Analysis of the ^{13}C T_1 Relaxation Times in n-Alkanes

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Summary ^{13}C T_1 nuclear magnetic relaxation times have been measured for a series of n-alkanes and analysed in terms of rotational diffusion coefficients for the molecule as a whole and for motion about individual carbon–carbon bonds.

LONG-CHAIN alkanes have often been studied as simple models to help in the understanding of the dynamics of polymer molecules.[1] We report here the measurement and analysis of ^{13}C nuclear magnetic relaxation times, T_1, in some liquid n-alkanes. Unlike other techniques which allow only the determination of average motional properties, ^{13}C n.m.r. allows the study of individual carbon nuclei in the backbone of the molecule.

In molecules as flexible as the n-alkanes, many motions contribute to the observed spin–lattice relaxation times, and it is not possible to separate out these contributions intuitively, The work of Woessner[2] and of Wallach[3] has, however, been extended[4] to allow the calculation of dipolar spin–lattice relaxation times in molecules with many internal motions, where the molecule as a whole reorients isotropically. This approach has been applied[5] to the analysis of the ^{13}C relaxation times of phosphatidylcholines in aqueous dispersions,[6] where the phosphatidylcholine molecules form spherical, isotropically tumbling vesicles. We have now extended this approach in order to calculate dipolar relaxation times in anisotropically reorienting molecules with multiple internal motions.[7]

For the n-alkanes from C_6H_{14} to $C_{10}H_{22}$, all the carbon resonances can be resolved at 25·1 MHz. ^{13}C T_1 relaxation times were measured on degassed samples, using a Varian XL100/15 spectrometer and a Fourier transform technique, with a (π–t–$\pi/2$) pulse sequence as described by Freeman and Hill,[8] where t is the time in seconds between the π and $\pi/2$ pulses. The chemical shift assignments of Grant and Paul were used.[9] In molecules of this type, dipolar relaxation will be dominant for ^{13}C.[10] The T_1 values obtained are given in Table 1.

The results have been analysed in terms of the diffusion coefficients for rotation about the C–C bonds and for rotation of the molecule as a whole. The alkane molecule can be considered to behave hydrodynamically as an axially symmetric prolate ellipsoid, with $D_x = D_y < D_z$, where D_x, D_y, and D_z are the rotational diffusion coefficients about the x, y, and z axes, respectively. The ratio D_z/D_x has been set equal to the ratio of the moments of inertia about the x and y axes, obtained from the molecular geometry. This implies that the carbon skeletons are in the all-*trans* configuration.

^{13}C T_1 relaxation times have been calculated for a wide range of values of D_z (and thus D_x) and D_i, where D_i is the diffusion coefficient about the ith C–C bond. The simplest model which fits the data to within the experimental error is one in which the diffusion coefficients for motion about all the C–C bonds are equal, except for the terminal C–C bond, about which motion is faster. The values of the diffusion coefficients obtained are given in Table 2. Only a ±15% variation in these diffusion coefficients was possible if the T_1 values for all the carbons were to be fitted to within experimental error. Since the product $D_z\eta$ is essentially constant, the chain length dependence of D_z can be explained by the chain length dependence of viscosity.

Despite the fact that the values of D_i are considerably less than the corresponding values of D_z, an appreciable gradient of T_1 values along the chain is obtained. The pattern of T_1 values in hexane is particularly interesting in that the T_1 value for carbon 2 (counting from the terminal methyl group as carbon 1) is slightly but reproducibly shorter than that for carbon 3. This behaviour is attributed to the fact that $D_i < D_x$ for hexane. The transformation along the chain effectively attenuates the correlation function of the molecular motion, leading to an increase in the spectral density at high frequencies, and for carbon 2 this increase is greater than the accompanying decrease in spectral density due to the internal motions (since $D_i < D_x$) resulting in a net increase in the spectral density at high frequencies and thus to a reduction in T_1. The more usual situation, with $D_i > D_x$, as exemplified by octane and decane, gives rise to a monotonic decrease in spectral density at high frequencies for successive carbons, leading to the observed monotonic increase in T_1.

For longer chain alkanes, only the resonances of carbons

TABLE 1.

^{13}C relaxation times T_1 (s) for liquid n-alkanes at 31°.

n-Alkane	Carbon number[a]				
	1[b]	2	3	4	$[CH_2]_n$
Hexane	21·22 ± 0·69	14·78 ± 0·99	15·87 ± 0·92		
Octane	12·76 ± 0·14	10·94 ± 0·38	10·11 ± 0·30	9·58 ± 0·22	
Decane	8·74 ± 0·14	6·64 ± 0·11	5·71 ± 0·10	4·95 ± 0·07	4·36 ± 0·29
Hexadecane	6·52 ± 0·24	2·94 ± 0·08	2·40 ± 0·15	1·71 ± 0·04	1·25 ± 0·03

[a] Counting from the terminal methyl as carbon 1.
[b] Multiplied by 3/2 to facilitate comparison with the other values.

near the ends of the chains are resolved. The values of D_i then obtained are those that give a good fit for the T_1 data at the end of the chains, so that a slight gradient of D_i values along the chain cannot be excluded. The values of the diffusion coefficients for hexadecane are also given in Table 2. Comparison of these diffusion coefficients *Di* with those found[5] for the fatty acid chains in a dipalmitoylphosphatidylcholine bilayer shows that the rates of motion about bonds near the terminal methyl are very similar to those in the n-alkanes. Motions about C–C bonds near the glycerol groups of the lipids in the bilayer, however, are at least an order of magnitude lower than in the n-alkanes, This suggests that recent attempts to characterise the hydrocarbon region of the bilayer with a single 'microviscosity coefficient' may be inappropriate.[11,12]

TABLE 2.

Rotational diffusion coefficients calculated for n-alkanes.

n-Alkane	D_z $(10^{11}s^{-1})$	$D_z\eta$[a]	$D_x(=D_y)$ $(10^{11}s^{-1})$	D_i $(10^{11}s^{-1})$	D_w[b] $(10^{11}s^{-1})$
Hexane	2·6	0·7	0·35	0·20	0·9
Octane	1·4	0·7	0·113	0·17	0·3
Decane	1·0	0·75	0·064	0·115	0·3
Hexadecane	—	—	—	0·09	0·6

[a] η = viscosity. Values taken from the International Critical Tables. [b] Diffusion coefficient about the bond to the terminal methyl.

The results presented here show both the considerable potential of ^{13}C relaxation measurements for obtaining motional information about flexible molecules in solution, and the dangers inherent in using T_1 values directly as a guide to motional gradients within such molecules. A direct comparison of ^{13}C T_1 values between hexane and hexadecane might have suggested a much greater change in diffusion coefficients D_i and D_w than is in fact obtained by a complete analysis. Further, the pattern of T_1 values within the hexane molecule is very different to the gradient of motions within that molecule (Table 2). The details of the necessary calculations are given elsewhere;[4,7] though they are somewhat lengthy, they are straight forward enough to encourage the belief that they will find wider applicability in studies of molecular motion in solution.

The diffusion coefficients obtained as a result of the analysis are associated unambiguously with a particular motion of the molecule. Methods other than ^{13}C n.m.r. for measuring molecular motion in liquids give diffusion coefficients which cannot be identified with single motions (see, for example, ref. 13).

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