# $^{13}$C NMR Relaxation Study of Molecular Motions in Tetraphenyltin and Tetra(*p*-tolyl)tin in Solution

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The Woessner approach is applied to the $^{13}$C relaxation data for tetraphenyltin (**1**) and tetra(*p*-tolyl)tin (**2**) in $CDCl_3$ solution over the temperature range 5−42 °C to obtain correlation times for rotational motions and hence the activation barriers. Quantum mechanical computations were carried out to obtain the rotational energy barriers for comparison. For **2** the relaxation data indicate (1) slower ring rotation than in **1**, (2) highly hindered internal rotation of the methyl group. IR and chemical shift data support the hypothesis of hyperconjugation of the methyl correlated with interaction between the $\pi$-electrons and the 5d orbitals of tin in the (*p*-tolyl)Sn moiety to account for the hindrances to the rotations of the ring and the methyl. The activation barrier for the tolyl group rotation is found to be much higher than that for the phenyl rotation. However, the Woessner approach yields an anomalously high barrier for the methyl rotation. An explanation based on correlated rotations of the tolyl ring and the methyl is offered.

## Introduction

Analysis of carbon-13 nuclear magnetic resonance relaxation data can yield detailed information about the overall and internal motions of molecules in solution. Woessner's theoretical treatment of nuclear spin relaxation in spheroids[1] has been used to interpret $^{13}$C relaxation data for near spheroidal molecules: specifically, tetraphenylmethane and tetraphenylsilane, in which correlation times for the overall motion of the molecule and for internal rotation of the phenyl groups have been obtained.[2]

The $r^{-6}$ dependence of the dipole−dipole relaxation mechanism ensures that the relaxation of hydrogen-bearing carbons is dominated by interactions with directly bonded protons. Under extreme narrowing conditions the rate of dipolar relaxation is given by

$$1/T_1^{\mathrm{dd}} = (\mu_o/4\pi)^2 N(\gamma_C\gamma_H)^2(h/2\pi)^2 r_{CH}^{-6}\tau_c \qquad (1)$$

where $T_1^{\mathrm{dd}}$ is the dipolar contribution to the spin−lattice relaxation time $T_1$. In eq 1 $\gamma_C$ and $\gamma_H$ are the $^{13}$C and $^1$H magnetogyric ratios, respectively, $r_{CH}$ is the carbon−hydrogen internuclear distance, $N$ is the number of directly attached protons, and $\tau_c$ is the effective correlation time for rotational reorientation.[3,4] Equation 1 assumes equal C−H bond distances and neglects nonbonded interactions; it applies to molecular tumbling when only one correlation time $\tau_c$ is involved, which implies a rigid body undergoing isotropic motion. This simple scheme breaks down as soon as the molecule as a whole undergoes anisotropic motion or when the molecule possesses groups which undergo fast internal motion.[5]

Based on Woessner's treatment of internal rotation,[1] eq 1 can be used to deal with internal rotation of a phenyl group attached to a large spherical molecule which tumbles isotropically by replacing the isotropic tumbling correlation time $\tau_c$ with an effective correlation time $\tau_e$:[2]

$$1/T_1^{\mathrm{dd}} = (\mu_o/4\pi)^2 N(\gamma_C)^2(\gamma_H)^2(h/2\pi)^2(r_{CH})^{-6}\tau_e \qquad (2)$$

In eq 2 the quantities appearing are

$$\tau_e = A\tau_a + B\tau_b + C\tau_c$$

$$A = (1/4)(3\cos^2\Delta - 1)^2$$

$$B = 3\sin^2\Delta\cos^2\Delta$$

$$C = (3/4)\sin^4\Delta$$

$$\tau_a = \tau_S$$

$$\tau_b = (\tau_S^{-1} + \tau_G^{-1})^{-1}$$

$$\tau_c = (\tau_S^{-1} + 4\tau_G^{-1})^{-1}$$

in which the angle $\Delta$ is that between the C−H vector and the rotation axis, $\tau_S$ is the correlation time for rotation of the sphere, and $\tau_G$ is the correlation time for internal rotation of the phenyl group. The correlation times are related to diffusion coefficients $D$ through $\tau_S = 1/(6D_S)$ and $\tau_G = 1/D_G$. Because $\Delta = 0$ for the para C−H bond so that $A = 1$ and $B = C = 0$, $T_1^{\mathrm{dd}}$(para) is independent of $\tau_G$ and eq 2 can be used to calculate $\tau_S$. For the meta C−H bond $\Delta = 60°$ so that $A = 1/64$, $B = 9/16$, and $C = 27/64$. The values of $T_1^{\mathrm{dd}}$(ortho) and $T_1^{\mathrm{dd}}$(meta) depend on both $\tau_S$ and $\tau_G$, but the equations can be solved for $\tau_G$ once the known value of $\tau_S$ is inserted.[2] To interpret the $T_1$ data adequately, it is necessary to take into account these two correlation times.

The nuclear Overhauser effect (NOE) depends entirely on dipolar relaxation; hence $T_1^{\mathrm{dd}}$ can be determined directly from

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the observed $T_1$ and NOE measurements using the relationship

$$T_1^{dd} = 1.988T_1/\eta \quad (3)$$

where $\eta$ = NOE − 1.[5]

In this research we report the results of $^{13}C$ $T_1$ and NOE measurements on $CDCl_3$ solutions of tetraphenyltin ($Ph_4Sn$) (**1**), tetra(*p*-tolyl)tin ((*p*-tolyl)$_4$Sn) (**2**) and diphenyldi(*p*-tolyl)tin ($Ph_2$(*p*-tolyl)$_2$Sn (**3**). Dilute solutions were used to reduce effects of viscosity variations. The Woessner approach was used to obtain correlation times of rotational motions and hence the activation barriers. Quantum mechanical computations were carried out to obtain the energy barriers for the internal rotations, to allow for comparison with the NMR results. The validity of the Woessner approach in determining the activation barrier for the methyl rotation in **2** is examined.

## Experimental Section

The tin compounds used in this study were synthesized and purified according to procedures described in the literature.[6,7] Samples in $CDCl_3$ were prepared at the following concentrations: for **1** at 0.32 mol % (or 0.040 M) as solubility was limited; for **2** and **3** at 0.75 mol % (0.094 M). The samples in 10 mm NMR tubes were thoroughly degassed by five freeze−pump−thaw cycles on a vacuum line and sealed under vacuum.

$^{13}C$ NMR spectra were recorded on a JEOL EX90A spectrometer, operating at 22.50 MHz. Temperatures in the probe insert were checked with a standard methanol sample for temperature calibration. To confirm chemical shift assignments, proton-coupled $^{13}C$ NMR spectra were also obtained on a JEOL GSX270 spectrometer operating at 67.94 MHz. The $^{13}C$ $T_1$ spectra were measured using the inversion−recovery method with a set of typically 10 recovery ($\tau$) periods. For each $\tau$ value the number of repetitive scans varied from at least 100 scans to at least 150 scans for the more dilute solution. The relaxation delay was at least 5 $T_1$ plus the acquisition time. The $\tau$ values were varied up to 1.5 $T_1$. The $T_1$ values were calculated from the raw signal intensity data using standard software. The final $T_1$ value was the average of two final experiments, which were carried out after one or more preliminary experiments were made to estimate the magnitude of the value. Reproducibility of the $T_1$ values was 4% or better in most cases. The relaxation measurements were confined to carbons with at least one directly bonded hydrogen. If there is no directly bonded proton, then interactions with protons in other molecules could compete against interactions with more distant protons in the same molecule, thereby giving rise to problems of interpretation.

The NOE of a $^{13}C$ resonance was obtained from two successive measurements, one under continuous proton decoupling conditions and the other under gated proton-decoupling conditions in which the NOE was eliminated. The pulse delay was 6 $T_1$ in the first measurement and 10 $T_1$ in the second, in addition to the acquisition time. For good signal-to-noise ratios, the number of spectral accumulations was varied from 1700 to 2500 for the two solutions. The digital resolution was 0.030 Hz. Zero-filling was applied to the FID data prior to Fourier transformation, but no sensitivity or resolution enhancement was applied. The total area under the signal was accurately measured on an expanded spectrum using Simpson's rule.[8] As the Lorenztian line shape of the NMR signal has a wide base, the signal was recorded over a sufficiently wide frequency range so that no intensity was neglected in the area measurement. The experiments were repeated and reproducibility of both peak areas was better than 5%. The NOE was obtained by dividing the total area in the continuously decoupled spectrum by the total area in the gated decoupled spectrum.

Six to seven measurements of both $T_1$ and NOE were made over the range of temperature (5−42 °C). These data are shown in Tables 2−4. The correlation times for the rotational motions were obtained using eq 2. The barrier ($E_a$) to a rotational motion is obtained by fitting the diffusion rates $D_i$ to the Arrhenius equation

$$D_i = A \exp(-E_a/RT) \quad (4)$$

The infrared spectra of (*p*-tolyl)$_4$Sn (**2**) and toluene in chloroform solution were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. The vibrational absorptions of the solvent were subtracted from the solution spectrum. From the difference IR spectrum the vibrational absorption frequencies of the deforma-

**TABLE 1: $^{13}C$ and $^{119}Sn$ Chemical Shifts, $\delta$ (ppm),[a] for Tetraphenyltin and Tetra(*p*-tolyl)tin[b]**

| compound | ipso (C-1) | ortho (C-2/C-6) | meta (C-3/C-5) | para (C-4) | methyl (C-7) | $^{119}Sn$ |
|---|---|---|---|---|---|---|
| **1** | 137.80 | 137.28 | 128.69 | 129.17 | | −130.65 |
| **2** | 134.48 | 137.18 | 129.43 | 138.81 | 21.51 | −124.88 |

[a] $\delta$ (ppm): $^{119}Sn$ referenced to $(CH_3)_4Sn$ at $\delta = 0$; $^{13}C$ referenced to $(CH_3)_4Si$ at $\delta = 0$. [b] In $CDCl_3$ solution at 27 °C; **1**, 0.040 M; **2**, 0.094 M.

**TABLE 2: $^{13}C$ $T_1$[a] and NOE[b] Data for Tetraphenyltin in $CDCl_3$[c] at 22.50 MHz**

| | ortho[d] | | meta[d] | | | para[d] | | |
|---|---|---|---|---|---|---|---|---|
| temp (°C) | $T_1$ (s) | $\eta$ | $T_1$ (s) | $\eta$ | $\tau_G$ (ps) | $T_1$ (s) | $\eta$ | $\tau_S$ (ps) |
| 5 | 2.96 | 1.99 | 2.81 | 1.99 | 35.5 | 0.78 | 1.99 | 57.0 |
| 12 | 3.28 | 1.98 | 3.12 | 1.97 | 33.5 | 0.96 | 1.98 | 49.0 |
| 19 | 3.70 | 1.94 | 3.51 | 1.94 | 30.0 | 1.13 | 1.95 | 40.9 |
| 27 | 4.06 | 1.92 | 3.84 | 1.94 | 29.0 | 1.30 | 1.93 | 35.1 |
| 32 | 4.38 | 1.93 | 4.12 | 1.92 | 27.0 | 1.42 | 1.93 | 32.2 |
| 37 | 4.58 | 1.91 | 4.38 | 1.92 | 25.0 | 1.50 | 1.93 | 30.4 |
| 42 | 4.83 | 1.92 | 4.60 | 1.92 | 23.5 | 1.61 | 1.93 | 28.4 |

[a] $T_1$, observed data. [b] NOE = 1 + $\eta$. [c] Concentration: 0.32 mol % solute (or 0.040 M). [d] For conventional numbering of the carbons, see Table 1.

**TABLE 3: Relaxation Data and Correlation Times for Tetraphenyl-Substituted Compounds at 37 °C in $CDCl_3$ Solution**

| compound | bond length C−X (×$10^{10}$ m) | $\chi$[a] | $\tau_S$ (ps) | $\tau_G$ (ps) | $D_S$[b] ($ns^{-1}$) |
|---|---|---|---|---|---|
| $Ph_4Sn$ | 2.14[16] | 3.00 | 30 | 25 | 5.5 |
| $Ph_4Si$[c] | 1.87 | 2.41 | 31 | 37 | 5.4 |
| $Ph_4C$[c] | 1.47 | 1.47 | 33 | 132 | 5.1 |

[a] $\chi = T_1^{dd}(o,m)/T_1^{dd}(p)$. [b] $D_S = 1/6\tau_S$. [c] Reported results from data obtained at 25.2 MHz magnetic field and 37 °C.[2]

**TABLE 4: $^{13}C$ $T_1$[a] and NOE[b] Data for Tetra(*p*-tolyl)tin in $CDCl_3$[c] at 22.50 MHz**

| | ortho[d] | | meta[d] | | | methyl[d] | | | |
|---|---|---|---|---|---|---|---|---|---|
| temp (°C) | $T_1$ (s) | $\eta$ | $T_1$ (s) | $\eta$ | $\tau_G$ (ps) | $T_1$ (s) | $\eta$ | $\tau_G$ (ps) | $\tau_S$ (ps) |
| 5 | 1.95 | 1.99 | 1.90 | 1.99 | 62.0 | 2.15 | 1.60 | 9.0 | 69 |
| 12 | 2.22 | 1.99 | 2.19 | 1.99 | 53.1 | 2.39 | 1.57 | 7.9 | 61 |
| 19 | 2.60 | 1.95 | 2.51 | 1.95 | 45.9 | 2.81 | 1.57 | 6.9 | 53 |
| 27 | 2.92 | 1.94 | 2.79 | 1.92 | 39.0 | 3.06 | 1.57 | 6.2 | 47 |
| 34 | 3.31 | 1.95 | 3.24 | 1.95 | 33.7 | 3.39 | 1.55 | 5.5 | 43 |
| 42 | 3.78 | 1.95 | 3.68 | 1.95 | 29.0 | 3.74 | 1.53 | 4.9 | 39 |

[a] $T_1$, observed data. [b] NOE = 1 + $\eta$. [c] Concentration: 0.75 mol % solute (or 0.094 M). [d] For conventional numbering of the carbons, see Table 1.

**TABLE 5: Vibrational Absorption Frequencies ($cm^{-1}$) of the $CH_3$ Group**

| | deformation mode | | |
|---|---|---|---|
| compound | asymmetric | symmetric | rocking mode |
| toluene | 1460.0 | 1379.9 | 1042.0 |
| (*p*-tolyl)$_4$Sn | 1446.7 | 1389.8 | 1070.5 |

tion and rocking modes of the methyl groups were obtained. The data are shown in Table 5.

### Computation Methods

Quantum mechanical computations were carried out for the tin compounds **1** and **2** and for the methyl group rotation in 4-methyl-9-fluorenone (**4**). For the phenyl- and tolyl-substituted tin compounds, ab initio and density functional theory (DFT) methods were employed. The ab initio method is second-order Møller−Plesset perturbation (MP2) theory,[9] and the hybrid DFT/Hartree−Fock method is B3LYP. The latter incorporates Becke's three parameter functional[10] (B3) with the Lee, Yang, and Parr (LYP) correlation functional.[11] The basis sets used here are LanL2DZ, which are of effective core potential (ECP) plus double-$\zeta$ (DZ) quality. For the H and C atoms, the LanL2DZ basis sets are actually Dunning's DZ basis sets,[12] and for the Sn atom, we use Wadt and Hay's ECP plus DZ basis set.[13] Equilibrium geometries were fully optimized with each method. To evaluate the internal rotation barrier, the phenyl (or tolyl) group was rotated by changing the corresponding dihedral angle. The other internal coordinates were fixed. Because the whole molecule was not relaxed when rotating, the computed energy barrier should be an upper bound; that means the true barrier should be lower. The computation allowing the whole molecule to relax when rotating would require very large computer capacity which was not available. Hence an energy barrier closer to the true value was not obtained. The computations were carried out at University of Georgia, using the Gaussian 94 Program suite (1995).

### Results and Discussion

**A. Computations.** The results of the computations are summarized below, with the computational method or method/basis set used given in parentheses:

(1) For the phenyl group rotation in $Ph_4Sn$ (**1**), the upper bound values of the energy barriers are 27.2 kJ $mol^{-1}$ (B3LYP) and 30.1 kJ $mol^{-1}$ (MP2).

(2) In (*p*-tolyl)$_4$Sn (**2**) the upper bound values of the energy barrier for tolyl group rotation is 26.4 kJ $mol^{-1}$ (B3LYP) and 28.0 kJ $mol^{-1}$ (MP2). The energy barrier for the methyl group rotation is 0.94 kJ $mol^{-1}$ (0.22 kcal $mol^{-1}$). Although an upper bound in the computations, this value for the methyl rotation is expected to be close to the true value, because the geometrical changes in the other parts of the molecule should be very small when the methyl group is rotating.

(3) In 4-methyl-9-fluorenone (**4**) the computed energy barriers for the methyl group rotation are 8.4 kJ $mol^{-1}$ (B3LYP/DZP), 10.3 kJ $mol^{-1}$ (MP2/DZP), and 10.0 kJ $mol^{-1}$ (MP2/6-311G**). This energy barrier is attributed to steric interaction with the hydrogen at the 5-position in the molecule. These results are similar to those computed for substituted toluenes.[14]

The energy barrier for the methyl group rotation in **4** has been determined by $^{13}$C NMR using the Woessner approach and the reported value is $7.8 \pm 0.9$ kJ $mol^{-1}$.[15] This value is in fair agreement with the computed values given above. Although the computed values are more relevant to the gas phase, the fair agreement with the NMR solution state value does confirm that the NMR method based on eq 2 is valid for the determination of activation barriers to the internal rotation of a small group which is *directly attached* to a rigid backbone that tumbles isotropically. The validity of eq 2 for the internal rotation of the methyl in the tolyl group in which the methyl is conjoined to another internal rotor is examined in the results for (*p*-tolyl)$_4$Sn (**2**).

**B. Tetraphenyltin** (**1**). There are two motions to consider: the overall reorientational motion (tumbling) of the molecule as a unit and the internal rotation of the phenyl groups. Table 2 shows the expected temperature dependence of the $T_1$ and NOE $\eta$ values. The $\eta$ values are near maximum, indicating that the dipole−dipole relaxation mechanism is dominant. As the preferred rotation is around the $C_2$ axis, which should not affect the para carbon, the smaller $T_1$ value observed for this carbon is accounted for by the overall reorientational motion. The relaxation data for tetraphenylmethane ($Ph_4C$) and tetraphenylsilane ($Ph_4Si$) which have been reported[2] are included in Table 3 for comparison. In the calculation of the correlation time using eq 2, the expectation value of the C−H bond length in the phenyl group is used, with the value $\langle r \rangle = 0.1092$ nm.[2] The correlation time $\tau_S$ is calculated with $T_1^{dd}$(para) and $\tau_G$ is calculated with $T_1^{dd}$(meta). The $T_1^{dd}$ values (1.44−1.55 s) for the para carbons are essentially equal in the three compounds $Ph_4X$ (where X = C, Si or Sn) in $CDCl_3$ solution at 37 °C. Hence, the $\tau_S$ for the overall reorientational motion with values of 30, 31, and 33 ps are equal within experimental error. Thus the overall reorientational motion is not affected by the difference in the phenyl-C−X bond lengths[16] or the nature of X. However, the correlation time of the internal rotation, $\tau_G$, of the phenyl moiety greatly depends on the C−X bond length, with the value in $Ph_4C$ a factor of 5 higher than that for $Ph_4Sn$, which has the longest C−X bond length among the three compounds. The longer C−X bond length presumably reduces steric interactions of the phenyl rings and thus allows them to rotate more freely (or more anisotropically). In $Ph_4C$ and $Ph_4Si$ $\tau_G > \tau_S$, indicating that the internal motion is slower than the overall reorientational motion; but in $Ph_4Sn$ (**1**) the internal motion is faster, as seen by the values $\tau_G = 25$ ps and $\tau_S = 30$ ps in $CDCl_3$ solution at 37 °C.

The anisotropy of the internal rotation of a phenyl group in an axially symmetric molecule can be assessed by taking the ratio of the average of the $T_1^{dd}$ values of the ortho and meta carbons to that of the para carbon.[17] In the limit of very fast rotation this ratio $\chi = 64$, whereas in the case of isotropic rotational motion $\chi = 1$.[18] Below the limit of anisotropic motion this model can be applied only approximately for descriptions of the moderate anisotropic internal rotations in the phenyl-substituted compounds. This ratio, represented by $\chi$ in Table 3, varies from 1.47 for $Ph_4C$ to 3.00 for $Ph_4Sn$, indicating that the degree of anisotropy of the internal motion increases as the bond length of C−X increases.

The overall reorientational diffusion rate $D_S = 1/(6\tau_S)$, and the average value in the three compounds is $D_S = 5.3$ $(ns)^{-1}$ at 37 °C. The plot of ln $D_G$ vs $1/T$ for the meta carbon in Figure 1 (plot B) gives a lower activation barrier for the internal rotation of the phenyl group ($7.8 \pm 0.4$ kJ $mol^{-1}$) than that (plot D) for the overall reorientational motion ($13.8 \pm 0.6$ kJ $mol^{-1}$). These values, determined using the Woessner approach, are expected to be reliable as discussed earlier. The activation barrier for the phenyl group rotation is, as expected, less than the computed (upper bound) values. Steric interactions no doubt account for part of this activation barrier. However, if there is contribution of p$\pi$−d$\pi$ bonding in the Sn−C bond, the $\pi$-bond character

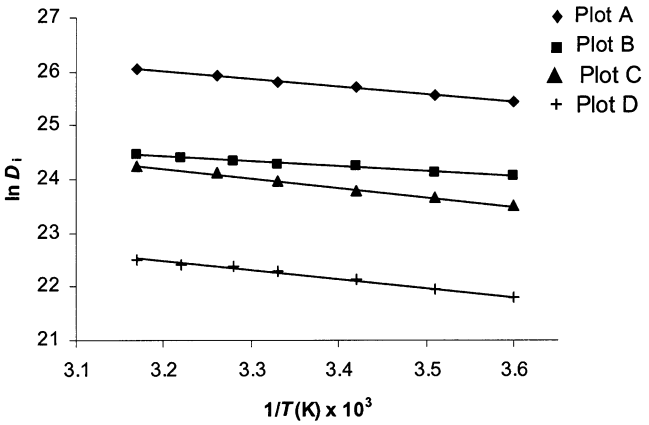


**Figure 1.** Plots of ln $D_i$ vs $1/T$ (K) for rotational motions: (A)−(C) $D_i = D_G = (1/\tau_G)$; (D) $D_i = D_S = (1/6\ \tau_S)$. (A) Rotation of the methyl in (*p*-tolyl)$_4$Sn (**2**). (B) Rotation of the phenyl ring in $Ph_4Sn$ (**1**). (C) Rotation of the tolyl ring in **2**. (D) Overall reorientational motion of **1**.

would also contribute to the barrier. Rationalization for the incidence of $\pi$-bonding is given below in the discussion of internal rotations in (*p*-tolyl)$_4$Sn (**2**).

**C. Tetra(*p*-tolyl)tin (2).** Table 4 shows that the observed relaxation data for the ortho and meta carbons follow the same trend as the corresponding carbons in **1,** except that in **2** the $T_1$ values are 25−40% smaller, whereas the NOE is essentially full in both compounds. As the para carbon in **2** is a quaternary carbon, its relaxation data were not determined, so that the overall reorientation correlation time $\tau_S$ is not directly available. However, the $\tau_S$ can be approximated from the corresponding value for a closely related molecule, diphenyldi(*p*-tolyl)tin (**3**), in which the phenyl has a hydrogen bearing para carbon. The $T_1$ and NOE values for the para carbons provide, through eq 2, the $\tau_S$ values shown in Table 4. As these values are about 10 ps longer than those in **1**, they are considered reasonably good approximations for the overall reorientational motion of **2**.

The striking feature in the data in Table 4 is that the observed $T_1$ values for the methyl carbon are unusually low (compared to the ortho and meta carbons) and that the NOE for the methyl carbon is unusually high ($\eta = 1.55$) for a methyl carbon in a tolyl group, considering that the corresponding value in toluene is 0.61[19] or 0.69.[2] This high $\eta$ and the relatively low $T_1$ values are consistent with a significant hindrance to the internal rotation of the methyl in **2**. Another feature is that the $T_1$ data for the ring carbons clearly imply that the rotation of the tolyl ring is more hindered than that of the phenyl in **1**.

The hindrance to the rotation of a methyl group can be indicated by the ratio of its $T_1^{dd}$ to that of a methine (CH) group, provided that the latter belongs to the rigid backbone of the molecule. For a completely locked $CH_3$ group the ratio $T_1^{dd}(CH_3)/T_1^{dd}(CH) = 1/3$, whereas for a freely rotating $CH_3$ the ratio is 3.[20] In the case of **2** in $CDCl_3$ solution at 34 °C, the ratio is 1.33, using the average of the data for ortho and meta carbons. This ratio is 1.77 in toluene, as calculated using reported data.[2] The lower ratio in **2** is another indication that the internal rotation of the methyl is more hindered than in the case of toluene.

The existence of hindrance to the rotation of the methyl is further supported by the computed energy barrier of 0.94 kJ mol$^{-1}$ as discussed above. As this value is more relevant to the gas phase, in the solution state the barrier is expected to be higher because of intermolecular effects. Further this value does indicate that in the (*p*-tolyl)Sn moiety the methyl energy barrier is significantly higher than the essentially zero value in toluene.[21]

The infrared spectra of **2** and toluene provide further information on the methyl groups. The vibrational frequencies of the deformation and the (in-plane) rocking modes of the methyl groups are shown in Table 5. It is well documented that the $CH_3$ group in hydrocarbons gives rise to the asymmetric deformation mode at 1460 cm$^{-1}$ and the symmetric deformation mode has a characteristic absorption frequency in the range 1385−1370 cm$^{-1}$.[22] The latter is highly sensitive to the electronic structure along the C−X bond, where X is the group to which the methyl is bonded. The data in Table 5 show that there is a 10 cm$^{-1}$ difference in the symmetrical deformation frequencies of the methyl groups in **2** and toluene, indicating that the electronic structure in the C−$CH_3$ group in **2** is significantly different from that in toluene. The methyl group attached to an aromatic ring has a very specific rocking frequency near 1042 cm$^{-1}$.[22] The methyl in **2** has a value of this frequency which is 28.5 cm$^{-1}$ higher than that in toluene, as shown in Table 5. The higher frequency in **2** indicates that the force constant for the rocking vibration of the methyl is greater than that in toluene. That is, the **C**−**C**$H_3$ bond is "stiffer" in the *p*-tolyl−Sn moiety.

The $^{119}$Sn and $^{13}$C chemical shifts for **1** and **2** are shown in Table 1. In **2** the ipso-carbon is 3.32 ppm more shielded, and the para-carbon is 9.64 ppm less shielded than the corresponding nuclei in **1**. The IR and chemical shift data and the computed energy barrier for the rotation of the methyl are consistent with significant changes in electronic structure in the **C**−**C**$H_3$ bond in tetra(*p*-tolyl)tin (**2)** which may be attributed to hyperconjugation.[23] The IR and NMR data also suggest that a higher degree of hyperconjugation exists in **2** than in toluene. This hyperconjugation necessarily accounts for the hindrance to the methyl rotation as observed.

The presence of the *p*-methyl in **2** also results in the $^{119}$Sn nucleus becoming 5.77 ppm less shielded than that in **1**. Tin is highly electropositive (Pauling electronegativity 1.82). There is some evidence that in phenyltin compounds interaction occurs between the $\pi$-electrons of the phenyl groups and the 5d orbitals of tin; that is, in the sp$^2$-C−Sn bond there is significant (p→d)-$\pi$ contribution.[24,25] Presumably, the extent of p$\pi$−d$\pi$ bonding is greater in the (*p*-tolyl)Sn moiety than in the phenyl−Sn because of correlation with the hyperconjugation of the methyl. It is likely that the correlation of the two phenomena leads to mutual enhancement, judging from the hindrances to the rotations of the tolyl ring and the methyl. This situation predicts a higher activation barrier for the rotation of the tolyl ring.

The calculation of the correlation time $\tau_G$ for the rotation of the tolyl ring follows that in **1**. Using the $\tau_S$ found in **3** and the $T_1^{dd}$ for the meta carbon in **2**, eq 2 is solved for $\tau_G$. The results are shown in Table 4. In the temperature range studied (5−42 °C) $\tau_G < \tau_S$, but both $\tau_G$ and $\tau_S$ are larger than the corresponding values in **1**, indicating slower motions in **2**. As the diffusion rate $D_G = 1/\tau_G$, the plot of ln $D_G$ vs $1/T$ in Figure 1 (plot C) yields an activation barrier $E_a = 14.8 \pm 0.5$ kJ mol$^{-1}$ for the rotation of the tolyl group. This value, obtained using the Woessner approach, is expected to be reliable, as discussed earlier, and is also expected to be lower than the computed (upper bound) values. Although a higher value than the corresponding one in **1** is expected from the observed $T_1$ data, the difference (7.0 kJ mol$^{-1}$) in the $E_a$ values found is unexpectedly large. Steric interactions are not expected to be that much more severe in **2** than in **1**. Presumably, this high $E_a$ value in **2** is the result of higher $\pi$-bond character in the Sn−C bond.

**D. Rotational Activation Energy for the Methyl Group.** The calculation of the correlation time for the rotation of the methyl, $\tau_G$, using eq 2 presents a problem in that the tolyl ring to which it is attached does not constitute a rigid backbone. An attempt is made by ignoring the rotation of the tolyl ring and assuming that the methyl is attached to a rigid backbone that tumbles isotropically with the $\tau_S$ data which are derived from **3**. Then using $T_1^{dd}$ data for the methyl carbon and the $\tau_S$ data, eq 2 yields the correlation times $\tau_G$ shown in Table 4. The results indicate that the methyl rotation is only a factor of 6−7 times faster than the tolyl ring rotation. Specifically the data at 27 °C are: $\tau_G$(methyl) = 6.2 ps, $\tau_G$(tolyl) = 39 ps and $\tau_S$(overall) = 47 ps. In the case of toluene, $\tau_G$ has been estimated to be 0.3 ps at 37 °C in $CDCl_3$ solution, where $\tau_G$ refers to motion relative to the phenyl ring.[2] The diffusion rate $D_G$ is related to $\tau_G$ and the plot of $\ln D_G$ vs $1/T$ in Figure 1 (plot A) yields an activation barrier $E_a = 11.8 \pm 0.4$ kJ mol$^{-1}$ for the rotation of the methyl group. The relatively high value of $\tau_G$(methyl) is consistent with hindrance to the rotation as discussed, but the $E_a$ value is unreasonably high. It is far too high compared with the computed value of 0.94 kJ mol$^{-1}$, which can be used as a reference. The following discussion attempts to explain how this anomalous result comes about.

Tetra(*p*-tolyl)Sn (**2**) has two conjoined internal rotors in each *p*-tolyl group: the rotating methyl is attached to the tolyl ring which itself is rotating, and the whole molecule tumbles isotropically in solution. There is an inherent problem in interpreting the effective correlation time ($\tau_e$) for the methyl carbon in eq 2; it should be pertinent to the local environment in which the spin−lattice relaxation occurs. It is expected that the rotation of the tolyl ring and that of the methyl group are correlated, in view of the hyperconjugation and the resulting hindrance to the methyl rotation. Hence the rate of rotation of the methyl relative to the tolyl ring would be less than when the tolyl ring is stationary (or its intrinsic rate of rotation in the laboratory frame of reference). This situation implies that the effective correlation time of the methyl in a molecule-fixed frame of reference becomes longer than what it would be in the laboratory frame. Consequently the relaxation of the methyl carbon via the dipolar mechanism becomes unusually efficient. This result is equivalent to the situation where the rotation of the methyl becomes retarded. The unusually high NOE ($\eta$ = 1.55 at 27 °C) found in $CDCl_3$ is consistent with this expectation. This effective correlation time of the methyl carbon, as obtained from its relaxation data, is therefore dependent on or dominated by the rate of rotation of the tolyl ring. As is well-known, the activation barrier to the tolyl group rotation is much larger than that for the rotation of the methyl (relative to the tolyl ring), so that the temperature dependence of the rate of rotation of the tolyl ring is correspondingly greater. This will result in the effective correlation time of the methyl carbon following closely that temperature dependence and thus yield a spurious high barrier to the rotation of the methyl, a value that would actually reflect the barrier to the tolyl group rotation. This expectation is consistent with the unusually high activation barrier evaluated from the methyl carbon relaxation data; a value which is three-fourths of that for the rotation of the tolyl group.

## Conclusions

The present analysis shows that in a molecule having two conjoined internal rotors in which the two rotations are correlated, the effective correlation time for the internal rotation of the end rotor is poorly defined. In the case of the tolyl group in **2** the relaxation data of the methyl carbon can be interpreted as arising from the correlation of two internal rotations, and the Woessner approach, in such a situation, may *not* lead to a correct value of the barrier to the internal rotation of the methyl.

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## References and Notes

(1) Woessner, D. E. *J. Chem. Phys*. **1962**, *36*, 1−4.
(2) Harris, R. K.; Newman, R. H. *Mol. Phys*. **1985**, *54*, 1021−1034 and references therein.
(3) Werbelow, L. G.; Grant, D. M. *J. Chem. Phys*. **1975**, *63*, 4742−4749.
(4) Kuhlmann, K. F.; Grant, D. M. *J. Chem. Phys*. **1971**, *55*, 2998−3007.
(5) Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Longman Scientific & Technical: Harlow, Essex, U.K., 1986; Chapter 4.
(6) Zimmer, H.; Lubke, K. *Chem. Ber*. **1952**, *85*, 1119−1121; *Chem. Abstr*. **1952**, *47*, 12280.
(7) Gilman, H.; Rosenberg, S. D. *J. Org. Chem*. **1953**, *18*, 1554−1560; *Chem. Abstr*. **1952**, *48*, 13648.
(8) Anton, H. *Calculus*, 6th ed.; John Wiley: New York, 1999; pp 557−562.
(9) Møller, C.; Plesset, M. S. *Phys. Rev*. **1934**, *46*, 618.
(10) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648.
(11) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(12) Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer H. F., Ed.; Plenum: New York, 1976; p 1.
(13) Wadt, W. R.; Hay, P. J. *J. Chem. Phys*. **1985**, *82*, 284.
(14) Rio, A. D.; Boucekkine, A.; Meinnel, J. *J. Comput. Chem*. **2003**, *24*, 2093−2100.
(15) Wilson, N. K. *Magn. Reson. Chem*. **1985**, *23*, 12−15.
(16) Chieh, P. C.; Trotter, J. *J. Chem. Soc. A* **1970**, 911−914.
(17) Lyerla, J. R.; Levy, G. C. In *Topics in Carbon-13 NMR Spectroscopy*; Levy, G. C., Ed.; John Wiley: New York, 1974; Vol. 1, Chapter 3, pp 113−115.
(18) Levy, G. C.; Cargioli, J. D.; Anet, F. A. L. *J. Am. Chem. Soc*. **1973**, *95*, 1527−1535.
(19) Levy, G. C., *J. Chem. Soc. Chem. Commun*. **1972**, 47−48.
(20) Allerhand, A.; Doddrell, D.; Komoroski, R. *J. Chem. Phys*. **1971**, *55*, 189−198.
(21) Lambert, J. B.; Nienhuis, R. J.; Finzel, R. B. *J. Phys. Chem*. **1981**, *85*, 1170−1172.
(22) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Methuen: London, 1966; pp 20−25.
(23) Weinhold, F. *Nature* **2001**, *411*, 539−541 and references therein.
(24) Poller, R. C. *The Chemistry of Organotin Compounds*; Academic Press: New York, 1970; pp 4−9 (see also references therein).
(25) McFarlane, W.; Maire, J. C.; Delmas, M. *J. Chem. Soc. Dalton* **1972**, 1862−1865.