

Nuclear Spin-Spin Interactions. ^{14}N - ^1H Spin-Spin Coupling in Quaternary Enammonium Salts¹

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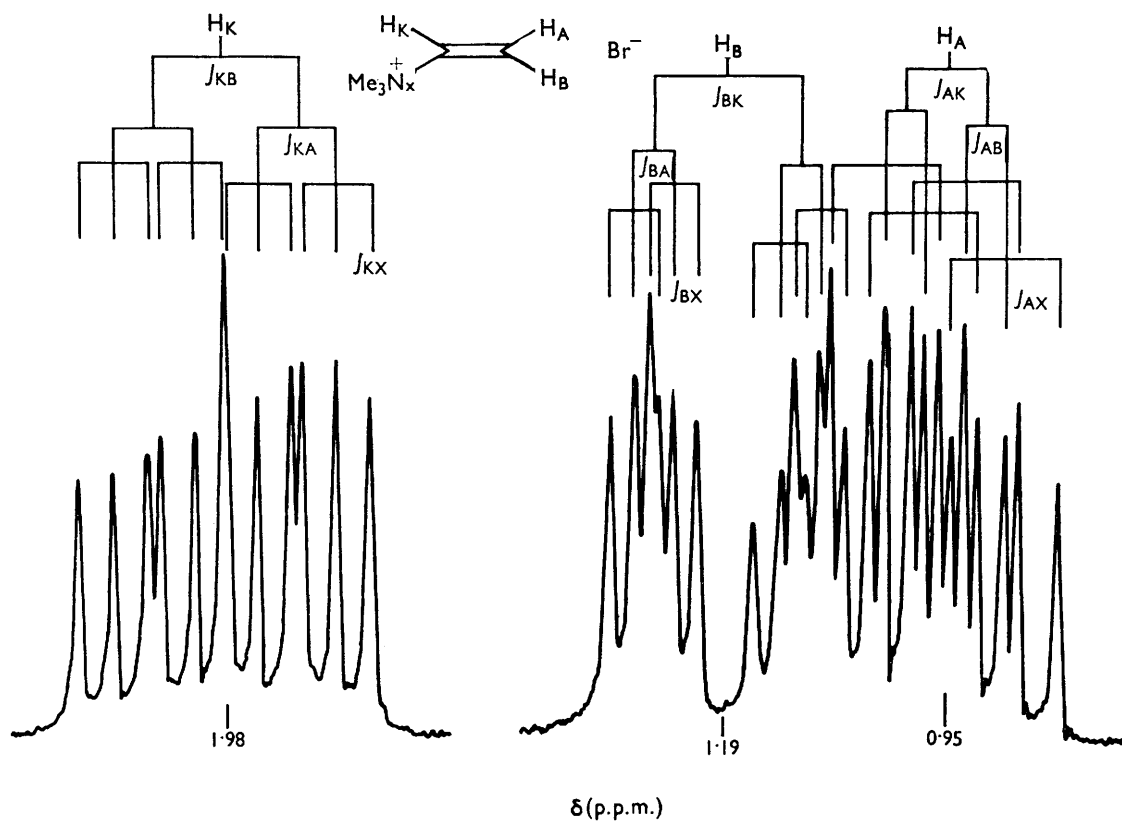
Slow quadrupolar relaxation of the ^{14}N nucleus in certain tetra-alkylammonium salts permits the observation of spin-spin coupling between the ^{14}N and ^1H nuclei.^{1,2} When the rate of quadrupolar relaxation increases, the couplings gradually disappear.^{1,3} The observation of N-H coupling is therefore directly related to the electric-field gradients at the ^{14}N nucleus.

We report the observation of ^{14}N - ^1H couplings in several enammonium salts.⁴

The spectrum of the vinylic region of trimethylvinylammonium bromide, $\text{Me}_3\overset{+}{\text{N}}\text{-CH}=\text{CH}_2$, Br^- (I), is shown in the Figure. It is of the ABKX type and is formed by three subspectra of the ABK type, each corresponding to one of the spin states of the nitrogen nucleus. This is confirmed by double irradiation $\{^{14}\text{N}\}$ - ^1H at the nitrogen resonance frequency: the observed pattern of the vinylic protons is then an ABK spectrum, identical to the subspectrum corresponding to the nitrogen spin state 0 in the single-resonance spectrum.

The measured splittings are given in the Table. A triplet splitting of *ca.* 0.5 c./sec. is also observed for the CH_3 signal. This points to a highly symmetrical environment of the ^{14}N nucleus, and one can calculate³ a lower limit of *ca.* 1 sec. for the quadrupolar relaxation time of the ^{14}N nucleus. From the existing correlations between substituent electronegativity⁵ and $J_{\text{H,H}}$ in substituted ethylenes⁶ it is reasonable to assume the relative order: $|J_{\text{H,H}}|(\text{trans}) > |J_{\text{H,H}}|(\text{cis}) > |J_{\text{H,H}}|(\text{gem})$ for the H,H couplings in compound (I) $J_{\text{H,H}}(\text{trans})$ and $J_{\text{H,H}}(\text{cis})$ being positive and $J_{\text{H,H}}(\text{gem})$ being presumably negative. It is seen that the N-H couplings follow a different order: $|J_{\text{N,H}}|(\text{trans}) > |J_{\text{N,H}}|(\text{gem}) > |J_{\text{N,H}}|(\text{cis})$.

In compound (I) the N-H (*trans*) coupling corresponds to a dihedral angle of 180° and may be considered as a measure of $^3J_{\text{N,H}}(\text{trans})$ in ethylammonium salts.² Using then the value $^3J_{\text{N,H}} = 2.2$ c./sec. measured for $\text{Me}_3\overset{+}{\text{N}}\text{Et}_3 \text{Br}^-$, one may calculate $^3J_{\text{N,H}}(\text{gauche}) \sim 0.5$ c./sec. It thus



FIGURE

Vinyl proton pattern in the n.m.r. spectrum of $\text{Me}_3\text{N}^+\text{-CH}=\text{CH}_2 \text{Br}^-$ at 100 Mc/sec.

TABLE

Chemical shifts (in p.p.m. downfield from H_2O) and coupling constants (in c./sec.) for D_2O solutions of compounds:^a

Compound	Chemical Shifts	Coupling $J_{\text{H,H}}$	Constants
			$J_{\text{N,H}}$
(I) A = B = K = H Y = Br	$\delta_{\text{A}} = 0.95$ $\delta_{\text{B}} = 1.19$ $\delta_{\text{K}} = 1.98$	$J_{\text{A,B}} = \mp 4.1$ $J_{\text{A,K}} = \pm 8.5$ $J_{\text{B,K}} = \pm 15.0$	$J_{\text{N,A}} = 5.6$ $J_{\text{N,B}} = 2.6$ $J_{\text{N,K}} = 3.6$
(II) A = B = H K = Y = Br	$\delta_{\text{A}} = 1.50$ $\delta_{\text{B}} = 1.92$	$J_{\text{A,B}} = \mp 6.3$	$J_{\text{N,A}} \sim 3.5$ $J_{\text{N,B}} = \text{b}$
(III) A = B = H K = Y = Cl	$\delta_{\text{A}} = 1.30$ $\delta_{\text{B}} = 1.48$	$J_{\text{A,B}} = \mp 6.3$	$J_{\text{N,A}} \sim 3.5$ $J_{\text{N,B}} = \text{b}$
(IV) A = B = H K = OEt, Y = Br	$\delta_{\text{A}} = -0.16$ $\delta_{\text{B}} = 0.18$	$J_{\text{A,B}} = \mp 6.6$	$J_{\text{N,A}} = 3.8$ $J_{\text{N,B}} = \text{b}$
(V) B = K = H A = CO_2H , Y = Br	$\delta_{\text{B}} = 1.75$ $\delta_{\text{K}} = 2.4$	$J_{\text{B,K}} = \pm 13.5$	$J_{\text{N,K}} \sim 2.5$ $J_{\text{N,B}} \sim 1.8$

^a Measured with an A-60 spectrometer at 90°, except for compound (I) (HA-100; 30°). The parameters given are from first-order analysis.

^b Couplings washed out by quadrupolar relaxation.

seems that vicinal N-H couplings also follow the general pattern for angular dependence of vicinal coupling constants.⁷

The spectral parameters of some derivatives⁸ of $\text{Me}^{\delta}\text{N}^{\delta+}\text{-CH}=\text{CH}_2\text{Br}^-$ are given in the Table. It is seen that the presence of substituents increases the electric-field gradient at the nitrogen nucleus, whose quadrupolar relaxation becomes fast enough to destroy the *cis*-N-H coupling even

at 90°. The *trans*-N-H coupling, though not resolved at 30°, is visible at 90°.⁹

Furthermore, both $|J_{\text{N,H}}|$ (*gem*) and $|J_{\text{N,H}}|$ (*trans*) decrease as H is replaced by a more electronegative substituent Br, OEt, or CO₂H. On the basis of the existing correlations between J and substituent electronegativity,⁶ one may suggest that $J_{\text{N,H}}$ (*gem*) and $J_{\text{N,H}}$ (*trans*) [and by analogy, also $J_{\text{N,H}}$ (*cis*)] are probably of the same sign, and positive.¹⁰

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¹⁰ (a) $^3J(^{14}\text{N-H})$ is positive in ethyl isonitrile (A. J. R. Bourn, D. G. Gillies, and E. W. Randall in "Nuclear Magnetic Resonance in Chemistry", ed. B. Pesce, Academic Press, New York, 1965, p. 280).

(b) $^3J(^{15}\text{N-H})$ is negative in [¹⁵N]acetonitrile (W. McFarlane, *Mol. Phys.*, 1966, **10**, 603); allowing for the opposite gyromagnetic ratios of ¹⁴N and ¹⁵N, the corresponding $^3J(^{14}\text{N-H})$ is positive.