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Barriers to Ring Rotation in 1,1′,4,4′-Tetra-*tert*-butyluranocene and 1,1′,3,3′-Tetra-*tert*-butylferrocene

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Abstract: The ^{1}H NMR spectra of 1,1′,4,4′-tetra-*tert*-butyluranocene show a singlet for the *tert*-butyl protons and three singlets for the ring protons. Coalescence occurs at −65 to −85 °C with splitting of each peak at lower temperatures, corresponding to $\Delta G^{\ddagger}$ of rotation of 8.3 kcal mol^{-1}. Coalescence was also observed for 1,1′,3,3′-tetra-*tert*-butylferrocene and a corresponding $\Delta G^{\ddagger}$ = 13.1 kcal mol^{-1} was obtained.

The energy barrier to ring rotation in sandwich organometallic complexes is generally quite small. The rotational barrier in ferrocene has been measured by several different methods: gas-phase electron diffraction, 0.9 ± 0.3 kcal mol^{-1};[2-5] IR, 0.9 kcal mol^{-1};[6] wideline ^{1}H NMR second-moment measurements, 1.8 ± 0.2 kcal mol^{-1}.[7-11] Similarly, second-moment studies have shown the corresponding barrier in nickelocene, cobaltocene, and chromocene to be 1.8 ± 0.2 kcal mol^{-1},[7] in ruthenocene, 2.3 ± 0.2 kcal mol^{-1},[10,11] in bisbenzenechromium, 4.56 kcal mol^{-1},[11] and in uranocene 0 kcal mol^{-1}.[8] Appropriate substitution of the rings would be expected to raise this barrier; however, data on barriers to internal rotation in substituted metallocenes are limited. Second-moment studies on several crystalline mono- and 1,1′-disubstituted ferrocenes have indicated internal rotation barriers of 0.9–5.0 kcal mol^{-1}.[12-16] A gas-phase electron diffraction study has recently shown the barrier to be 1.0 ± 0.3 kcal mol^{-1} for decamethylferrocene.[17] An equally low barrier has been assumed for 1,1′,3,3′,5,5′,7,7′-octamethyluranocene from X-ray structural data.[18] We now report measurement of the barrier to ring rotation in the unsymmetrically tetra-*tert*-butyl substituted metallocenes 1,1′,4,4′-tetra-*tert*-butyluranocene (**1**) and 1,1′,3,3′-tetra-*tert*-butylferrocene (**2**) by variable-temperature ^{1}H NMR.

Table I. Least-Squares Linear Regression vs. T^{-1} of the Variable-Temperature ^{1}H NMR Data for 1,1',4,4'-Tetra-*tert*-butyluranocene

resonance	slope × 10^3	intercept	r^2
ring A	−7.72	−5.49	0.9985
ring B	−14.73	3.26	0.9970
ring C	−15.42	2.95	0.9983
t-Bu	−5.09	5.04	0.9980
ring A'	−3.73	−13.66	0.9991
ring A''	−8.17	−3.85	0.9986
ring B'	−9.40	−4.14	1.0000
ring B''	−19.31	17.37	0.9985
ring C'	−11.87	−3.04	0.9999
ring C''	−17.41	10.25	0.9989
t-Bu'	−3.86	0.17	1.0000
t-Bu''	−5.76	9.31	1.0000

Variable-temperature ^{1}H NMR spectra of 1,1′,4,4′-tetra-*tert*-butyluranocene[19] show that we were successful in "freezing out" ring rotation on the NMR time scale (Figure 1). Above −30 °C, where ring rotation is rapid, the spectrum consists of four singlets with an area ratio of 18:2:2:2, corresponding to the *tert*-butyl protons and three sets of nonequivalent ring protons. In the low-temperature spectrum below −80 °C, the compound is conformationally rigid on the NMR time scale, and the spectrum

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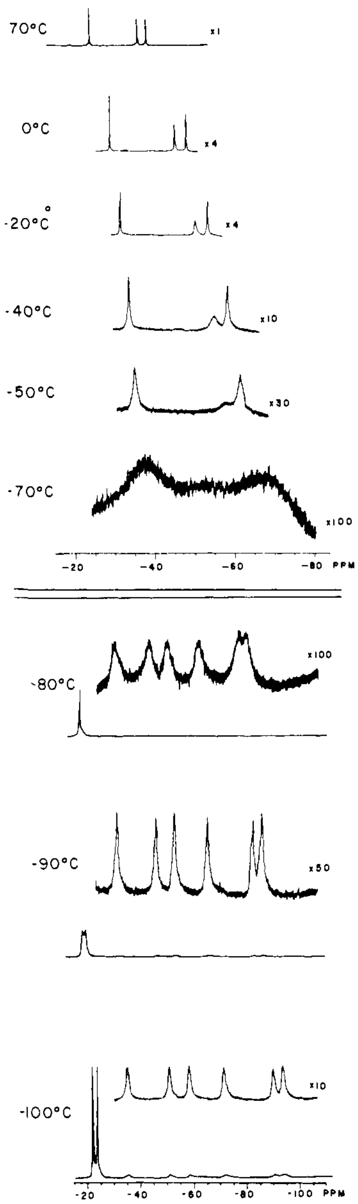

Figure 1. ^1H NMR spectra of 1,1′,4,4′-tetra-*tert*-butyluranocene as a function of temperature. The upper group of spectra show only the ring protons with the assignment order left to right: A, B, C. The spectra at low temperatures show the *tert*-butyl group as well.

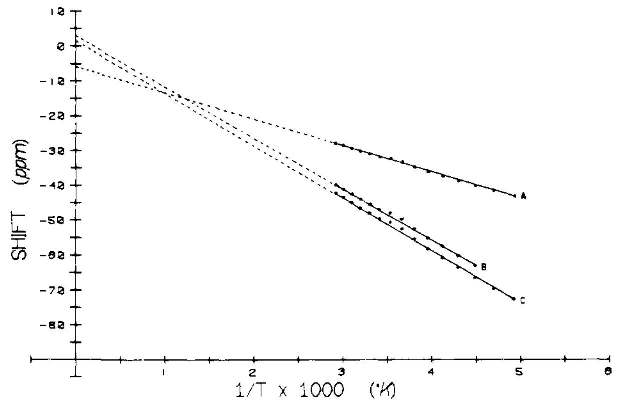

Figure 2. Temperature dependence of ring proton ^1H NMR shifts above coalescence showing linearity in $1/T$ and extrapolation to $1/T = 0$.

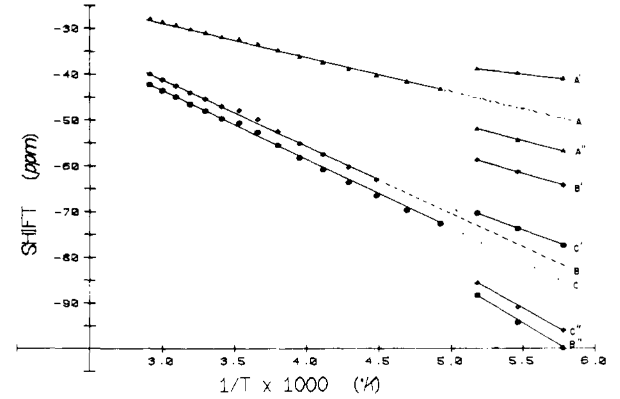

Figure 3. Proton shifts before and after coalescence. The primed letters after coalescence correspond to the unprimed letters before coalescence for the determination of $\Delta\sigma$ at coalescence.

Table II. Calculation of Rotation Barrier in 1,1',4,4'-Tetra-*tert*-butyluranocene

proton	coalescence temp, °C	isotropic shift,[a] ppm		$\Delta G^{\ddagger}$, kcal mol^{-1}
t-Bu	−85	−20.37	−21.33	8.61
ring A	−70	−33.49	−47.31	8.25
ring B	−65	−49.36	−75.46	8.20
ring C	−70	−61.52	−75.52	8.25
				av 8.3 ± 0.2

[a] Extrapolated to coalescence temperature from shifts of the conformationally "frozen" molecule at lower temperatures.

consists of eight singlets with area ratios of 9:9:1:1:1:1:1:1, corresponding to two kinds of *tert*-butyl groups and six distinct sets of ring protons. Labeling the three ring proton resonances in the high-temperature spectrum A–C, from low field to high field, the B resonance coalesces first, followed by virtually simultaneous coalescence of the A and C resonances and eventual coalescence of the *tert*-butyl group as the temperature is lowered.

The coalescence temperature is dependent on the difference in frequency of the resonance signals in the low-temperature spectrum of the conformationally "frozen" molecule. The standard equation at coalescence (eq 1) implies that the larger the difference

$$\text{at coalescence:}\quad k_c = \pi(\Delta\nu)/\sqrt{2} \qquad (1)$$

in frequency ν, the higher the coalescence temperature.

Because of the paramagnetic uranium center, all of the observed resonances are highly temperature dependent but the isotropic shifts are linear in T^{-1}.[20] These linear T^{-1} dependences for the ring protons both before and after coalescence are shown in Figures 2 and 3. All sets could be readily extrapolated to the coalescence temperatures to obtain each $\Delta\nu$ (Table I). The assignment of the primed resonances below coalescence in Figure 3 was made on the basis that the average of each assigned pair best fits the extrapolated value of the corresponding unprimed resonance. Thus, the uranocene system is a unique example in which the uranium center serves effectively as an internal paramagnetic shift reagent to clearly resolve all of the nonequivalent proton resonances both in the limit of rapid and slow ring rotation. Accordingly, $\Delta G^{\ddagger}$ for internal rotation can be calculated from four distinct sets of coalescence data (Table II) to give an average value of 8.3 kcal mol^{-1} at −70 °C. If the corresponding $\Delta S^{\ddagger}$ derives principally from hindering the rotations of the two *tert*-butyl groups passing each other in the transition state, we can estimate a contribution of 2–3 eu per group or a total $\Delta S^{\ddagger}$ of about −5 eu.[21] Correspond-

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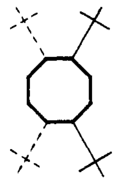
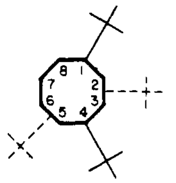
(21) Based on Table 27-11 of Lewis, G. N.; Randall, M. "Thermodynamics", 2nd ed.; McGraw-Hill: New York, 1961; p 444. For a large group like *tert*-butyl $1/Q$ is small and we use the left side of the table. Reasonable values of barrier heights in the middle portion of the table give entropy changes of the order of 2–3 eu. We thank Professor K. S. Pitzer for a helpful discussion.

ingly, $\Delta H^{\ddagger}$ is about 7 kcal mol^{-1}.

We cannot definitively assign the specific ring proton resonances; however, observation of six ring proton resonances at low temperature eliminates **1a** as the low temperature conformation of 1,1′,4,4′-tetra-*tert*-butyluranocene since it contains a plane of symmetry. Inspection of molecular models suggests that **1b** or a similar structure is the most reasonable conformation of the two rings and undoubtedly corresponds to the low-temperature conformation. Moreover, this structure does suggest some partial assignments of the frequencies. Ring protons H-2 and H-3 differ little in the equilibrating structures **1b** and **1c** and may be assigned to A′ and A″ which show the smallest $\Delta\delta$ and are also furthest downfield; the presence of a *tert*-butyl group directly beneath in the ring below appears to produce a downfield shift.[20] On this basis B″ and C″ correspond to H-7 or H-8 in **1b** but no further detail seems appropriate at this time.


1a



1b

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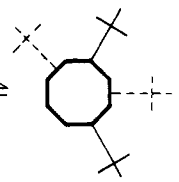
1c

Our success in measuring the rotational barrier in 1,1′,4,4′-tetra-*tert*-butyluranocene suggested that the rotational barrier in the ferrocene analog, 1,1′,3,3′-tetra-*tert*-butylferrocene, could be measured in a similar manner. One would expect the barrier in the ferrocene analog to be larger since the ring–ring distance in ferrocene is 0.52 Å smaller than in uranocene. Surprisingly, although 1,1′,3,3′-tetra-*tert*-butylferrocene has been prepared several times,[22-24] and its structure has been elucidated by single-crystal X-ray diffraction,[25] the ring rotational barrier has not been reported. In fact, we could not find any report in the literature concerning the determination of ring rotational energy barriers of substituted ferrocenes in solution by variable-temperature ^{1}H NMR.

At 30 °C, the ^{1}H NMR spectrum of 1,1′,3,3′-tetra-*tert*-butylferrocene consists of one *tert*-butyl resonance (1.218 ppm, s, 18 H) and two ring proton resonances split by 1,3 coupling (3.822 ppm, t, 2 H, J = 1.46 Hz; 3.097 ppm, d, 4 H, J = 1.46 Hz), indicating rapid ring rotation relative to the NMR time scale. Below −35 °C two distinct *tert*-butyl resonances are observed at 1.231 and 1.206 ppm (Figure 4). Unfortunately, the resonances of the nonequivalent ring protons in the conformationally "frozen" molecule could not be resolved. At −60 °C the high-field ring proton resonance is a broad singlet while the low-field resonance is a broad doublet and, thus, only the *tert*-butyl resonance can be used to calculate $\Delta G^{\ddagger}$.

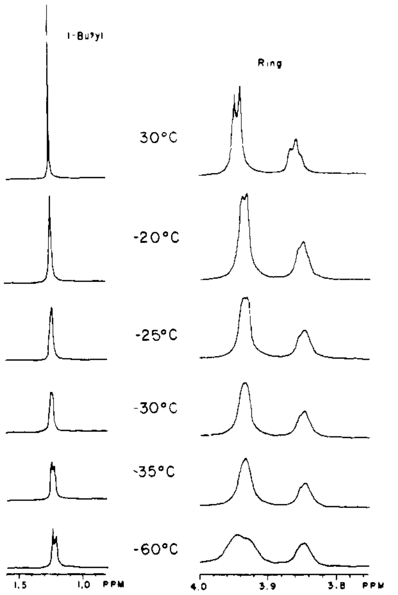

Figure 4. ^{1}H NMR spectra of 1,1′,3,3′-tetra-*tert*-butylferrocene as a function of temperature.

Taking its coalescence temperature at −27.5 °C, the calculated $\Delta G^{\ddagger}$ for ring rotation is 13.1 kcal mol^{-1}. As expected, both the coalescence temperature is higher and $\Delta G^{\ddagger}$ is larger in the ferrocene than in the corresponding uranocene.

Experimental Section

^{1}H NMR spectra were run on the Berkeley 180-MHz FT spectrometer equipped with a variable-temperature probe. All uranocene spectra were run in toluene-d_8. The temperature of the probe was monitored by a precalibrated thermocouple 5 mm from the sample tube, and could be held to ±0.3 °C over the dynamic temperature range. The data for 1,1′,4,4′-tetra-*tert*-butyluranocene are shown in Figures 1 and 2. The least-squares regression lines of Figure 2 are summarized in Table II.

1,1′,4,4′-Tetra-*tert*-butyluranocene was prepared by Miller.[19] 1,1′,3,3′-Tetra-*tert*-butylferrocene was prepared by the method of Leigh[22] by treatment of ferrocene with 4 equiv of *tert*-butyl chloride and 4 equiv of $BF_3 \cdot Et_2O$ in refluxing hexane for 24 h. The tri-*tert*-butylferrocene was removed by reduced-pressure short-path distillation followed by two recrystallizations from CH_2Cl_2: yield 23%, mp 196–197 °C (lit.[22] 198 °C).

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