Nitrogen-14 Couplings in Aliphatic Nitramines

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LAMBERTON *et al.*[1] have recently given details of the n.m.r. spectra of a series of aliphatic nitramines. They concluded that the shielding effect of the $-N(NO_2)-$ group is very similar to that of oxygen in *O*-alkyl compounds. They also stated that in two cases out of over twenty compounds examined, they observed that protons on carbon atoms alpha to the nitramino group showed a small ^{14}N-coupling. Thus the methyl protons of dimethylnitramine showed a triplet splitting, $J = 1{\cdot}4$ c./sec. whilst the CH_3N and CH_2N signals of ethylmethylnitramine showed coupling of 1·3 and 1·7 c./sec. respectively.

We also have examined some aliphatic nitramines by n.m.r. and by using ^{14}N double irradiation techniques it is possible to show that coupling between nitrogen and protons on the alpha carbon atoms in the nitramines is quite general. However, this coupling usually results only in a broadening of the proton signals. For all compounds shown in the Table, simultaneous application of R_F power at the ^{14}N resonant frequency (7·22 Mc./sec. for protons observed at 100 Mc./sec.) caused some sharpening of all peaks due to protons on alpha carbon atoms. The increases in peak amplitudes caused by the ^{14}N irradiation ranged from about 15% for the CH_3 group of compound 6 up to about 120% for the CH_2 group of compound 7. In compound 1, dimethylnitramine, we found the same splitting of 1·4 c./sec. reported by Lamberton and in this case ^{14}N irradiation causes the collapse of the triplet to a single line.

By analogy with other systems where coupling between ^{14}N nuclei and β-CH protons has often been found to be stronger than that between ^{14}N nuclei and α-CH protons (see reference 1 for references), Lamberton[1] reasoned that in the nitramines the observed coupling is probably due to the ^{14}N nucleus of the nitro-group rather than that of the amino-group. By measuring the critical ^{14}N irradiation frequency that most effectively removes the splitting or broadening of the signal due to the protons on the alpha carbon atoms, the chemical shift of the coupled ^{14}N nucleus can be derived.[2] These are shown in the Table. The ^{14}N chemical shifts are quoted with respect to that of the nitrate nitrogen of 4·5M-ammonium nitrate in aqueous 3N-hydrochloric acid, *i.e.* the reference used by Herbison-Evans and Richards for their collection of ^{14}N data.[3] Also shown in the Table are the chemical shifts of protons on the alpha carbon atom, *i.e.* those showing the ^{14}N coupling. These proton values support Lamberton's observation[1] that the shielding effect of the nitramine group is very similar to that of oxygen. It can be seen that the ^{14}N shifts fall between 20—30 p.p.m. Such

^{1}H *and* ^{14}N *Chemical shifts of coupled nuclei in some nitramines*

	Compound	Solvent	^{1}H chemical shifts (δ)				^{14}N chemical shift (p.p.m.)
			CH$_3$N	CH$_2$N	CHN	NH	of coupled ^{14}N nucleus
1.	$\mathrm{Me_2N\cdot NO_2}$	CDCl$_3$	3·41				21·8 ± 1·5
2.	$\mathrm{NC\cdot[CH_2]_3\cdot NH\cdot NO_2}$	CDCl$_3$		3·53		9·0	28 ± 10
3.	$\mathrm{HO_2C\cdot CH_2\cdot NH\cdot NO_2}$[a]	D$_2$O		3·89			21 ± 4
4.	$\mathrm{EtO_2C\cdot CH_2\cdot NH\cdot NO_2}$[b]	D$_2$O		4·04			21 ± 7
5.	$\mathrm{H_2N\cdot CO\cdot CH_2\cdot NH\cdot NO_2}$	D$_2$O		4·13			24 ± 3
6.	$\mathrm{HO_2C\cdot CH_2\cdot NMe\cdot NO_2}$	D$_2$O	3·48	4·59			26 ± 4
7.	$\mathrm{NC\cdot CH_2\cdot NMe\cdot NO_2}$	D$_2$O	3·49	4·88			24 ± 3
8.	$\mathrm{(Me\underset{\vert}{C}H\cdot NH\cdot NO_2)_2}$	acetone			4·50	10·5	26 ± 7

[a] di-K salt; [b] mono K salt.

values are typical of the ^{14}N nuclei of nitro-groups, but are over 100 p.p.m. lower than the values expected for the ^{14}N nuclei in the amino-group.[3] Clearly therefore, the nitro-group nitrogen nuclei are responsible for the observed couplings in the aliphatic nitramines.

Presumably, the nuclear quadruple relaxation rate of the nitro-group nitrogen nucleus determines whether splitting or merely broadening of the resonances of the coupled protons on the alpha carbon atom is found. Only when the rate is slow will splitting be observed. The broadening generally found in the nitramines indicates that an intermediate quadrupole relaxation rate is normally the case. For very fast relaxation rates, the ^{14}N nucleus would be effectively decoupled from the alpha protons and the double irradiation experiment would have no effect.

Most of the compounds in the Table were examined in D$_2$O and under these conditions the NH protons of the nitramine group were not observed. Thus the NH protons must be reasonably labile. Lamberton found this also. In compounds 2 and 8, examined in CDCl$_3$ and acetone respectively, broadened NH proton signals were found at low field. These NH proton signals were not affected by ^{14}N irradiation. This is expected if the exchange rate for these protons is fast enough to effectively decouple them from the ^{14}N nucleus.

A Varian HA 100 Spectrometer was used with the probe doubly-tuned to accept the ^{14}N frequency which was derived from a Schomandl synthesiser. Full details of the apparatus and the experimental procedures for obtaining the ^{14}N chemical shifts have been given already.[2]

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[2] P. Hampson and A. Mathias, *Mol. Phys.*, 1966, **11**, 541.

[3] D. Herbison-Evans and R. E. Richards, *Mol. Phys.*, 1964, **8**, 19.