The Sign of Indirect ^{14}N–^{1}H Spin Couplings in Trimethylvinylammonium Bromide[1]

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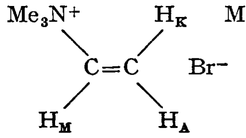
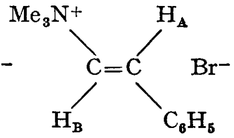
SEVERAL workers have found[2] and discussed[3,4] the fact that indirect ^{14}N–C–H and ^{14}N–C–C–H spin couplings are clearly observed in some tetra-alkylammonium ions in which the electric field at the ^{14}N atom is highly symmetrical and the quadrupole relaxation time of the ^{14}N nucleus is relatively long. So far as we are aware, such ^{14}N–^{1}H spin couplings have not been reported for other compounds except alkyl isonitriles,[5] in which the signs of $J(^{14}N\text{–C–C–H})$ and $J(\text{H–C–C–H})$ (positive) were reported to be opposite to that of $J(^{14}N\text{–C–H})$.[6]

We have found that spin couplings between ^{14}N and the vinyl protons as well as between ^{14}N and the methyl protons [at τ 6·65, $|(^{14}N\text{–}CH_3)| = 0{\cdot}5_0$ c./sec.] are clearly observed in the p.m.r. spectrum of trimethylvinylammonium bromide (I) in deuterium oxide even at ordinary probe temperature.



(I)



(II)

As shown in the Figure, the signals of three vinyl protons appear as 36 well-resolved lines (the AKM part of an AKMX system) at 100 Mc./sec. On the basis of the correlation of J(H,H) with the substituent electronegativities in monosubstituted ethylenes,[7] we can assume the order of the magnitude of J(H,H) between vinyl protons as follows from the electronegativity of $N^{+}Me_3$ (3·16) obtained earlier;[4] $J[\text{H,H}(trans)] > J[\text{H,H}(cis)] > |J[\text{H,H}(gem)]|$ (probably negative). Although the relative signs of $J(^{14}N,H)$ to J(H,H) cannot be determined owing to the lack of the ^{14}N spectral pattern,[8] the relative signs of J(H,H) and those of $J(^{14}N,H)$ were determined by ^{1}H–$\{^{1}H\}$ double resonance "tickling" experiments demonstrated by Freeman and Anderson.[9] Of the sixteen different possibilities in the arrangement of the energy levels of this AKMX spin system, the one which reasonably accounts for the results of the experiments[10] is that in which $J[\text{H,H}(trans)]$ and $J[\text{H,H}(cis)]$ are of like signs opposite to the sign of $J[\text{H,H}(gem)]$ and which all $J(^{14}N,H)$ have the same sign. The observed coupling constants are as follows (in c./sec.);

$J[H_K,H_M\ (trans)] = \pm 14{\cdot}8$, $J[H_A,H_M\ (cis)] = \pm 8{\cdot}3$,
$J[H_A,H_K\ (gem)] = \mp 4{\cdot}1$
$J[^{14}N,H_A\ (trans)] = \pm 5{\cdot}5$, $J[^{14}N,H_K\ (cis)] = \pm 2{\cdot}6$,
$J[^{14}N,H_M\ (gem)] = \pm 3{\cdot}5$

We have also observed the splittings of vinyl proton signals at τ 3·09 and 2·72 by the ^{14}N nucleus in trimethyl-(*trans*-β-phenylvinyl)ammonium bromide (II) in deuterium oxide at 100°c. The coupling constants obtained are as follows (in c./sec.);

$J[H_A,H_B(trans)] = 14{\cdot}2$, $J[^{14}N,H_A(cis)] = 2{\cdot}2$,
$J[^{14}N,H_B(gem)] = 2{\cdot}9$

The absolute values of these J's are smaller than the corresponding values in (I), respectively. The J(H,H)-values are known to show a negative trend with increasing electronegativity of the substituent X in CHR=CHX.[7b] The negative shift of the $J[\text{H,H}(trans)]$-value from (I) to (II) can be explained by the higher electronegativity of the phenyl group than that of the hydrogen. Pople and Brothner-By interpreted this fact about $J[\text{H,H}(gem)]$ using the molecular-orbital theory.[11] Thereafter, McLauchlan and Schaefer have extended

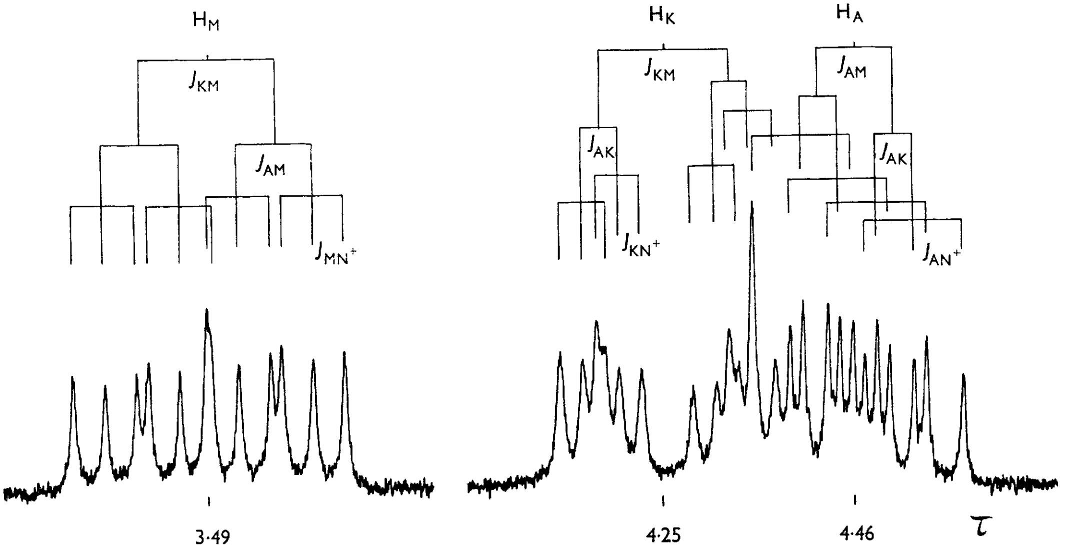


FIGURE *The vinyl proton signals in the p.m.r. spectrum of trimethylvinylammonium bromide in deuterium oxide at* 100 *Mc./sec.*

the theory to the case of $J[^{13}C,H(gem)]$ to account for experimental data in a qualitative way.[12] We can reasonably assume that a similar correlation holds also between $J[^{14}N^+,H(gem)]$ and the electronegativity of the substituent X in $Me_3N^+CH{=}CHX$. Therefore, the sign of all the $J(^{14}N,H)$'s is suggested to be positive as the value of $J[^{14}N,H(gem)]$ is smaller in (II).

All the $J(^{31}P,H)$'s in trivinylphosphine were reported to have the same sign (positive).[13] However, the relative sequence in their magnitudes is different from that of $J(^{14}N,H)$'s in (I) presented here. This difference might arise mainly from the difference in hybridization between the neutral ^{31}P atom and the cationic ^{14}N atom. The sign of $J(^{31}P\text{–}C\text{–}H)$ was reported to be absolutely positive or negative depending on hybridization of the ^{31}P or the C atom.[14,15] We have confirmed that the sign of $J(^{14}N\text{–}C\text{–}H)$ can also be changed by hybridization of the ^{14}N or the C atom.

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[10] The double resonance experiments were performed by using a Varian HA-100 spectrometer operating at 100 Mc./sec. in the frequency sweep and the external Me_4Si locked mode with a Hewlett–Packard HP-200ABR audio-oscillator. The line positions (from sodium 3-trimethylsilylpropane-1-sulphonate as an internal reference in D_2O) were measured directly by using a Hewlett–Packard HP-5212A electronic counter with accuracies of ±0·1 c./sec. or less.

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