extended term of the Debye-Hückel equation for the activity coefficient (*4*).

The standard potentials were evaluated using the IBM 7.0.002 polynomial curve fitting program. The left hand side of Equation 3 was taken as ordinate and $m^{1/2}$ as the abscissa. The curve fitting program gives results which are in excellent agreement with the results of linear extrapolations (*4*). The standard potentials were evaluated from the first term of the polynomial. The degree of polynomial used for extrapolation purposes was determined by comparing the graphs and the trends in the values of the activity coefficients. The standard potentials are listed in Table II. The values should be good to ±0.2 mv. for the 8.68 and 17.81% monoglyme systems, to ±0.6 mv. for the 46.52% monoglyme system, and for the 67.03% monoglyme system to ±1.0 mv.

Table III contains the values of mean activity coefficients calculated from Equation 3. The activity coefficients in this case are referred to unity at infinite dilution in the mixed solvent system and are defined by Harned and Owen (*1*). The activity coefficients were evaluated using E_{obsd} values as calculated from the polynomials used for extrapolations. The values were then smoothed with respect to temperature. The values of primary and secondary medium effects as defined by Owen (*2*) are tabulated in Tables IV and V.

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Electronic Effects in the Ferrocene Ring System by Proton Magnetic Resonance Spectroscopy

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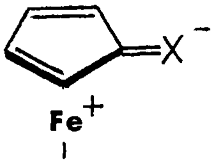
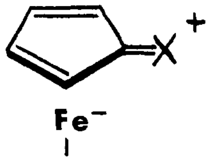
Results of a proton magnetic resonance study of the chemical shifts of ring protons of representative monosubstituted ferrocene compounds are reported. The substituents cover a span from strongly electron-donating groups to strongly electron-withdrawing. Some relationships appear to exist between the ring-proton chemical shifts in these compounds and those reported for the corresponding monosubstituted benzene compounds. The chemical shifts recorded were precisely measured. As such, they serve to revise the data reported while this work was in progress.

RECENTLY, estimates of electronic effects in metallocene ring systems have been forthcoming from PMR spectroscopy (*3, 4, 8, 10, 14*). In the case of the ferrocene ring system, abundant data are available to illustrate the deshielding effect of substituents containing a carbonyl group attached to the ring (*9, 12, 13*); however, substituent effects in the PMR spectra of other types of monosubstituted ferrocenes (particularly those containing electron-donating substituents) had not been reported at the time this work was initiated. A possible representation of resonance contribution to the ferrocene ring system of an electron-withdrawing group is shown in structure I; that of an electron-donating group is in structure II. Electron withdrawal, represented by the extreme formal-charge structure I, suggests deshielding of the substituted ring protons. Likewise, electron donation as in formal-charge structure II suggests shielding of the substituted ring protons will be observed. Structure II is, however, rendered less satisfactory than I because of the necessity of placing a negative formal charge on the iron atom.



I



II

The results of a PMR study are reported for several representative monosubstituted ferrocene compounds; the substituents cover a span from strongly electron-donating groups (—NH_2) to strongly electron withdrawing (—CHO). A rough, nonlinear correlation is shown between the chemical shifts of protons at the 2 and 3 positions and the chemical shifts of protons at, respectively, the ortho and para positions of the corresponding benzene compounds (*15*).

The compounds employed were either commercial samples (acetylferrocene and carbomethoxyferrocene) or were pre-

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Table I. 60 Mc. Chemical Shifts in CCl_4 Relative to Ferrocene[a]

Substituent	2-Position[b]	3-Position[b]	1′-Position[b]
$-CHO$	−39.6	−25.7	−9.2
$-CO_2CH_3$	−39.2(−38.4)	−13.4(−13.2)	−4.4(−4.2)
$-COCH_3$	−36.8(−33.0)	−18.5(−16.2)	−4.4(−1.8)
$-I$	−16.9(−13.2)	−0.4(+3.0)	−3.5(−1.2)
$-Br$	−16.8(−16.8)	+3.0(+3.0)	−5.5(−6.0)
$-C_2H_5$	+6.5(+12.0)	+6.5(+12.0)	+3.8(+10.2)
$-NH_2$	+19.7(+21.0)	+14.1(+15.0)	+3.9(+6.0)

[a] Ferrocene at 242.9 c.p.s. Levenberg and Richards (*7*) cite a value of 246 c.p.s. for this solvent, while Dvoryantseva *et al.* (*4*) cite a value of 243 c.p.s. [b] Values in parentheses are those of Russian authors (*4*).

pared by known procedures. Aminoferrocene was synthesized by the treatment of an ethereal solution of lithioferrocene with methoxyamine (*1*) and by the Curtius rearrangement (*2*). Iodoferrocene was prepared by treatment of chloromercuriferrocene with iodine (*11*) and bromoferrocene by a recently published modification of this procedure (*5*). Ferrocenecarboxaldehyde was obtained by the phosphorus oxychloride-*N*-methyl formanilide method (*6*). An extensively purified sample of each of these substances was prepared as a solution ca. 10% (w./w.) in CCl_4. All spectra were taken on a Varian A-60 spectrometer at an ambient sample temperature of ca. 36° C. Chemical shifts were measured relative to tetramethylsilane (TMS) as an internal reference by means of conventional audio-sideband interpolation techniques. The precision and therefore, presumably, the accuracy of frequency measurements was better than 0.1 c.p.s.

The chemical shifts obtained are presented in Table I and compared there with the results of Russian workers (*4*). The assignment of chemical shifts to protons at position 2 or 3 has been made by analogy to known substituent effects on shifts of ortho and para protons, respectively, on monosubstituted benzenes. Apparently, a rough correlation does indeed exist, but would exist were the assignment for the 2- and 3-position reversed. However, assignment of the 2-position triplet to that appearing furthest downfield in acyl-type ferrocenes is conclusive (*4, 7-9, 12, 13*).

In favorable cases, the PMR spectra of these monosubstituted ferrocenes characteristically exhibited two apparent triplets for protons in the 2- and 3-positions and a single line for the five equivalent protons in the unsubstituted ring. A close approximation—i.e., to within 0.5 c.p.s.—to the chemical shifts of the protons at the 2- and 3-positions of these compounds was obtained by taking frequencies of the center line of each apparent triplet. These three peak multiplets, rather than a more complicated pattern generally characteristic of the A_2B_2 spin system, results from the near equality of the small vicinal—i.e., between protons 2-3 and 4-5—and cross-ring—i.e., between protons 2-5, 3-5, and 2-4—spin coupling constants (*7*).

The spectra of the ethyl, amino, and carboxaldehyde derivatives of ferrocene were less resolved. Ethylferrocene exhibited only one line for the 2- and 3-position proton signal. Apparent triplet structure for these positions in ferrocenecarboxaldehyde and aminoferrocene could not be resolved; rather, two wide (ca. 5 c.p.s.) lines of equal integrated intensity were observed. This feature may have arisen because of formation of a precipitate which could not be removed by filtering and could not be prevented from occurring by any means attempted. The authors do not believe this line broadening can be attributed to any exchange process, since a temperature study (HR 60) of the aldehyde spectrum, for example, showed no change to take place over a temperature range of −10° to 60° C.

The PMR spectrum of aminoferrocene was also determined on an A-56/60; somewhat better resolution was obtained on this instrument. The spectrum of aminoferrocene is remarkable in that it shows an upfield shift for the protons at both the 2 and 3 positions, suggesting that contributing structures such as II may have some meaning. The significant features of this spectrum are recorded in Figure 1.

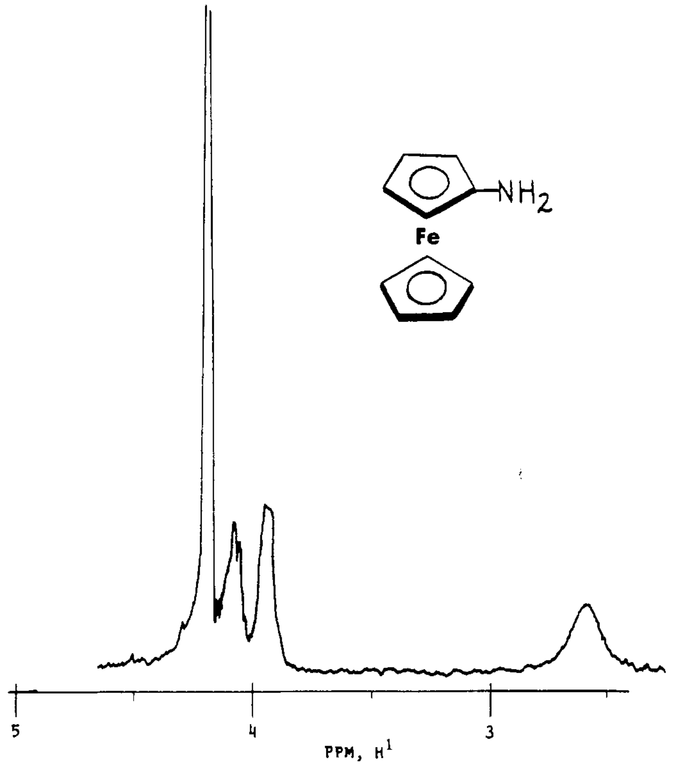

Figure 1. PMR spectrum of aminoferrocene in $CDCl_3$ vs. TMS

The assignment of chemical shifts to the 2 and 3 positions in other than acyl-type ferrocenes is to be made secure by studies on deuterium-labeled compounds.

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