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Conformation and electrochemistry of some *β*-[alkyl-bridged biferrocenyl]-*α*,*β*-unsaturated ketones

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Abstract—The geometrical and conformational isomerism of some *β*-[alkyl-bridged biferrocenyl]-*α*,*β*-unsaturated ketones was discussed on the basis of their IR and ^{1}HNMR spectra. They exist in *s-cis* conformation. The electrochemistry of the title compounds was also studied using cyclic voltammetry. Two distinct consecutive pairs of one-electron reversible redox peaks centered on the two non-equivalent ferrocenyl fragments were observed. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: *β*-[alkyl-bridged biferrocenyl]-*α*,*β*-unsaturated ketones; conformational study; electrochemistry.

INTRODUCTION

Binuclear ferrocene derivatives have aroused many researches in recent years as redox active entities with potential application in fields such as materials for molecular electronics and as biologically active compounds [1–3]. Zanello's group has done some work on alkyl-bridged biferrocene compounds [4, 5]. As a continuation of our previous studies on alkyl-bridged biferrocene [6], we now report here the condensation reactions of alkyl-bridged biferrocenyl formaldehyde with aryl ketones, which afford several *β*-[alkyl-bridged biferrocenyl]-*α*,*β*-unsaturated ketones (Scheme 1). Their conformational and electrochemical properties are discussed as well.

EXPERIMENTAL

2,2-Diferrocenyl propane, 2,2-diferrocenyl butane and the corresponding formaldehyde derivatives were prepared as before [6]. Other chemicals were of analytical grade. The instruments used were the same as those described in the literature [6]. Cyclic voltammetric experiments were performed on a BAS-100B electrochemical analyzer equipped with a three electrode assembly with 0.1 mol/l -*n*-Bu_4NPF_6 as support electrolyte and CH_2Cl_2 as solvent. The working electrode was a platinum disk of 1.5 mm in diameter embedded in a cobalt glass seal and was polished consecutively with polishing alumina and diamond suspensions between runs. The reference electrode was a KCl saturated calomel electrode. A platinum filament was used as an auxiliary electrode. The solutions were saturated and blanketed with N_2 before the first scan. Measurements were made at room temperature.

Synthesis of β-[alkyl-bridged biferrocenyl]-α,β-unsaturated ketones

Taking compound **1** as an example: A solution of 2,2-propinyl-bridged biferrocene formaldehyde (4.84 g, 1.1 mmol) and *p*-aminopheylmethylketone (2.97 g, 2.2 mmol) in 95% EtOH (35 cm^3) was stirred at room temperature for 8–12 h in the presence of KOH (0.168 g, 3 mmol). The reaction mixture was then extracted by CH_2Cl_2, washed to neutral by water

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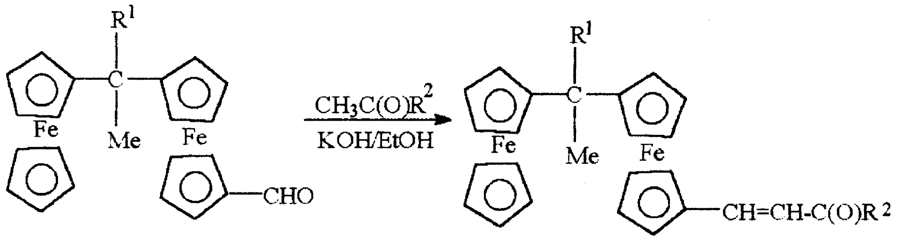


1. $R^1=CH_3$, $R_2=p\text{-}NH_2C_6H_4$; 2. $R^1=CH_3$, $R_2=C_6H_5$; 3. $R^1=C_2H_5$, $R_2=p\text{-}NH_2C_6H_4$
4. $R^1=C_2H_5$, $R_2=C_6H_5$; 5. $R^1=C_2H_5$, $R_2=Fc$.

Scheme 1. The preparation of the title compounds.

and dried with anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the dark red residue was dissolved in a minimum amount of benzene and chromatographed on alumina using C_6H_6 and C_6H_6–Et_2O (2:3) as eluents successively. The resulting product was recrystallized by EtOH–H_2O. **2**–**5** are synthesised analogously. Yield >90%.

RESULTS AND DISCUSSION

All the β-[alkyl-bridged biferrocenyl]-α,β-unsaturated ketones are red solids stable in the air. Their analytical and melting points are listed in Table 1. Their IR, ^{1}H NMR and UV spectra data are listed in Tables 2–4, respectively.

IR spectra

The KBr disk IR spectra of the β-[alkyl-bridged biferrocenyl]-α,β-unsaturated ketones show two strong bands at about 1650 and 1590 cm^{-1}, due to the carbonyl and ethylenic stretching vibration respectively. The two peaks in the region 1000–1077 cm^{-1} were allocated as $\delta_{CH=CH}$ of olefin with a *trans* configuration [7]. While in CCl_4 solution, $\nu_{C=O}$ and $\nu_{C=C}$ bands split, indicating the existence of an equilibrium between *s-cis* and *s-trans* conformation. Their IR spectral data in CCl_4 solution were listed in Table 2.

In compounds **1**–**5**, a conformational equilibrium may occur by the rotation around both C(1′)–C(β) and C(α)–C(CO) bonds. There are two favored coplanar forms, *s-cis* (**1**) and *s-trans* (**2**), as illustrated in Scheme 2. IR spectra is often used to study the equilibrium between *s-cis* and *s-trans* [8, 9]. Investigation of many substituted monoferrocene analogues have been reported [10, 11].

The *s-cis* form is preferred because there may be strong steric repulsion between H(β) and the *ortho*-hydrogens on the phenyl group in *s-trans* conformation. There are sharp carbonyl bands and intensified $\nu_{C=CH}$ bands in the IR spectra of their CCl_4 solutions. On the basis of the empirical rules suggested by Shorter and Hayes *et al.* [8, 9], the existence of the equilibrium and the predominance of the *s-cis* conformation in solution could be inferred. This conclusion is also supported by their ^{1}H NMR spectra.

^{1}H NMR *spectra*

^{1}H NMR spectra of the new compounds are recorded at room temperature. As the cyclopentadienyl protons are in almost the same chemical environment, their signals overlap and form an multiplet. In the ^{1}H NMR spectra of the title compounds, the olefinic protons give a doublet, corresponding to an AB type absorption. The coupling constant is 15 Hz, indicating they exist in *trans*-configuration, in which the biferrocenyl and the carbonyl groups take the opposite

Table 1. Physical properties and elemental analyses data for the title compounds

		Found (calcd) (%)		
Compounds	M.p. (°C)	C	H	N
1	180–181	69.0 (69.0)	5.6 (5.3)	2.9 (2.5)
2	83–84	70.9 (71.2)	5.6 (6.1)	–
3	35–37	69.0 (68.4)	6.3 (5.5)	2.4 (2.4)
4	40–41	71.0 (70.4)	6.2 (6.3)	–
5	82–83	66.7 (67.1)	5.8 (5.8)	–

Table 2. IR Data in CCl_4 solution for the title compounds (cm^{-1})

Compounds	*s-cis*		*s-trans*		
	$\nu_{C=O(1)}$	$\nu_{C=C(1)}$	$\nu_{C=O(2)}$	$\nu_{C=C(2)}$	$\delta_{CH=CH}$
1	1676 (s)	1552 (vs)	1620 (s)	1585 (vs)	1003 (s)
2	1686 (s)	1558 (vs)	1661 (s)	1593 (s)	1002 (vs)
3	1659 (s)	1549 (s)	1651 (vs)	1580 (s)	1014 (vs)
4	1716 (s)	1551 (vs)	1657 (vs)	1596 (s)	
5	1648 (s)	1551 (s)	1610 (vs)	1605 (s)	
FcCH=CHC(O)Bu-*n*[a]	1685	1600	1663	1617	
FcCH=CHC(O)Ph	1661	–	1635	–	
FcCH=CHC(O)C_6H_4-4-Me[a]	1659	–	1636	–	

[a] From Ref.[10].

Table 3. ^1H NMR data for the title compounds (δ, ppm)

Compounds	Bridged alkyl	Cp	Olefinic		Ph	NH_2
			α	β		
1	1.9 (s, 6H)	4.1–4.6 (m, 17H)	7.0 (d, 1H)	7.6 (d, 1H)	7.2 (m,2H), 7.9 (m,2H)	3.8 (s, 2H)
2	1.3–1.6 (m, 6H)	3.9–4.6 (m, 17H)	7.0 (d, 1H)	7.7 (d, 1H)	7.2–7.9 (m, 5H)	
3	0.7 (m, 3H), 1.6 (s, 3H), 1.9 (m, 2H)	4.1–4.6 (m, 17H)	7.0 (d, 1H)	7.6 (d, 1H)	7.2–7.8 (m, 4H)	3.8 (s, 2H)
4	0.8 (m, 3H), 1.6 (s, 3H), 1.9 (m, 2H)	4.1–4.7 (m, 17H)	7.0 (d, 1H)	7.6 (d, 1H)	7.2 (m,2H), 7.8 (m,3H)	
5	0.8 (m, 3H), 1.6 (s, 3H), 1.9 (m, 2H)	4.1–4.4 (m, 26H)	6.8 (d, 1H)	7.6 (d, 1H)		

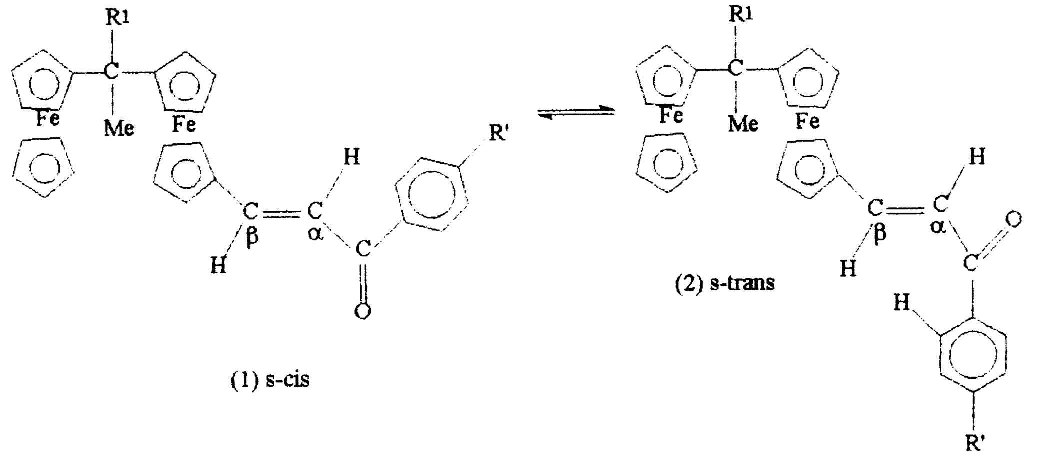
Table 4. UV absorptions of the title compounds and their related precursors (λ_{max}, nm)

Compounds	π–π^*(ε_{max})			d–d(ε_{max})
1	202 (88610)	249 (16750)	367 (32790)	505 (4580)
2	204 (139800)	252 (63830)	322 (44370)	482–541 (7570–7060)
3	202 (86540)	255 (18200)	369 (35760)	504 (6910)
4	204 (145600)	253 (59630)	330 (46280)	488–540 (7580–6140)
5	204 (204600)		332 (113520)	483–505 (4830–2690)
FcC(Me)$_2$FcCHO	204 (130100)		275 (62710)	437–467 (7570–6550)
FcC(Me)(Et)CHO	204 (128900)		282 (59670)	437–472 (7260–6680)

position of the double bond. This is in accordance with their monoferrocenyl analogues reported in the literature [10]. Both H(α) and H(β) signals are shifted upfield. If the *s-trans* rotamer is favored, H(α) is in the shielding area of the carbonyl group and H(β) is closer to the aryl ring, whose anisotropy would increase the shielding about H(β). Their δ values could not be so high. Consequently, the *s-cis* conformation is the favored conformation.

UV spectra

The UV spectra of the title compounds were recorded in 95% EtOH and are summarized in Table 4,



Scheme 2. Conformational equilibrium of the title compounds.

together with some related literature reported ferrocene derivatives. The strongest absorption bands at 322–369 nm can be assigned to the π–π^* transition of the α,β-unsaturated ketone conjugated with the ferrocene nucleus. The d–d transition, appears at a longer wavelength in the region 482–541 nm as a broad peak. The two ferrocenyl groups are indistinguishable by UV spectra. The large bathochromic shifts are ascribed to the extensive conjugation of α,β-unsaturated ketone with the ferrocenyl moiety and the interaction of the nonbonding d-orbital of iron with the substituents on the ferrocenyl group. In addition, such large bathochromic shifts may also involve the bridging alkyl group, which play some role in electronic interactions. This could be inferred from their electrochemical behavior also.

Electrochemical studies

The cyclic voltammetric behaviours of the compounds were studied using CH_2Cl_2 as solvent and 0.1 mol l^{-1} TBAFB(Bu_4NBF_4) as supporting electrolyte. The measurements were carried out at 13°C. The scan rate was 100 mV s^{-1}. The $\overline{E}_{p1}$ [$\overline{E}_{p1} = 1/2(E_{pa1}+E_{pc1})$], $\overline{E}_{p2}$ [$\overline{E}_{p2} = 1/2(E_{pa2}+E_{pc2})$] and their differences $\Delta\overline{E}_p = \overline{E}_{p2} - \overline{E}_{p1}$, together with the K_{con} and Robin–Day classification [12, 13, 14] are given in Table 5. For comparison, ferrocene, 2,2-diferrocenylpropane (DFP), 2,2-diferrocenyl butane (DFB), diferrocenylketone (DFK) [4] and bisferrocene (BF) [4] were also included in the measurements and the results are listed in Table 5. The CV curves of **1** and **5** are illustrated in Figs 1 and 2.

The following could be inferred from Table 5.

1. There are two pairs of redox peaks in the cyclic voltammograms of all the compounds studied.
2. The $\overline{E}_{p1}$ values of the first redox peak are all lower than that of ferrocene. This is attributed to the monosubstituted ferrocenyl group. The bridging alkyl and the other ferrocenyl group exert mainly an electron-donating effect, which makes it easier to be oxidized.

Table 5. Electrochemical characteristics for the oxidation process of the title compounds and related molecules with the Robin–Day classification of the relevant mix-valent species

Compounds	$\overline{E}_{p1}$ (V)	$E_{pc1}-E_{pa1}$ (mV)	$\overline{E}_{p2}$ (V)	$E_{pc2}-E_{pa2}$ (mV)	$\Delta\overline{E}_p$ (V)	K_{con} ($\times 10^4$)	Robin–Day class
1	0.355	89	0.548	75	0.193	0.18	II
2	0.359	103	0.553	71	0.194	0.19	II
3	0.386	72	0.671	78	0.285	6.6	II–III
4	0.389	80	0.676	73	0.281	7.0	II–III
5	0.376	63	0.628	75	0.262	2.7	II–III
DFP	0.355	81	0.551	76	0.196	0.20	II
DFB	0.328	74	0.551	73	0.223	0.59	II
DFK[a]	0.55		0.74		0.19	0.10	II
BF[a]	0.44		0.79		0.35	80	III
Ferrocene	0.44	99					

[a] From Ref.[4].

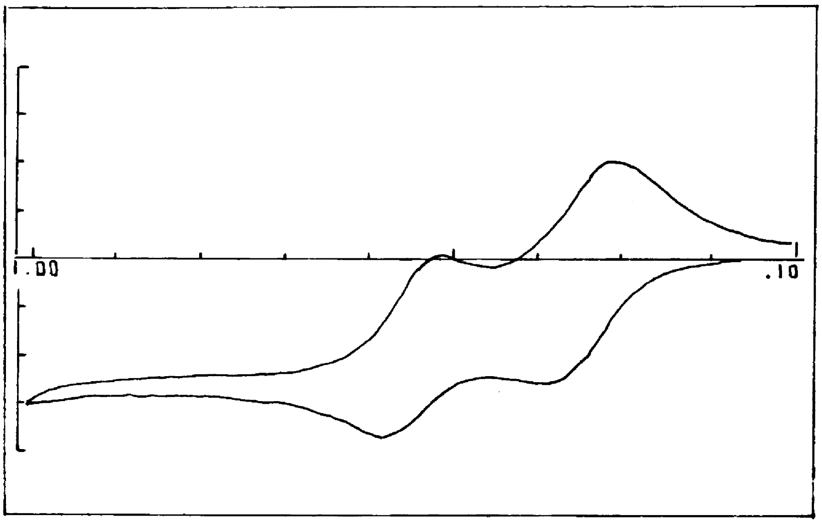


Fig. 1. Cyclic voltammogram obtained in CH_2Cl_2 (0.1 mol/l Bu_4NBF_4) at room temperature at a potential sweep rate of $100\,mV\,s^{-1}$ for **1**. The initial potential was set at 0.100 V and the switching potential was 1.000 V.

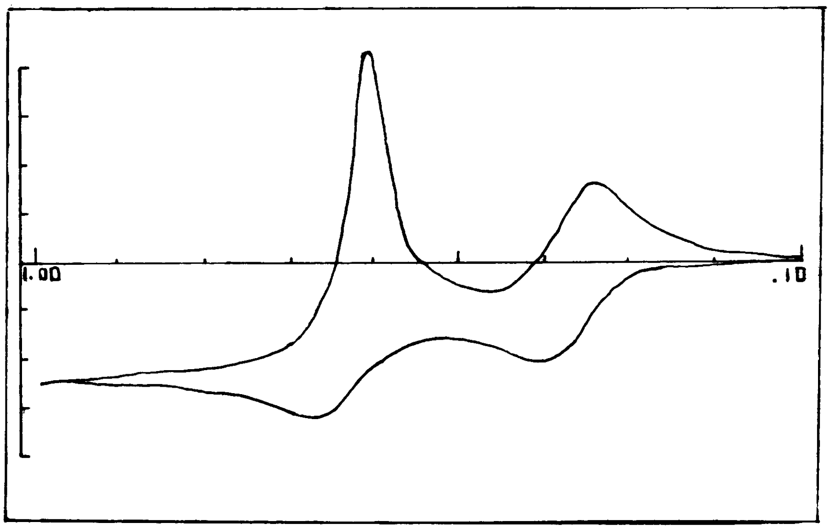


Fig. 2. Cyclic voltammogram obtained in CH_2Cl_2 (0.1 mol/l Bu_4NBF_4) at room temperature at a potential sweep rate of $100\,mV\,s^{-1}$ for **5**. The initial potential was set at 0.100 V and the switching potential was 1.000 V.

3. The $\overline{E_{p2}}$ value of the second redox peak increases in the order 1→2→5→3→4 and $\Delta\overline{E_p}$ increases in the same order, indicating the more deformation from tetrahedral configuration the parent compounds [15] is, the more non-equivalent the two ferrocenyl groups are. The amino group is an electron-donating group and, as a result, **1** and **3** are oxidized slightly easier than **2** and **4**.
4. The $\Delta\overline{E_p}$ values of **1** and **2** reveal that the interaction between the two Fe sub-units is slight, the monocation is a slightly delocalized, weakly interacting class II mix valent species according to Robin–Day classification [4, 12, 13]. While in **3**–**5**, the two subunits interact more, thus causing extensive delocalization. They are classified between the weakly-interacting class II and strong-interacting class III within the Robin–Day classification.
5. For the redox of compounds with two or more ferrocenyl groups, a number of factors affecting the behavior of the ferrocenyl moieties concur. In the occurrence of two waves, through-space and through-bridge interactions and substituent effects coexist. The through-bridge interactions, however, seemed to be predominant. The more deformation

from regular tetrahedral configuration caused by the bridging group, the larger the difference in the electrochemical behaviors of the ferrocenyl groups.

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