^2H Spin–Lattice Relaxations at Axial and Equatorial Deuterons in 2,2,6,6-Tetradeuterio-4-*tert*-butylcyclohexanone

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Abstract: The relaxation times of the axial and equatorial deuterons of 2,2,6,6-tetradeuterio-4-*tert*-butylcyclohexanone, whose signals are unresolved, are measured by a technique employing the paramagnetic shift reagent $Pr(fod)_3$. The relaxation time ratio, T_{ax}/T_{eq}, is 1.09 for the uncomplexed molecule, in good agreement with the theoretical value, 1.093, obtained from Woessner's theory of relaxation. The experimental T_{ax}/T_{eq} ratio for the completely complexed species is 0.59. The inversion of the ratio T_{ax}/T_{eq} observed for the uncomplexed relative to complexed species is consistent with a bent angle of ca. 160° between the carbonyl bond and the weak oxygen metal complexing bond.

Recently the utilization of paramagnetic shift reagents for the simultaneous determination of deuteron relaxation times of accidentally isochronous deuterium resonances was described.[1] The application of this technique to the problem of simultaneous determination of the ^2H relaxation times of the axial and equatorial deuterons of 2,2,6,6-tetradeuterio-4-*tert*-butylcyclohexanone (**1**), whose signals at 13.82 MHz are not completely resolved, is described in the present work. Compound **1** has a chair conformation and the diastereotopic deuterons in question are bonded to the same carbon along two vectorial directions which have distinct direction cosines with respect to the principal inertial axes of the molecule. The anisotropy of the molecule would suggest that the relaxation times of axial and equatorial deuterons should differ. With available theory it is possible not only to estimate the ratio of axial to equatorial spin–lattice relaxation times (T_{ax}/T_{eq}) but also to estimate the effect that the addition of shift reagent should have on this ratio. The latter in turn can be used to verify the geometry of the complex of **1** with lanthanide shift reagents which has been suggested from ^1H and ^{13}C chemical shift data by Schneider and Weigand.[2]

Theoretical Predictions

The deuteron relaxation rates ($1/T_1$) are related to the molecular correlation time τ in the extreme narrowing limit (where $1/\tau$ is much greater than the magnetic resonance frequency) by the relation,

$$\frac{1}{T_1} = \tfrac{3}{8}(1 + \eta^2/3)\left[\frac{e^2qQ}{\hbar}\right]^2 \tau \qquad (1)$$

where $e^2qQ/\hbar$ is the quadrupole coupling constant and η is the asymmetry parameter. Quadrupole coupling constants for carbon–deuterium bonds have been measured by various workers.[3-5] The asymmetry parameter has a value[6] of ca. 0.2 and is usually neglected in most calculations ($\eta^2/3 \sim 0$). Thus, a theoretical estimate of $1/T_1$ is obtainable from a theory of molecular reorientation time (τ), such as developed by Woessner,[7] in connection with eq 1. For compound **1**, Woessner's theory predicts

$$\tau = C_+\tau_+ + C_-\tau_- + \sum_{i=1}^{3} C_i\tau_i \qquad (2)$$

where $C_\pm$ and C_i are well defined functions of the direction cosines of the bond vector of interest whose orientations are defined with respect to the Cartesian diffusion axes. The quantities $\tau_\pm$ and τ_i are the following functions of the rotational diffusion coefficients:

$$\tau_i = \frac{1}{3(D_i + D)}$$

$$\tau_\pm = \frac{1}{6(D \pm (D^2 - L^2)^{1/2})}$$

$$D = \tfrac{1}{3}\sum_{i=1}^{3} D_i$$

$$L^2 = \tfrac{1}{3}\sum_{i>j} D_iD_j$$

where D_i is the ith rotational diffusion coefficient.

In the formation of the shift reagent complex of compound **1**, the metal of the shift reagent coordinates with the carbonyl oxygen of **1** along a line which coincides with the assumed threefold symmetry axis of the shift reagent. Structurally, the complex should closely approximate a prolate ellipsoid ($D_1 < D_2 = D_3$) with internal rotation of **1** about the local threefold symmetry axis of the shift reagent for which Woessner's theory[7] predicts

$$\tau = \frac{\tfrac{3}{4}\sin^4\phi}{2D_2 + 4(D_1 + D')} + \frac{3\sin^2\phi\cos^2\phi}{5D_2 + D_1 + D'} + \frac{(\tfrac{1}{2}(3\cos^2\phi - 1))^2}{6D_2} \qquad (3)$$

where ϕ is the angle between the internal rotation axis and bond vector undergoing reorientation, and D' is the rotational diffusion coefficient for internal rotation.

The prediction of relaxation rates from eq 1, 2, and 3 requires estimates of rotational diffusion coefficients and quadrupole coupling constants. Since estimates of all these quantities are not readily available, only the ratios of relaxation rates of the axial and equatorial deuterons are predicted. The quadrupole coupling constants are, to a good approximation, the same for the axial and equatorial deuterons andd the ratio of their relaxation times is equal to the inverse ratio of their correlation times. This, in turn, depends only on the ratio of rotational diffusion coefficients and the direction cosines of the carbon deuterium bond vectors.

In order to evaluate the quantities in eq 2 and 3 which are dependent on the angle between the bond vector and the various diffusion axes, it was assumed that the diffusion axes are coincident with the principal axes. This assumption has previously been successfully employed.[8-10] In order to estimate ratios of rotational diffusion coefficients it was assumed that rotational diffusion coefficients are, in the first-order approximation, inversely proportional to the square root of the corresponding moments of inertia. A theoretical basis for this assumption has been presented by Steele[11] in terms of rotational friction coefficients. Bauer et al.,[12] in studies on aromatic compounds, have shown that in-plane rotations which displace very little solvent are faster than out-of-plane rotations which displace a larger volume of solvent. This latter work concludes that factors other than moments of inertia influence rotational diffusion. Compound **1** and its shift reagent complex are bulky species in which all rotations displace large amounts of solvent and it should not be expected that significant solvent anisotropic effects would be observed as have been observed by Bauer et al.[12] in more compact planar compounds. Thus the assumption that the rotational diffusion coefficients are inversely proportional to the square roots of the corresponding moments of inertia is probably valid for compound **1.**

Detailed geometric data on compound **1,** required to apply eq 2 and 3, were calculated with the program STRAIN[13] such that the strain energy was minimized. The presence of the *tert*-butyl group results in small differences between the coordinates calculated for the cyclohexanone portion of compound **1** and the coordinates obtained for cyclohexanone in an earlier calculation by Allinger et al.[14] The differences are insignificant when the coordinates are applied to the calculations of T_{ax}/T_{eq} for compound **1** but are quite significant when applied to the same calculation for the shift reagent complex of compound **1.**

The calculated coordinates predict the principal moments of inertia of compound **1** to be 246, 813, and 901 amu Å^2. Using these data to estimate ratios of rotational diffusion coefficients and eq 2, one obtains T_{ax}/T_{eq} = 1.093. In the shift reagent complex, compound **1** uundergoes internal rotation about the weak O-M bond (M represents the metal in the shift reagent). The moment of inertia I' about this internal rotation axis is the following function of the C=O—M bond angle θ,

$$\begin{aligned} I' = 306.610\cos^2(\theta - 31.132) \\ + 675.942\sin(\theta - 31.132)\cos(\theta - 31.132) \\ + 2800.008\sin^2(\theta - 31.132) \quad (4) \end{aligned}$$

Since no detailed structural data are available for the shift reagent complex of compound **1,** its moments of inertia are approximated as 52 200, 31 600, and 31 600 amu- Å^2, using molecular volumes and crystallographic lattice parameters[15] of the shift reagent and calculated coordinates of compound **1.** These data, eq 3 and 4, and the assumed square root relation between rotational diffusion coefficients and moments of inertia predict T_{ax}/T_{eq} = 1.11, 0.80, and 0.57 for θ = 180, 160, and 140°, respectively. When the above values are compared with T_{ax}/T_{eq} = 1.093 for compound **1,** the postulated bent θ angle of about 160° proposed by Schneider and Weigand[2] implies a significant reversal of T_{ax}/T_{eq} upon addition of shift reagent.

Since the moments of inertia used to obtain estimates of ratios of rotational diffusion coefficients of the complex (D_1/D_2 = 0.778 and D'/D_2 = 6.85, 4.61, and 3.68 for θ = 180, 160, and 140°, respectively) are approximate, other calculations of T_{ax}/T_{eq} were performed which allowed for considerable deviations from these estimates. Essentially the same predictions with regard to the reversal of T_{ax}/T_{eq} for $\theta \sim 160°$ are obtained. It is found that T_{ax}/T_{eq} is nearly independent of D_1/D_2 for $0.5 \leq D_1/D_2 \leq 2$, and results of these calculations listed in Table I show that the reversal of T_{ax}/T_{eq} is substantial for all $D'/D_2 \geq 3$ for θ = 160°, that it rapidly becomes less pronounced for larger θ, and is negligible for $170° \leq \theta \leq 180°$

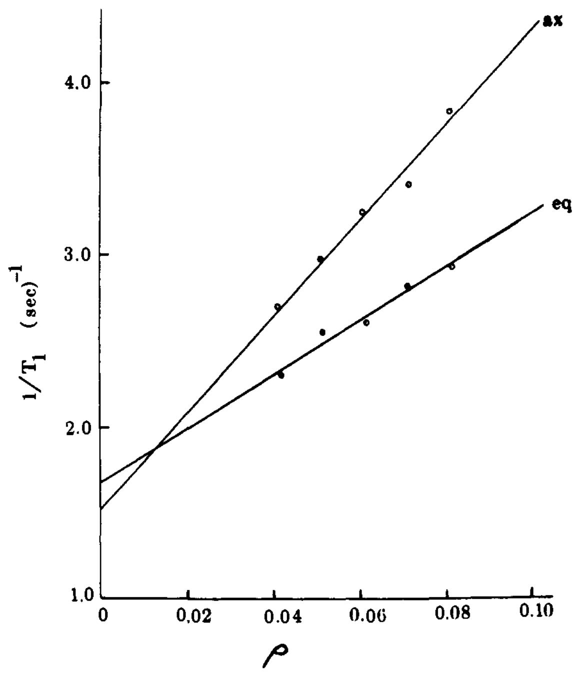

Figure 1. The least-squares linear plots of relaxation rate for axial and equatorial deuterons vs. ρ.

Table I. Estimated Ratios, T_{ax}/T_{eq}, for the Shift Reagent Complex

	θ =					
D'/D_2	140°	150°	160°	165°	170°	180°
1	0.82	0.88	0.93	0.96	0.99	1.04
2	0.70	0.78	0.88	0.94	0.99	1.07
3	0.61	0.72	0.85	0.92	0.98	1.08
4	0.55	0.66	0.82	0.90	0.98	1.09
5	0.50	0.62	0.79	0.89	0.98	1.10
10	0.36	0.48	0.70	0.84	0.97	1.11
20	0.24	0.34	0.57	0.76	0.96	1.10

Experimental Section

The relaxation times of the axial and equatorial deuterons of 2,2,6,6-tetradeuterio-4-*tert*-butylcyclohexanone were determined in five solutions containing the paramagnetic shift reagent Pr(fod)$_3$ (Norell Chemical Co., Inc., Landisville, N.J.) to the extent of ρ = 0.04 to 0.08, ρ being the molar ratio of shift reagent to substrate molecule **1.** The samples were prepared by weighing the required amount of shift reagent and dissolving it in 2 ml of a 0.50 M solution of **1** in cyclohexane containing a trace of perdeuteriocyclohexane (internal reference). The relaxation measurements were performed using the Freeman-Hill modification[16] to the standard inversion recovery pulse sequence with a Bruker HX-90 spectrometer operating at a resonance frequency of 13.82 MHz. A total of 20 transients containing 4K data points were acquired for each spectrum with a spectral width of 400 Hz. Operating with a single-coil configuration, the 90° pulse width was 12 μs. The samples were confined to the RF coil in 10 mm cylindrical cells. The temperature of the sample probe was regulated at 30 °C. The spectrometer was locked on the proton resonance of cyclohexane. For each sample, two or three repetitions were made on different dates of at least five successive T_1 determinations.

Results and Discussion

Figure 1 shows the least-squares linear plots of relaxation rate of axial and equatorial deuterons vs. ρ. Each point on the plot corresponds to the average of 15 measurements performed at a given concentration of shift reagent. The range of ρ values was limited to 0.04-0.08 for the following reasons: below ρ = 0.04 resolution precluded simultaneous determination of T_1 and above ρ = 0.08 the standard deviation from linear correlation increased significantly. In the range of ρ studied there was an excellent linear correlation between the chemical shifts and ρ (correlation coefficient $\geq$ 0.998).

Savitsky et al. / 2,2,6,6-Tetradeuterio-4-tert-Butylcyclohexanone

The linear least-squares correlations of relaxation rates with ρ for the deuterons are:

$$1/T_{ax} = 27.57\rho + 1.546$$
$$1/T_{eq} = 15.50\rho + 1.686 \qquad (5)$$

with standard deviations of 0.158 and 0.101 s^{-1} respectively for axial and equatorial relaxation rates. The estimate of the ratios of T_1 values (T_{ax}/T_{eq}) in the uncomplexed and complexed compound can be estimated by setting $\rho = 0$ and $\rho = 1$, respectively. Using standard statistical procedures[17] for estimating uncertainties of the extrapolated values, the ratios (90% confidence interval) are:

$$\begin{aligned} T_{ax}/T_{eq} &= 1.09 \pm 0.08 \quad \text{(uncomplexed molecule)} \\ T_{ax}/T_{eq} &= 0.59 \pm 0.05 \quad \text{(complexed molecule)} \end{aligned} \qquad (6)$$

The experimental value of 1.09 for T_{ax}/T_{eq} of the uncomplexed molecule agrees with the theoretical value of 1.093.[18] Comparison of $T_{ax}/T_{eq} = 0.59$ for the complexed molecule with the above value of 1.09 shows that the inversion of T_{ax}/T_{eq} upon addition of shift reagent occurs as is predicted from theory for a bent C=O—M angle. A comparison of 0.59 with the theoretical values in Table I would suggest even a more bent C=O—M angle (~150°) than the value ~160° proposed by Schneider and Weigand.[2] However, because of the approximations involved, this should not be viewed as a serious discrepancy. As in the previously reported case,[1] the paramagnetic dipolar relaxation effects usually associated with shift reagents appear to be completely dominated by the quadrupolar relaxation mechanism as verified by separate experiments employing the diamagnetic La(fod)$_3$ reagent.

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(13) The program STRAIN (Cf. E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95,** 8005 (1973), and J. D. Andose and K. Mislow, *ibid.*, **96,** 2168 (1974)) was kindly provided by Professor Kurt Mislow. Results of the calculation which are particularly critical to the evaluation of T_{ax}/T_{eq} for the shift reagent complex of **1** are the bond distances and bond angles associated with the carbonyl group and its attached methylene groups. Bond distances (denoted by *r*) are r_{CO} = 1.224 Å, r_{CC} = 1.507 Å, r_{CH} = 1.098 Å; bond angles are ∠CCO = 122.8°, ∠CCH(axial) = 106.5°, ∠CCH(equatorial) = 108.4°; and dihedral angles are ∠HCCO(axial) = 115.2°, ∠HCCO(equatorial) = −1.0°

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Gaseous Ionic Acetylation of Some Substituted Anisoles. Evidence for an Intermediate π Complex

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Abstract: Rates of reaction of CH_3CO^+, $CH_3CO(COCH_3)CH_3^+$, and $CH_3COCO(COCH_3)CH_3^+$ with methyl- and halogen-substituted anisoles were measured. The rates are not always less than the ADO limit, but for the methylanisoles and the cresols reported previously an excellent linear relation between rates for different reagent ions holds for unsubstituted and para-substituted neutrals. For the more closely substituted neutrals, a different relation holds. The interpretation totally consistent with results requires a π complex with transfer to oxygen. The halogenated anisoles react with these ions too slowly to measure, behaving similarly to other halogenated aromatics; ions corresponding to the mass of the products expected from them were shown in some cases to be products of reactions of ions derived from the aromatic compound.

The nature of interactions in the collision complex between an ion and a molecule when both are moderately complex has not been greatly explored. When molecules approach the size of interest to the physical organic chemist, however, relationships not seen in reactions of very simple species have been observed. We wish to report a striking example detected in the last set of compounds from a large series which we have investigated over the past several years.

Others have noted that the rates of gas-phase reactions of aromatic compounds with the $(CH_3CO)_2\cdot^+$ ion may be correlated roughly with the Hammett σ function, the substituent of the aromatic compound influencing the rate in a way suggesting an electrophilic attack upon the ring.[1] The range of observed rates is rather small, about two, in comparison to the range of effects in solution, which may be many orders of magnitude larger. The absolute values of these rate constants were not reported, but the rate of attack of $(CH_3CO)_2\cdot^+$ on pyrrole was found to be 4.3×10^{-10} cm^3 molecule^{-1} s^{-1},[2] which is about 30% of the calculated[3] rate; many other rates of acetylation of aromatic compounds are no more than two orders of magnitude less than the calculated rate of collision.

Likewise, it was found that proton transfer from toluene to allyl anion in the gas phase, which has a rate constant of 7.5