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THE ^{1}H AND ^{13}C NUCLEAR MAGNETIC RESONANCE AND IR ADSORPTION SPECTRA OF SUBSTITUTED POLYMETHYLFERROCENES

R.B. MATERIKOVA *, V.N. BABIN, I.R. LYATIFOV, T.Kh. KURBANOV, E.I. FEDIN, P.V. PETROVSKII and A.I. LUTSENKO

Institute of Organo-Element Compounds, Academy of Sciences, Moscow (U.S.S.R.)

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Summary

The NMR and IR spectra of *sym*-polymethylferrocenes have been studied. The abnormal shifts observed of the ^{13}C signals from the adjacent methyl groups are discussed in terms of spatial interactions between these groups, which cause charge redistribution in the vicinity of the ^{13}C nuclei.

Until now, none of the series of substituted ferrocenes in which the number of substituents successively increases up to a fully substituted species has been subjected to systematic study. Such a study of, e.g. symmetric heteroannular polymethylferrocenes would provide insight into the specific features of electron density distribution and hence contribute to a deeper understanding of the nature of interactions between the methyl group and the ferrocene aromatic system.

As the compounds discussed here contain two identically substituted rings in a molecule, then taking into consideration that these rings undergo free rotation * we may as first approximation neglect the heteroannular effects by the substituents and restrict the analysis to interactions between the nonclassic aromatic five-membered ring and the methyl groups.

Figure 1 gives a schematic representation of the proton NMR spectra of ferrocene and its polymethyl-substituted analogues: 1,1′-dimethylferrocene, $(MeCp)_2Fe$; 1,3,1′,3′-tetramethylferrocene, $(1,3\text{-}Me_2Cp)_2Fe$; 1,2,4,1′,2′, 4′-hexamethylferrocene, $(1,2,4\text{-}Me_3Cp)_2Fe$; *sym*-octamethylferrocene, $(Me_4Cp)_2Fe$, decamethylferrocene, $(Me_5Cp)_2Fe$. The chemical shift values are summarized in Table 1. By considering the peak area ratios, the methyl proton signals at 1.79 and 1.76 ppm in the proton NMR spectrum of $(1,2,4\text{-}Me_3Cp)_2Fe$ can unambiguously be assigned to the 4- and 1,2-methyl groups, respectively. Note that the signal from the vicinal CH_3 groups appears at the higher field. An increase in the

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* The ^{13}C peak widths in the spectrum of decamethylferrocene are practically independent of temperature in the range +30° to —60°C.

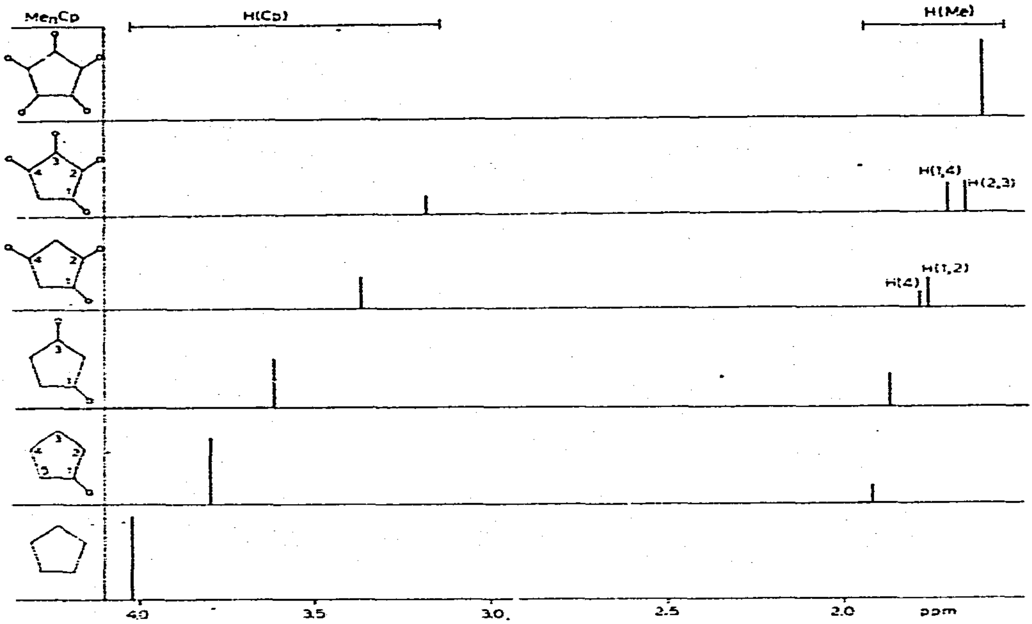

Fig. 1. A schematic representation of the ^{1}H NMR spectra of ferrocene and its polymethyl homologues.

number of electron releasing methyl substituents successively shifts all the signals of polymethylferrocenes upfield. The difference in the chemical shift values, $\Delta\delta$(H) between the adjacent members of the series amounts to 0.18—0.24 ppm for H(Cp) and to 0.05—0.11 ppm for H(Me) (cf. the data in refs. 4—6). The δ values are not strictly additive, possibly because of spatial effects and variation in contributions from the lowest free molecular orbitals to the electron distribution, which increase with the number of methyl substituents in the ferrocene molecule.

Spatial interactions between the methyl groups might be expected to have observable effects on the IR spectra of polymethylferrocenes. The IR data (KBr

TABLE 1

PROTON CHEMICAL SHIFTS IN THE ^{1}H NMR SPECTRA OF *sym*-POLYMETHYLFERROCENES (in CS_2)

Compound	Ring proton chemical shifts δ (ppm)	CH_3 proton chemical shifts δ (ppm)	Literature
Ferrocene	4.02		4.008 [1]
1,1'-Dimethylferrocene	3.80	1.92	
1,1',3,3'-Tetramethylferrocene[a]	3.62	1.88	
1,1',2,2',4,4'-Hexamethylferrocene	3.38	1.79	
		1.76	
sym-Octamethylferrocene	3.19	1.72	
		1.66	
Decamethylferrocene		1.61	1.62 [2]

[a] For the data on 1,1',2,2'-tetramethylferrocene and *sym*-octamethylferrocene ($CDCl_3$) see ref. 3.

discs, UR-10 spectrophotometer, 700—3200 cm^{-1}) are summarized in Table 2. As the number of methyl substituents increases, the molecular symmetry first successively falls and then successively increases. The number of the observed IR bands changes accordingly. The effect is most evident in the region of 800 cm^{-1} (the out-of-plane ring C—H bendings) and 1400 cm^{-1} (the E_{1g} and E_{1u} vibrations of the ferrocene system) [9]. The introduction of CH_3 somewhat lowers the ring C—H stretches (3000—3100 cm^{-1}). On the contrary, the C—H stretching frequencies of the methyl groups (2800—3000 cm^{-1}) suffer only insignificant displacements under the action of the adjacent ferrocene ring, except for the 2900 and 2872 cm^{-1} bands. The latter one undergoes resonance splitting, as may be expected for the Me group attached to the conjugate system [10]. Small systematic variations of vibrational frequencies and band intensities are observed in the region of symmetric and asymmetric bending vibrations of the methyl groups (1385—1375 and 1455—1475 cm^{-1}); no drastic changes in the IR spectrum, however, occur in passing from unsubstituted ferrocene to the decamethyl derivative. The data obtained are insufficient for any conclusions about the presence (or

TABLE 2

IR ABSORPTION SPECTRA OF *sym*-POLYMETHYLFERROCENES $[(CH_3)_nC_5H_{5-n}]_2Fe$ (cm^{-1})

H	CH_3 [a]	1,3-$(CH_3)_2$ [a]	1,2,4-$(CH_3)_3$	$(CH_3)_4$	$(CH_3)_5$
790m	780w (sh)	767w 786w	742w	690w 787vw	
820s	810s 846m	809m 830w (sh) 839s 865w	825s 844s	823s	
	918w 926w	928w 932w 955m	931m 979w	930w 975m	
1005s	1023s		1027s		1038vs
1055w	1034s	1037s		1031s	1073m
1110s			1115w 1187m	1113w	
	1225m	1275m			
			1300m		
	1343w		1308m (sh)		
	1358m		1338m	1325m	
	1370w	1348m	1342m (sh)		
	1380w	1378s	1365s	1362s	1365m
	1384w (sh)		1380m	1378s	1375vs
1415m	1435w		1423w (sh)	1423m	1427m
		1440m	1440s	1442m	1450m
	1455m (sh)	1459s	1459m	1466m	1476m
	1468m	1494m	1495w	1472m	
	1475m		1498w	1487m	
	2845w	2865s	2865s	2862m	2857s
	2885m	2890s	2886s (sh)	2865m	2882s (sh)
	2920m	2923s	2910s	2902s	2900s
	2943m	2947s	2937s	2948s	2945s
	2967m	2967s	2960s	2969s	2968s
3100m	3078m	3072m	3057w		
	3090w	3076m	3070m	3070m	

[a] The IR spectra of similar t-butyl homologues are given in ref. 7; for the IR spectrum of 1,1′-dimethylferrocene see also ref. 8.

absence) of direct Van der Waals interactions to be made.

Other factors that may influence the ^{13}C and ^{1}H NMR spectra of the compounds studied are the following: first, spatial electrostatic interactions between the methyl groups, which affect diamagnetic shielding of the adjacent atoms and atomic groups; second, contributions due to magnetic anisotropy. Comparison of proton decoupled and undecoupled ^{13}C NMR spectra provides an unambiguous assignment of the signals (see Fig. 2 and Table 3). Thus, the signal at δ 67.99 ppm observed in the spectrum of $(MeCp)_2Fe$ may with certainty be assigned to the C(3,4) nuclei on the grounds that the $^{1}J(^{13}C-^{1}H)$ and $^{2,3}J(^{13}C-^{1}H)$ constants remain near their values in unsubstituted ferrocene (rather weak perturbation of the ferrocene electronic system [17]) and from consideration of signal multiplicities: the C(3,4) signal represents a well resolved quartet, unlike the C(2,5) one which is considerably broadened due to couplings with the methyl protons [11—13]. Comparison of the chemical shift values and of the $^{1}J(^{13}C-^{1}H)$ constants observed in the spectra of $(MeCp)_2Fe$ and $(1,3\text{-}Me_2Cp)_2Fe$, as well as the relative intensities of the Cp ring carbon signals in the spectrum of the latter compound, show the tetramethylferrocene signal at 69.87 ppm to arise from C(4,5) [12]. The $^{13}C-\{^{1}H\}$ NMR spectrum of 1,2,4,1′,2′,4′-hexamethylferrocene contains two methyl carbon signals and two signals from the key atoms of the Cp ring, with the peak area ratio of 2/1 for each pair of signals. With the Me groups, the more intense signal (that of vicinal substituents) is again shifted upfield, while the signal of the adjacent ring carbon atoms (the stronger key atom peak) is displaced to the lower field region (the shifts are referred to the respective isolated groupings).

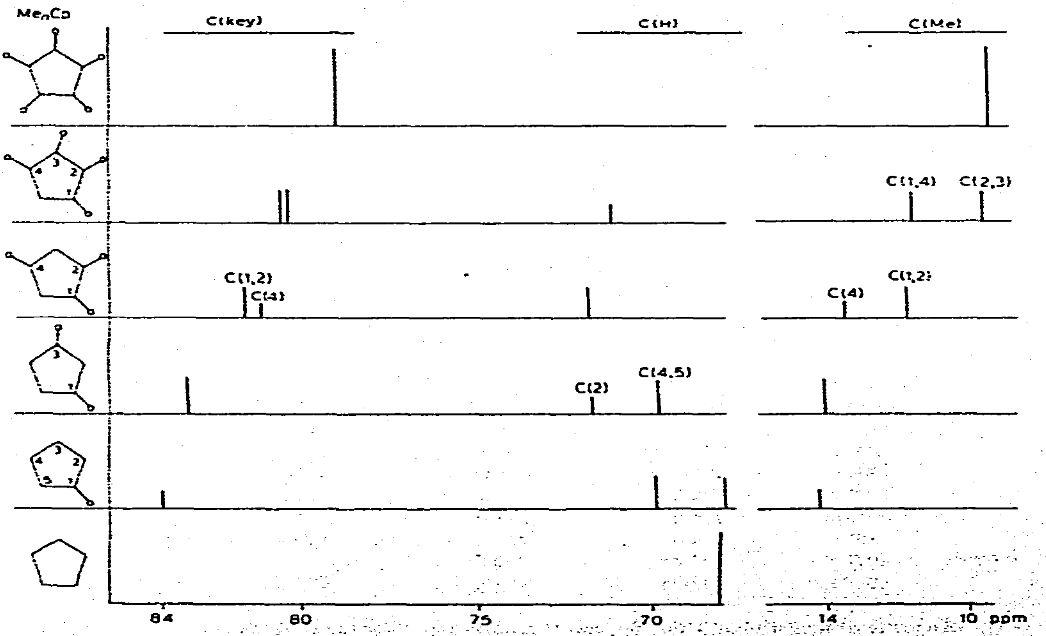

Fig. 2. A schematic representation of the ^{13}C NMR spectra of ferrocene and its polymethyl homologues.

TABLE 3

THE ^{13}C NMR DATA ON *sym*-POLYMETHYLFERROCENES (solvent and internal reference CH_2Cl_2)

Compound	Key atoms		Unsubstituted atoms			Methyl atoms		References
	δ (ppm)	$^{2,3}J(^{13}C-^{1}H)$ (Hz)	δ (ppm)	$^{1}J(^{13}C-^{1}H)$ (Hz)	$^{2,3}J(^{13}C-^{1}H)$ (Hz)	δ (ppm)	$^{1}J(^{13}C-^{1}H)$ (Hz)	
Ferrocene			68,12	175,0	6,6			11–16
1,1′-Dimethylferrocene	84,04	7.3	69,94 67,99	172,8 174.3	7.3	14.32	126.5	11–14
1,3,1′,3′-Tetramethylferrocene	83,36	6,1	71,82 69,87	170.2 171.3		14.19	126.5	
1,2,4,1′,2′,4′-Hexamethylferrocene	81,76 81,18		71,89	167,7		13,67 11,85	127,2 125,7	
sym-Octamethylferrocene	80,66 80,47		71,17	163,2		11,59 9,64	125,0 125,0	
Decamethylferrocene	78,98					9,48	125,7	

The dependence of the C(Me) chemical shifts on the number of methyl substituents is interesting. In general, the C(Me) signals, as expected, progressively shift upfield as the extent of substitution increases; the shifts however remain rather small while only isolated methyl substituents are present: δ(Me) decreases by $\Delta\delta$(Me) 0.13 ppm on passing from $(MeCp)_2Fe$ to $(1,3\text{-}Me_2Cp)_2Fe$. However, the first vicinal substituent displaces the ^{13}C(Me) NMR signal to the higher field by 2.0 to 2.4 ppm. With two vicinal substituents in the molecule, the effect is twice as strong (see Fig. 2). Thus, according to the δ value observed, we may distinguish three types of methyl substituents: isolated Me groups (δ 14.4 to 13.6 ppm), Me substituents with one vicinal group (δ 11.9 to 11.6 ppm), and Me groups having two vicinal substituents (δ 9.7 to 9.5 ppm).

Using the correlation between the ^{13}C and ^{1}H chemical shifts [17], we carried out a similar analysis of the ^{1}H signals. The singlet at 1.66 ppm observed in the spectrum of $(Me_4Cp)_2Fe$ has been assigned to the CH_3 group having two vicinal methyl substituents. It should be noted that considerable upfield shifts of the signals of the vicinal methyl substituents (the "*ortho* effect") is also characteristic for polymethylbenzenes [15,18,19].

In general, shielding of the ^{13}C nuclei in the compounds studied reveals the following trends. The introduction of the first methyl group into the Cp ring shifts the key atom signals downfield by 15.92 ppm from unsubstituted ferrocene (cf. ref. 20). Further substitutions progressively shift the key atom signals to the higher field region. The methyl carbon signals also shift upfield. The first and the second vicinal substituents each shift the signal by 2 ppm upfield. The $^1J(^{13}C—^1H)$ constants of the Me groups remain almost unaffected. The unsubstituted ring carbon atoms behave very differently from the methyl and key carbon atoms. A nonmonotonic shift of their signals to the lower field occurs as the number of substituents increases. Simultaneously, the $^1J(^{13}C—^1H)$ constants successively decrease because of *s*—*p* electron density redistribution on the Cp—Fe bonds [17].

The simplest additive scheme based on the increment values derived from the ^{13}C NMR spectra of ferrocene and 1,1'-dimethylferrocene provides an adequate description of the number, intensity, and mutual positions of the signals of unsubstituted and key atoms in the spectra of all compounds studied. It is reasonable to calculate the spectra of methyl carbon atoms using the increment values determined from the spectra of deca- and octa-methylferrocenes. The most serious qualitative discrepancy between the calculation and experimental results is observed for the key carbon atoms: the calculations predict progressive downfield shifting of these signals as the number of substituents increases, whereas the experiment testifies to the contrary.

A similar pattern has been observed by Grant and co-workers [18,19] for the methyl carbon signals in polymethylbenzenes. It is likely that the same factors are responsible for the effects observed in both series. It may well be that charge redistribution in the vicinity of a spatially perturbed ^{13}C(Me) nucleus is the most important one among these factors. Polymethylferrocenes comprising five-membered rings afford more opportunity for analyzing the effect of the angle between the adjacent substituents on the observed shifts: in the ferrocene series, the difference between the $\Delta\delta$(Me) values decreases on going from a methyl group having one vicinal substituent to that with two vicinal neighbours as referred to appropriate difference in benzene series.

At present, we are studying the dependence of the chemical shifts of unsubstituted and key carbon atoms on the nature of the alkyl substituents, on the metal, and on the charge of the central atom. These studies, we believe, will provide added insight into the patterns of chemical shift variations in the polymethylferrocene series, in particular, into the features that distinguish methylferrocenes from other alkylsubstituted species, such as downfield shifts of the α-C signals and upfield shifts of the key atom signals as the number of the substituents increases.

The ^{1}H NMR spectra (CS_2) were obtained on a Hitachi—Perkin—Elmer R-20 instrument operated at 60 MHz, 34°C. The ^{13}C NMR spectra were recorded with a Bruker HX-90 spectrometer, using CH_2Cl_2 as solvent and internal reference. The operating conditions were 22.635 MHz, 30°C.

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