BRIDGED FERROCENES
III*. THE VISIBLE AND NEAR ULTRAVIOLET ABSORPTION SPECTRA OF [m]FERROCENOPHANES AND RELATED COMPOUNDS

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(Received August 6th, 1968)

SUMMARY

The visible and near ultraviolet absorption spectra of a range of heteroannularly bridged ferrocene derivatives have been recorded and compared with those of analogous non-bridged compounds. The results have shown that the absorption bands appearing in this region are sensitive to the presence of ring substituents, particularly those capable of conjugative interaction with the cyclopentadienyl system. The band appearing at 440 nm in the ferrocene spectrum also responds to ring-tilt deformation of the ferrocene nucleus. The findings are discussed in relation to current theories of the electronic structure of ferrocene.

INTRODUCTION

Within the framework of the various bonding theories, the electronic absorption spectrum of ferrocene has been discussed in several publications[2-7]. The long wavelength region of this spectrum is characterised by the presence of two broad relatively weak maxima at 325 nm ($\varepsilon \sim 50$) and 440 nm ($\varepsilon \sim 90$) and it is generally agreed that these bands represent symmetry-forbidden excitations of electrons from orbitals of pronounced metals d character**. These transitions gain allowance through vibrational distortion in the molecule. Weaker bands ($\varepsilon < 10$), which appear as shoulders on the low energy tail of the 440 nm band, have also been detected[3-5] and these have been attributed to spin-forbidden singlet→triplet transitions arising through spin orbital coupling[3,5].

The precise nature of the electronic transitions responsible for the 325 nm and 440 nm absorptions is a topic of controversy within the general debate regarding the electronic structure of ferrocene. They were originally interpreted by Jaffé as intramolecular charge transfer bands involving promotion of electrons from iron d orbitals to ring π orbitals[9]. From consideration of a ligand field model, this conclusion has been questioned by Scott and Becker who have assigned[10] these bands respectively to

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* For Part I, see ref. 1a; Part II, see ref. 1b.
** A different view has been taken by Lundquist and Cais who have assigned these bands to electronic transitions in the ring–metal bonds[8].

$$e_{2g}(3d_{xy, x^2-y^2}) \rightarrow e_{1g}(3d_{xz, yz}) \text{ and } a_{1g}(3d_{z^2}) \rightarrow e_{1g}$$

transitions between iron orbitals split by the perturbing field of the cyclopentadienyl ligands*.

An essentially similar conclusion has been reached by McGlynn[11] and Schacht-schneider[12] and their coworkers from semi-empirical MO calculations. These treatments concur in assigning the a_{1g} level as a relatively pure Fe $3d_{z^2}$ orbital but a small significant contribution of cyclopentadienyl orbital character to the e_{1g} and e_{2g} levels is inherent to these descriptions. Earlier ferrocene bonding theories have been critically discussed by Rosenblum[13] and correlated with spectral data by Scott and Becker[3].

Details of the electronic spectra of a large number of substituted ferrocenes have been described[14-17]. These studies have shown that the bands in the visible region are sensitive to the presence and nature of substituents and that resonance interaction between the ferrocene rings is minimal. We have carried out a systematic investigation of the visible and near ultraviolet absorption spectra of ferrocene derivatives in which the rings are linked by bridging groups of various types (*i.e.* [m]-ferrocenophanes). These compounds possess much less conformational freedom than non-bridged analogues[1b] such that interpretation of the modes of substituent interaction in their spectral properties may be made more readily. The effect of cyclopentadienyl ring tilting has also been studied and the results have been analysed in the light of current electronic theories.

EXPERIMENTAL

All of the spectra were recorded at ambient temperature using balanced 1 cm silica cells on a Unicam SP800A spectrometer calibrated against holmium film. Absolute ethanol solutions were used. At least two determinations of each spectrum were carried out and reproducible results were obtained. Sample purity was checked by thin-layer chromatography. The methods of preparation of most of the compounds have been described previously[1a,18]. The new derivatives cited have been fully characterised (analysis, etc.) and their syntheses will be described in a forthcoming publication.

RESULTS AND DISCUSSION

For convenience, the bands appearing at 325 nm and 440 nm in the ferrocene spectrum will be referred to as Band I and Band II respectively. A further weak band, appearing as a shoulder on the lower energy side of Band II, was detected in all of the spectra examined. Because of the imprecision in determining the position and intensity of this absorption, it has not been studied further. In the following discussion, the spectra of alkyl-, alkenyl-, acyl-, and diacyl-ferrocenes will be considered in turn.

Alkylferrocenes. The absorption bands appearing in the spectra of a range of heteroannularly substituted dialkylferrocenes are given in Table 1. With non-bridged

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* An earlier ligand field treatment by Matsen[2] led to different and intrinsically less acceptable conclusions (see refs. 3, 10).

TABLE 1

ABSORPTION MAXIMA OF ALKYLFERROCENES[a]

| Compound	Band I		Band II	
	λ_{max} (nm)	ε	λ_{max} (nm)	ε
Ferrocene	325	50	440	90
Non-bridged alkylferrocenes				
1,1'-Dimethylferrocene	325	60	437	100
1,1'-Diethylferrocene	325	70	438	105
1,1'-Diisopropylferrocene	322	90	439	100
1,1'-Di(tert-butyl)ferrocene	326	275	442	105
1,1'-Dibenzylferrocene	324[d]	105[d]	438	125
1,1'-Di(methoxymethyl)ferrocene	324	75	434	110
Bridged alkylferrocenes[b]				
I (R = Me, n=0)	326	105	466	460
I (R = H, n = 1)	319	85	442	185
I (R = H, n = 2)	323	70	433	100
I (R = H, n = 3)	329	110	448	110
II (R = H)	320	85	443	220
II (R = Me)[c]	321	80	443	215
III (R = H)	320	80	442	225
III (R = Ph)[c]	320	90	442	225
IV	324[e]	105[e]	438	105
V	317[e]	115[e]	444	210

[a] In absolute EtOH. [b] Formulae in text. [c] Stereoisomeric forms give identical spectra. [d] Shoulder. [e] Inflection.

compounds, the modest progressive intensification of Band I, which occurs as the rings are substituted in turn by Me, Et, iso-Pr, and tert-Bu groups, parallels the relative electron-releasing capacities of these substituents when attached to an aromatic nucleus[19]. The intensity of Band II, on the other hand, is relatively insensitive to the presence of alkyl substituents and the position of maximum absorption for both bands varies little through the series*. The spectra of those compounds containing a CH_2R groups (e.g. R = OMe) attached to each ring are similar to that of the diethyl derivative (R = Me).

(I)   (II)   (III)

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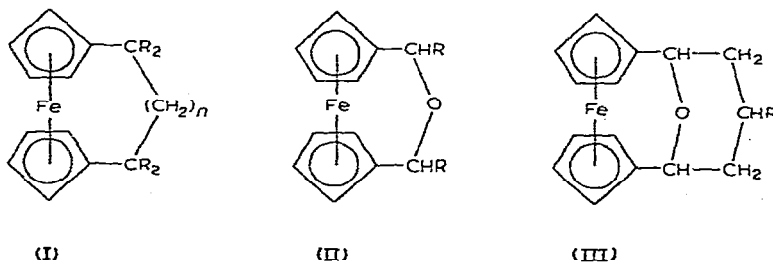
* From semi-empirical MO calculations, a red shift has been predicted for the ferrocene low energy bands when electron-donor groups are substituted in the rings[11].

As discussed briefly elsewhere[1b], much greater variation is shown in the spectra of heteroannularly alkyl-bridged ferrocenes. Thus, while the spectra of [4]- and [5]ferrocenophane (I; R = H, n = 2 and 3 respectively) are similar to those of non-bridged models*, a marked intensification of Band II is observed for related derivatives containing a 3-carbon (I; R = H, n = 1) and 2-carbon (I; R = Me, n = 0) bridge. This is much more pronounced with the latter compound whose maximum has also undergone a strong bathochromic shift. The spectra of the 2-oxa[3]ferrocenophanes (II; R = H and Me) and the related bridged tetrahydropyrans (III; R = H and Ph) show a similar effect and this is well demonstrated by the values for the isomeric ethers (IV) and (V); Band II is twice as intense and appears at longer wavelength in the spectrum of the heteroannularly bridged isomer (V). The position and intensity of Band I in the spectra of all of these ferrocenophanes, on the other hand, are similar to the values for analogous non-bridged derivatives.

(IV)   (V)
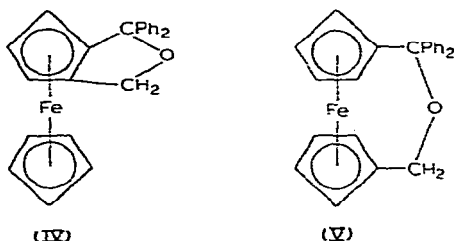
The sensitivity of Band II to interannular bridging and more particularly to the length of the connecting bridge cannot be rationalised in terms of variations in molecular symmetry or vibrational freedom. Since both Bands I and II represent symmetry-forbidden transitions (see Introduction) a qualitatively similar response to alterations in either of these variables would be expected whereas the latter absorption is selectively affected. The results can neither be satisfactorily attributed to differences in the inductive characteristics of the various bridging groups since the spectra of the non-bridged compounds have shown (*vide supra*) that Band I is the more sensitive to electronic influences of this nature.

Crystallographic studies have revealed that the ferrocene rings are displaced from their preferred parallel plane arrangement when they are connected by short ($\leqslant$ 3 atom) chains. The dihedral angle of ring tilt has been found to be *ca.* 9° in the case of the [3]ketone (IX; n = 1)[20] and *ca.* 23° for the [2]ferrocenophane (I; R = Me, n = 0)[21]. From these data and from inspection of Dreiding models, it can be inferred that the ferrocene nucleus would remain undistorted in the presence of longer bridges (*i.e.* I; n > 1). Further, it is clear from the results discussed above that the intensification of Band II in the spectra of [m]ferrocenophanes parallels the extent by which the cyclopentadienyl rings deviate from their normal sandwich geometry.

From MO calculations, Ballhausen and Dahl have concluded[22] that the strength of metal-ring bonding in metallocenes is relatively unaffected by ring-tilt

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* Comparison of the spectra of related derivatives in the [4]-and [5]-series (*cf.* I, VIII, IX, and X) has shown that the Band II maximum for a compound of the former type consistently appears at shorter wavelength (up to *ca.* 15 nm) than that of the analogue of longer bridge length.

distortion provided that the dihedral angle between ring planes does not exceed 45°. In such a situation, the altered molecular geometry promotes mixing of the non-bonding a_{1g} and e_{2g} levels. Since Bands I and II in the ferrocene spectrum apparently (see Introduction) represent electronic excitations from these energy levels, ring-tilt induced changes in their relative location would be reflected in accompanying changes in visible absorption. A qualitatively similar conclusion would derive from the ligand field formalism[10] since the splitting of the iron d orbitals would vary with the relative positioning of the rings about the metal atom.

The experimental results discussed above lead to the conclusion that the a_{1g} level in ferrocene is the more sensitive of the non-bonding orbitals to ring-tilt deformation since Band II is selectively affected. Correlation of these findings with further calculations based both on the ligand field and MO treatments should provide insight into the relative merits of these approaches.

Alkenylferrocenes. The electronic spectra of simple non-bridged alkenylferrocenes contain five distinct absorption maxima of which the three short wavelength bands most probably represent transitions of the $N \rightarrow V$ type. Bands I and II in these spectra are enhanced compared with the values for alkylferrocenes (Table 2). The

TABLE 2

ABSORPTION MAXIMA OF ALKENYLFERROCENES[a]

Compound	Band I		Band II	
	λ_{max} (nm)	ε	λ_{max} (nm)	ε
Non-bridged compounds				
Vinylferrocene	333[c]	505[c]	446	250
trans-(3-Phenyl-1-propenyl)ferrocene	334[c]	605[c]	446	300
trans-Styrylferrocene	352[c]	2360[c]	455	1000
Bridged compounds[b]				
VI	329	90	448	110
VII	327	85	448	110
VIII (R = OAc, n = 1)	318[c]	100[c]	443	200
VIII (R = OAc, n = 2)	327[d]	295[d]	429	120
VIII (R = OAc, n = 3)	334[c]	295[c]	439	155
VIII (R = H, n = 3)	334[c]	270[c]	440	145

[a] In absolute EtOH. [b] Formulae in text. [c] Shoulder. [d] Inflection.

former appears as a shoulder or inflection on the tail of a broad intense UV band which is extremely sensitive both in position and intensity to the nature of the substituent conjugated with the cyclopentadienyl ring. This absorption has been assigned as a $\pi \rightarrow \pi^*$ transition by Schlögl whose group has reported[16] a detailed study of the absorption spectra of a range of unsaturated ferrocenes. The overlap of these bands, however, precludes accurate assessment of the position and intensity of Band I and the uncorrected values given in Table 2 may be misleading.

In agreement with previous findings[16a], Band II undergoes a progressive blue shift with intensification as conjugation in the substituent group is extended. This is apparent from the values for ferrocene, vinylferrocene, and *trans*-styrylferrocene. This marked sensitivity to conjugative influences suggests that some measure of charge

transfer (metal → ring) character is associated with this transition. These results, therefore, are in accord with the conclusion[11,12] (see Introduction) that the e_{1g} level in ferrocene contains a significant contribution from ligand orbitals. They do not, however, necessarily invalidate the ligand field model[10] since the splitting pattern of the Fe d orbitals would be affected by variations in electron density distribution (and hence electrostatic field) associated with the cyclopentadienyl ligands.

(VI)   (VII)   (VIII)
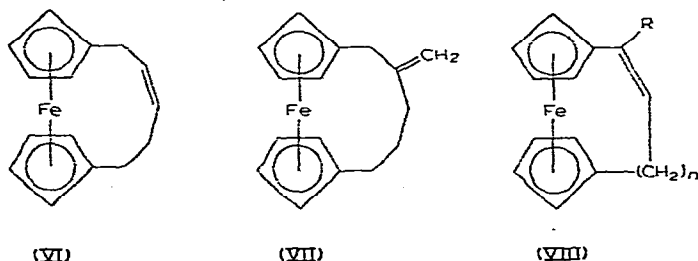
The $\beta\gamma$-unsaturated [5]ferrocenophanes (VI and VII) give spectra essentially identical with that of the saturated parent compound (I; R = H, n = 3). Thus, although the unsaturated centres in these molecules are constrained to environments close to the metal, there is no evidence of interaction between filled Fe d orbitals and empty π^* orbitals associated with the double bonds.

From study of the UV spectra of bridged alkenyl-ferrocenes of the type (VIII), we have previously shown[1a] that conjugation between the cyclopentadienyl ring and an attached double bond is conformationally possible in the [5]-series (VIII; n = 3). In contrast, the double bond in the [3]-analogue (VIII; n = 1) is unable to attain a conformation in the adjacent ring plane and conjugative interaction is precluded[23]. The visible absorption characteristics of these compounds are also affected by conjugation. By comparison with the respective values for the corresponding saturated analogues (I; R = H, n = 1–3) given in Table 1, it is apparent that the intensities of both Bands I and II for the ferrocenophanenes (VIII; n = 1–3) increase with increasing bridge length.

TABLE 3

ABSORPTION MAXIMA OF ACYLFERROCENES[a]

Compound	Band I Region				Band II	
	λ_{max} (nm)	ε	λ_{max} (nm)	ε	λ_{max} (nm)	ε
Non-bridged compounds						
Acetylferrocene	337	1190	358[d]	745[d]	458	470
Acryloylferrocene	373	1550	—	—	484	1105
trans-Crotonoylferrocene	369	1655	—	—	478	1055
trans-Cinnamoylferrocene	386	1840	—	—	504	1820
Bridged Compounds[b]						
IX (n = 1)	336	935	—	—	448	305
IX (n = 2)	340	1415	—	—	443	490
IX (n = 3)	343	1330	368[d]	705[d]	456	525
X (n = 1)	317	500	—	—	436	110
X (n = 2)	308[c]	640[c]	—	—	450	125

[a] In absolute EtOH. [b] Formulae in text. [c] Shoulder. [d] Inflection.

Acylferrocenes. The long wavelength absorption bands for a series of acylferro-cenes and ferrocenophanones are given in Table 3. These data show that the presence of a carbonyl group attached to the ferrocene nucleus causes a blue shift and intensi-fication of Band II. These effects both become more pronounced as conjugation in the substituent group is extended (*cf.* values for acetyl-, acryloyl-, and *trans*-cinna-moyl-ferrocene).

(IX)   (X)
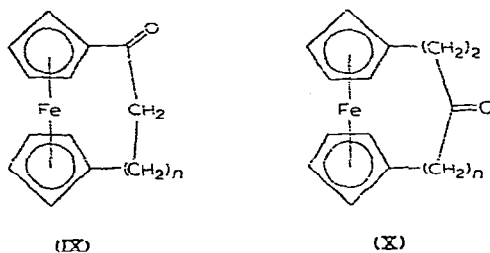
As in the case of the bridged alkenylferrocenes discussed above, conjugation between the carbonyl and cyclopentadienyl π-systems in the bridged ketones (IX; $n = 1$–3) is reduced as the bridge is shortened and the oxygen atom thereby displaced from the ring plane (*cf.* crystal structure[20]). In the spectra of these compounds, the response of Band II to conjugative influence can be seen from the increase in intensity as the bridge is lengthened and p_π–p_π orbital overlap becomes more significant. With the keto-ferrocenes (X; $n = 1$ and 2), intensity of Band II is unaffected.

Investigation of the behaviour of Band I in the spectra of acylferrocenes is complicated by the presence of an overlapping band which has been noted in other studies[7,14c] and has been interpreted[14c] as an intramolecular charge transfer absorp-tion associated with the carbonyl chromophore. In the spectra of the ketones examined in the present study, Band I is either obscured or appears as an *inflection on the low* energy side of this additional band and an accurate estimate of its position and intensity could not be obtained.

TABLE 4

ABSORPTION MAXIMA OF DIACYLFERROCENES[a]

Compound	Band I Region				Band II	
	λ_{max} (nm)	ε	λ_{max} (nm)	ε	λ_{max} (nm)	ε
Non-bridged compounds						
1,2-Diformylferrocene	334	1045	381	1380	458	1045
1,1'-Diformylferrocene	333	1665	371[d]	840[d]	470	600
1,2-Diacetylferrocene	340[c]	1080[c]	370	1310	451	690
1,1'-Diacetylferrocene	332	1755	365[c]	900[c]	464	510
1-Acetyl-1'-acryloylferrocene	348[c]	1645[c]	362	1680	476	855
Bridged compounds[b]						
XI (R = R' = H)	342	1880	—	—	462	345
XI (R = H, R' = Ph)	348	2025	—	—	455	300
XI (R = Me, R' = H)	341	1865	—	—	465	365
XI (R = CH₂OEt, R' = H)	342	1965	—	—	465	385

[a] In absolute EtOH. [b] Formulae in text. [c] Shoulder. [d] Inflection.

Diacylferrocenes. The absorption spectra of diacylferrocenes (Table 4) are broadly similar in feature to those of the related monoacyl derivatives. Thus, only a relatively small further intensification and blue shift of Band II occurs on substitution of an acyl group in the unsubstituted ring of an acylferrocene. The results are at variance, therefore, with the suggestion[17b] that the position and intensity of Band II for heteroannularly disubstituted ferrocenes can be calculated on the assumption that each substituent causes an additive modification of the spectrum. Substitution of a second acyl group in the 2-position of an acyl-substituted ring causes a greater intensification of Band II which is red-shifted compared with the value for the heteroannularly substituted isomer.
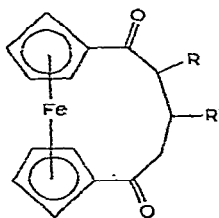
(XI)

The spectra of [5]ferrocenophane-1,5-diones (XI) are interesting in that the intensity of Band II is significantly depressed compared with the values for related monoketones (*e.g.* IX; $n = 3$). This may be due to conformational constraints in the dione bridges which hinder the attainment by the carbonyl groups of coplanarity with the adjacent rings.

As with monoacylferrocenes (*vide supra*), the Band I spectral region for the non-bridged diketones contains two overlapping absorptions which are particularly distinct in the spectra of 1,2-diacylferrocenes. Although only one maximum is discernible in the spectra of the bridged diketones (XI), the presence of an obscured absorption band appears probable. Unambiguous interprepation of these absorption curves is consequently difficult and further analysis has not been carried out.

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