

## Nuclear Magnetic Resonance Relaxation Times of Chemically Shifted Protons

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**Summary** Proton relaxation times  $T_2$  for chemically shifted nuclei measured by a refined Carr-Purcell method compare well with  $T_1$  values except in aromatic compounds where significant differences appear in dilute solutions.

MEASUREMENT of the individual relaxation times  $T_1$  and  $T_2$  for the different protons of organic molecules could give useful chemical information, but the traditional spin-echo technique is limited because the normal pulse parameters give a frequency spread which effectively spans the entire proton spectrum.

We have extended the spin-echo technique so as to be able to distinguish typical chemical shifts but not fine coupling constants.<sup>1</sup> This method has successfully yielded values of  $T_2$  for chemically shifted nuclei, although experimental difficulties prevented quantitative  $T_1$  measurements. A field-frequency locked high resolution n.m.r. spectrometer using a Perkin-Elmer R10 magnet and a programmed digital pulse generator were built. This apparatus contains several innovations.

The pulse widths are much greater than normal, so that spectral resolution is correspondingly improved. There is, however, a systematic conflict between resolution and the lowest relaxation times that can be accurately measured.<sup>1c</sup> The values taken as a reasonable compromise were  $90^\circ = 30$  ms,  $180^\circ = 60$  ms, giving a spectral resolution of about 8 Hz and permitting  $T_2$  measurements down to about 3 s. A sideband technique was used with the signals recovered by

phase sensitive detection. During reception of the echo train an additional phase detection system was used to monitor the signal in dispersion mode and thus enable the spectrometer to be field-frequency locked on to the echoes. Because of the high field homogeneity and spectral resolution the duration of each echo was much longer than usual (*ca.* 1 s) and thus the echo train could be recorded directly with a medium speed pen recorder. A fuller account of the apparatus will be published.<sup>1a</sup>

Using the Meiboom-Gill modification<sup>2</sup> of the Carr-Purcell sequence<sup>3</sup> we have obtained a series of  $T_2$  measurements which may be compared with the corresponding  $T_1$  values already in the literature.<sup>4-8</sup> These refer to measurements at various frequencies, on pure liquids or solutions in  $\text{CS}_2$  normally at ambient temperature. Our results were obtained at 40 MHz and  $33.3^\circ$ ; all samples were thoroughly degassed before use. The accuracy of the  $T_2$  measurements is estimated as *ca.* 5%.

Frequency and temperature differences must be considered in the interpretation of corresponding pairs of values of  $T_1$  and  $T_2$ . Frequency is probably unimportant because (for the dipolar relaxation mechanism at least) the correlation time will be sufficiently short for the approximation  $\tau_c \ll 1/\omega$  to be equally valid at any normally used frequency. The temperature difference is significant, but as measurements were all made at fairly similar temperatures, the effect will be small. Thus a direct comparison of corresponding  $T_1$  and  $T_2$  values from the Table is reasonable as a first approximation.

## Measured relaxation times (in seconds)

Compound	$T_1(\text{pure})$	$T_2(\text{pure})$	$T_1(\infty)$	$T_2(\infty)$	$T_{1\text{ref.}}$
Benzene	22	21	107	67	4
Toluene-aliphatic	9.8	10.1	16	16.1	} 4,5,6,7
Toluene-aromatic	16.2	17.5	67	22	
<i>o</i> -Xylene-aliphatic	6.8	6.5	13.5	14.3	
<i>o</i> -Xylene-aromatic	13.3	13.4	61	21	} 4
<i>p</i> -Xylene-aliphatic	7.5	7.6	11.9	12.3	
<i>p</i> -Xylene-aromatic	14.6	14.3	43	22	} 4,5
Mesitylene-aliphatic	5	6.2 <sup>a</sup>	10.6	9.2	
Mesitylene-aromatic	10	10.5	40	15	} 4,5,6,8

<sup>a</sup> May be subject to unusually high instrumental error.  $T_1(\infty)$  and  $T_2(\infty)$  are values at infinite dilution in  $\text{CS}_2$ .

The values given in the Table show that, subject to experimental error and the above conditions,  $T_1 = T_2$  for aliphatic protons in all the cases investigated throughout the entire concentration range. It has been demonstrated<sup>4</sup> that the aliphatic  $T_1$ 's of these compounds can quite well be predicted by calculations for the dipolar relaxation mechanism, although the spin-rotational mechanism may become significant at elevated temperatures.<sup>7,9</sup> Our own results for the corresponding  $T_2$ 's show that the same mechanism dominates the spin-spin relaxation also.

The behaviour of the aromatic protons is different. For the pure liquids  $T_1 = T_2$ , but at infinite dilution  $T_2 < T_1$  in all cases investigated.

The explanation of this phenomenon may not be straightforward. The aromatic  $T_1$  values are reasonably well predicted using the dipolar relaxation mechanism, as are the aliphatic values.<sup>4</sup> It appears that for the aromatic protons an additional relaxation mechanism is in operation but affecting only the spin-spin relaxation times. According to relaxation theory—in particular that of Redfield<sup>10</sup>—such

behaviour would indicate that the relaxing field is spatially anisotropic or that it has a long correlation time.

Whatever the nature of the effect, it is seen only for the aromatic protons. Scalar relaxations seem unlikely because although there exists coupling between ring protons, a possible source of the necessary modulation of this coupling is unknown. A possible mechanism can be advanced which considers the effect of the aromatic ring currents.<sup>11</sup> As the molecules are buffeted by Brownian motion, the supplementary field will also fluctuate. This field will be slight (*ca.*  $10^{-2}$  G) and very rapid such that any "direct" relaxation effect would be minimal. However, it might give rise to a "pseudo" spin-rotational interaction in that the averaged value of this fluctuating field would alter whenever rotational motion of the molecule is interrupted, and thus give rise to the expected long correlation time. This mechanism is tentative and needs theoretical justification to have proper validity.

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