VIII.Primer for Estimating T_1 Values Theoretically

[by cg fry: revised 28-Oct-98: the following is a problem given in Chem. 626, followed by the solution.]

A. Estimate from theory T_1 for the singlet aromatic ^1H of pamoic acid.

Assume relaxation is dominated by dipole-dipole interactions and the correlation time for pamoic acid, $t_c \approx 10^{-11}$ s. From pg. 193 of T. C. Farrar, Introduction to Pulse NMR Spectroscopy we can derive:

$$\frac{1}{T_1} \cong \frac{\left(\overset{t}{g}_H\right)^4}{r^6} t_c \times 1.11 \times 10^{10}\, s^{-1}$$

where $\overset{t}{g}_H = 2.67$, r has units of Å and τ_c is in sec.

B. Quickly measure T_1 of the ^1H's of interest for Pamoic acid.

1. Follow directions in section II (Rapid Determination of T_1, by Inversion Recovery Null Method, p. 44) of the T_1 chapter in the Bruker User's Guide.
2. Include with turned-in solutions null times and T_1 values for longest and fastest relaxing ^1H on pamoic acid. Give two reasons why the T_1 estimate made in part A might differ from the value you just measured [hint: think about assumptions made in part A, and how the sample has been prepared].

Solution:

Using the last equation on pg. 193 of T. C. Farrar, Introduction to Pulse NMR Spectroscopy (Farragut, 1989):

$$R_1 \equiv \frac{1}{T_1} = S(S+1)\frac{\left(\overset{t}{g}_I\,\overset{t}{g}_S\right)^2}{r_{IS}^6}\left[\frac{t_c}{1+w_-^2 t_c^2} + \frac{3t_c}{1+w^2 t_c^2} + \frac{6t_c}{1+w_+^2 t_c^2}\right] \times 1.1126 \times 10^9\, s^{-1}$$

where $w_- = w_I - w_S = 0$ and $w_+ = w_I + w_S = 2w_o$. Since $\omega_0 = 2.5 \times 10^8 \times 2\pi$ and $\tau_c = 10^{-11}$, we can see that $w_o t_c \approx 10^{-2} \ll 1$, so that

$$\frac{1}{T_1} \cong \frac{3}{4}\frac{\left(\overset{t}{g}_H\right)^4}{r^6} 10 t_c \times 1.1126 \times 10^9\, s^{-1}$$

On pg. 192, Farrar gives the *correct* units for this equation, where $\overset{t}{g}_H = 2.67$, so all we need is r in Å.

Use C-H = 1.1Å, and C-C(aromatic) = 1.4Å then elementary geometry gives:

H^4 to H^6 distance = 2×1.4×cos30° = 2.4Å

$$\frac{1}{T_1} \cong \frac{3}{4}\frac{(2.67)^4}{2.4^6} 10 \times 10^{-11} \times 1.1126 \times 10^9\, s^{-1} \qquad \boxed{\Rightarrow\ T_1 = 45s}$$

(Actually, I believe the 1.1126 constant is a mistake in Farrar's text, and should be 1.48... giving T_1 = 33 s, which I'll use now.)

Similarly, we could have calculated the protons, as

H^6 to H^7 distance = 1.4 + 2×1.1×sin30° = 2.5Å

$\Rightarrow \quad T_1 = 18\,s$ (add rates for both H^7 and H^4 $\Rightarrow$ $R_1 = \frac{1}{33} + \frac{1}{42} = 0.054\,s^{-1}$!!)

–CH_2– to H^7 distance = 2.4 - 1.1 + out-of-plane ~ 1.7 to 2.1Å

so for H^7 we have $R_1(H^7)$ = 1/42 + 1/8[for 1.9Å] $\boxed{\Rightarrow \quad T_1(H^7) = 6.8\,s}$

Finally, we have H-C-H = 2×sin(109.5°/2)×1.1Å = 1.80Å, so

for –C(H *toward* H^7)H– R_1(*toward*) = 1/8 + 1/5.8[for 1.8Å] $\boxed{\Rightarrow \quad T_1(toward) = 3.3\,s}$

and –C(H *away* H^7)H– R_1(*away*) = 1/5.8[for 1.8Å] $\boxed{\Rightarrow \quad T_1(away) = 5.8\,s}$

The primary reasons for differences in the estimated values and measured values are:

i) lack of careful degassing to remove oxygen, or other contamination in solution;

ii) incorrect estimate for the correlation time (in fact, measuring T_1 is one of the best methods for obtaining correlation times).