

# Carbon-13 Spin-Lattice Relaxation in Benzene and Substituted Aromatic Compounds<sup>1</sup>

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**Abstract:** Measurements of <sup>13</sup>C spin-lattice relaxation times ( $T_1$ ) and nuclear Overhauser effects at 25 MHz are reported for a number of aromatic compounds and are discussed in terms of four relaxation mechanisms: dipole-dipole (DD), chemical shift anisotropy (CSA), spin rotation (SR), and scalar (SC). Examples are given of compounds with carbons dominantly relaxed by all of these mechanisms. Protonated ring carbons are largely relaxed by the DD mechanism; nonprotonated ring carbons are relaxed by both the DD and SR mechanisms, with the exception of <sup>79</sup>Br-bonded carbons, which can relax entirely by the SC mechanism. For bromine-bonded carbons, the relaxation is nonexponential since the  $T_1$ 's are different for the two bromine isotopes. The CSA mechanism is negligible in these compounds but is the dominant relaxation mechanism for the central acetylenic carbons in diphenyldiacetylene, as shown by experiments at 25 and 63 MHz. The large contributions of DD and SR relaxation and nearly insignificant CSA contribution for the nonprotonated carbon of toluene were approximately determined from 25- and 63-MHz experiments. Dipole-dipole relaxation of protonated aromatic ring carbons in substituted benzenes is strongly affected by ring substitution. Large or polar substituents reduce molecular tumbling, lengthening the molecular correlation time,  $\tau_c$ , thereby shortening observed  $T_1$ 's. Anisotropic motion has an easily observable effect on the DD contribution to  $T_1$  and can form the basis for spectral assignments, as in 3-bromobiphenyl. With phenol and aniline, strong solvent effects owing to molecular association or protonation are found and affect not only the absolute values of  $T_1$ , but also the ratios of  $T_{1\text{om}}/T_{1\text{p}}$ .

Carbon-13 spin-lattice relaxation measurements obtained from specialized pulsed Fourier transform nmr experiments have indicated great promise in structural and dynamic studies of organic molecules.<sup>2</sup> Spin-lattice relaxation times ( $T_1$ ) are affected by immediate and remote molecular structural features, as well as by consideration of rapid ( $>10^8$ – $10^{10}$  sec<sup>-1</sup>) dynamic processes occurring in the specific system studied. In particular,  $T_1$  studies can yield useful information about rapid molecular motions on a time scale that is far shorter than is available with conventional nmr techniques.

The process of spin-lattice relaxation is an energy exchange between nuclear spins and the "lattice," tending toward establishment of an equilibrium state of the populations of the nuclear spin energy levels.<sup>3</sup> For nuclei of spin  $1/2$ , this energy exchange results from the perception by these spins of fluctuating localized magnetic fields. There are four sources of these fluctuating fields, corresponding to four spin-lattice relaxation mechanisms: dipole-dipole interactions, spin-rotation, scalar interaction, and chemical shift anisotropy. In many organic compounds, <sup>13</sup>C–<sup>1</sup>H dipole-dipole (DD) interactions dominate carbon  $T_1$  processes.<sup>4</sup> Of the

remaining three mechanisms, only spin-rotation is commonly encountered, and then only in small molecules or with freely spinning groups in larger molecules.

This paper presents  $T_1$  and associated nuclear Overhauser effect (NOE) data on various types of substituted aromatic compounds. Analysis of these data gives insight into the four <sup>13</sup>C  $T_1$  processes and also further demonstrates the utility of  $T_1$  measurements for determinations of molecular motion arising from symmetry, stereochemical, and chemical bonding considerations.

## Experimental Section

**<sup>13</sup>C Nmr Spectra.** <sup>13</sup>C nmr spectra were recorded on a Varian Associates XL-100-15 spectrometer equipped for pulsed Fourier transform (FT) operation at 25.16 MHz and on a 63.1-MHz superconducting solenoid nmr spectrometer.<sup>5</sup> Chemical shifts when reported<sup>6</sup> were determined relative to the internal standard TMS. The system computer on the Varian XL-100 spectrometer (Varian 620-i, 16K core) allowed acquisition of 8K data points, thus yielding 4K (4096) output data points in the transformed, phase corrected real spectrum ( $\sim 1.3$  Hz per data point in a 5000-Hz spectrum). For experiments performed at 63.1 MHz, data acquisition (8K data points) and Fourier transform were carried out by a Data General Nova computer. <sup>13</sup>C spectra were generally obtained with complete <sup>1</sup>H decoupling.

**Spin-Lattice Relaxation Measurements.** Spin-lattice relaxation times ( $T_1$ ) for all carbons were determined simultaneously by the inversion-recovery pulse method, modified by Freeman and Hill (Varian Associates)<sup>7a</sup> for the measurements made at 25 MHz. The pulse sequence utilized in these measurements was ( $T$ –90°– $T$ –180°– $t$ –90°)<sub>z</sub>, where  $t$  is experimentally varied and  $T$  is set greater than three to four times the longest  $T_1$  to be measured.

In the Freeman-Hill modified program, the log of ( $S_\infty - S_t$ ) is

(5) F. A. L. Anet, V. J. Basus, C. H. Bradley, and A. K. Cheng, Abstracts, 12th Experimental Nmr Conference, Gainesville, Fla., 1971.

(6) Many substituted benzene <sup>13</sup>C chemical shifts were reported in G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Amer. Chem. Soc.*, **94**, 3089 (1972).

(7) (a) R. Freeman and H. D. W. Hill, "Molecular Spectroscopy 1971," Institute of Petroleum, London, 1971, p 105; also ref 2a; (b) R. Freeman, H. D. W. Hill, and R. Kaptein, *J. Magn. Resonance*, **7**, 327 (1972).

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(1) Preliminary reports (a) G. C. Levy, *Chem. Commun.*, **47** (1972); (b) G. C. Levy, D. M. White, and F. A. L. Anet, *J. Magn. Resonance*, **6**, 453 (1972); (c) G. C. Levy, *Chem. Commun.*, 352 (1972); (d) G. C. Levy, *J. Magn. Resonance*, **8**, 122 (1972).

(2) (a) R. Freeman and H. D. W. Hill, *J. Chem. Phys.*, **54**, 3367 (1971); (b) A. Allerhand, D. Doddrell, and K. Komoroski, *ibid.*, **55**, 189 (1971); (c) other references cited in G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, N. Y., 1972.

(3) Spin-lattice relaxation ( $T_1$ ) must be distinguished from spin-spin relaxation ( $T_2$ ) which does not require energy transfer ( $T_2$  defines the natural spectral line width in the absence of field inhomogeneities).  $T_2$  processes will not be discussed further in this paper.

(4) The <sup>13</sup>C–<sup>1</sup>H dipole-dipole relaxation contributions can be directly evaluated from <sup>13</sup>C{<sup>1</sup>H} NOE measurements: K. F. Kuhlmann and D. M. Grant, *J. Chem. Phys.*, **52**, 3439 (1970).

plotted against  $t$ , where  $S_\infty$  and  $S_t$  are the transformed signals from the  $90^\circ_\infty$  and  $90^\circ_t$  pulses, thus yielding only positive peaks in the spectral display.  $T_1$  is the time,  $t$ , at which  $(S_\infty - S_t)$  reaches 0.368 ( $\equiv 1/e$ ) of  $(S_\infty - S_t)$  for  $t = 0$  ( $\equiv 2S_\infty$ ). Because the effective  $^{13}\text{C}$  rf field of the XL-100-15 is under 2 kHz ( $90^\circ$  pulse  $\cong 130$   $\mu\text{sec}$ ), spin-lattice relaxation experiments were restricted to spectral widths  $<1500$  Hz. When larger widths were required, separate experiments were run on each spectral region. For each determination six to ten sets of measurements were taken. Reproducibility of  $T_1$  values was considerably better than  $\pm 10\%$  in most cases. Accuracy limitations depend in each instance on solute concentration and the length of data acquisition. In the higher accuracy studies (stated probable error limits  $<10\%$ ) very high signal:noise ratios were achieved ( $>100$ ). Repetitive experiments on separate, equivalent samples yielded  $T_1$  values within one-third to one-half the stated maximum probable error limits. Systematic errors due to sample size (liquid column height) were found to be insignificant in experiments obtained on the crossed coil Varian spectrometer.  $T_1$  values for the four carbons of toluene were measured at three liquid column heights. The results are shown in Table I. If dif-

Table I.  $T_1$  as a Function of Sample Geometry. Toluene

Sample column height <sup>b</sup>	$T_1$ , sec <sup>a</sup>			
	C-1	C-2	C-3	C-4
2	87	24	24	17.5
3.5	84	23	23	17.5
5	83	26	27	18.5

<sup>a</sup> 90% toluene; 10% cyclohexane- $d_{12}$ ;  $\text{N}_2$  degassed.  $T_1$  measured at 25.2 MHz and  $38^\circ$ . <sup>b</sup> In cm. Liquid column measured from the beginning of 12-mm o.d. dimension (excludes the rounded bottom of the nmr tube) up to the meniscus.

fusion effects were significant, the observed  $T_1$  for the nonprotonated carbon C-1 (86 sec) could be expected to change appreciably at 5 cm liquid sample depth. Within experimental error ( $\sim 5\%$ ) no change in  $T_1$  for C-1 was noted.

The  $T_1$  measurements at 63.1 MHz were carried out with a single coil system. A  $90^\circ$  pulse was obtained in 40  $\mu\text{sec}$ . The conventional  $180^\circ$ - $t$ - $90^\circ$  pulse sequence was used with an appropriate waiting time between sequences. Care was taken to have a constant spinning speed in order to prevent any mixing of the sample which was inside the receiver coil region with that outside the coil. A rapid stream of nitrogen gas was passed around the sample tube (10 mm) to prevent the formation of temperature gradients along the length of the tube. Even so, the proton decoupling power (ca. 5 W in  $T_1$  measurements) was probably sufficient to set up small thermal convection currents. These mixing effects will give rise to spuriously short  $T_1$ 's, especially for liquids of low viscosity and  $T_1$ 's longer than 25 sec. For shorter  $T_1$ 's or more viscous liquids, the errors are less than the random measurement errors and can be neglected.

**NOE Measurements.** The absolute nuclear Overhauser enhancement determined at 25.2 MHz was recorded by dividing individual integrated peak intensities in  $^1\text{H}$  decoupled cmr spectra by the total integrated band intensities in the coupled cmr spectra. In cases of band overlap in the coupled spectra appropriate integration assignments were made. In all cases, the pulse interval was longer than 5 ( $T_1$ ) for the slowest relaxing carbon being measured. This ensured complete relaxation of all nuclei between pulses. In some cases experiments were repeated three to four times. Reproducibility of both decoupled and coupled peak integrations was generally  $\pm 5\%$  and always better than  $\pm 15\%$ . The accuracy obtained in these NOE measurements was largely due to the very high signal:noise ratios obtained with concentrated solutions of low molecular weight symmetrical molecules.

Some of the NOE determinations were made after gating the decoupler, to allow interrupted (pulse modulated)  $^1\text{H}$  decoupling. Using the technique<sup>7b</sup> of decoupling just before the short  $^{13}\text{C}$  pulses and during short ( $<1$  sec) acquisitions of the free-induction decays while leaving the decoupler off for the long ( $\geq 4T_1$ ) pulse intervals allowed direct measurements of NOE's from  $^1\text{H}$  decoupled spectra where the  $T_1$ 's are greater than 5 sec.

**Materials.** Compounds were generally reagent grade and were used without further purification. Samples were not degassed unless noted. When degassing was required,  $\text{N}_2$  was bubbled

through the solution for 0.5–1 min or the sample was vacuum degassed (freeze–pump–thaw cycles).

## Results and Discussion

The spin-lattice relaxation (and NOE) data for benzene are given in Table II.

Table II.  $T_1$  and NOE Data for Benzene<sup>a</sup>

	$T_1$ , sec	NOE ( $\eta$ ) <sup>c</sup>
Undegassed	23	1.30
Degassed <sup>b</sup>	29.3	1.60

<sup>a</sup> Solvent, benzene- $d_6$ . Determined at  $38^\circ$  and 25.2 MHz.

<sup>b</sup> Vacuum degassed (freeze–thaw cycles). <sup>c</sup> Average of two to three measurements on each of several samples; probable accuracy  $\pm 0.05$  (deviations from reported values  $<0.05\eta$ ).

The experimentally observed NOE's indicate that  $^{13}\text{C}$ - $^1\text{H}$  dipole–dipole interactions dominate ring carbon relaxation with appreciable contributions from other mechanisms.<sup>8</sup> Arguments similar to those given below for toluene suggest that the remaining relaxation ( $\sim 20\%$  contribution) in degassed benzene is spin-rotation (SR) relaxation. This is consistent with the variable-temperature  $T_1$  study of Olivson and Lippmaa on benzene and benzene- $d_6$ .<sup>9</sup> In undegassed benzene, dissolved  $\text{O}_2$  results in a contribution of ca. 25% to relaxation of the benzene carbons, corresponding to a  $^{13}\text{C}$ - $\text{O}_2$  (DD) relaxation rate,  $R_1 \equiv 1/T_1$ , of ca. 100 sec. Jaeckle, Haeberlen, and Schweitzer<sup>10</sup> estimated a similar relaxation contribution from  $\text{O}_2$  at 63 MHz for toluene and benzene.

**Toluene.** Spin-lattice relaxation times and NOE's for several toluene samples are given in Table III. Several things can be learned from comparisons of the data from different samples, and from single sample measurements at different temperatures and magnetic fields.  $T_1$ 's for the C–H ring carbons of toluene are comparable with, but somewhat shorter than, the C–H carbon  $T_1$ 's in benzene because the increased molecular size and solution viscosity give rise to slower molecular tumbling.<sup>11</sup> The short  $T_1$  observed for C-1 in undegassed samples of toluene results from an  $\text{O}_2$  relaxation contribution comparable with that calculated for benzene. The NOE's observed for C–H ring carbons in toluene indicate that  $^{13}\text{C}$ - $^1\text{H}$  dipole–dipole interactions do not completely dominate the relaxation behavior.

Two independent lines of argument show that the chemical shift anisotropy (CSA) contribution to relaxation must be very small, even for C-1. For reasons mentioned in the Experimental Section, the  $T_1$  value of 65 sec found for C-1 at 63 MHz may have a small contribution from thermal convection effects, and therefore should be considered a minimum value. By making use of the dependence of  $T_1^{\text{CSA}}$  on the square of

(8) T. D. Alger and D. M. Grant, *J. Phys. Chem.*, **75**, 2538 (1971), concluded that  $^{13}\text{C}$ - $^1\text{H}$  dipole–dipole relaxation was more nearly complete. It was not noted whether their sample was degassed. For this reason our measurements were repeated several times to minimize experimental errors (Table II).

(9) A. Olivson and E. Lippmaa, *Chem. Phys. Lett.*, **11**, 241 (1971).

(10) J. Jaeckle, U. Haeberlen, and D. Schweitzer, *J. Magn. Resonance*, **4**, 198 (1971).

(11) It is important to understand the connection between molecular motion and spin-lattice relaxation.<sup>20</sup> For all of the molecules discussed in this paper, and under the conditions employed (*i.e.*, mobile solution), faster effective motion (rotation) results in less efficient relaxation interaction between dipoles. Therefore,  $T_1$  values for nuclei undergoing increased motion get longer.

Table III.  $T_1$  and NOE Data for Toluene

Sample	Freq, MHz	Temp, °C	$T_1$ , sec <sup>a</sup>					NOE ( $\eta$ ) <sup>a</sup>				
			C-1	C-2	C-3	C-4	CH <sub>3</sub>	C-1	C-2	C-3	C-4	CH <sub>3</sub>
Neat (undegassed)	25.2	38	58	20	21	15	16.3	0.43	1.32	1.32	1.70	0.61
85% in acetone- <i>d</i> <sub>6</sub>	25.2	38	89	23.6	24.5	17.3		0.56	1.63	1.73	1.63	
	25.2	10	84	17.2	17.2	14.2		0.67	1.63	1.61	1.74	
	63.1	38	65 <sup>b</sup>	24	24	18						
90% in cyclohexane- <i>d</i> <sub>12</sub>	25.2	38	84	23	23	17.5		0.4	1.4	1.4	1.3	
20% in toluene- <i>d</i> <sub>8</sub> <sup>c</sup>	25.2	38	85	24	23	18						
9% in toluene- <i>d</i> <sub>8</sub> <sup>c</sup>	25.2	38	85									

<sup>a</sup> Probable errors in  $T_1$  5–10%; NOE's  $\pm$  0.1. Samples degassed unless noted. <sup>b</sup> See Discussion for possible errors. <sup>c</sup> Toluene-toluene *d*<sub>8</sub> with 10% (v/v) cyclohexane-*d*<sub>12</sub>.

the spectrometer frequency,<sup>12</sup> the data in Table III allow a calculation of  $T_1^{\text{CSA}}$  for C-1 of 180 sec at 63 MHz. However, the value calculated is highly dependent on the difference between two large numbers; thus if the measured  $T_1$  were actually 75 instead of 65 sec, then  $T_1^{\text{CSA}}$  would be  $\approx$  360 sec. It is clear that  $T_1^{\text{CSA}}$  has a minimum value of about 200 sec at 63 MHz and therefore a minimum value of 1200 sec at 25 MHz.

An estimate of  $T_1^{\text{CSA}}$  can be obtained by a different procedure as follows. With the assumption of isotropic motion, and making use of  $T_1$ 's and  $\eta$ 's for ring carbons in toluene, we can calculate a correlation time ( $\tau_c$ ) for random molecular tumbling of about  $1.5 \times 10^{-12}$  sec from the expression in eq 1. The <sup>13</sup>C chem-

$$\tau_c = \eta r_{\text{C-H}}^6 / 2\gamma_{\text{C}}^2 \gamma_{\text{H}}^2 \hbar^2 T_1 \quad (1)$$

ical shift anisotropy in solid benzene, which is about 180 ppm,<sup>13</sup> can be taken as an approximate value for toluene. Treating the system as an axially symmetric one, for simplicity, we can calculate  $T_1^{\text{CSA}}$  from the following equation.<sup>12</sup>

$$1/T_1^{\text{CSA}} = (2/15)\gamma^2 H_0^2 (\sigma_{\parallel} - \sigma_{\perp})^2 \tau_c \quad (2)$$

With  $\sigma_{\parallel} - \sigma_{\perp} = 180 \times 10^{-6}$ , a  $T_1^{\text{CSA}}$  of 1000 sec at 63 MHz is obtained. Increasing the anisotropy to 250 ppm reduces  $T_1^{\text{CSA}}$  to 500 sec. At 25 MHz the values of  $T_1^{\text{CSA}}$  will be 6.25 times longer than at 63 MHz. These considerations strongly suggest that  $T_1^{\text{CSA}}$  at 25 MHz for toluene must be about 3000 sec or longer, and is thus negligible even for the nonprotonated C-1 carbon.<sup>14</sup>

The remaining relaxation for the toluene ring carbons is almost certainly caused by the spin-rotation mechanism. A  $T_1^{\text{SR}}$  of 140 sec fits both the protonated and unprotonated ring carbons, as shown in Table IV. The components of  $T_1^{\text{obsd}}$  obey the relationship,  $1/T_1^{\text{obsd}} = 1/T_1^{\text{DD}} + 1/T_1^{\text{CSA}} + 1/T_1^{\text{SR}}$ .

(12) T. C. Farrar and E. D. Becker, "Pulse and Fourier Transform NMR," Academic Press, New York, N. Y., 1971, Chapter 4.

(13) A. Pines, M. G. Gibby, and J. S. Waugh, Abstracts, 13th Experimental NMR Conference, Asilomar, Calif., 1972.

(14) A  $T_1^{\text{CSA}}$  at 25 MHz of the order of 160 sec has been reported for the ring carbons in isodurene and hemimellitene: T. D. Alger, D. M. Grant, and R. K. Harris, *J. Phys. Chem.*, **76**, 281 (1972). These compounds have  $T_1^{\text{DD}}$ 's for the protonated ring carbons about three times shorter than those of toluene, so that  $1/\tau_c$  and therefore  $T_1^{\text{CSA}}$  should also be three times shorter; i.e.,  $T_1^{\text{CSA}}$  should be  $>1000$  sec instead of 160 sec. In fact, a  $T_1^{\text{CSA}}$  of 160 sec for these compounds corresponds to a CSA of about 700 ppm, which certainly seems to be too large by at least a factor of 2. The estimate given for  $T_1^{\text{CSA}}$ , it should be noted, was obtained by a comparison of data at 15 and 25 MHz. The calculation involves differences between large numbers which themselves have relatively large errors, and thus the result may have very large errors. Unpublished variable temperature and variable field studies by workers at the Max Planck Institute, Heidelberg, show very long  $T_1^{\text{CSA}}$  at room temperature for toluene ring carbons: D. Schweitzer, personal communication; see also section of the present paper on diphenyldiacetylene.

Table IV. Dissection of  $T_1$  (in sec) at 25 MHz for Toluene at 38°

Carbon	$T_1^{\text{obsd}}$	$T_1^{\text{DD}}$	$T_1^{\text{CSA}}$	$T_1^{\text{SR}}$
C-1	89	270 <sup>a</sup>	$>3000$	140
(C-2, C-3, C-4) <sub>av</sub>	22	27 <sup>a</sup>	$>3000$	140

<sup>a</sup> Calculated from  $2T_1^{\text{obsd}}/\eta$ .

Spin-rotation relaxation for the CH<sub>3</sub> carbon in toluene has been indicated from theoretical works<sup>15</sup> and inferred from experimental studies on polymethylbenzenes.<sup>14,16</sup> The NOE observed for the CH<sub>3</sub> carbon in toluene (Table III) can be used to calculate  $T_1^{\text{DD}}$  ( $\approx$  80 sec).  $T_1$  and NOE measurements on the CH<sub>3</sub> carbon at +70° (14 sec and  $\eta = 0.4$ , respectively, compare with the 38° data in Table III) confirm that the spin-rotation interaction dominates CH<sub>3</sub> carbon relaxation.

It is generally thought that *intermolecular* <sup>13</sup>C-<sup>1</sup>H dipole-dipole interactions do not contribute significantly to <sup>13</sup>C relaxation in most organic molecules. In order to test this belief, dilute samples of toluene in toluene-*d*<sub>8</sub> were studied (Table III). Deuterium nuclei are far less effective than protons for DD relaxation; thus dilution of toluene in perdeuteriotoluene would eliminate intermolecular dipole-dipole relaxation if it were significant for neat toluene. The observed  $T_1$ 's for C-1 at 20 and 9% concentrations in toluene-*d*<sub>8</sub> are experimentally indistinguishable from the data for toluene itself. Intermolecular DD relaxation even for the nonprotonated C-1 carbon in toluene is thus experimentally insignificant,  $T_1^{\text{DD-inter}} \lesssim 1500$  sec! For the protonated (C-H) carbons intermolecular contributions would be vanishingly small.

**Substituted Benzenes.**  $T_1$ 's and NOE's for toluene and nine other mono- and disubstituted benzenes are summarized in Table V. In the monosubstituted benzenes all C-H  $T_1$ 's are shorter than the  $T_1$  observed for benzene reflecting longer molecular correlation times ( $\tau_c$ ) due to (a) larger size, (b) greater solution viscosity, (c) electrostatic solute-ordering effects, and (d) solute aggregation. The three low molecular weight, nonpolar hydrocarbons (X = CH<sub>3</sub>, CH=CH<sub>2</sub>, C≡CH) have relatively long  $T_1$ 's. The polar nitro substituent results in increased electrostatic ordering of solute molecules, lengthening  $\tau_c$ , and shortening  $T_1$ 's. Groups such as OH and NH<sub>2</sub> that can form strong hydrogen bonds with solvent or other solute molecules further slow molecular tumbling.  $T_1$ 's for aggregated low molecular weight molecules are often shorter than  $T_1$ 's for noninteracting large molecules.

(15) C. F. Schmidt, Jr., and S. I. Chan, *J. Magn. Resonance*, **5**, 151 (1971).

(16) K. F. Kuhlmann and D. M. Grant, *J. Chem. Phys.*, **55**, 2998 (1971).

Table V. Relaxation Behavior for Substituted Benzenes

Substituent	$T_1$ , sec <sup>a</sup>						NOE, $\eta^b$					
	C-1	C-2	C-3	C-4	$\alpha$	$\beta$	C-1	C-2	C-3	C-4	$\alpha$	$\beta$
CH <sub>3</sub> <sup>c</sup>	58	20	21	15	16.3		0.43	1.32	1.32	1.70	0.61	
<i>t</i> -Bu <sup>c</sup>		10.3	10.3	5.8								
CH=CH <sub>2</sub> <sup>c,d</sup>	75	14.8	14.8	11.9	17.0	7.8	1.1	2.0	2.0	2.0	2.0	2.0
C≡CH <sup>e</sup>	56	13.2	13.2	9.0	53	8.5	0.46	1.89	1.92 <sup>h</sup>	1.92 <sup>h</sup>	0.51	1.95
C≡CH (degassed) <sup>f</sup>	107	14.0	14.0	8.2	132	9.3	0.8	2.0	1.9	1.9	0.90	2.0
Ph <sup>d,f</sup>	61	5.9	5.9	3.2			0.9	2.0	2.0	2.0		
NO <sub>2</sub> <sup>c</sup>	56	6.9	6.9	4.8			0.8	2.0	1.9	1.9		
OH <sup>c</sup>	18.4	2.8	2.8	1.9								
NH <sub>2</sub> <sup>c</sup>		5.4	5.3	4.4								
2-NO <sub>2</sub> -1-CO <sub>2</sub> H	C-1	C-2	C-3	C-4	C-5	C-6						
			3.0	1.9	2.8	2.9						
3-NO <sub>2</sub> -1-CO <sub>2</sub> H		1.5		0.95	1.5	1.35						

<sup>a</sup> Samples not degassed unless noted.  $T_1$ 's  $\pm$  5–10%. <sup>b</sup> Absolute NOE unless noted, estimated maximum error  $\pm$ 0.15. <sup>c</sup> Neat. <sup>d</sup> Not absolute NOE: relative NOE; based on the assumption that for each protonated carbon,  $\sim$ 2.0. <sup>e</sup> C<sub>6</sub>D<sub>6</sub> solvent. <sup>f</sup> CD<sub>3</sub>COCD<sub>3</sub> solvent. <sup>g</sup> CCl<sub>4</sub> solvent, 6:1 mol ratio CCl<sub>4</sub>:PhOH. <sup>h</sup> Two carbons determined together.

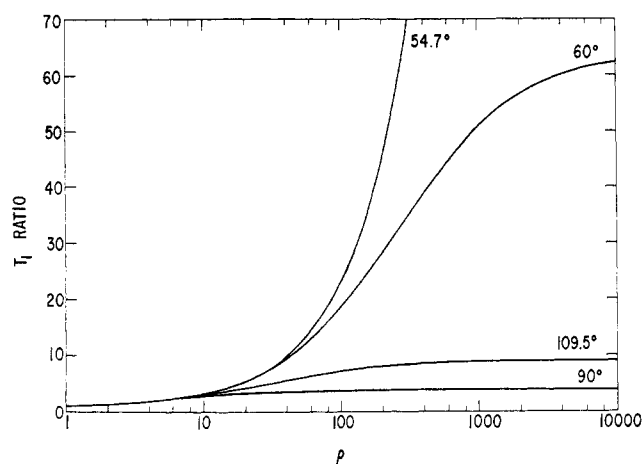


Figure 1. Calculated  $T_1$  ratios as a function of the tumbling or spinning ratio ( $\rho$ ) for four geometries ( $\theta = 54.7$  (magic angle),  $60^\circ$ ,  $90^\circ$ , and  $109.5^\circ$ ).

**Anisotropic Motion.** The overall tumbling of small molecules is often anisotropic<sup>17</sup> resulting in nonsystematic variation of protonated carbon  $T_1$  values. In molecular systems where the motional behavior is qualitatively predictable, <sup>13</sup>C  $T_1$  measurements can yield quantitative data on internal motions as well as overall molecular tumbling characteristics. From Tables III and V it can be seen that  $T_1$  for the para carbon in a monosubstituted benzene is always shorter than  $T_1$  for the meta or ortho carbons of the same phenyl ring. In monosubstituted benzenes rotation around the  $C_2$  molecular symmetry axis coincident with the C–X bond is preferred. This results from two effects: (a) the moment of inertia around the C–X bond axis is lower (inertial effect) and (b) fewer solvent molecules are disturbed by rotation around the C–X axis (frictional effect). The size, polarity, bonding ability, and symmetry of the ring substituent determine the degree of anisotropy of motion. Anisotropic motion results in different  $T_1$  values for ring C–H carbons aligned and not aligned with preferred rotational axes. Rotation around the  $C_2$  symmetry axis does not lead to any modulation in the direct dipole–dipole interaction of the para <sup>13</sup>C and its directly attached proton, and therefore

(17) (a) W. T. Huntress, Jr., *J. Chem. Phys.*, **48**, 3524 (1968); (b) D. E. Woessner, *ibid.*, **36**, 1 (1962); **42**, 1855 (1965).

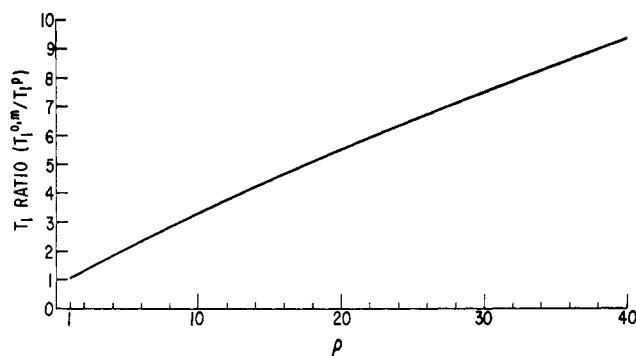


Figure 2. Calculated  $T_1$  ratios (expanded scale),  $\rho = 1$  to 40 for benzene ring geometry ( $\theta = 60^\circ$ ).

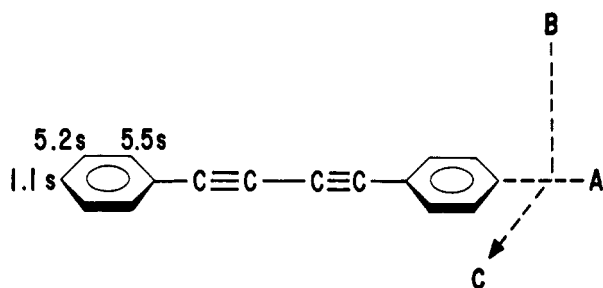
does not contribute to relaxation of that carbon. However, such a rotation does lead to relaxation for the ortho and meta carbons because the C–H bonds in these instances make angles ( $\theta$ ) of  $60^\circ$  and  $120^\circ$  with the  $C_2$  axis. In the limit of very much faster rotation about the long axis than about the shorter axes of these molecules,  $T_1$  for the ortho and meta carbons should be increased by a factor of  $[1/2(3 \cos^2 \theta - 1)]^{-2}$  (i.e., 64 for  $\theta = 60^\circ, 120^\circ$ ), over  $T_1$  for the para carbon.<sup>2b</sup> Below the limit of anisotropic motion, calculations can predict motional anisotropy from observed  $T_1$  values.<sup>2b</sup> Figure 1 gives the tumbling ratios vs. observed  $T_1$  ratios for four cases:  $\theta = 54.7^\circ$  (the magic angle),  $60^\circ$  (substituted benzenes),  $90^\circ$  (substituted ferrocenes<sup>18</sup>), and  $109.5^\circ$  (methyl groups). Figure 2 shows an expanded view useful for estimating tumbling ratios from  $T_1^{0,m}/T_1^p$  ratios in monosubstituted benzenes. As the tumbling ratio,  $\rho$ , approaches infinity,  $T_1^{0,m}/T_1^p$  approaches 64. The calculations used to construct Figures 1 and 2 were derived for axially symmetric molecules<sup>19</sup> and thus apply only approximately for descriptions of moderate anisotropic motion in monosubstituted benzenes.

In the rod-shaped molecule diphenyldiacetylene (DPDA) motional anisotropy is sufficient to result in  $T_1$  for the para carbons five times shorter than  $T_1$  for the ortho and meta carbons.<sup>1b</sup> This corresponds to rota-

(18) G. C. Levy, *Tetrahedron Lett.*, 3709 (1972).

(19) The system is treated as being axially symmetrical, which should be a good approximation. In any case, since all the nuclei in one benzene ring are in one plane, it is not possible to solve the problem in a more rigorous fashion.

tion about the long molecular axis (A) being  $\sim 17$  times faster than rotation about the short axes B or C (from Figure 2).



DPDA (25% in acetone- $d_6$ ,  $T_1$ 's in sec)

For the monosubstituted benzenes in Table V, anisotropic motion is not as marked. Nevertheless, expected trends hold (effects of substituent size, polarity, etc.). In styrene ( $X = \text{CH}=\text{CH}_2$ ), the substituent is not axially symmetric and the tumbling motions of styrene are nearly isotropic. The para carbon  $T_1$  is only slightly shorter than the  $T_1$  for the ortho and meta carbons. Also, the vinyl CH and  $\text{CH}_2$   $T_1$  values are approximately in the expected 2:1 ratio.<sup>2b,c</sup>

Polysubstituted benzenes can act as if they have a preferred rotational axis for each substituent. In meta unsymmetrically disubstituted benzenes, for example, the effective rotational rates around the different axes depend on the relative size, etc., of the two substituents. (However, small substituents involved in strong solute-solvent or solute-solute hydrogen bonding interactions behave like large substituents.) Table V lists  $T_1$ 's for two disubstituted benzenes, *o*- and *m*-nitrobenzoic acid. In ortho di- and trisubstituted benzenes the molecular tumbling does not appear to be simply described by assumption of independent axes of preferred rotation. However, carbons para to the various substituents do exhibit shorter  $T_1$  values.

**Structure Analysis of Substituted Benzenes Using  $T_1$  Measurements.** In substituted phenyl compounds where the motional behavior is predictable,  $^{13}\text{C}$  spin-lattice relaxation measurements can be used to identify individual molecular fragments, or individual  $^{13}\text{C}$  resonance lines. Ambiguous spectral assignments may often be verified using  $T_1$  data. An illustrative example is 3-bromophenyl (I). In cyclohexane- $d_{12}$  solvent only eight resonance lines of a possible ten were observed for this compound ( $^1\text{H}$ -decoupled  $^{13}\text{C}$  FT spectrum, Figure 3a).<sup>2c</sup> Spectral assignments for five or six resonance lines can be made based on chemical shift considerations.<sup>6</sup> The shoulder observed on one high intensity peak indicated accidental chemical shift equivalence for two to three carbons. The  $^1\text{H}$ -decoupled  $^{13}\text{C}$  spectrum of I run in dimethyl- $d_6$  sulfoxide (DMSO- $d_6$ ) is shown in Figure 3b; the two missing carbon lines are completely resolved. Assignments of the three resonances (C-2, C-4, and C-5) based on chemical shifts are impractical since the total chemical shift range is under 2 ppm; unambiguous assignments for C-2', C-3', C-4, and C-6 (see Figure 3b) cannot be made for the same reason. Determination of  $^{13}\text{C}$  spin-lattice relaxation times allows unambiguous assignment for all carbons except C-2' and C-3' where the assignments may be interchanged.

The observed  $T_1$  values for 3-bromobiphenyl are given in Figure 3b. Carbons 4 and 4' have the shortest

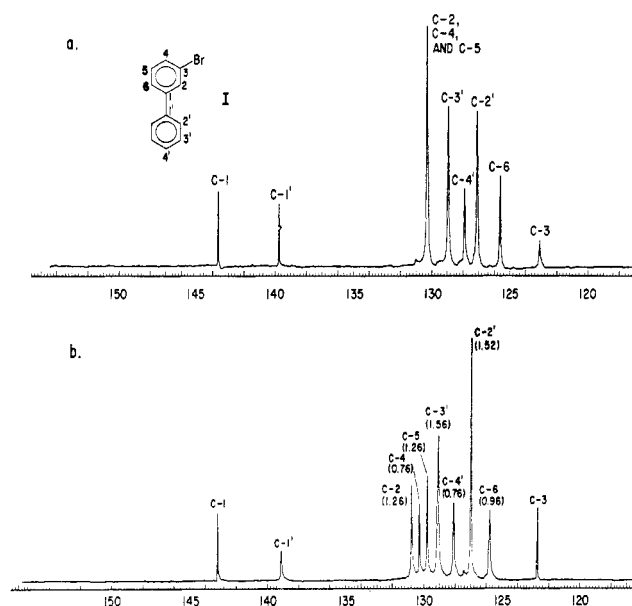
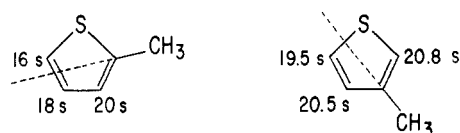


Figure 3.  $^{13}\text{C}$  Fourier transform nmr spectrum of 3-bromobiphenyl (I): (a) in cyclohexane- $d_{12}$ ; (b) in DMSO- $d_6$ . Chemical shifts relative to TMS. Spectral width 1000 Hz; 4096 spectral data points (8K transform). Spin-lattice relaxation times given in parentheses (in sec,  $\pm 10\%$  absolute;  $\pm < 5\%$  relative).<sup>2c</sup>

$T_1$ , 0.76 sec, as a result of their alignment with the long biphenyl axis. For C-6,  $T_1$  is shortened (0.96 sec) because it is para to the (large) bromine. Both C-2 and C-5 are unaligned with any preferred axis of rotation ( $T_1 = 1.26$  sec); differentiation is based on anticipated deshielding of C-2 (ortho to Br).<sup>6</sup> As expected, rotation of the ring containing bromine is slower than rotation of the other ring. This is evidenced by the longer  $T_1$  values for the off-axis carbons on the latter (C-2' and C-3';  $T_1 = 1.56$  sec).

Because of the strong directing influence of the nitro group, resonance line assignments are more straightforward for 3-nitrobiphenyl. The relaxation behavior of the protonated carbons in 3-nitrobiphenyl mirrored the situation in the bromo compound. For C-4 ( $\sim 122$  ppm) and C-4' (128.5 ppm),  $T_1$  was 1.6 sec, compared with 2.1 sec for C-6 (133 ppm), 2.5 sec for C-2 (121.2 ppm) and C-5 (130 ppm), and 3.0 sec for C-2' (127 ppm) and C-3' (129.2 ppm).

**Heteroaromatics.** The relaxation times of protonated ring carbons in five-membered heteroaromatic compounds show moderate to small differences as a result of anisotropic tumbling. The smaller effect results from the ring geometry. There are no para C-H bonds exactly aligned with the preferred molecular rotational axis coincident with a substituent-ring bond. The ring carbons across from a substituent may, however, experience somewhat reduced motion. The ring carbon relaxation times for 2- and 3-methylthiophene are illustrative ( $T_1$  values indicated in seconds).



In the unsubstituted six-membered heteroaromatic pyridine, the protonated carbon relaxation times are somewhat different,  $C_\alpha$  and  $C_\beta$  being somewhat longer

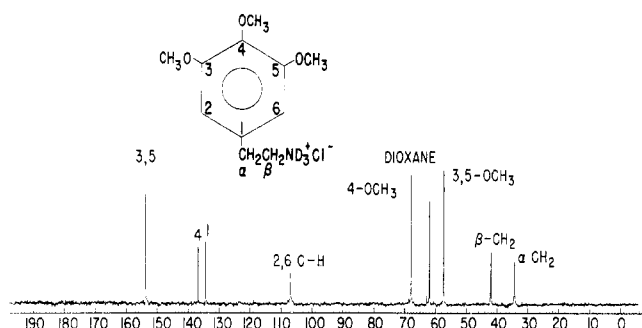
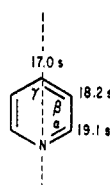


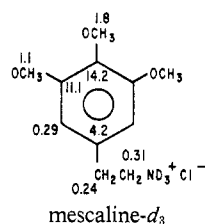
Figure 4.  $^{13}\text{C}$  FT nmr spectrum of mescaline (2 g in  $\text{D}_2\text{O}$ , total volume  $\sim 4$  ml). Chemical shifts relative to TMS, internal dioxane ( $\delta$  67.4) standard.

than  $C_\gamma$ . A word of caution is advisable for molecules



such as pyridine, however, where very small differences in relaxation times are noted. Small variations in C-H bond lengths may have a significant effect on observed  $T_1$ 's (because of the  $1/r^6$  dependence). For example, in pyridine the  $\gamma$ -carbon-H bond length is shorter than the other C-H bonds.<sup>20</sup> Almost half of the differential between  $T_{1\alpha}$ ,  $T_{1\beta}$ , and  $T_{1\gamma}$  can be accounted for based on the variation in  $r_{\text{C-H}}$ . In the case of pyridine, the  $T_1$  behavior is not conclusive evidence for anisotropic molecular tumbling as discussed above.

In large, polysubstituted aromatic compounds it becomes practical to augment carbon chemical shift data with  $T_1$  measurements of both C-H and nonprotonated carbons. The relaxation times for all carbons in mescaline (3,4,5-trimethoxyphenethylamine hydrochloride) are illustrative.



If mescaline molecules tumbled as *rigid bodies* in a more or less isotropic manner, then the ring substituent  $\text{CH}_2$  and  $\text{CH}_3$  carbons would have  $T_1$ 's of *ca.* 0.15 and 0.10 sec, respectively (from 0.29 sec  $T_1$  for the CH ring carbon). The somewhat long  $T_1$ 's observed for the two  $\text{CH}_2$  carbons result from increased freedom of motion relative to the ring. The inner and outer methoxy groups exhibit a further stereochemical feature similar to that observed for rotating  $\text{CH}_3$  groups in polymethylbenzenes<sup>16</sup> (even though the simple rotational axis is lost with the methoxy groups). The outer (3 and 5)  $\text{OCH}_3$  carbons have somewhat more restricted motion than the 4- $\text{OCH}_3$  (although all three  $\text{OCH}_3$  carbons are considerably more mobile than the ring or  $\text{CH}_2$  substituent carbons). The three nonprotonated carbons in mes-

caline (Figure 4) are easily assigned using  $T_1$  data.  $^{13}\text{C}$ - $^1\text{H}$  DD interactions dominate relaxation behavior even for nonprotonated ring carbons in mescaline (observed NOE's,  $\sim 2.0$ ). Ortho protons are most efficient owing to their proximity. Ring carbon-4 with no ortho protons has the longest  $T_1$  (14.2 sec) while C-3 and C-5 each with one ortho proton have faster  $T_1$ 's (11.1 sec). Two protons ortho to C-1 make it the fastest relaxing C-X carbon—4.2 sec (significant contribution is also expected from the  $\alpha$ - $\text{CH}_2$  protons).

**Chemical Shift Anisotropy. Diphenyldiacetylene.** Even with nonprotonated carbons (such as C-1 in toluene, see above) chemical shift anisotropy rarely dominates  $^{13}\text{C}$  relaxation behavior. In fact, the only compound that has been shown to have carbons dominantly relaxed at 23.5 kG near room temperature by the CSA mechanism is diphenyldiacetylene, DPDA.<sup>1b</sup> In DPDA the central acetylenic carbons are far removed from available proton nuclei ( $>3$  Å). Table VI

Table VI.  $T_1$  Data for Acetylenic Carbons<sup>a</sup>

	Approx. concn (w/v), %	$\nu$ , MHz	$\alpha$	$\beta$
$\alpha$ $\beta$				
PhC $\equiv$ CH	80	25.2	132	9.3
$\alpha$ $\beta$	30	25.2	75	125
PhC $\equiv$ C—C $\equiv$ CPh	25	25.2	82	136
	25	63.1	15	30

<sup>a</sup> Samples dissolved in acetone- $d_6$  and degassed.  $T_1$ 's determined at 38°.

lists  $T_1$ 's for phenylacetylene and DPDA.

The  $T_1$  for the  $\beta$  carbons in DPDA is 125 sec (30% sample) which is two orders of magnitude longer than  $T_1$  for the para carbon (1.1 sec; see previous text). The very long relaxation time for  $C_\beta$  allowed measurement of  $T_1$  outside of the spectrometer magnetic field, the sample being placed in the magnet only for initial polarization and, very briefly, for final measurement (single 90° pulse) of the remaining magnetization after a time,  $t$ , outside the magnet. The weak field  $T_1$  determined in that way was  $340 \pm 70$  sec. Since relaxation by the CSA mechanism depends on the square of the magnetic field, over 60% of the relaxation rate for  $C_\beta$  at 23 kG magnetic field comes from this mechanism. At high fields (*e.g.*, 59 kG/63 MHz)  $T_1$  for  $C_\beta$  drops to *ca.* 30 sec (Table VI) with 90% of the relaxation occurring by the CSA mechanism. The chemical shift anisotropy for  $C_\beta$  in DPDA is calculated from the present data to be *ca.* 270 ppm, a reasonable value for  $^{13}\text{C}$  where the chemical shifts span several hundred parts per million. For comparison, the  $^{13}\text{C}$  chemical shift anisotropies for  $\text{CS}_2$  and COS have been found to be 430 and 370 ppm, respectively.<sup>21-23</sup> For benzene,  $^{13}\text{C}$  chemical shift anisotropy of *ca.* 180 ppm has been reported.<sup>13</sup> In  $\text{CS}_2$ , which is the only previous example where  $^{13}\text{C}$  CSA relaxation has been established,<sup>20</sup> it is only at low temperatures and at very high magnetic fields that this mechanism becomes dominant, because of competing

(21) H. W. Spiess, D. Schweitzer, U. Haebleren, and K. H. Haussner, *J. Magn. Resonance*, **5**, 101 (1971).

(22) A. Pines, W. K. Rhim, and J. S. Waugh, quoted in ref 21.

(23) F. H. DeLeeuw and A. Dymanus, *Chem. Phys. Lett.*, **7**, 288 (1970).

spin-rotation relaxation. The latter mechanism is expected to be quite unimportant for DPDA.

The nuclear Overhauser effect (NOE) for the  $\beta$  carbon in DPDA was measured by integration of Fourier transform spectra with and without proton noise decoupling and found to be  $0.5 \pm 0.1\eta$ . This NOE value together with the  $T_1$  value for  $C_\beta$  allows the following dissection of  $T_1$  at 23 kG (30% sample):  $T_1^{\text{CSA}} 200 \pm 80$  sec,  $T_1^{\text{DD}} 500 \pm 100$  sec,  $T_1$  (other) 600 to  $>5000$  sec. Another and independent measure of  $T_1^{\text{DD}}$  can be made as follows. From the angle of  $38^\circ$  made by the  $C_\beta$ -proximal ortho H line with the  $A$  axis in DPDA, the C-H distance (3.54 Å), and the reorientation times obtained from the protonated ring carbons, a  $T_1^{\text{DD}}$  of 470 sec can be calculated, in agreement with the value obtained above.

The unassigned relaxation for the  $\beta$  carbon in DPDA may be spin rotation and/or relaxation by unpaired electrons (e.g., traces of free radicals or unremoved oxygen) or may reflect experimental errors.

**Scalar Relaxation. Bromobenzene.** Spin-lattice relaxation of  $^{13}\text{C}$  nuclei as a result of scalar interaction with a nucleus, X, does not occur in most molecules because of stringent requirements needed to make this mechanism competitive with the other relaxation mechanisms. The efficiency of scalar relaxation follows the relations given in eq 3, where  $J$  is the scalar coupling

$$R_1^{\text{SC}} = 1/T_1^{\text{SC}} = \frac{8}{3} \pi^2 J^2 S(S+1) \frac{T_1^{\text{X}}}{1 + \Delta\omega^2(T_1^{\text{X}})^2} \quad (3)$$

constant between the  $^{13}\text{C}$  and X nucleus,  $S$  is the spin of X,  $T_1^{\text{X}}$  is the spin-lattice relaxation time of X, and  $\Delta\omega$  is the difference in radians  $\text{sec}^{-1}$  between the Larmor frequencies of  $^{13}\text{C}$  and X nuclei.

Unless the Larmor frequencies for  $^{13}\text{C}$  and X are very close, the denominator in eq 3 becomes very large. Even when the Larmor frequencies are close, the X nucleus<sup>24</sup> must have a quadrupolar  $T_1$  of the appropriate magnitude (comparable to  $\Delta\omega$ , the difference between the Larmor frequencies of  $^{13}\text{C}$  and X). Scalar spin-lattice relaxation is thus a rare phenomenon. Scalar spin-spin relaxation, however, is described by a somewhat different equation (eq 4). The addition of

$$R_2^{\text{SC}} = 1/T_2^{\text{SC}} = \frac{4}{3} \pi^2 J^2 S(S+1) \left[ \frac{T_1^{\text{X}}}{1 + \Delta\omega^2(T_1^{\text{X}})^2} + T_1^{\text{X}} \right] \quad (4)$$

the independent  $T_1^{\text{X}}$  term (multiplier) in eq 4 enables  $T_2$  scalar relaxation to be competitive even in cases where  $\Delta\omega$  is large (if  $T_1^{\text{X}}$  is reasonably long). It is for this reason that resonance lines of  $^{13}\text{C}$  nuclei attached to quadrupolar nuclei (e.g.,  $^{14}\text{N}$ ) can be extensively broadened (short  $T_2$ ).

Several nuclei have more or less appropriate nuclear characteristics but scalar  $T_1$  relaxation of  $^{13}\text{C}$  nuclei has been confirmed only for  $^{13}\text{C}$  nuclei bonded to  $^{79}\text{Br}$  nuclei.<sup>25,26,1e,7</sup> Scalar relaxation for  $^{13}\text{C}$  nuclei di-

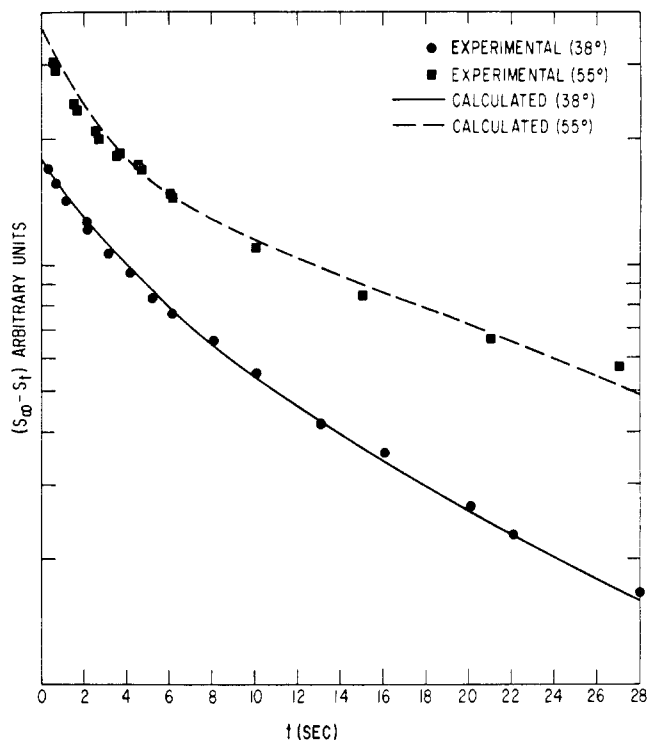


Figure 5. Experimental and calculated determination of  $T_1$  for the C-1 carbon of bromobenzene.<sup>1e</sup>

rectly bonded to bromine nuclei in bromomethanes<sup>25,26</sup> and *p*-bromobenzonitrile<sup>7</sup> has been reported, but no differentiation between  $^{13}\text{C}$ - $^{79}\text{Br}$  and  $^{13}\text{C}$ - $^{81}\text{Br}$  nuclei could be made in those studies. Differentiation of  $^{13}\text{C}$ - $^{79}\text{Br}$  and  $^{13}\text{C}$ - $^{81}\text{Br}$  relaxation has been reported in bromobenzene.<sup>1e</sup>

The spin-lattice relaxation time for C-1 in bromobenzene determined in the usual way results in an apparent nonexponential decay of magnetization following variable pulse intervals,  $t$  (see Experimental Section). The near equivalence of natural isotopic abundances for  $^{79}\text{Br}$  and  $^{81}\text{Br}$  (50.5 and 49.5%) results in an experimentally observed curve (Figure 5)<sup>1e</sup> rather than the usual straight line (see Figure 6). Using a linear combination of 2 exponential terms, it was possible to fit the observed curves ( $T_1$  was determined at 3 temperatures) and thus determine close estimates for  $T_1(^{13}\text{C}$ - $^{79}\text{Br})$  and  $T_1(^{13}\text{C}$ - $^{81}\text{Br})$  (Table VII).

Table VII.  $^{13}\text{C}$  Spin-Lattice Relaxation in Bromobenzene (C-1 Carbon)<sup>a</sup>

Temp, °C	$T_1(^{13}\text{C}$ - $^{79}\text{Br})$	$T_1(^{13}\text{C}$ - $^{81}\text{Br})$	NOE ( $\eta$ ) <sup>b</sup>
38	3.6	16	0.0
55	2.2	22	
125	1.2	~26	0.0

<sup>a</sup> Determined at 25.2 MHz; degassed ( $\text{N}_2$  method).  $T_1$  in sec; calculated from experimental curve (see Figure 5 and text); estimated maximum error 20%.  $T_1$  for the ortho and meta carbon atoms was 10.7 sec and for the para-carbon, 6.8 sec ( $38^\circ$ ). <sup>b</sup> Determined from total integrated peak intensity ratios; probable error  $<0.1$ . The NOE ( $\eta$ ) for all protonated carbons was complete (2.0).

It is not possible from the experiments performed to differentiate quantitatively between  $^{13}\text{C}$ - $^{81}\text{Br}$  scalar relaxation and  $^{13}\text{C}$ - $^{81}\text{Br}$  dipole-dipole relaxation. The

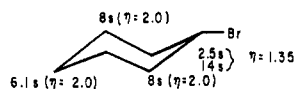
(24) We treat here only scalar relaxation "of the second kind" according to A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961. To date,  $^{13}\text{C}$  scalar spin-lattice relaxation of the first kind (e.g., chemical exchange) has not been observed.

(25) J. R. Lyerla, Jr., D. M. Grant, and R. D. Bertrand, *J. Phys. Chem.*, **75**, 3967 (1971).

(26) T. C. Farrar, S. J. Druck, R. R. Shoup, and E. D. Becker, *J. Amer. Chem. Soc.*, **94**, 699 (1972).



NOE measurements (Table VII) indicate that  $^{13}\text{C}$ – $^1\text{H}$  dipole–dipole interactions do not contribute significantly to relaxation of the C-1 carbon of bromobenzene. For *protonated* carbons bonded to bromine the longer C–Br bond length and somewhat lower magnetic moments for the bromine isotopes make  $^{13}\text{C}$ –Br dipole–dipole interactions ineffective for relaxation of the  $^{13}\text{C}$  nuclei. In bromobenzene, however, the  $^{13}\text{C}$ – $^{81}\text{Br}$  bond distance ( $\sim 1.85$  Å) is shorter than the  $^{13}\text{C}$ –ortho  $^1\text{H}$  internuclear distance ( $\sim 2.7$  Å). Taking into account the presence of two ortho protons, the difference between  $^1\text{H}$  and  $^{81}\text{Br}$  magnetic moments, and the estimated internuclear distances,  $^{13}\text{C}$ – $^{81}\text{Br}$  DD relaxation dominates over  $^{13}\text{C}$ – $^1\text{H}$  relaxation by a factor of *ca.* 5 (but neither can compete with the more efficient  $^{13}\text{C}$ – $^{79}\text{Br}$  scalar interaction for those carbons bonded to  $^{79}\text{Br}$ ).<sup>27</sup> It is likely that some contribution from  $^{13}\text{C}$ – $^{81}\text{Br}$  scalar relaxation is present. In compounds where protonated carbons are bonded to bromine the situation becomes somewhat less complex. In 1-bromocyclohexane, for example, the  $T_1$  observed for the 1-carbon is nonexponential. Estimated  $T_1$ 's for  $^{13}\text{C}$ – $^{79}\text{Br}$  and  $^{13}\text{C}$ – $^{81}\text{Br}$  carbons were  $\sim 2.5$  and  $\sim 14$  sec, respectively. NOE measurements on C-1 ( $\eta = 1.35$ ) indicated that for  $^{13}\text{C}$ – $^{81}\text{Br}$  carbons,  $^{13}\text{C}$ – $^1\text{H}$  dipole–dipole interactions dominated relaxation, while for  $^{13}\text{C}$ – $^{79}\text{Br}$  carbons, scalar and  $^{13}\text{C}$ – $^1\text{H}$  DD interactions competed with one another (65% scalar; 35% DD).



(27) If the results of anisotropic tumbling are included in this estimate then the  $^{13}\text{C}$ - $^1\text{H}$  DD contributions are more nearly comparable ( $\sim 3:1$ ).

PhOH in	$T_1$ , sec <sup>a</sup>			
	C-1	C-2	C-3	C-4
CCl <sub>4</sub>				
CCl <sub>4</sub> :PhOH Mol Ratio				
1	16.7	2.4	2.4	1.4
2	19.9	2.9	2.9	2.1
5.9	21	4.2	3.9	2.4
12		5.5	5.3	3.1
25 <sup>b</sup>		6.4	7.4	5.4
H <sub>2</sub> O and D <sub>2</sub> O				
(% w/w PhOH)				
H <sub>2</sub> O (88) <sup>c</sup>	17.8	2.8	2.8	2.0
(85)	19.2	2.9	2.9	2.15
(90)	18.4	2.8	2.8	1.9
D <sub>2</sub> O (87) <sup>c,d</sup>	27.0	2.45	2.45	1.65
Acetone				
Mol ratio 1:1	33.0	5.0	5.2	4.3

Normally,  $^{13}\text{C}$   $T_1$  data would not be reported to the precision given in Table VIII. The  $\text{H}_2\text{O}-\text{D}_2\text{O}$  PhOH experimental  $T_1$ 's were of particularly high accuracy, aided by the high concentrations of PhOH, and by per-

*Journal of the American Chemical Society* / 95:5 / March 7, 1973



Table IX.  $T_1$  Data for Aniline in Inert, Hydrogen-Bonding, and Acidic Solvent Systems

Solvent	Concn, % v/v	Visc, cP <sup>b</sup>	$T_1$ , sec <sup>a</sup>			$T_{1^{o,m}}/T_{1^p}$
			Ortho	Meta	Para	
Neat		3.62	5.4	5.3	4.4	1.32
CCl <sub>4</sub>	20	2.6	11.5	11.7	8.8	1.32
Benzene- <i>d</i> <sub>6</sub>	20	0.886	13.4	12.7	10.5	1.24
Acetone- <i>d</i> <sub>6</sub>	20	0.602	10.5	11.7	11.2	0.99
DMSO- <i>d</i> <sub>6</sub>	20	2.08	3.5	3.55	2.85	1.24
	10	2.0	3.5	3.47	3.13	1.11
CH <sub>3</sub> CO <sub>2</sub> H	20	5.08	1.29	1.35	0.44	3.00
	10	2.99	1.65	1.8	0.62	2.78
CF <sub>3</sub> CO <sub>2</sub> H	20	6.26	1.21	1.07	0.26	4.42

<sup>a</sup> 38°, 25.2 MHz. Samples undegassed. <sup>b</sup> Viscosities in centipoise calculated from solution densities and capillary viscometer measurements.

sistent attention to experimental details. Precision in duplicate runs with separate samples was <2%. <sup>13</sup>C  $T_1$  data plots for the C-H carbons of PhOD in D<sub>2</sub>O are given in Figure 6. In this case the ( $T-90^\circ_\infty-T-180^\circ-t-90^\circ_t$ )<sub>z</sub> pulse sequence was repeated 16 times for each data point set. The decay was followed for  $\approx 2 \times T_1$  at which time only 13.5% of the initial magnetization remains.

The last solvent system investigated for PhOH was CH<sub>3</sub>COCH<sub>3</sub>. Geometries of phenol-ketone complexes have not been elucidated. The  $T_{1^{o,m}}/T_{1^p}$  ratio observed for 1:1 PhOH-CH<sub>3</sub>COCH<sub>3</sub>, 1.2, is significantly lower than the ratios observed in PhOH-CCl<sub>4</sub> or PhOH-H<sub>2</sub>O solutions ( $\sim 1.5-1.7$ ). This indicates that PhOH-CH<sub>3</sub>COCH<sub>3</sub> complexes may be "folded," or that the complex lifetime is short compared with the time for overall molecular reorientation of the PhOH molecules.

Relaxation behavior analogous to that observed for phenol is observed for aniline in inert and hydrogen-bonding solvents (Table IX). When aniline is pro-

tonated in acid solution the ring carbon  $T_1$ 's decrease markedly, out of proportion to macroscopic viscosity measurements. In addition, the molecular tumbling of the anilinium ion becomes highly anisotropic, the  $T_{1^{o,m}}/T_{1^p}$  ratio being *ca.* 3 (tumbling ratio  $\approx 9$ ) *vs.* 1.0-1.3 for aniline itself. The strongly anisotropic molecular motion arises from the ion being "locked" into the solvent lattice by ion pairing and electrostatic interactions.<sup>29</sup>

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(29) G. C. Levy, *Chem. Commun.*, 768 (1972).

## Analysis of Isomerization in Compounds Displaying Restricted Rotation of Aryl Groups<sup>1</sup>

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**Abstract:** A general and systematic approach to the topological analysis of isomerism and isomerization has been developed for compounds belonging to the triaryl systems Ar<sub>3</sub>ZX (*e.g.*, Ar<sub>3</sub>CH, Ar<sub>3</sub>P) and Ar<sub>3</sub>Z (*e.g.*, Ar<sub>3</sub>B), and also for the diaryl systems Ar<sub>2</sub>ZXY (*e.g.*, Ar<sub>2</sub>CHCl, Ar<sub>2</sub>PH), Ar<sub>2</sub>ZX<sub>2</sub> (*e.g.*, Ar<sub>2</sub>CH<sub>2</sub>, Ar<sub>2</sub>O), and Ar<sub>2</sub>ZX (*e.g.*, Ar<sub>2</sub>CO, Ar<sub>2</sub>O), where X and Y represent ligands or pseudo-ligands. The results may be displayed in the form of graphs, as illustrated by application to several examples from the literature. This method of analysis is broadly applicable to a large variety of molecular structures.

Recent years have witnessed the study of a great diversity of chemical systems which demonstrate isomerism due to restricted internal motions.<sup>2</sup> One group of compounds evincing such behavior consists of molecules containing two or more aromatic ring

systems (Ar) bonded to a central atom (Z). Although these compounds often differ greatly in their constitution, they are all related in the elements giving rise to isomerism and in the pathways for interconversion of isomers (isomerization). The present paper presents an approach to a general, systematic, and exhaustive analysis of isomerism and isomerization in such systems, allowing a facile interpretation of relevant experimental data. The sometimes complex interconversion

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(2) See, for example, I. O. Sutherland, *Annu. Rep. NMR (Nucl. Magn. Resonance) Spectrosc.*, **4**, 71 (1971).