

The per cent of enol in diethyl oxaloacetate neat and of oxaloacetic acid in methanol and in water was determined by using the integrator on the CH_2 and $=\text{CH}$ peaks. The per cent of enol of diethyl oxaloacetate in methanol and the per cent of enol of oxaloacetic acid in 40% water-methanol was determined from the CH_2 and $=\text{CH}$ peak heights and widths, as this method appeared more accurate than using the integrator because of the interference of the strong methyl signal from the solvent.

The large difference between the 79% enol in neat diethyl oxaloacetate and the 8% enol in oxaloacetic acid in water solution is in keeping with the shift towards the enol form of compounds in the pure state or in nonpolar solvents as compared with the per cent of enol in water. Acetyl acetone neat, is 80%¹⁶ enol but only 15%¹⁷ enol in water.

The NMR spectrum of diethyl fluoroaxaloacetate which was measured neat is of interest in this connection. It contains peaks for the CH_3 , CH_2 and $\text{F}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{H}$ hydrogens only and indicates the compound is of high purity. It contains no peak for an enolic hydrogen and the peak for the hydrogen on the carbon to which fluorine is attached is split into two peaks which have a separation of 47 c.p.s. This is the amount of separation in keeping with what is expected for a spin-spin splitting resulting from a fluorine atom on the same carbon atom. The NMR spectrum therefore indicates this compound is 100% keto.

It is interesting that substitution of a fluorine for a hydrogen in diethyl acetoacetate would have such a large effect that it increased the per cent of keto from 21 to 100%. It is not without precedence, however, for introduction of a halogen to increase the per cent of keto in a compound. Introduction of a bromine into acetylacetone increases the per cent of keto from 84.5 to 91.9% when both are measured in water.

Of considerable interest is the finding that although we start out with what is quite pure oxaloacetic acid, the NMR spectrum of the water solution indicates the presence of peaks which are not accounted for by the enol and keto forms of oxaloacetic acid. When the total amount of hydrogen in oxaloacetic acid is measured in deuterium oxide using the integrator, about 80% shows up as HDO, indicating it has exchanged, while 20% is present as some other form that has not exchanged. As we used 0.1 g. of oxaloacetic acid in 1.0 g. of deuterium oxide, the number of equivalents of deuterium calculated to be present is $1.0 \times 2/20 = 0.1$ and the number of equivalents of hydrogen from the oxaloacetic acid is $0.1 \times 4/132 = 0.003$. If the exchange takes place on a purely statistical basis, then $(0.003 \times 100/0.1 = 3\%)$ only 3% of the hydrogen should show up in forms other than HDO. The fact that 20% of the hydrogen has not exchanged indicates appreciable amounts of other species are present in water solutions of oxaloacetic acid and their nature is a matter for further study.

SAN FRANCISCO, CALIF.
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(16) J. B. Conant and A. F. Thompson, Jr., *J. Am. Chem. Soc.*, **54**, 4039 (1932).

(17) G. Schwarzenbach and E. Felder, *Helv. Chim. Acta*, **27**, 1044 (1944).

[CONTRIBUTION FROM THE DETROIT RESEARCH LABORATORIES OF ETHYL CORPORATION AND THE DEPARTMENT OF CHEMISTRY, ISRAEL INSTITUTE OF TECHNOLOGY]

Ultraviolet Spectra of Organometallic Compounds^{1,2}

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Evidence is presented for the existence of electronic absorption bands typical of the transition metal-carbon bond. This evidence is based on a correlative qualitative study of the ultraviolet spectra of organo derivatives of iron, manganese, chromium, and molybdenum. The characteristic features of these spectra are described.

The discovery of dicyclopentadienyliron (ferrocene)⁴ and the subsequent proposal⁵ of the *pi*-

bonded "sandwich" structure for this compound has led to the synthesis of a large number of new com-

(1) A preliminary report of this paper was presented at the Meeting of the XVIIth International Congress of Pure and Applied Chemistry, Munich, September 1959, see M. Cais and R. T. Lundquist, Abstracts of Papers, A104; and the 7th Detroit Anachem Conference, Detroit, Mich., October 1959.

(2) "Organometallic Studies," part VI in the Israel Institute of Technology Series. Part V, M. Cais and M. Feldkimmel, *Tetrahedron Letters*, **13**, 444 (1961).

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(4) T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).

(5) R. B. Woodward, M. Rosenblum, and M. C. Whiting, *J. Am. Chem. Soc.*, **74**, 3458 (1952).

pounds containing different types of metal-carbon bonds. Simultaneously, the application of various physicochemical techniques to these new compounds has provided data which allowed for the proposal of chemical structures and which cast new light on the different theories of the metal-carbon bonds.

The measurement of the electronic absorption spectra of this new type of compound appeared to be a physicochemical method which could provide useful data about the electronic interactions in the transition metal-carbon bonds. A literature search yielded few data on the ultraviolet spectra of organometallics. Therefore, the spectra of representative types of compounds were measured to provide a possible basis for structure-spectral correlations. The compounds studied can be roughly divided into the following groups: metallocarbonyls, substituted metallocarbonyls (σ -bonded), substituted metallocarbonyls (π -bonded), alkyl substituted ferrocenes, and phenyl substituted ferrocenes.

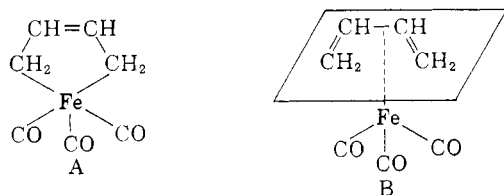
EXPERIMENTAL

Absorption spectra between 214 $m\mu$ and 700 $m\mu$ were obtained using a Cary Model 10-S recording spectrophotometer. Approximately 15 mg. of sample, accurately weighed, was dissolved in 95% ethanol. Appropriate dilutions were made to obtain transmittances in the range of 10 to 80%. The spectra were recorded using 1-cm. quartz cells with the solvent in the reference beam.

The molar extinction coefficients and their logarithms were then determined at intervals of 4 $m\mu$ using a Burroughs E-102 digital computer.

RESULTS AND DISCUSSION

The formation of butadieneiron tricarbonyl (I) was first reported by Reihlen *et al.*,⁶ who suggested structure A for this compound. Recently, Hallam and Pauson⁷ prepared butadieneiron tricarbonyl and cyclohexadieneiron tricarbonyl (II).



On the basis of chemical evidence structure B was suggested. Subsequently, Mills and Robinson⁸ determined the structure of butadieneiron tricarbonyl by X-ray methods. They also concluded that the bonding, as shown in B, is that of a π -complex.

Hallam and Pauson reported an intense maximum for I at 211 $m\mu$ (in ethanol), $\log \epsilon$ 4.36, and a

maximum for II at 207 $m\mu$, $\log \epsilon$ 4.36. They compared these data to the maximum at 217 $m\mu$ in the spectrum of butadiene gas.⁹ They assumed that the 211- $m\mu$ band was the K-band¹⁰ expected of a conjugated diene system, which would further confirm structure B.

In the present study, measurements of the ultraviolet spectrum of I did not give the maximum at 211 $m\mu$ because of the limitation of the instrument used, but did give a highly intense end absorption at 214 $m\mu$, $\log \epsilon$ 4.33. To investigate the effect of the iron tricarbonyl moiety on the spectrum of I, we measured the spectrum of iron pentacarbonyl (III), which can be regarded as the parent compound of I. The spectra of other metal carbonyls, such as chromium hexacarbonyl (IV) and manganese pentacarbonyl dimer (V), also were measured.

The spectra of Figure 1 show highly intense end

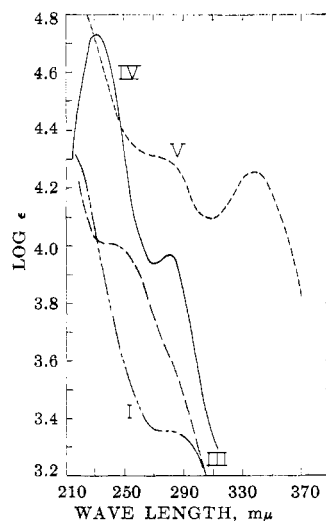


Fig. 1. Metal carbonyls

- I. (1,3-Butadiene)iron tricarbonyl
 III. Iron pentacarbonyl
 IV. Chromium hexacarbonyl
 V. Manganese pentacarbonyl dimer

absorption for III and V in the region of 210–230 $m\mu$ and a well defined maximum for IV (λ_{\max} 230 $m\mu$, $\log \epsilon$ 4.73). Furthermore, all compounds containing the metal-carbonyl moiety were found to exhibit this highly intense end absorption. The experimental conditions and results obtained—namely, the instrument used, the reproducible results with concentration variations, and the intensity of the end absorptions—preclude the possibility that these maxima are due to scattered light. Consequently, assignment of structures such as B to compounds of type I on the basis of the short wave length bands is of doubtful validity.

The spectrum of butadieneiron tricarbonyl (I) showed an absorption band of much lower intensity ($\log \epsilon$ 3.39) at 278 $m\mu$; this band was not reported

(6) H. Reihlen, A. Gruhl, G. V. Hessling, and O. Pfengle, *Annalen*, **482**, 161 (1930).

(7) B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 642 (1958).

(8) O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 421 (1960).

(9) A. Smakula, *Angew. Chem.*, **47**, 657 (1934).

(10) A. E. Gillam and E. S. Stearn, "Electronic Absorption Spectroscopy," Edward Arnold Ltd., London, 2nd Ed., 1957, p. 128.

by Hallam and Pauson.⁷ A band of similar intensity ($\log \epsilon$ 3.58) in the form of an inflection at 282 $m\mu$ was shown by iron pentacarbonyl (III) and a more intense absorption ($\log \epsilon$ 3.97) at 280 $m\mu$ was shown by chromium hexacarbonyl (IV) (Fig. 1). Similar bands were observed in the absorption spectra of all the organometallic compounds studied. These bands may appear over a wide range of the spectrum and both the wave length maxima and the intensities of absorption vary with the type of organic moiety as well as with the metal atom. It is suggested that these bands may be due to electronic transitions involving the transition metal-carbon bond and consequently could be a characteristic feature of all compounds containing such bonds. For convenience, these bands will be referred to as MC (metal-carbon) bands. This study was limited to the longer wave length MC-bands. The highly intense end absorptions of the carbonyl derivatives very likely are also MC-bands, but their properties were not studied as the instrument and techniques used were not suitable for measurements below 214 $m\mu$.

MC-bands in the spectra of methylmanganese pentacarbonyl (VI), (tri-fluoromethyl)manganese pentacarbonyl (VII), acetylmanganese pentacarbonyl (VIII), and (trifluoroacetyl)manganese pentacarbonyl (IX) are shown in Fig. 2. Replacement of

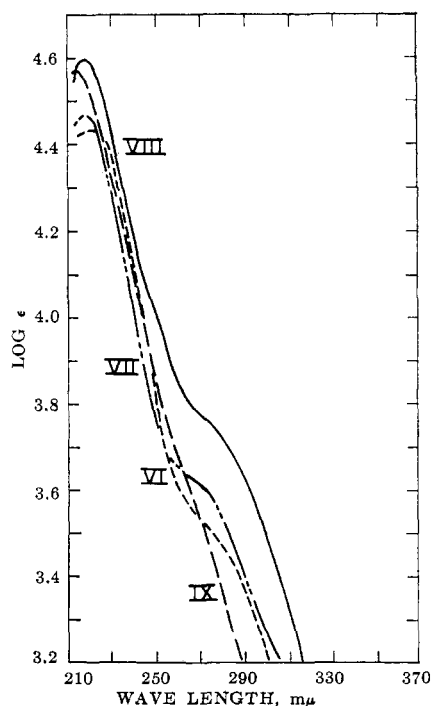
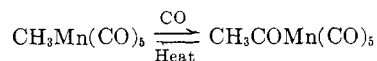


Fig. 2. Substituted manganese pentacarbonyl derivatives
VI. Methylmanganese pentacarbonyl
VII. (Trifluoromethyl)manganese pentacarbonyl
VIII. Acetylmanganese pentacarbonyl
IX. (Trifluoroacetyl)manganese pentacarbonyl

the electron-releasing methyl group in VI by the strongly electron-withdrawing group in VII causes a hypsochromic shift of the MC-band from 278 $m\mu$ to

270 $m\mu$. A smaller hypsochromic shift, from 278 $m\mu$ to 274 $m\mu$, is observed when the methyl group of VI is replaced by the electronegative carbonyl group in VIII.

The introduction of a carbonyl group between the alkyl radical and the manganese pentacarbonyl moiety causes a noticeable increase in the intensity of the MC-band. This effect suggests that the additional ketonic carbonyl group takes on, at least partially, the same character as the other five metal-carbonyl groups in VIII and as such it has a similar effect in increasing the intensity of the MC-band. Tracer studies¹¹ of the reaction:



support this suggestion and one could envisage a resonating structure¹² such as:

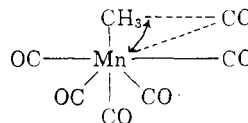


Fig. 3 shows the spectra of cyclopentadienylmanganese tricarbonyl (X), (methylcyclopenta-

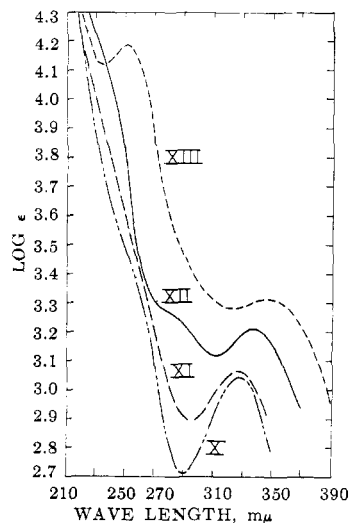


Fig. 3. Cyclopentadienylmanganese tricarbonyl and derivatives

- X. Cyclopentadienylmanganese tricarbonyl
XI. (Methylcyclopentadienyl)manganese tricarbonyl
XII. (Acetylcyclopentadienyl)manganese tricarbonyl
XIII. (Benzoylcyclopentadienyl)manganese tricarbonyl

dienyl)manganese tricarbonyl (XI), (acetylcyclopentadienyl)manganese tricarbonyl (XII), and (benzoylcyclopentadienyl)manganese tricarbonyl (XIII). The appearance of the MC-band is well illustrated by these spectra. A comparison of these spectra with those of the manganese pentacarbonyl derivatives in Fig. 2 shows two interesting effects:

1. A marked decrease in the intensity of absorp-

(11) T. H. Coffield, J. Kozikowski, and R. D. Closson, *Chem. Soc. Spec. Publ.*, No. 13, 126 (1959).

(12) P. L. Pauson, *Proc. Chem. Soc.*, 303 (1960).

tion. This effect might be ascribed to the smaller number of carbonyl groups attached to the metal atom (three instead of five). It is apparent that the number of carbonyl groups attached to the metal atom has a direct influence on the intensity of absorption of the MC-band.

2. A large bathochromic shift of the MC-band, from about 280 $m\mu$ to about 330 $m\mu$. This shift might be ascribed to the conjugative effect of the aromatic cyclopentadienyl moiety. The bathochromic shift of the MC-band is analogous to and of similar magnitude to the bathochromic shift of the R- and K-bands¹⁰ in such cases. The magnitude of the bathochromic shift of the MC-band is further affected by additional conjugative effects of substituents on the cyclopentadienyl ring, as illustrated in Table I. These effects will be discussed further in connection with the spectra of ferrocene derivatives.

TABLE I
BATHOCHROMIC SHIFT OF MC-BAND FROM INCREASED CONJUGATION

Compound	MC-Band	
	λ_{max} , $m\mu$	ϵ
$(CO)_3MnC_5H_5$	328	1120
$(CO)_3MnC_5H_4C(=O)CH_3$	338	1640
$(CO)_3MnC_5H_4C(=O)C_6H_5$	348	2040
$(CO)_3Mn$ -indenyl	375	1415
$C_5H_5FeC_5H_5$	325	49
$C_5H_5FeC_5H_4C(=O)CH_3$	337	1713

Fig. 4 shows the spectra of several sulfur derivatives.¹³ The sulfonyl group has only a slight effect on the position of the MC-band of cyclopentadienylmanganese tricarbonyl derivatives. The spectra in Fig. 5 agree with recently published¹⁴ ultraviolet spectral data for several arylchromium tricarbonyl derivatives. Spectra of mesitylenechromium tricarbonyl (XVI) and mesitylenemolybdenum tricarbonyl (XIX) are compared in Fig. 6. These spectra exhibit similar features but the molybdenum derivative shows slightly lower intensities.

From the data discussed above it becomes apparent that in all compounds containing a metal-carbonyl moiety, the effect of the latter predominates in the wave length region below 300 $m\mu$, irrespective of whether the organic moiety is a conjugated diene, a cyclopentadienyl ring, or a benzene ring.

Several authors¹⁵⁻¹⁸ have discussed the spectra of

(13) M. Cais and J. Kozikowski, *J. Am. Chem. Soc.*, **82**, 5667 (1960).

(14) R. Ercoli and A. Mangini, *Ricerca Sci.*, **28**, 2135 (1958).

(15) G. Wilkinson, M. Rosenblum, M. C. Whiting, and R. B. Woodward, *J. Am. Chem. Soc.*, **74**, 2125 (1952).

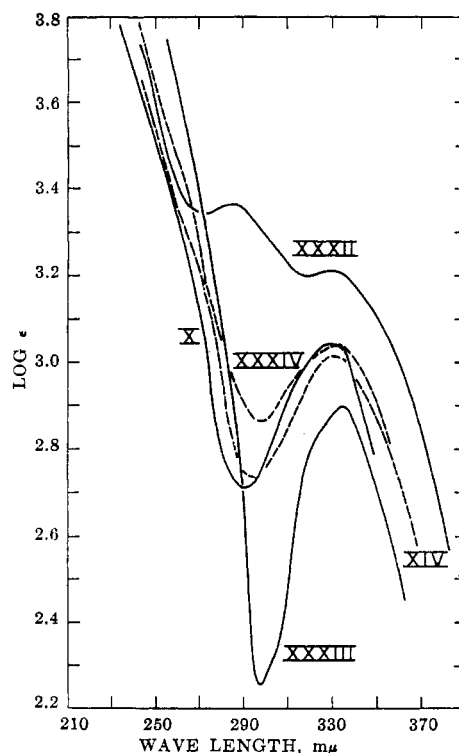


Fig. 4. Sulfonyl derivatives of cyclopentadienylmanganese tricarbonyl

X. Cyclopentadienylmanganese tricarbonyl

XIV. [(Methylsulfonyl)cyclopentadienyl]manganese tricarbonyl

XXXII. [(Chlorosulfonyl)cyclopentadienyl]manganese tricarbonyl

XXXIII. [(*p*-Tolylsulfamoyl)cyclopentadienyl]manganese tricarbonyl

XXXIV. (Sulfinocyclopentadienyl)manganese tricarbonyl

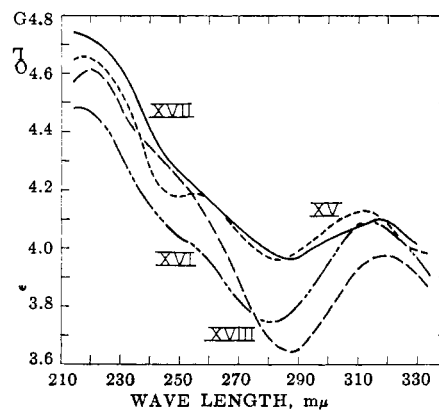


Fig. 5. Benzenechromium tricarbonyl and derivatives

XV. Benzenechromium tricarbonyl

XVI. Mesitylenechromium tricarbonyl

XVII. Anilinechromium tricarbonyl

XVIII. *N,N*-Dimethylanilinechromium tricarbonyl

ferrocene and some of its derivatives. In discussing the electronic structure of ferrocene, Jaffé¹⁸ attributes the longest wave length absorption band (440 $m\mu$) to a charge-transfer transition, and explains

(16) L. Kaplan, W. L. Kester, and J. J. Katz, *J. Am. Chem. Soc.*, **74**, 5531 (1952).

(17) K. L. Rinehart, K. L. Motz, and Sung Moon, *J. Am. Chem. Soc.*, **79**, 2749 (1957).

(18) H. H. Jaffé, *J. Chem. Phys.*, **21**, 156 (1953).

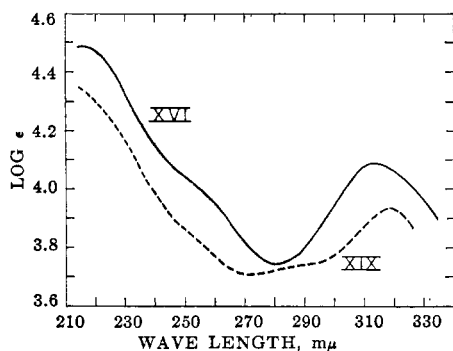


Fig. 6. Mesitylenemetal tricarbonyls
XIX. Mesitylenemolybdenum tricarbonyl
XVI. Mesitylenechromium tricarbonyl

that the low intensity (ϵ 87) is due to a forbidden transition that occurs only because the symmetry is distorted by vibrational motion. He further suggests that the second absorption band (λ_{\max} 326 $m\mu$, ϵ 50) may be of the same nature as the first band, it also being a forbidden transition.

Our data show that the two cyclopentadienyl rings in ferrocene tend to absorb independently. Thus only the 326- $m\mu$ band occurs in the spectrum of cyclopentadienylmanganese tricarbonyl, which contains only one ring. Furthermore, the intensity of this band in the spectrum of cyclopentadienylmanganese tricarbonyl is much higher (ϵ 1120, compared to ϵ 50 for ferrocene). This significant change in the intensity of absorption which occurs when the $-\text{M}(\text{C}_5\text{H}_5)$ moiety is replaced by $-\text{M}(\text{CO})_3$ suggests that for ferrocene and its derivatives the 326- $m\mu$ and 440- $m\mu$ maxima are associated with electronic transitions in the metal-carbon bonds between the cyclopentadienyl rings and the iron atom. The assumption that each ring in ferrocene tends to absorb independently is supported by the data in Table II. Both the 325- $m\mu$ and 440- $m\mu$

TABLE II

EFFECT OF UNSATURATED AND PHENYL RING SUBSTITUENTS
LONG WAVE LENGTH BANDS OF FERROCENE

Compound ^a	λ_{\max} , $m\mu$	ϵ	λ_{\max} , $m\mu$	ϵ
F—H	325	49	440	91
F—COH	342	1339	464	590
F—COCH ₃	337	1713	456	544
F—COOH	(342)	361	445	223
F—CH=CHCH ₂ OH	(345)	470	449	315
F—COCH=CHC ₆ H ₅	383	1960	488	1660
F—CH=CHCOC ₆ H ₅	387	3120	490	2970
F—C ₆ H ₅	(327)	1264	450	380
F—C ₆ H ₄ NO ₂	395	2835	503	2690
F—C ₆ H ₄ CO ₂ Et	362	3100	456	1180
C ₆ H ₅ C ₆ H ₄ FeC ₅ H ₄ C ₆ H ₅	(346)	1674	451	617

^a F = C₅H₅FeC₅H₅.

bands of ferrocene are shifted bathochromically when unsaturated alkyl groups are substituted on the cyclopentadienyl ring. There does not appear to be any particular regularity about this batho-

chromic shift. The intensity of the 325- $m\mu$ band, however, always increases much more than that of the 440- $m\mu$ band.

Irregularities in the bathochromic shifts of the 325- $m\mu$ and 440- $m\mu$ bands were also observed for some phenyl-substituted compounds (Table II). Spectra of some of the ferrocene derivatives are given in Fig. 7 and 8. The data in Table I show that

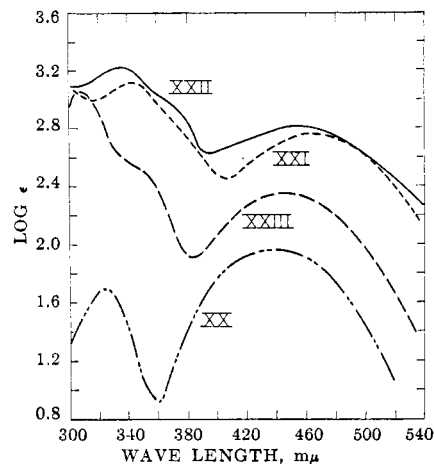


Fig. 7. Dicyclopentadienyliron and some alkyl derivatives
XX. Dicyclopentadienyliron
XXI. Cyclopentadienyl(formylcyclopentadienyl)iron
XXII. Cyclopentadienyl(acetylcyclopentadienyl)iron
XXIII. Cyclopentadienyl(carboxycyclopentadienyl)iron

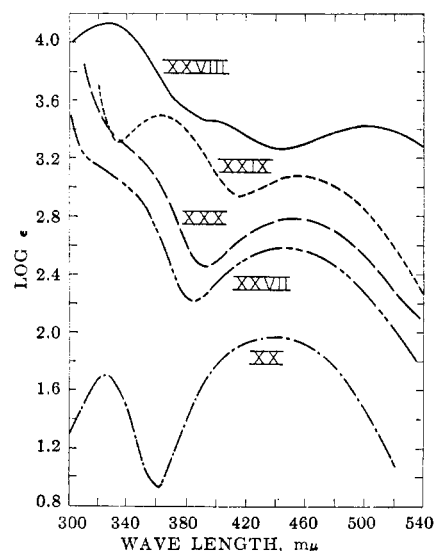


Fig. 8. Dicyclopentadienyliron and some phenyl derivatives

XX. Dicyclopentadienyliron
XXVII. Cyclopentadienyl(phenylcyclopentadienyl)iron
XXVIII. Cyclopentadienyl[(*p*-nitrophenyl)cyclopentadienyl]iron
XXIX. Cyclopentadienyl[(*p*-ethoxycarbonylphenyl)cyclopentadienyl]iron
XXX. Bis(phenylcyclopentadienyl)iron

the 325- $m\mu$ band of both ferrocene and cyclopentadienylmanganese tricarbonyl is affected similarly by substitution of an acetyl group on the ring.

The high intensity bands in the ultraviolet absorption spectra of phenyl-substituted ferrocenes

(Fig. 9-11) show several interesting effects. Two such bands (λ_{\max} 238 $m\mu$, ϵ 18,190 and λ_{\max} 278 $m\mu$, ϵ 11,370) appear in the spectrum of cyclopentadienyl(phenylcyclopentadienyl)iron¹⁹ (XXX);

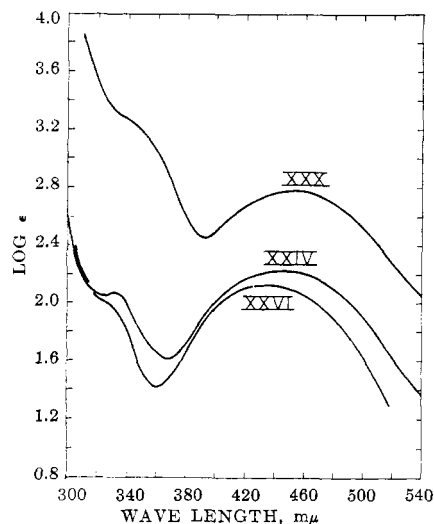


Fig. 9. Some phenyl derivatives of dicyclopentadienyliron

- XXIV. Bis[(α,α -dimethylbenzyl)cyclopentadienyl]iron
 XXVI. Bis(benzylcyclopentadienyl)iron
 XXX. Bis(phenylcyclopentadienyl)iron

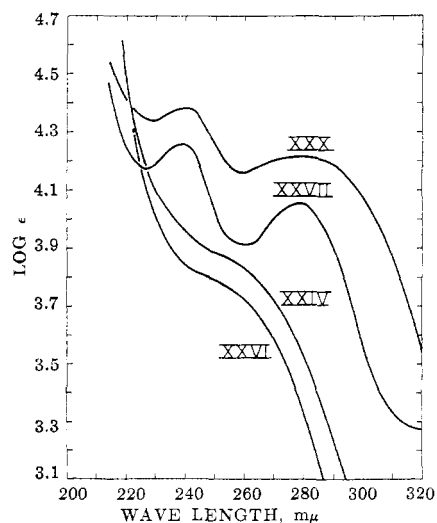


Fig. 10. Some phenyl derivatives of dicyclopentadienyliron

- XXIV. Bis[(α,α -dimethylbenzyl)cyclopentadienyl]iron
 XXVI. Bis(benzylcyclopentadienyl)iron
 XXVII. Cyclopentadienyl(phenylcyclopentadienyl)iron
 XXX. Bis(phenylcyclopentadienyl)iron

tadienyl(phenylcyclopentadienyl)iron¹⁹ (XXVII); these bands are very slightly displaced, though of higher intensity, in the spectrum of bis(phenylcyclopentadienyl)iron¹⁹ (XXX), (λ_{\max} 240 $m\mu$, ϵ 24,190 and λ_{\max} 279 $m\mu$, ϵ 16,315). On the other hand, bis(benzylcyclopentadienyl) iron (XXVI), in which the benzene chromophore is insulated from the ring by a methylene group, has essentially a ferrocene spectrum (Fig. 10).

Thus it appears that each phenylcyclopentadienyl chromophore absorbs as an entity and the

(19) P. L. Pauson, *J. Am. Chem. Soc.*, **76**, 2187 (1954).

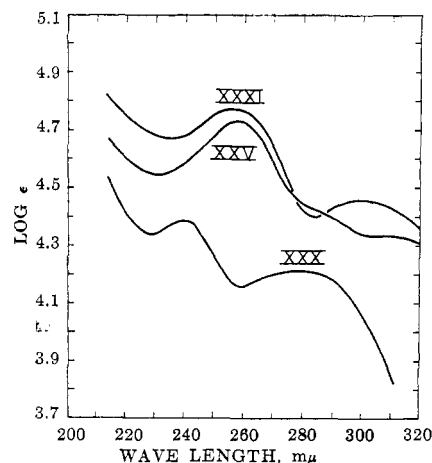


Fig. 11. Some phenyl derivatives of dicyclopentadienyliron

- XXV. Bis(1,3-diphenylcyclopentadienyl)iron
 XXX. Bis(phenylcyclopentadienyl)iron
 XXXI. Bis(1,2,4-triphenylcyclopentadienyl)iron

presence of two such chromophores, connected through the iron atom, as in XXX, causes mainly an additive effect on the intensity of these bands. Consequently, one may conclude that although the iron atom might have some effect in increasing the conjugation on connecting two phenylcyclopentadienyl moieties, this effect is a small one. Compare, for example, the strong bathochromic shifts in passing from $C_6H_5COC_6H_5$ (λ_{\max} 253 $m\mu$, ϵ 18,600)²⁰ through $p-C_6H_5-C_6H_4COC_6H_5$ (λ_{\max} 291 $m\mu$, ϵ 23,200)²⁰ to $p-C_6H_5-C_6H_4COC_6H_4-C_6H_5-p$ (λ_{\max} 333 $m\mu$, ϵ 56,230)²¹ where the biphenyl moieties are connected through a carbonyl group. This is an important point because it has been shown chemically^{13,22} that substitution in one ligand has a definite effect, which is transmitted through the metal atom, on the second ligand of "sandwich" type compounds.

As is to be expected, the two high intensity bands in the spectra of bis(1,3-diphenylcyclopentadienyl)iron¹⁹ (XXV) and of bis(1,2,4-triphenylcyclopentadienyl) iron¹⁹ (XXXI) (Fig. 11) are shifted to longer wave lengths.

It should be interesting to study the absorption spectra of phenyl-substituted ferrocenes with different substituents on the phenyl groups to ascertain whether these bands are predominately benzenoid-type absorptions or displaced ferrocene bands.

Acknowledgment. The authors are greatly indebted to Dr. J. M. Vandenberg, Prof. M. Orchin, Prof. E. A. Halevi, Prof. P. L. Pauson, and the late Dr. A. Burawoy for many helpful discussions.

We also wish to express our thanks to Prof. P. L. Pauson and Prof. R. A. Benkeser, who have kindly supplied most of the substituted ferrocene samples.

(20) H. H. Szmant and C. McGinnis, *J. Am. Chem. Soc.*, **74**, 240 (1952).

(21) L. C. Anderson and C. M. Gooding, *J. Am. Chem. Soc.*, **57**, 999 (1935).

(22) M. Rosenblum, *Chem. & Ind.*, **72** (1957).