

^{13}C Nuclear Magnetic Relaxation Studies at 62 MHz

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An apparatus suitable to measure ^{13}C relaxation times T_1 and T_2 in liquids at 62 MHz is described. The required field of 58 kG is generated by a superconducting magnet. Results of T_1 measurements on a variety of liquids, including benzene, derivatives of benzene, saturated rings, CS_2 and others are reported. They are discussed in terms of dipole-dipole interactions, spin-rotation interactions and anisotropic chemical shifts, the latter of which turn out to play only a minor role. Intramolecular dipole-dipole interactions are found to provide by far the most important spin-lattice relaxation mechanism, whenever protons are bound directly to the carbons under investigation, even when the samples contain dissolved oxygen.

INTRODUCTION

In the last few years numerous studies on ^{13}C NMR spectra have been published. A wealth of chemical shifts and C-H and C-F coupling constants has been accumulated, but measurements of ^{13}C spin-lattice and spin-spin relaxation times are still very scarce in the literature. The only recent data we know of are from Jones (1) and Lippmaa *et al.* (2, 3).

Here we describe an apparatus suitable for the measurement of ^{13}C relaxation times and report first results. T_1 and T_2 measurements of ^{13}C add to our knowledge of the dynamic interactions of carbon nuclei with their surroundings. They are also important for purely spectroscopic investigations since T_1 and T_2 must be known for the best choice of the various spectrometer adjustments. This is true for conventional as well as for Fourier-transform techniques and the latest development, the DEPT method (4).

The main difficulty in ^{13}C relaxation measurements arises from the low sensitivity of ^{13}C as compared to ^1H . In order to take advantage of the gain in sensitivity of high fields most of our measurements have been done at the Larmor frequency of 62 MHz corresponding to a field of 58 kG, which was generated by a superconducting magnet. A time average computer was used for further enhancement of the signal-to-noise ratio.

A ^{13}C enriched toluene sample (60% enrichment, methyl carbon only) which contained 20% of the free radical DBNO in order to shorten its relaxation times was used to search for the resonance field and to adjust the spectrometer. So far we could not exploit the potential signal-to-noise enhancement by proton-noise decoupling. At a ^{13}C Larmor frequency of 62 MHz it requires a powerful rf irradiation at 248 MHz over a relatively big sample (7.5 mm diameter, 20 mm length).

One purpose of these measurements is to provide data of ^{13}C relaxation rates in pure and O_2 -loaded liquids and to study the contributions of various possible inter-

actions to ^{13}C relaxation rates. Another is the determination of ratios of ^{13}C to proton relaxation rates in various molecules. In order to study the influence of the anisotropic chemical shift on the ^{13}C relaxation rate data have been collected at 15 MHz and 62 MHz from a ^{13}C enriched toluene sample (60% enrichment, methyl carbon only). All other measurements have been performed at 62 MHz on samples with ^{13}C in natural abundance. This paper deals with T_1 results only. T_2 measurements have been performed also, but will be discussed on a later occasion.

EXPERIMENTAL

A Bruker pulse spectrometer BK-R-306-S with a frequency range of 12–62 MHz was used. A Siemens superconducting magnet (SUMA 75/50/280 H, maximum field 80 kG) provided the magnetic field of approximately 58 kG for the measurements at 62 MHz. Its homogeneity as deduced from the width of a spin echo signal is 5 ppm over a cylindrical sample of 0.75 cm diameter \times 1.5 cm. A special NMR probe was built for the geometry of the superconducting magnet (see Fig. 1).

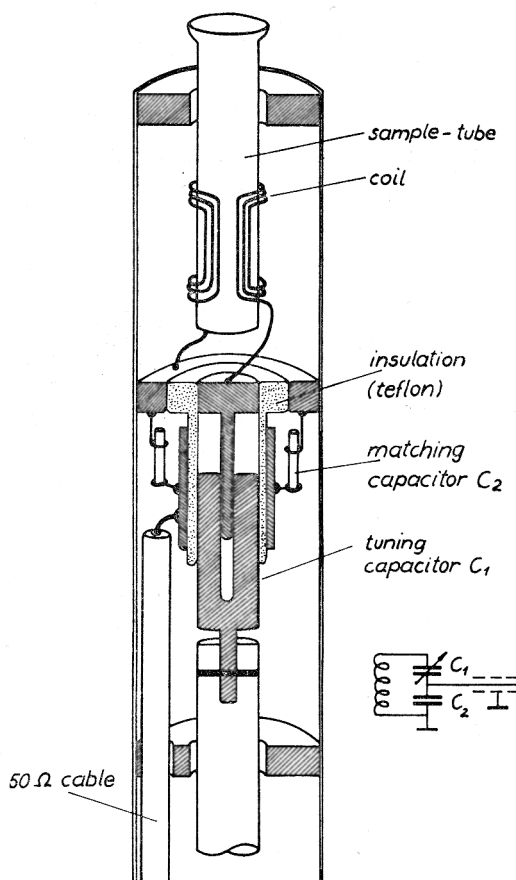


FIG. 1. 62 MHz NMR probe for the field geometry of superconducting solenoids. Outer diameter 30 mm, 8 mm sample tubes.

A single coil circuit was chosen in order to get the highest possible H_1 field with the rf pulse power available from the spectrometer and to allow the use of large samples. The bending of the turns (see Fig. 1) which is necessary to introduce the samples impairs the rf homogeneity to a negligible extent only. Impedance matching with the cable is obtained by capacitive voltage dividing. The rotating component of the rf field is about 30 G. It is about five times larger than the width of the spectra to be excited (≈ 100 ppm).

A signal-to-noise ratio of at least 15 could be obtained with a sample of cyclohexane when the receiver bandwidth was set to 1 kHz (see Fig. 2a). In many of the molecules studied, the chemical shift differences are considerably bigger than 1 kHz; therefore,

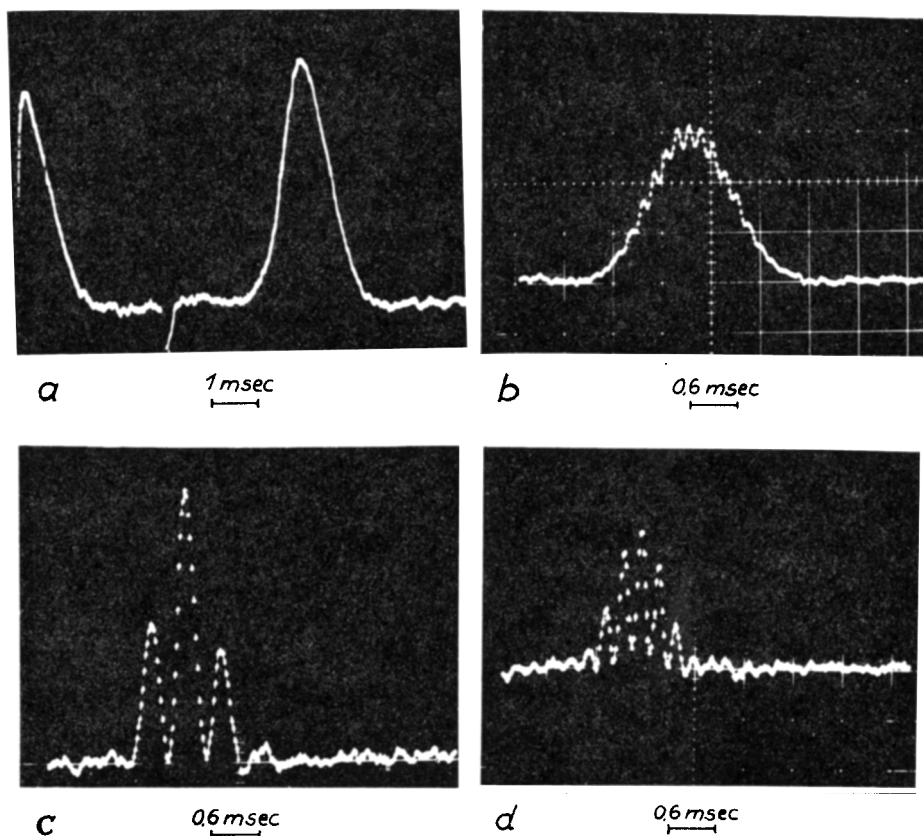


FIG. 2. ^{13}C NMR signals from samples with ^{13}C in natural abundance.

- (a) Free induction decay and spin echo of cyclohexane, single run, receiver bandwidth 1 kHz.
- (b) Echo of toluene. Small sample size (8.10^{-2} cm³), 2048 runs, bandwidth 10 kHz. The reference frequency of the lock-in was set at exact resonance of the ring ^{13}C . The chemically shifted signal from the methyl ^{13}C is out of resonance and accounts for the beat.
- (c) Echo of tetramethylpiperazine at resonance of methyl ^{13}C , 16 runs, bandwidth 10 kHz. Beat from signal of ring ^{13}C .
- (d) Echo of trimethyltrioxane at resonance of ring ^{13}C , 16 runs. Beat from signal of methyl ^{13}C .

most measurements have been performed with a receiver bandwidth of 3 or 10 kHz. For signal-to-noise enhancement a Fabritek model 1071 time averaging computer was used. Averaging over 16 or 32 runs proved to be sufficient in most cases (see Figs. 2b, c, d).

A $90^\circ\text{-}\tau_1\text{-}180^\circ\text{-}\tau\text{-}90^\circ\text{-}\tau_1\text{-}180^\circ\text{-}\dots$ pulse sequence was chosen for the T_1 measurements. This sequence is equivalent to the more familiar $90^\circ\text{-}\tau\text{-}90^\circ\text{-}\dots$ sequence. The job of the extra 180° pulses following the 90° pulses after a constant time interval $\tau_1 \ll T_2$ is to generate echoes the amplitudes of which can be measured with more ease and accuracy than the ordinary Bloch decay. The criterion for the adjustment of the 90° impulse was a zero spin-echo amplitude after a $90^\circ\text{-}\tau_1\text{-}180^\circ$ pulse pair which is applied shortly after the 90° impulse to be adjusted. This procedure ensures $M_z = 0$ after every 90° impulse. After phase sensitive detection the spin echo displays a beat structure whenever the molecules under study contain ^{13}C nuclei in inequivalent sites. The beat is due to the frequency differences of the various signal components from chemically shifted ^{13}C . Setting the reference frequency ν_{ref} of the phase sensitive detector exactly equal to the resonance frequency of one particular signal component μ makes the echo of this component a dc echo, as is the entire echo of cyclohexane shown in Fig. 2a. The echos in Figs. 2b, c and d clearly display a dc component.

By setting ν_{ref} equal to the various nuclear resonance frequencies and measuring the amplitude of the dc component of the spin echoes it is thus possible to measure the spin-lattice relaxation times of ^{13}C nuclei in different molecular sites separately. In an effort to get stable conditions all samples were sealed.

RESULTS

Table 1 shows the ^{13}C spin-lattice (T_1) relaxation times of various compounds. Benzene and toluene samples with dissolved free radicals (di-tert-butyl-nitroxide = DBNO, and bis-diphenyl-*p*-chlorophenyl-allyl = *p*-Cl-BPA) have also been studied. The relaxation times refer to the underlined carbons. The proton spin-lattice relaxation times listed in Table 1 for purposes of comparison have been measured at 62 MHz also. Identical samples have been used for ^{13}C and ^1H measurements. Whenever the molecules contain protons in different sites, the T_1 values given represent a weighted average for all protons¹ obtained from about the first decade of the usual plot of $\log(M_z(\infty) - M_z(\tau))$ versus τ . A systematic deviation from linearity was not obvious in these plots. All results in Table 1 have been obtained at $(13 \pm 2)^\circ\text{C}$.

In Fig. 3 the spin-lattice relaxation time T_1 of the methyl carbon of the ^{13}C enriched toluene sample, measured at 15 and 62 MHz, is plotted against the temperature.

DISCUSSION

Four mechanisms are known which can contribute to the spin-lattice relaxation rate of ^{13}C spins—the dipolar and scalar interactions of ^{13}C with the spins of other nuclei or electrons, the spin-rotation interaction, and the anisotropic chemical shift. By measuring the temperature and frequency dependence of T_1 one is able to decide, in principle, which mechanism or which combination of mechanisms is responsible

¹ Green and Powles (5) have measured separate T_1 's of ring and methyl protons in toluene and mesitylene using the fast adiabatic passage technique.

TABLE 1
 ^{13}C SPIN-LATTICE (T_1) RELAXATION TIMES OF VARIOUS LIQUIDS^a

		^{13}C T_1 (sec)	^1H T_1 (sec)
Benzene $\underline{\text{C}}_6\text{H}_6$	Pure	28	13.4
	with O_2	23	3.6
	with 20% DBNO	0.28	0.015
Toluene $\underline{\text{C}}_6\text{H}_5\text{CH}_3$	Pure	28	14
	with O_2	19	3.0
	with 20% DBNO	0.25	0.015
	with 10^{-2} mole/l BPA	11.5	
$\text{C}_6\text{H}_5\underline{\text{C}}\text{H}_3$	Pure	17	
	with O_2	12.5	
	with 20% DBNO	0.25	
	with 10^{-2} mole/l BPA	10	
Mesitylene $\text{C}_6\text{H}_3(\underline{\text{C}}\text{H}_3)_3$	Pure	12	5.4
	with O_2	10	2.3
$\underline{\text{C}}_6\text{H}_3(\text{CH}_3)_3$	Pure	15	
	with O_2	12	
2, 4, 6-Trimethyltrioxane ($\underline{\text{C}}\text{HCH}_3\text{O}$) ₃	Pure	2.6	1.9
	with O_2	2.2	1.3
$(\underline{\text{C}}\text{HCH}_3\text{O})_3$	Pure	4.0	
	with O_2	3.2	
2, 3, 5, 6-Tetramethylpiperazine ($(\underline{\text{C}}\text{HCH}_3)_2\text{NH}$) ₂	Pure	1.4	0.84
	with O_2	1.3	0.50
	Pure	1.4	
	with O_2	1.3	
Cyclohexane $\underline{\text{C}}_6\text{H}_{12}$	Pure	21	4.0
	with O_2	17	3.7
<i>n</i> -Pentane $\underline{\text{C}}_5\text{H}_{12}$	Pure	24	12
	with O_2	20	5.2
<i>n</i> -Hexane $\underline{\text{C}}_6\text{H}_{14}$	Pure	24	5.4
	with O_2	15.5	3.2
$\underline{\text{C}}\text{S}_2$	Pure	36 ± 1	—

^a The T_1 's refer to the underlined carbons. The last column shows proton T_1 's, averaged over all protons of the molecule. All data have been taken at $(13 \pm 2)^\circ\text{C}$, which is the equilibrium temperature in the bore of the superconducting solenoid. The statistical errors are estimated to be of the order of $\pm 5\%$.

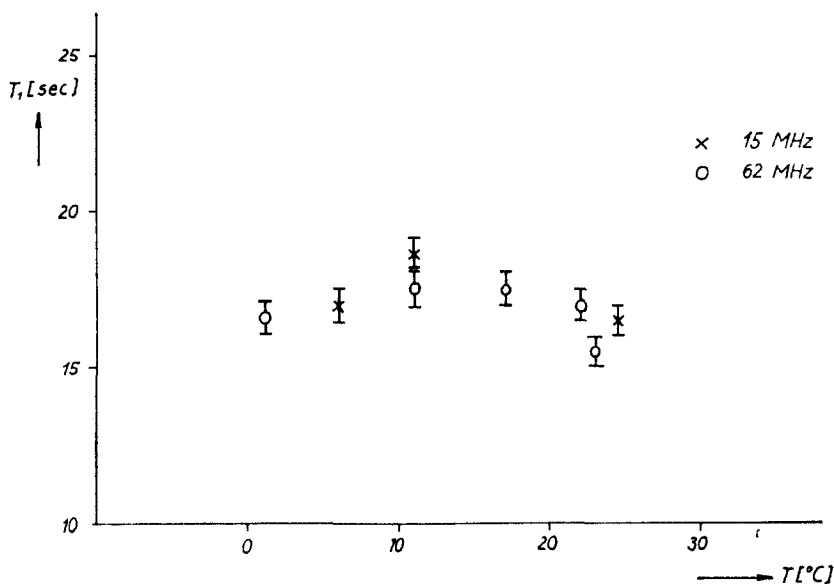


FIG. 3. Spin-lattice relaxation time of methyl ¹³C in toluene versus temperature at 15 and 62 MHz.

for the observed relaxation rates. Because of experimental difficulties we could vary the temperature and frequency only to a limited extent. However, with the data collected so far, a number of conclusions can be reached, especially by taking into account the proton-relaxation times measured also in this study.

Benzene

The contribution of the ¹³C-¹H dipole-dipole (DD) interactions to the ¹³C relaxation rate of benzene can be calculated in the following way. As usual inter- and intramolecular interactions are treated separately. We first turn to the intramolecular ones. Because of the r^{-6} dependence of the DD interactions it is sufficient to take into account only the proton which is directly bound to the ¹³C. All other protons together contribute only about 4% to the relaxation rate. ¹³C and ¹H form a two-spin system to which Eqs. [1] and [2] apply (6):

$$\frac{d\langle I_Z \rangle}{dt} = -\frac{1}{T_1^{II}} (\langle I_Z \rangle - I_0) - \frac{1}{T_1^{IS}} (\langle S_Z \rangle - S_0) \quad [1]$$

$$\frac{d\langle S_Z \rangle}{dt} = -\frac{1}{T_1^{SI}} (\langle I_Z \rangle - I_0) - \frac{1}{T_1^{SS}} (\langle S_Z \rangle - S_0). \quad [2]$$

S denotes protons, *I* carbons. Here $1/T_1^{SS}$ includes—by contrast to the notation of Abragam (6, p. 295)—not only the ¹³C-¹H intramolecular DD mechanism, but also all other mechanisms by which proton spins are relaxed. If we insert, tentatively, the measured proton and ¹³C relaxation rates for $1/T_1^{SS}$ and $1/T_1^{II}$, respectively, put $1/T_1^{SI} = 1/T_1^{IS} = 1/2T_1^{II}$ (extreme narrowing) and solve Eqs. [1] and [2] for the initial conditions of the experiment, then we find that $\langle I_Z(t) \rangle$ indeed relaxes exponentially with sufficient accuracy, and that the time constant is approximately T_1^{II} .

For extreme narrowing

$$\frac{1}{T_1^{II}} = \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \frac{4}{3} \tau_c \frac{1}{r_{CH}^6}. \quad [3]$$

τ_c is the correlation time of the molecular tumbling, and $r_{CH} = 1.085 \text{ \AA}$ (7) is the distance between the proton and the carbon. Green and Powles (5) succeeded in determining τ_c by measuring the proton-relaxation rate in mixtures of C_6H_6 and C_6D_6 . They obtained $\tau_c = 1.7 \times 10^{-12} \text{ sec}$ at $13^\circ C$. Inserting τ_c and r_{CH} in Eq. [3] yields $1/T_1^{II} = 1/27 \text{ sec}^{-1}$.

Turning now to the intermolecular DD interactions we assume that the protons of the neighbouring molecules approach the carbon and the proton spins of the reference molecule equally closely. This assumption probably leads to an overestimation of the intermolecular DD relaxation rate. It gives

$$\frac{1}{T_{1,C}} (\text{inter}) = (\gamma_C/\gamma_H)^2 \frac{2}{3} \frac{1}{T_{1,H}} (\text{inter}) \approx \frac{1}{600} \text{ sec}^{-1}. \quad [4]$$

The $2/3$ factor arises from the fact that one of the two relaxation rates which are related by Eq. [4] is due to heteronuclear interactions ($1/T_{1,C}$) whereas the other one stems from homonuclear interactions ($1/T_{1,H}$). According to (5) we have put $T_{1,H}(\text{inter}) = 25 \text{ sec}$. We conclude that the intermolecular DD relaxation rate contributes less than 5% to the total DD relaxation rate.

For $1/T_{1,C}$ we find experimentally $1/28 \text{ sec}^{-1}$. This result is in excellent agreement with the theoretical value. It means that the ^{13}C spins in benzene are predominantly relaxed by DD interactions with the directly bound protons. Other interactions do not seem to play an important role at $13^\circ C$ in the ^{13}C spin-lattice relaxation of benzene.

An estimation of the ^{13}C relaxation rate due to O_2 can be obtained with Eq. [5]:

$$\frac{1}{T_{1,C}} (O_2) \approx (\gamma_C/\gamma_H)^2 \cdot \frac{1}{T_{1,H}} (O_2). \quad [5]$$

Here we assumed again that the magnetic moment of O_2 approaches carbon nuclei as close as protons. Equation [5] differs from Eq. [4] by the factor $2/3$, because it relates two relaxation rates arising both from interactions between unlike spins. $1/T_{1,H}(O_2)$ is the relaxation rate of the protons due to O_2 . From the measured data we get $1/T_{1,H}(O_2) = 1/3.6\text{--}1/13.4 \approx 1/5 \text{ sec}^{-1}$ which, when inserted into Eq. [5], gives $1/T_{1,C}(O_2) = 1/80 \text{ sec}^{-1}$. Adding this rate to the rate measured in pure benzene gives $1/T_{1,C}(\text{with } O_2) = 1/21 \text{ sec}^{-1}$.

The measured rate is $1/23 \text{ sec}^{-1}$. We conclude that the comparatively low sensitivity of ^{13}C relaxation rates to O_2 —which is surprising at first sight—is mainly due to the fact that, because of the very small C–H internuclear distance intramolecular DD interactions are much stronger than intermolecular ones, even if the interaction partner is an electron spin. Benzene is no exception in this respect, as is manifest from Table 1.

Toluene

Ring protons and ring carbons behave, with respect to spin-lattice relaxation, equally in toluene and benzene, and therefore we restrict our discussion here to the methyl group.

Buchner and Emmerich (8) have shown that the three protons of the methyl group may be replaced, in as much as ¹³C relaxation is concerned, by a fictitious spin on the symmetry axis of the methyl group if the correlation time of the rotational motion of the methyl group (τ_M) is much shorter than the correlation time τ_c of the tumbling of the entire molecule and if $\omega_0\tau_c \ll 1$. For toluene at room temperature $\tau_c \approx 1.8 \times 10^{-12}$ sec (5) and, according to Burke and Chan (9), $\tau_M \approx 6 \times 10^{-14}$ sec. The latter value is, however, rather uncertain. The fictitious spin has the same magnetogyric ratio as protons, its spin quantum number S can be 1/2 or 3/2, and its distance from the ¹³C nucleus has to be chosen as $r_{CH} \cdot 3^{1/3}$.

Inserting τ_c and the parameters of the fictitious spin into Eq. [3] gives

$$\frac{1}{T_1^{II}}(\text{methyl}) = \frac{1}{190} S(S+1) \text{ sec}^{-1}. \quad [6]$$

The probabilities for the fictitious spin to be in the states $S = 1/2$ and $S = 3/2$ are equal, hence the average relaxation rate is

$$\left\langle \frac{1}{T_1^{II}}(\text{methyl}) \right\rangle_{\text{Av}} = \frac{1}{190} \cdot \frac{1}{2} \left(\frac{3}{4} + \frac{15}{4} \right) = \frac{1}{85} \text{ sec}^{-1}. \quad [7]$$

The standard method (6, 10) to calculate $1/T_1^{II}$ is to treat the interactions of the ¹³C nucleus with each of the three protons separately and simply to add the rates. The advantage is that τ_M need not be smaller than τ_c , but the disadvantage is that no distinction is made between the $S = 1/2$ and $S = 3/2$ states of the methyl group. This distinction is essential for the explanation of a new Overhauser multiplet effect discovered by Buchner and Emmerich.

A calculation along the same lines as in (10) gives, for extreme narrowing,

$$\frac{1}{T_1}(\text{methyl}) = \frac{1}{3} \gamma_C^2 \gamma_H^2 \hbar^2 r_{CH}^{-6} (\tau_c + 8\tau_{CM}), \quad [8]$$

where $\tau_{CM}^{-1} = \tau_c^{-1} + \tau_M^{-1}$.

For $\tau_M \ll \tau_c$, Eq. [8] leads to the same result as Eq. [7]. Inserting $\tau_M = 6 \times 10^{-14}$ sec (9) into Eq. [8] yields the revised value $1/67 \text{ sec}^{-1}$ for $1/T_1(\text{methyl})$. The intermolecular interactions can be assumed to be roughly the same as in benzene, hence we get for the dipolar relaxation rate $1/T_1(\text{DD}) = 1/60 \text{ sec}^{-1}$.

We have measured $1/17 \text{ sec}^{-1}$ for the total relaxation rate. Anisotropic chemical shifts can be excluded as an explanation for the discrepancy, because the difference of the relaxation rates at 15 and 62 MHz is at most $1/300 \text{ sec}^{-1}$ (see Fig. 3). The relaxation rate $1/T_1(\text{CS})$ due to an axially symmetric anisotropic chemical shift is given by Eq. [9] [see (6, Eq. VIII, p. 141)]:

$$\frac{1}{T_1}(\text{CS}) = \frac{2}{15} \omega_0^2 \left(\frac{3}{2} \delta_z \right)^2 \tau_c. \quad [9]$$

$3/2 \delta_z$ is the difference of the chemical shift parallel and perpendicular to the axis of the shift tensor. Inserting $\tau_c = 1.8 \times 10^{-12}$ sec and $1/T_1(\text{CS}) = 1/300 \text{ sec}^{-1}$ into Eq. [9] gives 200 ppm as an upper limit for δ_z . This value appears to be reasonable in view of the range of measured isotropic ¹³C chemical shifts. Figure 3 shows that in the range of 0 to 25°C the dependence on temperature of T_1 is hardly beyond the error limits of the experiment. Jones (1) found that T_1 of the methyl carbon of a number of

other substances decreases with rising temperature. This indicates that internal spin-rotation interactions also play a role and are responsible, at least in part, for the difference between the measured relaxation rate and the calculated DD rate. Measurements of the dynamic ^{13}C nuclear polarization (8) also lead to this conclusion.

Mesitylene

To discuss the spin relaxation of mesitylene we compare the ^{13}C and ^1H T_1 's of mesitylene with those of toluene and define for convenience of reference the following ratios (compare Table 1):

$$V_1 = \frac{T_{1,\text{C}}(\text{ring, tol.})}{T_{1,\text{C}}(\text{ring, mes.})} = 1.85; V_2 = \frac{T_{1,\text{C}}(\text{methyl, tol.})}{T_{1,\text{C}}(\text{methyl, mes.})} = 1.4; V_3 = \frac{T_{1,\text{H}}(\text{tol.})}{T_{1,\text{H}}(\text{mes.})} = 2.5.$$

The relaxation rates of the ring ^{13}C , to which protons are attached, characterize excellently the rotational motion of the molecules and its correlation time as we have seen in the discussion of toluene and benzene. Thus we conclude that the ratio of the correlation times τ_c^{M} and τ_c^{T} of mesitylene and toluene is equal to V_1 .

The Stokes-Einstein equation

$$\tau_c = \frac{4\pi\eta a^3}{3kT} \quad [10]$$

makes this understandable, at least qualitatively: mesitylene is somewhat bigger and more viscous than toluene.

V_2 is smaller than V_1 . This can be explained qualitatively by noting that the methyl ^{13}C is relaxed not only by intramolecular DD interactions but also by spin-rotation interaction. It is reasonable to assume that spin-rotation interactions are essentially the same in toluene and mesitylene, being largely independent of τ_c .

V_3 is the biggest of the three ratios. Two explanatory reasons can be put forth: First, $T_{1\text{H}}(\text{methyl})$ is smaller than $T_{1\text{H}}(\text{ring})$ in toluene as well as in mesitylene (5). The measured average proton-relaxation rate is shorter, since there are more methyl protons in mesitylene than in toluene. Second, the intermolecular DD interaction is the most efficient proton-relaxation mechanism for benzene and toluene. Because of the higher proton density it is even more effective in mesitylene.

2, 4, 6-Trimethyltrioxane (TMT), 2, 3, 5, 6-tetramethyl-piperazine (TMP)

The ^1H and ^{13}C relaxation rates of TMT and TMP are substantially bigger than those of the molecules discussed so far. The same is true for their viscosities, which are for TMT and TMP at 20°C 1.1×10^{-2} and 3.7×10^{-2} poise, respectively, as compared to 0.59×10^{-2} poise for toluene. Spin-relaxation rates and viscosities reflect their bigger correlation times.

n-Pentane, n-hexane, and cyclohexane

The ^{13}C relaxation rates of these molecules are very similar to each other and are mainly due to intramolecular DD interactions between the carbons and the directly bound protons. A detailed discussion, which is not attempted here, will have to take into account the flexibility and the internal motions of these molecules.

Carbon disulfide

McConnell and Holm (11) were the first to comment on T_1 of CS_2 . They suggested that the difference between the spin-lattice relaxation rates of CS_2 and CCl_4 is due to the fact that the ^{13}C chemical shift in CS_2 can be, and almost certainly is, anisotropic, whereas the ^{13}C shift in the symmetric CCl_4 molecule is necessarily isotropic.

New measurements of Jones (1) at 15 MHz, much more precise than those available to McConnell and Holm, gave $T_1(\text{CS}_2) = 44.5 \pm 1$ sec at 25°C and $T_1(\text{CCl}_4) = 170 \pm 10$ sec at 27°C . Lippmaa *et al.* (3) found similar values. We found at 62 MHz and 13°C $T_1(\text{CS}_2) = 36 \pm 1$ sec. These values clearly demonstrate that the different ^{13}C relaxation rates of CS_2 and CCl_4 can be due only to a small extent to the anisotropic chemical shift of CS_2 . A more careful study of the temperature and frequency dependence of T_1 on a ^{13}C enriched CS_2 sample is now under progress.

CONCLUDING REMARKS

It is well-known and has been stated repeatedly that ^{13}C spectroscopy often is superior to proton spectroscopy because the analysis of the ^{13}C spectra usually is simpler. Thus ^{13}C spectroscopy is at least a valuable complement to proton spectroscopy. The major difficulty is sensitivity. We would like to point out that these statements hold true also for ^{13}C and proton *relaxation* studies: Sensitivity is also a problem, of course, but ^{13}C data are likely to be interpreted more easily, because often there is no need to divide measured relaxation rates into intra- and intermolecular contributions, a need which renders the analysis of proton-relaxation times often so hard a task. This tends to be the case when protons are covalently bound to the carbons in question. Then, due to the short C-H distance, the intramolecular interactions usually override all intermolecular ones.

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