# $^{13}C$ Spin–Lattice Relaxation Studies of Perfluoroalkanes

**J. R. Lyerla, Jr.,[1] and David L. VanderHart***

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**Abstract:** To obtain information on the rigidity of perfluoroalkanes in the liquid state, $^{13}C$ spin-lattice relaxation times ($T_1$) and $^{13}C$-$^{19}F$ nuclear Overhauser enhancements (NOE) of individual carbon atoms in liquid $n$-$C_6F_{14}$, $n$-$C_7F_{16}$, and $n$-$C_8F_{18}$ have been measured at 39 °C. Analysis of the relaxation results indicates that the only internal motion occurring on the time scale of overall molecular reorientation is rotation of the $CF_3$ group. Comparison of these results with $n$-alkane relaxation data provides evidence for higher intramolecular rotational potential barriers in the perfluoroalkyl chain. In addition to the relaxation results chemical shifts and resonance assignments are reported for the three perfluoroalkanes as well as 1H-$n$-$C_7F_{15}$.

It is generally accepted that the polytetrafluoroethylene (PTFE) chain is less flexible and more extended than the polyethylene (PE) chain.[2,3] However, calculations of the configurational characteristics of isolated perfluoro-$n$-alkane chains indicate that the perfluoroalkyl chain is by no means rigid.[3] Unfortunately, the lack of solvents for PTFE near room temperature has severely limited experimental attempts to obtain indications of chain flexibility and experiments on the characteristics of the molecular motion in the appropriate model compounds, the perfluoro-$n$-alkanes, are lacking.

Recently, carbon-13 spin-lattice relaxation times ($T_1$) (in the temperature range 30–40 °C) were used to study[4,5] molecular motion in neat liquid $n$-alkanes thru $C_{20}H_{42}$. Analysis of the $T_1$ data yielded information on the overall and internal reorientational motion in these systems, thus providing qualitative information on the flexibility of an $n$-alkane chain. Presuming that results on perfluoro-$n$-alkanes can be used to provide insight into the physical properties of PTFE much in the manner of $n$-alkanes and PE, we have measured $^{13}C$ $T_1$ values for $C_nF_{2n+2}$ compounds in the liquid state in order to obtain a qualitative indication of the degree of chain motion in perfluoroalkyl chains. The results of a preliminary study on molecular mobility in $C_6F_{14}$, $C_7F_{16}$, and $C_8F_{18}$ as assessed by $^{13}C$ $T_1$ measurements are reported herein.

## Results

In Figure 1 is shown the fluorine-decoupled $^{13}C$ spectrum of perfluoroheptane. As in the corresponding $n$-alkane, each nonequivalent carbon gives rise to a $^{13}C$ resonance line. A similar result is found for $C_6F_{14}$ and $C_8F_{18}$. The chemical shift data and assignments for the three compounds are presented in Table I. (There is a paucity of data in the literature on $^{13}C$ chemical shifts in fluoroalkanes;[6] therefore, resonance assignments had to be made and the rationale for these assignments is given in the Experimental Section.) The constancy of the $^{13}C$ chemical shifts indicates that parameterization of the fluoroalkane chemical shifts using schemes analogous to those employed for $n$-alkanes[7,8] should be possible once a larger collection of data becomes available. Two notable differences in chemical shift behavior between the perfluoroalkanes and the $n$-alkanes are: (1) the apparent absence of a "$\gamma$ effect"[9] in the perfluoro compounds ($CF_2$ resonances appear at higher fields in an orderly way, the closer the $CF_2$ unit is to the $CF_3$ group), and (2) the observation that the $CF_3$ carbon is the least shielded carbon in the perfluoro-$n$-alkanes while the $CH_3$ carbon is the most shielded carbon in the $n$-alkanes.

In each of the three perfluoroalkanes $^{13}C$ spin-lattice relaxation times (Table II) were determined for the resolved carbon lines from inversion-recovery (180–$\tau$–90) Fourier transform spectra. Experiments were performed at 39 °C in order to facilitate comparison with $n$-alkane results. To complement the relaxation measurements, $^{13}C\{^{19}F\}$ nuclear Overhauser enhancements[10] (NOE) were determined from integrated line intensities of continuous-decoupled and gated-decoupled spectra. In all cases, a maximum NOE ($2.87 \pm 0.3$) was found indicating that the carbon relaxation in the perfluoroalkanes is dominated by the C–F heteronuclear dipolar mechanism and that rotational reorientation is such that the extreme narrowing condition is valid, i.e., $(\omega_C + \omega_F)^2\tau_r^2 \ll 1$, where $\tau_r$ is a reorientational correlation time and $\omega_C$ and $\omega_F$ are the respective Larmor frequencies. Under these conditions an effective rotational correlation time ($\tau_{eff}$) for the vector connecting the directly bonded C and F atoms is given by[4,11]

$$\tau_{eff} = r_{CF}^6/KT_1N_F \tag{1}$$

where $r_{CF}$ is the internuclear distance, $N_F$ is the number of attached fluorines, and $K$ is a constant equal to $3.15 \times 10^{-4}$ nm$^6$ s$^{-2}$. Isotropic reorientation is also assumed in eq 1. Values of $\tau_{eff}$ for the three perfluoro compounds are listed in Table II.

## Discussion

The link between molecular dynamics and measured $\tau_{eff}$ values is clearly established for the case of a spherical molecule, i.e., $\tau_{eff} = (6D)^{-1}$, where $D$ is the rotational diffusion coefficient of the sphere. However, for a polymer chain a distribution of correlation times ($\tau_i$) is required to describe the complex motion of a C–H or C–F vector[12] and the single $\tau_{eff}$ parameter must be viewed as a weighted average of these correlation times, i.e., $\tau_{eff} = \Sigma_i c_i \tau_i$, where the $c_i$ are orientation-dependent coefficients.[4] Rigorous interpretation of $\tau_{eff}$ requires a detailed model of chain motion. While such detailed models are unavailable, we will use the following simplied equation to interpret $\tau_{eff}$:

$$\tau_{eff}^{-1} = \tau_0^{-1} + \tau_i^{-1} \tag{2}$$

where $\tau_0^{-1}$ is the reorientation rate for the rigid molecule and $\tau_i^{-1}$ is the reorientation rate for internal motions. This equation was used successfully in the analysis of $\tau_{eff}$ data in a series of $n$-alkanes ranging from $C_7H_{16}$ to $C_{20}H_{42}$.[4] In this model, reorientation of a C–H vector is separated into contributions from internal motions within the alkyl chain and overall motion of the molecule (considered rigid). The internal motions originate from conformational changes

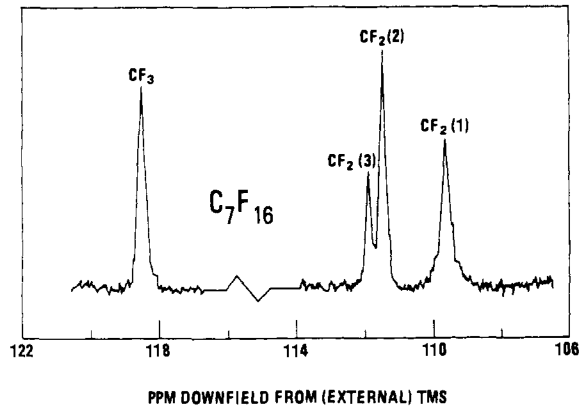

Figure 1. Fluorine-decoupled 15.08 MHz $^{13}C$ spectrum of perfluoro-*n*-heptane at 39 °C. The spectrum is the result of 16 scans at a recycle time ($t$) of 100 s using a (90–$\tau$) pulse sequence. Assignments of resonance lines are given above the individual peaks. Numbering of $CF_2$ resonance is explained in the Experimental Section.

**Table I.** $^{13}C$ Chemical Shifts[a,b] in Several Perfluoroalkanes at 39 °C

| Compd | Carbon in chain | | | |
|---|---|---|---|---|
| $C_nF_{2n+2}$ | 1, ($n$) | 2, ($n-1$) | 3, ($n-2$) | 4. ($n-3$) |
| $C_6F_{14}$ | 118.1 | 109.4 | 111.1 | |
| $C_7F_{16}$ | 118.1 | 109.4 | 111.1 | 111.7 |
| $C_8F_{18}$ | 118.1 | 109.4 | 111.2 | 111.8 |

[a] In ppm relative to external TMS, converted using $\delta_{TMS}$(external) = $\delta_{CS_2}$ + 193.7. [b] Estimated error ±0.1 ppm.

and internal rotations within a conformation. These motions are largely determined by intramolecular potential barriers that are independent, to a first approximation, of chain length. On the other hand, the overall molecular motion is a function of both molecular weight and viscosity and is subject to chain-length dependent, intermolecular barriers.

The following systematic trends in the *n*-alkane data[4] were noted: (1) $\tau_{eff}$ increased progressively for a carbon in a given chain position ($C_1$, $C_2$, etc.) as chain length increased, (consistent with a decrease in overall motion with molecular weight and viscosity); (2) $\tau_{eff}$ increased from chain ends toward the center for each alkane. As the chain length was increased, the fractional rate of increase in $\tau_{eff}$ was least at the chain ends (consistent with a greater degree of internal rotational freedom at chain ends). In fact, a detailed analysis of the $\tau_{eff}$ data also indicated that the internal reorientational modes were (within experimental error) independent of chain length.

It is the gradation in $CH_2$ carbon $\tau_{eff}$ values (trend 2 above) in a given *n*-alkane that provides direct evidence of the considerable flexibility of the *n*-alkane chain. Examination of the data in Table II reveals no such gradation in $\tau_{eff}$ values for the $CF_2$ carbons in the three perfluoroalkanes; within experimental error all $CF_2$ $\tau_{eff}$ values in a given perfluoro compound are equal. This result suggests there are no significant conformational changes in the perfluoro compounds which have lifetimes comparable to or less than the compounds' rotational lifetime. Consistent with this conclusion are the $T_1$ values calculated for $CF_2$ carbons in $C_6F_{14}$ and $C_7F_{16}$, assuming models of rigid molecules undergoing rotational diffusion.[14] For a rigid molecule undergoing isotropic reorientation, the Gierer–Wirtz[15] modification (the so-called "micro-viscosity" correction) to the Stokes–Einstein equation for calculation of rotational diffusion constants gives rotational diffusion constants,[16] $D$, for $C_6F_{14}$ and $C_7F_{16}$ of $3.2 \times 10^{10}$ and $2.1 \times 10^{10}$ s$^{-1}$. Calculation of $\tau_{eff}$ values from the relation $\tau_{eff} = \frac{1}{6}D$ and using these $D$ values along with eq 1 yields $T_1$ values of 19.6 and 12.8 s respectively for $CF_2$ carbons in $C_6F_{14}$ and $C_7F_{16}$, in excellent agreement with experimental $T_1$ values. If the compounds are treated as axially symmetric rigid ellipsoids (to account for shape anisotropy) undergoing rotational diffusion, the equations of Woessner[17] can be used to calculate $T_1$ for $CF_2$ carbons. Using the geometry from a $15_7$ helix (the presumed geometry for PTFE above 19 °C),[18] $T_1$ values of 19.4 and 12.3 s are computed for $C_6F_{14}$ and $C_7F_{16}$ difluoromethylene carbons, respectively, again in reasonable agreement with the data.

In the *n*-alkanes,[4] both internal and overall reorientation contributed to $\tau_{eff}$, even when $\tau_{eff}$ was as short as 2 psec. As shown above, the results for $CF_2$ carbons are consistent with C–F reorientation rates given by $1/\tau_{eff} = 1/\tau_0$. Since overall reorientation rates ($1/\tau_0$) are slower in a $C_nF_{2n+2}$ compound relative to its $C_nH_{2n+2}$ counterpart, it is clear that internal motion in the perfluoroalkyl chain is considerably slower than in the *n*-alkyl chain, i.e. intramolecular potential barriers are larger in $C_nF_{2n+2}$ compounds. While these $^{13}C$ relaxation results are experimental verification of the reduced flexibility of the perfluoroalkyl chain relative to the *n*-alkyl chain, semiquantitative estimates of the degree of internal reorientational motion obviously require $^{13}C$ $T_1$ studies of $C_nF_{2n+2}$ compounds with $n > 8$, i.e., compounds in which $1/\tau_0$ is sufficiently small that $1/\tau_i$ (see eq 2) would contribute significantly to the relaxation process.

In the case of a rigid molecule undergoing isotropic reorientation, the $CF_3$ carbon spin–lattice relaxation time should be ⅔ that of a $CF_2$ carbon. In the three compounds studied, the ratio of $CF_3/CF_2$ $T_1$'s is nearly constant at 0.75 ± 0.03 rather than 0.67. This discrepancy, which is outside of experimental error, could be accounted for if the C–F bond in a $CF_3$ moiety were 0.0025 nm longer than in a $CF_2$ moiety ($r_{C-F} = 0.136$ nm) so as to reduce the relative efficiency of each C–F dipolar interaction in the $CF_3$ group. However, available evidence[19] indicates the contrary may be true, i.e., the C–F bond in a $CF_3$ group may be 0.134 nm. (Values of $\tau_{eff}$ for the $CF_3$ carbon corresponding to both $r_{CF} = 0.134$ nm and $r_{CF} = 0.136$ nm are listed in Table II.) The $CF_3$ $T_1$ data might also be explained using the ellipsoidal model if the angle ($\theta$) which the one unique C–F vector of a rigid

**Table II.** $^{13}C$ Spin–Lattice Relaxation Times $T_1$[a] and Calculated $\tau_{eff}$ Values[b] for Three Perfluoroalkanes at 39 °C

| Compd | Carbon in chain | | | | |
|---|---|---|---|---|---|
| $C_nF_{2n+2}$ | 1, $n$<br>$T_1(\tau_{eff})$ | 2, ($n-1$)<br>$T_1(\tau_{eff})$ | 3, ($n-2$)<br>$T_1(\tau_{eff})$ | 4. ($n-3$)<br>$T_1(\tau_{eff})$ | $\tau_{eff}$[c] (av) |
| $C_6F_{14}$ | 14.3 (4.3,[d] 4.7[e]) | 18.6 (5.4) | 18.8 (5.3) | | 5.4[c] |
| $C_7F_{16}$ | 9.6 (6.4,[d] 7.0[e]) | 13.2 (7.6) | 13.3 (7.5) | 13.2 (7.6) | 7.6[c] |
| $C_8F_{18}$ | 6.9 (8.9,[d] 9.7[e]) | 9.3 (10.8) | 9.1 (11.0) | 9.3 (10.8) | 10.9[c] |

[a] In seconds; estimated error is ±7% of $T_1$. [b] In picoseconds. [c] Average $\tau_{eff}$ for the $CF_2$ carbons. [d] $\tau_{eff}$ calculated using $r_{CF} = 0.134$ nm. [e] $\tau_{eff}$ calculated using $r_{CF} = 0.136$ nm.

$CF_3$ group makes with the long axis of the ellipse was such that this C-F interaction was less efficient than the other two interactions. However, in the $15_7$ helical configuration, the unique C-F interaction ($\theta = 33°12'$) is ca. 1.2 times more efficient than each of the other interactions ($\theta = 86°48'$).

The only other explanation for the $CF_3$ $T_1$ data is that internal reorientation motion about the $CF_3$-$CF_2$ bond reduces the relaxation efficiency of the C-F interactions in the $CF_3$ moiety. In the *n*-alkanes,[4,5] $CH_3$ internal reorientation was found to be reflected in the $CH_3$ $\tau_{eff}$ data. An estimate of this reorientation rate was obtained[4] from the differences in $(\tau_{eff})^{-1}$ values for the methyl carbon and the first methylene unit of the alkane chain. The value of this rate was found to be independent of chain length and directly related to the barrier to methyl rotation ($V_3$ = 2.6-3.0 kcal).[20] A similar analysis of the perfluoroalkane $\tau_{eff}$ data indicates that the rate ascribed to $CF_3$ internal reorientation is about the same in $C_7F_{16}$ and $C_8F_{18}$ but about twice as large in $C_6F_{14}$ relative to the other two compounds. However, these differences in internal $CF_3$ reorientation rates are hardly significant, because the differences between $\tau_{eff}^{-1}$ ($CF_3$) and $\tau_{eff}^{-1}$($CF_2$) are only 10-20% and have a rather large uncertainty. (See Table II.) In addition, $\tau_{eff}$ depends on the choice of $r_{CF}$ for the $CF_3$ and $CF_2$ groups.

Potential barriers for $CF_3$ bond rotation have been claimed to lie in the 3.5-4.2 kcal range.[21] In assessing the importance of $CF_3$ internal reorientation in the perfluoroalkane data, it is necessary to determine whether motion subject to such a potential barrier would be expected to influence the $CF_3$ carbon relaxation rate. Woessner[22,23] has treated the effects of internal motion on nuclear relaxation rates of $CH_3$ groups attached to an isotropically reorienting body or an axially symmetric rigid ellipsoid. Two models of methyl internal motion have been examined by Woessner: reorientation by a stochastic diffusion process and a jump process (between three equivalent positions differing by 120°). As the $T_1$ values of the $CF_2$ carbons of $C_6F_{14}$ calculated from an isotropic reorientation model and an axially symmetric rigid ellipse were in good agreement with experimental results, the $T_1$ of the $CF_3$ carbon in this compound was calculated from Woessner's equations using the parameters deduced from $CF_2$ $T_1$'s and an internal rotation rate derived from the rate of reorientation of a $CF_3$ rotor subjected to a barrier of 3.5 kcal.[24] For the isotropic model, the $CF_3$ $T_1$ values calculated for the stochastic and jump internal processes are 13.9 and 13.7 s, respectively. These values are to be compared with a calculated value of 13.1 s for a rigid $CF_3$ group and a measured value of 14.3 s. For the ellipsoidal model, the $CF_3$ $T_1$ values for the stochastic and jump processes are 13.1 and 12.7 s, respectively, while that for a rigid $CF_3$ moiety is 12.5 s. The general trend of the computed $T_1$ values indicates that inclusion of $CF_3$ internal reorientation (subject to a 3.5-kcal barrier) about the $CF_3$-$CF_2$(1) bond can account for the observed $CF_3$ $T_1$ value in $C_6F_{14}$.[25] Indeed it seems to us that invoking internal $CF_3$ reorientation is the only way to resolve the differences between $CF_3$ and $CF_2$ $\tau_{eff}$'s. However, the results of the calculations should not be viewed as quantitative measure of the rate of $CF_3$ internal reorientation in reducing the efficiency of the C-F interactions in the $CF_3$ group of perfluoroalkanes, since the calculations are subject to considerable assumption and were carried out for the case of greatest influence of the internal motion (i.e., lowest barrier).[26]

## Conclusions

These experiments demonstrate that resonance lines corresponding to individual carbon sites can be resolved in the perfluoroalkanes and that $^{13}C$ spin-lattice relaxation times can provide information on the chain dynamics of C-F vectors along the perfluoroalkane chain. Internal motion in the $C_nF_{2n+2}$ chain is much reduced relative to its alkane counterpart, i.e., the $C_nF_{2n+2}$ chain appears rigid on the time scale for overall motion, except for evidence of $CF_3$ reorientation about the $CF_3$-$CF_2$ bond. More quantitative estimates of degree of backbone motion in the perfluoroalkane chain will require experiments on longer chain compounds at various temperatures.

## Experimental Section

The three perfluoroalkanes were obtained commercially and the $^{13}C$ NMR spectra of $C_6F_{14}$ and $C_7F_{16}$ samples gave no indication of impurities. The $C_8F_{18}$ sample contained possibly as high as 15% isomeric impurity. Samples were prepared by pipeting the compounds in 10-mm tubes, purging with dry nitrogen, and plugging (to prevent vortexing). Although the procedure of purging with dry nitrogen as opposed to vacuum degassing might be questioned on the basis of recent fluorocarbon $T_1$ measurements,[27] we believe that oxygen effects here are minimal in view of the full Overhauser effects measured. In all cases, the sample volume was restricted to 1.4 ml, ensuring that the entire sample would lie within the volume of the transmitter-receiver coil. Experiments were performed on a "home-built" pulse-Fourier transform spectrometer (described previously)[28,29] operating at 15.08 MHz. Sample temperature was maintained at 39 °C using a commercial temperature controller. The probe and noise decoupler were tuned to decouple $^{19}F$ at 56.4 MHz. All spectra were obtained with a spectral width of 1.5 kHz and 8K Fourier transformation (yielding a digital resolution of ~0.37 Hz).

Owing to the large separation in $^{19}F$ chemical shifts of $CF_3$ vs. $CF_2$ groups (ca. 2200 Hz in $C_7F_{16}$)[30] and the large magnitude of direct C-F couplings (ca. 260-290 Hz),[30] it proved impossible to obtain good fluorine decoupling over the entire range of perfluoroalkane $^{19}F$ resonances with the instrument's presently available noise-decoupling capability. This necessitated performing two experiments on each compound to obtain the entire $^{13}C$ spectrum. (The spectrum of $C_7F_{16}$ in Figure 1 is a composite of two such experiments.) In one experiment the noise-decoupler was centered at about the fluoromethyl resonance ($\delta_F$ = −81.6 ppm relative to $CF_3COOH$);[30] this gives rise to a singlet in the $^{13}C$ spectrum at ~118 ppm (downfield from external TMS). In the second experiment, the decoupler was centered at about the midpoint of the $CF_2$ $^{19}F$ resonances (range 122.2-126.9 ppm from $CF_3COOH$);[30] this gives rise to singlets in the carbon spectrum in the range 109-111 ppm. In both experiments a noise modulation frequency of 2.7 kHz was employed which proved effective in removing the nondirectly bonded couplings ($J_{CCF} \approx 30$ Hz).[31,32]

**A. Chemical Shift Assignments.** The required decoupling procedures outlined above readily enabled the $CF_3$ carbon to be assigned to the resonance at 118.1 ppm. If the $CF_2$ carbons are denoted, as $CF_2(i)$, $i$ = 1-3, where the index $i$ indicates the position of the $CF_2$ group from the end $CF_3$, then assignment of $CF_2$(3) to the resonance line at 111.7 ppm is consistent with the absence of a peak at this position in $C_6F_{14}$, the presence of a peak of unit intensity in $C_7F_{16}$, and the presence of a peak of double intensity in $C_8F_{18}$. Distinguishing the $CF_2$(1) from $CF_2$(2) resonances was aided by the $^{13}C$ chemical shifts of the compound 1-hydroperfluoroheptane (Figure 2). The spectrum of this compound is readily analyzed through the intensities of resonance lines and doublet splittings due to C-H couplings. The $HCF_2$ carbon is a doublet ($J_{CH}$ = 193.6 Hz) centered at 108.5 ppm, $CF_2$(1) is a doublet ($J_{CCH}$ = 6.9 Hz) centered at 110.9 ppm, $CF_2$(2) is coincident with $CF_2$(3) at 111.8 ppm with a nonresolvable splitting ($J_{CCCH}$ < 1.0 Hz), and the remaining three carbons (the nonsubstituted end) have chemical shift values the same as the corresponding carbons in $C_7F_{16}$. The only set of assignments of $CF_2$ resonances in $C_7F_{16}$ consistent with the $^{13}C$ chemical shifts and C-H couplings in 1-hydroperfluoroheptane is $CF_2$(1) at 109.4 ppm and $CF_2$(2) at 111.1 ppm. This set of assignments is also consistent with the result that the $^{13}C$ resonance at 109.4 ppm is a little broader (2-3 Hz) than that at 111.1 ppm (1.5-2.0 Hz) in all three perfluoroalkane spectra since this additional broadening presumably arises from some residual $J_{CCF}$ coupling of $CF_2$(1) to the $CF_3$ fluorines.

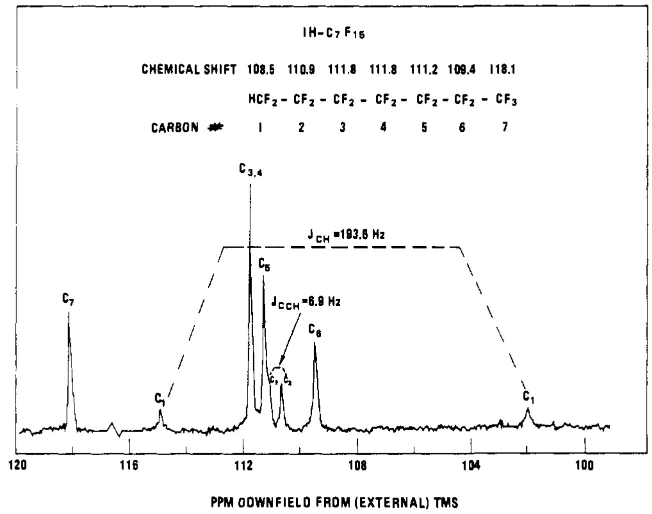

**Figure 2.** Fluorine-decoupled 15.08 MHz $^{13}C$ spectrum of 1-hydroperfluoro-*n*-heptane at 39 °C. The spectrum is the result of 64 scans at a recycle time ($t$) of 100 s using a ($90-\tau$) pulse sequence. Chemical shift values and assignments are listed above the skeletal diagram and resonance lines, respectively. Appropriate C-H couplings are also indicated.

**B. Spin-Lattice Relaxation Times.** Relaxation experiments were performed using standard $180-\tau-90$ pulse sequences with a ($5T_1 + \tau$) repetition rate. Free induction decays were accumulated for each value of $\tau$ in the relaxation experiment sequence (between 6 and 10 values of $\tau$ were employed). For each perfluoro compound, the $CF_3$ $T_1$ value and $CF_2$ $T_1$ values were determined in separate experiments owing to the problems associated with the fluorine noise decoupling discussed previously. $T_1$ values were calculated by least-squares analysis of integrated line intensities and were reproducible to ±7%. The fact that there was incomplete decoupling of long-range ($J_{CCF}$) fluorine interactions for $CF_2(1)$ or $CF_3$ (depending upon experiment) did not affect the $T_1$ or NOE measurements since there was sufficient decoupling power at these nonmeasured sites to collapse the multiplets into a broad line of half-width 30-40 Hz which certainly implies that all fluorines were saturated.

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