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schematic structures of substituted ferrocene rings with protons labeled H_a, H_b, H_c, substituent X, and Fe

Figure 1: schematic structures of substituted ferrocene rings with protons labeled H_a, H_b, H_c, substituent X, and Fe

Abstract

Full Text

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N.M.R. Spectra of Ferrocene Derivatives

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In order to study the nature of the influence of substituents in ferrocene derivatives, in previous works we measured the integral intensities of the C—H bonds of five-membered rings and of certain characteristic vibrations of functional groups in the i.r. spectra of mono- and heteroannular disubstituted ferrocenes ([1],[2]), and also determined the oxidation-reduction potentials of these compounds ([3],[4]) and the dissociation constants of substituted ferrocenecarboxylic acids ([5]). The data obtained made it possible to draw conclusions about the nature of the transmission of the electronic influence of substituents from one five-membered ring to the other in the ferrocene molecule. Along with this, the study of the influence of substituents on hydrogen atoms located in different positions of the five-membered ring is of undoubted interest.

For this purpose, in the present work we measured the chemical shifts of proton signals in high-resolution n.m.r. spectra of a series of mono- and heteroannular disubstituted ferrocenes. In the proton-resonance spectra of all monosubstituted ferrocenes, there is observed a singlet from the five equivalent protons (a) of the unsubstituted five-membered ring and two triplets of the (b)- and (c)-protons of the substituted ring, with a spin-spin coupling constant $I \simeq 1.5$ Hz.

The observed spin-spin splitting belongs to the A_2B_2 type. The spectra of heteroannular disubstituted compounds contain only two triplets of the protons of the substituted rings.

Table 1 gives the chemical shifts of the signals of the (a)-, (b)-, and (c)-protons of monosubstituted ferrocenes in ppm relative to the singlet of the protons of unsubstituted ferrocene (4.05 ppm), and, for comparison, the chemical shifts of the signals of the ortho-, meta-, and para-protons of the corresponding benzene derivatives described in the literature ([6]). According to the nature of their n.m.r. spectra, the monosubstituted ferrocenes studied are divided into three types. In the spectra of ferrocene derivatives with strongly electron-accepting substituents (Table 1, Nos. 10–14), the proton signals are shifted entirely toward relatively weaker fields (negative values of δ for all protons). By analogy with the influence of substituents on the chemical shifts of the ortho-protons of the phenyl nucleus, we assigned the signal observed in the region of the weakest field to the (b)-protons of the substituted five-membered ring in compounds of this type. This assignment was confirmed by comparison of the intensities of the signals of the (b)- and (c)-protons in the n.m.r. spectra of ferrocenyl-

amide and homoannular alkylferrocenylamides of established structure (7) and is consistent with the assignment of proton signals in the spectra of isomeric alkylacetylferrocenes (8).

The second type includes ferrocenes with electron-donor substituents (Table 1, Nos. 2-4), the spectra of which are shifted entirely toward

Table 1

Chemical shifts of proton signals of five-membered rings in monosubstituted ferrocenes
$C_5H_5FeC_5H_4X$, in ppm

No.	–X	H_a	H_c	H_b	δ_a	δ_c	δ_b	δ_m	δ_p	δ_o
1	–H	4.05	–	–	0.00	0.00	0.00	0.00	0.00	0.00
2	–C_2H_5	3.88	3.85	3.85	+0.17	+0.20	+0.20	+0.13*	+0.17*	+0.17*
3	–NH_2	3.95	3.80	3.70	+0.10	+0.25	+0.35	+0.22		+0.68
4	–OCH_3	4.05	3.95	3.69	0.00	+0.10	+0.36	+0.10	+0.33	+0.42
5	–$OCOCH_3$	4.11	3.82	4.35	–0.06	+0.23	–0.30			
6	–$OCOC_6H_5$	4.12	3.85	4.48	–0.07	+0.20	–0.43			
7	–Cl	4.05	3.86	4.19	0.00	+0.19	–0.14	+0.06	+0.13	–0.05
8	–Br	4.15	4.00	4.33	–0.10	+0.05	–0.28	+0.11	+0.06	–0.22
9	–J	4.07	4.00	4.27	–0.02	+0.05	–0.22	+0.22		–0.41
10	–$COCH_3$	4.08	4.32	4.60	–0.03	–0.27	–0.55			
11	–$COOCH_3$	4.12	4.27	4.69	–0.07	–0.22	–0.64	–0.10	–0.20	–0.74
12	–CN	4.27	4.28	4.57	–0.22	–0.23	–0.52	–0.13		–0.35
13	–$SO_2C_6H_5$	4.45	4.37	4.62	–0.40	–0.32	–0.57			

No.	–X	H_a	H_c	H_b	δ_a	δ_c	δ_b	δ_m	δ_p	δ_o
14	–NO_2	4.26	4.37	5.13	−0.21	−0.32	−1.08	−0.21		−0.98

Note. H_a, H_b, H_c are the chemical shifts of the proton signals of the five-membered rings in monosubstituted ferrocenes, measured relative to the proton signal in $(CH_3)_4Si$. δ_a, δ_b, δ_c are the chemical shifts of the signals of the same protons relative to the proton signal in unsubstituted ferrocene. δ_m, δ_o, δ_p are the chemical shifts of the signals of the meta-, ortho-, and para-protons under the influence of substitution in a benzene nucleus relative to the proton signal in unsubstituted benzene (6).

* Data for X = CH_3.

relatively stronger fields (positive values of δ for all protons)*. Obviously, the signal in the region of the strongest fields in these compounds should be assigned to the (b)-protons of the substituted ring.

Finally, the third type comprises ferrocene derivatives (Table 1, Nos. 5-9), in whose spectra signals are observed both in the region of weaker and in the region of stronger fields in comparison with the signal of unsubstituted ferrocene; in this case the singlet from the (a)-protons is located between the triplets of the (b)- and (c)-protons. Apparently, the triplet in the region of relatively weaker field belongs to the (b)-protons of the substituted ring.

From the data in Table 1 it is evident that the absolute values of the chemical shifts of the protons of most monosubstituted ferrocenes are arranged in the series $\delta_b > \delta_c > \delta_a$ in order of decreasing sensitivity to the influence of substituents. At the same time, the influence on the protons of the unsubstituted ring is, as a rule, several times weaker than on the protons of the substituted ring.

Qualitative consideration shows that the chemical shifts of the protons of the unsubstituted ring are determined mainly by the inductive effect of the substituents. A plot of the dependence of the measured values of δ_a on the inductive constants of the substituents σ_i (9) (see Fig. 1) is a straight line with correlation coefficient $r = 0.978$, corresponding to the equation:

$$\delta_a = -0.59\sigma_i + 0.15; \qquad n = 9. \tag{I}$$

Significant deviations from this line are observed for the values of δ_a in the spectra of iodo- and chloroferrocenes.

* In the spectrum of ethylferrocene, two signals are observed at 3.88 (five protons) and 3.85 ppm (four protons), corresponding to the protons of the unsubstituted and substituted rings.

Examination of the NMR spectra of some symmetrically heteroannularly disubstituted ferrocenes shows that in most cases the introduction of the same type of substituent into the second ring only slightly changes the positions of the signals of the (*b*)- and (*c*)-protons (Table 2, Nos. 1-4). Thus, the influence of substituents on the chemical shifts of the protons of the other ring in these compounds is also weak. At the same time, the additivity rule is obeyed only for the chemical shifts of protons in compounds with strong electron-acceptor substituents.

The observed values of δ_b and δ_c in the NMR spectra of monosubstituted ferrocenes indicate a significant influence of the substituent conjugation effect on the chemical shifts of the protons of the substituted ring. Thus, for example, the positive values of the chemical shifts of the (*c*)-protons in compounds of the third type can be explained only by the predominant influence of the $+C$-effect of these substituents. When the values of δ_c are correlated with the induction constants of substituents σ_i, considerable deviations from the straight line (I) are observed. In this case the points lying below the straight line correspond to substituents possessing a $-C$-effect, and the points lying above the straight line correspond to substituents with a $+C$-effect. From the vertical deviation of the points from the straight line (I), corresponding to $\delta_c - \delta_a$, one can estimate the contribution of the substituent conjugation effect. We correlated the value $\delta_c - \delta_a$ with the substituent constants σ_c (9). In the graph (see Fig. 2) two intersecting straight lines are obtained, one containing the electron-acceptor substituents and the other predominantly the donor substituents. The electron-donor influence of substituents having a free pair of electrons is substantially reduced in the ferrocenyl nucleus in comparison with the phenyl nucleus. The interaction of these substituents with the ferrocenyl nucleus is analogous to their interaction with a phenyl nucleus containing, in the para position, functional

Fig. 1. Dependence of the chemical-shift values of the signals of the protons of the unsubstituted rings on the induction constants of substituents

Table 2*

Chemical shifts of the proton signals of five-membered rings of heteroannularly disubstituted ferrocenes $XC_5H_4FeC_5H_4X$, in ppm

No.	$-X$	H_b	H_c	Found δ_b	Found δ_c	Calculated δ_b	Calculated δ_c
1	$-C_2H_5$	3.82		+0.23	+0.23	+0.37	+0.37
2	$-OCOCH_3$	4.35	3.82	−0.30	+0.23	−0.36	+0.17
3	$-COCH_3$	4.62	4.35	−0.57	−0.30	−0.58	−0.30
4	$-COOCH_3$	4.74	4.34	−0.69	−0.29	−0.71	−0.29
5	$-Cl$	4.27	4.02	−0.22	+0.03	−0.14	+0.19

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* In Table 2 the same designations are used as in Table 1.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

groups with free electron pairs. This agrees with the known electron-donor properties of ferrocenyl. Indeed, when, for these substituents, instead of the σ_p values determined from the dissociation constants of benzoic acids (10), we took the σ_p^* values obtained from the dissociation constants of phenols (11), the points corresponding to these substituents lay on the common straight line with the electron-acceptor substituents:

$$\delta_c - \delta_a = -0.81(\sigma_p - \sigma_i) + 0.008; \quad n = 8; \quad r = 0.988. \tag{II}$$

Thus, the chemical shifts (c) of the protons of substituted five-membered rings are determined by a linear combination of the induction effect and the conjugation effect of the substituents:

$$\delta_c = -0.81\sigma_c - 0.59\sigma_i + 0.158. \tag{III}$$

The same effects, but in another linear combination, determine the chemical shifts (b) of the protons under the influence of substituents. In the graph of Fig. 3 the results are presented of the correlation of the values δ_b with Hammett’ s σ_p constants. In this case as well, the points corresponding to substituents with a $+C$-conjugation effect lie on a common straight line:

Fig. 2. Dependence of the quantities $\delta_c - \delta_a$ on the conjugation constants of substituents $\sigma_c = \sigma_p - \sigma_i$. The dashed line shows the straight line obtained for the values of σ^* determined from the dissociation constants of benzoic acids

Fig. 3. Dependence of the values of the chemical shifts of signals of the (b) protons of substituted rings on Hammett substituent constants σ_p

$$\delta_b = -1.47\sigma_p + 0.13; \quad r = 0.985, \quad n = 10 \tag{IV}$$

only when the values σ_p^*, determined from the dissociation constants of phenols, are used. The dependence of the values of the chemical shifts (b) of the protons of substituted rings is determined by the relation:

$$\delta_b = -1.47\sigma_c - 1.47\sigma_i + 0.13. \tag{V}$$

The results of the present work make it possible to draw a substantial analogy between the magnitude and character of the influence of substituents on the (*a*)-, (*b*)-, and (*c*)-hydrogen atoms of the ferrocenyl nucleus and, respectively, on the meta-, ortho-, and para-hydrogen atoms of the phenyl nucleus.

The NMR spectra of the compounds studied were measured in 10–15% solutions in CCl_4 on an INM-C-60 NMR spectrometer (60 MHz).

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