Contribution from the Department of Chemistry and Biochemistry,
University of Windsor, Windsor, Ontario N9B 3P4, Canada

# Evidence for an Anisotropic Contact Shift. Proton NMR Study of Line Shapes in Uranocene and (C5H5)3UCl Powders

Bruce R. McGarvey* and Steven Nagy

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The proton NMR spectra of solid powders of uranocene and $(C_5H_5)_3UCl$ were measured from 90 to 298 K. The line shapes of both systems became increasingly anisotropic as the temperature was lowered. The cyclooctatetraene rings in uranocene were found to be rotating at a frequency greater than 100 kHz down to 90 K. The $(C_5H_5)_3UCl$ molecules were found to be reorienting rapidly above 220 K, but below 140 K the NMR spectra were characteristic of a rigid lattice with no rotation of the cyclopentadienyl rings. The spectra of both compounds could be simulated by assuming an axial paramagnetic shift tensor and an orientation-dependent line width. Comparison of the experimental shift tensor with that calculated for a point dipolar interaction revealed a large and very anisotropic paramagnetic shift for uranocene due to unpaired spin transferred into the ligand orbitals. The shift was large when the magnetic field was along the 8-fold symmetry axis of the molecule and nearly zero perpendicular to the axis. It appears conclusive that the "contact shift" in uranocene is not isotropic at all. A similar anisotropy in the "contact shift" associated with the cyclopentadienyl rings is evident also in the results for $(C_5H_5)_3UCl$. The average solid-state shift of uranocene agreed with the solution shift, within experimental error, but the solid-state shift of $(C_5H_5)_3UCl$ was 42 ppm greater than the solution shift at 298 K, indicating a difference in molecular geometry between the crystalline state and solution.

## Introduction

The solution NMR of lanthanide and actinide organometallics has been interpreted by most chemists in terms of theories and concepts that were originally developed for use with transition-metal complexes. These theories assumed that the orbital angular momentum was quenched and that the spin–orbit coupling was only a second-order effect, which is definitely not the case for the lanthanide and actinide systems (except for the f⁷ configuration). The isotropic shifts observed in solution spectra are recognized to consist of two contributions. The first is the long-range dipolar interaction between the ligand nuclei and the unpaired electrons in the f orbitals of the central metal ion. If the magnetic susceptibility tensor is not isotropic, this interaction will not average to zero, and the result is often termed the pseudocontact shift in the literature. This term is generally treated properly in the more recent literature except there is sometimes a tendency to assume axial symmetry (to make the problem easier) when there is no valid reason to do so.

The second term is where most of the problems arise. This is the shift that results from the interaction between unpaired electron spin that has been transferred (by some mechanism) to atomic orbitals centered either on the ligand nucleus being studied or the adjacent nucleus. It has been assumed (because this was true for quenched transition-metal systems) that the dipolar contribution from spin in p or d orbitals would average out in solution and therefore only the contribution from spin in s orbitals (Fermi contact interaction) would be seen. For this reason, most chemists refer to the transferred spin component of the shift as the "contact" shift.

It has been known for a long time by chemists and physicists doing solid-state EPR and ENDOR spectroscopy that when the electronic angular momentum is not quenched, it is possible to encounter ground states in which the contribution of the Fermi contact interaction to the hyperfine interaction is definitely not isotropic and the dipolar contribution from the p and d orbitals has an isotropic component. A review article on this problem has recently appeared.[1] A dramatic illustration of the effect occurs[2] in the ¹⁹F hyperfine interaction with Yb³⁺ in octahedral and cubic crystal fields.

Another problem with the analysis that normally is found in the literature on the NMR of organometallics is the attempt to deduce a hyperfine constant from the "contact" shift. The equation normally used is

$$\Delta H/H_0 = -\bar{g}\beta_e S(S+1)A/3kTg_N\beta_N \qquad (1)$$

where $\bar{g}$ is the average electronic g factor, $g_N$ is the nuclear g factor,

$\beta_e$ and $\beta_N$ are the electronic and nuclear magnetons, $S$ is the electronic spin, $k$ is the Boltzmann constant, and $A$ is the isotropic hyperfine interaction constant. In this equation and in this paper $\Delta H = H - H_0$, where $H$ is the resonance field of the paramagnetic sample at a fixed frequency and $H_0$ is the resonance field for the diamagnetic reference. This equation was first proposed by McConnell and Chestnut[3] for quenched transition-metal systems with no thermally accessible excited states. The only way this equation could be valid for the lanthanide and actinide systems is if $A$ were the same for all thermally accessible crystal field states and there were no hyperfine matrix components between the ground state and these crystal field states. Since neither of these conditions is generally fulfilled, the value of $A$ calculated from (1) generally should have no close relation to $A$ values found by EPR for related ligand radicals (as is commonly assumed in the literature).

NMR of lanthanide and actinide compounds in the solid state is generally dominated by the dipolar interaction between spin on the metal atom and the ligand nuclei. This gives large shifts, which change dramatically with orientation in single crystals or large anisotropic line shapes in powder spectra. Studies of the ¹⁹F NMR in a series of lanthanide fluorides[4] show evidence of an anisotropic transferred spin shift, but lack of knowledge about the magnetic susceptibility tensor makes it difficult to calculate the dipolar shift accurately enough. Proton NMR[5] on two erbium hydrates could be explained entirely by the dipolar contribution alone. The authors know of no experimental evidence (other than the work presented here) for an anisotropy in the transferred spin component of the paramagnetic shift of protons.

The organometallic "sandwich" compound of uranocene, bis-($\eta^8$-1,3,5,7-cyclooctatetraenediyl)uranium(IV), has excited considerable interest since its discovery in 1968.[6] The solution proton NMR and its temperature dependence was first measured by Edelstein et al.[7] and that of the related octamethyluranocene, bis-($\eta^8$-1,3,5,7-tetramethyl-1,3,5,7-cyclooctatetraenediyl)uranium(IV), was measured by Streitweiser et al.[8] The temperature dependence was remeasured by Luke and Streitweiser.[9] Edelstein

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* To whom correspondence should be addressed.

et al.[7] calculated the "contact" shift contribution by estimating the pseudocontact shift from the magnetic susceptibility and preliminary crystallographic data[10] on uranocene. In this calculation they assumed $\chi_\perp = 0$. Luke and Streitweiser[9] and Fischer[11] calculated the pseudocontact shift from NMR measurements on a series of substituted uranocenes and from improved crystallographic data[12] on uranocene. Their analyses indicated that $\chi_\perp \neq 0$ but was much smaller than $\chi_\parallel$. McGarvey[13] has attempted to calculate the isotropic shift due to spin transfer into the ligand molecular orbitals and has concluded that the reported "contact" shifts cannot be used to show any involvement of the f orbitals in covalent bonding.

There has been considerable uncertainty as to the ground state of the uranocene molecule. U(IV) has an $f^2$ configuration with the lowest state being $^3H_4$. The 8-fold symmetry of the molecule gives a crystal field that splits the $^3H_4$ state into the five states $|4,\pm M_J\rangle$. Karraker[14] predicted a $|4,\pm4\rangle$ ground state based on theoretical considerations, which was confirmed by Hayes and Edelstein[15] in their analysis of the magnetic susceptibility. Amberger et al.[16] fitted their susceptibility data to a model in which the ground state was $|4,0\rangle$ with the $|4,\pm1\rangle$ state only 17 $cm^{-1}$ above it. Edelstein et al.[17] repeated the low-temperature susceptibility measurements and found that they agreed with the earlier calculations of Hayes and Edelstein but not with that of Amberger et al. Fischer[11] has estimated $(\chi_\parallel - \chi_\perp)$ from the pseudocontact shift and claims it agrees with the ground state being $|4,\pm3\rangle$. Dallinger et al.[18] found with Raman studies that the first excited state was at 466 $cm^{-1}$ and differed from the ground state by $\Delta M_J = \pm1$. They found using this value for the excited state that the best fit between theory and experiment for the temperature dependence of the magnetic susceptibility was obtained when the ground state was $|4,\pm4\rangle$ and the first excited state was $|4,\pm3\rangle$. Barron and Vrbancich[19] have reported that their measurement of the magnetic optical activity of the electronic resonance Raman spectra of the 466-$cm^{-1}$ band confirms the $M_J = \pm4$ level is below the $\pm3$ level.

There is one report[20] on the proton NMR of uranocene in a solid powder at room temperature. The second moment was measured at 60 MHz and was found to be consistent with rapidly rotating cyclooctatetraene rings. No mention was made of any anisotropy of the sort found in this work, but this would be difficult to detect at the temperature and frequency used for the measurement.

The solution proton NMR spectra of $Cp_3UX$, tris($\eta^5$-cyclopentadienyl)uranium(IV), and their temperature dependences have been reported.[21-23] Calculation of the pseudocontact term has proven difficult. Amberger[24] has derived the crystal field pattern for $Cp_3UCl$ from optical and magnetic susceptibility data and has used this to calculate $\chi_\parallel$ and $\chi_\perp$. These values along with crystallographic data[25] were then used to estimate the pseudo-
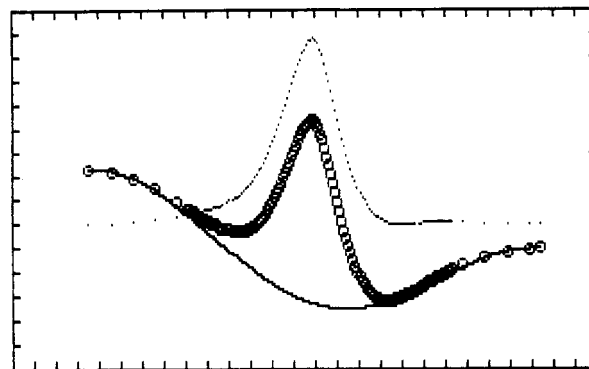


**Figure 1.** Correction of base-line roll. Open circles are selected points from the experimental transformed absorption spectrum in which first- and second-order phase corrections were done manually. Solid curve is the base line due to pulse breakthrough determined by the method discussed in the text. Dotted curve is the spectrum corrected for base-line roll.

contact shift. This calculation assumed a small deviation from $T_d$ symmetry, and this has become suspect. Amberger et al.[26] has recently repeated these calculations without the $T_d$ restrictions for new data on the perdeuteriated compound. Magnetic susceptibility has been measured by several others.[27-29]

This work was originally begun with the idea that the anisotropy in the line shape of the proton NMR of uranocene would be dominated by the dipolar interaction and that the comparison of it with calculated line shapes would enable us to determine the anisotropy in the magnetic susceptibility, $\chi_\parallel - \chi_\parallel$. As will be seen below, we ended up measuring instead a very large anisotropy in the transferred spin shift of the proton.

**Experimental Section**

The uranocene powder was given to us by Dr. A. Streitweiser, University of California, Berkeley, CA. The $Cp_3UCl$ was prepared by using the method of Reynolds and Wilkinson.[27] Both finely divided powders were placed in sealed spherical containers to eliminate shifts due to demagnetization effects. The NMR spectra were obtained on a Bruker CXP-90 FT NMR spectrometer with a flowing-gas ($N_2$) variable-temperature control unit that had been modified to give temperatures down to 85 K. The temperatures reported are ±1 K except at the lower temperatures (<140 K) where the error is ±2 K.

The spectrometer's resonant circuit had been slightly detuned to give a linear response over a bandwidth in excess of 1 MHz and the 90° pulse width was 2.5 μs, which is sufficient for the 250 kHz sweep width used in quadrature detection. Even so, considerable difficulty was experienced in obtaining reliable absorption spectra due to pulse breakthrough in the first 5 μs after the pulse. This meant that the first three points in the FID were unreliable and would introduce considerable base-line roll if retained, but if they were excluded, important information would be lost about the tails in the absorption curve. Attempts to overcome this problem by using spin echo or solid-state echo techniques were fruitless because rapid motions in the solid resulted in the shape of the transformed echo depending on the interval of time between the two pulses.

The problem was eventually overcome by using techniques suggested by Henrichs et al.[30] In this method the first-order phase correction is done manually with the relative phase knob of the spectrometer. This adjustment is done by using a narrow signal located in the center of the spectrum, usually the sample itself at room temperature. The equivalent of the second-order phase correction was then done by changing the magnetic field enough to bring the resonance line to either end of the spectrum and adjusting the time interval between the pulse end and the beginning of data collection until just the absorption spectrum could be seen for any offset of the field. This corrected for the time delay caused by the filter circuits. For a sweep width of 250 kHz, our spectrometer required a delay of 0.9 μs. The spectrometer was now tuned to give an absorption spectrum without any phase manipulations by the computer

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FIELD SWEEP IN KHZ
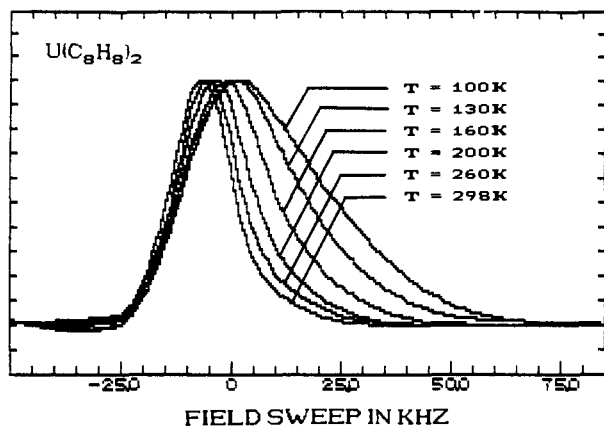
**Figure 2.** Absorption NMR spectra at 90 MHz for uranocene powder at different temperatures. Sweep scale has the magnetic field increasing to the right.



FIELD SWEEP IN KHZ

**Figure 3.** Absorption NMR spectra at 90 MHz for $(C_5H_5)_3UCl$ powder at different temperatures. Sweep scale has the magnetic field increasing to the right.

and any base-line roll was due to pulse breakthrough only.

For sequential quadrature detection the base-line roll in the absorption curve due to three points in the FID will have the form

$$A_0 + A_1 \sin (\pi \nu / \nu_0) + A_2 \cos (2\pi \nu / \nu_0) \qquad (2)$$

where $\nu$ is the frequency of each point in the transformed spectrum measured from the center, $\nu_0$ is the sweep width for the spectrum, and $A_n$ are essentially the magnitudes of the first three points in the FID due to pulse breakthrough. Additional points in the FID will introduce terms of the form $A_n \sin (n\pi\nu/\nu_0)$ for $n$ = odd and $A_n \cos (n\pi\nu/\nu_0)$ for $n$ = even. The sweep width is chosen to be wide enough so that the first and last quarter of the spectrum would be flat base line if no pulse breakthrough has occurred. The $A_n$ parameters are then determined by a least-squares fit of points in the first and last quarter of the spectrum to (2). The resulting base line is then subtracted from the experimental spectrum to get the correct spectrum. An example of the raw spectrum, fitted base line, and corrected spectrum is shown in Figure 1. It is important when using this method that one determine carefully how many points in the FID are seriously affected by pulse breakthrough and use a series with no more parameters $A_n$ than this number. Furthermore, a well-space collection of points from both the first and last quarters of the spectrum must be used for the least-squares fitting. If a good fit is not obtained for all the points, the original tuneup procedure should be checked and redone.

## Results

**A. Powder Spectra.** Representative spectra at different temperatures for uranocene are shown in Figure 2 and similar spectra for Cp₃UCl are shown in Figure 3. The sweep axis is for magnetic field sweep given in frequency units with zero arbitrarily chosen near the center of the spectrum at room temperature. For frequency sweep the signs would be reversed so that frequency increases from right to left. For uranocene the room-temperature spectrum has a width of about 15 kHz and a small tail extending to higher field. As the temperatue is lowered there is an increase in the line width with an increase in the anisotropy of the shape toward higher fields. A similar broadening and increase in anisotropy is observed for Cp₃UCl except the anisotropy is now toward lower fields. Also the line width above 260 K is almost liquidlike indicating not only rotation of the Cp rings but also reorientation of the molecule itself in the lattice at a rapid rate. This reorientation of the molecule is consistent with the room-temperature X-ray study,[25] which showed the molecules to be loosely packed and found very large temperature factors for the carbon atoms in the Cp ring.

**B. Simulation of Line Shapes.** We wish to extract the principal paramagnetic shifts from these spectra and compare them to those predicted from the dipolar interaction. The way to do this is to simulate the spectra and adjust the parameters of the simulation until we have a good match between simulated and experimental spectra. The spectra appear to be nearly axial in nature (two of the three principal shifts are almost the same), and preliminary attempts were made to simulate the spectra by making this assumption and assuming a constant broadening (Gaussian or Lorentzian) independent of the orientation of the magnetic field.
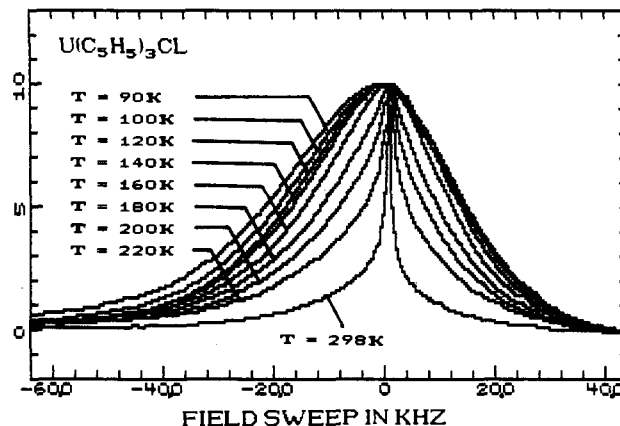
These preliminary attempts gave very poor fits, and it became apparent that one would have to use a simulation that included a broadening function whose line width varied greatly with orientation of the magnetic field.

The source of this orientation-dependent broadening is not hard to find. One major contribution to the broadening is the magnetic dipolar interaction between proton spins in the cyclooctatetraene (COT) ring in uranocene or the Cp ring in Cp₃UCl. Van Vleck[31] has shown us how to calculate the second moment of lines broadened by this spin–spin mechanism from geometric factors alone. His equation shows us that for a set of spins oriented in a circular ring, the second moment will be proportional to $(3 \cos^2 \alpha - 1)^2$ and therefore the line width to $|3 \cos^2 \alpha - 1|$. The angle $\alpha$ is the angle between the magnetic field and the axis perpendicular to the plane of the ring. It should be noted that this line width is maximum when $\alpha = 0°$ and half of the maximum width when $\alpha = 90°$; it is zero when $\alpha = 54.7°$, the "magic angle".

We have successfully simulated all the line shapes measured by assuming each crystallite in the powder gives a Gaussian line shape with a second moment of the form

$$\langle \Delta \nu^2 \rangle = C(3 \cos^2 \alpha - 1)^2 + D \qquad (3)$$

and an axial paramagnetic shift tensor. This gives us four parameters to adjust in our simulation: $C$, $D$, $\Delta H_\parallel$, and $\Delta H_\perp$. Examples of the fitted versus experimental line shapes are given in Figure 4 for uranocene at room temperature and at 90 K while a fit for Cp₃UCl at 100 K is shown in Figure 5. Fits were done only for temperatures below 140 K in the case of Cp₃UCl since above this temperature the reorientational motions of the molecule affected the line shape. In all cases the fits appear to be excellent.

The simulation described above assumed that the parallel axis for the paramagnetic shift tensor was the same as the axis perpendicular to the rings. This is proper for uranocene as we shall see below but may not be correct in the case of Cp₃UCl. If the Cp rings are not rotating (as it appears is the case), then the large downfield shift identified as $\Delta H_\parallel$ would be close to the U–H vector, which is not perpendicular to the ring axis. Nevertheless the simulation model seems to work well with the Cp₃UCl system.

For uranocene parameter $C$ in (3) is essentially constant for all temperatures measured, while $D$ is temperature dependent. This is illustrated in Figure 6 where the half-width of Gaussian lines having second moments of $C$ and $D$ are plotted against $T^{-1}$. The average value of $C$ gives a C–H bond distance of 1.08 Å from Van Vleck's equation if we assume the ring to be rotating. It appears that the COT rings are rotating rapidly on the NMR time scale down to 90 K. Anderson[20] has calculated the intramolecular contribution to the second moment in uranocene when the rings are rotating, and this contribution is close to the values of $D$ found at room temperature. The temperature-dependent part of $D$ must result from $T_1$ broadening originating from the magnetic inter-

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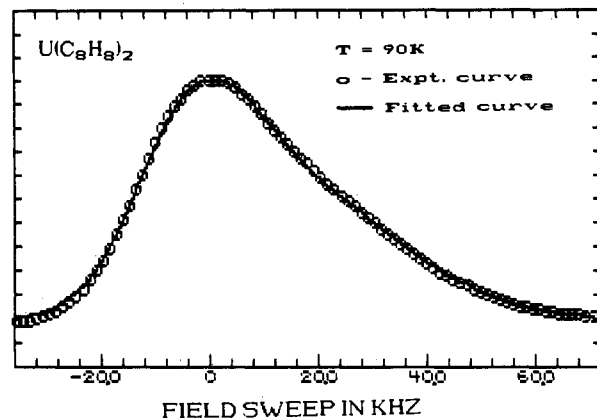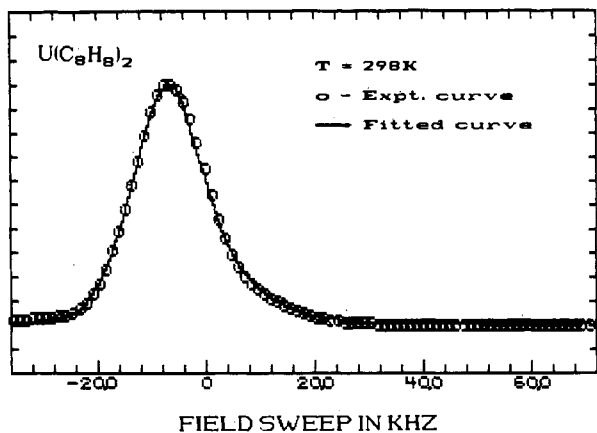


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**Figure 4.** Comparison between experimental and simulated absorption curve for uranocene at 298 (top) and 90 K (bottom). Solid line is a simulation.
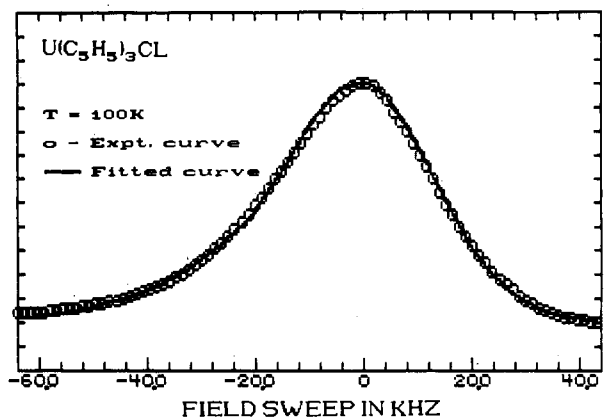


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**Figure 5.** Comparison between experimental and simulated absorption curve for $(C_5H_5)_3UCl$ at 100 K. Solid line is a simulation.

action between the uranium ion and the proton.

For Cp$_3$UCl the temperature interval examined below 140 K is too small to detect any temperature dependence. The line widths associated with the $C$ and $D$ parameters are both about 19 kHz. We estimate for a nonrotating Cp ring that the line width should be 18 kHz. It thus appears that the rings are not rotating below 140 K.

In Figure 7 are given the paramagnetic shift terms $\Delta H_\parallel$ and $\Delta H_\perp$ for uranocene as well as the average shift. For comparison purposes the solution results of Luke and Streitweiser[9] and the chemical shift for thorocene[9] are also plotted. The agreement between the solid-state average shift and the solution shifts demonstrates that the use of a spherical container has indeed removed the effect of demagnetization fields. It is of interest to note that a linear least-squares fit of the $\Delta H_\parallel$ and $\Delta H_\perp$ points produces two lines with intercepts at the thorocene shift within experimental error. It also should be noted that the perpendicular
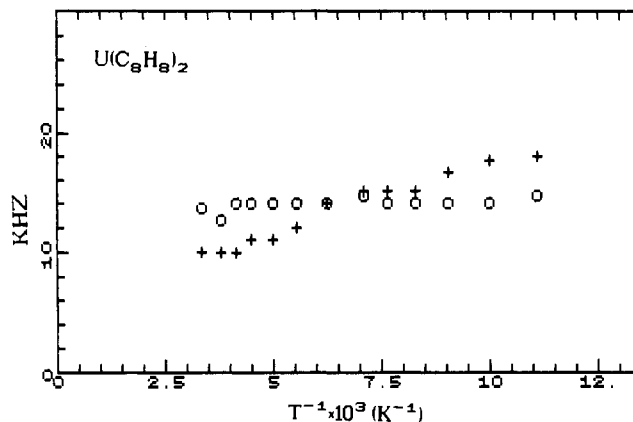


**Figure 6.** Temperature dependence of line widths for Gaussian broadening functions used in the simulation of uranocene powder NMR spectra. Open circles are the perpendicular line width for the orientation-dependent part. Crosses are for the orientation-independent part.
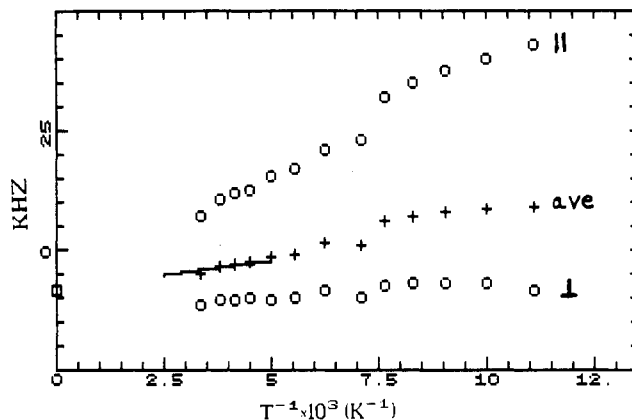


**Figure 7.** Temperature dependence of the uranocene powder paramagnetic shift tensor. Open square on the left axis is the solution shift for thorocene. Straight line is the solution shift as reported in ref 9.
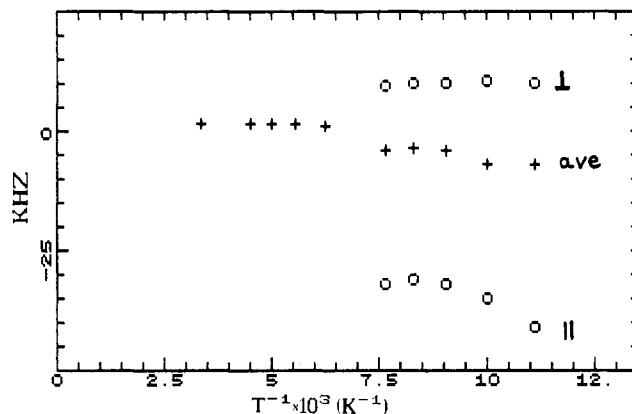


**Figure 8.** Temperature dependence of the $(C_5H_5)_3UCl$ powder paramagnetic shift tensor. Average shifts at higher temperatures where there is no $\Delta H_\parallel$ or $\Delta H_\perp$ are simply positions of the top of the absorption peak.

shift is essentially independent of temperature.

In Figure 8 is given the equivalent plot for Cp$_3$UCl. As for uranocene the perpendicular shift is independent of temperature. The parallel shift, however, does seem to follow a linear $T^{-1}$ dependence over the small temperature interval measured.

**C. Calculation of Dipolar Shift in Uranocene.** The basic equation[32] for calculating the point dipole contribution from the metal ion susceptibility tensor $\chi_{ij}$ is

$$(\Delta H/H_0)_{ij} = -R^{-3}[3(\cos\,\theta_i)(\sum_m \chi_{mj}\cos\,\theta_m) - \chi_{ij}] \qquad (4)$$

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**Table I.** Summary of Calculations and Experiment on $U(C_8H_8)_2$

| | | | exptl, kHz | | cryst calcd,[b] kHz | | | molec, kHz | |
|---|---|---|---|---|---|---|---|---|---|
| $T$, K | $10^{-27}\chi_\parallel,^a$ emu | $10^{-27}\chi_\perp,^a$ emu | $\Delta H_\parallel$ | $\Delta H_\perp$ | $\Delta H_1$ | $\Delta H_2$ | $\Delta H_3$ | $\Delta H_\parallel$ | $\Delta H_\perp$ |
| 298 | 11.385 | 1.067 | 15.7 | −2.9 | 2.79 | 0.02 | −0.67 | 1.21 | −0.06 |
| 260 | 13.197 | 1.134 | 19.2 | −2.1 | 3.22 | 0.03 | −0.75 | 1.40 | −0.06 |
| 240 | 14.379 | 1.168 | 20.7 | −2.0 | 3.51 | 0.04 | −0.81 | 1.53 | −0.06 |
| 220 | 15.774 | 1.201 | 21.2 | −1.6 | 3.84 | 0.06 | −0.87 | 1.67 | −0.06 |
| 200 | 17.440 | 1.232 | 24.2 | −1.8 | 4.23 | 0.08 | −0.95 | 1.85 | −0.07 |
| 180 | 19.467 | 1.259 | 25.7 | −1.3 | 4.71 | 0.11 | −1.04 | 2.07 | −0.07 |
| 160 | 21.984 | 1.282 | 29.7 | 0.2 | 5.31 | 0.15 | −1.16 | 2.33 | −0.07 |
| 140 | 25.198 | 1.299 | 31.7 | −1.3 | 6.06 | 0.20 | −1.30 | 2.67 | −0.07 |
| 130 | 27.167 | 1.306 | 40.7 | 1.2 | 6.53 | 0.23 | −1.39 | 2.88 | −0.07 |
| 120 | 29.456 | 1.311 | 43.7 | 1.4 | 7.07 | 0.27 | −1.49 | 3.12 | −0.07 |
| 110 | 31.837 | 1.315 | 46.2 | 1.5 | 7.63 | 0.31 | −1.60 | 3.38 | −0.07 |
| 100 | 35.386 | 1.318 | 48.7 | 1.4 | 8.46 | 0.37 | −1.76 | 3.75 | −0.07 |
| 90 | 39.329 | 1.320 | 51.7 | 0.0 | 9.39 | 0.44 | −1.93 | 4.17 | −0.07 |

[a] Calculated from equations in ref 18. [b] Calculated from summation over neighboring uranocene molecules using crystal data from ref 12.

where $R$ is the distance from the metal ion and $\cos\theta_i$ is the direction cosine for the vector $\mathbf{R}$ of the $i$th coordinate. This is not a symmetric tensor and cannot be diagonalized by an orthogonal rotation to a principal axis system. If we define a symmetric tensor, $(\Delta H/H_0)_s$, and an antisymmetric tensor, $(\Delta H/H_0)_a$, as

$$[(\Delta H/H_0)_s]_{ij} = [(\Delta H/H_0)_{ij} + (\Delta H/H_0)_{ji}]/2 \quad (5)$$

$$[(\Delta H/H_0)_a]_{ij} = [(\Delta H/H_0)_{ij} - (\Delta H/H_0)_{ji}]/2 \quad (6)$$

we find that $(\Delta H/H_0)_s$ is the only one we detect experimentally because when the vectors $\mathbf{I}_H$ and $\mathbf{H}$ are parallel to each other then $\mathbf{I}_H \cdot (\Delta H/H_0)_a \cdot \mathbf{H} = 0$.

The biggest contribution for an individual proton will be from the uranium atom to which the COT ring is bonded. For this calculation we choose a coordinate system in which the $z$ axis is the $C_8$ axis perpendicular to the COT rings (the parallel axis). The $x$ axis is defined such that the proton is in the $xz$ plane. We define the angle between $z$ and the $\mathbf{R}$ vector connecting U and H as $\alpha$. The shift tensor components calculated from (4) and (5) are then

$$(\Delta H/H_0)_{xx} = (1 - 3\sin^2\alpha)\chi_\perp R^{-3}$$

$$(\Delta H/H_0)_{yy} = \chi_\perp R^{-3}$$

$$(\Delta H/H_0)_{zz} = (1 - 3\cos^2\alpha)\chi_\parallel R^{-3} \quad (7)$$

$$(\Delta H/H_0)_{xz} = (\Delta H/H_0)_{zx} = -\tfrac{3}{2}(\sin\alpha\cos\alpha)(\chi_\parallel + \chi_\perp)R^{-3}$$

$$(\Delta H/H_0)_{xy} = (\Delta H/H_0)_{yx} = (\Delta H/H_0)_{yz} = (\Delta H/H_0)_{zy} = 0$$

The three principal shifts are then

$$(\Delta H/H_0)_2 = (\Delta H/H_0)_{yy} \quad (8)$$

$$(\Delta H/H_0)_{1,3} = [(\Delta H/H_0)_{xx} + (\Delta H/H_0)_{zz}]/2 \, ● $$
$$\tfrac{1}{2}\{[(\Delta H/H_0)_{xx} - (\Delta H/H_0)_{zz}]^2 + 4(\Delta H/H_0)_{xz}^2\}^{1/2} \quad (9)$$

The principal values predicted by these equations are far from the axial values found. This is readily seen by making the following reasonable assumptions. We assume $\chi_\perp = 0$ since $\chi_\perp$ is much smaller than $\chi_\parallel$, and since crystallographic data[12] indicates that $\alpha$ is near the "magic angle", we assume $\cos^2\alpha = \frac{1}{3}$. These approximations give principal shifts of $0$, $\pm 2^{1/2}\chi_\parallel/R^{-3}$, which are very far from axial. Any reasonable values of $\chi_\perp$ and $\alpha$ come up with similar results. Also the spread of resonances is much larger than the line widths observed.

If we assume that the COT rings are rotating (or simply jumping between the eight equivalent orientations) we obtain an axial shift tensor with the principal values of

$$(\Delta H/H_0)_\parallel = (1 - 3\cos^2\alpha)\chi_\parallel R^{-3} \quad (10)$$

$$(\Delta H/H_0)_\perp = -\tfrac{1}{2}(1 - 3\cos^2\alpha)\chi_\perp R^{-3} \quad (11)$$

Since $\alpha$ is near the "magic angle", the above equations give much smaller principal shifts than those found experimentally.

Since in the rotating case the contribution from the nearest uranium is almost canceled out, we considered it necessary to calculate the contribution of other nearby uranium atoms to the dipolar shift. A computer program was devised to do this for the rigid lattice, and the contribution of all uranium atoms within 15 Å was computed. This was done for each of the eight protons in the ring, and then the average of all eight tensors was computed to give the tensor for a rotating ring. The results of this calculation are given in Table I along with the experimental results (which are measured relative to the solution thorocene result). The values of $\chi_\parallel$ and $\chi_\perp$ used in the calculations are listed in Table I and were obtained by using equations from Dallinger et al.[18] for a ground state of $M_J = \pm 4$. Attempts to use slightly different combinations of $\chi_\parallel$ and $\chi_\perp$, but the same average $\chi$, showed the dipolar calculation to be rather insensitive to the exact values chosen for $\chi_\parallel$ and $\chi_\perp$. Also included in the table are the results calculated for a single molecule (eq 10 and 11). It will be noted that the inclusion of the intermolecular terms removes the axial symmetry in the shift tensor. Two of the principal shifts are close enough, however, that it would be difficult to detect the lower symmetry in the sort of simulations done here.

**D. Calculation of Dipolar Shift in $Cp_3UCl$.** Only the intramolecular calculation was done for $Cp_3UCl$. The investment in time to do the intermolecular calculation was deemed to be of little value for two reasons. One, the quality of the crystallographic data[24] is poor, and two, the intermolecular contribution will be a much smaller percentage of the total than was the case for uranocene. The calculation of the shift tensor components from (4) and (5) is straightforward, but the resulting equations are more complex because they require the specification of the position of the proton in the Cp ring since this affects the angle between the U–H vector and the molecular $C_3$ symmetry axis. For the rotating case the three principal shifts are

$$\Delta H/H_0 = \tfrac{1}{2}(3\cos^2\gamma - 1)\chi_\perp R^{-3} \quad (12)$$

$$\Delta H/H_0 = \tfrac{1}{4}(3\cos^2\gamma - 1)R^{-3}\{-3(\chi_\parallel - \chi_\perp)\cos^2\alpha + \chi_\parallel - 2\chi_\perp \pm [3(\chi_\parallel^2 - \chi_\perp^2)\cos^2\alpha + 9\bar\chi^2]^{1/2}\} \quad (13)$$

where $\alpha$ is the angle between the $C_3$ symmetry axis of the molecule and the vector between the center of the Cp ring and the uranium atom, $\gamma$ is the angle between the U–H vector and U–Cp ring vector, and $\bar\chi$ is the average value of $\chi$. In Table II are given the shift values calculated from (12) and (13) along with the experimental values. The experimental values have been referenced against the diamagnetic $C_5H_5^-$ resonance. The values of $\chi_\parallel$ and $\chi_\perp$ given in Table II are from calculations done by Amberger et al.[26] Also given in Table II are the shifts calculated for the rotating and nonrotating case when one assumes the magnetic susceptibility to be isotropic. It should be noted that the average shift, $(\Delta H_\parallel + 2\Delta H_\perp)/3$, in the isotropic case is zero as expected. The rotating case gives a spread of shifts considerably below what is found experimentally. The problem is considerably more complex in the case of the nonrotating rings when there is an anisotropy in the susceptibility. We have calculated the principal shifts for the

**Table II.** Summary of Conclusions and Experiment on U(C$_5$H$_5$)$_3$Cl

| T, K | 10$^{-27}$χ$_\parallel$,$^a$ emu | 10$^{-27}$χ$_\perp$,$^a$ emu | exptl, kHz | | ring rot. calcd, kHz | | | χ$_{iso}$, kHz | | χ$_{iso}$, kHz | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | ΔH$_\parallel$ | ΔH$_\perp$ | ΔH$_1$ | ΔH$_2$ | ΔH$_3$ | ΔH$_\parallel$ | ΔH$_\perp$ | ΔH$_\parallel$ | ΔH$_\perp$ |
| 130 | 1.988 | 13.14 | −22.3 | 18.2 | −19.1 | 1.8 | 9.8 | −14.1 | 7.1 | −45.1 | 22.6 |
| 120 | 1.850 | 13.73 | −20.3 | 18.7 | −19.9 | 1.7 | 10.3 | −14.6 | 7.3 | −46.8 | 23.4 |
| 110 | 1.710 | 14.27 | −22.3 | 18.7 | −20.7 | 1.7 | 10.7 | −15.1 | 7.5 | −48.3 | 24.1 |
| 100 | 1.558 | 14.80 | −26.3 | 19.2 | −21.5 | 1.6 | 11.1 | −15.6 | 7.8 | −49.7 | 24.9 |
| 90 | 1.381 | 15.34 | −32.3 | 18.7 | −22.3 | 1.5 | 11.5 | −16.0 | 8.0 | −51.2 | 25.6 |

$^a$ From ref 26.

**Table III.** Three Principal Shifts for Cp$_3$UCl at 91 K Calculated for Nonrotation

| atom$^a$ | ΔH$_1$, kHz | ΔH$_2$, kHz | ΔH$_3$, kHz |
|---|---|---|---|
| 1 | −44.7 | 19.3 | 36.6 |
| 2 | −71.4 | 4.4 | 36.6 |
| 3 | −57.1 | 12.5 | 36.6 |
| 4 | −72.9 | 3.6 | 36.6 |
| 5 | −40.7 | 21.3 | 36.6 |
| 6 | −70.5 | 4.9 | 36.6 |
| 7 | −61.7 | 10.0 | 36.6 |
| 8 | −65.4 | 7.9 | 36.6 |
| 9 | −59.0 | 11.5 | 36.6 |
| 10 | −34.5 | 24.4 | 36.6 |
| 11 | −67.5 | 6.6 | 36.6 |
| 12 | −62.8 | 9.4 | 36.6 |
| 13 | −62.4 | 9.6 | 36.6 |
| 14 | −66.8 | 7.1 | 36.6 |
| 15 | −31.3 | 26.0 | 36.6 |
| av | −57.9 | 11.9 | 36.6 |

$^a$ Number corresponds to numbers for carbon atoms given in ref 25.

15 different protons for 91 K only, and these are tabulated in Table III. It can be seen that in the nonrotating case the average range of shifts is considerably larger than that found experimentally.

## Discussion

**A. Uranocene.** In the case of uranocene, it is quite clear that the COT rings are rotating rapidly enough to average out much of the dipolar shift anisotropy for all temperatures studied. This is evident, not only from the $C$ value needed for (3) in the simulation but also from the axial symmetry found for the shift tensor. In the nonrotating case our calculations reveal the dipolar shift tensor would give an anisotropy that would be very easy for us to detect in these experiments. Thus the frequency of rotation must be higher than 100 kHz even at 90 K, which indicates a very low barrier to internal rotation in the solid state. This rapid rotation also explains our difficulty in obtaining consistent line shapes from the solid-state echo technique even for pulse intervals as low as 30 $\mu$s for the two pulses.

Examination of Table I shows that $\Delta H_\parallel$ is more than five times larger than that predicted by the dipolar interaction. The reason for the smallness of the dipolar shift is found in the nearness of $\alpha$ to the "magic angle" of 54.7°. In calculating this angle from the X-ray data, we assumed the hydrogen atoms to be in the same plane and at a distance from each other consistent with the value of $C$ in (3) as determined from Van Vleck's equation.[31] We can increase the dipolar value of $\Delta H_\parallel$ by bending the C–H bonds toward the uranium atom (thus increasing $\alpha$). We have done the complete crystal calculation for different assumed positions of the H atom and find we can attain dipolar shifts similar to the experimental shifts only by bending the C–H bond by more than 20°. We consider this extent of C–H bending out of the COT plane to be most unreasonable; therefore, we are forced to conclude that the bulk of the anisotropy we have observed in the uranocene NMR spectra is due to a large anisotropy in the transferred spin component of the paramagnetic shift. If this transferred spin shift results primarily from the Fermi contact interaction, then our results show that, for uranocene, the "contact shift" is not isotropic at all. It is very large in the direction of the parallel axis of the molecule and is nearly zero in the plane of the COT rings. It should be noted for those whose belief in the isotropic nature of

the contact shift is so strong that they would prefer our results to be a proof of a very large bending of the C–H bond that they are then giving up the notion of a contact shift in uranocene because our results then show that the solution shift is entirely accounted for by the pseudocontact shift. This is because our experiments show very little paramagnetic shift in the perpendicular direction, which is consistent with the dipolar contribution but not with a sizable isotropic contact shift.

**B. Cp$_3$UCl.** For Cp$_3$UCl the conclusions are less clear cut. The narrowness of the NMR lines at the higher temperatures clearly indicate that there is more motion than just the rotation of the rings. Either the molecule is tumbling in the solid just like a liquid or at the very least there is a rotation of the molecule about the U–Cl axis of the molecule. At temperatures below 140 K, the spectra appear on the NMR time scale to be that of rigid solids. The parameter $C$ in (3) has a value suggesting nonrotation of the rings, but as has been mentioned earlier, the assumption made in the simulation that the axis perpendicular to the Cp ring is also the parallel axis of the shift tensor is not necessarily true (particularly for the dipolar shift) and this could affect the value of $C$. It is our opinion that such a mismatch between the rotation axis and the parallel axis would mostly produce lower values of the $C$ parameter rather than larger values; therefore, we think that on balance the evidence is strong for nonrotating rings.

Because we are not completely certain about the motion of the Cp rings, we have given the dipolar calculation results for both cases in Tables II and III. It is clear that there is an anisotropy in the transferred spin component of the shift in either case, but the exact nature of the shift is not the same. If the rings are not rotating (which we assume to be the case), then the experimental anisotropy in the shift is considerably less than that predicted for the dipolar shift, which means that the transferred spin component has a sign that tends to cancel out some of the anisotropy. The dipolar shifts calculated from Amberger et al.[26] predict large enough deviations from axial symmetry that we should have found it necessary to include it in our simulations. We think our results show a much smaller anisotropy in the magnetic susceptibility, and it would be better to compare our experimental results to the dipolar shift predicted from the isotropic $\chi$ calculation included in Table II. In this case the transferred shift contribution to $\Delta H_\parallel$ would be somewhat greater than +20 kHz and to $\Delta H_\perp$, approximately −5 kHz.

One surprising result is the magnitude of the average paramagnetic shift in the solid state as compared to the solution results. At 298 K the paramagnetic shift is 4.7 kHz or is +52 ppm, which is an order of magnitude greater than the value of 9.6 ppm reported[11] for the solution NMR. This could be due to demagnetization factors that were not eliminated by using spherical samples, but since we observed no comparable effect in uranocene, where the solid state and solution results agreed within experimental error, this appears unlikely. More likely there is a difference in molecular geometry between the solution and the solid that makes a pronounced difference in the pseudocontact shift. If this is the case, it points up one of the dangers in using crystallographic data to estimate the pseudocontact shift.

**Registry No.** (C$_5$H$_5$)$_2$U, 11079-26-8; (C$_5$H$_5$)$_2$UCl, 72042-61-6.