The Effect of Paramagnetic Species on the Nuclear Magnetic Resonance Spectra of Nitrogen-15

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Summary In addition to appreciable gains in sensitivity resulting from reduction of long spin-lattice relaxation times, the addition of small amounts of paramagnetic material eliminates the possibility of low or zero intensities arising from partial quenching of the negative nuclear Overhauser effect when relaxation mechanisms other than dipole–dipole interactions are present.

Various workers have recently demonstrated the possibility of observing n.m.r. spectra of the nitrogen-15 isotope in its natural abundance.[1] Apart from the obvious limitations imposed by the low sensitivity of this nucleus, the results have shown that there are two major problems inhibiting its routine detection. One arises as a result of the long nitrogen-15 spin-lattice relaxation times, particularly notable in cases where there are no protons directly bonded to the ^{15}N nucleus.[2] The problem is equally severe when the pulsed-mode is employed, since the small flip angles and/or long delays between successive pulses needed to obtain the free induction decay reduce the gain in sensitivity normally expected from using this technique.[3] The second problem is a consequence of the negative nuclear Overhauser effect resulting from incoherent irradiation of the proton resonances[4] when dipole–dipole interaction of the ^{15}N nucleus with the protons is the dominant relaxation mechanism. The Overhauser effect can be a considerable asset since an approximately fourfold increase in intensity of nitrogen resonances may be obtained in favourable cases. However, competing relaxation mechanisms can result in intensities varying anywhere between normal positive signal and full Overhauser inversion. Consequently there is a significant possibility of obtaining reduced or even zero intensities,[5] unlike the situation for ^{13}C n.m.r. Our preliminary observations suggest that reduction of nitrogen spin-lattice relaxation times may be achieved with complete 'quenching' of the nuclear Overhauser effect by the addition of small amounts of paramagnetic reagent. Our work was prompted by the successful application of such reagents to more tractable problems in carbon-13 spectroscopy.[6] Of the various transition-metal species used for these studies, the properties and general attributes of tris (acetylacetonato)chromium (III)[6b] appeared to be most suitable for the current investigations.

Table 1. *Variation in* ^{15}N *signal intensities as a function of added paramagnetic for benzonitrile* (**1**) *and 4-bromobenzonitrile* (**2**)

Cr(acac)$_3$[a]	S/N(**1**)[b]	S/N(**2**)[b]
0	6	11
0·03	23	29
0·06	34	38
0·09	40	43
0·11	43	46
0·13	39	44

[a] Molar concentration; [b] Mean peak height divided by root-mean-square noise. Values obtained for 512 pulses using an acquisition time of 0·4 s.

All measurements were made on a Bruker HFX 13 spectrometer operating at 9·12 MHz. All samples were contained in 5 mm spinning tubes and degassed initially to remove the effects of molecular oxygen. An external sample of hexafluorobenzene provided the ^{19}F resonance for field-frequency stabilization.

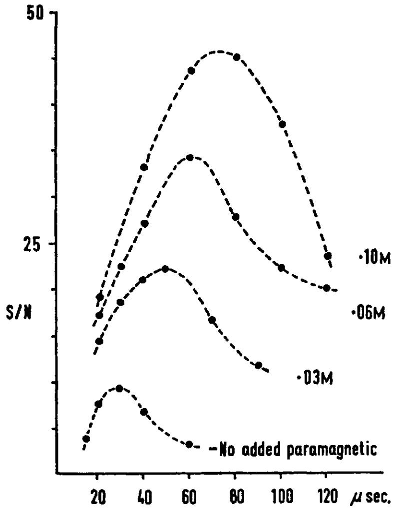

Figure. *The dependence of the* ^{15}N *signal intensity in 4-toluonitrile on pulse duration for different concentrations of paramagnetic additive.*

The data in Table 1 show the variation in signal intensities as a function of added paramagnetic for 1M solutions of some freshly-prepared ^{15}N-enriched benzonitrile derivatives in deuteriochloroform. The ^{15}N nucleus in benzonitrile is known to have a very long T_1 value[2] and the almost complete absence of dipole–dipole interactions with the ring protons render proton decoupling unnecessary thus conveniently eliminating the complications due to a variable Overhauser effect. Fairly rapid pulsing in the Fourier mode was employed using single-coil detection and all variables were kept constant apart from the pulse length which was optimized to produce maximum signal intensity for each different solution. The Figure shows the depend-

Table 2. *Variation of the nuclear Overhauser enhancement of N-methyl*[^{15}N]*formamide with added* Cr(acac)$_3$

Cr(acac)$_3$[a]	I/I_0[b]
0	−3·5
0·01	−1·8
0·03	−0·8
0·05	0·0
0·07	+0·7
0·09	+0·9
0·11	+1·0
0·13	+1·0

[a] Molar concentration; [b] Ratio of the observed intensity to the limiting intensity, $I_0 \pm 0·2$.

ence of the optimum pulse length on molar concentration of Cr(acac)$_3$ for a solution of 4-toluonitrile.

In all cases studied useful gains in intensity were obtained for concentrations of Cr(acac)$_3$ up to 0·1M after which the effect of line broadening became apparent; in the case of benzonitrile the signal-to-noise ratio was increased by a factor of seven at the optimum concentration. The gains obtained in the other two cases were not quite as substantial and could result from shorter initial T_1 values. However, integrated intensity ratios were difficult to obtain and therefore quantitative predictions based on signal-to-noise ratios should be treated cautiously since under the given experimental conditions coarse sampling of the frequency spectrum could be responsible in part for the minor variations observed. In all cases small upfield shifts in the order of a few Hz were noted over the concentration range studied.

A second experiment was conducted to determine the effect of the paramagnetic species on the nuclear Overhauser effect. A 2M solution of ^{15}N-enriched N-methyl formamide in deuteriochloroform was used. Spectra were obtained in the frequency sweep mode and protons were decoupled using noise modulation centred at the CW frequency (for NH proton). Single sweep integrated intensities were obtained using sweep rates of 0·12 Hz s^{-1} while keeping H_1 well below saturation level (Table 2).

Progressive addition of Cr(acac)$_3$ resulted in gradual reduction in intensity of the inverted signal through zero to a positive value, at which stage relaxation of the nitrogen nucleus presumably proceeds mainly *via* the unpaired electrons of the chelated complex. No further intensity changes were observed at concentrations greater than 0·11M in Cr(acac)$_3$ although slight line broadening became apparent. The maximum value of I/I_0 may be attributed to the nuclear Overhauser enhancement in the absence of paramagnetic molecules provided that I_0 corresponds to the intensity obtained without decoupling, a reasonable assumption in the absence of a 'three spin effect'.[7] The difference between the observed value and the maximum theoretical value ($-3·94$) could be due to small contributions to the spin-lattice relaxation as a result of exchange modulation of the scalar N–H spin–spin coupling or even spin rotation interactions.

These results suggest that use of this technique can ensure predictable positive intensities for proton decoupled nitrogen-15 resonance in addition to substantial gains in sensitivity when T_1 values are long.

We thank the S.R.C. for the spectrometer, a research assistantship (A.I.W.), and a fellowship (L.F.F.).

(*Received*, 21*st August* 1972; *Com.* 1458.)

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