PROTON SPIN LATTICE RELAXATION RATES OF SUBSTITUTED FERROCENE DERIVATIVES;

ASSIGNMENT OF RESONANCES AND DETERMINATION OF MOTIONAL CORRELATION TIMES

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SUMMARY

Proton spin lattice relaxation rates have been used to assign the proton resonances of the substituted cyclopentadienyl ring of two ferrocenyl-sugar conjugates. Comparison between the R_1-values of the protons of the substituted and unsubstituted rings shows that the latter ring is spinning more rapidly about the Cp—Fe—Cp axis.


The ^{1}H n.m.r. spectrum of an achiral, monosubstituted ferrocene derivative invariably shows two multiplets, each from a pair of equivalent protons {α,α^- and β,β^-}, together with a sharp singlet for the five equivalent protons of the unsubstituted ring. When both rings are substituted by the same achiral substituent, only two resonances are observed, both rings being essentially identical. For chiral, mono or 1,1'-di-substituted derivatives all four proton resonances of these rings are intrinsically inequivalent as first observed by Kursanov [1] for chiral cymantrene systems. Although in some cases a reasonable assignment of such resonances can be inferred by inspection, for many systems not even a tentative assignment can be made; we now report that

proton spin latice relaxation rates (R_1- values) provide direct evidence
for unequivocal assignments. As an added bonus those same data automatically
provide information concerning the relative mobilities of the substituted
and unsubstituted cyclopentadienyl rings.

Although to our knowledge, no results have previously been reported
for organometallic π complexes, an ample body of data exists for
organic molecules which shows that the spin lattice relaxation of the
protons of most diamagnetic organic molecules is dominated, generally
exclusively, by the dipole-dipole mechanism [2], which has the general
form

$$R_1(D,R) \propto \frac{\gamma_D^2\, \gamma_R^2}{r^6(D \rightarrow R)} \cdot \tau_c(D \rightarrow R) \tag{1}$$

where $R_1(D,R)$ is the specific relaxation contribution between a donor
nucleus (D) and a receptor nucleus (R), γ_D and γ_R are the gyromagnetic
ratios of those two nuclides, $r(D \rightarrow R)$ is the distance separating them and
$\tau_c(D \rightarrow R)$ is the motional correlation time of the vector joining D and R.
For most diamagnetic molecules protons are the only nuclear species with
a high gyromagnetic ratio and for that reason the relaxation of each
proton generally occurs via the other protons of the system; working
at high dilution in a solvent which contains no protons ensures that
intramolecular proton relaxation is dominant. Under these circumstances
it is possible to use the experimentally determined values of $R_1(D,R)$ to
measure either the relative interproton distances or the relative rates
of motion of the various proton-containing moieties.
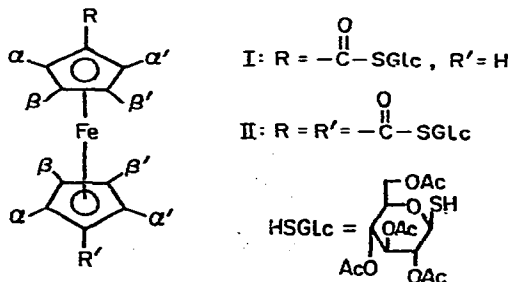
In the context of ferrocene chemistry, two useful items of information can be obtained from a simple, qualitative interpretation of proton R_1 values. Because protons which are α to a substituent have only one neighbouring proton whereas those which are β have two, the latter will be characterized by their larger R_1 values. And if it is assumed that all C-H bond lengths and bond-angles are identical, intercomparison of the R_1 values can show which cyclopentadienyl ring is rotating about the Cp-Fe-Cp axis more rapidly. For brevity we shall illustrate these points here using the mono- and bis-substituted sugar derivatives I and II.

The 270 MHz proton resonance spectra of compounds I and II are shown in (Fig. 1) and the relevant proton R_1 values are summarized in (Table 1). It is clear that although the R_1-values of the resonances at 4.77 ppm and 4.68 ppm of I are closely similar, both these are relaxing at approximately
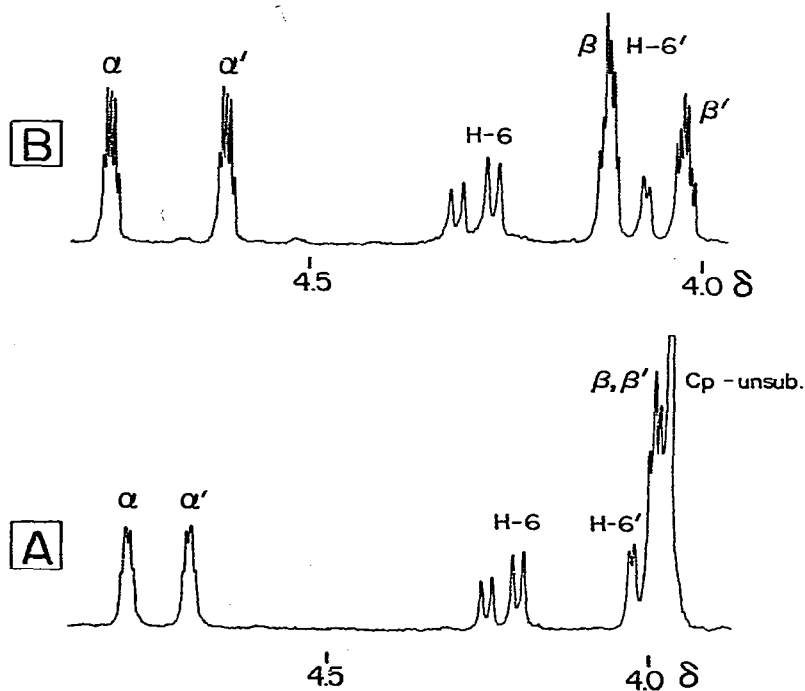

Fig. 1. Partial ^{1}H n.m.r. spectra (270 MHz) of I and II in deuteriobenzene (<0.05 molar) measured at 20°C {t_{90}°= 6.5μsec., NA= 100, AT= 5.439sec.}

TABLE 1

PROTON SPIN LATTICE RELAXATION RATES[a] R_1 sec^{-1}

	α, α'	β, β'	Cp(unsub)
I R=$-\overset{\overset{\text{O}}{\|}}{\text{C}}$-SGlc, R'=H	0.258±0.001 0.280±0.005	0.426±0.008	0.185±0.004
II R=R'=$-\overset{\overset{\text{O}}{\|}}{\text{C}}$-SGlc	0.483±0.004, 0.482±0.005	0.84±0.15[b], 0.780±0.015	–

[a] Uncertainty are from printout of computer fit and reflect errors
caused by noise only. There are many other sources of error,
however, which can only be estimated by repeating the experiment
several times.

[b] Due to an accidental overlap with a sugar resonance this rate was
estimated from null point determinations and therefore has a much
higher uncertainty.

half the rate of the resonances at 3.99 ppm. Clearly the latter resonances

must correspond to β,β',their enhanced R_1-values being ascribed to the fact

that they each have two neighbouring protons. A similar relationship

pertains for II, the interpretation being only marginally complicated by

the accidental overlap between the β resonance and one of the protons of

the sugar ring.

Assignment of which protons are on the same side of the cyclopentadienyl

ring, that is the pairing of α with β and α' with β' in II, is trivially

accomplished by homonuclear decoupling. Unfortunately it is not easy to

ultimately assign each resonance to a particular proton and we can think

of no simple method whereby this can be accomplished.

Although not directly related to the main thrust of the work presented

thus far, we would like to illustrate to the reader not familiar with this

technique, the conformational information [2] obtainable from relaxation
rates by examining the R_1-values for protons of the appended sugar ring in I
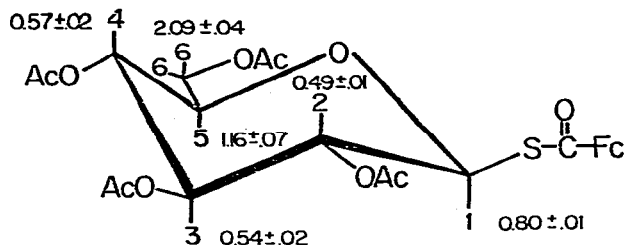(Fig. 2). As shown earlier in equation (1), the relaxation rate is

Fig. 2. Conformational structure and proton R_1-values for the appended
sugar moiety in I.

dependent upon the distance between protons and because of the r^{-6}
dependence the relaxation contributions drop off sharply as the distance
is increased. Due to this, the vicinal trans-diaxial interactions, present
between neighbouring protons in this particular sugar ring, are small and
contribute little to the R_1-values of the ring protons. The R_1-value for
H_6 is the largest observed because there is very efficient relaxation
between the closely spaced geminal protons and there is a large contribution
from H_5 as well. The R_1-value of H_5 is the next largest since it gets
relaxation contributions from both H_6 protons and the two syn-diaxial protons
H_1 and H_3. The R_1-values for protons H_4 and H_1 provide an interesting com-
parison. Since H_1 has 1,3-diaxial interactions with both H_3 and H_5, it
relaxes more rapidly than H_4 which has only the diaxial interaction with
H_2. As expected the R_1-value of H_2 is the smallest since it gets relaxation
only from H_4 while H_4 gets some additional relaxation from the H_6 protons.
The rate for H_3 seems a little low since it has two 1,3-diaxial interactions
with H_5 and H_1 but it is still within reason and, since there may well be
a larger systematic error in the R_1-values of H_2 and H_3 because they are
partially overlapping and strongly coupled [5], it is not worth discussing
this point further. It should be clear from the above that conformational

information can be readily obtained via the relaxation technique for
ferrocene and other classes of organometallic compounds as well.

Information concerning the relative rates of spinning motion of the
substituted and unsubstituted cyclopentadienyl rings about the Cp-Fe-Cp
axis can be inferred directly from the proton R_1-values. Simply, the
observation that the β protons of the substituted ring relax faster
than the protons of the unsubstituted ring immediately implies that the
latter is rotating faster than the former. A value for this rate difference
can be approximated in the following way. Using equation (2) the relaxation

$$R_1(R) = \frac{3}{2} \Sigma\rho(D,R) \qquad (2)$$

contribution $\rho(D,R)$ of the donor nucleus to the receptor, can be calculated
from the observed R_1-value of the receptor nucleus. After first calculating
$\rho(\alpha,\beta) = 0.18$ this can then be used to calculated a value for $\rho(\beta,\beta) = 0.11$;
and $\rho(H,H) = 0.62$ can be calculated separately for the unsubstituted cyclo-
pentadienyl ring. From the relationship,

$$\rho(D,R) = 4/3\ I_R(I_R+1)\ \frac{\gamma_D^2\gamma_R^2\hbar^2}{r^6(D\to R)}\ \tau_c(D\to R) \qquad (3)$$

where I is the nuclear spin and other terms are as for (1), one can calculate
the motional correlation time for the two interproton vectors $\alpha\to\beta(\tau_c=1.22\times10^{-10}$
sec/rad.) and $\beta\to\beta(\tau_c=0.71\times10^{-10}$ sec/rad.), using a value of the interproton
distance $r = 2.7\overset{o}{A}$; this distance need not be accurate since only relative
rates are being calculated. An average value for the correlation time of
the interproton vectors for the unsubstituted ring is calculated from
$\rho(H,H)$ to be 0.42×10^{-10} sec/rad. By comparing the average value of
$\tau_c(\alpha\to\beta)$ and $\tau_c(\beta\to\beta)$ for the substituted ring with the average τ_c value
obtained for the unsubstituted ring it is clear that the unsubstituted
ring is rotating about the Cp-Fe-Cp axis approximately 2.3 times more
rapidly than the substituted ring. In this calculation it has been assumed
that other molecular motions of the molecules contributing to the relaxation

rates of these ring protons are approximately the same for both rings, and
therefore effectively cancel, leaving the difference in these rates
affected mainly by their rotational rates about the Cp-Fe-Cp axis.
This rate difference is intuitively reasonable and the differential
can be ascribed to the increased size and inertial moment of the
substituted ring. It is also worth noting that a two-factor differential
exists between the R_1-values for the α protons of I and II and for the
β counterparts. Once again the sense of this differential indicates that
the larger molecule II is tumbling more slowly overall than its smaller
counterpart I; this probably reflects the increased drag associated
with the second sugar substituent.

Two concluding statements seem to be appropriate. First, that the
proton R_1 values of many different classes of organometallic substances
are likely to be amenable to the same simple, useful interpretations as
those given here. Second, that since it is possible to extend the relaxation
experiment to a quantiative measurement of interproton distances with an
accuracy which under favourable conditions can [4] approach that of
a neutron diffraction study, use of this technique to identify the positions
of the hydride substituents of certain metal-hydrides clearly merits attention.

Experimental

The synthesis of compounds I and II has been reported elsewhere [5].
Solutions for n.m.r. were made in deuteriobenzene (99.8%, Mercke, Sharp
and Dohme) at solute concentrations of <0.05 molar, and were degassed
using five freeze-pump-thaw cycles.

The n.m.r. measurements were made with a home-built 270 MHz spectro-
meter based on an Oxford Instruments solenoid, a Nicolet 1180 computer,
and a modified 293A pulse programmer. Relaxation data were obtained using
the standard Nicolet software for the phase alternating inversion recovery
experiment $(180_x^0 - \tau - 90_x^0 - Acq-Delay - 180_{-x}^0 - \tau - 90_x^0 - Acq-Delay)_{n/2}$ and the R_1-values
were calculated using a $\ln(M_\infty - M_\tau)$ vs τ plot [6]. Only pre-null point
relaxation data was used in these plots to accomodate the initial slope
approximation [7]. The relaxation rates obtained from these plots were

also checked by roughly estimating the rates from the null points of individual resonances in the partially relaxed spectra using the relationship

$$R_1 = \frac{0.69}{\tau}$$

where τ is a short delay after the 180° pulse to allow the nuclear spin to partially relax.

Acknowledgements

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