ml. of 1-phenylethyl bromide as described above for 1-isopropoxy-2-(1-phenylethoxy)ethane. The product was obtained in approximately 10 ml. yield and had b.p. 100–108° (1 mm.).

*Anal.* Calcd. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.01; H, 9.81.

**1-Phenylethyl neopentyl ether** was prepared in approximately 30% yield by mixing 8.8 g. (0.1 mole) of neopentyl alcohol, 20 g. (0.1 mole) of 1-phenylethyl bromide, and 13 g. (0.1 mole) of silver oxide. After the initial exothermic reaction had subsided, 3 g. more of silver oxide and 5 ml. more of 1-phenylethyl bromide were added and the reaction mixture was heated on the steam bath for 24 hr. The mixture was cooled and the product isolated as described for 1-isopropoxy-2-(1-phenylethoxy)ethane. The crude ether had b.p. 86–91° (16 mm.) and was contaminated with appreciable quantities of 1-phenylethyl bromide. Purification was effected by dissolving the mixture of halide and ether in di-ethyl ether, and allowing the solution to stand over sodium for 24 hr. The solution was decanted from the unreacted sodium and redistilled. The n.m.r. spectrum of this material was consistent with the assigned structure.

**1-Phenylethyl ethyl ether** was prepared in these laboratories by Dr. F. Kaplan.

**2-Methyl-2-phenylbutane** was prepared in poor yield by reaction of approximately 0.2 mole of isopropylmagnesium bromide with an equivalent amount of 1-phenylethyl bromide in ether. The reaction mixture was hydrolyzed with saturated aqueous ammonium chloride solution, and the ether layer from the hydrolysis was dried and distilled in the usual manner to yield approximately 2 ml. of the desired hydrocarbon, b.p. 85–105° (18 mm.). The principal product of this reaction is 2,3-diphenylbutane, apparently arising from a metal–halogen exchange reaction between isopropyl Grignard reagent and 1-phenylethyl bromide.

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# An Analysis of the Nuclear Magnetic Resonance Spectra of Substituted Ferrocenes[1]

By Milton I. Levenberg and J. H. Richards[2]

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A detailed analysis of the n.m.r. spectra of a series of alkylacetylferrocenes in a variety of solvents has been carried out. This has allowed a determination of the coupling constants between the various protons in these substances. For protons attached to the same ring, the following values are generally observed: $J_{25} \sim 2.5$ c.p.s. and $J_{24} \sim 1.3$ c.p.s. The magnetic anisotropy of the carbonyl group in 2-acetyl-1,1'-trimethyleneferrocene is also discussed.

## Introduction

Though significant work has appeared on the high resolution n.m.r. spectra of various metallocenes,[3,4] no detailed analysis of these systems with three or four dissimilar proton interactions on the same ring has been reported. Detailed analyses have, however, been reported for many other aromatic systems, *e.g.*, 2-fluoro-4,6-dichlorophenol,[5] 2,3-lutidine,[6] *o*-dichlorobenzene,[7] pyridine,[8] furan and pyrrole,[9] and thiophene.[10] The purpose of the present work was to examine homoannularly disubstituted and monosubstituted ferrocene derivatives, treating them as representative ABX and ABCD systems, respectively.[11] To this end, the n.m.r. spectra of a series of acetylalkylferrocenes have been studied in a variety of solvents and the chemical shifts and coupling constants are reported.

## Experimental

**N.m.r. Spectra.**—The spectra of 1–5% solutions in spectral grade benzene, chloroform, and carbon tetrachloride were observed on a Varian Associates A-60 n.m.r. spectrometer.

The spectra were calibrated against ferrocene as an internal standard, and the chemical shifts in Table III are reported on this basis. The chemical shifts of ferrocene from tetramethylsilane in the various solvents used are reported in Table II to allow facile comparison of the chemical shifts observed by us with those reported by other authors.

### Table I

#### Compounds Studied



### Table II

#### Chemical Shift of Ferrocene Relative to Tetramethylsilane[a]

| Solvent | $CCl_4$ | $CHCl_3$ | $C_6H_6$ |
|---|---|---|---|
| Chemical shift[b] | 246 | 252 | 243 |

[a] Measurements made with ~10 mg. of ferrocene and 0.04 ml. of TMS together in 1 ml. of solvent. [b] Reported in cycles per second downfield from TMS.

**Chemicals.**—1-Acetyl-3-methylferrocene (I), 3-acetyl-1,1'-dimethylferrocene (II), and 2-acetyl-1,1'-trimethyleneferrocene (V) were prepared by published procedures.[12]

1,1'-Diacetyl-3,3'-dimethylferrocene (III) and 1,1'-diacetyl-2,2'-dimethylferrocene (IV) were prepared by the acetylation of dimethylferrocene using standard Friedel–Crafts techniques.[13–16]

(1) Contribution No. 3070.

(2) Alfred P. Sloan Foundation Fellow.

(3) M. Rosenblum, A. K. Banerjee, N. Danieli, R. W. Fish, and V. Schlatter, *J. Am. Chem. Soc.*, **85**, 316 (1963).

(4) K. L. Rinehart, Jr., D. E. Bublitz, and D. H. Gustafson, *ibid.*, **85**, 970 (1963).

(5) H. S. Gutowsky, C. H. Holm, A. Saika, and G. A. Williams, *ibid.*, **79**, 4596 (1957).

(6) H. J. Bernstein, J. A. Pople, and W. G. Schneider, *Can. J. Chem.*, **35**, 65 (1957).

(7) J. A. Pople, W. G. Schneider, and H. J. Bernstein, *ibid.*, **35**, 1060 (1957).

(8) W. G. Schneider, H. J. Bernstein, and J. A. Pople, *ibid.*, **35**, 1487 (1957).

(9) R. J. Abraham and H. J. Bernstein, *ibid.*, **37**, 1056 (1959).

(10) R. J. Abraham and H. J. Bernstein, *ibid.*, **37**, 2095 (1959).

(11) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 98.

(12) E. A. Hill and J. H. Richards, *J. Am. Chem. Soc.*, **83**, 4216 (1961).

(13) E. A. Hill, Ph.D. Thesis, California Institute of Technology, Pasadena, 1961, pp. 113–120.

TABLE III

N.m.r. Parameters[a]

| Compound[b] | Solvent | $\nu'$ | $\nu_2$ | $\nu_3$ | $\nu_4$ | $\nu_5$ | $J_{23}$ | $J_{24}$ | $J_{25}$ | $J_{34}$ | $J_{35}$ | $J_{45}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I | CCl₄ | 0.0 | −32.7 | ..... | −13.5 | −29.5 | .. | 1.0 | 1.4 | .. | .. | 2.5 |
|  | CHCl₃ | +1.6 | −32.3 | ..... | −16.6 | −31.3 | .. | 1.1 | 1.5 | .. | .. | 3.1 |
|  | C₆H₆ | +10.2 | −30.2 | ..... | −2.4 | −30.6 | .. | 1.45 | 1.4 | .. | .. | 2.45 |
| II | CCl₄ | +9.4 | −24.4 | ..... | −8.1 | −24.6 | .. | 1.5 | 1.1 | .. | .. | 2.5 |
|  | CHCl₃ | +10.2 | −24.7 | ..... | −9.7 | −25.5 | .. | 1.03 | 1.5 | .. | .. | 2.77 |
|  | C₆H₆ | +16.0 | −23.6 | ..... | +1.8 | −27.4 | .. | 1.5 | 1.4 | .. | .. | 2.5 |
| III | CCl₄ | .... | −22.4 | ..... | −6.4 | −24.5 | .. | 1.6 | 1.3 | .. | .. | 2.3 |
|  | CHCl₃ | .... | −22.2 | ..... | −8.2 | −25.4 | .. | 1.6 | 1.2 | .. | .. | 2.6 |
|  | C₆H₆ | .... | −14.8 | ..... | +11.5 | −20.2 | .. | 1.5 | 1.2 | .. | .. | 2.5 |
| IV | CCl₄ | .... | ..... | −5.6 | −6.6 | −20.1 | .. | .. | .. | 2.5 | 1.3 | 2.5 |
|  | CHCl₃ | .... | ..... | −6.5 | −7.0 | −20.8 | .. | .. | .. | 2.5 | 1.6 | 2.6 |
|  | C₆H₆ | .... | ..... | +10.7 | +11.2 | −3.7 | .. | .. | .. | 2.5 | 1.6 | 2.6 |
| V[c] | CCl₄ | .... | ..... | −6.7 | −6.1 | −23.8 | .. | .. | .. | 2.5 | 1.5 | 2.6 |
|  | C₆H₆ | .... | ..... | +1.8 | −1.2 | −15.4 | .. | .. | .. | 2.5 | 1.3 | 2.7 |
| V[d] | CCl₄ | .... | +26.25 | −4.06 | +8.91 | +13.70 | 2.37 | 1.24 | 1.22 | 2.41 | 1.20 | 2.40 |
|  | C₆H₆ | .... | +27.63 | +1.37 | +11.62 | +21.94 | 2.39 | 1.23 | 1.23 | 2.48 | 1.22 | 2.45 |

[a] Reported in c.p.s. from ferrocene.   [b] See Table I for structures.   [c] Acetylated ring.   [d] Unacetylated ring.

The products were separated by a series of chromatographies and identified by infrared and n.m.r. spectra and by melting points.

Compound III exists in what is called the *trans* isomer by Rinehart,[16] and IV is an almost equal mixture of *cis* and *trans* isomers. The infrared spectra of the *cis* isomers of both III and IV have been reported[16] to be identical with the infrared spectra of their *trans* isomers, and one would expect very little difference in their n.m.r. spectra. We have observed a slight splitting of the methyl and acetyl proton peaks in the n.m.r. spectrum of IV in benzene. They are each split by about 1 c.p.s. into two peaks of about equal magnitudes.

Compound IV was chromatographed on deactivated alumina, and the leading and trailing portions of the band were isolated. These showed a change of about 20% in the relative intensities of the two acetyl peaks in the n.m.r. spectrum of one fraction as compared to the other, indicating a slight enrichment of one of the isomers over the other.

## Results

The n.m.r. spectrum of 1,1'-diacetyl-3,3'-dimethyl-ferrocene (III) in benzene is presented in Fig. 1. The cluster of peaks at lower magnetic field has twice the area of the higher field multiplet. The substance was, therefore, treated as an ABX system with the protons defined as in VI, an assignment which is also consistent with the expected effect of the acetyl substituent on the chemical shifts of the various protons.

The carbonyl group in acetylferrocene is normally coplanar with the cyclopentadienyl ring.[3,15] Because of the magnetic anisotropy of the carbonyl groups,[17] one would expect the protons adjacent ($\alpha$) to the acetyl group to be more strongly deshielded than the $\beta$-proton. That the methyl group does not substantially perturb the ring proton resonance is indicated by the fact that the ring protons in methylferrocene all appear at 238 c.p.s. relative to TMS with no significant difference in chemical shift between the $\alpha$- and $\beta$-protons. This would

VI
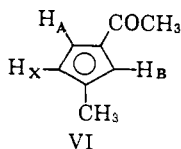
(14) M. Rosenblum and R. B. Woodward, *J. Am. Chem. Soc.*, **80**, 5443 (1958).

(15) K. L. Rinehart, Jr., K. L. Motz, and S. Moon, *ibid.*, **79**, 2749 (1957).

(16) K. L. Rinehart, Jr., and K. L. Motz, *Chem. Ind.* (London), 1150 (1957).

(17) L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, pp. 123–125.

lead one to expect the two $\alpha$-protons to appear at lower field than the single $\beta$-proton, which is borne out by the relative areas of the two absorptions. The analysis of this spectrum by the procedure of Pople, *et al.*,[18] leads to the parameters: $J_{AB}$ = 1.2 c.p.s., $J_{AX}$ = 2.5 c.p.s., $J_{BX}$ = 1.5 c.p.s., $\nu_A - \nu_B$ = 5.4 c.p.s., $\nu_{AB} - \nu_X$ = 29 c.p.s.
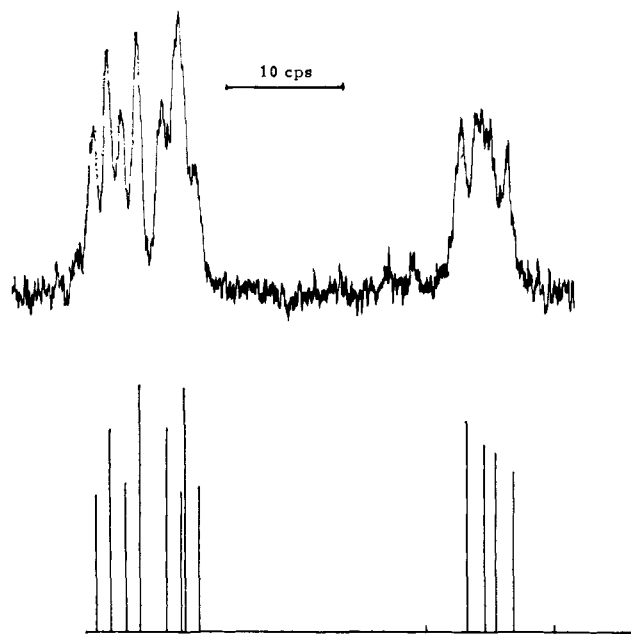


Fig. 1.—The n.m.r. spectrum of 1,1'-diacetyl-3,3'-dimethyl-ferrocene in benzene.

Though the experimental spectrum does not contain enough information to determine the absolute sign of any coupling constant, $J_{AX}$ and $J_{BX}$ must have the same sign. This consideration applies to all the ABX systems reported in this paper and all coupling constants have been arbitrarily assigned positive values.

In a similar fashion the parameters were obtained for the other systems and are reported in Table III. The parameters so obtained were used to calculate a theoretical spectrum using the Wiberg computer program[19] on an IBM 7090. The spectrum calculated for III is

(18) Reference 11, pp. 132–138.

(19) K. B. Wiberg and B. J. Nist, "The Interpretation of N.M.R. Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962.
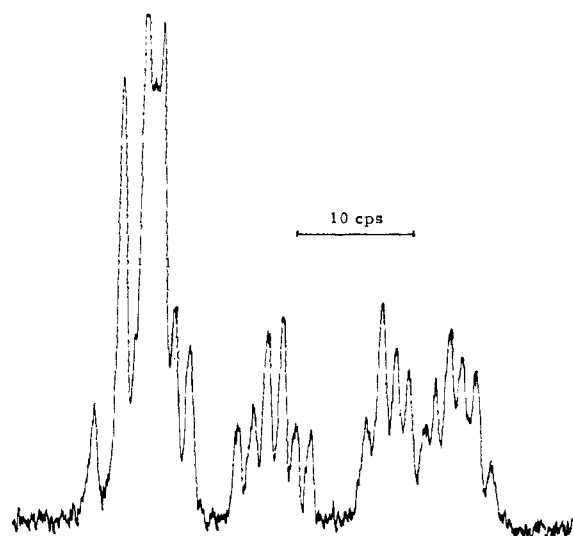
10 cps



Fig. 2.—The n.m.r. spectrum of the unacetylated ring of 2-acetyl-1,1'-trimethyleneferrocene in benzene. The first multiplet of the experimental spectrum also includes the AB portion of the other ferrocene ring.

shown in Fig. 1. In all cases the calculated and experimental spectra were in good agreement.

A different approach was used to analyze the spectrum of the monosubstituted ring of V. Reasonable values were assigned to the coupling constants between each set of protons in what is essentially an ABCD system. Likely sets of chemical shifts were chosen, and theoretical spectra were calculated using the Wiberg program. Several sets of parameters predicted spectra remarkably similar to the observed one. This ambiguity is coincidental and due to the unusual circumstance that coupling constants $J_{23} \approx J_{34} \approx J_{45} \approx 2J_{24} \approx 2J_{25} \approx 2J_{35}$.

The problem was complicated by the fact that the multiplet from one of the protons is hidden under the AB multiplet of the other ring. The difficulty was resolved by observing the n.m.r. spectrum of V at 100 Mc.[20] where the multiplets were shifted enough to allow a unique assignment of parameters. The correct combination was chosen on the basis of relative peak intensities. The approximate parameters were entered into a computer program of Swalen[21] which, by application of a reiterative technique, determined that set of parameters most closely fitting the experimental spec-

(20) For this we thank the Varian Associates.
(21) J. D. Swalen and C. A. Reilly, J. Chem. Phys., 37, 21 (1962).

trum. The resulting parameters are included in Table III, and the experimental and theoretical spectra of V are shown in Fig. 2.

These calculations do not specify whether the acetyl group is over the 2'-proton or the 5'-proton. Consideration of the magnetic anisotropy of the carbonyl later in this paper suggests that the acetyl is over the 2'-proton, as indicated in Table III.
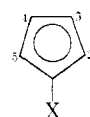
### Discussion

An interesting feature of these results is the close similarity between the coupling constants observed between the protons on the aromatic cyclopentadienyl ring of ferrocene and between the protons attached to various aromatic five-membered heterocycles, e.g., furan,[9] pyrrole,[9] and thiophene.[10] In these cases the following range of coupling constants has been reported



X = O, S, NH

$J_{23}$ 1.3–5.0 c.p.s.
$J_{24}$ 0.9–1.5 c.p.s.
$J_{25}$ 2.7 c.p.s.
$J_{34}$ 2.8–3.5 c.p.s.

These are to be compared with the analogous coupling constants of ferrocene derivatives.



X

$J_{23}$ 2.3–3.1 c.p.s.
$J_{24}$ 1.0–1.6 c.p.s.
$J_{25}$ 1.1–1.5 c.p.s.
$J_{34}$ 2.5 c.p.s.

The coupling constants of protons attached to some six-membered benzenoid systems have also been measured,[5-8] and typical values for coupling between ortho, meta, and para protons are: $J_o = 5.0$–8.6 c.p.s., $J_m = 1.3$–2.7 c.p.s., $J_p = 0.0$–0.9 c.p.s. From these comparisons, it is clear that the coupling between protons adjacent to each other on a five-membered aromatic system are consistently and significantly lower than analogous couplings between protons bonded to benzenoid rings. A similar ring-size effect has been observed on cis-cycloolefins.[22,23]

Another interesting result is the effect of solvent on the observed coupling constants. If there is an acetyl residue attached to the ring in question, the solvent can have a significant effect on the coupling constants as well as on the relative chemical shifts. In those rings which do not have acetyl substituents, however, this effect is sharply diminished. The explanation clearly lies in the nonuniform solvation caused by the acetyl group, which results in nonuniform magnetic shieldings at the various ring positions and variations in local electron distributions. Coupling constants in some other systems have previously been observed to depend on the electronegativity of adjacent groups.[24]

A correlation was sought between the observed chemical shifts of the ring protons in 1-acetyl-2,1'-trimethyleneferrocene and the shifts anticipated on the basis of the magnetic anisotropy of the carbonyl group. The distance and angle from the carbonyl group to each proton for all possible orientations of the acetyl group was calculated on the basis of an X-ray structure for α-ketotrimethyleneferrocene.[25] The magnetic aniso-

(22) (a) O. L. Chapman, J. Am. Chem. Soc., 85, 2014 (1963); (b) G. V. Smith and H. Kriloff, ibid., 85, 2016 (1963).
(23) P. Laszlo and P. von R. Schleyer, ibid., 85, 2017 (1963).
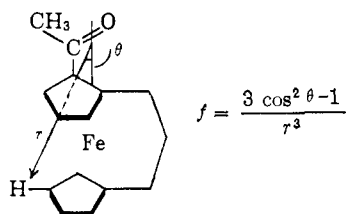(24) K. L. Williams, ibid., 85, 516 (1963).
(25) R. Marsh, N. Jones, and J. H. Richards, unpublished results.

tropy of the carbonyl group was approximated by a dipole–dipole interaction, $f$, of the form:

$$f = \frac{3 \cos^2 \theta - 1}{r^3}$$

between the center of the carbon–oxygen bond and the proton in question.[17,26] For each proton, $f$ will be a function of the angle between the plane of the acetyl group and the plane of the cyclopentadienyl ring. This function is shown in Fig. 3.

Spectroscopic evidence[4,15] has shown the acetyl group in 1-acetyl-2-alkylferrocenes to be nearly planar with the cyclopentadienyl ring. Moreover, solvolysis experiments on methyl-2-(1,1'-trimethyleneferrocenyl)-carbinyl acetates and related compounds[12] indicate a high degree of steric interference to an orientation where the acetyl methyl group is near the bridge as in VIIa.
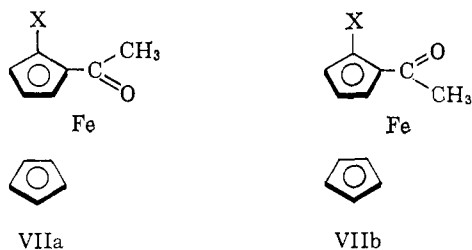
VIIa

VIIb

Nuclear magnetic resonance evidence indicates a rapid conversion between structures VIIa and VIIb for acetylferrocene (X = H); however, steric factors favor structure VIIb for compound V. This would correspond to an angle near 0° in Fig. 3.

If one assumes that the carbonyl magnetic anisotropy of the acetyl group is the dominant factor selectively affecting the protons on the unacetylated ring of compound V, several conclusions may be drawn about the proton assignment and the orientation of the acetyl group. An examination of Fig. 3 shows that between −40° and +70° the 2'-proton will be more shielded than proton 3'. Moreover, between +30° and +60° the chemical shifts of all of the protons on the bottom ring are in one of the sequences anticipated from the theoretical analysis of the spectrum. (At ≈50° the agreement is quantitative.) Moreover, at any orientation of the acetyl group from −50 to +50° the calculated chemical shifts of the protons on the acetylated ring of V are in the sequence experimentally observed. (At ≈0° the agreement is quantitative.)

Thus, a range of angles will give the correct relative order of the various protons, but no single angle of the

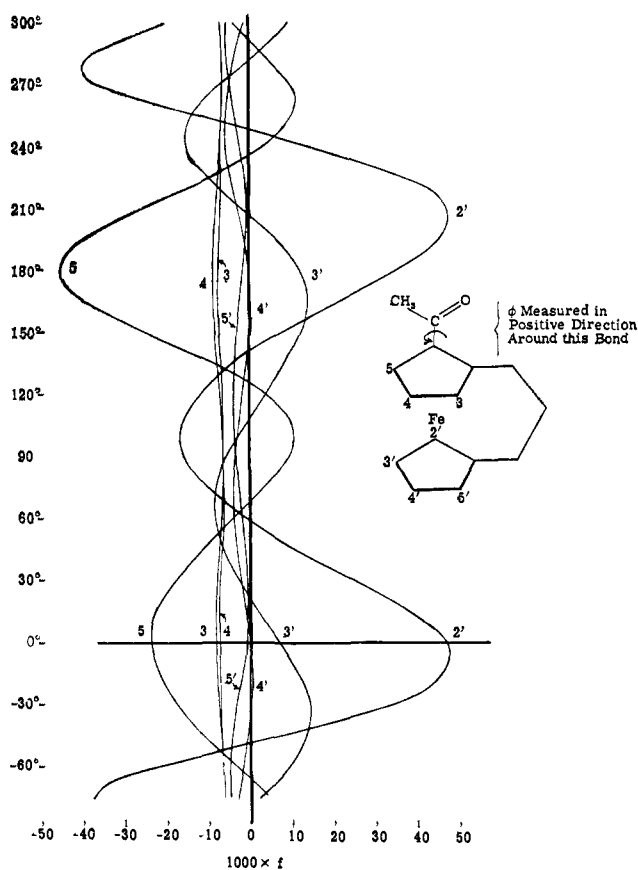(26) H. M. McConnell, J. Chem. Phys., **27**, 226 (1957).



Fig. 3.—Dipole–dipole interaction, $f$, of carbonyl on ring protons in acetylferrocenes.

carbonyl group predicts the quantitative aspects of the spectrum in detail. Surely, other factors, e.g., nonuniform resonance or inductive effects, will perturb significantly any model based solely on considerations of magnetic anisotropy. However, the fact that one can obtain such good qualitative agreement suggests strongly that the magnetic anisotropy of the carbonyl group plays a dominant role in determining the relative chemical shifts of the various hydrogens.

These results confirm and amplify Rinehart's qualitative argument.[4] However, an additional important point is that the chemical shift assignments which we find for compound V do not agree with the assignments suggested by Rinehart[4] for the same compound (his compound II). Our analysis of the spin–spin coupling constants demonstrates that the multiplet Rinehart lists at $\tau = 5.76$ is due to protons at ring positions 3, 4, and 3' rather than protons 4, 2', and 3', as he indicates.

The data presented in this paper on the theoretical contribution to chemical shifts due to the carbonyl magnetic anisotropy should be directly applicable to any ferrocene system having the same relative positions of the two cyclopentadienyl rings and the carbonyl group.