of Naphthalenoferrocenophanes

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Several naphthalenoferrocenophanes, in which the two cyclopentadienyl rings are linked by two naphthalene rings, were synthesized *via* intramolecular reductive coupling of the corresponding formyl compounds with a low valent titanium reagent. Their structures are deduced from IR, NMR, and UV spectra. Transannular π-electronic interaction between the two naphthalene rings is discussed on the basis of electronic spectra.

Recently a wide variety of cyclophanes with stacked aromatic nuclei have widely been studied as pertinent model compounds for π-electronic interactions.[1] From this point of view, we have previously reported of a synthesis of several ferrocenophanes containing aromatic nuclei: benzene[2] and biphenyl.[3] If one or two benzene rings are replaced by naphthalene ring, which has a larger molecular surface and a lower ionization potential than benzene, it is expected that such ferrocenophanes will show stronger transannular interactions. In this report, as a part of our studies on the metallocenophane chemistry, we describe of synthesis and properties of naphthalenoferrocenophanes **1a**—**d**, in which the two cyclopentadienyl rings are linked by one or two naphthalene rings.

Results and Discussion

Synthesis. Previous successful use of a reductive coupling reaction on appropriate carbonyl compounds for synthesis of [2.2.2] paracycloferrocenophanes[2] and biphenyloferrocenophanes[3] promoted us to attempt the synthesis of **1a**—**d** by this method. In connection with the synthesis of **1a**—**d**, it was desirable to synthesize in quantity intermediary compounds: 1,1′-bis(5-formyl-1-naphthyl)ferrocene (**2a**), 1,1′-bis(6-formyl-1-naphthyl)ferrocene (**2b**), 1,1′-bis(7-formyl-1-naphthyl)ferrocene (**2c**), and 1-(*p*-formylphenyl)-1′-(4-formyl-1-naphthyl)ferrocene (**2d**). The synthesis of intermediates **2a**—**c** was carried out by Gomberg's arylation of ferrocene with diazonium salts **3a**—**c** derived from 5-amino-naphthoic acid (**4a**), 5-amino-2-naphthoic acid (**4b**), and 8-amino-2-naphthoic acid (**4c**), followed by esterification, reduction with $LiAlH_4$, and oxidation with active MnO_2 in chloroform. On the other hand, the synthesis of the intermediate **2d** was carried out by Gomberg's arylation of (*p*-ethoxycarbonyl)ferrocene (**6**) with diazonium salts derived from 4-ethoxycarbonyl-1-naphthylamine (**7**), followed by reduction with $LiAlH_4$, and oxidation with active MnO_2 in chloroform.

The reductive coupling reactions of dialdehydes **2a**—**c** with low valent titanium reagents ($TiCl_4$–Zn[4]) using the high dilution method led to the formation of unsaturated naphthalenoferrocenophanes, [2](1,5)naphthaleno[0](1,1′)ferroceno[0](1,5)-naphthalenophan-1-ene (**5a**), [2](2,5)naphthaleno-[0](1,1′)ferroceno[0](1,6)naphthalenophan-1-ene (**5b**), and [2](2,8)naphthaleno[0](1,1′)ferroceno[0](1,7)-naphthalenophan-1-ene (**5c**), accompanied by the formation of reduction products of dialdehydes **2a**—**c**, respectively. The catalytic hydrogenation of the unsaturated ferrocenophane **5a**—**c** afforded the saturated naphthalenoferrocenophanes, [2](1,5)-naphthaleno[0](1,1′)ferroceno[0](1,5)naphthalenophane (**1a**), [2](2,5)naphthaleno[0](1,1′)ferroceno[0](1,6)-naphthalenophane (**1b**), and [2](2,8)naphthaleno-[0](1,1′)ferroceno[0](1,7)naphthalenophane (**1c**), respectively. However, the intramolecular reductive coupling of **2d**, for preparing the unsaturated ferrocenophane **5d**, was unsuccessful and led to the formation of reduction products of **9d**. Therefore, the saturated ferrocenophane, [2]paracyclo[0](1,1′)-ferroceno[0](1,4)naphthalenophane (**1d**), was prepared by ring closure of 1-[*p*-(bromomethyl)phenyl]-1′-[4-(bromomethyl)-1-naphthyl]ferrocene (**8**) with butyllithium.

Structures. The structures of the ferrocenophanes **1a**—**d** and **5a**—**d** were determined on the basis of IR, NMR, and mass spectra and elementary analyses. The ^1H NMR and IR spectral data of all the ferrocenophanes and the reference compounds are summarized in Tables 1 and 2, respectively. For the unsaturated ferrocenophane **5a**, the configuration of the olefinic bond has been confirmed to be cis because the IR spectrum of **5a** exhibits a band at 720 cm^{-1} chracteristic of *cis*-vinylene linkage and because the characteristic C–H out of deformation modes of *trans*-vinylene linkage around 960 cm^{-1} are absent. With the ^1H NMR spectrum of **5a**, it is noteworthy that the downfield shift of vinylene protons(δ=7.56) is observed, as with the case of [2.2.2](1,3,5)cyclophane-1,9,17-triene(vinylene protons, δ=7.37).[5] For both **1a** and **5a**, two possible conformations are considered from their ^1H NMR spectra, syn or skew. In addition, **1a** and **5a** have the same conformation so that **1a** could be synthesized from **5a** by catalytic hydrogenation, in which the

Table 1. ^{1}H NMR spectra of the ferrocenophanes **1a**—**d** and **5a**—**c** and the reference compounds **9a**—**d** (δ from TMS, in $CDCl_3$)

Compound	Aromatic ring protons	Ferrocene ring protons	Other protons
1a	6.57—7.01 (m, 8H, Ha—c, e) 7.42 (m, 2H, Hd) 7.64 (m, 2H, Hf)	4.32 (m, 4H, H_β) 4.56 (m, 4H, H_α)	2.74 (m, 4H, $-CH_2-$)
5a	6.49—6.95 (m, 8H, Ha—c, e) 7.52 (m, 2H, Hd) 7.85 (m, 2H, Hf)	4.39 (m, 4H, H_β) 4.54 (m, 2H, H_α) 4.70 (m, 2H, H_α)	7.56 (s, 2H, $-CH=CH-$)
9a	7.19—7.66 (m, 8H, Ha—c, e) 7.90 (m, 2H, Hd) 8.32 (m, 2H, Hf)	4.38 (m, 4H, H_β) 4.58 (m, 4H, H_α)	2.62 (s, 6H, $-CH_3$)
1b	6.02 (m, 2H, He) 6.64—7.41 (m, 10H, Ha—d, f)	4.27 (m, 2H, $H_{\alpha'}$) 4.40 (m, 4H, H_β) 4.84 (m, 2H, H_α)	3.44 (m, 4H, $-CH_2-$)
5b	6.21 (m, 2H, He) 6.88—7.78 (m, 10H, Ha—d, f)	3.48 (m, 2H, $H_{\alpha'}$) 4.31 (m, 4H, H_β) 4.78 (m, 2H, H_α)	7.28 (s, 2H, $-CH=CH-$)
9b	6.68—7.48 (m, 10H, Ha—e) 7.85 (m, 2H, Hf)	4.27 (t, 4H, H_β) 4.58 (t, 4H, H_α)	2.31 (s, 6H, $-CH_3$)
1c	7.18—7.75 (m, 10H, Ha—e) 7.82 (m, 2H, Hf)	4.36 (m, 4H, H_β) 4.75 (m, 4H, H_α)	3.46 (s, 4H, $-CH_2-$)
5c	7.18—7.68 (m, 10H, Ha—e) 7.78 (m, 2H, Hf)	4.32 (m, 4H, H_β) 4.98 (m, 4H, H_α)	6.49 (s, 2H, $-CH=CH-$)
9c	7.11—7.44 (m, 6H, Ha, b, e) 7.56—7.78 (m, 4H, Hc, d) 8.28 (m, 2H, Hf)	4.38 (m, 4H, H_β) 4.63 (m, 4H, H_α)	2.33 (s, 6H, $-CH_3$)
1d	5.41 (d, J=8 Hz, 1H, Ha′) 6.26 (d, J=8 Hz, 1H, Hb′) 6.52 (d, J=8 Hz, 1H, Ha) 6.89 (d, J=7 Hz, 1H, Hc) 7.00 (d, J=8 Hz, 1H, Hb) 7.21 (d, J=7 Hz, 1H, Hd) 7.41 (m, 2H, Hf+Hg) 7.98 (m, 1H, Hh) 8.25 (m, 1H, He)	4.26 (m, 2H, H_β) 4.36 (m, 2H, H_δ) 4.52 (m, 1H, H_α) 4.68 (m, 1H, H_γ) 4.80 (m, 1H, H_α) 4.92 (m, 1H, $H_{\gamma'}$)	3.13 (m, $-CH_2-+H_{exo}$) 4.00 (m, 1H, H_{endo})
6d	7.06 (d, J=8 Hz, 2H, Ha) 7.30 (m, 2H, Hf+Hg) 7.42 (d, J=7 Hz, 1H, Hc) 7.47 (d, J=8 Hz, 2H, Hb) 7.70 (d, J=7 Hz, 1H, Hd) 8.02 (m, 1H, Hh) 8.49 (m, 1H, He)	4.22 (t, 2H, H_β) 4.30 (t, 2H, H_δ) 4.50 (t, 2H, H_α) 4.61 (t, 2H, H_γ)	2.29 (s, 3H, $-C_6H_4-\mathbf{CH_3}$) 2.69 (s, 3H, $-C_{10}H_6-\mathbf{CH_3}$)

rotation of syn to skew at the 5-position of naphthalene ring is made impossible by bridging. The smaller upfield shift of protons Ha and Hd relative to protons Hb, Hc, He, and Hf in the naphthalene ring would be expected if **5a** had a skew form as with[2.2](1,5)naphthalenophane.$^{6)}$ In the ^{1}H NMR spectra of **5a**, however, all the protons of naphthalene rings appear at higher fields than the corresponding protons of the reference compound, 1,1′-bis(5-methyl-1-naphthyl)ferrocene (**9a**), showing a shielding effect by the opposite naphthalene ring. This phenomenon suggests a *syn*-conformation for both **1a** and **5a** rather than a skewed one (**10**). In **1a** and **5a**, the molecule probably exists in such a conformation that the naphthalene rings approximately parallel to one another and approximately coplanar to the cyclopentadienyl ring. In ferrocene, the distance between the two cyclopentadienyl rings is 3.32 Å,$^{7)}$ while the Van der Waals separation between parallel π-systems is 3.345 Å.$^{8)}$ Thus, in **1a** and **5a**, a substantial repulsive interaction must exist between the two naphthalene rings which are bound together by ethylene or vinylene bridges at both the 5-positions. In the ^{1}H NMR spectra of both **1b** and **5b**, the aromatic protons He and Hf are shifted to higher field by about 0.9 ppm, compared with those of the reference compound, 1,1′-bis(6-methyl-1-naphthyl)ferrocene (**9b**). However, the signals of protons Ha, Hb, Hc, and Hd are observed at nearly the same positions as those of **9b**. These data support

Table 2. IR spectra of ferrocenophane and reference compounds

Compound	KBr, $\tilde{\nu}$/cm^{-1}
1a	3100, 805 (1,1′-disubstituted ferrocene ring), 1600, 1580, 780, 770 (naphthalene ring), 715, and 685 (distorted naphthalene ring).
5a	3100, 805 (1,1′-disubstituted ferrocene ring), 1600, 1580, 785, 775 (naphthalene ring), 1620, 720 (cis -CH=CH-), 710, and 685 (distorted naphthalene ring).
9a	3100, 805 (1,1′-disubstituted ferrocene ring), 1590, and 770 (naphthalene ring).
1b	3100, 805 (1,1′-disubstituted ferrocene ring), 1590, 780, and 765 (naphthalene ring).
5b	3100, 805 (1,1′-disubstituted ferrocene ring), 1600, 1580, 775 (naphthalene ring), 1625, and 720 (cis -CH=CH-).
9b	3100, 810 (1,1′-disubstituted ferrocene ring), 1590, 785, and 770 (naphthalene ring).
1c	3100, 810 (1,1′-disubstituted ferrocene ring), 1600, and 830 (naphthalene ring).
5c	3100, 810 (1,1′-disubstituted ferrocene ring), 1590, 830 (naphthalene ring), 1620, and 735 (cis -CH=CH-).
9c	3100, 810 (1,1′-disubstituted ferrocene ring), 1600, and 830 (naphthalene ring).
1d	3100, 810 (1,1′-disubstituted ferrocene ring), 1600, 1580, 840, 820, 765 (naphthalene ring+*p*-disubstituted benzene ring), 725, and 695 (distorted aromatic ring).
9d	3100, 800 (1,1′-disubstituted ferrocene ring), 1600, 1580, 820, and 760 (naphthalene ring+*p*-disubstituted benzene ring).

the view that both **1b** and **5b** exist exclusively in the *anti*-conformation rather than in the *syn*-conformation owing to a π-π repulsive instabilization in the latter conformation. Furthermore, in **1b** and **5b**, the cyclopentadienyl protons Hα′ are shifted to higher field by about 0.5 and 1.0 ppm, respectively, compared with those of **9b**. The remarkable upfield shifts of protons Hα′ in **1b** and **5b** are probably due to a diamagnetic shielding effect on the opposed naphthalene ring and clearly indicate the *anti*-conformation rather than the vertically stacked conformation (**1b′**). In the ^{1}H NMR spectra of both **1c** and **5c**, the aromatic proton signals, except for Hf, are observed at nearly the same positions as those of the reference compound, 1,1′-bis(7-methyl-1-naphthyl)-ferrocene (**9c**). On the other hand, the aromatic protons Hf are shifted to higher fields by about 0.45 ppm, compared with those of the reference compound **9b**. These data suggest that, in both **1c** and **5c**, the two naphthalene rings are held not in a face to face conformation but in an *anti*-conformation. On the other hand, the ferrocenophane **1d** shows its signals of the bridge ethylene protons to be roughly divided into two groups of multiplets. Of these, the lower field multiplet is associated with the endo proton of methylenes attached to the condensed aromatic ring for the 1,4-bridged systems. The downfield shift of the proton is explained in terms of the large deshielding effect of the neighboring condensed aromatic ring. The phenyl protons show upfield shifts compared with those of the reference compound, 1-(*p*-tolyl)-1′-(4-methyl-1-naphthyl)-ferrocene (**9d**), and may reasonably be assigned by considering the diamagnetic anisotropy of the opposite aromatic ring. In the ferrocenophane **1d**, the upfield shifts (1.21 and 1.65 ppm) of the phenyl protons Ha′ and Hb′ are drastic as compared with those of protons Ha (0.47 ppm) and Hb (0.54 ppm), suggesting that protons Ha′ and Hb′ are situated above the center of the opposite naphthalene ring. The naphthalene protons Hc and Hd show reasonable upfield shifts. However, protons Hf and Hg show absorptions at a rather lower field and shifts of protons He and Hh are negligible. These data are best accounted for on the basis of the conformation **1d**, in which the benzene and naphthalene rings are approximately parallel to each other and are held face to face in close proximity by the ethylene bridges at both the 4-positions.

Electronic Spectra. Toluene and 1-methylnaphthalene show no absorption in the long wavelength region above 300 nm.[9] Figures 1,2,3, and 4 show the electronic spectra of naphthalenoferrocenophanes

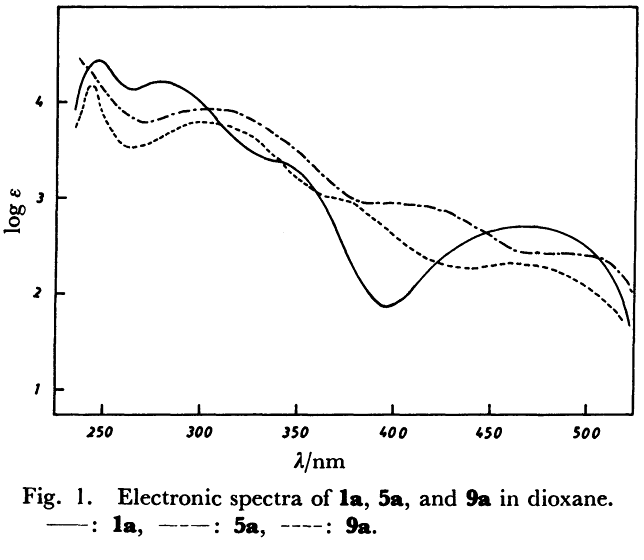


Fig. 1. Electronic spectra of **1a**, **5a**, and **9a** in dioxane.
——: **1a**, ——–: **5a**, ----: **9a**.

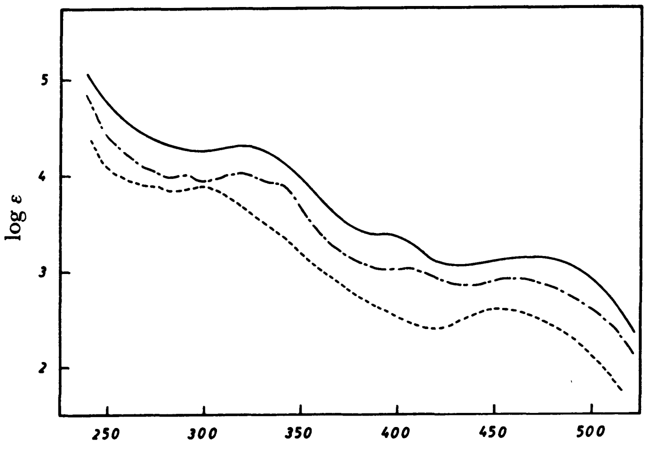


Fig. 2. Electronic spectra of **1b**, **5b**, and **9b** in dioxane. ——: **1b**, —·—: **5b**, ----: **9b**.

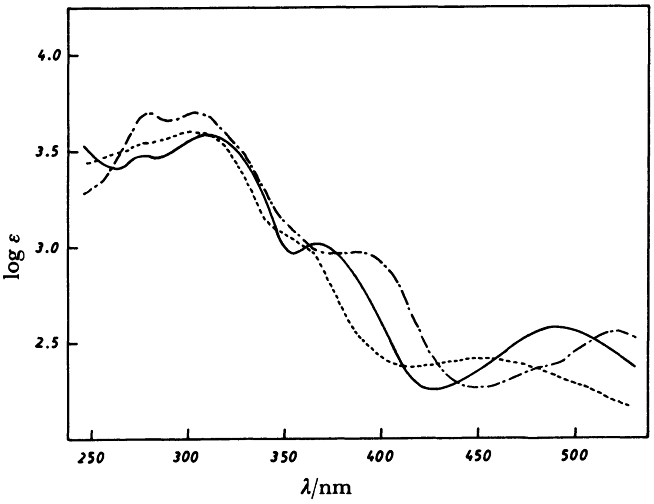


Fig. 3. Electronic spectra of **1c**, **5c**, and **9c** in dioxane. ——: **1c**, —·—: **5c**, ----: **9c**.

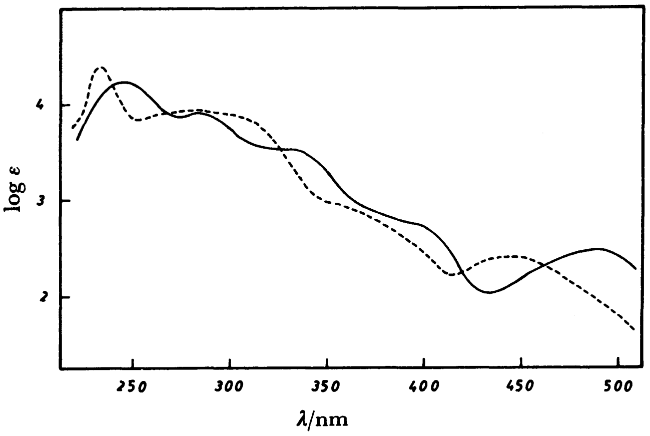
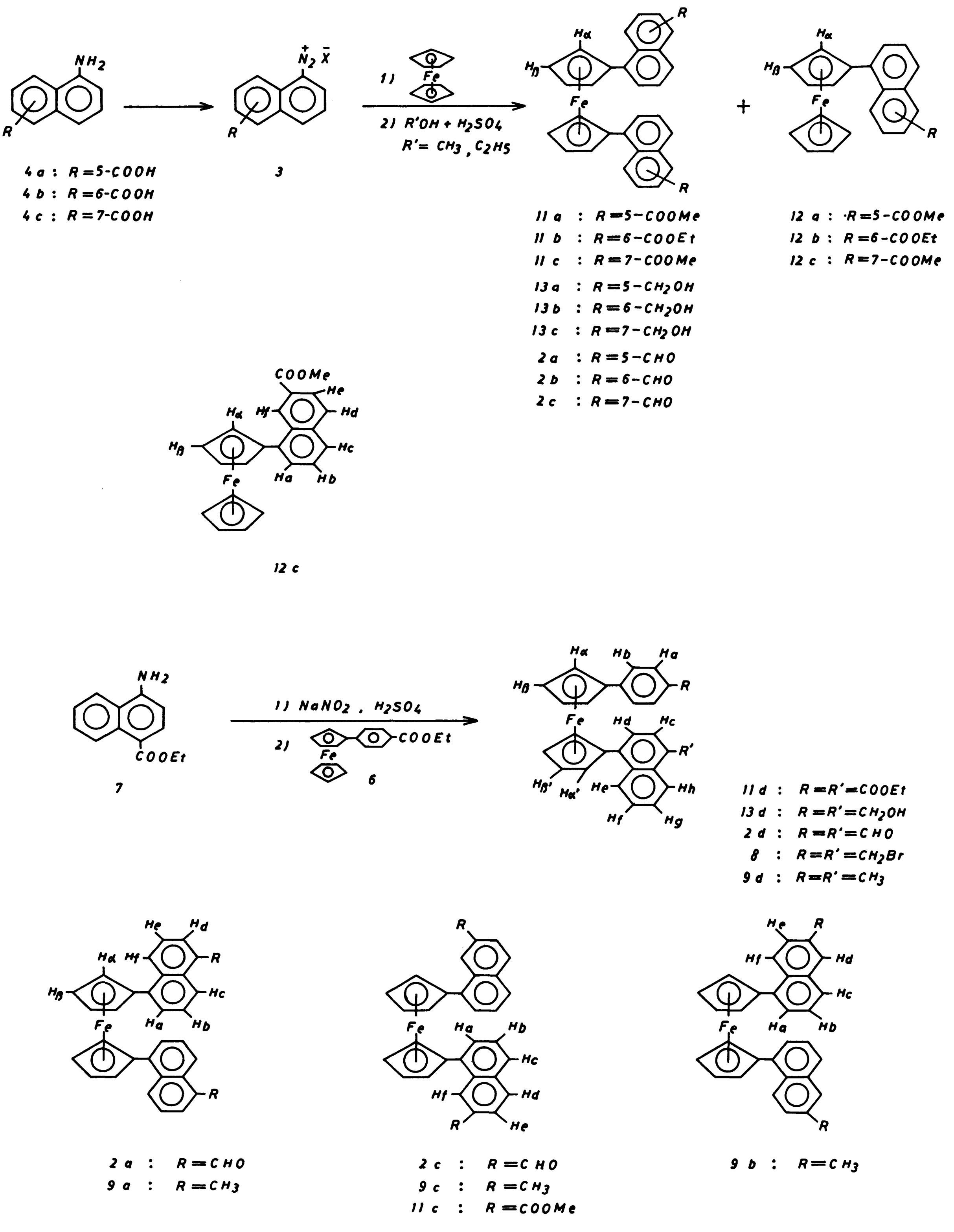


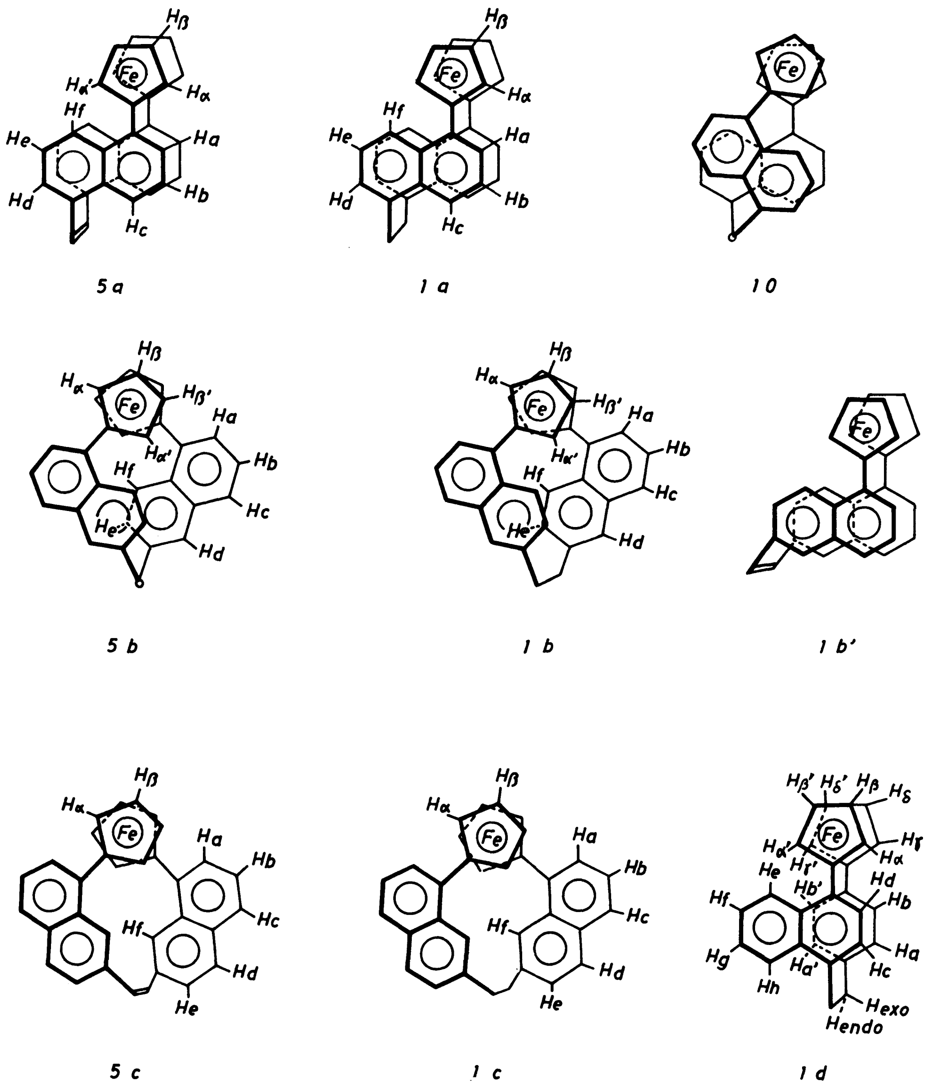
Fig. 4. Electronic spectra of **1d** and **9d** in dioxane. ——: **1d**, ----: **9d**.

1a—**d** and **5a**—**c** together with those of the reference compounds **9a**—**d**. The electronic spectra of **1a**, **1b**, **5a**, and **5b** show somewhat bathochromic and hyperchromic shifts in the range 220—320 nm, compared with those of the reference compounds **9a** and **9b**, respectively. This may be due to transannular π-electronic interactions between the two naphthalene chromophores in **1a**, **1b**, **5a**, and **5b**. Furthermore, in **1a**, **1b**, **5a**, and **5b**, the bathochromic shifts of the unsaturated series are more significant than those of the saturated series, suggesting that the two naphthalene rings in the unsaturated ferrocenophanes **5a** and **5b** are closer in orientation to vertical stacking than those of the saturated ferrocenophanes **1a** and **1b**. On the other hand, in the 220—320 nm region, the electronic spectra of **1c** and **5c** are similar to the spectra of the reference compound 9c. This phenomenon and the small shielding effects on all the aromatic protons but proton Hf in the NMR spectra, indicate that the interactions between the two naphthalene rings in **1c** and **5c** are relatively weak. The electronic spectrum of ferrocene has two main absorptions at 325 and 440 nm. It has been shown that both the position and intensity of the 440 nm band are particularly sensitive to ferrocene ring-tilt distortion.[10] In the 330—500 nm region, the electronic spectra of the ferrocenophanes **1a**—**d** and **5a**—**c** show an increased intensity and a bathochromic shift to longer wavelengths, compared with those of the reference compounds **9a**—**d** bearing an untilted ferrocene ring. These phenomena suggest that, in all ferrocenophanes, ferrocene ring-tilt distortion will occur. In compounds **1a**, **5a**, and **1d**, the ferrocene ring-tilt distortion may be caused by the strong π-π repulsions between the two faced naphthalene rings or between the benzene and naphthalene rings. In **1b** and **5b**, the planes of the cyclopentadienyl and naphthalene rings probably have a nonplanar orientation owing to the short length of the side chain which is bridging at the 6-position of the naphthalene ring, and the ferrocene ring-tilt distortions may be caused by the repulsions between the B rings in the two naphthalene rings. On the other hand, in compounds **1c** and **5c**, the interactions between the two naphthalene rings are relatively weak, and accordingly the ferrocene ring-tilt distortions may be caused by the strain due to the short length of the side chain which is bridging at the 7-position in naphthalene rings.

Infrared Spectra. IR spectra of the [2.2]paracyclophane system are known to reveal obvious features. One is the increase in the intensity of a band in the 1580—1600 cm^{-1} region, which is related to the increased double-bond character due to the distortion of the benzene ring.[11] The other is the appearance of a strong new maximum in the 710 cm^{-1} region. Longone and Warren[11b] reported that the strong maxima at 725 cm^{-1} in [2.2]paracyclophane and 710 cm^{-1} in 4,7,12,15-tetramethyl[2.2]paracyclophane might be characteristic bands associated with the distorted benzene ring in the [2.2]paracyclophane system. We also reported of the same phenomenon in the [2]paracyclo[0](1,1′)ferroceno[0]paracyclophane bearing the distorted benzene ring.[2] The naphthalenophanes **1a**, **5a**, and **1d** exhibit characteristic bands



Scheme 1.



Scheme 2.

around 700 cm^{-1}, whereas the reference compounds **9a** and **9d** bearing strain-free aromatic rings exhibit no bands in this region. This phenomenon may be due to the distortion of the aromatic rings in **1a**, **5a**, and **1d**. On the other hand, near 700 cm^{-1}, the IR spectra of **1b**, **5b**, **1c**, and **5c** are similar to those of the open-chain models **9b** and **9c**. This may be due to the lack of distortion of the aromatic rings in **1b**, **5b**, **1c**, and **5c** (see Table 2).

Experimental

Materials and Measurements. All melting points are uncorrected. 5-Amino-1-naphthoic acid (**4a**),[12] 5-amino-2-naphthoic acid (**4b**),[13] 8-amino-2-naphthoic acid (**4c**),[13] (*p*-ethoxycarbonylphenyl)ferrocene (**6**),[14] and 4-ethoxycarbonyl-1-naphthylamine (**7**)[15] were prepared by the methods described in the literature. IR, ^{1}H NMR, mass, and electronic spectra were recorded with Hitachi 260-10, Hitachi R-22, Hitachi RMU-6M, and Hitachi 200-10 spectrometers, respectively.

*1,1'-Bis[5-(methoxycarbonyl)-1-naphthyl]ferrocene (**11a**).* The amine **4a** (9.36 g, 50 mmol) was diazotized in 10% sulfuric acid at 0—5 °C with sodium nitrite (3.45 g, 50 mmol). After the diazotization the solution was added dropwise to a solution of ferrocene (3.72 g, 20 mmol) in acetic acid (150 cm^3) under a nitrogen atmosphere. The resulting dark brown solution was stirred overnight at room temperature and then poured into water. The precipitates formed were filtered off, washed with water, dried at room temperature, and then esterified in refluxing methanol (300 cm^3) containing 5 cm^3 of concd H_2SO_4 under a nitrogen atmosphere. After removal of the solvents *in vacuo*, the residue was extracted with chloroform and the chloroform extracts were washed with 5% sodium hydrogencarbonate solution and brine, dried over anhyd $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography (silica gel).

The first elution with benzene gave the starting material ferrocene (1.12 g, 30%), mp 173 °C.

The second elution with benzene afforded 1.17 g (15.9%

yield based on ferrocene) of (5-methoxycarbonyl-1-naphthyl)-ferrocene (**12a**): orange yellow crystal; mp 114—115 °C; IR (KBr) 3100, 1100, 1000, 805 (monosubstituted ferrocene ring), 1710 (-COOCH$_3$), 1600, 1500, 810, 790, and 770 cm^{-1} (naphthalene ring); ^{1}H NMR (CDCl$_3$) δ=3.96 (s, 3H, -C$\underline{H}_3$), 4.13 (s, 5H, $\underline{H}_\gamma$), 4.36 (t, 2H, $\underline{H}_\beta$), 4.57 (t, 2H, $\underline{H}_\alpha$), and 7.31—8.80 (m, 6H, Ar-$\underline{H}$). Found: C, 71.13; H, 4.81; M$^+$, 370. Calcd for C$_{22}$H$_{18}$FeO$_2$: C, 71.27; H, 4.89; M, 370.

The third elution with benzene gave 1.58 g (14.2% yield based on ferrocene) of reddish crystals, mp 156—158 °C, which were determined to be 1,1′-bis(5-methoxycarbonyl-1-naphthyl)ferrocene (**11a**): IR (KBr) 3100,805 (1,1′-disubstituted ferrocene ring), 1720 (-COOCH$_3$), 1600, 1500, 820, 790, and 770 cm^{-1} (naphthalene ring); ^{1}H NMR (CDCl$_3$) δ=3.91 (s, 6H, -C$\underline{H}_3$), 4.42 (m, 4H, $\underline{H}_\beta$), 4.58 (m, 4H, $\underline{H}_\alpha$), and 7.32—8.50 (m, 12H, Ar-$\underline{H}$). Found: C, 73.53; H, 4.56; M$^+$, 554. Calcd for C$_{34}$H$_{26}$FeO$_4$: C, 73.65; H, 4.72; M, 554.

*1,1′-Bis[6-(ethoxycarbonyl)-1-naphthyl]ferrocene (**11b**).* Gomberg's arylation of ferrocene with diazonium salts derived from **4b**, followed by esterification in ethanol, was carried out in the same way as described above, and (6-ethoxycarbonyl-1-naphthyl)ferrocene (**12b**) (orange yellow crystals, mp 98—99 °C) and **11b** (reddish crystals, mp 130—132 °C) were obtained in 14 and 8% yields, respectively.

11b: IR (KBr) 3100, 810 (1,1′-disubstituted ferrocene ring), 1720 (-COOEt), 1600, 1500, 780, and 770 cm^{-1} (naphthalene ring); ^{1}H NMR (CDCl$_3$) δ=1.38 (t, 6H, -C$\underline{H}_3$), 4.40 (t, 4H, $\underline{H}_\beta$), 4.44 (q, 4H, -C$\underline{H}_2$-), 4.61 (t, 4H, $\underline{H}_\alpha$), and 7.20—8.49 (m, 12H, naphthalene ring protons). Found: C, 74.39; H, 5.26; M$^+$, 582. Calcd for C$_{36}$ H$_{30}$ FeO$_4$: C, 74.23; H, 5.19; M, 582.

12b: IR (KBr) 3100, 1100, 1000, 805 (monosubstituted ferrocene ring), 1720 (-COOEt), 1600, 1500, 780, and 770 cm^{-1} (naphthalene ring); ^{1}H NMR (CDCl$_3$) δ=1.38 (t, 3H, -C$\underline{H}_3$), 4.12 (s, 5H, $\underline{H}_\gamma$), 4.37 (t, 2H, $\underline{H}_\beta$), 4.41 (q, 2H, -C$\underline{H}_2$), 4.60 (t, 2H, $\underline{H}_\alpha$), and 7.34—8.60 (m, 6H, naphthalene ring protons). Found: C, 71.75; H, 5.17; M$^+$, 384. Calcd for C$_{23}$H$_{20}$FeO$_2$: C, 71.88; H, 5.24; M, 384.

*1,1′-Bis[7-(methoxycarbonyl)-1-naphthyl]ferrocene (**11c**).* Gomberg's arylation of ferrocene with diazonium salts derived from **4c**, followed by esterification in methanol, was carried out in the same way as described for **11a**, and (7-methoxycarbonyl-1-naphthyl)ferrocene (**12c**) (orange yellow crystals, mp 90—92 °C) and **11c** (reddish orange crystals, mp 152—153 °C) were obtained in 12.5 and 6.2% yields, respectively.

11c: IR (KBr) 3100, 800 (1,1′-disubstituted ferrocene ring), 1720 (-COOCH$_3$), 1600, 1500, 835, and 740 cm^{-1} (naphthalene ring); ^{1}H NMR (CDCl$_3$) δ=3.96 (s, 6H, -C$\underline{H}_3$), 4.50 (t, 4H, $\underline{H}_\beta$), 4.90 (t, 4H, $\underline{H}_\alpha$), 7.11—7.93 (m, 10H, $\underline{H}_{a-e}$), and 9.57 (br-s, 2H $\underline{H}_f$). Found: C, 73.51; H, 4.58; M$^+$, 554. Calcd for C$_{34}$H$_{26}$FeO$_4$: C, 73.65; H, 4.72; M, 554.

12c: IR (KBr) 3100, 1100, 1000, 805 (monosubstituted ferrocene ring), 1720 (-COOCH$_3$), 1600, 1500, 835, and 740 cm^{-1} (naphthalene ring); ^{1}H NMR (CDCl$_3$) δ=3.92 (s, 3H, -C$\underline{H}_3$), 4.19(s, 5H, $\underline{H}_\gamma$), 4.42 (t, 2H, $\underline{H}_\beta$), 4.66 (t, 2H, $\underline{H}_\alpha$), 7.29—8.11 (m, 5H, $\underline{H}_{a-e}$), and 8.56 (br-s, 1H, $\underline{H}_f$). Found: C, 71.22; H, 4.74; M$^+$, 370. Calcd for C$_{22}$H$_{18}$FeO$_2$: C, 71.37; H, 4.90; M, 370.

*1-(p-Ethoxycarbonylphenyl)-1′-(4-ethoxycarbonyl-1-naphthyl)-ferrocene (**11d**).* The amine **7** (3.01 g, 14 mmol) was diazotized in 5% sulfuric acid (830 cm^3) at 0—5 °C with sodium nitrite (1.0 g, 14.4 mmol). After the diazotization the diazotized salt solution was added rapidly to a solution of compound **6** (4.01 g, 12 mmol) in acetic acid (600 cm^3) in an atmosphere of nitrogen. The resulting dark brown solution was stirred overnight at room temperature and then poured into water. The reaction mixture was extracted with chloroform and the chloroform extracts were washed with 5% aqueous sodium hydrogencarbonate solution and with brine, dried over anhyd MgSO$_4$, filtered, and concentrated. The residue was purified by column chromatography with silica gel.

The first elution with hexane–diethyl ether (4:1) afforded the starting material **6** (0.78 g, 19.4%), mp 87—88 °C.

The second elution with hexane–diethyl ether (4:1) afforded 0.98 g (15.3% yield based on **6**) of **11d** in reddish oil: IR (CHCl$_3$) 3100, 805 (1,1′-disubstituted ferrocene ring), 1720 (-COOEt), 1600, 1500, 780, and 730 cm^{-1} (aromatic ring); 1H NMR (CDCl$_3$) δ=1.37 (t, 3H, -C$\underline{H}_3$), 1.44 (t, 3H, -C$\underline{H}_3$), 4.31(t, 2H, $\underline{H}_\beta$), 4.38(t, 2H, $\underline{H}_{\beta'}$), 4.41(m, 4H, -C$\underline{H}_2$-), 4.57 (t, 2H, $\underline{H}_\alpha$), 4.69 (t, 2H, $\underline{H}_{\alpha'}$), and 7.34—8.94 (m, 10H, aromatic protons). Found: C, 72.06; H, 5.18; M$^+$, 532. Calcd for C$_{32}$H$_{28}$FeO$_4$: C, 72.18; H, 5.30; M, 532.

*1,1′-Bis[5-(hydroxymethyl)-1-naphthyl]ferrocene (**13a**).* To a suspension of LiAlH$_4$ (0.42 g, 11 mmol) in anhyd diethyl ether (50 cm^3) was added dropwise a solution of **11a** (2.21 g 4 mmol) in dry benzene (50 cm^3) at room temperature over 1 h, and the reaction mixture was then heated under reflux for an additional 4 h. After the mixture was decomposed with a amall amount of cold water, the organic layer was washed successively with 5% hydrochloric acid, 5% sodium hydrogencarbonate solution, and brine, and dried over anhyd MgSO$_4$. After removal of the solvents, the residue was purified by column chromatography on silica gel (benzene–diethyl ether, 1:1) to afford **13a** as orange yellow crystals, which were recrystallized from ethanol, mp 168—169 °C, in 72% yield: IR (KBr) 3100, 805 (1,1′-disubstituted ferrocene ring), 3400, 1020 (-OH), 1600, 820, 780, and 770 cm^{-1} (naphthalene ring); ^{1}H NMR (CDCl$_3$) δ=1.72 (br-s, 2H, -O$\underline{H}$), 4.42 (t, 4H, $\underline{H}_\beta$), 4.62 (t, 4H, $\underline{H}_\alpha$), 5.08 (s, 4H, -C$\underline{H}_2$-), and 7.12—8.48 (m, 12H, naphthalene ring protons). Found: C, 77.28; H, 5.21; M$^+$, 498. Calcd for C$_{32}$H$_{26}$FeO$_2$: C, 77.12; H, 5.26; M, 498.

*1,1′-Bis[6-(hydroxymethyl)-1-naphthyl]ferrocene (**13b**).* A reduction of **11b** with LiAlH$_4$ was carried out in the same way as described above, and **13b** (orange yellow crystals, mp 163—164 °C) was obtained in 66% yield: IR (KBr) 3100, 805 (1,1′-disubstituted ferrocene ring), 3350, 1020 (-OH), 1590, 825, 780, and 760 cm^{-1} (naphthalene ring); ^{1}H NMR (CDCl$_3$) δ=1.72 (br-s 2H, -O$\underline{H}$), 4.42 (t, 4H, $\underline{H}_\beta$), 4.58 (t, 4H, $\underline{H}_\alpha$), 4.74 (s, 4H, -C$\underline{H}_2$-), and 6.91—8.39 (m, 12H, naphthalene ring protons). Found: C, 77.21; H, 5.35; M$^+$ 498. Calcd for C$_{32}$H$_{26}$FeO$_2$: C, 77.12; H, 5.26; M, 498.

*1,1′-Bis[7-(hydroxymethyl)-1-naphthyl]ferrocene (**13c**).* A reduction of **11c** with LiAlH$_4$ was carried out in the same way as described for the ruduction of **11a** with LiAlH$_4$ and the product **13c** (orange yellow crystals, mp 136—137 °C) was obtained in 51% yield: IR (KBr) 3100, 810 (1,1′-disubstituted ferrocene ring), 3450, 1020 (-OH), 1590, 835, and 740 cm^{-1} (naphthalene ring); ^{1}H NMR (CDCl$_3$) δ=1.80 (br-s, 2H, -O$\underline{H}$), 4.39 (t, 4H, $\underline{H}_\beta$), 4.66 (s, 4H, -C$\underline{H}_2$-), 4.78 (t, 4H, $\underline{H}_\alpha$), and 7.11—8.70 (m, 12H, naphthalene ring protons). Found: C, 69.96; H, 5.13; M$^+$, 498. Calcd for

$C_{32}H_{26}FeO_2$: C, 77.11; H, 5.25; M, 498.

1-[p-(Hydroxymethyl)phenyl]-1′-[4-(hydroxymethyl)-1-naphthyl]ferrocene (13d). A reduction of **11d** with $LiAlH_4$ was carried out in the same way as described for the reduction of **11a** with $LiAlH_4$, and the product **13d** (orange yellow crystals, mp 60—62 °C) was obtained in 90% yield: IR (KBr) 3100,805 (1,1′-disubstited ferrocene ring), 3300, 1000 (–OH), 1600, 820, and 760 cm^{-1} (naphthalene ring); ^{1}H NMR ($CDCl_3$) δ=1.89 (s, 2H, -O$\underline{H}$), 4.30 (t, 2H, $\underline{H}_\beta$), 4.34 (t, 2H, $\underline{H}_{\beta'}$), 4.57 (m, 4H, –C$\underline{H}_2$–+$\underline{H}_\alpha$), 4.63 (t, 2H, $\underline{H}_\alpha$), 5.09 (s, 2H, -C$\underline{H}_2$–), 7.06 (d, J=8 Hz, 2H, $\underline{H}_a$), and 7.23—8.48 (m, 8H, $\underline{H}_b$+naphthalene ring protons). Found: C, 76.46; H, 5.50; M$^+$, 448. Calcd for $C_{28}H_{24}FeO_2$: C, 76.37; H, 5.40; M, 448.

*1,1′-Bis(5-formyl-1-naphthyl)ferrocene (**2a**).* At room temperature, active manganese(IV) oxide (49 g) was added to a solution of **13a** (2.59 g, 5.2 mmol) in chloroform (150 cm^3) and the mixture was stirred in the dark for 12 h. After filtration to remove MnO_2, the reddish chloroform solution was evaporated to dryness and the residue was chromatographed by elution of chloroform on silica gel to afford reddish crystals **2a** (1.80 g, 70% yield): mp 175—176 °C; IR (KBr) 3100, 805 (1,1′-disubstituted ferrocene ring), 1680 (–CHO), 1590, 780, and 770 cm^{-1} (naphthalene ring); ^{1}H NMR ($CDCl_3$) δ=4.50 (t, 4H, $\underline{H}_\beta$), 4.59 (t, 4H, $\underline{H}_\alpha$), 7.24—8.73 (m, 10H, $\underline{H}$a, b, d, e, f), 9.14 (d, 2H, $\underline{H}$c), and 10.33 (s, 2H, –C$\underline{H}$O). Found: C, 77.86; H, 4.55; M$^+$, 494. Calcd for $C_{32}H_{22}FeO_2$: C, 77.75; H, 4.49; M, 494.

*1,1′-Bis(6-formyl-1-naphthyl)ferrocene (**2b**).* An oxidation of **13b** with active manganese(IV) oxide was carried out in the same way as described above, and reddish crystals **2b** (mp 191—193 °C) were obtained in 81% yield: IR (KBr) 3100, 800 (1,1′-disubstituted ferrocene ring), 1690 (–CHO), 1590, 830, and 790 cm^{-1} (naphthalene ring); ^{1}H NMR ($CDCl_3$) δ=4.46 (t, 4H, $\underline{H}_\beta$), 4.63 (t, 4H, $\underline{H}_\alpha$), 7.20—8.52 (m, 12H, naphthalene ring protons), and 10.02 (s, 2H, –C$\underline{H}$O). Found: C, 77.91; H, 4.58; M$^+$, 494. Calcd for $C_{32}H_{22}FeO_2$: C, 77.74; H, 4.48; M, 494.

*1,1′-Bis(7-formyl-1-naphthyl)ferrocene (**2c**).* An oxidation of **13c** with active manganese(IV) oxide was carried out in the same way as described for the oxidation of **13a** with active MnO_2, and reddish crystals **2c** (mp 204—205 °C) were obtained in 66% yield: IR (KBr) 3100, 800 (1,1′-disubstituted ferrocene ring), 1690 (–CHO), 1590, 830, and 760 cm^{-1} (naphthalene ring); ^{1}H NMR ($CDCl_3$) δ=4.51 (t, 4H, $\underline{H}_\beta$), 4.78 (t, 4H, $\underline{H}_\alpha$), 7.13—7.74 (m, 10H, $\underline{H}$a, b, c, d, e), 9.02 (s, 2H, $\underline{H}$f), and 9.81 (s, 2H, –C$\underline{H}$O). Found: C, 77.62; H, 4.35; M$^+$, 494. Calcd for $C_{32}H_{22}FeO_2$: C, 77.75; H, 4.49; M, 494.

*1-(p-Formylphenryl)-1′-(4-formyl-1-naphthyl)ferrocene (**2d**).* An oxidation of **13d** with active manganese(IV) oxide was carried out in the same way as described for the oxidation of **13d** with active MnO_2, and reddish crystals **2d** (mp 168—170 °C) were obtained in 64% yield: IR (KBr) 3100, 805 (1,1′-disubstituted ferrocene ring), 1690 (–CHO), 1590, 830, 760, and 730 cm^{-1} (aromatic ring); ^{1}H NMR ($CDCl_3$) δ=4.46 (t, 2H, $\underline{H}_\beta$), 4.50 (t, 2H, $\underline{H}_{\beta'}$), 4.72 (T, 2H, $\underline{H}_\alpha$), 4.76 (t, 2H, $\underline{H}_{\alpha'}$), 7.23—8.92 (m, 10H, aromatic ring), 10.06 (s, 1H, –C$\underline{H}$O), and 10.21 (s, 1H, –C$\underline{H}$O). Found: C, 75.81; H, 4.59; M$^+$, 444. Calcd for $C_{28}H_{20}FeO_2$: C, 75.69; H, 4.54; M, 444.

1-[p-(Bromomethyl)phenyl]-1′-[4-(bromomethyl)-1-naphthyl]ferrocene (8). In an atmosphere of nitrogen, chlorotrimethylsilane (8.47 g, 78 mmol) was added to a solution of anhyd lithium bromide (5.82 g, 67 mmol) in dry acetonitrile (210 cm) with stirring at room temperature. The alcohol **13d** (8.06 g, 18 mmol) was then added and the reaction mixture was heated under reflux for 0.5 h. After cooling, the mixture was extracted with diethyl ether (500 cm^3), and the extract was washed successively with water, 5% sodium hydrogencarbonate solution, and brine, and dried over anhyd $MgSO_4$. After removal of the solvents, the residue was purified by column chromatography on silica gel (dichloromethane) to afford **8** in reddish oil in 56% yield: IR ($CHCl_3$) 3100, 805 (1,1′-disubstituted ferrocene ring), 1600, 1500, 840, and 760 cm^{-1} (aromatic ring); ^{1}H NMR ($CDCl_3$) δ=4.28 (t, 2H, $\underline{H}_\beta$), 4.31 (t, 2H, $\underline{H}_\beta$), 4.38 (s, 4H, –C$\underline{H}_2$–), 4.48 (t, 2H, $\underline{H}_\alpha$), 4.54 (t, 2H, $\underline{H}_{\alpha'}$), 7.18 (d, 2H, $\underline{H}$a), and 7.24—8.54 (m, 8H, $\underline{H}$b+naphthalene ring protons). Found: C, 58.46; H, 3.77; M$^+$ 574. Calcd for $C_{28}H_{22}Br_2Fe$: C, 58.57; H, 3.86; M, 574.

*Intramolecular Reductive Coupling of **2a** with $TiCl_4$–Zn.* In an atmosphere of nitrogen, zinc dust (1.17 g, 18 mmol) was added in small portions to a stirred solution of $TiCl_4$ (1.80 g, 9 mmol) in dry THF (50 cm^3) at 0—5 °C. After the mixture was refluxed for 1.5 h, a solution of **2a** (0.89 g, 1.8 mmol) and dry pyridine (0.10 g) in dry THF (200 cm^3) was added over 14 h under reflux and the mixture was allowed to reflux for an additional 10 h and then quenched by addition of 50 cm^3 of saturated potassium carbonate solution. The mixture was stirred for 0.5 h, diluted with chloroform, and filtered through Celite. The chloroform layers were washed with brine and dried over anhyd $MgSO_4$. After removal of the solvents, the residue was dissolved in hexane and chromatographed on silica gel.

The first fraction, eluted with hexane-ether (5:1) and subjected to evaporation and recrystallization from ethanol, gave yellow orange crystals (0.09 g, 10.7%), mp 135—137 °C, which were determined to be 1,1′-bis(5-methyl-1-naphthyl)ferrocene(**9a**). Found: C, 82.56; H, 5.69; M$^+$, 466. Calcd for $C_{32}H_{26}Fe$: C, 82.41; H, 5.62; M, 466.

The second fraction, eluted with hexane–diethyl ether (5:1) and subjected to evaporation and recrystallization from benzene, gave reddish crystals (0.15 g, 18.0%), mp 241—242 °C, which were determined to be *syn*-[0](1,5)-naphthaleno[2](1,5)naphthaleno[0](1,1′)ferrocenophan-9-ene (**5a**). Found: C, 83.21; H, 4.96; M$^+$, 462. Calcd for $C_{32}H_{22}Fe$: C, 83.13; H, 4.80; M, 462.

The third fraction, eluted with chloroform and subjected to evaporation and recrystallization from ethanol, gave orange yellow crystals (0.21 g, 23% yield), mp 168—169 °C, which were identified with 1,1′-bis(5-hydroxymethyl-1-naphthyl)ferrocene (**4a**) by comparison of IR, NMR, and mass spectra and a mixed-melting-point value with those of the authentic sample **4a**.

*Reaction of **2b** with $TiCl_4$–Zn.* The reductive coupling of **2b** with $TiCl_4$–Zn was carried out in the same way as has been described above, and the products were separated by chromatography on silica gel.

The first fraction, eluted with benzene-hexane (1:1) and subjected to evaporation and recrystallization from ethanol, gave orange yellow crystals, mp 175—177 °C (8% yield), which were determined to be 1,1′-bis(6-methyl-1-naphthyl)ferrocene (**9b**). Found: C, 82.55; H, 5.72; M$^+$, 466. Calcd for $C_{32}H_{26}Fe$: C, 82.41; H, 5.62; M, 466.

The second fraction, eluted with benzene and subjected to evaporation and recrystallization from ethanol, gave deep reddish crystals, mp 224—226 °C (37.5% yield), which were determined to be *anti*-[0](1,6)naphthaleno[2](2,5)naphthaleno[0](1,1′)ferrocenophan-9-ene (**5b**). Found: C, 83.25; H, 4.93; M+, 462. Calcd for $C_{32}H_{22}Fe$: C, 83.13; H, 4.80; M, 462.

The third fraction, eluted with chloroform and subjected to evaporation and recrystallization from ethanol, gave yellowish crystals (mp 163—164 °C, 26% yield), which were identified with **4b** by comparison of IR, NMR, and mass spectra and a mixed-melting-point value with those of the authentic sample **4b**.

Reaction of **2c** *with* $TiCl_4$*-Zn.* The reductive coupling of **2c** with $TiCl_4$-Zn was carried out in the same way as has been described for the reductive coupling of **2a** with $TiCl_4$-Zn, and the products were separated by chromatography on silica gel. The first fraction, eluted with hexane and subjected to recrystallization from ethanol, gave orange yellow crystals (mp 60—62 °C, 4.3% yield), which were determined to be 1,1′-bis(7-methyl-1-naphthyl)ferrocene (**9c**). Found: C, 82.28; H, 5.56; M+ 466. Calcd for $C_{32}H_{26}Fe$: C, 82.40; H, 5.61; M, 466.

The second fraction, eluted with hexane–THF (5:1) and subjected to evaporation and recrystallization from ethanol, gave deep reddish crystals (mp 246—247 °C, 20% yield), which were determined to be *anti*-[0](1,7)-naphthaleno[2](2,8)naphthaleno[0](1,1′)ferrocenophan-9-ene (**5c**). Found: C, 83.02; H, 4.67; M+, 462. Calcd for $C_{32}H_{22}Fe$: C, 83.13; H, 4.80; M, 462.

The third fraction, eluted with chloroform and subjected to evaporation and recrystallization from ethanol, gave yellowish crystals (mp 136—137 °C, 14% yield), which were identified with **4c** by comparison of IR, NMR, and mass spectra and a mixed-melting-point value with those of the authentic sample **4c**.

Reaction of **2d** *with* $TiCl_4$*-Zn.* The reaction of **2d** with $TiCl_4$-Zn was carried out in the same way described for the reductive coupling of **2a** with $TiCl_4$-Zn, and the products were separated by chromatography on silica gel. The first fraction, eluted with hexane and subjected to evaporation and recrystallization from ethanol, gave reddish orange crystals (mp 51—52 °C, 32% yield), which were determined to be 1-(*p*-tolyl)-1′-(4-methyl-1-naphthyl)-ferrocene(**9d**). Found: C, 80.85; H, 5.94; M+, 416. Calcd for $C_{28}H_{24}Fe$: C, 80.78; H, 5.81; M, 416.

Catalytic Hydrogenation of **5a**. In a mixture of dioxane (100 cm^3) and ethanol (100 cm^3), compound **5a** (0.50 g) was hydrogenated with PtO_2 (0.01 g) at room temperature under the ordinary pressure. The reaction mixture was filtered to remove the catalyst and the filtrate was evaporated to dryness *in vacuo*. The residue was chromatographed on silica gel with hexane to give reddish orange crystals (mp 182—184 °C, 82% yield), which were determined to be [0](1,5)naphthaleno[2](1,5)naphthaleno-[0](1,1′)ferrocenophane (**1a**). Found: C, 82.90; H, 5.35; M+, 464. Calcd for $C_{32}H_{24}Fe$: C, 82.77; H, 5.21; M, 464.

Catalytic Hydrogenation of **5b**. The catalytic hydrogenation of **5b** was carried out in the same way as described above, and the product was purified by column chromatography on silica gel with benzene to give reddish orange crystals (mp 233—235 °C (dec), 80% yield), which were determined to be [0](1,6)naphthaleno[2](2,5)-naphthaleno[0](1,1′)ferrocenophane(**1b**). Found: C, 82.90; H, 5.35; M+, 464. Calcd for $C_{32}H_{24}Fe$: C, 82.77; H, 5.21; M, 464.

Catalytic Hydrogenation of **5c**. The catalytic hydrogenation of **5c** was carried out in the same way as described for the catalytic hydrogenation of **5a**, and the product was purified by column chromatography on silica gel with benzene to give reddish crystals (mp 237—238 °C, 85% yield), which were determined to be [0](1,7)-naphthaleno[2](2,8)naphthaleno[0](1,1′)ferrocenophane(**1c**). Found: C, 82.70; H, 5.08 ; M+ 464. Calcd for $C_{32}H_{24}Fe$: C, 82.76; H, 5.20; M, 464.

Intramolecular Coupling of **8** *with Butyllithium.* In an atmosphere of nitrogen, a 15% solution of butyllithium in hexane (16 cm^3) was added dropwise to a solution of **8** (4.50 g, 7.84 mmol) in dry THF (450 cm^3) at −50 °C, and stirred at the same temperature for 2 h and then at 0 °C for 4 h. After a successive addition of water (50 cm^3) and 1 M hydrochloric acid (70 cm^3) (1 M=1 mol dm^{-3}), the mixture was extracted with chloroform. The chloroform extracts were washed successively with 1 M hydrochloric acid, brine, 5% sodium hydrogencarbonate solution, and brine, and dried over anhyd $MgSO_4$. After removal of the solvents, the residue was chromatographed on silica gel with hexane–diethyl ether (4:1) to give reddish crystals (mp 220 °C (dec), 20.5% yield), which were determined to be [2]paracyclo[0](1,1′)ferroceno[0](1,4)naphthalenophane(**1d**). Found: C, 81.25; H, 5.46; M+, 414. Calcd for $C_{28}H_{22}Fe$: C, 81.17; H, 5.35; M, 414.

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