THE NMR SPECTRA OF ACETYLATED [3]FERROCENOPHANES: AN EXAMPLE OF NON-BONDING ORBITAL ANISOTROPY

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Summary

The nuclear magnetic resonance spectra of a series of mono- and di-acetyl-[3]ferrocenophanes have been investigated by computer matching and NMR shift reagents. Accurate chemical shifts and coupling constants have been obtained. Changes in chemical shift of the "aromatic" or "ring" protons induced by the introduction of an acetyl group into various positions of the cyclopentadiene rings cannot be explained solely by the anisotropy of the acetyl groups. These differences in chemical shift have been interpreted in terms of the anisotropy of the non-bonding hybridized "*d*" orbitals of the iron atom and the perturbations of these orbitals caused by the introduction of the acetyl group.

Introduction

The effect of substituents on the nuclear magnetic resonance chemical shifts in ferrocene systems has been extensively studied [1]. The effect produced by compressing and tilting the rings by tying them together to make ferrocenophanes has also been investigated [2]. However, the combination of these effects has not been systematically studied. The series of mono- and di-acetyl[3]ferrocenophanes provide a model system for the investigation of this combination of effects.

Rinehart, Bublitz and Gustafson [3] offered the first interpretation of

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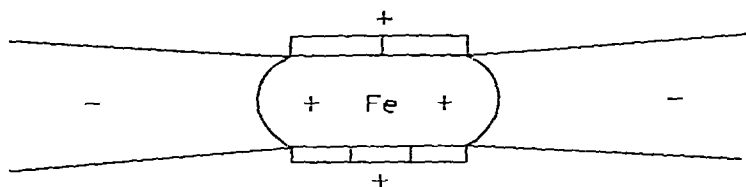* Author to whom correspondence should be addressed.

Fig. 1.

the NMR spectra of acetylated [3]ferrocenophanes. Levenberg and Richards [4] measured the chemical shifts of 2-acetyl[3]ferrocenophane (II) relative to ferrocene and rationalized the chemical shifts of the protons on the unsubstituted ring on the basis of the anisotropy of the acetyl carbonyl. The NMR spectra of a series of homoannularly bridged ferrocenophanes have been studied by Turbitt and Watts [5]. Their data were in general agreement with the picture of anisotropsy of the ferrocene molecule (Fig. 1) based on the magnetic susceptibility measurements of Mulay and Fox [6].

We have made a systematic investigation of the effect of acetylation on the NMR chemical shift of protons on both the substituted and unsubstituted rings of [3]ferrocenophane systems. Only the "aromatic" or ring protons have been investigated.

Experimental

All of the ferrocenophanes used in this investigation have been prepared previously in this laboratory [7] with the exception of the 3-ethyl[3]ferrocenophane. This compound was prepared by the reduction of 3-acetyl[3]ferrocenophane with lithium aluminum hydride and aluminum chloride according to the method of Nystrom and Berger [8]. The 3-ethyl[3]ferrocenophane was crystallized from methanol and had a melting point range of 24-25°C.
Anal. found: C, 70.73; H, 7.20; Fe, 22.21. $C_{15}H_{18}Fe$ calcd: C, 70.89; H, 7.14; Fe, 21.97%.

All compounds were purified, immediately before obtaining spectra, by column chromatography on neutral alumina with spectral grade carbon tetrachloride (CCl_4) as eluent. All spectra were obtained in CCl_4 solution on a Varian A-60 spectrometer, using tetramethylsilane (TMS) as an internal standard, and on a Varian HA-100 spectrometer using TMS as an internal lock signal. Chemical shifts were measured using sideband techniques and are considered to be accurate to ± 0.02 Hz.

Assignments of chemical shifts and coupling constants were made by matching the experimental 100 MHz spectra using the LAOCN-3 computer program [9] modified for use on the Burrough's B-5500 computer. This program was also expanded to include a plotting subprogram, SUBPLOT [10]. Matching was considered to be satisfactory when line positions were reproduced to within 0.003 Hz.

Shift reagent experiments were carried out by standard techniques using $Eu(fod)_3$ as reagent and CCl_4 as solvent. Experiments on 2-acetyl[3]ferrocenophane (II) could not be carried to the equivalence point due to the insolubility of the II—$Eu(fod)_3$ complex.

Calculations of the anisotropic shielding effects of the acetyl group were made according to the method of ApSimon and others [11] and included both radial and multi-angular dependence. Measurements were made assuming a time averaged, in-plane configuration of the acetyl carbonyl; i.e., measurements were taken from both the in-plane positions, the $\Delta\delta$'s calculated and averaged.

Results

The NMR spectra of a series of mono- and di-acetyl[3]ferrocenophanes have been examined to determine the effect of the acetyl group on the "aromatic" protons on both the acylated ring and on the unsubstituted ring. The chemical shifts and coupling constants were assigned so as to best fit the iterative computer analysis of the entire series of compounds. These assignments were then corroborated by shift reagent and spin decoupling experiments. The data have been summarized in Tables 1 and 2. Examples of NMR spectra (100 MHz) and the matching computer generated line spectra for 2-acetyl[3]ferrocenophane and 3-acetyl[3]ferrocenophane are shown in Figs. 2 and 3 respectively.

The results of these experiments can be summarized as follows:

1. All protons on the acylated ring are deshielded, the *ortho* protons to a larger degree than the *meta*.
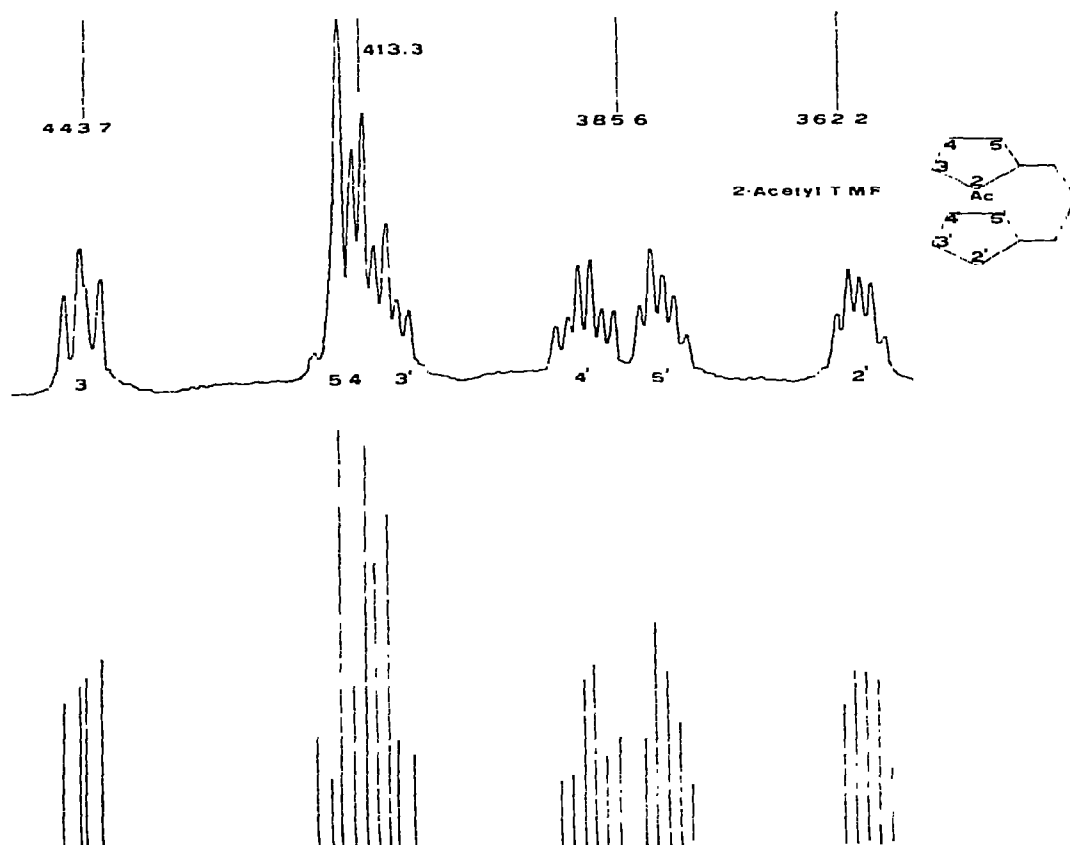

Fig. 2. The NMR spectrum of 2-acetyl[3]ferrocenophane with computer matching.
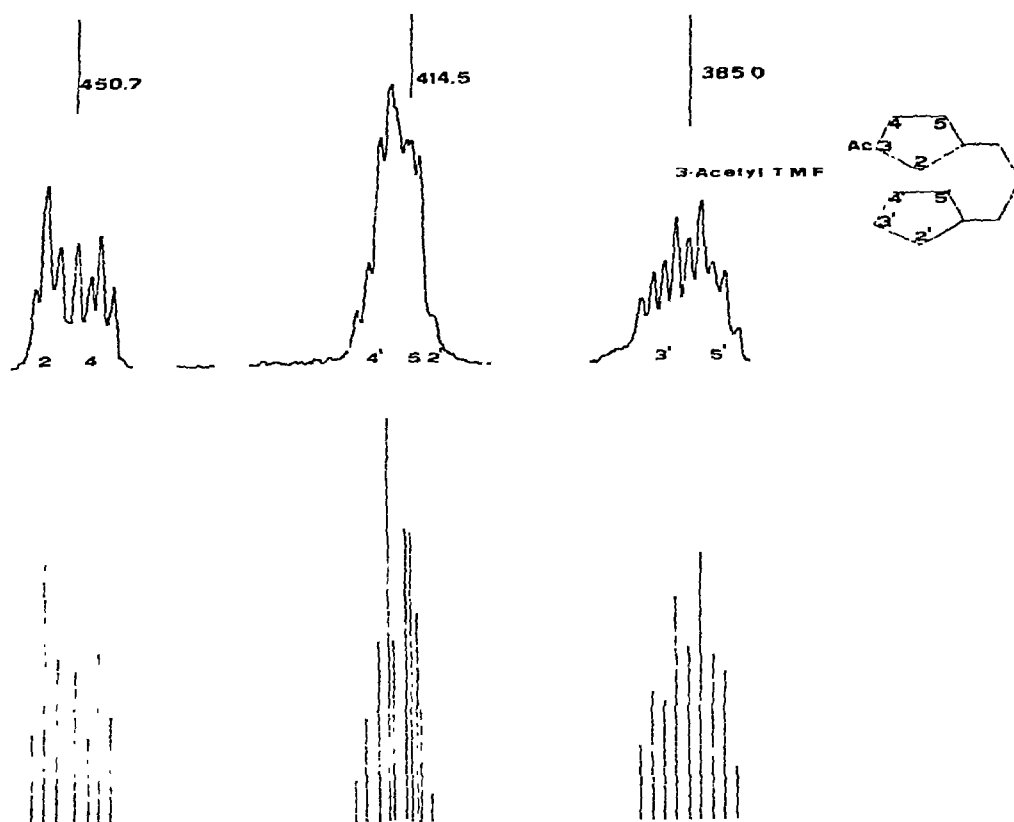
Fig. 3. The NMR spectrum of 3-acetyl[3]ferrocenophane with computer matching.

2. The acetyl group causes a deshielding of the proton on the unacylated ring which lies directly beneath it, i.e., eclipsed by it (see Table 5).

3. The acetyl group causes a deshielding of the protons on the unacylated ring which are adjacent to the eclipsed position.

4. *Ortho* coupling constants range between 2.40 and 2.80 Hz.

5. *Meta* coupling constants are 1.33 ± 0.05 Hz. The only exception to this occurs on the acylated ring when the acyl group is in the α position to the bridge. In this case the coupling constant, $J_{meta} = 1.48$ Hz.

Discussion

Levenberg and Richards [4] measured the chemical shifts of 2-acetyl[3]-ferrocenophane relative to ferrocene and explained the relative shift differences on the basis of the anisotropy of the acetyl carbonyl. The chemical shift assignments used in our study, when taken relative to ferrocene, agree in both magnitude and direction with those used by Levenberg and Richards. However, we *do not consider ferrocene to be the best choice for a model compound* as it does not account for those effects of ring tilt [2] or restricted rotation [12] imposed by the trimethylene bridge. Therefore, [3]ferrocenophane itself has been selected as the model compound.

The initial attempts to computer match the series of mono- and di-acetyl-[3]ferrocenophanes (Tables 1 and 2) based on the assignments for 2-acetyl[3]-ferrocenophane (II) and 3-acetyl[3]ferrocenophane (III) previously published by Rinehard et al. [3] gave rather unsatisfactory results. If, however, one transposes the assignments of the 2' and the 5 protons in the spectrum of II and those of the 2' and 3' protons in the spectrum of III, one obtains a self-consistent set of assignments which give satisfactory computer matching for all of the compounds listed in Table 1. This hypothetical set of assignments was then tested for II and III by measuring the relative changes in the resonance of the protons upon the addition of Eu(fod)₃ shift reagent and by the spin decoupling of the shifted spectra. These experiments have been summarized in Tables 3 and 4.

The assignments for II have been made as a result of these experiments as follows. The proton resonating at 8.17 ppm can be seen to be coupled to only two other protons, viz. those resonating at 6.40 ppm and at 6.07 ppm (Table 4). The magnitude of the coupling constants indicated that the proton at 8.17 ppm is *ortho* to the proton at 6.40 ppm and *meta* to the one at 6.07. These three resonances, therefore, must belong to the three protons on the acetylated ring with the 4 proton being at 6.07 ppm. The relative rate of δ shift (Table 3) indicates that the 8.17 ppm resonance is the 3 proton. Therefore, the 5 proton must be the one at 6.40 ppm.

Irradiation of 5.20 ppm resonance (equivalent to 2 protons) causes the 7.70 ppm resonance to collapse to a doublet with $J \approx 2.5$ Hz. This indicates that it (the proton at 7.70 ppm) is coupled to a proton at 6.07 ppm with the J value for *ortho* coupling. (The 6.07 ppm resonance is equivalent to 2 protons; one of which is on the acetylated ring). The appearance of a triplet at 7.70 ppm upon decoupling the resonance at 6.07 shows that the 7.70 ppm proton is coupled equivalently to two other protons both at 5.20 ppm. The coupling constant, $J \approx 1.2$ Hz, indicated that it (7.70 ppm resonance) is *meta* to those protons at 5.20 ppm. Thus, the 7.70 ppm resonance must correspond to either the 2' or the 5' proton. The relative rate of shift (Table 4) indicates that the 2' proton, rather than the 5', is the one at 7.70. Thus the 5.20 ppm resonance must correspond to the 4' and 5' protons (*meta* to the 2' proton) and the 3' proton, then, is at 6.07 ppm. A similar treatment of the data in Tables 3 and 4 leads to the assignments for III that are listed in Tables 1 and 3. These assignments are identical with those chosen to best fit the entire series of computer matching experiments.

If one now calculates the electric screening and anisotropic effects of the acetyl carbonyl, based on the methods proposed by ApSimon et al. [11], it is obvious that these effects explain neither the magnitude nor the direction of differences in the chemical shifts between analogous protons of acetylated and non-acetylated [3]ferrocenophanes. For example, in the case of II, calculations predict that the 3' proton should be shielded by approximately 10 Hz. It can be seen from Table 5 that this proton is actually deshielded by 21.5 Hz; a discrepancy of over 31 Hz. Similar discrepancies between calculated and experimental values for other protons in II, III and IV have been illustrated in Table 5. Some particular mention should be made of the 3-ethyl[3]ferrocenophane (VIII). The inductive effect of the ethyl group would be opposite that of the acetyl

TABLE 1

CHEMICAL SHIFTS[a] OF MONO- AND DI-ACETYL[3]FERROCENOPHANES
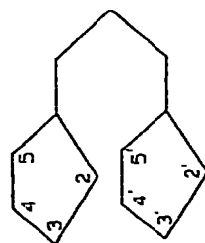
Compound	Acetyl position	H$_2$	H$_3$	H$_4$	H$_5$	H$_2$'	H$_3$'	H$_4$'	H$_5$'
[3]Ferrocenophane I	—	3.839	3.894	3.894	3.839	3.839	3.894	3.894	3.839
2-Acetyl[3]-ferrocenophane II	2	—	4.430	4.136	4.155	3.596	4.109	3.892	3.811
3-Acetyl[3]-ferrocenophane III	3	4.541	—	4.490	4.156	4.155	3.871 (3.925)[b]	4.176	3.827
2,3'-Diacetyl[3]-ferrocenophane IV	2,3'	—	4.389	4.341	4.131	4.334	—	4.431	4.106
2,4'-Diacetyl[3]-ferrocenophane V	2,4'	—	4.681	4.065	4.423	3.870	4.686	—	4.485
2,5'-Diacetyl[3]-ferrocenophane VI	2,5'	—	4.470	4.308	3.880	3.880	4.308	4.470	—
3,4'-Diacetyl[3]-ferrocenophane VII	3,4'	4.498	—	4.392	4.405	4.405	4.392	—	4.498
3-Ethyl[3]-ferrocenophane VIII	—	c	c	c	c	3.902	3.710	3.937	3.796
Ferrocene X					4.042				

[a] Chemical shifts expressed in ppm. [b] Spectrum taken at −30° C. [c] No computer matching done on these protons.

TABLE 2
COUPLING CONSTANTS OF MONO- AND DI-ACETYL[3]FERROCENOPHANES
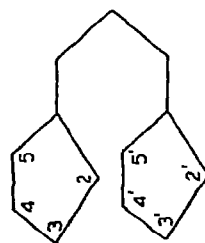
Compound		Acetyl position	$J_{2,3}$	$J_{2,4}$	$J_{2,5}$	$J_{3,4}$	$J_{3,5}$	$J_{4,5}$	$J'_{2,3}$	$J'_{2,4}$	$J'_{2,5}$	$J'_{3,4}$	$J'_{3,5}$	$J'_{4,5}$
[3]Ferrocenophane	I		2.07	1.58	0.39	0.47	1.58	2.07	2.07	1.58	0.39	0.47	1.58	2.07
2-Acetyl[3]-ferrocenophane	II	2				2.71	1.49	2.49	2.45	1.27	1.28	2.47	1.27	2.48
3-Acetyl[3]-ferrocenophane	III	3		1.32	1.24			2.43	2.52	1.30	1.28	2.55	1.32	2.53
2,3'-Diacetyl[3]-ferrocenophane	IV	2,3'				2.66	1.47	2.67		1.36	1.36			2.56
2,4'-Diacetyl[3]-ferrocenophane	V	2,4'				2.70	1.45	2.68	2.68		1.41		1.39	
2,5'-Diacetyl[3]-ferrocenophane	VI	2,5'				2.54	1.49	2.53	2.53	1.49		2.54		
3,4'-Diacetyl[3]-ferrocenophane	VII	3,4'		1.38	1.38			2.79	2.79		1.38		1.38	
3-Ethyl[3]-ferrocenophane	VIII								2.41	1.25	1.25	2.45	1.09	2.45

275

TABLE 3

RESULTS OF ADDITION OF Eu(fod)$_3$

Proton	Orgnal δ (ppm)	Shifted δ (ppm)	Δδ (ppm)
2-Acetyl[3]ferrocenophane			
3	4.44	8.17	3.73
4	4.14	6.07	1.93
5	4.16	6.40	2.24
2'	3.60	7.70	4.10
3'	4.11	6.07	1.96
4'	3.89	5.20	1.31
5'	3.81	5.20	1.39
3-Acetyl[3]ferrocenophane			
2	4.54	10.57	6.03
4	4.49	9.53	5.04
5	4.16	6.10	1.94
2'	4.15	6.10	1.95
3'	3.87	7.48	2.61
4'	4.18	6.10	1.92
5'	3.83	5.01	1.18

group. However, the NMR spectrum of VIII shows qualitatively the same effects on the unsubstituted ring as III; i.e., a shielding of the 3' and 5' protons and a deshielding of the 2' and 4' protons (Table 6). This would seem to eliminate the transmission of any inductive effects through the iron as having any major influence on the NMR spectrum of the unsubstituted ring protons.

The differences between the calculated chemical shifts and those experimentally determined can be rationalized if a non-bonding orbital is assumed to exhibit a magnetic anisotropsy effect similar in nature, though not necessarily in magnitude, to the effect exhibited by a bonding orbital; i.e., deshielding along its major axis and shielding about its minor axes. Such an anisotropy would be in agreement with the overall magnetic susceptibility described by Mulay and Fox [6] and Turbitt and Watts [5] (Fig. 1). The model proposed by Balhausen and Dahl [13], has been chosen to represent the [3]ferrocenophane system.

TABLE 4

SPIN DECOUPLING OF SHIFTED SPECTRA

Resonance irradiated (ppm)	Resonance viewed (ppm)	Result
2-Acetyl[3]ferrocenophane		
6.40	8.17	doublet $J \approx 2.5$ Hz
6.07	8.17	doublet $J \approx 1.5$ Hz
5.20	7.70	doublet $J \approx 2.5$ Hz
6.07	7.70	triplet $J \approx 1.2$ Hz
6.07	5.20	doublet $J \approx 1.2$ Hz
3-Acetyl[3]ferrocenophane		
6.10	10.57	doublet $J \approx 1.3$ Hz
6.10	9.53	doublet $J \approx 1.3$ Hz?
6.10	7.48	doublet $J \approx 1.3$ Hz
5.01	7.48	triplet $J \approx 2.5$ Hz

TABLE 5

DISCREPANCIES BETWEEN CALCULATED AND EXPERIMENTAL VALUES FOR PROTONS IN COMPOUNDS II-VII

Compound	Proton	Calculated Δ^a (Hz)	Experimental Δ (Hz)	$\Delta\Delta$ (Hz)
2-Acetyl[3]ferrocenophane (II)	2'	+ 25.66	+ 24.25	− 1.41
	3'	+ 9.90	− 21.47	− 31.37
	5		− 7.5	− 7.5
3-Acetyl[3]ferrocenophane (III)	2'	+ 10.10	− 31.60	− 41.70
	3'	+ 18.75	+ 2.31	− 16.44
	4'	+ 8.12	− 28.12	− 36.24
2,3'-Diacetyl[3]ferrocenophane (IV)	3'^{b}	+ 18.75	+ 4.92	− 13.83
	4'^{b}	+ 8.12	− 20.47	− 28.59
	2'^{c}	+ 25.66	+ 20.69	− 4.97
	5'^{c}		− 28.90	− 28.90
2,4'-Diacetyl[3]ferrocenophane (V)	3'^{b}	+ 8.12	− 24.21	− 32.33
	4'^{b}	+ 18.75	+ 7.12	− 11.63
	5'^{b}	+ 10.0	− 36.79	− 46.79
	2'^{c}	+ 25.66	+ 28.59	+ 2.93
	3'^{c}	+ 9.90	− 19.65	− 29.45
2,5'-Diacetyl[3]ferrocenophane (VI)	4'^{b}	+ 9.90	− 17.13	− 27.03
	5'^{b}	+ 25.66	+ 27.54	+ 1.98
	2'^{b}	+ 25.66	+ 27.54	+ 1.98
	3'^{b}	+ 9.90	− 17.13	− 27.03
3,4'-Diacetyl[3]ferrocenophane (VII)	2'^{c}	+ 8.12	+ 4.28	− 3.84
	4'^{c}	+ 18.75	+ 9.90	− 8.85
	5'^{c}	+ 10.10	− 24.91	− 35.01
	2'^{c}	+ 10.10	− 24.91	− 35.01
	3'^{c}	+ 18.75	+ 9.90	− 8.85
	5'^{c}	+ 8.12	+ 4.28	− 3.84

^{a} Anisotropic shifts, on 100 MHz scale. Calculated as described in ref. 11. ^{b} As compared to analogous protons in 2-acetyl[3]ferrocenophane. ^{c} As compared to analogous protons in 3-acetyl[3]ferrocenophane.

TABLE 6

COMPARISON OF THE PROTON SHIFTS IN COMPOUNDS I. III AND VIII

Compound	Substitution site	Proton on the unsubstituted ring (ppm)			
		2'	3'	4'	5'
[3] Ferrocenophane (I)		3.839	3.894	3.894	3.839
3-Acetyl [3]-ferrocenophane (III)	3	4.156	3.871	4.109	3.827
3-Ethyl [3] ferrocenophane (VIII)	3	3.902	3.710	3.937	3.796

This model shows three hybridized orbitals lying in the xy plane and strongly oriented toward the opening of the ferrocenophane system (Fig. 4).

A consideration of the perturbation of such a model (Fig. 4) by the acetylation of one or both of the cyclopentadienyl rings and the effects these perturbations would have on the chemical shifts of the ring protons leads to at least a qualitative rationalization of the results summarized in Table 5.

An example of this interpretation for 3-acetyl[3] ferrocenophane (III) is as follows. Here the introduction of an acetyl group into the 3 position would have a major effect on both lobes "a" and "b". Both lobes will be somewhat deflected below the xy plane (Fig. 5) and the angle between them will be increased; i.e., lobe "a" will be pushed toward the y axis and lobe "b" will be pushed toward the −y axis. The interaction between lobes "b" and "c" can be minimized by the deflection of lobe "c" somewhat toward the −y axis and slightly above the xy plane. The predominant effect of this perturbation is the deshielding of 2' and 4' protons caused by their being now closer to lobes "a" and "b". This is true also, to a somewhat lesser extent, for the 3' proton. The deflections of both lobes "b" and "c" away from proton 4 coupled with the deflection of lobe "a" somewhat toward proton 2, result in the shielding of the 4 proton to the extent that it resonates at a higher field than the 2 proton even though the 2 proton is α to the trimethylene bridge.

The chemical shifts for the ring protons of the other compounds in this series (Table 1) can be rationalized in an analogous fashion.
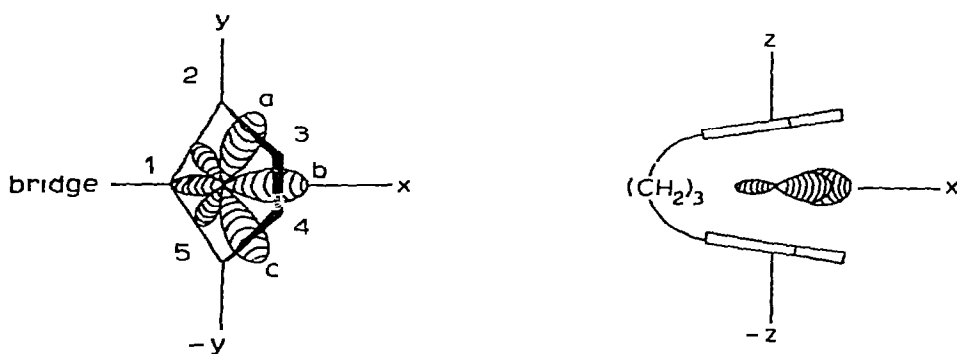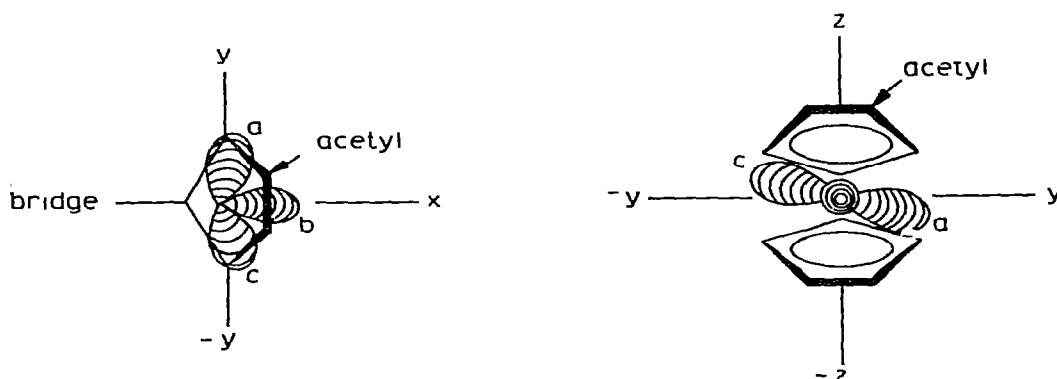

Fig. 4.

Fig. 5.

Fig. 6.

It should be noted that the perturbations of the iron non-bonding orbitals are probably quite small, perhaps only a few degrees at best. The angular displacements in the xy plane would probably be greater than displacements above and below the xy plane. This is a result of increased interaction with the iron-cyclopentadienyl ring bonding orbitals tending to minimize such displacements above and below the xy plane. All perturbations would be maximized during rotation of the acetyl groups out of the plane of the cyclopentadienyl rings. The effect of slowing down this transition (Fig. 6) is seen in the spectrum of 3-acetyl-[3] ferrocenophane (III) at −30°C. Slowing the rate of rotation would decrease the amount deflection of lobes "a" and "b". The major effect would be a decrease in the angle between these lobes, which would bring both lobes "a" and "b" closer to the 3′ proton. This can be seen in a further deshielding of the 3′ proton by about 5.4 Hz at the lower temperature (Table 1).

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