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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

Three series of diacylferrocenes (I) and ferrocenylidene acetophenones (II) and monoalkyl ferrocenes (III) were synthesised 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 that have been assigned (1) to symmetry forbidden electronic transitions of the type $N \rightarrow Q$ that 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 orbital 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 that are highly localized on the metal atom¹⁻³. 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 $N \rightarrow Q$. 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.

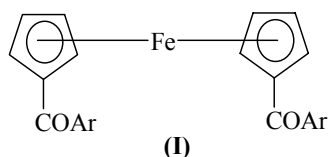


TABLE 1. Spectral data for diacylferrocenes

Compd.	Ar	λ_1/nm ($\{\epsilon\}$)	$\tilde{\nu}_1$ (cm^{-1})	λ_2/nm ($\{\epsilon\}$)	$\tilde{\nu}_2$ (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 frame⁵.

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 ferrocenylidene acetophenones (II) and monosubstituted 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.

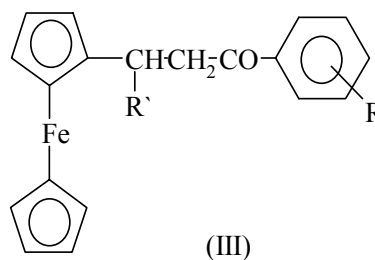
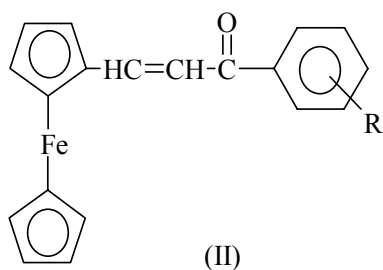
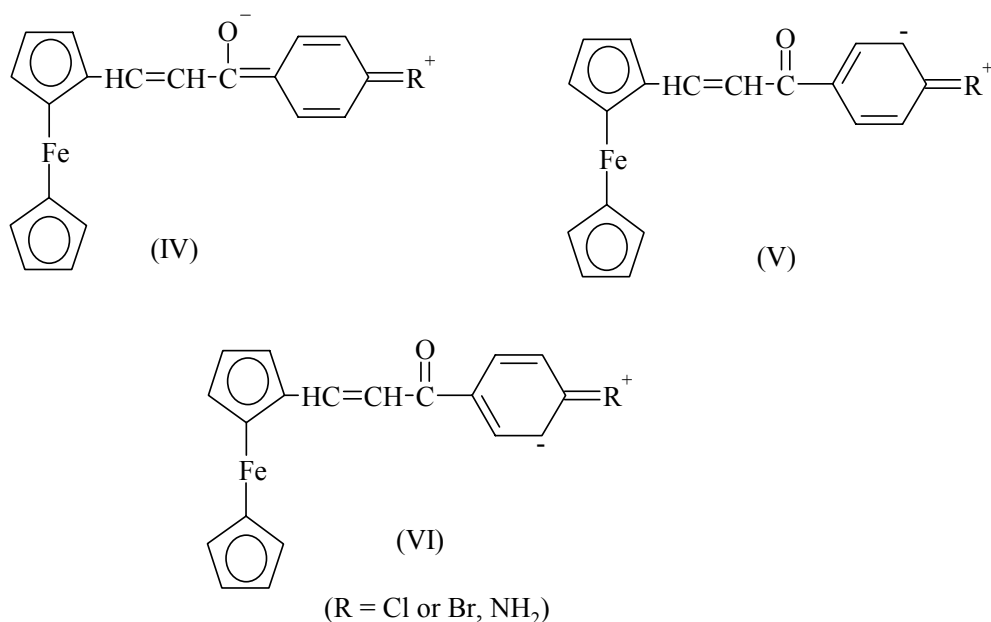


Table II. The spectral data of ferrocenylidene acetophenones (II) and mono-substituted ferrocene (III) in n-hexane solution.

Compd.	R	λ_1/nm ($\{\epsilon\}$)	$\tilde{\nu}_1$ (cm^{-1})	λ_2/nm ($\{\epsilon\}$)	$\tilde{\nu}_2$ (cm^{-1})	σ
IIa	H	381(3800)	36250	467(2920)	21000	0
IIb	p-CH ₃	381(4320)	26250	475(3000)	21050	-0.17
IIc	p-OCH ₃	378(3990)	26450	468(2490)	21360	-0.27
IId	p-Cl	388(4250)	25770	484(3520)	20660	0.23
IIe	p-Br	387(4560)	25830	483(3800)	20700	0.23
IIf	p-CN	399(4300)	25060	502(5000)	19920	0.63
IIg	m-OCH ₃	381(5170)	26250	477(3720)	20960	0.12
IIh	p-NH ₂	339(64214)	29500	489(4950)	20450	-0.66
IIIa	R = p-CH ₃ R' = PhCHCN	322(330)		430(265)		
IIIb	R = p-Br R' = PhCHCN	325(350)		445(280)		
IIIc	R = p-Br R' = PhCHCOPh	327(340)		439(250)		

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 molecule⁶. 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 explaining 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 substituents 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.



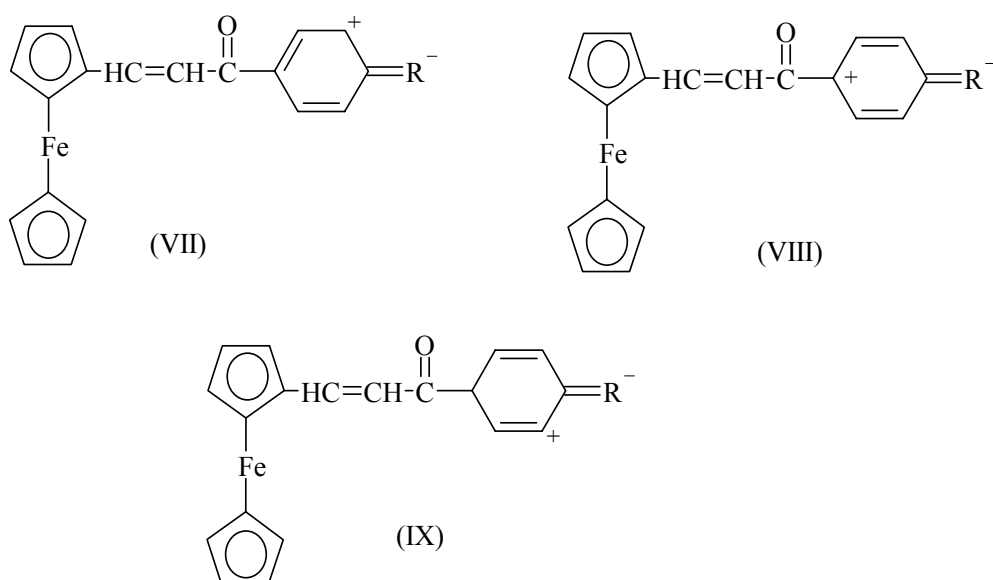
Scheme 1
Resonance structures for ferrocenylidene acetophenone IIId, IIe and IIh

Structures (IV) to (VI) probably contribute more to the excited state than to the ground state due to through conjugation 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 ($R = \text{CN}$), the resonance structures (VII to IX) can be constructed.



Scheme 2

Resonance structures for ferrocenylidene acetophenone IIIf

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 result a high extinction coefficient for compound IIIf ($R = \text{CN}$).

The Hammett equation has been found to correlate oxidation potentials of substituted ferrocenes⁷⁻¹⁰.

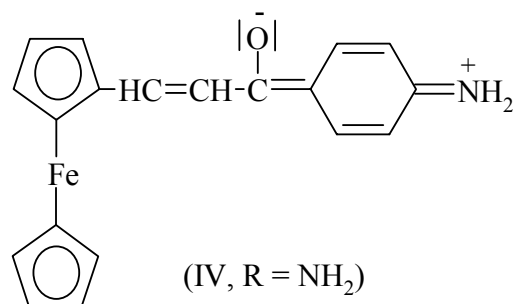
More recently, the Mossbauer parameters¹¹ of dibromoboryl ferrocenes and dichloroboryl ferrocenes with Hammett substitute constants were reported.

Also $\Delta E_{1/2}$, $E_{1/2}$ (Fe^{III} / Fe^{II}) of complexes¹² containing ferrocenylpyridine change sharply and clearly with Hammett substitute constants (δ).

In the present investigation, the correlation between $\tilde{\nu}_1$ and $\tilde{\nu}_2$ of ferrocenylidene acetophenones with the Hammett substitute constant σ is produced.

A plot of $\tilde{\nu}_1$ against the Hammett substituent constant σ is shown in Fig. 1a while in Fig. 1b a plot of $\overline{\tilde{\nu}}_1$ 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 $\tilde{\nu}_1$ and $\overline{\tilde{\nu}}_1$ 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 $\tilde{\nu}_2$ and $\overline{\tilde{\nu}}_2$ against the Hammett substitute 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 $\tilde{\nu}_2$ and $\overline{\tilde{\nu}}_2$ against the Hammett substitute constant σ after omitting the value of NH_2 . Now the correlation is fair good with linearity ($R = 0.968$)



Negative slopes (The second parameter ρ) explain the probability of electronic transition is more difficulty by electron withdrawal.

EXPERIMENTAL

All the melting points are uncorrected. The IR spectra were recorded on a Unicam SP-1200 spectrophotometer using the KBr Wafer technique; ¹H-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. TLC checked the purity of all the synthesized compounds.

Diacylferrocenes (Ia-d) were prepared by a method previously reported in the literature⁴.

Compounds IIa, IIc and IIe were prepared as previously described according to ref. 13, and IIb, IId and IIg were prepared according to ref. 14. 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*-amino-acetophenone (0.01 mol) and ferrocenyaldehyde (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 ^1H -NMR spectra.

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

The ^1H -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, H_3 and H_4 of substituted cyclopentadienyl ring), δ 4.55 (2H, t, $J = 1.4$ Hz, H_2 and H_5 of substituted cyclopentadienyl ring), two doublet at δ 6.7 and δ 6.9 (AB system of olefinic protons), two doublet at δ 7.5 and δ 7.7 (A_2B_2 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 cm^3) was treated with aqueous NaOH (20 %, 5 cm^3) 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 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 ^1H -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} ($\nu_{\text{C}=\text{O}}$), and 2200-2215 cm^{-1} ($\nu_{\text{C}=\text{N}}$).

The ^1H -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), 4.45 (5H, m, unsubstituted cyclopentadienyl ring); δ 4.52 (2H, m, H_3 , H_4 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 $\tilde{\nu}_{\max}$ of two carbonyl groups. The characterization data of II_f, II_h and III_{a-c} are presented in Table III.

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

Compd.	M.p. °C	Yield/%	Mol. Formula (M. Wt.)	w _i (calc.)/%	w _i (found)/%
II _f	171	75	C ₂₀ H ₁₅ NOFe	70.38	4.39
			(341)	70.16	4.65
II _h	226	62	C ₁₉ H ₁₇ NOFe	68.88	5.13
			(331)	68.77	5.52
III _a	192	55	C ₂₈ H ₂₅ NOFe	75.16	5.59
			(447)	75.21	5.64
III _b	182	57	C ₂₇ H ₂₂ NOBrFe	63.28	4.29
			(512)	63.27	4.44
III _c	195	52	C ₃₃ H ₂₇ O ₂ BrFe	67.00	4.56
			(591)	67.47	4.89

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Figure captions:

Figure 1:

- a) $\tilde{\nu}_1$ of substituted ferrocenylidene vs. the Hammett constant σ with the NH_2 value
- b) $\tilde{\nu}_1$ of substituted ferrocenylidene vs. the Hammett constant σ with the NH_2 value
- c) $\tilde{\nu}_1$ of substituted ferrocenylidene vs. the Hammett constant σ without the NH_2 value
- d) $\tilde{\nu}_1$ of substituted ferrocenylidene vs. the Hammett constant σ without the NH_2 value

Figure 2:

- a) $\tilde{\nu}_2$ of substituted ferrocenylidene vs. the Hammett constant σ with the NH_2 value
- b) $\tilde{\nu}_2$ of substituted ferrocenylidene vs. the Hammett constant σ with the NH_2 value
- c) $\tilde{\nu}_2$ of substituted ferrocenylidene vs. the Hammett constant σ without the NH_2 value
- d) $\tilde{\nu}_2$ of substituted ferrocenylidene vs. the Hammett constant σ without the NH_2 value

$\underline{\sigma}$	$\{\widetilde{\nu}_1\}$	$\underline{\sigma}\{\widetilde{\nu}_1\}$	$\underline{\sigma}^2$	$\{\widetilde{\nu}_1^2\}$	$\underline{\sigma}$	$\{\widetilde{\nu}_1\}$
-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
$\Sigma \underline{\sigma}$	$\Sigma \{\underline{\nu}\}$	$\Sigma \underline{\sigma} \underline{\nu}$	$\Sigma \underline{\sigma}^2$	$(\Sigma \underline{\sigma})^2$	$\Sigma \{\underline{\nu}^2\}$	$(\Sigma \{\underline{\nu}\})^2$
0.11	21.136	-0.02682	1.0545	0.0121	55.96325	446.7305

$$\{\rho\} = -0.30147 \quad \{\nu_o\} = 2.646145 \quad \underline{n} \Sigma \{\underline{\nu}\} \underline{\sigma} - (\Sigma \underline{\sigma})(\Sigma \{\underline{\nu}\}) = -2.53952 \quad \underline{n} \Sigma \underline{\sigma}^2 - (\Sigma \underline{\sigma})^2 = 8.4239$$

$$(\underline{n} \Sigma \underline{\sigma}^2 - (\Sigma \underline{\sigma})^2)^{0.5} = 2.902396 \quad \underline{n} \Sigma \{\underline{\nu}\}^2 - \{\Sigma \underline{\nu}\}^2 = 0.975536 \quad (\underline{n} \Sigma \{\underline{\nu}\}^2 - \{\Sigma \underline{\nu}\}^2)^{0.5} = 0.987692$$

$$\{\underline{\nu}_1\} = \{\underline{\nu}_o\} + \{\rho\} \underline{\sigma} \quad R = -0.88588 \quad R^2 = 0.784777913$$

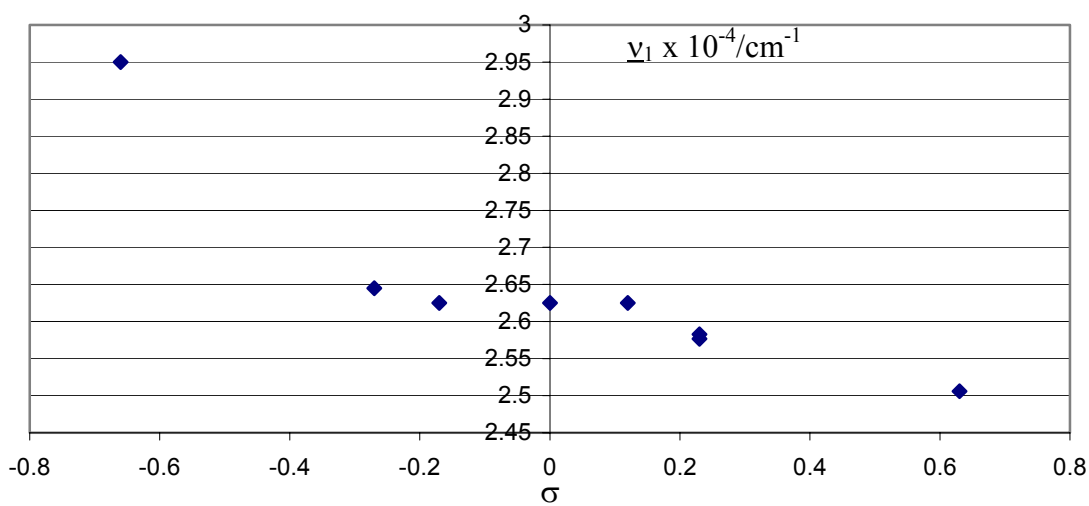
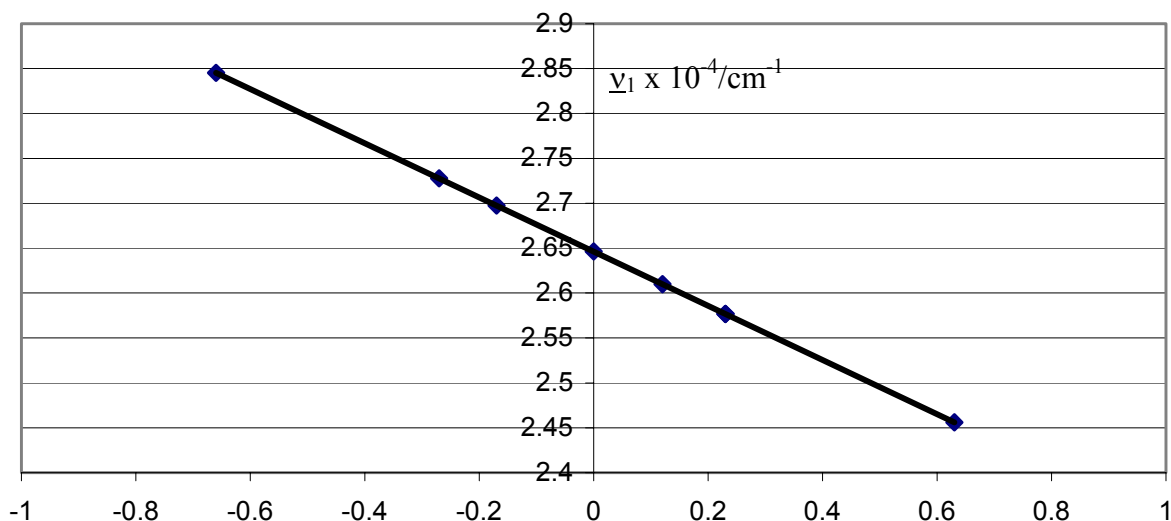


Figure 1a



Figs. 1a and b. Wave numbers $\widetilde{\nu}_1$ and $\widetilde{\nu}_1$ of ferrocenylidene vs. the Hammett constant $\underline{\sigma}$ with the NH_2 value.

$\underline{\sigma}$	$\{\tilde{\nu}_1\}$	$\underline{\sigma}\{\tilde{\nu}_1\}$	$\underline{\sigma}^2$	$\{\tilde{\nu}_1^2\}$	$\underline{\sigma}$	$\{\tilde{\nu}_1\}$
-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	0.230000	2.579966
0.230000	2.58300	0.59409	0.0529	6.671889	0.230000	2.579966
0.630000	2.50600	1.57878	0.3969	6.280036	0.630000	2.519854
$\Sigma \underline{\sigma}$	$\Sigma \{\underline{\nu}\}$	$\Sigma \underline{\sigma \nu}$	$\Sigma \underline{\sigma}^2$	$(\Sigma \underline{\sigma})^2$	$\Sigma \{\underline{\nu}^2\}$	$(\Sigma \{\underline{\nu}\})^2$
0.77000	18.18600	1.92018	0.6189	0.5929	47.26075	330.7306

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

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

$$\{\nu_1\} = \{\nu_o\} + \{\rho\} \underline{\sigma} \quad R = -0.94443 \quad R^2 = 0.891951953$$

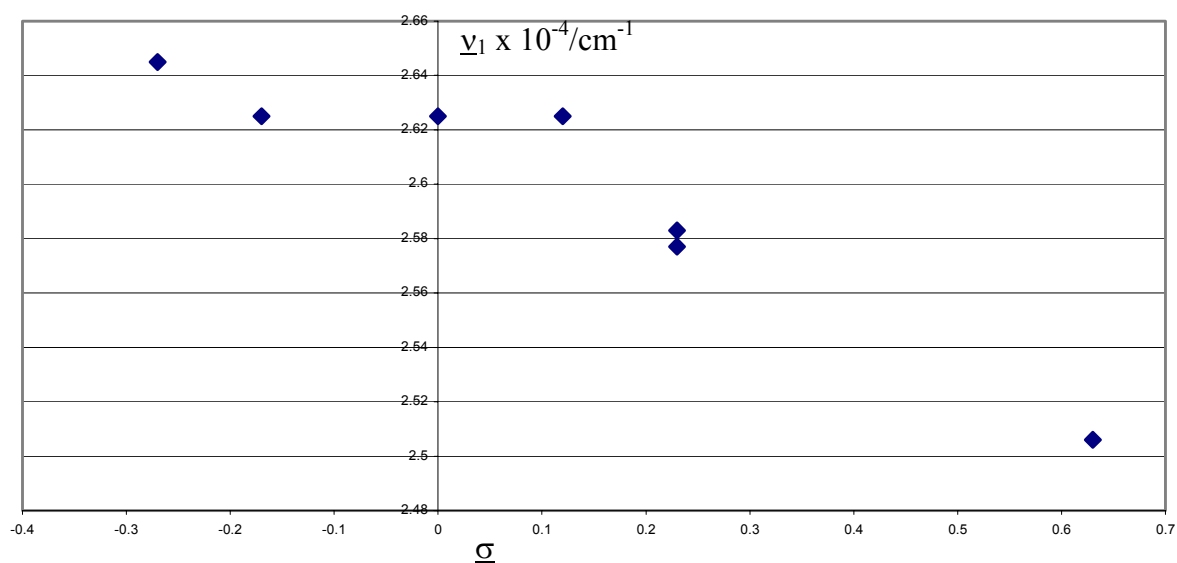
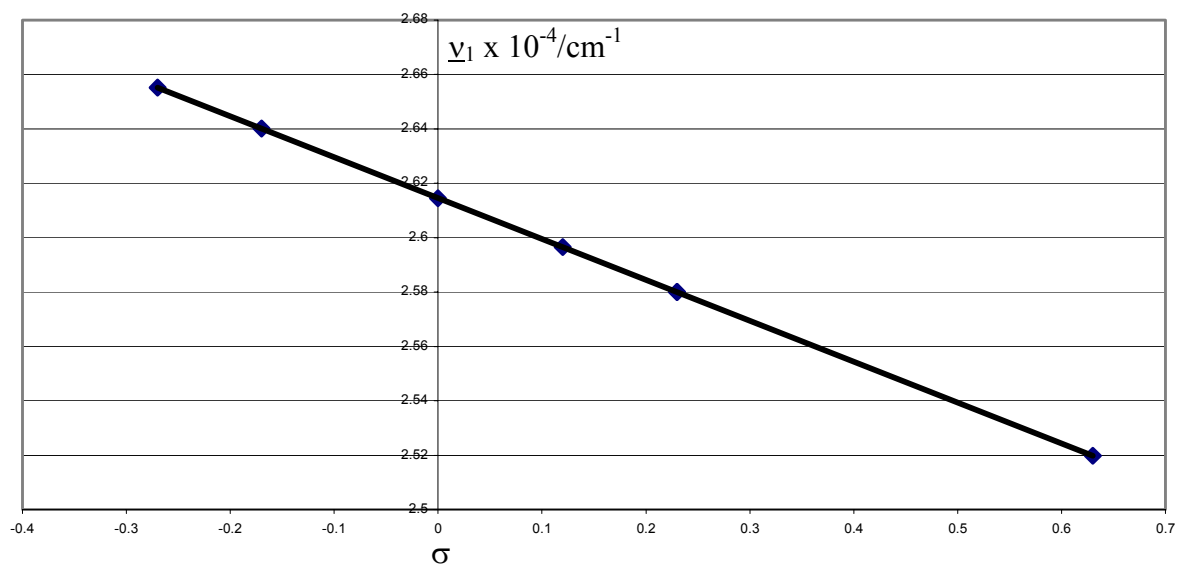


Figure 1c



Figs. 1c and d. Wave numbers $\tilde{\nu}_1$ and $\bar{\nu}_1$ of ferrocenylidene vs. the Hammett constant $\underline{\sigma}$ without the NH_2 value.

$\underline{\sigma}$	$\{\tilde{\nu}_2\}$	$\underline{\sigma}\{\tilde{\nu}_2\}$	$\underline{\sigma}^2$	$\{\tilde{\nu}_2^2\}$	$\underline{\sigma}$	$\{\tilde{\nu}_2\}$
-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
$\Sigma \underline{\sigma}$	$\Sigma \{\underline{\nu}\}$	$\Sigma \underline{\sigma \nu}$	$\Sigma \underline{\sigma}^2$	$(\Sigma \underline{\sigma})^2$	$\Sigma \{\underline{\nu}^2\}$	$(\Sigma \{\underline{\nu}\})^2$
0.11	16.61	017349	1.0545	0.0121	34.50008	275.8921

$$\{\rho\} = -0.05213 \quad \{\nu_o\} = 2.076967 \quad \underline{n} \Sigma \{\underline{\nu}\} \underline{\sigma} - (\Sigma \underline{\sigma})(\Sigma \{\underline{\nu}\}) = -0.43918 \quad n \Sigma \underline{\sigma}^2 - (\Sigma \underline{\sigma})^2 = 8.4239$$

$$(\underline{n} \Sigma \underline{\sigma}^2 - (\Sigma \underline{\sigma})^2)^{0.5} = 2.902396 \quad \underline{n} \Sigma \{\underline{\nu}\}^2 - \{\Sigma \underline{\nu}\}^2 = 0.108556 \quad (\underline{n} \Sigma \{\underline{\nu}\}^2 - \{\Sigma \underline{\nu}\}^2)^{0.5} = 0.329478$$

$$\{\underline{\nu}_1\} = \{\underline{\nu}_o\} + \{\rho\} \underline{\sigma} \quad R = -0.45926 \quad R^2 = 0.210920151$$

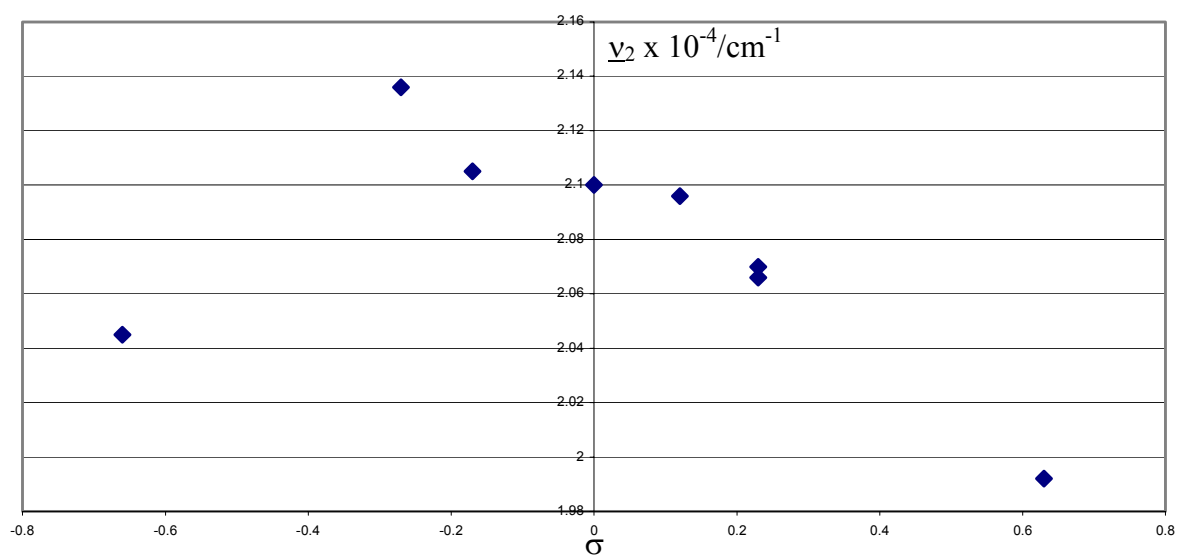
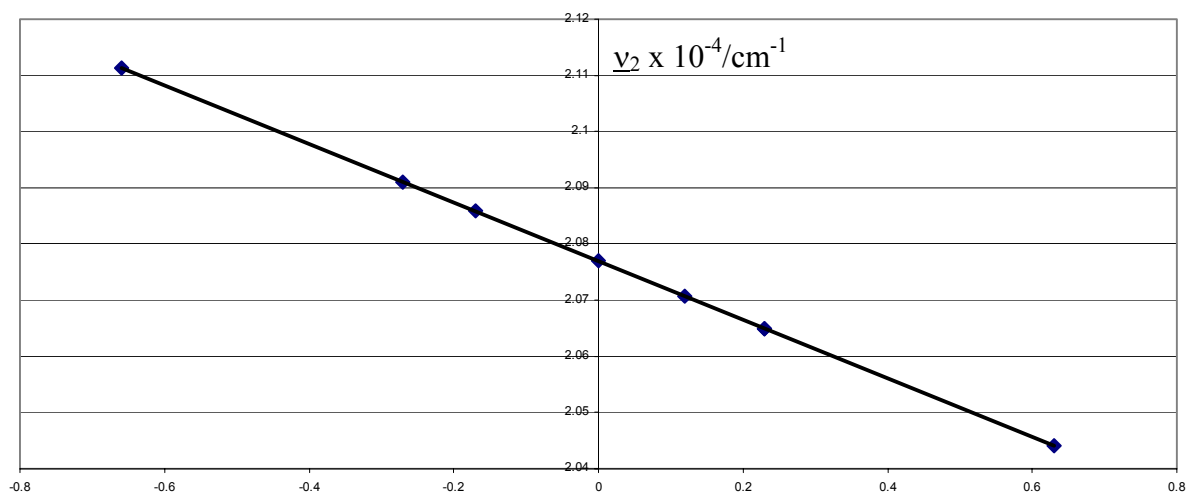


Figure 2a



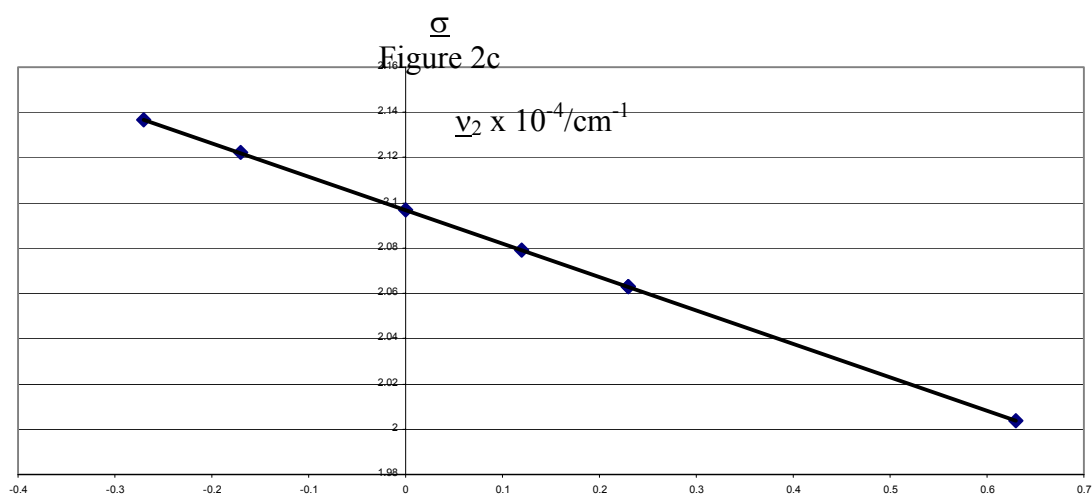
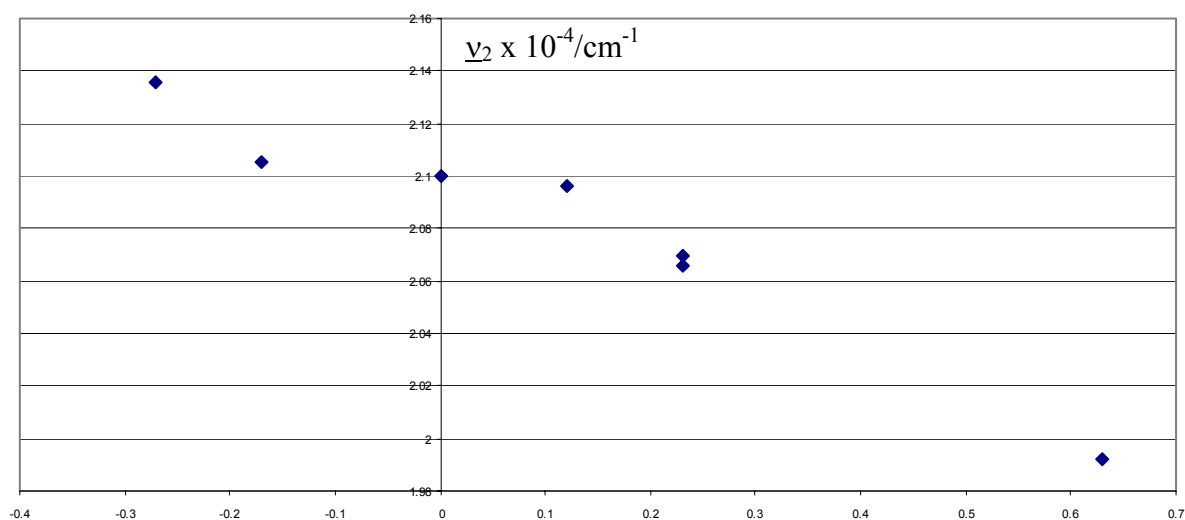
Figs. 2a and b. Wave numbers $\tilde{\nu}_2$ and $\tilde{\nu}_2$ of ferrocenylidene vs. the Hammett constant $\underline{\sigma}$ with the NH_2 value.

$\underline{\sigma}$	$\{\tilde{\nu}_2\}$	$\underline{\sigma}\{\tilde{\nu}_2\}$	$\underline{\sigma}^2$	$\{\tilde{\nu}_2^2\}$	$\underline{\sigma}$	$\{\tilde{\nu}_2\}$
-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	0.23000	2.062977
0.230000	2.07000	0.4761	0.0529	4.2849	0.23000	2.062977
0.630000	1.99200	1.25496	0.3969	3.968064	0.63000	2.003853
$\Sigma \underline{\sigma}$	$\Sigma \{\underline{\nu}\}$	$\Sigma \underline{\sigma} \underline{\nu}$	$\Sigma \underline{\sigma}^2$	$(\Sigma \underline{\sigma})^2$	$\Sigma \{\underline{\nu}^2\}$	$(\Sigma \{\underline{\nu}\})^2$
0.77000	14.56500	1.52319	0.6189	0.5929	30.31806	212.1392

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

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

$$\{\nu_1\} = \{\nu_o\} + \{\rho\} \underline{\sigma} \quad R = -0.96808 \quad R^2 = 0.937176654$$



Figs. 2c and d. Wave numbers $\tilde{\nu}_2$ and $\tilde{\nu}_2^-$ of ferrocenylidene vs. the Hammett constant $\underline{\sigma}$ without the NH_2 value.