

Carbon-13 Spin-Lattice Relaxation in Benzene and Substituted Aromatic Compounds¹

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Abstract: Measurements of ¹³C 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 ⁷⁹Br-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, τ_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 $T_1^{\text{ortho}}/T_1^{\text{para}}$.

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.² 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⁻¹) 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.³ 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, ¹³C–¹H dipole-dipole (DD) interactions dominate carbon T_1 processes.⁴ 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 ¹³C 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

¹³C Nmr Spectra. ¹³C 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.⁵ Chemical shifts when reported⁶ 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 (~ 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. ¹³C spectra were generally obtained with complete ¹H 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)^{7a} for the measurements made at 25 MHz. The pulse sequence utilized in these measurements was (T – 90°_ω – T – 180° – t – 90°)_z, 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 ¹³C 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 ¹³C–¹H dipole-dipole relaxation contributions can be directly evaluated from ¹³C{¹H} NOE measurements: K. F. Kuhlmann and D. M. Grant, *J. Chem. Phys.*, **52**, 3439 (1970).

plotted against t , where S_∞ and S_t are the transformed signals from the 90°_∞ and 90°_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 $(S_\infty - S_0)$ for $t = 0$ ($\equiv 2S_0$). Because the effective ^{13}C rf field of the XL-100-15 is under 2 kHz (90° pulse $\cong 130$ μsec), 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 ^b	T_1 , sec ^a			
	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

^a 90% toluene; 10% cyclohexane- d_{12} ; N_2 degassed. T_1 measured at 25.2 MHz and 38° . ^b 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° pulse was obtained in 40 μsec . The conventional 180° - t - 90° 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 ^1H 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) ^1H decoupling. Using the technique^{7b} of decoupling just before the short ^{13}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 ^1H 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, 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^a

	T_1 , sec	NOE (η) ^c
Undegassed	23	1.30
Degassed ^b	29.3	1.60

^a Solvent, benzene- d_6 . Determined at 38° and 25.2 MHz. ^b Vacuum degassed (freeze–thaw cycles). ^c Average of two to three measurements on each of several samples; probable accuracy ± 0.05 (deviations from reported values $<0.05\eta$).

The experimentally observed NOE's indicate that ^{13}C - ^1H dipole–dipole interactions dominate ring carbon relaxation with appreciable contributions from other mechanisms.⁸ 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 .⁹ In undegassed benzene, dissolved O_2 results in a contribution of ca. 25% to relaxation of the benzene carbons, corresponding to a ^{13}C - O_2 (DD) relaxation rate, $R_1 \equiv 1/T_1$, of ca. 100 sec. Jaeckle, Haebleren, and Schweitzer¹⁰ estimated a similar relaxation contribution from 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.¹¹ The short T_1 observed for C-1 in undegassed samples of toluene results from an O_2 relaxation contribution comparable with that calculated for benzene. The NOE's observed for C–H ring carbons in toluene indicate that ^{13}C - ^1H 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^{CSA} on the square of

(8) T. D. Alger and D. M. Grant, *J. Phys. Chem.*, **75**, 2538 (1971), concluded that ^{13}C - ^1H 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. Haebleren, and D. Schweitzer, *J. Magn. Resonance*, **4**, 198 (1971).

(11) It is important to understand the connection between molecular motion and spin-lattice relaxation.^{2c} 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 ^a					NOE (η) ^a				
			C-1	C-2	C-3	C-4	CH ₃	C-1	C-2	C-3	C-4	CH ₃
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> ₆	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 ^b	24	24	18						
90% in cyclohexane- <i>d</i> ₁₂	25.2	38	84	23	23	17.5		0.4	1.4	1.4	1.3	
20% in toluene- <i>d</i> ₈ ^c	25.2	38	85	24	23	18						
9% in toluene- <i>d</i> ₈ ^c	25.2	38	85									

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

the spectrometer frequency,¹² the data in Table III allow a calculation of T_1^{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^{CSA} would be \approx 360 sec. It is clear that T_1^{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^{CSA} can be obtained by a different procedure as follows. With the assumption of isotropic motion, and making use of T_1 's and η 's for ring carbons in toluene, we can calculate a correlation time (τ_c) for random molecular tumbling of about 1.5×10^{-12} sec from the expression in eq 1. The ¹³C 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,¹³ can be taken as an approximate value for toluene. Treating the system as an axially symmetric one, for simplicity, we can calculate T_1^{CSA} from the following equation.¹²

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

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

The remaining relaxation for the toluene ring carbons is almost certainly caused by the spin-rotation mechanism. A T_1^{SR} of 140 sec fits both the protonated and unprotonated ring carbons, as shown in Table IV. The components of T_1^{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^{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^{DD} 's for the protonated ring carbons about three times shorter than those of toluene, so that $1/\tau_c$ and therefore T_1^{CSA} should also be three times shorter; i.e., T_1^{CSA} should be >1000 sec instead of 160 sec. In fact, a T_1^{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^{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^{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^{obsd}	T_1^{DD}	T_1^{CSA}	T_1^{SR}
C-1	89	270 ^a	>3000	140
(C-2, C-3, C-4) _{av}	22	27 ^a	>3000	140

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

Spin-rotation relaxation for the CH₃ carbon in toluene has been indicated from theoretical works¹⁵ and inferred from experimental studies on polymethylbenzenes.^{14,16} The NOE observed for the CH₃ carbon in toluene (Table III) can be used to calculate T_1^{DD} (\approx 80 sec). T_1 and NOE measurements on the CH₃ 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 CH₃ carbon relaxation.

It is generally thought that *intermolecular* ¹³C-¹H dipole-dipole interactions do not contribute significantly to ¹³C relaxation in most organic molecules. In order to test this belief, dilute samples of toluene in toluene-*d*₈ 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*₈ 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 (τ_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 = CH₃, CH=CH₂, C≡CH) have relatively long T_1 's. The polar nitro substituent results in increased electrostatic ordering of solute molecules, lengthening τ_c , and shortening T_1 's. Groups such as OH and NH₂ 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 ^a						NOE, η^b					
	C-1	C-2	C-3	C-4	α	β	C-1	C-2	C-3	C-4	α	β
CH ₃ ^c	58	20	21	15	16.3		0.43	1.32	1.32	1.70	0.61	
<i>t</i> -Bu ^c		10.3	10.3	5.8								
CH=CH ₂ ^{c,d}	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 ^e	56	13.2	13.2	9.0	53	8.5	0.46	1.89	1.92 ^h	1.92 ^h	0.51	1.95
C≡CH (degassed) ^f	107	14.0	14.0	8.2	132	9.3	0.8	2.0	1.9	1.9	0.90	2.0
Ph ^{d,f}	61	5.9	5.9	3.2			0.9	2.0	2.0	2.0		
NO ₂ ^c	56	6.9	6.9	4.8			0.8	2.0	1.9	1.9		
OH ^g	18.4	2.8	2.8	1.9								
NH ₂ ^c		5.4	5.3	4.4								
2-NO ₂ -1-CO ₂ H	C-1	C-2	C-3	C-4	C-5	C-6						
3-NO ₂ -1-CO ₂ H		1.5	3.0	1.9	2.8	2.9						
				0.95	1.5	1.35						

^a Samples not degassed unless noted. T_1 's \pm 5–10%. ^b Absolute NOE unless noted, estimated maximum error \pm 0.15. ^c Neat. ^d Not absolute NOE: relative NOE; based on the assumption that for each protonated carbon, \sim 2.0. ^e C₆D₆ solvent. ^f CD₃COCD₃ solvent. ^g CCl₄ solvent, 6:1 mol ratio CCl₄:PhOH. ^h Two carbons determined together.

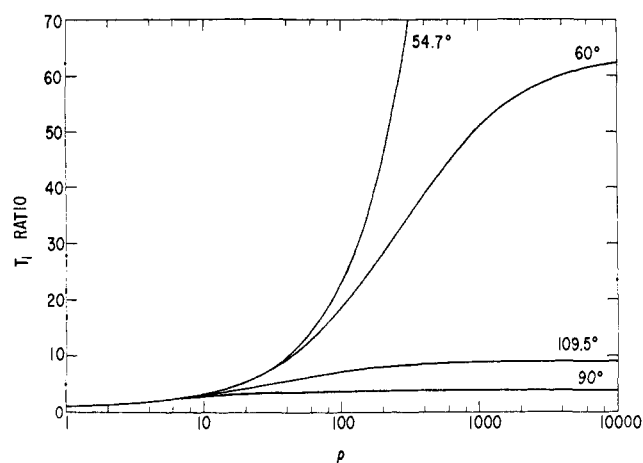


Figure 1. Calculated T_1 ratios as a function of the tumbling or spinning ratio (ρ) for four geometries ($\theta = 54.7$ (magic angle), 60° , 90° , and 109.5°).

Anisotropic Motion. The overall tumbling of small molecules is often anisotropic¹⁷ resulting in nonsystematic variation of protonated carbon T_1 values. In molecular systems where the motional behavior is qualitatively predictable, ¹³C 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 C₂ 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 C₂ symmetry axis does not lead to any modulation in the direct dipole–dipole interaction of the para ¹³C 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).

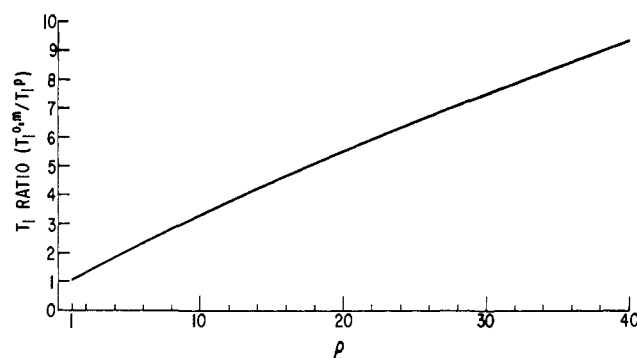


Figure 2. Calculated T_1 ratios (expanded scale), $\rho = 1$ to 40 for benzene ring geometry ($\theta = 60^\circ$).

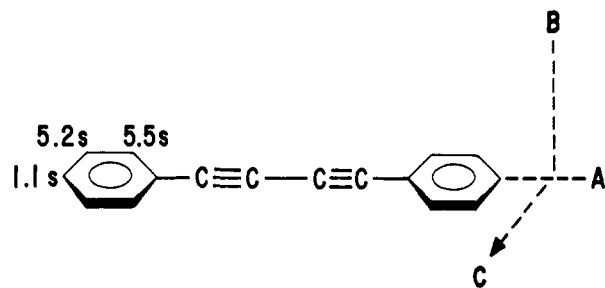
does not contribute to relaxation of that carbon. However, such a rotation does lead to relaxation for the ortho and meta carbons because the C–H bonds in these instances make angles (θ) of 60° and 120° with the C₂ axis. In the limit of very much faster rotation about the long axis than about the shorter 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.^{2b} Below the limit of anisotropic motion, calculations can predict motional anisotropy from observed T_1 values.^{2b} Figure 1 gives the tumbling ratios vs. observed T_1 ratios for four cases: $\theta = 54.7^\circ$ (the magic angle), 60° (substituted benzenes), 90° (substituted ferrocenes¹⁸), and 109.5° (methyl groups). Figure 2 shows an expanded view useful for estimating tumbling ratios from $T_1^{o,m}/T_1^p$ ratios in monosubstituted benzenes. As the tumbling ratio, ρ , approaches infinity, $T_1^{o,m}/T_1^p$ approaches 64. The calculations used to construct Figures 1 and 2 were derived for axially symmetric molecules¹⁹ 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.^{1b} 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 ~ 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 = CH=CH₂), 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 CH₂ T_1 values are approximately in the expected 2:1 ratio.^{2b,c}

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, ¹³C spin-lattice relaxation measurements can be used to identify individual molecular fragments, or individual ¹³C 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 (¹H-decoupled ¹³C FT spectrum, Figure 3a).²⁰ Spectral assignments for five or six resonance lines can be made based on chemical shift considerations.⁶ The shoulder observed on one high intensity peak indicated accidental chemical shift equivalence for two to three carbons. The ¹H-decoupled ¹³C 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 ¹³C 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

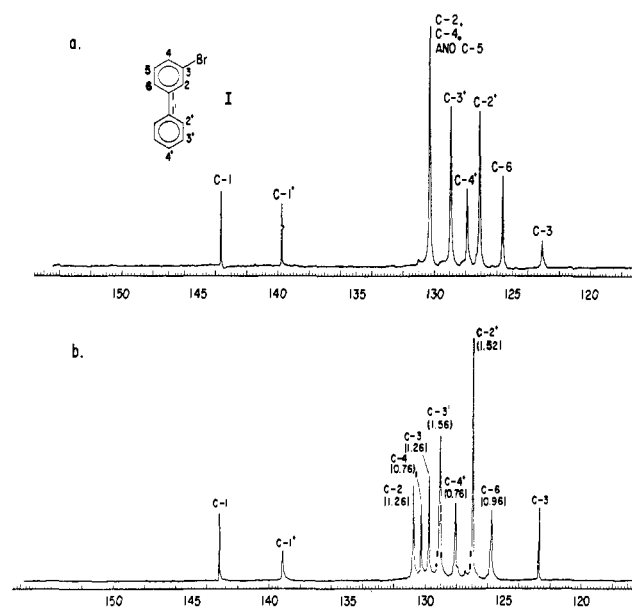
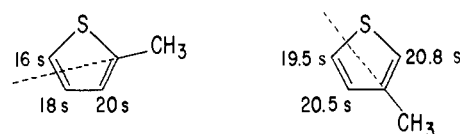


Figure 3. ¹³C Fourier transform nmr spectrum of 3-bromobiphenyl (I): (a) in cyclohexane- d_{12} ; (b) in DMSO- d_6 . Chemical shifts relative to TMS. Spectral width 1000 Hz; 4096 spectral data points (8K transform). Spin-lattice relaxation times given in parentheses (in sec, $\pm 10\%$ absolute; $\pm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

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).⁶ 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 (~ 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_α and C_β being somewhat longer

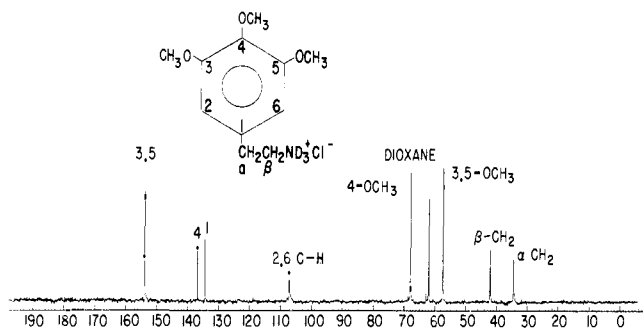
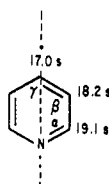


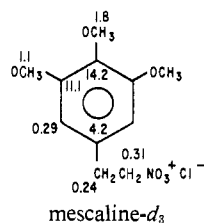
Figure 4. ^{13}C FT nmr spectrum of mescaline (2 g in D_2O , total volume ~ 4 ml). Chemical shifts relative to TMS, internal dioxane (δ 67.4) standard.

than C_γ . 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 γ -carbon-H bond length is shorter than the other C-H bonds.²⁰ 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 CH_2 and 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 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 CH_3 groups in polymethylbenzenes¹⁶ (even though the simple rotational axis is lost with the methoxy groups). The outer (3 and 5) OCH_3 carbons have somewhat more restricted motion than the 4- OCH_3 (although all three OCH_3 carbons are considerably more mobile than the ring or CH_2 substituent carbons). The three nonprotonated carbons in mes-

(20) B. Bak, L. Hansen-Nygaard, and J. Rastrup-Anderson, *J. Mol. Spectrosc.*, **2**, 361 (1958).

caline (Figure 4) are easily assigned using T_1 data. ^{13}C - ^1H DD interactions dominate relaxation behavior even for nonprotonated ring carbons in mescaline (observed NOE's, ~ 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 α - 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}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.^{1b} 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^a

	Approx. concn (w/v), %	ν , MHz	α	β
α β				
PhC \equiv CH	80	25.2	132	9.3
α β	30	25.2	75	125
PhC \equiv C-C \equiv CPh	25	25.2	82	136
	25	63.1	15	30

^a 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 β 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_β 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 ± 70 sec. Since relaxation by the CSA mechanism depends on the square of the magnetic field, over 60% of the relaxation rate for C_β at 23 kG magnetic field comes from this mechanism. At high fields (*e.g.*, 59 kG/63 MHz) T_1 for C_β drops to *ca.* 30 sec (Table VI) with 90% of the relaxation occurring by the CSA mechanism. The chemical shift anisotropy for C_β in DPDA is calculated from the present data to be *ca.* 270 ppm, a reasonable value for ^{13}C where the chemical shifts span several hundred parts per million. For comparison, the ^{13}C chemical shift anisotropies for CS_2 and COS have been found to be 430 and 370 ppm, respectively.²¹⁻²³ For benzene, ^{13}C chemical shift anisotropy of *ca.* 180 ppm has been reported.¹³ In CS_2 , which is the only previous example where ^{13}C CSA relaxation has been established,²⁰ 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. Hausser, *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 β 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_β 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^{DD} can be made as follows. From the angle of 38° made by the C_β -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^{DD} of 470 sec can be calculated, in agreement with the value obtained above.

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

Unless the Larmor frequencies for ^{13}C and X are very close, the denominator in eq 3 becomes very large. Even when the Larmor frequencies are close, the X nucleus²⁴ must have a quadrupolar T_1 of the appropriate magnitude (comparable to $\Delta\omega$, the difference between the Larmor frequencies of ^{13}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^{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^{X} is reasonably long). It is for this reason that resonance lines of ^{13}C nuclei attached to quadrupolar nuclei (e.g., ^{14}N) can be extensively broadened (short T_2).

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

(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}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).

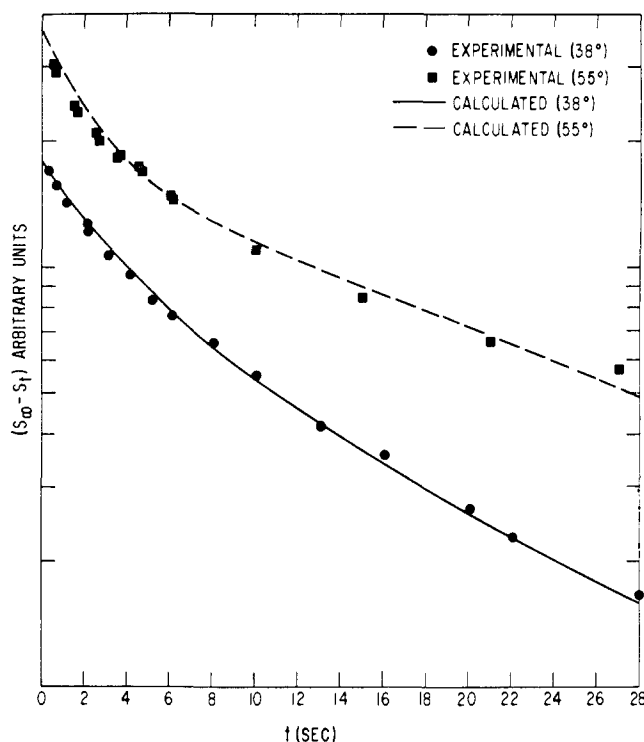


Figure 5. Experimental and calculated determination of T_1 for the C-1 carbon of bromobenzene.^{1c}

rectly bonded to bromine nuclei in bromomethanes^{25,26} and *p*-bromobenzonitrile⁷ 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.^{1c}

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}Br and ^{81}Br (50.5 and 49.5%) results in an experimentally observed curve (Figure 5)^{1c} 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}C Spin-Lattice Relaxation in Bromobenzene (C-1 Carbon)^a

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

^a Determined at 25.2 MHz; degassed (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°). ^b Determined from total integrated peak intensity ratios; probable error <0.1 . The NOE (η) 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

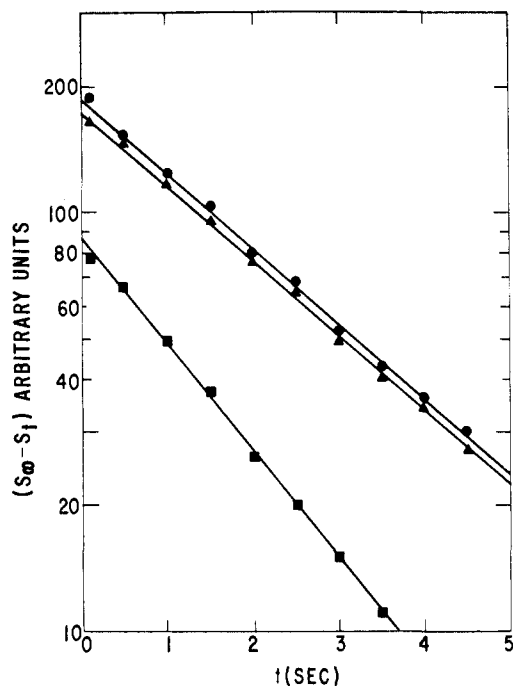
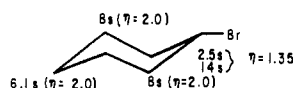


Figure 6. ^{13}C spin-lattice relaxation data for PhOD in D_2O :^{1d} (●) ortho, (▲) meta, (■) para carbons.

NOE measurements (Table VII) indicate that ^{13}C - ^1H 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}C -Br dipole-dipole interactions ineffective for relaxation of the ^{13}C nuclei. In bromobenzene, however, the ^{13}C - ^{81}Br bond distance ($\sim 1.85 \text{ \AA}$) is shorter than the ^{13}C -ortho ^1H internuclear distance ($\sim 2.7 \text{ \AA}$). Taking into account the presence of two ortho protons, the difference between ^1H and ^{81}Br magnetic moments, and the estimated internuclear distances, ^{13}C - ^{81}Br DD relaxation dominates over ^{13}C - ^1H relaxation by a factor of *ca.* 5 (but neither can compete with the more efficient ^{13}C - ^{79}Br scalar interaction for those carbons bonded to ^{79}Br).²⁷ It is likely that some contribution from ^{13}C - ^{81}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}C - ^{79}Br and ^{13}C - ^{81}Br carbons were ~ 2.5 and ~ 14 sec, respectively. NOE measurements on C-1 ($\eta = 1.35$) indicated that for ^{13}C - ^{81}Br carbons, ^{13}C - ^1H dipole-dipole interactions dominated relaxation, while for ^{13}C - ^{79}Br carbons, scalar and ^{13}C - ^1H DD interactions competed with one another (65% scalar; 35% DD).



Solvent Effects. Molecular Association. The relaxation behavior of phenol and aniline examined at various dilutions in different molecular environments (solvent

(27) If the results of anisotropic tumbling are included in this estimate then the ^{13}C - ^{81}Br and ^{13}C - ^1H DD contributions are more nearly comparable ($\sim 3:1$).

systems) illustrates the utility of substituted benzene T_1 studies for investigations of H-bonding and other strong intermolecular interactions.^{1d}

T_1 's for PhOH at five dilutions in CCl_4 are given in Table VIII. Intermolecular association of PhOH

Table VIII. ^{13}C Spin-Lattice Relaxation Behavior of Phenol

PhOH in	T_1 , sec ^a			
	C-1	C-2	C-3	C-4
CCl_4				
CCl ₄ :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 ^b		6.4	7.4	5.4
H_2O and D_2O				
(% w/w PhOH)				
H_2O (88) ^c	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_2O (87) ^{c,d}	27.0	2.45	2.45	1.65
Acetone				
Mol ratio 1:1	33.0	5.0	5.2	4.3

^aAt 25.2 MHz; 38°; samples not degassed. The effect of dissolved O_2 on the C-H carbons is negligible. Corrected T_1 's for C-1 should be longer by $\sim 15\%$ ($T_1^{\text{obsd}} = 17$ sec) to 30% ($T_1^{\text{obsd}} = 33$ sec). T_1 values ± 5 -10%; field/freq. control: *d*₆-acetone capillary. ^b T_1 values ± 15 -20%. ^cProbable exptl error $< 5\%$. ^d $> 95\%$ deuterium assay (PhOH dissolved in D_2O).

molecules is evidenced by the short T_1 's observed at high PhOH concentrations (owing to slower molecular tumbling of PhOH dimers and "aggregates"; part of this effect may arise, however, from changes in solution viscosity). The trend to longer T_1 's is quite evident at a 25:1 mol ratio of CCl_4 :PhOH. At lower concentrations ($\gg 25:1$) it is expected that the PhOH T_1 's would be significantly longer; however, measurements were not obtained at those dilutions.

In concentrated H_2O and D_2O solutions the PhOH T_1 's are similar to those in concentrated CCl_4 solution (Table VIII). Significant, but small changes of PhOH concentration in H_2O do not result in large changes in T_1 . However, the C-H carbons relax $\sim 15\%$ faster with 87% PhOD in D_2O vs. 88% PhOH in H_2O (approximately equivalent mol ratios). This change in T_1 's corresponds closely with the viscosity differential between D_2O and H_2O at $\sim 40^\circ$.²⁸ The T_1 for the non-protonated carbon C-1, on the other hand, increases in D_2O by $\sim 50\%$. This differential would increase to more than 100% if the contributions to relaxation of C-1 from dissolved O_2 and SR relaxation were taken into account (the NOE for C-1 is $\cong 1.3\eta$, for $T_1^{\text{obsd}} \approx 16.7$ sec). The $\text{D}_2\text{O}/\text{H}_2\text{O}$ effect on T_1 for C-1 indicates that the O-H proton (plus possibly "intermolecular" hydrogen-bonded H_2O and PhOH protons) is responsible for about half of the ^{13}C - ^1H DD relaxation of C-1; the remaining half arises from contributions from the two ortho protons.

Normally, ^{13}C T_1 data would not be reported to the precision given in Table VIII. The H_2O - D_2O PhOH experimental T_1 's were of particularly high accuracy, aided by the high concentrations of PhOH, and by per-

(28) J. R. Heiks, M. K. Barnett, L. V. Jones, and E. Orban, *J. Phys. Chem.*, **58**, 488 (1954).

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

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

^a 38°, 25.2 MHz. Samples undegassed. ^b 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%. ¹³C T_1 data plots for the C-H carbons of PhOD in D₂O are given in Figure 6. In this case the ($T-90^\circ_\infty-T-180^\circ-t-90^\circ_t$)_z 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 CH₃COCH₃. Geometries of phenol-ketone complexes have not been elucidated. The $T_{1^{o,m}}/T_{1^p}$ ratio observed for 1:1 PhOH-CH₃COCH₃, 1.2, is significantly lower than the ratios observed in PhOH-CCl₄ or PhOH-H₂O solutions ($\sim 1.5-1.7$). This indicates that PhOH-CH₃COCH₃ 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 ≈ 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.²⁹

Acknowledgments. The authors thank Russell Hill, Craig Robertson, and Miss Judith A. Halstead for assistance with the experimental work, and Dr. H. M. Relles for helpful discussion. The 63-MHz spectrometer was built with financial help from the United States Public Health Service and the National Science Foundation. Part of this work was done during the tenure of a visiting professorship at the General Electric Research and Development Center, summer 1971.

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

Analysis of Isomerization in Compounds Displaying Restricted Rotation of Aryl Groups¹

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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 Ar₃ZX (*e.g.*, Ar₃CH, Ar₃P) and Ar₃Z (*e.g.*, Ar₃B), and also for the diaryl systems Ar₂ZXY (*e.g.*, Ar₂CHCl, Ar₂PH), Ar₂ZX₂ (*e.g.*, Ar₂CH₂, Ar₂O), and Ar₂ZX (*e.g.*, Ar₂CO, Ar₂O), 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.² One group of compounds evincing such behavior consists of molecules containing two or more aromatic ring

(1) This work was supported by the National Science Foundation (GP-30257), and was presented as a Solvay Lecture at the Free University of Brussels, March 1972.

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

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