Viscosity Effects on the Internal Motion of Alkane Chains

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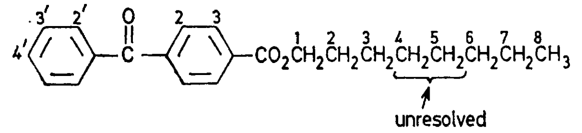
Summary ^{13}C Spin–lattice relaxation measurements on n-octyl 4-benzoylbenzoate demonstrate that the overall rate of molecular tumbling and the extent of segmental motion in the alkyl chain decrease with increasing viscosity.

^{13}C SPIN-LATTICE (T_1) relaxation measurements represent a powerful method for investigating dynamics of molecular motion in organic compounds.[1,2] Measurement of T_1 values have provided information about segmental motion in long chain alkanes.[3,4] However, more information can be obtained in cases where the alkyl group is attached to a heavy anchor,[5–7] particularly in cases where the anchor group contains carbon atoms whose T_1 values can provide a measure of the overall tumbling rate.[5]



(1)

The n-alkyl 4-benzoylbenzoates possess the chromophore as a heavy anchor. We have previously reported on the time-averaged conformation of the hydrocarbon chain in these molecules.[8] As an extension of that work to include information about the dynamics of motion, we have measured the spin–lattice relaxation times for n-octyl 4-benzoylbenzoate (**1**) in several solvents. The effective correlation times, τ_{eff}, show an interesting dependence on solution viscosity which can be interpreted in terms of varying sensitivities of specific group motions in the molecule to the viscosity of the medium.

TABLE. Effective correlation times, τ_{eff} (in picoseconds), for resolved proton-bearing carbons of n-octyl 4-benzoylbenzoate and estimated effective correlation times for overall tumbling (τ_{r}), methyl group spinning top rotation (τ_{ST}), and internal chain motion (τ_{int}).

Solvent	η_{B}[a]	$\tau_{\text{C}(2')}$[b]	$\tau_{\text{C}(3')}$	$\tau_{\text{C}(4')}$	$\tau_{\text{C}(2)}$	$\tau_{\text{C}(3)}$	τ_1	τ_2	τ_3	τ_6	τ_7	τ_8	τ_{r}[c]	τ_{ST}[d]	τ_{int}[e]
CD_3CN	4·29	17·5	18·5	20·9	22·8	24·6	16·4	15·6	12·4	5·49	4·49	2·68	22·7	6·6	5·6
$CDCl_3$	8·12	22·0	21·4	29·0	29·0	28·3	22·2	19·4	14·5	6·89	4·92	2·86	28·8	6·8	5·9
C_6D_{12}	10·68	24·4	22·9	38·8	33·1	36·4	28·0	21·6	16·7	7·56	6·14	3·13	36·1	6·4	7·4
CCl_4	12·81	35·3	27·8	49·0	42·7	43·1	34·6	26·4	17·0	8·16	6·73	3·23	44·9	6·2	7·9
CD_3CO_2D	14·10	37·0	35·1	52·8	54·0	54·7	36·2	30·6	19·5	8·87	7·25	3·28	53·8	6·0	8·4

[a] Bulk viscosity (in millipoise) of 0·5 M solution at 30 °C. Except for $CDCl_3$, measurements were made on the protic solvents. [b] Calculated from T_1 values using equation (1) and assuming $r_{\text{C–H}} = 1{\cdot}09$ Å. T_1 values were determined for 0·5 M solutions on a Varian CFT-20 spectrometer using the rapid inversion recovery pulse sequence (D. Canet, G. C. Levy, and I. R. Peat, *J. Magnetic Resonance*, 1975, **8**, 199). Typically, standard deviations in T_1 values were $<5\%$. [c] Average of $\tau_{\text{C}(4')}$, $\tau_{\text{C}(2)}$, and $\tau_{\text{C}(3)}$ (see text). [d] $\tau_{\text{ST}}^{-1} = \tau_8^{-1} - \tau_7^{-1}$. [e] $\tau_{\text{int}}^{-1} = \tau_7^{-1} - \tau_{\text{r}}^{-1}$.

Nuclear Overhauser effect measurements gave an enhancement factor of 3·0 ± 0·2 for all protonated carbon atoms, demonstrating the dominance of C–H dipole–dipole relaxation in the relaxation time, T_1. Therefore T_1 values can be used to determine an effective rotational correlation time for C–H bond reorientation[5] [equation (1)]. [Where N is the number of directly bonded hydrogen

$$\tau_{\text{eff}} = r_{\text{CH}}{}^6/N(h/2\pi)^2\gamma_{\text{C}}\gamma_{\text{H}}T_1 \qquad (1)$$

atoms ($\tau_{\text{eff}} = \tau_{\text{r}}$, the rotational correlation time, if the molecule tumbles isotropically)]. Values of τ_{eff} are summarized in the Table. The first important observation is that $\tau_{\text{C}(2)} \approx \tau_{\text{C}(3)} \approx \tau_{\text{C}(4')} > \tau_{\text{C}(2')} \approx \tau_{\text{C}(3')}$. The shorter correlation times for C(2′) and C(3′) indicate an additional mode of motion due to rotation of the unsubstituted phenyl group. This contributes to T_1 relaxation for C(2′) and C(3′) but not C(4′).[1] The nearly identical values for C(2), C(3), and C(4′) indicate an overall isotropic tumbling motion of the benzophenone segment (on which the phenyl rotation is superimposed). Therefore, the average of $\tau_{\text{C}(2)}$, $\tau_{\text{C}(3)}$, and $\tau_{\text{C}(4')}$ can be taken as the correlation time for isotropic tumbling τ_{r}. It is found that τ_{r} varies linearly with solution (or solvent) viscosity with the tumbling rate decreasing markedly with increasing solvent viscosity.†

The τ_{eff} values for the alkyl chain indicate increasing segmental motion with increasing distance from the alkyl chain. Lyerla *et al.* suggested that the difference in $\tau_{\text{eff}}{}^{-1}$ for a terminal Me group and the adjacent CH_2 group could provide τ_{eff} for methyl spinning top (ST) rotation, τ_{ST}.[3] They also used the difference of $\tau_{\text{eff}}{}^{-1}$ for the Me and internal CH_2 groups as a probe of segmental motion.[3] Our results allow an extension of this approach. The overall contributions to the motion of the methyl group can be factored into three parts: the overall tumbling motion of the molecule, the effect of rotation about internal C–C bonds, and the effects of the spinning top rotation of the methyl group. The first term is given by τ_{r}. The additional motion of the alkyl chain is given by[3] $\tau_{8,\text{r}}^{-1} = \tau_8^{-1} - \tau_{\text{r}}^{-1}$, where τ_8 is the effective correlation time for the methyl carbon. This can be further factored into $\tau_{8,\text{r}}^{-1} - \tau_{\text{ST}}^{-1} = \tau_{\text{int}}^{-1}$ where $\tau_{\text{ST}}^{-1} = \tau_8^{-1} - \tau_7^{-1}$. The term τ_{int} can be called the effective correlation time due to rotation about internal C–C bonds. τ_{ST} is essentially independent of viscosity (as observed previously[7]) and similar to values of τ_{ST} previously deduced for n-alkanes[3] and n-alkylammonium ions.[7] However, τ_{int} varies linearly and significantly with viscosity. This indicates a significant viscosity effect on internal motion of the chain. While contrary to previous conclusions from T_1 measurements,[7] this is intuitively reasonable since internal motion should require the molecule to sweep out a volume of solution (and should therefore depend on viscosity) while methyl rotation

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† A Stokes–Einstein plot of log τ_{r} *vs.* log η is linear with slope 1·1 for all but τ_{r} in acetonitrile. τ_{r} in this solvent shows a positive deviation. The origin of this deviation is under investigation.

does not involve swept volume. Investigations of diffusion-controlled radical recombination reactions in polymers have indicated that segmental motion of polymer chains is sensitive to viscosity.[9] Dielectric relaxation measurements on polymer solutions lead to similar conclusions.[10]

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