^{13}C Spin-lattice Relaxation in Substituted Benzenes

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Summary Spin-lattice relaxation of phenyl ring carbons in mono-substituted benzenes indicates that the tumbling of these molecules in solution is anisotropic; relaxation is dominated by dipole–dipole interactions with contributions from other mechanisms.

Pulsed Fourier transform n.m.r. methods are particularly suited for the study of ^{13}C nuclear spin-lattice relaxation under high resolution conditions, *i.e.*, determination of the ^{13}C spin-lattice relaxation time (T_1) for each identifiable carbon nucleus in a compound.[1] ^{13}C Spin-lattice relaxation occurs by several mechanisms—particularly dipole–dipole interactions with protons—but also through mechanisms involving ^{13}C chemical shift anisotropy, spin-rotation interactions, the presence of unpaired spins such as O_2, and sometimes arising from rapid chemical exchange situations. The nuclear Overhauser effect (NOE), which is a by-product of the proton decoupling irradiation in typical ^{13}C n.m.r. experiments, occurs only to the extent that the ^{13}C-^{1}H dipole–dipole (DD) interaction contributed to the total spin-lattice relaxation of a given ^{13}C nucleus. When the DD mechanism is entirely responsible for the spin-lattice relaxation of a nucleus, then the NOE for that nucleus is 2·99 (expressed as the integrated peak intensity with ^{1}H decoupling divided by the integrated peak intensity in the absence of ^{1}H irradiation). The actual contribution of the DD mechanism can be calculated if both T_1 and the experimental NOE are determined.[2] Variable magnetic field and variable temperature studies can be used to estimate the contributions of the various other relaxation mechanisms.

Few ^{13}C T_1 values of aromatic carbons have been reported in the literature.[3] We now report T_1 values and experimental NOE values for six mono-substituted benzenes and for benzene itself. The T_1 values were determined on a Varian XL-100-15-FT n.m.r. system at 25·2 MHz by the inversion–recovery technique (T-90°–T-180°–t-90°-pulse sequence).[4] The samples were not degassed except as noted.

Several points arise from the data (see Table): (i) The spin-lattice relaxation of benzene itself is dominated by the DD mechanism with significant contributions from other mechanisms.† In benzene, rapid rotation on the six-fold symmetry axis could lead to significant contribution from the spin rotation (SR) mechanism. Without further work it is not possible to confirm whether SR or the chemical shift anisotropy (CSA) relaxation mechanism is more important. Most of the non-DD relaxation in undegassed benzene results from the presence of dissolved O_2. The contribution of relaxation due to O_2, calculated from the increase in T_1 for degassed benzene, is $R_1 = 1/T_1 \simeq 1/100$s. (In approximate agreement with ref. 3a.)

T_1 *and* NOE *values for* X-*substituted benzenes*

X	T_1(sec)[a] C(1)	C(2)	C(3)	C(4)	α	β	NOE[b] C(1)	C(2)	C(3)	C(4)	α	β
–H[c]	23						2·30					
–H (degassed) . .	29·3						2·60					
$-CH_3$[d]	58	20	21	15	16·3		1·43	2·32[f]	2·32[f]	2·70	1·61	
$-CH{=}CH_2$[e,h] . .	75	14·8	13·5	11·9	17·0	7·8	2·1	3·0	3·0	3·0	3·0	3·0
$-C{\equiv}CH$[c]	56	13·2	13·2	9·0	53	8·5	1·46	2·89	2·92[f]	2·92[f]	1·51	2·95
$-C{\equiv}CH$ (degassed)[e]	107	14·0	14·0	8·2	132	9·3	1·8	3·0	2·9[f]	2·9[f]	1·9	3·0
–OH[g]	21·5	4·4	3·9	2·4			—	—	—	—		
$-NO_2$[e,h]	56	6·9	6·9	4·8			2·03	2·97	2·97	3·03		
–Ph[e,h]	61	5·9	5·9	3·2			1·9	3·0	3·0	3·0		

[a] Determined by inversion recovery pulse sequence. Samples not degassed unless noted. T_1 values ±5—10% (38°). [b] Absolute NOE unless noted. Expressed as the ratio of integrated intensities in ^{13}C {^1H} and undecoupled ^{13}C FT experiments; using pulse intervals = 5 times the longest T_1 value. Estimated maximum error ±0·1. [c] $(CD_3)_2CO$ solvent, *ca.* 20%. [d] Neat. [e] $(CD_3)_2CO$ solvent, *ca.* 20%. [f] Two carbons determined together. [g] CCl_4 solvent, 6 : 1 mole ratio CCl_4 : PhOH. [h] Not absolute NOE; relative NOE: based on the assumption each protonated carbon integration *ca.* 2·99 in a ^{13}C {^1H} experiment.

(ii) In the substituted benzenes all T_1 values for protonated carbons (carbons with directly attached protons) are shorter than the T_1 for benzene, reflecting longer molecular correlation times (τ_C) due to their larger size. The nuclear Overhauser enhancements of protonated ring carbons in the substituted benzenes are usually near the theoretical maximum, indicating domination of the dipole–dipole mechanism.‡ The longer T_1 values for non-protonated carbons result from less efficient dipole–dipole relaxation (dependent on $1/r^6$ where $r = {}^{13}C{-}{}^1H$ internuclear separation). As shown by the reduced NOE's (see Table), relaxation due to O_2 and CSA compete more favourably with DD relaxation for non-protonated carbons in these small molecules.§ (iii) Since no attempt was made to control variations in solution viscosity for the various substituted benzenes, it is impossible to correlate accurately absolute experimental T_1 values for different compounds. It is clear from the Table, however, that carbons *para* to the single substituent relax faster than do the carbons *ortho* or *meta* to that substituent. This results from preferred rotation around the axis bisecting the substituent and the ring.[5] (iv) The relaxation times for protonated substituent carbons were generally comparable to the T_1 values for the protonated ring carbons. Since the vinyl substituent in styrene is not axially symmetric, 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 CH_2 T_1 values are approximately in the expected 2 : 1 ratio.[1b,2]

Schmidt and Chan,[6] citing experimental work of Hill and Freeman (unpublished) theoretically derive dipole–dipole and spin–rotation contributions to the relaxation of the CH_3 group in toluene. Their calculations are in close agreement with the results of our T_1 and NOE measurements in toluene. T_1 Measurements at 70° confirm the domination of SR relaxation for the CH_3 group.[7]

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† A recent reference by Alger and Grant (ref. 3b) reports a higher NOE for benzene and, thus, lower contribution from mechanisms other than dipole–dipole relaxation. It was not noted whether their sample was degassed. We repeated our NOE determinations on 2 degassed benzene samples several times and feel that our maximum error is <0·07. The discrepancy between their measurements and ours and the significance of the benzene NOE values reported in the present study will be discussed in a future publication.

‡ Mono-substituted benzenes which have $T_1 > 15$—20 s for a protonated ring carbon should have significant contributions from CSA and dissolved oxygen. Integrations of the ^1H decoupled and undecoupled ^{13}C spectra of toluene indicate that the NOE is not complete for the *ortho* and *meta* carbons (T_1 *ca.* 20 s) (see Table).

§ Allerhand notes that in large, rigid molecules, DD relaxation often dominates even for non-protonated carbons. T_1 values in these large molecules range from 0·2 to several seconds.

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[6] C. F. Schmidt, jun., and S. I. Chan, *J. Magn. Resonance*, 1971, **5**, 151.

[7] G. C. Levy and F. A. L. Anet, unpublished data.