132. Motional Anisotropy of 1-Phenyladamantane

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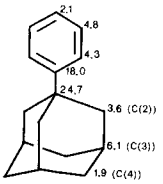
^{13}C-NMR longitudinal relaxation rates are analysed with the *Woessner* equations: in $CDCl_3$ solution at room temperature, 1-phenyladamantane has rotational diffusion coefficients $R_{\parallel} = 8.1 \times 10^{10}$ rad·s^{-1} and $R_{\perp} = 1.1 \times 10^{10}$ rad·s^{-1} corresponding to high motional anisotropy ($\sigma = 7.4$).

1. Introduction. – Whereas NMR chemical shifts continue to elude accurate theoretical treatments, relative NMR relaxation rates of symmetrical top molecules can often be predicted to high accuracy. Thus, they can be extremely useful in spectral assignment. Since we had an easy access to aryl-substituted adamantanes (see the accompanying paper [1]), we measured and analysed the ^{13}C-NMR longitudinal relaxation rates of 1-phenyl- and of 1,3-diphenyladamantane (**1** and **2**, resp.).

2. Experimental. – The samples, consisting of either 1-phenyladamantane (= 1-phenyltricyclo-[3.3.1.1^{3,7}]decane; **1**) or 1,3-diphenyladamantane (= 1,3-diphenyltricyclo[3.3.1.1^{3,7}]decane; **2**) in sat. $CDCl_3$ soln., were degassed and sealed in 5-mm (o.d.) tubes. The T_1 values are determined using a *Bruker AM 300* NMR spectrometer by the inversion-recovery technique at the operating temp. of 294 K. Each determination was based on a minimum of 12 data points, and the waiting time was 150 s [2]. The T_1 values (s) indicated below were provided by the standard program from the instrument manufacturer, with excellent fit to the inversion-recovery curves. These measurements suffer from a maximum uncertainty of ±10%, as a conservative estimate.



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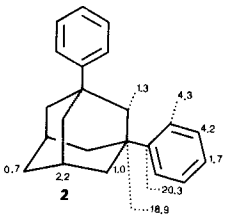

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3. Results and Discussion. – Both solutes **1** and **2** are sizeable enough that the ^{13}C-nuclei relax exclusively by the direct dipolar mechanism [3]. Longitudinal relaxation is thus governed only by ^{13}C–^{1}H interactions, modulated by the reorientational tumbling motions. Relaxation in the adamantyl skeleton comes from rotation of the molecule as a whole, aromatic C-atoms relax from combination of the overall reorientation with the (much faster) internal rotation of the phenyl ring.

The longest relaxation times are observed for the C-atoms not bearing protons. For proton-bearing C-atoms, relaxation is more efficient (shorter relaxation time) for CH_2 than for CH. To go further than these qualitative statements, one must consider the appropriate equations, which have been given long ago by *Woessner* [4]. It has been

pointed out that for 1-substituted adamantanes, the reorientation is diffusional in nature and that the inertial character is very small [5]. On the other hand, for monosubstituted benzene it is expected that the rotational diffusion model is not entirely valid [6]. The *Woessner* formalism [4] we used is adequate for diffusional motion. Therefore, we shall analyse only the data for the aliphatic C-atoms; additional assumptions and approximations would be required for the aromatic C-atoms.

For dipolar relaxation due to ^{13}C-^{1}H interactions in a rotating ellipsoidal molecule, in the extreme narrowing limit (the product $\omega^2\tau_c^2 = 3.2 \times 10^{-5}$ in the present case, is well below unity), the longitudinal relaxation rate is given by *Eqn. 1*:

$$\frac{1}{T_1} = \gamma_H^2 \gamma_C^2 \hbar r_{C-H}^{-6} R_\perp^{-1} \left(\frac{A}{6} + \frac{B}{5+\sigma} + \frac{C}{2+4\sigma} \right) \tag{1}$$

with $A = (1/4)\,(3(\cos\theta)^2 - 1)^2$, $B = 3(\cos\theta)^2(1 - (\cos\theta)^2)$, and $C = (3/4)\,((\cos\theta)^2 - 1)^2$.

θ is the angle formed by the C–H vector and the main axis of reorientation C_n, and σ is the motional anisotropy with $\sigma = R_\parallel/R_\perp$, $R_\parallel$ the reorientational diffusion coefficient about the main C_n axis and $R_\perp$ the reorientational diffusion coefficient about the two equivalent perpendicular axes.

Let us consider first case **1**: the only assumption made is that due to fast phenyl-group rotation the molecule belongs to the C_{3v} symmetry point group. We denote by p the relaxation rate of C-atoms whose C–H vectors make angles of 60 or 120° with the C_3 axis: C(2) and C(3) belong to this class. We denote by q the relaxation rate originating in a C–H vector parallel to the C_3 axis: C(4) bears one such bond. And r' is the part of the relaxation rate originating from non-nearest neighbor protons which, for simplicity and because of the r^{-6} dependence, we truncate to the second nearest neighbors only, of the type C–C–H. Thus:

$$\text{C(2)}: \; (3.6)^{-1} = 2p + r'$$

$$\text{C(3)}: \; (6.1)^{-1} = p + 4r'$$

$$\text{C(4)}: \; (1.9)^{-1} = p + q + 2r'$$

assumming additivity of the relaxation contributions (note that for C(3), two *non-nearest* C–H vectors are parallel to the C_3 axis and do not contribute to the relaxation).

This simple linear system of three equations gives $p = 0.135$, $q = 0.377$, and $r' = 7.2 \times 10^{-3}$. These values are easily checked: for C(1), the relaxation rate is $6r'$, which gives a calculated T_1 of 23.8 s, in excellent agreement with the observed value of 24.7 s. Due to the fast internal motion of the phenyl ring, the dipolar contribution from *ortho*-protons to the C(1) relaxation is expected to be negligeable.

The 'p case' corresponds to $\cos\theta = ½$, the 'q case' corresponds to $\cos\theta = 1$. The *Woessner Eqn. 1*, together with a C,H-bond lenght of 1.07 Å, gives: $R_\parallel = 8.1 \times 10^{10}$ rad·s^{-1}, $R_\perp = 1.1 \times 10^{10}$ rad·s^{-1}, and $\sigma = 7.4$.

The value of $R_\parallel$ is about the same as the diffusion coefficient for adamantane itself [7], which undergoes isotropic diffusional reorientation. The motional anisotropy $\sigma = 7.4$ is high, the bulky phenyl group constrains reorientation mostly around the C_3 axis. High motional anisotropies had been reported already for 1-substituted adamantanes, due to H-bonding between the substituent (COOH, OH, NH_2) and the solvent [5]. Here, 1-

phenyladamantane reorients predominantly around the three-fold axis of symmetry. Reorientation around each of the mutually perpendicular other two inertial axes is hindered by the need to push more solvent molecules out of the way.

Unfortunately, **2** cannot be analysed in like manner. The molecule is too symmetric, all C–H vectors make 60 or 120° angles with respect to the C_2 long axis, the problem is underdetermined. Only qualitative statements can be offered: obviously, **2** displays also a high degree of motional anisotropy, since, if reorientation was isotropic, the relaxation rates of C(2), C(4), and C(6) should be equal, but experimentally they differ almost by 100%!

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