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CARBON-13 SPIN-LATTICE RELAXATION. INTERNAL MOTIONS IN SUBSTITUTED FERROCENES

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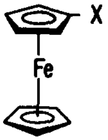
In suitable molecules carbon-13 spin-lattice relaxation measurements[1] give significant insight into preferred modes of molecular tumbling[2] and rapid, internal rotational motions[3,4]. In _mono_-substituted benzenes, for example, C-H ring carbons _para_ to the substituent have shorter spin-lattice relaxation times (T_1) than the other C-H ring carbons due to preferred rotation around the molecular symmetry axis coincident with the ring-substituent bond (C-X bond)[2]. The efficiency of a given preferred rotational motion in shortening the effective correlation time (and lengthening T_1) for a given off-axis C-H carbon is governed by the angle (θ) between the C-H bond vector and the preferred rotational axis.

Mono-substituted ferrocene molecules are large enough to act as more-or-less isotropic tumblers (i.e., no mode of overall rotation should be highly preferred)[5]. On the other hand, a substituent can effectively reduce rotation of the attached ring, simultaneously allowing relatively free spinning of the unsubstituted ring. The "anchoring" of the substituted ring (A ring) results from both inertial effects (loss of C_5 symmetry) and frictional effects. If the unsubstituted ring (B ring) is able to spin more rapidly than the A ring then longer T_1s will be observed for the B ring carbons. Infinitely fast internal rotation of ring B would result in T_1s four times those observed for the C-H carbons of ring A (assumes $\theta = 90^\circ$ and isotropic overall tumbling). Fast internal spinning of ring B that is not $\gtrsim 50$ times the spinning (tumbling) rate for ring A results in T_1s for ring B carbons ranging from >1 to <4 times observed T_1s for ring A.

Experimental results and derived relative spinning rates for A and B rings are given in Table 1 for acetyl and n-butyl ferrocene (overall tumbling rates for these compounds correspond to molecular correlation times of ~1.5 X 10^{-11} sec).

TABLE 1

^{13}C SPIN-LATTICE RELAXATION TIMES FOR ACETYL- AND n-BUTYL FERROCENE

	Carbons	T_1, sec[a]	Spinning ratio, $\frac{B}{A}$[b]
X=H		14.3	
X=acetyl	ring A	3.2, 3.2	
	ring B	6.2	~4
	CO$\underline{C}H_3$	7.9	
X=n-butyl	ring A	2.5, 2.6	
	ring B	6.0	
	α-CH_2	2.0	
	β-CH_2	2.0	~7
	γ-CH_2	2.8	
	δ-CH_3	3.6	

[a] Protonated carbons only. Determined by inversion-recovery pulse sequence (Varian XL-100 Spectrometer) at 25.2MHz and 38°. Probable expt'l error <15%. Solutes dissolved in benzene-d_6. The ^{13}C-^{1}H nuclear Overhauser effect (NOE) was measured for ferrocene and acetyl ferrocene (η=1.9 and ~1.4; theoretical maximum 2.0). The NOEs preclude large relaxation contributions from unpaired spins (Fe^{III}, etc.).

[b] Calculated from eq. 27 in ref. 3a (θ = 90°).

The data in Table 1 indicate that the B rings are indeed able to spin independently of overall molecular tumbling and A ring revolution. With the larger n-butyl substituent, the B ring rotates ca. 7 times faster than the A ring (Table 1). In n-butyl ferrocene another motion phenomenon is indicated. The increasing T_1s for the γ and δ chain carbons are due to internal or "segmental" motion. The effective correlation times for these carbons are shortened due to increased motional degrees of freedom near the free end of the chain[3a, 4].

The relatively free spinning of B rings in these substituted ferrocenes suggests that the energy barrier to independent B ring rotation is very small. Further work is underway to evaluate A and B ring motion in more restricted ferrocenyl systems and also to study the T_1 effects resulting from significant concentrations of free electrons (radicals).

APPENDIX: ^{13}C CHEMICAL SHIFTS[a]

	A Ring		B Ring	
	C-H	C-X	C-H	Other
Ferrocene			68.2	
Acetyl Ferrocene	69.8, 72.0	80.3	69.9	CH_3 27.2; CO 199.4
n-Butyl Ferrocene	67.3, 68.3	89.3	68.7	α-CH_2 33.7; β-CH_2 29.6; γ-CH_2 22.9; δ-CH_3 14.2

[a] Relative to internal TMS (38°); benzene-d_6 solvent.

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References and Footnotes

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5. If the sandwich compound tumbles somewhat preferentially around the destroyed ferrocenyl C_5 axis the conclusions reported in this paper are still valid.