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## Abstract

## Full Text

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# PROTON NMR SPECTRA OF FERROCENE COMPOUNDS AND THE MAGNETIC ANISOTROPY OF FERROCENE

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Earlier (1), high-resolution NMR spectra were recorded for the protons of ferrocene, ethylferrocene, tributylferrocene, and other compounds. Data on the chemical shifts are given in Table 1. In studying the NMR spectra of these compounds at temperatures of the order of 50 ÷ 60°, instead of the expected narrowing, broadening of the proton peak of the cyclopentadienyl (c.p.) rings of ferrocene was observed. This phenomenon can be explained if one takes into account that, according to the measurements of Muller and Fox (2), the principal molecular susceptibilities of ferrocene in the plane perpendicular to the axis of the rings differ somewhat from one another. As the temperature rises, the frequency of oscillations of the rings about the metal—ring direction increases. Under the condition that the frequency of the oscillations is less than the difference in the chemical shifts of protons in the positions corresponding to the principal susceptibilities, line broadening should be observed.

**Table 1**

Chemical shifts of protons, in ppm

| Compound | $H$ [[cyclopentadienyl ring]] | $H_{\mathrm{CH}}$ | $H_{\mathrm{CH_2}}$ | $H_{\mathrm{CH_3}}$ |
|---|---|---|---|---|
| Ferrocene | 6.06 | – | – | – |
| Ethylferrocene | 6.10 | – | 7.86 | 9.00 |
| Tributylferrocene | 6.13 | – | – | 8.82 |
| Bis-1,1′-ferrocenyl-di-1,1′-dicyclopentyl (17) | 6.10 | 8.40* | – | – |
| Diferrocenylethane-1,1′ | 6.09 | 7.36** | – | 8.86** |

| Compound | $H$ [[cyclopentadienyl ring]] | $H_{\mathrm{CH}}$ | $H_{\mathrm{CH_2}}$ | $H_{\mathrm{CH_3}}$ |
|---|---|---|---|---|
| Diferrocenylethane-1,2 | 6.09 | – | ? | – |

* The indicated chemical shift refers to a cyclopentyl proton.
** According to the data of work ($^{18}$), where the chemical shifts of hydrogens were determined using benzene as an internal standard, whose chemical shift is taken to be 2.72 ppm.

NMR spectra were recorded at a frequency of 24.458 MHz on a YaMR-KGU-1 spectrometer ($^{3}$), whose resolving power was $5 \cdot 10^{-8}$. The chemical shifts of crystalline compounds were determined in 20% (by volume) solutions in $CS_2$, and the shifts of ethylferrocene protons were found by extrapolation to infinite dilution in carbon disulfide. Chemical shifts are everywhere given in millionths of the applied field (ppm) on the Tiers scale with an accuracy of ±0.04 ppm. Line positions were measured by the "side-band"method, using tetramethylsilane as the internal standard. Samples were placed in cylindrical ampoules 3 mm in diameter made of zirconium glass.

Theoretical analysis of the NMR spectrum of ethylferrocene made it possible to obtain some information on the density of the $\pi$-electron current in the ring and on the diamagnetic anisotropy of ferrocene. These questions are of definite interest in connection with the study of the nature of the metal–ring bond in ferrocene.

The spectrum of ethylferrocene (Fig. 1), consisting of a sharp peak of the ring protons with $\tau = 6.10$ ppm, a methylene quartet with center at $\tau = 7.86$ ppm, and a methyl triplet with center at $\tau = 9.00$ ppm, indicates a noticeable paramagnetic influence experienced by the protons of the ethyl radical. If these values of the chemical shifts are compared with the positions

$> CH_2$ and $-CH_3$ groups in aliphatic compounds ($^{4}$), one can see that the methylene group of ethylferrocene is shifted to the left by 1.01 ppm, and the methyl group by 0.26 ppm.

Since the aromatic nature of ferrocene has been well established ($^{5}$), in explaining the chemical shifts in ferrocene derivatives it is necessary to take into account the influence of the $\pi$-electron current in the rings on the protons of the molecule. To estimate the chemical shifts $\Delta\tau_{\mathrm{magn}}$, expressed in parts per million (ppm), i.e., the difference between the resonance peaks of ethylferrocene and of a close analogue in which there is no circulating current but the hybridization of the bonds is the same, the formula ($^{6,7}$) was used:

$$\Delta\tau_{\mathrm{magn}} = \frac{ne^2}{6\pi mc^2 a} \cdot \frac{1}{\left[(1+\rho)^2 + z^2\right]^{1/2}} \left[K(k) + \frac{1-\rho^2-z^2}{(1-\rho)^2+z^2} \cdot E(k)\right].$$

Fig. 1. PMR spectrum of ethylferrocene at a temperature of ~ 19°C, $\nu_0 = 24.458$ MHz

Figure 1: Fig. 1. PMR spectrum of ethylferrocene at a temperature of ~ 19°C, $\nu_0 = 24.458$ MHz

Here $n$ is the number of circulating electrons, $\rho$ and $z$ are the cylindrical coordinates of the protons, calculated in units of the ring radius $a$, and $K$ and $E$ are complete elliptic integrals, with

$$k^2 = \frac{4\rho}{(1+\rho)^2 + z^2}.$$

In the course of the calculations it became clear that it was necessary to take into account the electric influence exerted on the protons by the electron cloud located between the rings. As was shown by the calculations of E. M. Shustorovich and M. E. Dyatkina ([8,9]), the dipole moment of the metal–ring bond is 0.55 D, and there is a certain effective positive charge on the central atom (+0.7), so that the electrons are partially displaced from the neutral metal atom toward the rings (−0.35 × 2). On the other hand, the calculations of Dahl and Ballhausen give an electron-density distribution of the form $\mathrm{Fe}^{-0.7}(\mathrm{C_5H_5}^{+0.35})_2$.

Fig. 1. PMR spectrum of ethylferrocene at a temperature of ~ 19°C, $\nu_0 = 24.458$ MHz

The estimate of the electric influence of the inter-ring cloud on the chemical shifts of the protons, $\Delta\tau_{\mathrm{el}}$, was carried out for both directions of the dipole according to Buckingham' s theory ([11]). From a comparison of the calculated chemical shifts with the experimental values, the number $n$ of electrons circulating in the rings of ferrocene was determined. Since the exact position of the methyl group in the ethylferrocene molecule was not known, the calculations were carried out for three cases: 1) the methyl in ethylferrocene rotates freely about the direction of the C–C bond lying in the plane of the ring, 2) the methyl undergoes vibrational motion predominantly above the axis of the molecule (the exo form of ethylferrocene), 3) this vibrational motion occurs mainly in the space between the rings of ferrocene (the endo form). At the same time, following the theory of McConnell ([12]), the magnetic anisotropy of ferrocene was calculated for the three cases described above. The calculations were carried out for the methyl, since in this case the McConnell formula, obtained in the dipole approximation, is better satisfied. In the calculations the influence of both rings was taken into account. The results of the calculations are presented in Table 2.

According to the measurements of Mulay and Fox, the magnetic anisotropy of ferrocene is equal to $\Delta\chi = \chi_{\parallel} - \chi_{\perp} = -49.5\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$. From comparison of this value with the data of Table 2 it can be seen that the experimental value of the anisotropy agrees with $\Delta\chi$ calculated for the endo form. However, it is difficult to decide which data on the charge distribution in ferrocene should be preferred. The magnetic anisotropy calculated from the data of Shustorovich and Dyatkina and from those of Dahl and Ballhausen is equally close to the experimental value, while the number of electrons in both cases (for the endo form) is somewhat less than five, which agrees with Pauling' s prediction (2).

**Table 2***

| No. | Conformation of ethylferrocene | $\Delta\tau_{mag}$ | $\Delta\tau_{el}\cdot10^{+6}$, according to (8, 9) | $\Delta\tau_{el}\cdot10^{+6}$, according to (10) | $n$, according to (8, 9) | $n$, according to (10) | $-\Delta\chi\cdot10^{+6}$, according to (8, 9) | $-\Delta\chi\cdot10^{+6}$, according to (10) |
|---|---|---|---|---|---|---|---|---|
| 1 | Free rotation of the methyl | $-0.039\cdot n$ | −0.012 | +0.012 | 6.35 | 6.97 | 67 | 73 |
| 2 | Exo form | $-0.033\cdot n$ | −0.006 | +0.006 | 7.7 | 8.1 | 93 | 96 |
| 3 | Endo form | $-0.058\cdot n$ | −0.015 | +0.015 | 4.2 | 4.75 | 47 | 53 |

* Calculations carried out by Musher' s formula (19): $\Delta\tau_{el} = -2.9\cdot10^{-13}\cdot E_z - 7.38\cdot10^{-19}\cdot E^2$, insignificantly change the data presented.

At the same time, the results obtained do not contradict the conclusions of Shustorovich and Dyatkina (8), confirming that in ferrocene the formation of donor–acceptor bonds occurs without substantial withdrawal of the $\pi$-electrons of the rings. It should be noted that if one follows the views of some German scientists (13–16), who adhere to the concept that all the $\pi$-electrons of the rings take part in bond formation with iron, it would be difficult to explain the observed chemical shifts in the NMR spectrum of ethylferrocene.

In order, following the hypothesis of ring currents in the cyclopentadienyl rings of ferrocene, to explain the chemical shift of the ring protons, equal to $\tau = 6.06$ ppm, it is necessary to compare this spectrum with the spectrum of a compound in which the protons would be under analogous conditions but would not experience the influence of the circulating current. Then it would be possible to determine more precisely the density of the $\pi$-electron current in the cyclopentadienyl rings. In our opinion, these conditions are satisfied by complexes of the type $FeCl_2\cdot C_2H_4$, which, unfortunately, we have not yet succeeded in obtaining.

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*Note: Figure translations are in progress. See original paper for figures.*