

Substituted ferrocenes: Synthesis and correlation of their electronic spectra with structure (LFER)

E. A. KASSAB, M. I. MARZOUK and M. EL-HASHASH

Faculty of Science, Ain Shams University, Cairo, Egypt and Industrial Education College, Ammeria, Cairo, Egypt

(Received 7 November 2001, revised 7 May 2002)

Abstract: Three series of diacylferrocenes (I) and ferrocenylidene acetophenones (II) and monoalkyl ferrocenes (III) were synthesized and their electronic spectra in the visible region were studied. The bands exhibited by compounds (II) show a good correlation between their wave numbers and the Hammett σ constants.

Keywords: substituted ferrocenes, synthesis of, electronic spectra of diacylferrocenes, ferrocenylidene acetophenones, mono- and disubstituted ferrocenes.

INTRODUCTION

The electronic spectra of ferrocene and its simple alkyl derivatives contain two weak bands ($\{\epsilon\} < 100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) at 325 nm and 440 nm which have been assigned¹ to symmetry forbidden electronic transitions of the type N→Q which derive their intensity from vibrational distortion in the molecule. Although both bands contain a great deal of d-orbital character, some involvement of ring molecular orbitals in the "325 nm" transition is indicated by the particular sensitivity of this absorption to substitution in the rings.

There is general agreement, however, that the band at "440 nm" represents a relatively pure (3d–3d) transitions involving energy levels which are highly localized on the metal atom.^{1–3} Also, the electronic spectra of benzoylferrocene and *p*-cyanobenzoylferrocene⁴ exhibit two bands at 365 nm ($\{\epsilon\}$, $1350 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 470 nm ($\{\epsilon\}$, $860 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). Their origin is forbidden electronic transitions of the type N→Q. The purpose of the present article is to report and comment upon the results obtained by measurements of the electronic spectra of 1,1'-diacylated ferrocenes and ferrocenylidene acetophenones. These two series of substituted ferrocene are appropriate for this study since the substituent groups: (1) ensure that the pertinent electronic spectra will appear in the visible region; (2) in diacylated series, the substituted groups are enough from the ferrocenoyl moiety to ensure that no steric interaction occurs.

RESULTS AND DISCUSSION

The absorption spectra of a series of diacylated ferrocenes were measured in hexane and the results are shown in Table I.

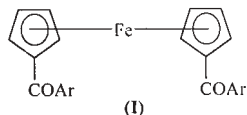
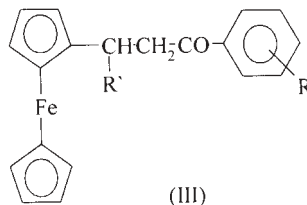
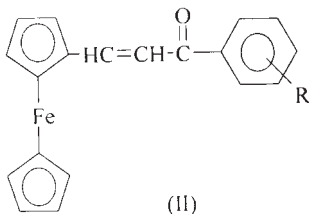


TABLE I. Spectral data for diacylferrocenes

Compound	Ar	λ_1/nm ($\{\epsilon\}$)	ν_1/cm^{-1}	λ_2/nm ($\{\epsilon\}$)	ν_2/cm^{-1}
Ia	$\text{CH}_3(\text{CH}_2)_9-$	315(2450)	31750	455(582)	21980
Ib	$\text{C}_6\text{H}_5\text{CH}_2-$	305(2320)	32790	461(470)	21690
Ic	$p\text{-Cl-C}_6\text{H}_4-$	355(4600)	28170	472(2020)	21190
Id	$p\text{-C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{-C}_6\text{H}_4-$	350(3660)	28570	470(950)	21280

The absorption intensity of the shorter wavelength band of the diacylferrocenes is increased and the half-width of the absorption band is reduced in Ic and Id. According to the Franck-Condon principle, the latter is a reliable indication of diminishing vibrational coupling between the π -electron system and the residual molecular frame.⁵

On the other hand, this band, origination from a (N-V) transition from a bonding orbital to an antibonding orbital is a particularly sensitivity to substitution in the rings *cf.* Ia and Ic. The red shift and rise of intensity of absorption for the longest wavelength absorption band of the diacylferrocenes are strong indication of increasing polarization of the molecule.



The π -electronic spectra of a series of ferrocenyldene acetophenones (II) and mono-substituted ferrocenes 1[(α -cyanophenylmethyl- β -4-methylbenzoyl) ethyl] ferrocene, 1[(α -cyanophenylmethyl- β -4-bromobenzoyl) ethyl] ferrocene and 1[(α -benzoylphenylmethyl- β -4-bromobenzoyl) ethyl] ferrocene (III a-c) were measured in hexane and the results are listed in Table II.

For a closely related series of compounds the extinction coefficient acts as a measure of the transition probability and, to some extent, of the polarization of the molecule.⁶ The extinction coefficients for compounds (II) were all found to be of the same order of magnitude, thus indicating that identical transitions are occurring throughout the series. Comparing the extinction coefficients of compounds II and III show that the extinction coefficients of compounds III are 10 to 15 times less than compounds II. This can be explained as

follows: A substitution on one ring of the metallocene nucleus may alter the electron density on that ring through its inductive field or resonance interaction with the ring. This change in electron density may be relayed through the ring-metal bonds to a substituent on the metal itself or on the second ring. Such transmission of effects will reflect the nature and polarizability of the ring-metal bonds. In compounds II a resonance interaction between heteroannular groups might be transmitted by the ring-metal bonds quite efficiently leads to high extinction coefficients. It is tentatively suggested that the high extinction coefficient attributed to a strong contribution from the polar structure IV for a series of compounds II. It is tentatively suggested that the high extinction coefficient attributed to a strong contribution from the polar structure IV.

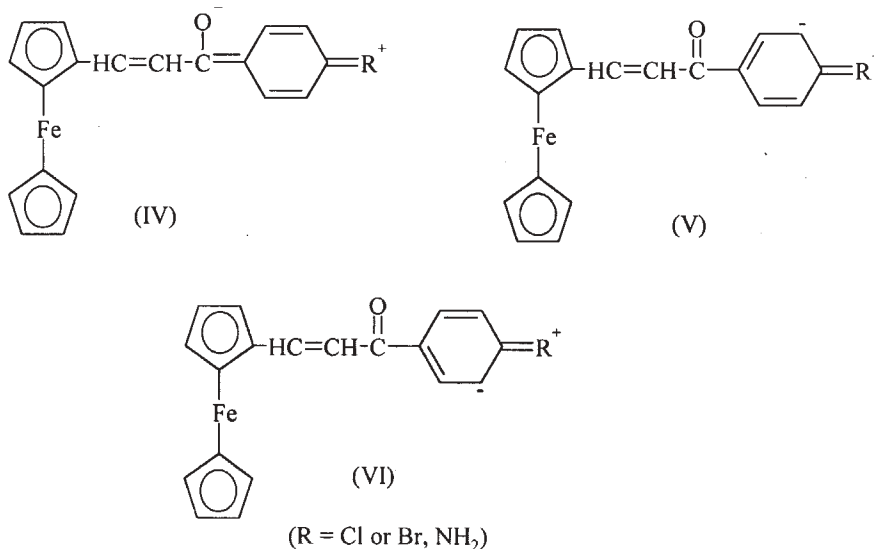
TABLE II. The spectral data of ferrocenylidene acetophenones (II) and mono-substituted ferrocene(III) in *n*-hexane solution

Compound	R	$\lambda_1/\text{nm} (\{\epsilon\})$	ν_1/cm^{-1}	$\lambda_2/\text{nm} (\{\epsilon\})$	ν_2/cm^{-1}	σ
IIa	H	381(3800)	36250	467(2920)	21000	0
IIb	<i>p</i> -CH ₃	381(4320)	26250	475(3000)	21050	-0.17
IIc	<i>p</i> -OCH ₃	378(3990)	26450	468(2490)	21360	-0.27
IId	<i>p</i> -Cl	388(4250)	25770	484(3520)	20660	0.23
IIe	<i>p</i> -Br	387(4560)	25830	483(3800)	20700	0.23
IIf	<i>p</i> -CN	399(4300)	25060	502(5000)	19920	0.63
IIg	<i>m</i> -OCH ₃	381(5170)	26250	477(3720)	20960	0.12
IIh	<i>p</i> -NH ₂	339(64214)	29500	489(4950)	20450	-0.66
IIIa	R = <i>p</i> -CH ₃ R' = PhCHCN	322(330)		430(265)		
IIIb	R = <i>p</i> -Br R' = PhCHCN	325(350)		445(280)		
IIIc	R = <i>p</i> -Br R' = PhCHCOPh	327(340)		439(250)		

Structures (IV) to (VI) probably contribute more to the excited state than to the ground state since due to conjugation the effect can be transmitted right through the substituent group R to the π electron of the phenyl group (V and VI) or to the oxygen of carbonyl group (IV) producing anionic resonance hybrids in which the formal charge can occupy a number of positions. The resonance structures involving the vinylferrocene moiety and carbonyl group alone are omitted, since they are common throughout the series.

In the ground state the electrons are displaced toward the substituent through an electron-attracting inductive effect, while in the excited state the substituent experiences a migration of electrons towards the ring through its resonance electron-donating property. Therefore the excitation energy should be lowered.

In the case of the electron-attracting substituent (R = CN), the resonance structures (VII to IX) can be constructed.

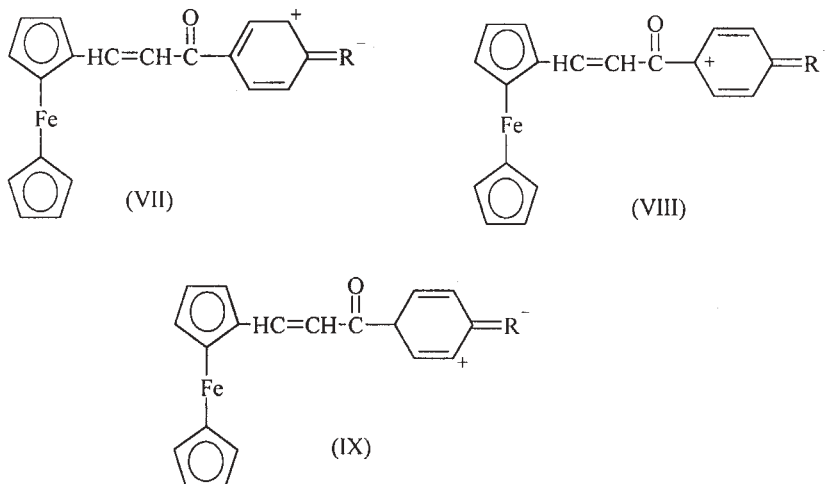


Scheme 1. Resonance structures for ferrocenylidene acetophenone IId, IIe and IIIh.

Here the substituent has only electron-withdrawing properties, and, consequently, the slight polarization in the ground state becomes considerably enhanced in the excited state leading to cationic resonance hybrids of canonical forms (VII–IX) in which the formal charge can occupy a number of positions, this would be expected to give as a result a high extinction coefficient for compound IIf (R = CN).

The Hammett equation has been found to correlate oxidation potentials of substituted ferrocenes.^{7–10} In the present investigation, the correlation between ν_1 and ν_2 of ferrocenylidene acetophenones with the Hammett substituent constant σ is produced.

A plot of ν_1 against the Hammett substituent constant σ is shown in Fig. 1a while in



Scheme 2. Resonance structures for ferrocenylidene acetophenone IIf.

σ	$\{\tilde{\nu}_1\}$	$\sigma\{\tilde{\nu}_1\}$	σ^2	$\{\tilde{\nu}_1^2\}$	σ	$\{\tilde{\nu}_1\}$
-0.66	2.95	-1.947	0.4356	8.7025	-0.66	2.845113
-0.27	2.645	-0.71415	0.0729	6.996025	-0.27	2.727541
-0.17	2.625	-0.44625	0.0289	6.890625	-0.17	2.697394
0	2.625	0	0	6.890625	0	2.646145
0.12	2.625	0.315	0.0144	6.890625	0.12	2.609969
0.23	2.577	0.59271	0.0529	6.640929	0.23	2.576808
0.23	2.583	0.59409	0.0529	6.671889	0.23	2.576808
0.63	2.506	1.57878	0.3969	6.280036	0.63	2.456222
$\Sigma\sigma$	$\Sigma\{\nu\}$	$\Sigma\sigma\nu$	$\Sigma\sigma^2$	$(\Sigma\sigma)^2$	$\Sigma\{\nu^2\}$	$(\Sigma\{\nu\})^2$
0.11	21.136	-0.02682	1.0545	0.0121	55.96325	446.7305

$\{\rho\} = -0.30147$ $\{\bar{\nu}_0\} = 2.646145$ $\rho \Sigma\{\tilde{\nu}_1\} - (\Sigma\sigma)(\Sigma\{\tilde{\nu}_1\}) = -2.53952$ $\rho \Sigma\sigma^2 - (\Sigma\sigma)^2 = 8.4239$
 $(\rho \Sigma\sigma^2 - (\Sigma\sigma)^2)^2 = 2.902396$ $\rho \Sigma\{\tilde{\nu}_1\}^2 - \{\Sigma\tilde{\nu}_1\}^2 = 0.975536$ $(\rho \Sigma\{\tilde{\nu}_1\}^2 - \{\Sigma\tilde{\nu}_1\}^2)^{0.5} = 0.987692$
 $\{\tilde{\nu}_1\} = \{\bar{\nu}_0\} + \{\rho\} \sigma$ $R = -0.88588$ $R^2 = 0.784777913$

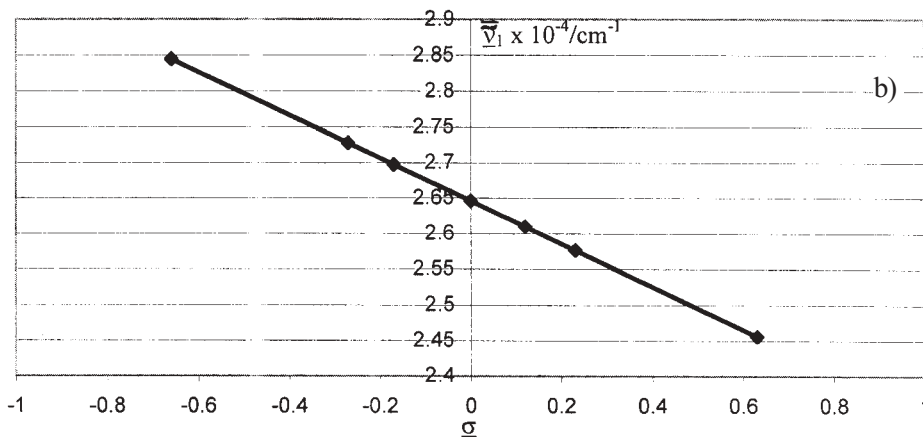
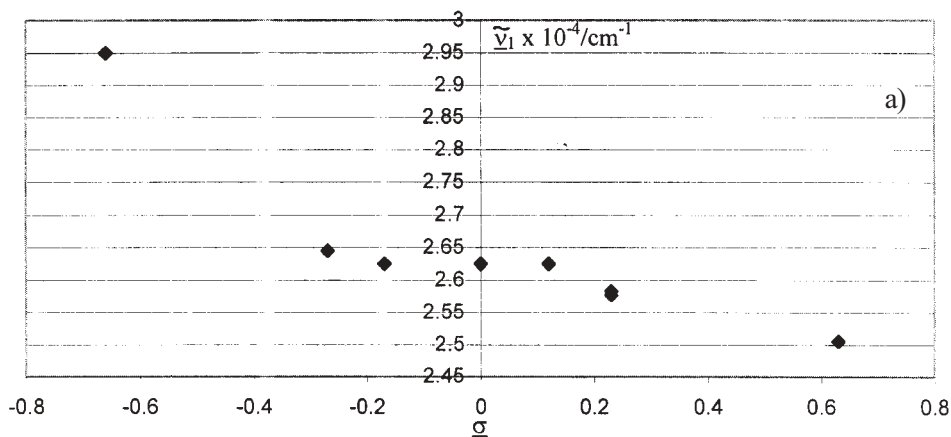


Fig. 1. a) ν_1 of substituted ferrocenyldiene vs. the Hammett constant σ with the NH_2 value; b) ν_1 of substituted ferrocenyldiene vs. the Hammett constant σ with the NH_2 value.

σ	$\{\tilde{\nu}_1\}$	$\sigma\{\tilde{\nu}_1\}$	σ^2	$\{\tilde{\nu}_1^2\}$	σ	$\{\tilde{\nu}_1\}$
-0.27000	2.64500	-0.71415	0.0729	6.996025	-0.27000	2.655107
-0.17000	2.62500	-0.44625	0.0289	6.890625	-0.17000	2.640079
0.000000	2.62500	0	0	6.890625	0.000000	2.614531
0.120000	2.62500	0.315	0.0144	6.890825	0.120000	2.596497
0.230000	2.57700	0.59271	0.0529	6.640929	0.23000	2.579966
0.230000	2.58300	0.59409	0.0529	6.671889	0.23000	2.579966
0.630000	2.50600	1.57878	0.3969	6.280036	0.63000	2.519854
$\Sigma\sigma$	$\Sigma\{v\}$	$\Sigma\sigma v$	$\Sigma\sigma^2$	$(\Sigma\sigma)^2$	$\Sigma\{v^2\}$	$(\Sigma\{v\})^2$
0.77000	18.18600	1.92018	0.6189	0.5929	47.26075	330.7306

$$\{\rho\} = -0.15028 \quad \{\tilde{\nu}_0\} = 2.614531 \quad \bar{n} \Sigma\{\tilde{\nu}\}\sigma - (\Sigma\sigma)(\Sigma\{\tilde{\nu}\}) = -0.56196 \quad \bar{n} \Sigma\sigma^2 - (\Sigma\sigma)^2 = 3.7394$$

$$(\bar{n} \Sigma\sigma^2 - (\Sigma\sigma)^2)^{0.5} = 1.933753 \quad \bar{n} \Sigma\{\tilde{\nu}\}^2 - \{\Sigma\tilde{\nu}\}^2 = 0.094682 \quad (\bar{n} \Sigma\{\tilde{\nu}\}^2 - \{\Sigma\tilde{\nu}\}^2)^{0.5} = 0.307704$$

$$\{\tilde{\nu}_1\} = \{\tilde{\nu}_0\} + \{\rho\} \sigma \quad R = -0.94443 \quad R^2 = 0.891951953$$

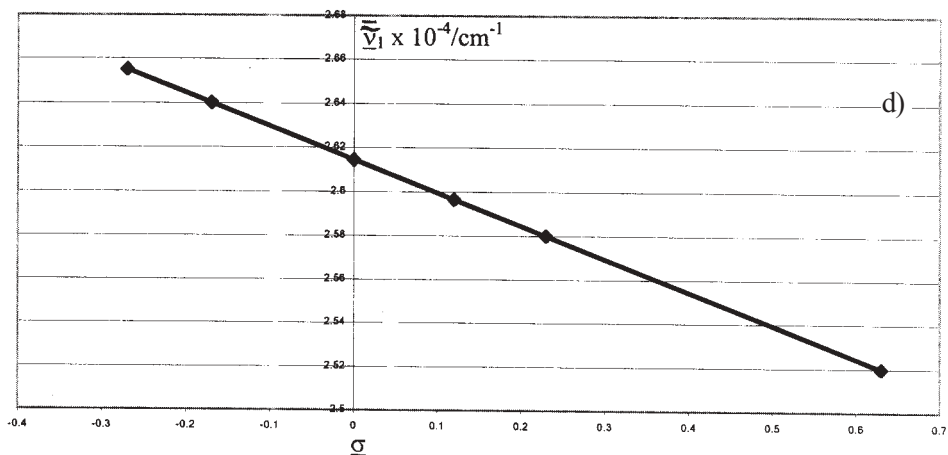
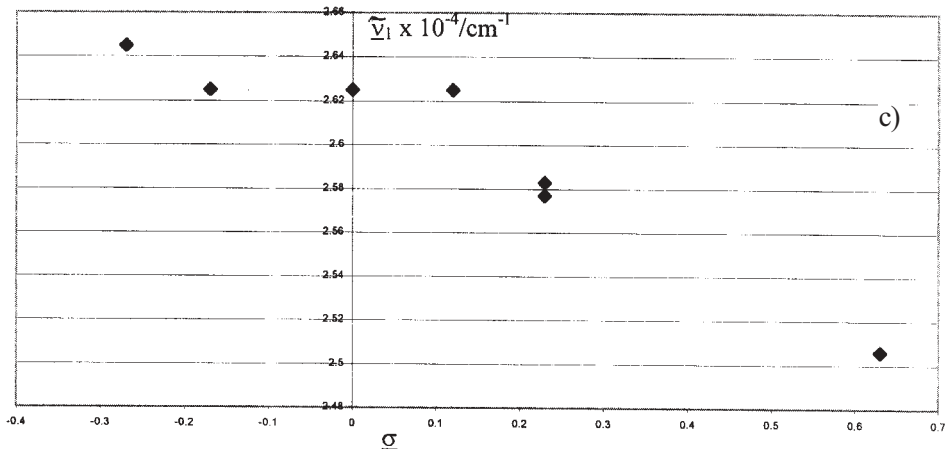


Fig. 1. ν_1 of substituted ferrocenylidene vs. the Hammett constant σ without the NH_2 value. d) ν_1 of substituted ferrocenylidene vs. the Hammett constant σ without the NH_2 value.

σ	$\{\tilde{\nu}_2\}$	$\sigma\{\tilde{\nu}_2\}$	σ^2	$\{\tilde{\nu}_2^2\}$	σ	$\{\tilde{\nu}_2\}$
-0.66	2.045	-1.3497	0.4356	4.182025	-0.66	2.111376
-0.27	2.136	-0.57672	0.0729	4.562496	-0.27	2.091043
-0.17	2.105	-0.35785	0.0289	4.431025	-0.17	2.08583
0	2.1	0	0	4.41	0	2.076967
0.12	2.096	0.25152	0.0144	4.393218	0.12	2.070711
0.23	2.066	0.47518	0.0529	4.268356	0.23	2.064976
0.23	2.07	0.4761	0.0529	4.2849	0.23	2.064976
0.63	1.992	1.25496	0.3969	3.968064	0.63	2.044122
$\Sigma\sigma$	$\Sigma\{\nu\}$	$\Sigma\sigma\nu$	$\Sigma\sigma^2$	$(\Sigma\sigma)^2$	$\Sigma\{\nu^2\}$	$(\Sigma\{\nu\})^2$
0.11	16.61	017349	1.0545	0.0121	34.50008	275.8921

$\{\rho\} = -0.05213$ $\{\tilde{\nu}_0\} = 2.076967$ $n \Sigma\{\tilde{\nu}\}\sigma - (\Sigma\sigma)(\Sigma\{\tilde{\nu}\}) = -0.43918$ $n \Sigma\sigma^2 - (\Sigma\sigma)^2 = 8.4239$
 $(n \Sigma\sigma^2 - (\Sigma\sigma)^2)^{-1} = 2.902396$ $n \Sigma\{\tilde{\nu}\}^2 - \{\Sigma\tilde{\nu}\}^2 = 0.108556$ $(n \Sigma\{\tilde{\nu}\}^2 - \{\Sigma\tilde{\nu}\}^2)^{-0.5} = 0.329478$
 $\{\tilde{\nu}_i\} = \{\tilde{\nu}_0\} + \{\rho\} \sigma$ $R = -0.45926$ $R^2 = 0.210920151$

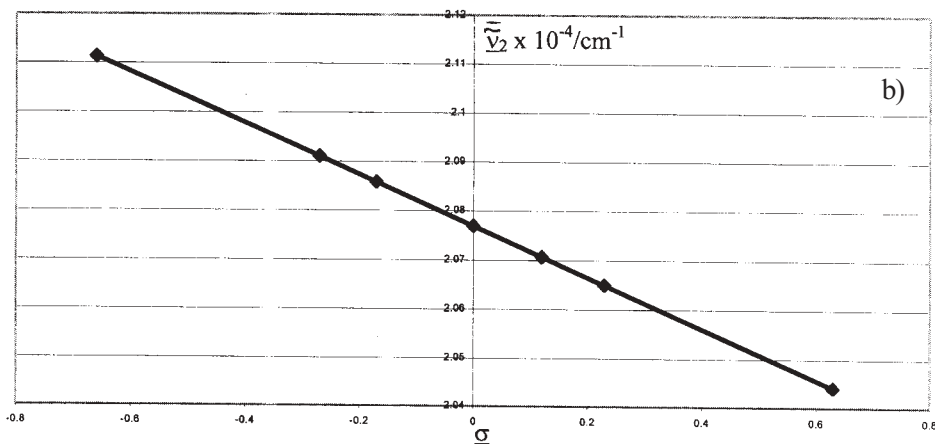
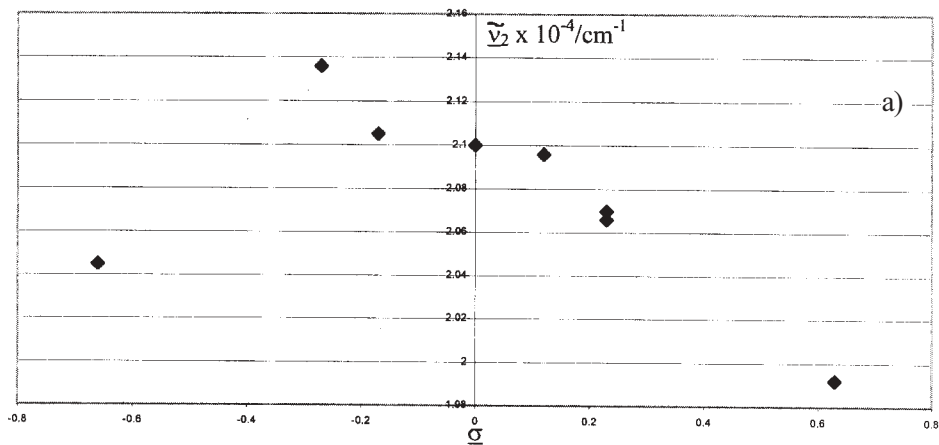


Fig. 2. a) ν_2 of substituted ferrocenyldiene vs. the Hammett constant σ with the NH_2 value; b) ν_2 of substituted ferrocenyldiene vs. the Hammett constant σ with the NH_2 value.

σ	$\{\tilde{\nu}_2\}$	$\sigma\{\tilde{\nu}_2\}$	σ^2	$\{\tilde{\nu}_2^2\}$	σ	$\{\tilde{\nu}_2\}$
-0.27000	2.13600	-0.57672	0.0729	4.562496	-0.27000	2.136882
-0.17000	2.10500	-0.35785	0.0289	4.431025	-0.17000	2.122101
0.000000	2.10000	0	0	4.41	0.000000	2.096973
0.120000	2.09600	0.25152	0.0144	4.393216	0.120000	2.079236
0.230000	2.06600	0.47518	0.0529	4.268356	0.230000	2.062977
0.230000	2.07000	0.4761	0.0529	4.2849	0.230000	2.062977
0.630000	1.99200	1.25496	0.3969	3.968064	0.630000	2.003853
$\Sigma\sigma$	$\Sigma\{\tilde{\nu}_2\}$	$\Sigma\sigma\tilde{\nu}_2$	$\Sigma\sigma^2$	$(\Sigma\sigma)^2$	$\Sigma\{\tilde{\nu}_2^2\}$	$(\Sigma\{\tilde{\nu}_2\})^2$
0.77000	14.56500	1.52319	0.6189	0.5929	30.31806	212.1392

$$\{\rho\} = -0.14781 \quad \{\tilde{\nu}_0\} = 2.096973 \quad \underline{n} \Sigma\{\tilde{\nu}_2\}\sigma + (\Sigma\sigma)(\Sigma\{\tilde{\nu}_2\}) = -0.55272 \quad \underline{n} \Sigma\sigma^2 - (\Sigma\sigma)^2 = 3.7394$$

$$(\underline{n} \Sigma\sigma^2 - (\Sigma\sigma)^2)^2 = 1.933753 \quad \underline{n} \Sigma\{\tilde{\nu}_2\}^2 - \{\Sigma\tilde{\nu}_2\}^2 = 0.087174 \quad (\underline{n} \Sigma\{\tilde{\nu}_2\}^2 - \{\Sigma\tilde{\nu}_2\}^2)^{0.5} = 0.295252$$

$$\{\tilde{\nu}_1\} = \{\tilde{\nu}_0\} + \{\rho\} \sigma \quad R = -0.96808 \quad R^2 = 0.937176654$$

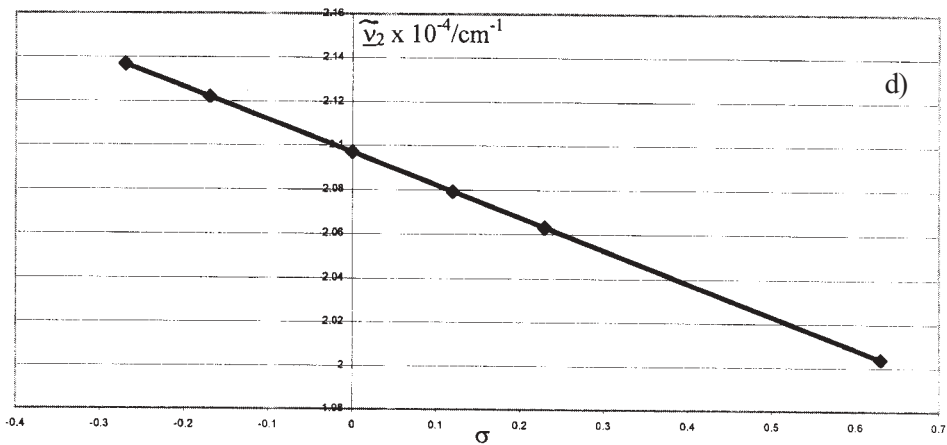
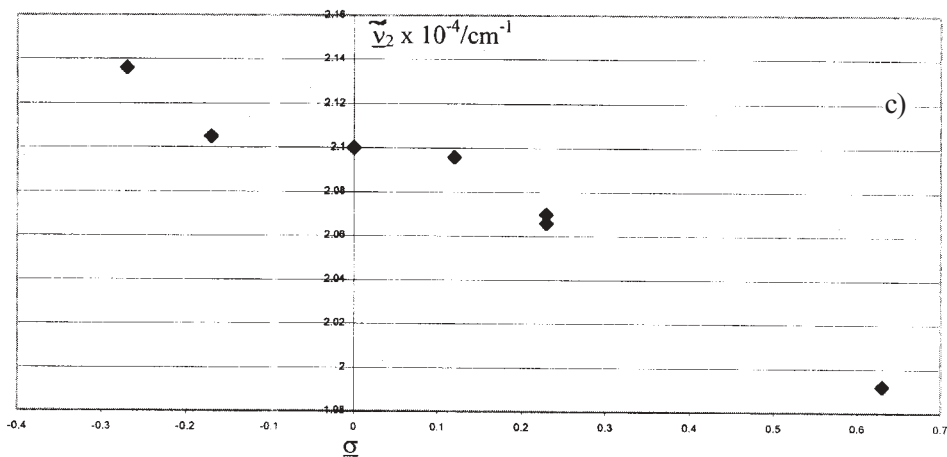
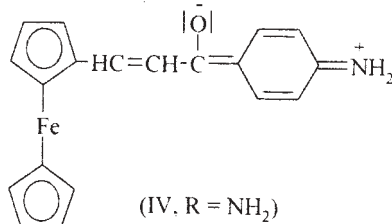


Fig. 2. ν_2 of substituted ferrocenylidene vs. the Hammett constant σ without the NH_2 value. d) ν_2 of substituted ferrocenylidene vs. the Hammett constant σ without the NH_2 value.

Fig. 1b a plot of ν_1 against the substituent constant σ is given. The correlation is quite good with linearity $R = 0.885$, with the exception of ferrocenylidene *p*-aminoacetophenone. This may be due to the electron donating nature of the *p*-amino group which interacts with the developing positive charge created in the excited state.

Plots of ν_1 and ν_1 against the Hammett substituent constant σ , after omitting the value of NH_2 are shown in Figs. 1c and 1d, respectively. Now the correlation seems to be typically linear, with linearity $R = 0.944$. Also in Figs. 2a and 2b are shown plots of ν_2 and ν_2 against the Hammett substituent constant σ . The correlation shows linearity $R = 0.459$ if the value of NH_2 is taken into consideration.



In Figs. 2c and 2d are shown plot of ν_2 and ν_2 against the Hammett substituent constant σ after omitting the value of NH_2 . Now the correlation is fair good with linearity $R = 0.968$.

EXPERIMENTAL

All the melting points are uncorrected. The IR spectra were recorded on a Unicam SP-1200 spectrophotometer using the KBr Wafer technique; $^1\text{H-NMR}$ spectra were run on a JEOL-JNM-FX-200 spectrometer. Elemental analysis was carried out in the microanalytical laboratory of the University of Texas at Dallas using a Richardson TX 75080 instrument. The electronic absorption spectra were measured using a Varian No. 952019-04 spectrophotometer. The purity of all the synthesized compounds was checked by TLC.

Diacylferrocenes (Ia-d) were prepared by a method previously reported in the literature.⁴

Compounds IIa, IIc and IIe were prepared as previously described according to Ref. 12, and IIb, IId and IIg were prepared according to Ref. 13. They were identified *via* melting point and mixed melting point measurement. Compounds IIf and IIh were prepared according to the following procedure:

A mixture of *p*-cyanoacetophenone and/or *p*-aminoacetophenone (0.01 mol) and ferrocenylidene (Aldrich) (0.01 mol) in absolute ethanol (50 cm³) was treated with aqueous sodium hydroxide (10%, 20 cm³) under vigorous stirring and cooling. The solid product that separated was filtered off and recrystallized from hexane in case of IIf and from benzene in case of IIh. The structures of compounds II, structures of compounds IIf and IIh were inferred from their IR and $^1\text{H-NMR}$ spectra.

IR spectra showed strong absorption bands in the region 1100–1120 cm⁻¹ (unsubstituted ferrocene ring), 1610–1625 cm⁻¹ ($\nu_{\text{C=C}}$), 1665–1670 cm⁻¹ ($\nu_{\text{C=O}}$), 2200 cm⁻¹ ($\nu_{\text{C=N}}$) for IIf and 3220 cm⁻¹ for IIh.

The $^1\text{H-NMR}$ spectrum of IIf in CDCl_3 showed the following signals: δ 4.25 (5H, *m*, unsubstituted cyclopentadienyl ring), δ 4.45 (2H, *t*, $J = 1.4$ Hz, H₃ and H₄ of substituted cyclopentadienyl ring), δ 4.55 (2H, *t*, $J = 1.4$ Hz, H₂ and H₅ of substituted cyclopentadienyl ring), two doublet at δ 6.7 and δ 6.9 (AB system of olefinic protons), two doublets at δ 7.5 and δ 7.7 (A₂B₂ system of phenyl moiety).

A mixture (0.01 mol) of the desired ferrocenylidene acetophenone (0.01 mol) and of the active methylene compound (benzyl cyanide or desoxybenzoin) (0.01 mol) in ethanol (50 cm³) was treated with aqueous NaOH (20%, 5 cm³) and the mixture was left for four days at room temperature. The solvent was then evaporated under reduced pressure. The residue was cooled and was triturated with a few drops of dilute hydrochloric

ric acid. The solid that separated was filtered off and crystallized from hexane. The structures of compounds IIIa and IIIb were inferred from their following IR and $^1\text{H-NMR}$ spectra.

The IR spectra of compounds IIIa and IIIb exhibited absorptions in the regions 1115–1130 cm^{-1} (unsubstituted ferrocene rings), 1670–1680 cm^{-1} ($\nu_{\text{C=O}}$), and 2200–2215 cm^{-1} ($\nu_{\text{C=N}}$).

The $^1\text{H-NMR}$ spectrum of IIIa in CDCl_3 showed the following signals: δ 2.4 (3H, *s*, Ar- CH_3), δ 2.7 (2H, *m*, non equivalent methylene protons), δ 2.9 (1H, *m*, methine proton), δ 4.45, (5H, *m*, unsubstituted cyclopentadienyl ring); δ 4.52 (2H, *m*, H₃, H₄ of substituted cyclopentadienyl ring); δ 4.60 (2H, *m*, H₂, H₅ of substituted cyclopentadienyl ring), δ 7.4–7.9 (9H, *m*, ArH protons).

IR spectrum of compound IIIc showed absorption bands at 1125 cm^{-1} (unsubstituted ferrocene ring), 1670 cm^{-1} , 1680 cm^{-1} attributable to ν_{max} of two carbonyl groups. The characterization data of II, III and IIIa-c are presented in Table III.

TABLE III. Physical constants data of the ferrocene derivatives (II) and (III)

Compound	M.p./ $^{\circ}\text{C}$	Yield/%	Mol. formula (M. wt.)	$w_f(\text{calcd.})/\%$	$w_f(\text{found})/\%$
II	171	75	$\text{C}_{20}\text{H}_{15}\text{NOFe}$	70.38	4.39
			(341)	70.16	4.65
III	226	62	$\text{C}_{19}\text{H}_{17}\text{NOFe}$	68.88	5.13
			(331)	68.77	5.52
IIIa	192	55	$\text{C}_{28}\text{H}_{25}\text{NOFe}$	75.16	5.59
			(447)	75.21	5.64
IIIb	182	57	$\text{C}_{27}\text{H}_{22}\text{NOBrFe}$	63.28	4.29
			(512)	63.27	4.44
IIIc	195	52	$\text{C}_{33}\text{H}_{27}\text{O}_2\text{BrFe}$	67.00	4.56
			(591)	67.47	4.89

ИЗВОД

СУПСТИТУИСАНИ ФЕРОЦЕНИ: СИНТЕЗА И КОРЕЛАЦИЈА ЊИХОВИХ ЕЛЕКТРОНСКИХ СПЕКТРА СА СТРУКТУРОМ

E. A. KASSAB, M. I. MARZOUK и M. EL-HASHASH

Faculty of Science, Ain Shams University, Cairo, Egypt and Industrial Education College, Ammeria, Cairo, Egypt

Синтетизоване су три серије диацилфероцена (I), фероценилиден ацетофенона (II) и моноалкил фероцена (III) и проучени њихови електронски спектри у видљивој области. Таласни бојеви апсорпционих трака једињења (II) су у доброј корелацији са Hammett-овим константама σ .

(Примљено 7. новембра 2001, ревидирано 7. маја 2002)

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