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## Abstract

## Full Text

## Chemistry

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# Integral Intensities of I.R. Absorption Bands of Certain Characteristic Vibrations of Cyclopentadienyl Rings in Ferrocene Derivatives

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It is known that certain vibrations appearing in the i.r. spectra of ferrocene derivatives are characteristic of the cyclopentadienyl ring and do not depend on vibrations of the rest of the molecule. Thus, the absorption band in the region of 3100 $\text{cm}^{-1}$ was assigned to the stretching vibrations of ring C—H bonds, and the band at 1108 $\text{cm}^{-1}$ to the symmetric stretching vibrations of the unsubstituted cyclopentadienyl ring ([1]). These data were confirmed by a calculation of the vibrations of cyclopentadienyl rings from the i.r. spectrum of ferrocene ([2]). The study of the frequencies and integral intensities of characteristic absorption bands in various ferrocene derivatives is of considerable interest for investigating the electron-donating properties of this peculiar aromatic system and its ability to transmit substituent effects. The data obtained may also be used for structural analysis in this series of compounds.

We have measured the frequencies and integral intensities of the absorption bands of stretching vibrations of C—H bonds and of the cyclopentadienyl ring in the i.r. spectra of ferrocene derivatives in carbon tetrachloride. The measurements were made on a double-beam i.r. spectrometer UR-10 with sodium chloride prisms in the region 1000—1200 $\text{cm}^{-1}$ and lithium fluoride in the region 3000—3200 $\text{cm}^{-1}$. The scanning rate did not exceed 12 $\text{cm}^{-1}$/min. The integral intensities were calculated by the extrapolation method of Wilson—Wells ([3,4]); corrections to the area under the wings of the bands were introduced according to Ramsay' s tables ([4]).

Table 1 gives the frequencies and integral intensities of the band of stretching vibrations of ring C—H bonds.

In the spectra of solutions of all the monosubstituted ferrocenes studied, irrespective of the nature of the substituent in the cyclopentadienyl ring (with the exception of nitroferrocene), one C—H band at 3100 $\text{cm}^{-1}$ is observed. In the spectra of crystals of these substances the band splits into 2-3 components, lying on average in the region 3070—3130 $\text{cm}^{-1}$. In heteroannular disubstituted derivatives, where half of the C—H bonds are in a neighboring position relative to the substituent, the C—H band also splits in solutions into two components lying in the region 3090–3120 cm$^{-1}$.

In contrast to the frequency, the integral intensity of the 3100 cm$^{-1}$ band depends substantially on the nature of the substituent in the cyclopentadienyl ring. Study of the substituent effect on the intensity of this band is complicated by the superposition of vibrations of C–H bonds located in different positions relative to the substituent. Only for ferrocene itself, where all C–H bonds are equivalent, can the value of the intensity corresponding both to one C–H bond and to the five C–H bonds of the unsubstituted cyclopentadienyl ring be determined reliably. For substituted ferrocenes such a calculation gives only a certain average value of the intensity. Nevertheless, for estimating the degree of influence of various substituents and the ability of the aromatic ferrocene system to transmit this influence,

**Table 1**

| Compound | $\nu_{max}$, cm$^{-1}$ | $A \cdot 10^{-3}$*, l mol$^{-1}$ cm$^{-2}$ | $\frac{A \cdot 10^{-3}}{n}$**, l mol$^{-1}$ cm$^{-2}$ | Compound | $\nu_{max}$, cm$^{-1}$ | $A \cdot 10^{-3}$, l mol$^{-1}$ cm$^{-2}$ | $\frac{A \cdot 10^{-3}}{n}$, l mol$^{-1}$ cm$^{-2}$ |
|---|---|---|---|---|---|---|---|
| Ferrocene | 3100 | 48.0 | 4.80 | Nitroferrocene | 3100–3125 | 21.0 | 2.3 |
| Ethylferrocene | 3099 | 49.0 | 5.4 | *p*-$C_6H_4NO_2$-ferrocene | 3100 | 35.5 | 3.9 |
| Biferrocenyl | 3100 | 97.0 | 5.4 | *m*-$C_6H_4NO_2$-ferrocene | 3098 | 38.5 | 4.3 |
| Bis(ferrocenyl)mercury | 3100 | 105.0 | 5.8 | *o*-$C_6H_4NO_2$-ferrocene | 3100 | 36.0 | 4.0 |
| Bis(ferrocenyl) ketone | 3100 | 70.0 | 3.9 | *p*-$C_6H_4OH$-ferrocene | 3096 | 45.3 | 5.0 |
| Formylferrocene | 3100 | 30.4 | 3.4 | 1,1′-Diacetylferrocene | 3112–3096 | 30.0 | 3.7 |
| Acetylferrocene | 3102 | 33.2 | 3.7 | 1,1′-Dipropionylferrocene | 3145–3090 | 30.3 | 3.8 |
| Propionylferrocene | 3100 | 34.0 | 3.8 | 1-Acetyl-1′-cyanoferrocene | 3112–3095 | 23.0 | 2.9 |
| Butyrylferrocene | 3102 | 32.7 | 3.6 | 1-Acetyl-1′-methoxycarbonylferrocene | 3114–3096 | 28.0 | 3.5 |

* The spectral slit width at 3100 cm$^{-1}$ was 3.5 cm$^{-1}$.
** $n$ is the number of non-equivalent C—H bonds in the molecule.

(continued)

| Compound | $\nu_{max}$, cm$^{-1}$ | $A \cdot 10^{-2}$, L · mol$^{-1}$ · cm$^{-2}$ | $\frac{A \cdot 10^{-2}}{n}$, L · mol$^{-1}$ · cm$^{-2}$ | Compound | $\nu_{max}$, cm$^{-1}$ | $A \cdot 10^{-2}$, L · mol$^{-1}$ · cm$^{-2}$ | $\frac{A \cdot 10^{-2}}{n}$, L · mol$^{-1}$ · cm$^{-2}$ |
|---|---|---|---|---|---|---|---|
| Ferrocenyl—$COOCH_3$ | 3100 | 31.6 | 3.5 | Ferrocenyl—$COC_2H_5$; ferrocenyl—$COOCH_3$ | 3116—3098 | 28.0 | 3.5 |
| Ferrocenyl—CN | 3100 | 22.0 | 2.4 | Ferrocenyl—$COC_3H_7$; ferrocenyl—$COOCH_3$ | 3118—3100 | 29.5 | 3.7 |

* The spectral width of the slit at 3100 cm$^{-1}$ was 3.5 cm$^{-1}$.
** $n$ is the number of ring C—H bonds in the molecule.

it is expedient to compare, for the C—H bonds of the unsubstituted ring, both the total intensities of the C—H band and the values averaged per one C—H bond (Table 1). Such a comparison shows that both of these quantities decrease regularly with increasing electron-acceptor properties of the substituent. A similar influence of electron-acceptor substituents on the intensity of the stretching-vibration band of C—H bonds has also been observed in other types of compounds ([5,6]). Electron-donor substituents increase the band intensity calculated per one C—H bond. On the basis of these data, the substituent —Hg—ferrocenyl possesses electron-donor properties, while —CO—ferrocenyl possesses weak electron-acceptor properties with respect to ferrocenyl.

The intensity values calculated on the average per one C—H bond correlate poorly with Taft' s $\sigma^*$ constants ([7]) and with Hammett' s $\sigma_m$ constants ([8,9]), and correlate considerably better with Hammett' s $\sigma_p$ constants ([8,9]) (see Fig. 1). This may indicate a certain similarity in the ability to transmit the influence of substituents between the aromatic systems of ferrocene and benzene.

**Fig. 1.** Dependence between the intensities of the IR absorption band at 3100,

Fig. 1. Dependence between the intensities of the IR absorption band at 3100, calculated on the average per one C—H bond in monosubstituted ferrocenes, and Hammett $\sigma_p$ constants

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calculated on the average per one C—H bond in monosubstituted ferrocenes, and Hammett $\sigma_p$ constants.

The presence of an influence of the substituent on the C—H bonds of the free ring is evident already from the fact that the total intensities of the C—H bands in ferrocenyl nitrile and nitroferrocene are smaller than the intensity of the C—H bonds in one cyclopentadienyl ring of ferrocene. This conclusion is consistent with the results we obtained in studying the intensities of characteristic vibrations of functional groups in heteroannular disubstituted ferrocenes ($^{10}$).

Introduction of an electron-acceptor substituent into the second cyclopentadienyl ring does not lead to a noticeable change in the intensity in the cal-

| R | $\nu_{\max}$, cm$^{-1}$ | $A \cdot 10^{-4}$, L · mol$^{-1}$ · cm$^{-2}$ | R | $\nu_{\max}$, cm$^{-1}$ | $A \cdot 10^{-4}$, L · mol$^{-1}$ · cm$^{-2}$ |
|---|---|---|---|---|---|
| $-H$ | 1108 | 0.15 | $-CN$ | 1108 | 0.11 |
| $-C_2H_5$ | 1107 | 0.15 | $-NO_2$ | 1108 | 0.10 |
| $-CHO$ | 1108 | 0.13 | $-C_6H_4-OH$ | 1108 | 0.15 |
| $-COC_2H_5$ | 1108 | 0.14 | $-C_6H_4-NO_2$ | 1108 | 0.15 |
| $-COC_3H_7$ | 1108 | 0.14 | $-C_5H_4FeC_5H_5$ | 1111 | 0.15 |
| $-COC_6H_5$ | 1108 | 0.13 | $-CO-C_5H_4FeC_5H_5$ | 1108 | 0.15 |

**Table 2**

per one C—H bond. The total intensities of the stretching-vibration bands of the ring C—H bonds in such compounds differ little from those calculated by the additivity rule from the corresponding monosubstituted derivatives.

The magnitudes of the intensity of the stretching-vibration band of the ring in monosubstituted ferrocenes also indicate transmission of the substituent effect to the second cyclopentadienyl ring (see Table 2). Although the band frequency is practically independent of the nature of the substituent, its integral intensity in ferrocene derivatives varies from 0.15 to $0.10 \cdot 10^4$ L • mol$^{-1}$ • cm$^{-2}$, decreasing symbatically with increasing electronegativity of the substituent. Electron-donor and weak electron-acceptor substituents have practically no effect on the intensity of this band. Therefore, measurement of this quantity can be used for structural analysis of ferrocene derivatives. In particular, the intensity may serve as a sufficiently reliable criterion for the correctness of assigning the band observed in the region of 1100 cm$^{-1}$ to stretching vibrations of the unsubstituted cyclopentadienyl ring, which often causes difficulties because of the presence of a large number of bands in this region of the spectrum. Thus, in the infrared spectrum of diferrocenyl in crystals, a doublet at 1111–1104 cm$^{-1}$ is observed. In the spectrum of the solution, at sufficiently high resolution, splitting of this band into two components, 1111–1106 cm$^{-1}$, can also be observed. Measurement of the integral intensities of these bands makes it possible to assign only the 1111 cm$^{-1}$ band to the symmetric vibrations of the free cyclopentadienyl rings.

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