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PROTON MAGNETIC RESONANCE SPECTRA OF HOMOANNULAR FERROCENES

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Summary

The proton magnetic resonance spectra of homoannular isomeric diethyl- and diacetyl-ferrocenes were studied. Chemical shifts were determined, and the results are discussed in terms of inductive and hyperconjugative effects of the substituent groups.

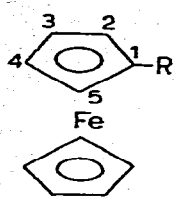
We have studied the PMR spectra of a series of ferrocene homologues (I) and found that the alkyl substituents possessed weak electron-donor properties [1-4]. Proton chemical shifts of the cyclopentadienyl (Cp) ring, in other words heteroannular effects of the alkyl groups, were found to be paralleled by hyperconjugation effects in the series Me > Et > i-Pr > t-Bu [3,4].

TABLE 1

PROTON CHEMICAL SHIFTS (ppm) IN ALKYL FERROCENES WITH RESPECT TO FERROCENE

Alkyl	H(1)	H(2,5)	H(3,4)	Ref.
CH_3[a,b]	0.077	0.109	0.146	5
CH_3[c]	0.079	0.108	0.143	
CH_3CH_2[a,b]	0.064	0.105	0.114	5
CH_3CH_2[c]	0.063	0.097	0.121	
$CH(CH_3)_2$[a]	0.050	0.114	0.114	5
$C(CH_3)_3$[a]	0.023	0.096	0.132	5
$C(CH_3)_3$[c]	0.013	0.132	0.086	4

[a] Recorded in CCl_4 at 20°C against a 2% TMS internal reference on a Varian 220 MHz instrument. [b] Assigned on the basis of the spectra of the respective 2-deuteriated derivatives [5]. [c] Recorded in C_6H_{12} at 20°C against an HMDS internal reference (HMDS 0.05 ppm) on a Bruker-HX-90 spectrometer.



R = Me, Et, i-Pr, t-Bu

(I)

The homoannular effect comprises both induction and hyperconjugation effects. Indeed, Slocum and Ernst showed later [5] that the protons 3 and 4 (R = Me, Et) were more strongly shielded than were the protons 2 and 5 (Table 1). The assignments [5] were made for Me, Et [5a] and t-Bu [5a,b], experimentally (Table 1). If the assignments were valid for a t-Bu group, a highfield doublet responsible for the equivalent protons 4 and 5 (cf. ref. 4) should arise in 1,3-di-t-butylferrocene as well as in 1,1',3,3'-tetra-t-butylferrocene. The experiment [4], however, suggests just the opposite arrangement, viz., the proton 2 triplet whose intensity is lower by a factor of 2 lies at higher fields [3]. The structure of 1,1',3,3'-tetra-t-butylferrocene was established by X-ray techniques [6]. In this paper we have studied the PMR spectra of homoannular isomeric diethyl- and diacetyl-ferrocenes (Table 2, Fig. 1).

The data demonstrate that the regularities stressed above hold in these molecules as well. This is most evident in the spectra of 1,3-diacetyl- and 1,2-diacetyl-ferrocenes where the triplet lies on the left of the doublet in the former compound, and on the right in the latter. In this connection it is especially interesting that 1,2-diethylferrocene synthetised from 1,2-diacetylferrocene has a spectrum that is almost identical to that of 1,3-di-t-butylferrocene. This agrees with the results obtained by Slocum for ethylferrocene and, at the same time, indicates unambiguously that no α—β-inversion of the NMR ^{1}H chemical shift is caused by a t-butyl substituent in the Cp ligand. The synthesis of the ferrocenes under study has been reported by us elsewhere [7,8].

Our data may suggest that the effect of electron-donor and electron-accep-

TABLE 2

PROTON CHEMICAL SHIFTS IN 1,2- AND 1,3-FERROCENE DERIVATIVES

Compounds	Proton chemical shifts								Ref.
	Unsubstituted Cp-ring	Substituted Cp-ring				Alkyl groups		Solvent	
		2	3	4	5	CH_3	CH_2		
1,2-$(C_2H_5)_2C_5H_3FeC_5H_5$ [a]	3.89		3.90	3.80(1)	3.90	1.18(6)	2.37(4)	CCl_4	This work
1,2-$(CH_3CO)_2C_5H_3FeC_5H_5$ [a]	4.28		4.91	4.63	4.1	2.49		$CHCl_3$	This work
1,3-$(CH_3CO)_2C_5H_3FeC_5H_5$	4.21	5.30		5.05	5.05	2.37		$CHCl_3$	This work
1,3-$(t\text{-}C_4H_9)_2C_5H_3FeC_5H_5$ [b]	4.04	3.80		3.87	3.87			C_6H_{12}	4
[1,3-$(t\text{-}C_4H_9)_2C_5H_3]_2Fe$ [b]		3.80		3.87	3.87			C_6H_{12}	2-4

[a] Recorded on a Cameca 250 MHz instrument in CCl_4 against a TMS internal reference. [b] Recorded in C_6H_{12} at 20°C against an HDMS internal reference (HDMS 0.05 ppm) on a Hitachi—Perkin—Elmer R-20 instrument.

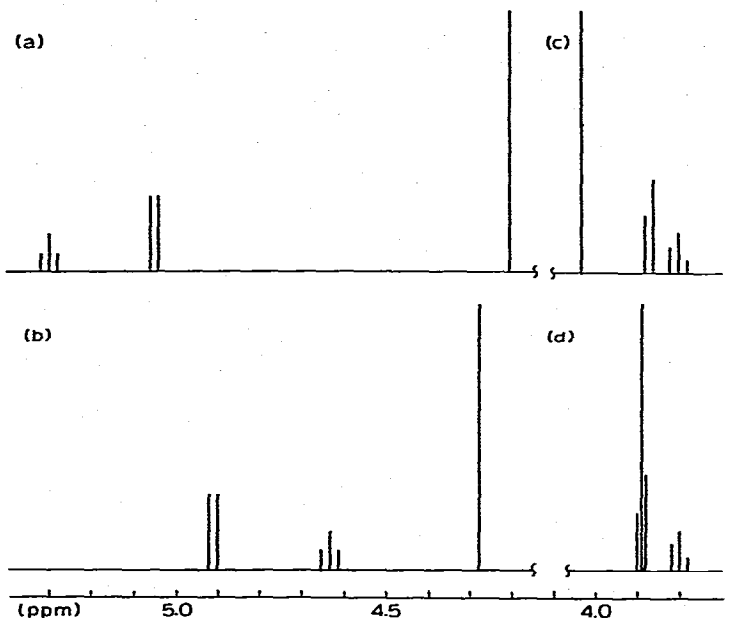


Fig. 1. Schematic representation of NMR spectra. (a) 1,3-Diacetylferrocene; (b) 1,2-diacetylferrocene; (c) 1,3-di-t-butylferrocene; (d) 1,2-diethylferrocene.

tor substituents on the electron density distribution in a molecule of this type is governed by the ratio of contributions of π- and σ-induction effects, conjugation and hyperconjugation, in the total electron effect of the substituents. With electron-donor alkyl substituents, whose induction effect increases in the series Me < Et < i-Pr < t-Bu, while the hyperconjugation effect operates in the opposite direction, the homoannular effect pattern and the location of the electron density maximum in the cyclopentadienyl ring are governed by the structure of the alkyl group. Methyl and ethyl groups, where hyperconjugation plays a role, shift the total electron density towards the β-position in the substituted ring. The isopropyl substituent exerts a weaker hyperconjugation which results in the α- and β-signals coinciding even when recorded on a 270 MHz instrument. These facts can hardly be assigned to the π-induction effect*. Effects of t-butyl and of electron-acceptor acetyl are mainly due to induction ($+I$ and $-I$, respectively): the substituent effect is at its strongest in the α-position of the substituted ring. With other electron-acceptor substituents, however, assignments of the PMR spectra may be different. The problem of homo- and hetero-annular effects of acceptor substituents requires further study.

* *Note added in proof.* It is evident from our ^{13}C NMR data [9,10,11] that the π-inductive effect is maximal for a t-Bu-substituent because its negative shielding of key Cp-carbon is the largest. For a Me-substituent this key-effect is minimal. Thus, we could arrange the alkyl groups in "right induction order" (t-Bu > i-Pr > Et > Me) for π-induction effect and after that it would be possible to reveal the opposite trend (Me > Et > i-Pr > t-Bu) for β-effects. Evidently, these arguments are purely qualitative.

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