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A SPECIFIC CHANGE OF THE ELECTRONIC AND ^{13}C NMR SPECTRA AND REDOX POTENTIALS IN 1,*n*-DITHIA[*n*]FERROCENOPHANES. A NOVEL INTERACTION BETWEEN THE SULPHUR ATOM AND THE FERROCENE NUCLEUS

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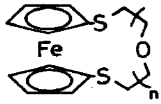
Summary

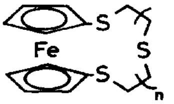
Of the 1,*n*-dithia[*n*]ferrocenophanes prepared from disodium 1,1′-ferrocenedithiolate and polymethylene dibromides, the ferrocenophane with $n = 7$ showed the largest shift in the electronic and ^{13}C NMR spectra and the largest decrease of the redox potential. This can be interpreted by a new type of stereoelectronic interaction between the sulfur atom and the ferrocene nucleus.

Many ferrocenophanes bridged by a polymethylene chain or by other similar chains between two cyclopentadienyl rings have been reported [1]. A few examples of ferrocenophanes in which the bridge-heteroatoms are attached directly to the cyclopentadienyl rings are also known [2–6]. Recently, some polyoxadithia[*n*]ferrocenophanes (**1**) [7] and polythia[*n*]ferrocenophanes (**2**) [8] have been prepared and 4-oxa-1,7-dithia[7]ferrocenophane and 1,4,7-trithia[7]ferrocenophane have been observed to show an abnormal spectral behavior in contrast to the other corresponding homologs. We now report the syntheses and the spectral properties of 1,*n*-dithia[*n*]ferrocenophanes (**3**), which are a simple system suitable for investigating the interaction between the sulfur atom and the ferrocene nucleus.

Disodium 1,1′-ferrocenedithiolate, prepared from 1,1′-ferrocenedithiol [9] and aqueous sodium hydroxide, reacted with polymethylene dibromides in ethanol under a high dilution condition to afford 1,*n*-dithia[*n*]ferrocenophanes (**3a**–**3f**). The results



(1)



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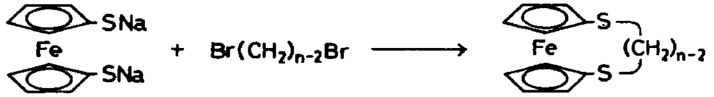

(3) a. n=4
b. n=5
c. n=6
d. n=7
e. n=8
f. n=10

are summarized in Table 1, along with the electronic spectral data. All the new compounds prepared showed satisfactory elemental analyses and mass and ^{1}H NMR spectral data for the assigned structures. For example, the molecular formula of **3d** was deduced to be $C_{15}H_{18}FeS_2$ by elemental analysis and mass spectroscopy ($M^+ = 318$). The ^{1}H NMR spectrum of **3d** showed the signals for the ferrocene ring protons as two broad triplets at δ 4.16 (4H) and 4.12 (4H) (J 1.8 Hz), while the signals of the methylene protons next to the sulfur atoms and the other methylene protons appeared as a triplet at δ 3.01 (t, 4H, J 6.3 Hz) and a multiplet at δ 1.90 (m, 6H), respectively. The extremely low yield of **3c**–**3d** is probably due to ring strain, similar to that observed in medium-sized ring compounds.

The electronic and ^{1}H and ^{13}C NMR spectral data of **3** are summarized in Tables 1 and 2, respectively. With increasing bridged chain length of **3**, the electronic spectral absorption band near 440 nm, corresponding to the *d*–*d* transition [10], gradually shifted to a longer wavelength region, exhibited the maximum bathochromic shift ($\Delta\lambda \sim 30$ nm) in **3d**, and then shifted to the original wavelength region. The absorption coefficient of this band showed the same trend (Table 1). Of the ^{13}C NMR spectra of **3**, that of **3d** (Table 2) showed the largest downfield shift of the bridge-head carbon and the largest upfield shift of the other cyclopentadienyl ring

TABLE 1

YIELDS, MELTING POINTS AND UV-VIS SPECTRAL DATA FOR 3

Compound	Yield (%)	M.p. (°C)	UV-VIS(CH_3CN)	
			λ_{max}(nm)	ϵ
3a [a]	37	138–139	436	152
3b	32	88–89	464	297
3c	3.5	116–118	467	309
3d	2.9	104–106	468	332
3e	1.8	61.5–63	454	237
3f	16	63–64	446	215

[a] Ref. 8.

carbons. A similar trend was also observed in the electronic and ^{13}C NMR spectra of 4-oxa-1,7-dithia[7]ferrocenophane [7] and 1,4,7-trithia[7]ferrocenophane [8], but not in 1,4,7-trioxa[7]ferrocenophane [6a] or 4-thia-1,7-dioxa[7]ferrocenophanes [6b] carrying an oxygen atom connected directly to the cyclopentadienyl ring.

In order to explain the spectral behavior mentioned above, two effects are considered. One is the tilting effect of two cyclopentadienyl rings in the ferrocene nucleus. It is well-known that the tilting of two cyclopentadienyl rings of ferrocene induces a bathochromic shift of the absorption at 440 nm and a large signal splitting of the α- and β-protons of the cyclopentadienyl ring [11]. In the present series of compound, the cyclopentadienyl rings may be tilted away from each other because of the repulsion of the lone pairs of the bridge sulfur atoms, since the sum of the Van der Waals radii of a sulfur atom (3.70 Å) is larger than the inter-ring distance (3.32 Å) [12]. As shown in Table 2, the difference between the α- and β-protons of the cyclopentadienyl rings, however, is rather smaller in **3c** and **3d** than in **3a** and **3b**. Therefore, an electronic interaction between the sulfur atom and the ferrocene nucleus remains to explain the phenomena observed in ferrocenophanes **3**. On considering the Dreiding molecular model of **3**, the bond between the bridge-head carbon of the ferrocene nucleus and the sulfur atom rotates little by little with the change in the bridge length, and the lone pair orbital of the sulfur atom seems to be perpendicular to the cyclopentadienyl ring in **3d**, resulting in a certain kind of stereoelectronic interaction between them.

An apparent analogy has been found between the chemical shift change of the benzene ring carbons caused by a substituent (substituent chemical shift, SCS) and that of the ferrocene ring carbons caused by the same substituents [13]. For example, the SCS values of the methoxyl group in methoxyferrocene are very similar to the corresponding ones in anisole (Table 3), suggesting the presence of an electron-donating $p\pi$–$p\pi$ interaction between the cyclopentadienyl ring and the oxygen atom,

TABLE 2

^{1}H AND ^{13}C NMR SPECTRAL DATA FOR DITHIA[*n*]FERROCENOPHANES 3

Compound	^{1}H NMR (90 MHz, $CDCl_3$, δ(ppm), J(Hz))	^{13}C NMR (22.5 MHz, $CDCl_3$, δ(ppm))
3a	4.38(t, 4H, J 1.9, H_α), 4.16(t, 4H, J 1.9, H_β), 3.28(s, 4H, CH_2)	85.0(C(1)), 69.9(C(2)), 68.7(C(3)), 31.1(CH_2)
3b	4.32(t, 4H, J 1.8, H_α), 4.12(t, 4H, J 1.8, H_β), 3.38(t, 4H, J 5.6, CH_2S), 1.98(m, 2H, CH_2)	89.2(C(1)), 69.9(C(2)), 67.7(C(3)), 33.4, 30.2(CH_2)
3c	4.13(s, 8H, $H_\alpha + H_\beta$), 3.04(t, 4H, J 5.6, CH_2S), 1.90(m, 4H, CH_2)	90.3(C(1)), 68.3(C(2)), 66.9(C(3)), 32.5, 25.7(CH_2)
3d	4.16(bt, 4H, H_α), 4.12(bt, 4H, H_β), 3.01(t, 4H, J 6.3, CH_2S), 1.90(m, 6H, CH_2)	91.8(C(1)), 67.2(C(2)), 66.4(C(3)), 32.8, 26.9 23.8(CH_2)
3e	4.12(t, 4H, J 1.8, H_α), 4.08(t, 4H, J 1.8, H_β), 3.00(t, 4H, J 6.4, CH_2S), 1.70(m, 8H, CH_2)	89.1(C(1)) 70.4(C(2)), 67.2(C(3)), 33.8, 26.4 23.9(CH_2)
3f	4.16(t, 4H, J 1.2, H_α), 4.15(t, 4H, J 1.2, H_β), 2.88(t, 4H, J 7.2, CH_2S) 1.50(m, 12H, CH_2)	86.7(C(1)), 72.0(C(2)), 68.1(C(3), 35.6, 27.4 26.2, 26.0(CH_2)

TABLE 3

SUBSTITUENT CHEMICAL SHIFTS (SCS) OF THE METHOXYL AND METHYLTHIO GROUPS (ppm)

Compound	C(1)	C(2)	C(3)	C(4)
Methoxyferrocene [a]	59.6	−13.0	−6.2	
Anisole [a]	31.4	−14.4	1.0	−7.7
Methylthioferrocene	16.2	3.4	0.5	
Thioanisole [b]	9.9	−2.0	0.1	−3.7

[a] Ref. 13. [b] Calculated from the data of ref. 20.

just like in anisole. Nevertheless, the absorption band corresponding to the *d–d* transition appeared at the same value of 440 nm as that of ferrocene itself [14], which seems to suggest that the *pπ–pπ* interaction exerts no influence on the HOMO level of ferrocene. On the other hand, as shown in Table 3, the SCS values of the methylthio group in thioanisole and those in methylthioferrocene are quite different from each other, i.e. the former are negative (−2.0 and −3.7) but the latter are positive (3.4 and 0.5), which means that the methylthio group is electron-donating in the benzene system but electron-attracting in the ferrocene system. Such an electronic effect of the methylthio group for the benzene ring in thioanisole has been confirmed by molecular orbital calculation [15] and photoelectron spectroscopy [16]. The electron-donating *pπ–pπ* interaction (**A** in Fig. 1) using the 3*p*-orbital of the sulfur atom in methylthioferrocene is considerably weak compared with that in thioanisole, while the electron-withdrawing *pπ–dπ* interaction (**B** in Fig. 1) between the molecular orbital of the cyclopentadienyl ring and the unoccupied *d*-orbital of the sulfur atom seems to play an important role in methylthioferrocene. This is probably because the electron density of the cyclopentadienyl ring in ferrocene is higher than that of benzene [17] and therefore the π-electron can easily move into

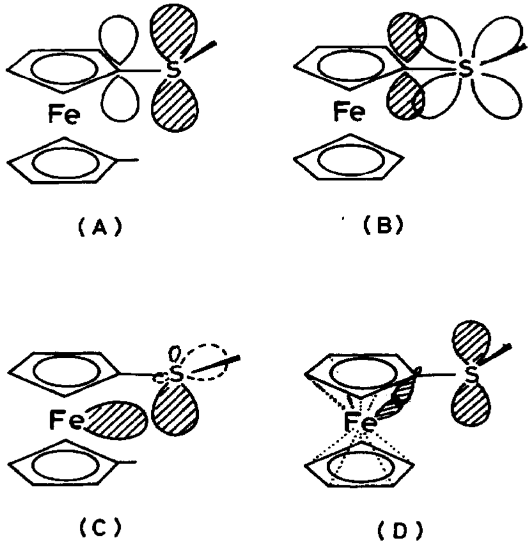

Fig. 1. Various interactions between a ferrocene nucleus and a sulfur atom.

TABLE 4

REDOX POTENTIALS OF 3

Compound	3a	3b	3c	3d	3e	3f
$E^{\ominus}$ (V)	0.27	0.16	0.08	−0.04	0.08	0.17

the sulfur atom of the methylthio group. However, the electron-attracting $p\pi$–$d\pi$ interaction does not explain the remarkable upfield shift of the C(2) and C(3) signals in the ^{13}C NMR spectrum of **3d**, and it is impossible for the $p\pi$–$d\pi$ interaction of no directing character to cause a stereoelectronic effect. Therefore, the $p\pi$–$p\pi$ and the $p\pi$–$d\pi$ interactions would play only a trivial role in the dithioferrocenophanes (**3**).

In order to examine the participation of the ferrocene nucleus HOMO orbital (a_{1g} or preferably e_{2g} *d*-orbital) [18] in the present interaction, the redox potentials ($E^{\ominus}$) of **3** were measured by cyclic voltammetry (Table 4). Of the ferrocenophanes **3**, the largest decrease of the redox potential, indicating a marked HOMO level elevation of the ferrocene nucleus, was observed in **3d**. The HOMO level elevation appears to be caused by the $d\pi$–$p\pi$ interaction between the HOMO orbital (non-bonding *d*-orbital) of the ferrocene nucleus and the occupied *p*-orbital of the sulfur lone pair, since the interaction between two occupied orbitals makes a less stable orbital than the original one. Therefore, some stereoelectric phenomena observed in **3** may be intrinsically due to the $d\pi$–$p\pi$ interaction (**C** in Fig. 1). However, the phenomena described above can also be fascinatingly explained by assuming a σ–π conjugated (**D** in Fig. 1) between the Fe–C σ bond of the ferrocene nucleus and the lone pair of the sulfur atom in **3d** [19]. The upfield shift of the C(2) and C(3) carbon atoms and the downfield shift of the C(1) atom seem to be successfully elucidated by the conjugation effect, and the HOMO level elevation would also be explained by the accumulation of an additional electron on the iron atom in terms of σ–π conjugation. Anyway, the phenomena observed here should be interpreted by the novel type of interaction involving both the sulfur atom and the iron atom of the ferrocene nucleus. At present, it is uncertain which type of interaction functions more practically. The investigation is currently being continued.

Experimental

General data and starting materials

The melting points are uncorrected. Electronic spectra were measured on a Hitachi 340 Spectrometer. Infrared spectra were measured on a JASCO IRA-2 Infrared Spectrometer. ^{1}H and ^{13}C NMR spectra were obtained on a JEOL FX-90Q Spectrometer, TMS being used as the internal standard. Mass spectra were recorded on a Hitachi M-80 Spectrometer.

1,1′-Ferrocenedithiol was prepared according to ref. 9. Polymethylene dibromides, obtained commercially, were used without further purification.

1,n-Dithia[n]ferrocenophanes

Standard procedure. All reactions were carried out under an atmosphere of nitrogen. All solvents were saturated with nitrogen. In a 1000-ml round-bottomed flask equipped with two dropping funnels, a stirring bar, and a nitrogen inlet, 500 ml of ethanol was placed. One dropping funnel was filled with a solution of 1,1′-ferrocenedithiolate prepared from 1,1′-ferrocenedithiol (0.50 g, 2 mmol) and 20% aqueous sodium hydroxide in ethanol (100 ml). The other dropping funnel was filled with a solution of polymethylene dibromide (2 mmol) in ethanol (100 ml). Both solutions were dropped into the flask at the same rate for a period of 5 h under stirring and then the mixture was stirred overnight at room temperature. The precipitate formed was filtered and washed with benzene (20 ml) three times. The combined filtrate and washings were evaporated under reduced pressure. The residue was chromatographed on silica gel, with benzene/hexane (2/1) as eluant. The crystalline compound that separated was recrystallized from cyclohexane to give the following compounds.

1,4-Dithia[4]ferrocenophane (3a). Orange needles (37%), m.p. 138–139°C [8].

1,5-Dithia[5]ferrocenophane (3b). Deep orange needles (32%), m.p. 88–89°C. Found: C, 53,73; H, 4.85. $C_{13}H_{14}FeS_2$ calcd.: C, 53.79; H, 4.87%. MS: m/z 290 (M^+, 100%). IR (KBr): 3100, 2950, 1420, 1395, 1360, 1300, 1260, 1170, 1040, 1030, 900, and 820 cm^{-1}.

1,6-Dithia[6]ferrocenophane (3c). Red needles (3.5%), m.p. 116–118°C. Found: C, 55.29; H, 5.52. $C_{14}H_{16}FeS_2$ calcd.: C, 55.26; H, 5.31%. MS: m/z 304 (M^+, 100%). IR (KBr): 3100, 2930, 1420, 1290, 1160, 1025, 890, and 820 cm^{-1}.

1,7-Dithia[7]ferrocenophane (3d). Deep red cubes (2.9%), m.p. 104–106°C. Found: C, 56.63; H, 5.77. $C_{15}H_{18}FeS_2$ calcd.: C, 56.60; H, 5.71%. MS: m/z 318 (M^+, 100%). IR (KBr): 3100, 2930, 1420, 1380, 1360, 1300, 1160, 1040, 1030, 900, and 820 cm^{-1}.

1,8-Dithia[8]ferrocenophane (3e). Red needles (1.8%), m.p. 61.5–63°C. Found: C, 57.79; H, 6.07. $C_{16}H_{20}FeS_2$ calcd.: C, 57.82; H, 6.08%. MS: m/z 332 (M^+, 100%). IR (KBr): 3100, 2900, 1420, 1380, 1370, 1295, 1275, 1160, 1030, 1020, 895, and 800 cm^{-1}.

1,10-Dithia[10]ferrocenophane (3f). Yellow needles (16%), m.p. 63–64°C. Found: C, 60.24; H, 6.77. $C_{18}H_{24}FeS_2$ calcd.: C, 59.99; H, 6.73%. MS: m/z 346 (M^+, 100%). IR (KBr): 3100, 2950, 1460, 1420, 1390, 1380, 1270, 1160, 1038, 900, and 820 cm^{-1}.

The electronic, ^1H and ^{13}C NMR spectral data of the compounds described above are summarized in Tables 1 and 2.

Measurement of redox potentials

Redox potentials were determined by cyclic voltammetry in a solution of 0.05 *M* tetrabutylammonium perchlorate in acetonitrile (dried over phosphorus pentoxide and distilled from calcium hydride) under nitrogen at 25°C, using a standard three-electrode cell. All potentials were measured vs. a $Ag/AgNO_3$ (0.05 *M*) electrode and the scan rate was 100 mV/s. The voltammograms showed that the redox reaction proceeds reversibly at a platinum electrode.

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