ELECTRONIC EFFECTS IN THE CYCLOPENTADIENYL RING. THE ^{13}C NMR SPECTRA OF MONOSUBSTITUTED FERROCENES *

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Summary

The chemical shifts of C(2,5) and C(3,4) carbons in the ^{13}C NMR spectra of monosubstituted ferrocenes have been assigned using deuterium labelling. An analogy is observed between the shielding of C(2,5) and C(3,4) carbons of ferrocene derivatives and *ortho*- and *para*-carbons of benzene derivatives with the same substituents. Electron-density distribution in the cyclopentadienyl ring is discussed on the basis of ^{13}C NMR data.

Introduction

Unlike benzene in which the effect of the substituent on the electron-density distribution of the phenyl ring has been the subject of many studies, its corresponding homocyclic aromatic system, cyclopentadienyl anion, has not been investigated in this respect. The data available on the electronic effects in a coordinated cyclopentadienyl ligand are rather few and generally concern the ferrocene system [3,4].

Two main approaches have been utilized in the investigation of substituent effects on the electronic-density distribution of the substituted ring in ferrocene derivatives (I). The first of these, the chemical method, is concerned with the
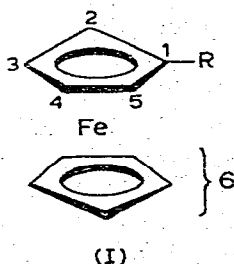
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study of the relative reactivity of the 2,5- and 3,4-positions in the substituted cyclopentadienyl ring, e.g. in acylation and metallation reactions.

The second is the spectroscopic approach based on the measurements of relative shielding of the H(2,5) and H(3,4) protons by the ^{1}H NMR method.

It should be noted that the relative reactivity is defined by the electronic effects in the transition state, while spectroscopy probes the ground state effects. However, the drawback to the ^{1}H NMR method is the sensitivity of the proton chemical shifts towards the magnetically anisotropic groups. Thus in acylferrocenes as well as in acylbenzenes the magnetic anisotropy effect of the carbonyl group causes deshielding of the ring protons closest to the substituent [5,6].

In recent years ^{13}C NMR spectroscopy has found wide application in the study of organic and organometallic compounds [7]. An important advantage of the ^{13}C NMR method over ^{1}H NMR spectroscopy is better signal resolution, and the relatively lower sensitivity of ^{13}C chemical shifts to the effects of magnetically anisotropic groups and ring current [8,9]. Moreover, ^{13}C NMR spectroscopy enables us to observe directly the skeleton of molecules and groups free of the hydrogen atoms.

Numerous examples have been described on the correlation of ^{13}C chemical shifts in monosubstituted benzenes with the electronic densities calculated by the MO method and σ Taft—Hammett constants [7]. The *para*-carbon chemical shifts show good correlations with the calculated electronic densities; the *ortho*-carbon correlations are essentially less satisfactory, whereas the chemical shifts of the directly substituted atoms exhibit only a rough correlation with the calculated charges. The *meta*-carbons are less sensitive towards the substituent influences, $\delta(C_m)$ 127—131.6 ppm, and their shielding is close to that of benzene carbons, δ 128.5 ppm.

Recently ^{13}C NMR spectra have been measured for the series of monosubstituted ferrocenes without assignment of C(2,5) and C(3,4) chemical shifts [10].

We now report a ^{13}C NMR study of the homoannular substituents effect in the ferrocene using deuterium labelling for unequivocal assignments for the chemical shifts in the ^{13}C NMR spectra.

Experimental

The 2,5-dideuterated ferrocenes were prepared by literature methods from *N*,*N*-dimethylaminomethylferrocene deuterated selectively by Hauser's method [11]. All ferrocene derivatives investigated have been described earlier.

The ^{13}C NMR spectra were recorded on a Bruker HX-90 spectrometer at 22.635 MHz under Fourier transform and [13]C—[1]H noise decoupling.

The ^{13}C signal assignment for amino- and methoxy-ferrocene was attained by a selective spin—spin proton decoupling. Slocum et al. have shown that H(3,4) protons in methoxy- [12] and amino-ferrocene [13] are more shielded with respect to H(2,5) protons.

Results and discussion

To make unequivocal assignment of the signals of C(2,5) and C(3,4) carbons in the monosubstituted ferrocenes we have synthesized 2,5-dideuterated deriva-

tives of the respective substituted ferrocenes: the deuterium-bearing carbon atoms were identified by loss of intensity of the appropriate signals. The ^{13}C chemical shifts of the monosubstituted ferrocenes are listed in Table 1. Comparative data on the effects of substituents in the ferrocene and benzene series are given in Table 2.

It can be seen from Table 1 that the C(1) carbons undergo the largest chemical shift variation and are shifted downfield from ferrocene. However, the C(1) carbons bearing an sp-hybridized carbon (cyanoferrocene, ferrocenylacetylene) are an exception. The C(6) chemical shifts in ferrocene derivatives change in a rather narrow region and resemble the meta-carbons in benzenes. In terms of the homoannular effect the data on shielding of C(2,5) and C(3,4) carbons are most in interesting.

In the alkylferrocenes the C(2,5) carbon signals are shifted upfield in the series methyl-, ethyl-, isopropyl- and t-butyl-ferrocene (δ(C(2,5)) 68.9, 67.2, 65.8 and 64.8 ppm, respectively). In the same series the C(1) signal shifts down-

TABLE 1

THE ^{13}C CHEMICAL SHIFTS OF SUBSTITUTED FERROCENES IN DICHLOROETHANE AND FERRO—CENYLCARBENIUM IONS IN CONCENTRATED H_2SO_4

Substituent R	^{13}C (ppm from TMS)				
	C(1)	C(2,5)	C(3,4)	C(6)	Substituent
H	67.7	67.7	67.7	67.7	
CH_3	83.4	68.9	66.8	68.4	14.4 (CH_3)
CH_2CH_3	90.7	67.2	66.7	68.2	22.0 (CH_2), 14.4 (CH_3)
$CH(CH_3)_2$	96.6	65.8	66.5	68.0	27.4 (CH), 23.2 (CH_3)
$C(CH_3)_3$	101.7	64.8	66.7	68.2	30.2 (C), 31.2 (CH_3)
$CH_2C(CH_3)_3$	85.3	69.9 [a]	66.9 [a]	68.2	44.6 (CH_2) 31.3 (C), 28.9 (CH_3)
$CH_2N(CH_3)_2$	83.9	70.0	67.8	68.6	58.3 (CH_2), 44.8 (CH_3)
CH_2OH	87.7	67.7	67.9	68.0	60.1 (CH_2)
$CH(OH)CH_3$	94.1	65.4	67.4	68.1	65.1 (CH), 23.4 (CH_3)
		66.0	67.5		
$CH(OH)CH_2CN$	90.0	65.5	68.1	68.3	65.6 (CH), 26.5 (CH_2), 117.5 (CN)
		66.2	68.2		
$CH(OH)C_6H_5$ [b]	93.9	65.3	67.7	68.2	71.6 (CH)
		67.0	67.8		
$C(OH)(CH_3)_2$	99.8	65.2	67.3	68.0	69.1 (C), 30.6 (CH_3)
$CH_2P^+(C_6H_5)_3\Gamma^{c,d}$	73.7	70.6	69.2	69.8	
$CH_2N^+(CH_3)_3\Gamma^c$	77.9	72.4	70.6	69.6	67.3 (CH_2), 52.8 (CH_3)
OCH_3	127.3	54.7	61.5	68.1	57.0 (CH_3)
CHO	79.2	68.0	72.6	69.2	192.2 (C=O)
$COCH_3$	79.3	69.2	71.8	69.5	200.1 (C=O), 26.9 (CH_3)
$COC(CH_3)_3$	76.6	70.7 [a]	70.9 [a]	69.4	208.5 (C=O), 44.1 (C) [c], 27.6 (CH_3)
$CH=CH_2$	83.2	66.4	68.4	68.9	134.4 (CH), 110.4 (CH_2)
cis-CH=CHCN	76.9	69.4	70.9	69.6	149.3, 141.2 (CH), 118.6 (CN)
trans-CH=CHCN	77.7	67.8	70.9	69.5	150.9, 141.2 (CH), 118.6 (CN)
C≡N	51.8	70.1	71.4	70.2	119.3 (CN)
C≡CH	63.5	68.3	71.2	69.6	82.2 (C), 73.5 (CH)
$^+CH_2$	110.6	84.6	94.4	82.3	87.7 (CH_2)
$^+C(CH_3)_2$	100.0	78.7	93.4	81.9	156.0 (C), 27.6 (CH_3)

[a] C(2,5) and C(3,4) signal assignments are not confirmed. [b] Phenyl: C_i, 143.6, C_o 137.7, C_m 126.9, C_p 125.8 ppm. [c] In CH_2Cl_2 solution. [d] Other ^{13}C signals (ppm). The value of the ^{13}C—^{31}P coupling constant is given in parentheses (Hz): CH_2 27.8 (45.6), C_i 117.9 (85.4), C_o 134.3 (10.3), C_m 130.3 (13.2); C_p 135.2 (4.4).

TABLE 2

A COMPARISON OF THE RELATIVE CHEMICAL SHIFTS IN THE RING OF MONOSUBSTITUTED FERROCENES AND BENZENES

| Substituent R | Ferrocene derivatives | | | Benzene derivatives | | | | |
| | ^{13}C (ppm from ferrocene) | | | ^{13}C (ppm from benzene) | | | | Ref. |
	C(1)	C(2)	C(2)	C(1)	C(2)	C(3)	C(4)	
CH_3	15.7	1.2	-0.9	9.3	0.8	0.0	-2.9	14
C_2H_5	23.0	-0.5	-1.0	15.7	-0.4	0.1	-2.6	14
$CH(CH_3)_2$	28.9	-1.9	-1.2	20.3	-1.9	0.1	-2.4	14
$C(CH_3)_3$	34.0	-2.9	-1.0	22.4	-3.2	-0.2	-2.9	14
$CH_2C(CH_3)_3$	17.6	2.2	-0.8	11.1	1.9	-0.6	-2.7	15
CH_2OH	20.0	0.0	0.2	13.0	-1.4	0.0	-1.2	16
$CH_2P^+(C_6H_5)_3$	6.0	2.9	1.5	0.0	3.7	1.4	1.1	17
CHO	11.5	0.3	4.9	8.6	1.3	0.6	5.5	18
$COCH_3$	11.6	1.5	4.1	9.1	0.1	0.0	4.2	18
$COC(CH_3)_3$	18.9	3.0	3.2	9.4	-1.1	-1.1	1.7	19
$CH=CH_2$	15.5	-1.3	0.7	9.7	-1.8	0.4	-0.3	19
$C{\equiv}CH$	-4.4	0.4	3.3	-6.1	3.8	0.4	-0.2	18
CN	-15.9	2.4	3.7	-16.3	3.6	0.6	3.9	18
$C^+(CH_3)_2$	32.3	11.0	25.7	11.5	13.9	4.8	27.4	20
OCH_3	59.6	-13.0	-6.2	31.4	-14.4	1.0	-7.7	18
NH_2	36.5	-8.9	-4.7	18.0	-13.3	0.9	-9.8	18
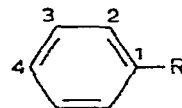
field with an alkyl group branching analogously to alkylbenzenes [14]. Thus excluding the methyl group all the alkyl substituents cause an upfield shift of the C(2,5) signal with respect to that of ferrocene (δ 67.7 ppm). The C(3,4) chemical shifts are observed relatively upfield (66.6—66.8 ppm). However, the shielding of the C(3,4) nuclei is less sensitive to the alkyl group nature than is that of the C(2,5) nuclei.

A comparison of the effect of the neopentyl group and a "big four" of the alkyl substituents shows that in view of the C(1) and C(2,5) chemical shifts the neopentyl group effect resembles a methyl rather than ethyl group effect.

Earlier in the study of alkylferrocenes by ^1H NMR it was observed that H(3,4) shielding is greater than that of H(2,5) [4]. Analogously to alkylferrocenes, the H(3,4) protons in amino- and methoxy-ferrocenes are more shielded. Since both the amino and methoxy groups are classically electron-donating substituents by resonance it has been proposed that a predominant of H(3,4) shielding protons in alkylferrocenes may be due to the alkyl group hyperconjugation [4].

However, the data of ^{13}C NMR spectra are inconsistent with such a conclusion. Thus if the C(3,4) carbons in methyl- and ethyl-ferrocenes are more shielded than the C(2,5) carbons, then in isopropyl- and t-butyl-ferrocene, on the contrary, the C(2,5) carbons are more shielded. Obviously the available data on the ^1H and ^{13}C shielding in alkylferrocenes cannot serve as conclusive evidence of the hyperconjugation [2].

When the relative inductive effects of the substituents are sufficiently different, by degree of C(3,4) carbon shielding the substituents are arranged in the order

expected: $CH_2CH_3 > CH_2N(CH_3)_2 \gtrsim CH_2OH > CH_2P^+(C_6H_5)_3I^- > CH_2N^+(CH_3)_3I^-$. A correlation between the substituent-inductive effect and C(2,5) carbon shielding is somewhat weaker, probably owing to a steric interaction between the bulky substituents and the 2,5-positions in the substituted ring. It could be pointed out further that if the given group is electron donating by induction then the C(3,4) carbons are more shielded with respect to ferrocene, and the relative shielding of C(2,5) and C(3,4) carbons may alter with the substituent (cf. ethyl- and neopentylferrocene).

In the case of the electron-withdrawing substituents by induction, then depending on their withdrawing strength only the signals from C(3,4) or from both C(3,4) and C(2,5) are shifted downfield from ferrocene. In $FcCH_2P^+(C_6H_5)_3I^-$ and $FcCH_2N^+(CH_3)_3I^-$ (Fc = ferrocenyl) the C(2,5) carbons are less shielded than the C(3,4). It is seen from Table 2 that a similar pattern is observed for the *ortho-* and *para*-carbons in benzene analogs.

In ferrocenyl carbinols the C(3,4) carbons are somewhat less shielded in comparison with the C(2,5). When a substituent has an asymmetric carbon atom, the 2,5- and 3,4-positions are pairwise diasteretopic. More differences in the chemical shifts were detected for the C(2) and C(5) closest to the substituent, which are equal to 0.6 and 4.2 ppm for $FcCH(OH)CH_3$ and $FcCH(OH)C(CH_3)_3$, respectively. Probably the steric substituent effects play a significant role in the shielding of the C(2,5) carbons in ferrocenes, analogously to the *ortho*-carbon shielding in benzenes.

Thus the inductive substituents, depending on their withdrawing or donating properties and relative strength, may produce essentially different effects on the relative ^{13}C shielding in the substituted cyclopentadienyl ligand. Even in alkylferrocenes where alkyl group effects should be close, the electron density is distributed over the ring in such a way as to provide sign inversion for the relative shielding of the C(2,5) and C(3,4) carbons on going from methyl- and ethylferrocene to isopropyl- and t-butyl-ferrocene (see above). The fact that the C(1) carbon shielding changes essentially in alkylferrocenes ($\Delta\delta(C(1))$ 18.3 ppm) while the difference in C(3,4) shielding is very small ($\Delta\delta(C(3,4))$ 0.4 ppm) may demonstrate that the π-inductive effect makes a considerable contribution to the electron density redistribution over the ring.

An interesting feature is revealed for the ^{13}C shielding in the ferrocenes with the electron-withdrawing substituents by resonance (CHO, CN etc.). In the ^{1}H NMR spectra of these compounds the H(2,5) protons are less shielded than the H(3,4) while the carbon spectra show the C(3,4) to have lower shielding than the C(2,5) carbons. For example in formylferrocene the C(2,5) and C(3,4) signals are observed at 68.0 and 72.6 ppm, respectively. These results are in agreement with the conclusion of Levenberg and Richards [6] that the magnetic anisotropy of the carbonyl group plays a dominant role in determining the relative chemical shifts of the H(2,5) and H(3,4) protons in acylferrocenes. However, this conclusion has often been ignored since and even in the review by Slocum and Ernst [3] ferrocene is revealed as an aromatic system which exhibits a response to all electron-withdrawing substituents principally in the 2,5-positions.

Analogously to acylferrocenes the predominant C(3,4) deshielding is observed in cyano-, vinyl-, *cis-β*-cyanovinyl-, *trans-β*-cyanovinyl-ferrocenes and ferrocenylacetylene as well. Thus the 3,4-positions instead of 2,5-positions (as it has been

suggested earlier [3]) are more response to the electron-withdrawing substituent by resonance. It is interesting that in the series of ferrocene derivatives FcCHO, FcCOCH$_3$ and FcCOC(CH$_3$)$_3$ the difference in C(2,5) and C(3,4) shielding is 4.6, 2.6 and 0.2 ppm respectively. Steric hindrance to the resonance is the most appropriate explanation of such behaviour: the coplanarity of the carbonyl group and cyclopentadienyl ring decreases with increasing bulk of the alkyl group. The shielding of *para*-carbons in the sterically hindered phenylalkylketones has also been explained by sterical reasons [20].

The predominant deshielding of C(3,4) carbons is most evident in ferrocenyl-carbenium ions. The relative C(2,5) and C(3,4) carbon shielding in the ferrocenyl-carbenium ions is similar to that in acylferrocenes or to the relative shielding of *ortho*- and *para*-carbons in phenylcarbenium ions and may serve as evidence of the predominantly resonance stabilization of the ferrocenylcarbenium ions [22].

It is seen from the data of Table 2 that the electron-withdrawing substituents by resonance are arranged in the same order of capability of deshielding the C(3,4) carbons both in ferrocenes and *para*-carbon in benzenes: C$^+$(CH$_3$)$_3$ > CHO > COCH$_3$ > CN.

However, the 3,4-positions exhibit a response not only to the electron-withdrawing substituents by resonance, but to an electron-donating substituent by resonance, although to a lesser extent than the 2,5-positions do. Thus in the amino- and methoxy-ferrocene the C(2,5) carbons are more shielded than C(3,4) carbons. Therefore for these substituents similar behaviour is observed for the C(2,5) and C(3,4) carbons in ferrocene, and for *ortho*- and *para*-carbons in benzene as well.

Conclusion

From these results the following conclusions may be drawn:

(*a*) in ferrocenes the 3,4-positions of the substituted cyclopentadienyl ring are more sensitive to electron-withdrawing substituents by resonance; the 2,5-positions are more sensitive to strong electron-donating groups by resonance;

(*b*) the 3,4-positions are sensitive to substituent inductive effects, but the relative shielding of C(2,5) and C(3,4) carbons depends on the substituent nature, and could alter even in alkylferrocenes;

(*c*) the opinion that "ferrocene is now revealed as an aromatic system which exhibits a response to all electron-withdrawing substituents principally in the 2,5-positions and response to strong or weak electron-donating substituents principally in the 3,4-positions" [3], is incorrect and should be revised;

(*d*) an apparent analogy is observed in the shielding of C(2,5) and C(3,4) carbons in ferrocenes and *ortho*- and *para*-carbons in benzenes with the same substituents. Therefore, we may associate the shielding of carbons in the ^{13}C NMR spectra of ferrocenes with an electron density distribution, as has been shown by numerous examples in the benzene series.

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