

MAGNETIC NON-EQUIVALENCE OF METHYLENE GROUP PROTONS

IN 1, 2-DISUBSTITUTED FERROCENES

G. Marr, R. E. Moore and B. W. Rockett

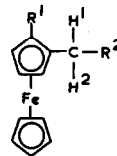
Department of Applied Science,
Wolverhampton College of Technology,
Wolverhampton, England.

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Continued interest in the origin of the magnetic non-equivalence of protons in methylene groups attached to asymmetric centres (1) prompts us to report our results with some 1, 2-disubstituted ferrocenes. Several factors, including molecular asymmetry (2), 2-substituent asymmetry (3), unequal conformer populations resulting from steric hindrance (1c, 4), and solvent (1a) and temperature effects (3) may contribute to the observed chemical shift differences between the methylene group protons.

Unlike the corresponding o-disubstituted benzenes (3), the non-equivalence in 1, 2-disubstituted ferrocenes is not confined to examples in which a plane of symmetry is absent from the side chain (R^1 in the Table). This difference may be ascribed, in part, to the inherent asymmetry of these ferrocenes (5) although the effect must be small since nearly half of the compounds examined showed an A_2 methylene pattern (see Table). The steric effect appears to be important (1c) since when the substituents on both the 2-position (R^1) and the methylene group (R^2) were either secondary or tertiary groups then an AB pattern was invariably observed. It is necessary to appreciate however that steric interactions are not of over-riding importance (1c) and in some cases an increase in the size of the 2-substituent may lead to a decrease in the chemical shift

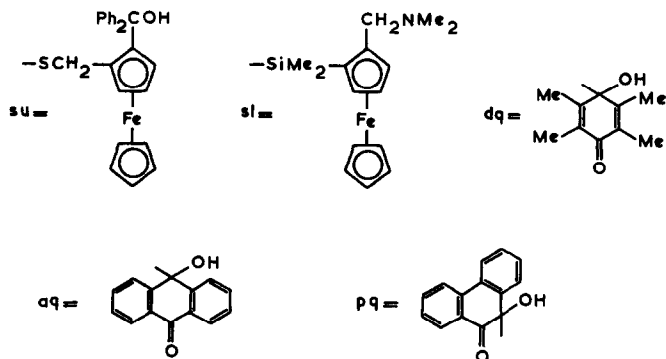
TABLE
P. m. r. absorptions (a) of the methylene groups of some
1, 2-disubstituted ferrocenes (b).



	R ¹	R ²	$\gamma_{1,p.p.m.}(c)$	$\gamma_{1,2}^{p.p.m.}$	$\gamma_{2,p.p.m.}$	$\delta_{1,2}^{c.p.s.}$	$J_{1,2}^{c.p.s.}$
I	CPh ₂ OH	N(CH ₂) ₄	2.935		3.835	54.04	13.6
II	CPh ₂ OH	N(CH ₂) ₅	2.74		3.84	66.06	13.4
III	CPh ₂ OH	su(e)		3.08			
IV	CPh ₂ OH	OH		4.98(d)			
V	CPh ₂ OH	OPh		4.26			
VI	SiMe ₃	N(CH ₂) ₅	2.97		3.66	35.36	12.8
VII	SiMe ₃	NMe ₂	2.97		3.406	26.24	12.8
VIII	sl(e)	NMe ₂	2.72		3.55	49.57	12.0
IX	SiMe ₃	NHPh		4.02			
X	SiMe ₃	OH		4.43(d)			
XI	SiMe ₃	OPh	4.765		4.955	9.45	10.6
XII	Cl	NMe ₂	3.45		3.61	9.17	13.6
XIII	Cl	NHPh		4.19			
XIV	Br	NMe ₂		3.48			
XV	Br	NHPh		4.18			
XVI	Br	OH		4.56			
XVII	I	OPh		4.80			
XVIII	I	NMe ₂		3.34			
XIX	CN	NMe ₂	3.50		3.62	6.74	13.4
XX	dq(e)	NMe ₂	2.80		4.145	80.87	12.4
XXI	aq(e)	NMe ₂	2.79		4.20	84.72	12.8
	R ¹	R ²	$\gamma_{1,p.p.m.}(c)$	$\gamma_{1,2}^{p.p.m.}$	$\gamma_{2,p.p.m.}$	$\delta_{1,2}^{c.p.s.}$	$J_{1,2}^{c.p.s.}$
XXII	pq(e)	NMe ₂	2.38		4.155	94.50	12.9
XXIII	B(OH) ₂	NMe ₂	2.90		4.14	74.54	12.6
XXIV(f)	CH ₂ OH	NMe ₂	2.70		4.73	80.98	12.3

a. Recorded at concentrations of 0.2M in deuteriochloroform at 35⁰ and 60Mc with tetramethylsilane (T.M.S.) as internal standard. b. The compounds were prepared and characterised as parts of other investigations (6, 7). c. γ_1, γ_2 -calculated chemical shifts downfield from T.M.S. for the constituent doublets of the AB quartets arising from the methylene protons; $\gamma_{1,2}$ -measured chemical shift for the methylene singlet; $\delta_{1,2}$ and $J_{1,2}$ -chemical shift differences and coupling constants, respectively, of the methylene protons 1 and 2. d. Partially obscured by other resonances.

e.



f. Recorded at 40 Mc.

differences between the methylene protons. Thus in the series of 2-(halogeno)dimethylamino-methylferrocenes (XII, XIV, XVIII) the chemical shift difference was largest in the presence of the smallest halogen (XII). In deuteriochloroform both the bromo- and iodo-ferrocenes (XIV and XVIII) gave A_2 methylene singlets, whilst in other solvents (8) the resonances in the bromo-ferrocene (XIV) were resolved as AB quartets. Therefore in these compounds the steric effects must be dominated by the differences in electron withdrawing power between the three halogen groups. As expected, the pseudohalogen substituted dimethylaminomethylferrocene (XIX) resembled the corresponding chloro compound (XII) in the chemical shift difference between the methylene protons. Furthermore the silyl-ferrocene (XI) showed inequivalence of the methylene protons whilst the sterically similar silyl-ferrocene (IX) and hydroxydiphenylferrocene (V) showed singlet absorptions.

The sterically small hydroxy-methyl substituent in the amine (XXIV) gave a chemical shift difference between the methylene protons comparable with the differences observed for compounds with large 2-substituents (XX-XXIII). This may be attributed to unequal population of the rotamer states through strong intramolecular OH...N hydrogen bonding. We have demonstrated previously the occurrence of such bonding in 1,2-disubstituted ferrocenes by infrared (6) and proton magnetic resonance (9) techniques. This effect may also contribute to the non-equivalence observed for hydroxy-amines (I, II, XX-XXIII).

We conclude that structural assignments of homoannularly disubstituted ferrocenes which are based on chemical shift differences between α -methylene protons must be treated with some reserve.

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