

^{14}N , ^1H and ^1H , ^1H Spin Couplings in Quaternary Enammonium Salts^{1,2}

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Abstract: The pmr spectra of trimethylvinylammonium bromide (I), trimethyl-(*trans*- β -phenylvinyl)ammonium bromide (II), trimethyl-(α -bromovinyl)ammonium bromide (III), trimethyl-(α -chlorovinyl)ammonium bromide (IV), and trimethyl-(α -ethoxyvinyl)ammonium bromide (V), and the ^{14}N nmr spectrum of I have been investigated. The ^1H , ^{14}N double-resonance spectra of I and II have also been determined. The relative signs of spin-coupling constants, $J_{\text{H,H}}$ and $J_{^{14}\text{N,H}}$ have been determined by the ^1H , ^1H spin-tickling method. The absolute signs of these J 's are inferred by employing substituent effects on J 's. The results are as follows; the sign of $J_{\text{H,H}(\textit{trans})}$ and $J_{\text{H,H}(\textit{cis})}$ (positive) is opposite to that of $J_{\text{H,H}(\textit{gem})}$ and all $J_{^{14}\text{N,H}}$'s have positive sign. Weak long-range spin couplings between the N-methyl and vinyl protons were observed. Structural effects on $J_{^{14}\text{N,H}}$'s are discussed and compared to the effects on $J_{\text{X,H}}$ values where X are some other nuclei. The quadrupolar relaxation of ^{14}N nucleus in the compounds examined is also discussed briefly.

Determination of magnitudes and signs of spin coupling constants, J , is of great importance in nmr spectroscopy because J values can provide much information about molecular structures and physical properties. There are a number of examples of determination of relative signs for various types of J 's between a proton and other nuclei.⁷

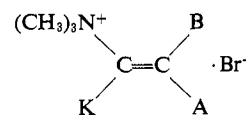
Determinations of the sign of indirect $J_{^{14}\text{N,H}}$ have been reported for a few alkylisocyanides, in which $J_{^{14}\text{N}-\text{C}-\text{H}}$ was determined to be opposite in sign to $J_{^{14}\text{N}-\text{C}-\text{C}-\text{H}}$ and $J_{\text{H}-\text{C}-\text{C}-\text{H}}$ (positive),⁸ and for a tetraethylammonium cation, where the $J_{^{14}\text{N}-\text{C}-\text{C}-\text{H}}$ value has been found to be positive.^{8d}

The spin coupling between ^{14}N and ^1H nuclei is in general washed out by rapid quadrupolar relaxation of the ^{14}N nucleus. However, several workers have reported that slow quadrupolar relaxation of the ^{14}N nucleus in some tetraalkylammonium salts,⁹ alkyliso-

cyanides,^{8,10} and nitramines,¹¹ in which the electric-field gradient at the ^{14}N is highly symmetrical, makes possible the observation of $J_{^{14}\text{N,H}}$. The presence of electronegative substituents or even short methylene chains substituted by electronegative groups, for example, $\text{Et}_3\text{N}^+(\text{CH}_2)_n\text{N}^+\text{Et}_3$ ($n \leq 4$),⁹ⁱ and highly strained $^{14}\text{N}^+$ atoms like those in some azabicyclic small-ring compounds^{9h,12} are known to make the observation of $J_{^{14}\text{N,H}}$ no longer possible.

In previous papers^{1,13} we briefly reported that the $J_{^{14}\text{N}^+, \text{H}}$'s between $^{14}\text{N}^+$ and vinyl protons and between the $^{14}\text{N}^+$ and methyl protons are clearly observed in trimethylvinylammonium bromide (I) even at ordinary probe temperature. Furthermore, $^{14}\text{N,H}$ couplings have recently been observed in some quaternary pyridinium¹⁴ and pyrazinium¹⁵ derivatives.

This paper deals with pmr studies of trimethylvinylammonium bromide (I), and its derivatives II-V. The ^{14}N nmr spectrum of I are reported and the ^1H , ^{14}N double-resonance spectra of I and II are also examined. The analyses of the pmr spectra are effected and the relative signs of the J 's in these molecules are determined by ^1H , ^1H spin-tickling experiments.¹⁶ The absolute signs for $J_{^{14}\text{N,H}}$'s are discussed in connection with substituent effects on the J values.



I, A = B = K = H
 II, B = K = H; A = C_6H_5
 III, A = B = H; K = Br
 IV, A = B = H; K = Cl
 V, A = B = H; K = OC_2H_5

(1) This paper was communicated in preliminary forms by (a) M. Ohtsuru and K. Tori, *Chem. Commun.*, 750 (1966); (b) J. M. Lehn and R. Seher, *ibid.*, 847 (1966).

(2) (a) Nmr Studies of Aliphatic Nitrogen-Containing Compounds. X. For part IX, see M. Ohtsuru and K. Tori, *J. Mol. Spectry.*, 27, 296 (1968); (b) Nuclear Spin-Spin Interactions. VIII. For part VII, see J. P. Kintzinger and J. M. Lehn, *Chem. Commun.*, 660 (1967).

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(7) For example, see J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1966.

(8) (a) See footnote 12 in S. L. Manatt, G. L. Juvinall, and D. D. Elleman, *J. Am. Chem. Soc.*, 85, 2664 (1963); (b) A. J. R. Bourn, D. G. Gillies, and E. W. Randall, "Nuclear Magnetic Resonance in Chemistry," B. Pesce, Ed., Academic Press, New York, N. Y., 1965, p 277; (c) J. P. Maher, *J. Chem. Soc., A*, 1855 (1966); (d) W. McFarlane, *ibid.*, 1660 (1967).

(9) (a) E. Grunwald, A. Loewenstein, and S. Meiboom, *J. Chem. Phys.*, 27, 630 (1957); (b) H. G. Herz and W. Spalthoff, *Z. Elektrochem.*, 63, 1096 (1959); (c) T. Nakagawa and K. Tori, *Ann. Rept. Shionogi Res. Lab.*, 12, 217 (1962); (d) E. A. LaLancette and R. E. Benson, *J. Am. Chem. Soc.*, 85, 2853 (1963); (e) J. M. Anderson, J. D. Baldeschwieler, D. C. Dittmer, and W. D. Phillips, *J. Chem. Phys.*, 38, 1260 (1963); (f) E. Bullock, D. G. Tuck, and E. J. Woodhouse, *ibid.*, 38, 2318 (1963); (g) M. Franck-Neumann and J. M. Lehn, *Mol. Phys.*, 7, 197 (1963); (h) P. G. Gassmann and D. C. Heckert, *J. Org. Chem.*, 30, 2859 (1965); (i) J. M. Lehn and M. Franck-Neumann, *J. Chem. Phys.*, 43, 1421 (1965); (j) E. W. Randall and D. Shaw, *Spectrochim. Acta*, 23A, 1235 (1967); (k) Y. Kawazoe, M. Tsuda, and M. Ohnishi, *Chem. Pharm. Bull.* (Tokyo), 15, 214 (1967).

(10) (a) I. D. Kuntz, Jr., P. von R. Schleyer, and A. Allerhand, *J. Chem. Phys.*, 35, 1533 (1961); (b) A. Loewenstein and Y. Margalit, *J. Phys. Chem.*, 69, 4152 (1965).

(11) A. H. Lambertson, I. O. Sutherland, J. E. Thorpe, and H. M. Yusuf, *J. Chem. Soc., B*, 6 (1968).

(12) J. P. Kintzinger and J. M. Lehn, to be published.

(13) K. Tori, T. Iwata, K. Aono, M. Ohtsuru, and T. Nagagawa, *Chem. Pharm. Bull.* (Tokyo), 15, 329 (1967).

(14) J. F. Biellmann and H. Callot, *Bull. Soc. Chim. France*, 397 (1967).

(15) T. Goto, M. Isobe, M. Ohtsuru, and K. Tori, *Tetrahedron Letters*, 1511 (1968).

(16) W. Brügel (BASF, Ludwigshafen am Rhein) and S. L. Manatt and coworkers (Jet Propulsion Laboratory, California Institute of Technology, Pasadena, Calif.) also analyzed the pmr spectrum of I; private communications.

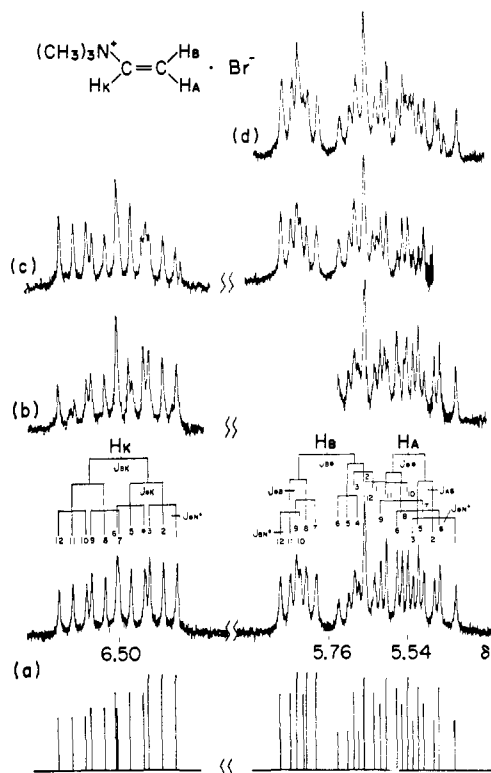


Figure 1. Pmr spectra of the vinyl protons of trimethylvinylammonium bromide (I) in D_2O at 100 MHz at 37° : (a) normal spectrum (experimental and calculated); (b) line B-8 has been irradiated and lines A-8, K-11, A-11, and K-5 become doublets; (c) line A-4 has been irradiated and lines B-4, K-1, B-1, and K-4 become doublets; (d) line K-1 has been irradiated and lines A-4, B-4, A-10, and B-10 become doublets.

Results

The preparation of the substrates I-V is reported in the Experimental Section. The structural proof of II-V is described in a later section.

Pmr Spectra. Figure 1a shows the signals of the vinyl protons in the pmr spectrum of I in D_2O at 100 MHz. Thirty-six well-resolved lines resulting from $^{14}N,H$ and H,H spin-spin coupling are clearly observed even at ordinary probe temperature. This pattern is the ABK part of an ABKX spectrum ($X = ^{14}N$; $I = 1$). It consists of three ABK subspectra, each corresponding to one of the spin states of the ^{14}N nucleus. The lines are numbered to facilitate the interpretation of the double-resonance experiments. A triplet with a splitting of 0.50 Hz is also observed for the signal of the methyl groups.¹⁷ The signals of the vinyl protons were assigned on the basis of the known correlation of $J_{H,H}$ with the substituent electronegativity in substituted ethylenes.¹⁸ It is reasonable to assume the following relative order from the electronegativity of $N^+(CH_3)_3$ (3.16) obtained earlier:¹⁸ $|J_{H,H}^{(trans)}| > |J_{H,H}^{(cis)}| > |J_{H,H}^{(gem)}|$ for the $J_{H,H}$ in I, $J_{H,H}^{(trans)}$ and $J_{H,H}^{(cis)}$ being positive and $J_{H,H}^{(gem)}$ being probably negative.

(17) Such a small splitting is also observed in a number of tetramethylammonium ions. See ref 9 and 13.

(18) (a) T. Schaefer, *Can. J. Chem.*, **40**, 1 (1962); (b) C. N. Banwell and N. Sheppard, *Discussions Faraday Soc.*, **34**, 115 (1962); (c) P. Laszlo and P. von R. Schleyer, *Bull. Soc. Chim. France*, 87 (1964), and references cited therein; (d) F. Hruska, G. Kotowycz, and T. Schaefer, *Can. J. Chem.*, **43**, 2827 (1965); (e) T. Schaefer and H. M. Hutton, *ibid.*, **45**, 3153 (1967).

Thus it is seen that the $J_{^{14}N,H}$'s follow a different order: $|J_{^{14}N,H}^{(trans)}| > |J_{^{14}N,H}^{(gem)}| > |J_{^{14}N,H}^{(cis)}|$.

In the pmr spectra of the substituted compounds II-V, the vinylic protons give rise to a broadened AB-type pattern. In no case are the $^{14}N,H$ couplings visible at ordinary probe temperature. When heating to $90-100^\circ$, both lines of the H_B and H_K doublets in the spectrum of II were split into triplets (see Figure 2). In similar conditions, the H_B signal of III-V remains a broadened doublet, whereas the H_A signal is a clear doublet of triplets for V and an ill-resolved, broadened doublet at triplets for III and IV. The value for $J_{^{14}N,A}$ in III and IV is, therefore, an approximate (minimum) value. The real value should lie near to $J_{^{14}N,A}$ in V. The chemical shifts and coupling constants for compounds I-V are collected in Table I.

Table I. Nmr Parameters for Compounds I-V^a

Compd	Chemical shift (δ)			Coupling constants (J)					
	H_A	H_B	H_K	H,H			$^{14}N,H$		
				<i>trans</i>	<i>cis</i>	<i>gem</i>	<i>trans</i>	<i>cis</i>	<i>gem</i>
I	5.54	5.76	6.50	15.12	8.18	-4.25	5.57	2.53	3.54
I ^b	5.56	5.99	6.88	15.10	8.32	-4.27	5.61	2.52	3.52
I ^c	15.62	8.30	-4.48	5.71	2.47	3.60
II ^d	...	6.96	6.75	14.2	2.2	2.9
				14.5 ^e					
III ^d	6.23	6.65	-6.3	~3.5	<i>f</i>	...
IV ^d	6.03	6.48	-6.5	~3.5	<i>f</i>	...
V ^d	4.55	4.90	-6.6	3.8	<i>f</i>	...

^a Chemical shifts are expressed in parts per million (ppm) downfield from internal DSS in D_2O . Coupling constants are in hertz; the signs are discussed in the text. The differences in the three results on I may arise from solvent and concentration effects. ^b Results obtained by Brügel.¹⁶ ^c Results obtained by Manatt, *et al.*¹⁶ (The spectrum was measured in a saturated solution of D_2O with about 15% DMSO and analyzed as an ABCD₂ spin system where all the nuclei are assumed $I = 1/2$, by using an NM-RENIT computer program.) ^d These values are for spectra taken at $90-100^\circ$. ^e Determined for the fluoroborate in nitromethane. See M. C. Caserio, R. E. Pratt, and R. J. Holland, *J. Am. Chem. Soc.*, **88**, 5747 (1966). ^f Couplings washed out by quadrupolar relaxation.

Vinyl isocyanide has been prepared recently.^{19a} The proton spectrum^{19b,c} of this compound is very complex and at least 28 lines are observable, indicating that splittings due to $^{14}N,H$ couplings are present as may be expected in view of the studies of alkyl isocyanides.¹⁰ Complete double resonance studies of this compound have already been performed to show that all the $^{14}N,H$ couplings are also positive.^{19d}

^{14}N Nmr Spectrum. The ^{14}N nmr spectrum of I was measured at a field of 21 kG on a 30% solution in D_2O . The spectrum shown in Figure 3 was obtained with field-frequency locking on the proton resonance of the $(CH_3)_3N^+$ group which simultaneously achieves heteronuclear $^1H, ^{14}N$ decoupling. Because of the small $^{14}N^+, CH_3$ geminal coupling (0.50 Hz) the fine structure of the ^{14}N resonance is much less apparent in the un-

(19) (a) D. S. Matteson and R. A. Bailey, *Chem. Ind. (London)*, 191 (1967); (b) D. S. Matteson and R. A. Bailey, *J. Am. Chem. Soc.*, **90**, 3761 (1968); (c) we thank Dr. D. S. Matteson for a copy of the pmr spectrum of vinyl isocyanide prior to publication; (d) S. L. Manatt, D. D. Elleman, and W. D. Cumming, unpublished work; we thank Dr. S. L. Manatt for information about the results prior to publication.

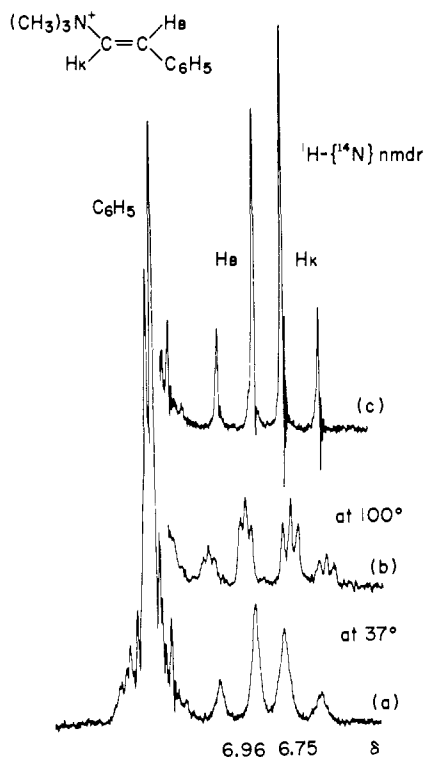


Figure 2. Pmr spectra of the vinyl protons of II in D_2O at 100 MHz: (a) at 37° ; (b) at 100° ; (c) $^1H,^{14}N$ double-resonance spectrum.

decoupled spectrum. The observed, partially overlapping, splittings are in agreement with the $J_{^{14}N,H}$ values obtained from the pmr spectrum. The ^{14}N resonance occurs at 317 ppm upfield from the NO_3^- resonance of an acidified aqueous ammonium nitrate solution, in agreement with reported values for other ammonium salts.⁷

$^1H,^1H$ Homonuclear Double-Resonance Spectra. In order to perform the complete analysis of the spectrum, the relative signs of the three $J_{H,H}$ constants have been determined by $^1H,^1H$ double-resonance "spin-tickling" experiments.²⁰ These experiments also yielded the signs of the three $J_{^{14}N,H}$ constants relative to each other. The signs of the $J_{H,H}$ constants relative to $J_{^{14}N,H}$ could not be determined, as $^1H,^{14}N$ double-resonance "tickling" experiments are needed.²¹ According to the theory,²⁰ only two spin-tickling experiments are necessary to enable us to select one energy-level diagram that reasonably accounts for the spectrum, out of the 16 possibilities in the arrangements of the energy levels of the present ABKX spin system. However, in the present study, more double-resonance experiments were performed to avoid possible ambiguities due to the complexity of the spectral pattern.

Figures 1b-d show the spectra obtained for the vinyl protons of I by spin-tickling experiments. The spectrum observed while irradiating transition B-8 is shown in Figure 1b. Transitions A-8 and K-11 are split into well-resolved doublets whereas transitions A-11



Figure 3. ^{14}N nmr spectrum of I in D_2O at 6.50 MHz with proton stabilization and simultaneous irradiation of the $(CH_3)_3N^+$ proton signal. The chemical shift is expressed in parts per million (ppm) upfield from the NH_4NO_3 resonance.

and K-5 are split into broadened doublets. From this experiment, it is possible to determine all the relative signs of the $J_{H,H}$'s, because spin-ticklings on the lines belonging to the zero spin state ($m_N = 0$) of the nitrogen nucleus are independent of the relative signs of the $J_{^{14}N,H}$'s. It follows that the sign of $J_{H,H(gem)}$ is *opposite* to those of $J_{H,H(trans)}$ and $J_{H,H(cis)}$ (positive) as expected. We confirmed this result from some other experiments, for example, irradiating transition K-2 and observing transitions A-5, A-11, B-5, and B-11.

We determined the relative signs of the $J_{^{14}N,H}$'s from the experiment shown in Figure 1c, where transition A-4 was irradiated. Transitions B-4 and K-1 are split into well-resolved doublets, whereas transitions B-1 and K-4 lead to broadened doublets. This result shows that all the $J_{^{14}N,H}$'s have the same sign. The same result was obtained by irradiating transition K-1 and observing transitions A-4, A-10, B-4, and B-10 (see Figure 1d) and so on.

Figure 4 shows the schematic energy-level diagram (neglecting second-order effects) appropriate to the ABKX system of I obtained from the above experimental results. From this energy-level assignment and the magnitudes of the first-order coupling constants and chemical shifts,¹ the final parameters were calculated by treating the spectrum as three simple ABK spectra, using Swalen-Reilly's NMREN1 and NMRIT program²² with an IBM 7090 computer. The calculated spectrum (the average deviation is about ± 0.04 Hz) is shown in Figure 1a and Table II and the nmr parameters are given in Table I. The $J_{^{14}N,H}$'s were deter-

(20) (a) W. A. Anderson and R. Freeman, *J. Chem. Phys.*, **37**, 85 (1962); (b) R. Freeman and W. A. Anderson, *ibid.*, **37**, 2053 (1962).

(21) For example, see E. W. Randall and J. D. Baldeschwieler, *J. Mol. Spectry.*, **8**, 365 (1962).

(22) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).

mined by the first-order analysis. Figure 5 provides a check of the analysis by comparing the experimental spectrum of the vinyl protons in I with that calculated²² for an operating frequency of 60 MHz.

Table II. The Pmr Spectrum^a of the Vinyl Protons of Trimethylvinylammonium Bromide (I) in D₂O at 100 MHz

Obsd	Calcd	Calcd intensity
547.7	547.71	0.684
551.9	551.81	1.135
556.0	556.04	0.916
560.1	560.14	1.258
566.0	565.99	1.057
570.0	570.09	0.554
580.8	580.76	1.343
584.9	584.86	1.053
639.0	639.00	1.311
647.4	647.33	1.076
653.7	653.78	0.861
662.1	662.10	0.741

^a Center lines of triplets corresponding to $m_N = 0$ are picked out here. All frequencies are expressed in hertz at 100 MHz downfield from internal DSS.

¹H,¹⁴N Double-Resonance Spectra. Double irradiation at the ¹⁴N resonance frequency of about 7.224 MHz while measuring the 100-MHz pmr spectrum of I leads to the vinyl-proton pattern shown in Figure 6c. This is an ABK spectrum corresponding to the subspectrum having the ¹⁴N in the spin state 0 in the single-resonance spectrum at the same operating frequency of 100 MHz. The most striking feature of this ¹H,¹⁴N double-resonance spectrum is the differences in line widths among the vinyl-proton signals. The broadest is the H_B signal and the narrowest is the H_A signal. Triple irradiation at the ¹⁴N+(CH₃)₃ signal and the ¹⁴N-resonance frequency demonstrated that each signal becomes sharper and shows good ringing as shown in Figure 6d. Double irradiation at the ¹⁴N+(CH₃)₃ signal even results in sharpening of every resonance line (compare Figures 6a with 6b). However, the so-called intramolecular nuclear Overhauser effect²³ was not observed, when irradiating the N-methyl signal under these experimental conditions.²⁴ Therefore, the presence of long-range spin couplings between the N-methyl and vinyl protons was revealed. The decreases in half-height line widths of each signal were measured to be about 0.30, 0.15, and 0.08 Hz for the H_B, H_K, and H_A signals, respectively.

Similarly, the ¹H,¹⁴N double-resonance spectrum of I corresponding to an ABC spectral pattern was obtained at 60 MHz on double irradiation at the ¹⁴N-resonance frequency of about 4.33 MHz as shown in Figure 5b. The experimental spectrum agrees well with that calculated by using the parameters listed in Table I as stated earlier.

Figure 2c shows the ¹H,¹⁴N double-resonance spectrum of II in D₂O. The signals of vinyl protons appear clearly as an AB-type quartet. The fact that the lower-

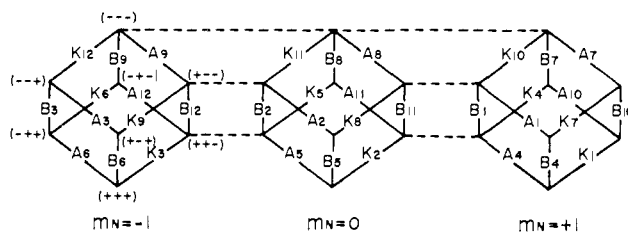


Figure 4. Energy-level diagrams and assignment of the vinyl-proton transitions for I, resulting from the spin-tickling experiments.

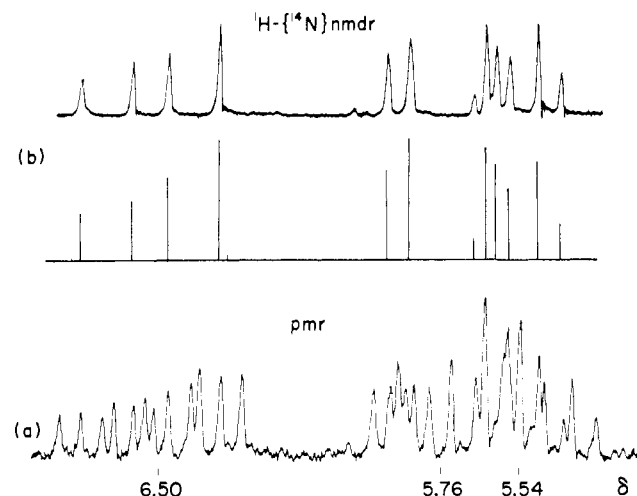


Figure 5. Pmr spectra of the vinyl protons of I in D₂O at 60 MHz at 37°: (a) normal spectrum; (b) experimental and calculated ¹H,¹⁴N double-resonance spectrum (at a reduced gain).

field peaks are somewhat broader indicates that they are due to the proton *cis* to the ¹⁴N⁺ nucleus in view of the long-range spin couplings between the N-methyl protons and H_B, and further, between the phenyl protons and H_B.²⁵

The present ¹H,¹⁴N double-resonance experiments can lead us to determine the relative chemical shifts of ¹⁴N⁺ nuclei of I and II in D₂O because the ¹⁴N-resonance signals are so narrow as shown above (see Figure 3). The ¹⁴N resonance in II occurs at about 14.5 ± 2 ppm downfield from that in I; this is due to the phenyl-substitution effect.

Discussion

Configurations of the Double Bond in Compounds II-V. The *trans* configuration of the substituents on the double bond in II follows immediately from the large $J_{H,H}$ value observed (Table I). The *gem* substitution in V results from the studies of Arens, Bouman, and Koerts.²⁶ The very similar J_{AB} values observed in V and in III and IV indicates that these latter compounds are also the *gem* isomers. This is also apparent from the chemical studies of Klages and Drerup.²⁷ Furthermore, the values of $J_{H,H}$ in III-V agree with

(23) F. A. L. Anet and A. J. R. Bourn, *J. Am. Chem. Soc.*, **87**, 5250 (1965).

(24) Recently, a nuclear Overhauser effect was observed on the O-methyl and vinyl proton *cis* to it on a double bond; see M. C. Woods, I. Miura, A. Ogiso, M. Kurabayashi, and H. Mishima, *Tetrahedron Letters*, 2009 (1968).

(25) G. P. Newsoroff and S. Sternhell, *Australian J. Chem.*, **21**, 747 (1968), and references cited therein.

(26) J. F. Arens, J. G. Bouman, and D. H. Koerts, *Rec. Trav. Chim.*, **74**, 1040 (1955).

(27) F. K. Klages and E. Drerup, *Ann.*, **547**, 65 (1941).

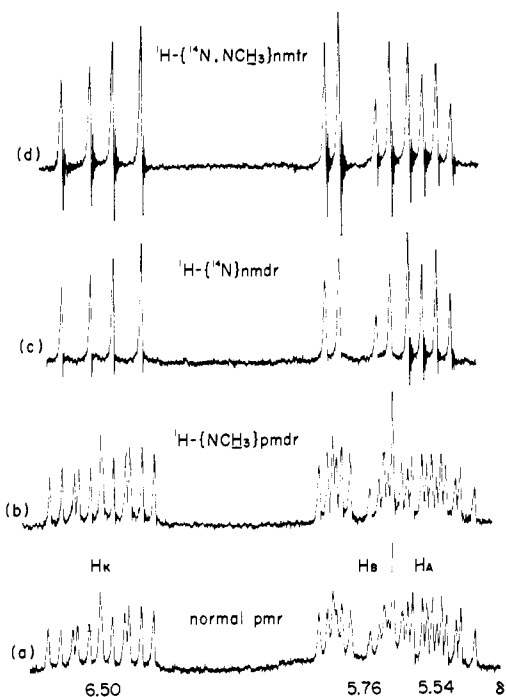


Figure 6. PMR spectra of the vinyl protons of I in D_2O at 100 MHz at 37° ; (a) normal spectrum; (b) $^1H, ^1H$ double-resonance spectrum irradiated at the $(CH_3)_3N^+$ proton signal; (c) $^1H, ^{14}N$ double-resonance spectrum (at a reduced gain); (d) $^1H, ^1H, ^{14}N$ triple-resonance spectrum irradiated at the $(CH_3)_3N^+$ proton and $^{14}N^+$ signals.

what may be expected for a vinylic geminal coupling from the effect of substituent electronegativity.¹⁸ The geminal $J_{H,H}$ value should decrease algebraically, *i.e.*, become more negative, when electronegative substituents are introduced on the double bond of I; this is what is observed for III–V (Table I).

Substituent Effects and Absolute Signs of J 's. Although it is impossible to determine the absolute sign of $J_{^{14}N,H}$ from the above experiments, the investigation of the substituent effects on $J_{^{14}N,H}$ values can be expected to give information about this point.

It is apparent from Table I that the absolute $J_{^{14}N,H}$ values in II–V are *smaller* than the corresponding values in I. The $J_{^{14}N,H(trans)}$ value is seen to decrease especially when electronegative substituents (Cl, Br, and OC_2H_5) are introduced on the double bond. It has well been established that the vicinal $J_{H,H}$ values in a vinyl group are *positive* and decrease, whereas the geminal $J_{H,H}$ value is *negative* or *positive* and decreases algebraically, becoming more negative, when electronegative substituents are introduced on the double bond.¹⁸ Correlations between substituent electronegativity and $J_{H,H}$ values in such systems have frequently been discussed in detail.¹⁸ In the present case, the correlations also hold for the $J_{H,H}$'s as can be seen from Table I. Pople and Bothner-By interpreted the behavior of geminal J_{H-C-H} using molecular orbital theory.²⁸ Thereafter, McLauchlan and Schaefer have extended the theory to the case of geminal $J_{^{13}C-C-H}$ to account for the experimental data in a qualitative way²⁹ (*vide*

(28) J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965).

(29) K. A. McLauchlan and T. Schaefer, *Can. J. Chem.*, **44**, 321 (1966).

Table III. Selected $J_{^{14}N^+-C-H(gem)}$ Values (in Hertz)

Compound	$J_{^{14}N-C-H(gem)}$	Ref
$CH_3N^+ \equiv C^-$	-2.3	8d
$CH_3CH_2N^+ \equiv C^-$	-2.0	8c
	-1.9	8d
$\begin{array}{c} H & & N^+ \equiv C^- \\ & \diagdown & / \\ & C = C & \\ & / & \diagdown \\ H & & H \end{array}$	+2.32	19d
$(CH_3)_3N^+CH_2CH_3 \cdot I^-$	$\leq \mp 0.3$	8c,d
$\begin{array}{c} \text{quinolinium ring} \\ \\ CH_2CH_3 \end{array} \cdot I^-$	-0.8 ^a (N, CH_2)	c
$\begin{array}{c} (CH_3)_3N^+ \\ \\ C = C \\ / \quad \backslash \\ H \quad \quad H \end{array} \cdot Br^-$	+3.54	This work
$\begin{array}{c} CH_3 \\ \\ NC \\ \\ H \end{array} = \begin{array}{c} H \\ \\ NC_6H_5 \end{array}$	$\left\{ \begin{array}{l} 6.00^{a,b} \text{ (N,H)} \\ \sim 0 \text{ (N,CH}_3\text{)} \end{array} \right.$	39
$\begin{array}{c} CH_3 \\ \\ NC \\ \\ CH_3 \end{array} = \begin{array}{c} H \\ \\ O \end{array}$	$\left\{ \begin{array}{l} +11.12^a \text{ (N,H)} \\ -0.78^a \text{ (N,CH}_3\text{)} \\ -0.85^a \text{ (N,CH}_3\text{)} \end{array} \right.$	8b, 36
$\begin{array}{c} H \\ \\ H_2NC \\ \\ O \end{array}$	+13.54 ^a	8b

^a These figures were converted from $J_{^{15}N,H}$. ^b This value is believed to be positive (see the text). ^c From $^1H, ^1H$ double-resonance studies the signs of $J_{^{15}N-CH_2}$ (1.1 Hz) and $J_{^{15}N-C-CH_3}$ (3.2 Hz) have been determined to be opposite in ^{15}N -quinolinium ethiodide (M. Ohtsuru and K. Tori, unpublished results). Then, the positive value was taken for $J_{^{15}N-CH_3}$, according to ref 8. Also refer to K. Tori, M. Ohtsuru, K. Aono, Y. Kawazoe, and M. Ohnishi, *J. Am. Chem. Soc.*, **89**, 2765 (1967).

infra). Assuming that a similar correlation holds for the geminal $J_{^{14}N^+,H}$ in the present systems, all the $J_{^{14}N^+,H}$ values are suggested to be *positive* in I–V.³⁰

It is generally accepted that the vicinal H,H coupling in substituted ethanes is positive, *i.e.*, of the same sign as the vicinal couplings between vinyl protons.⁷ The above suggestion of the positive sign for $^{14}N,H$ couplings in a vinyl group is then in conformity with the determination of the positive sign for the vicinal $^{14}N,H$ couplings in the isocyanides and the tetraethylammonium cation.⁸

Incidentally, the angular dependence of the vicinal $^{14}N^+,H$ coupling suggested earlier^{1b} has recently been confirmed for $J_{^{14}N^+-C-C-H}$ by using some rigid bicyclic

(30) (a) Quite recently, an $^1H, ^{14}N$ double-resonance study of I by using the ^{14}N indor method has been reported by W. McFarlane and R. R. Dean, *J. Chem. Soc., A*, 1187 (1968); they have confirmed our results regarding the absolute signs of $J_{^{14}N,H}$'s; (b) Dr. S. L. Manatt^{1b} has informed us that he and coworkers also performed the $^1H, ^1H, ^{14}N$, and $^1H, ^1H, ^{14}N$ double- and triple-resonance experiments on I which yielded the same results as those by McFarlane and Dean,^{30a} and by us; we thank Dr. S. L. Manatt for the information and data (in Table I) on the spectrum of I prior to publication.

quaternary ammonium salts.³¹ Thus, the $^{14}\text{N}^+-\text{C}-\text{C}-\text{H}$ coupling also appears to follow the general pattern for angular dependence of vicinal X,H couplings.^{7,31}

Structural Effects on Geminal $J_{^{14}\text{N}-\text{C}-\text{H}}$. Table III lists some selected geminal $J_{^{14}\text{N}-\text{C}-\text{H}}$ values. Structural effects on these J 's will be compared to those on geminal $J_{\text{H}-\text{C}-\text{H}}$, $J_{^{13}\text{C}-\text{C}-\text{H}}$, and $J_{^{31}\text{P}-\text{C}-\text{H}}$. Since the magnitudes of N,H couplings have recently been found to depend strongly upon the orientation of lone-pair electrons on the N atom concerned,³² the present discussion will be limited to $J_{^{14}\text{N}-\text{C}-\text{H}}$ where the nitrogen atom is positively charged (no lone-pair electrons).

As described in the above section, the correlations of $J_{\text{H}-\text{C}-\text{H}}$ with the s character of bonding orbitals of the intervening C atom and/or the electronegativity of substituents on the C atom have well been established both experimentally³³ and theoretically;²⁸ $J_{\text{H}-\text{C}-\text{H}}$ values increase algebraically, *i.e.*, show a positive trend, with an increase of the s character. A similar trend has also been reported on $J_{^{13}\text{C}-\text{C}-\text{H}}$.^{34,35}

An nmr study of N,N-dimethylformamide- ^{15}N has shown that the geminal $J_{^{15}\text{N}-\text{CO}-\text{H}}$ is negative (-15.6 Hz), whereas the two $J_{^{15}\text{N}-\text{CH}_3}$ are positive ($+1.2$ and $+1.1$ Hz).^{35,36} By taking into account of the opposite signs of the magnetogyric ratios of ^{14}N and ^{15}N nuclei, $J_{^{14}\text{N}-\text{CO}-\text{H}}$ becomes positive (see Table III). Then the increase of $J_{\text{H}-\text{C}-\text{H}}$ from -12.4 in methane^{33,37} through about $+2.3$ in ethylene³³ to about $+42$ Hz in formaldehyde,³³ and that of $J_{^{13}\text{C}-\text{C}-\text{H}}$ from -4.5 in $^{13}\text{CH}_3\text{CH}_3$ ³⁸ through $+3.2$ in $^{13}\text{CH}_3\text{CH}=\text{CCl}_2$ ³⁵ to $+26.6$ Hz in $^{13}\text{CH}_3\text{COH}$ ³⁵ are reflected in the change of $J_{^{14}\text{N}-\text{C}-\text{H}}$ from very small values in ethylammonium salts through $+3.5$ in I to 11.1 Hz in N,N-dimethylformamide and in that from about -2.0 in ethyl isocyanide^{38,c,d} to $+2.3$ Hz^{19d} in vinyl isocyanide (Table III). It should, however, be noted that the electronic structures at the nitrogen sites are not directly comparable in the present case. The value of $J_{^{14}\text{N}-\text{C}-\text{H}}$ in N,N-dimethyl-N-phenylformamidine³⁹ is probably positive by analogy with the others discussed here. A similar discussion has been given for the effect of substituents on the C atom upon $J_{^{31}\text{P}-\text{C}-\text{H}}$ ⁴⁰ and $J_{^{31}\text{P}^+-\text{C}-\text{H}}$ values.⁴¹

The effects of substituents on the X atom upon $J_{\text{X}-\text{C}-\text{H}}$ are quite complex; they have been discussed for

$J_{^{13}\text{C}-\text{C}-\text{H}}$ ^{34,35} and for $J_{^{31}\text{P}-\text{C}-\text{H}}$ ⁴⁰⁻⁴² and have been correlated with the change in hybridization of the X atom; such effects become even more complex when d orbitals are present on the X atom as discussed on $J_{\text{Sn}-\text{C}-\text{H}}$.⁴³

From the values listed in Table III, it appears that the geminal $J_{^{14}\text{N}-\text{CH}_2}$ shows a negative trend, when the ^{14}N atom is changed from an sp^3 hybridization in ethylammonium cation through the sp^2 state in quinolinium ethiodide to the sp state in ethylisocyanide. This change is entirely analogous to the variation observed for $J_{^{13}\text{C}-\text{C}-\text{H}}$, when the ^{13}C atom goes through the sp^3 , sp^2 , and sp states. In fact, the $J_{^{13}\text{C}-\text{CH}_3}$ values are respectively equal to -4.5 , -7.2 , and -10.6 Hz in $\text{CH}_3^{13}\text{CH}_3$,³⁸ $\text{CH}_3^{13}\text{CH}=\text{CCl}_2$,³⁵ and $\text{CH}_3^{13}\text{C}\equiv\text{CH}$.⁴⁴

These analogies suggest that the electronic effects studied by Pople and Bothner-By²⁸ in the case of $J_{\text{H}-\text{C}-\text{H}}$ are also operative in the case of $J_{^{14}\text{N}-\text{C}-\text{H}}$.

Comparison of $^{14}\text{N},\text{H}$ and X,H Couplings in Compounds of $\text{XCH}=\text{CH}_2$ Type. In order to compare the $J_{^{14}\text{N},\text{H}}$ values obtained to other $J_{\text{X},\text{H}}$ values in compounds of $\text{XCH}=\text{CH}_2$ type, several data on $J_{\text{X},\text{H}}$'s selected from the literature are listed in Table IV. Table IV also lists normalized coupling constants, $J'_{\text{X},\text{H}} = (J_{\text{X},\text{H}}/\gamma_{\text{X}}\gamma_{\text{H}}) \cdot (\mu_0^2/\hbar)$, where γ is the magnetogyric ratio and μ_0 is the nuclear magneton, so as to compare the couplings only by the electronic properties of bonds.^{37,45}

In Table IV, all $J'_{\text{X},\text{H}(\text{trans})}$ and $J'_{\text{X},\text{H}(\text{cis})}$ were assumed to be positive and $J'_{\text{X},\text{H}(\text{trans})}$ are always larger than $J'_{\text{X},\text{H}(\text{cis})}$. Furthermore, these J' values apparently increase with an increase of the atomic number,⁴⁶ although direct comparison does not seem justified because of the variety of substituents on X atom and on the vinyl group. On the other hand, it seems difficult to correlate the $J'_{\text{X},\text{H}(\text{gem})}$ values with the atomic number only. At this stage, more data are necessary for a complete discussion to be worthwhile.

Nitrogen Quadrupolar Relaxation. As a last point, it is of considerable interest to note that the quadrupolar relaxation in I is slow enough to allow the 0.50 Hz splitting of the $^{14}\text{N}^+(\text{CH}_3)_3$ proton signal and the fine structures in the ^{14}N -nmr spectrum to be observed. Using the general line shapes calculated by Pople⁴⁷ and by Suzuki and Kubo,⁴⁸ one may estimate a lower limit of about 1 sec for the quadrupolar relaxation time T_{q} of the ^{14}N nucleus in I. In comparable experimental conditions no such coupling is observed in $(\text{CH}_3)_3^{14}\text{N}^+\text{C}_6\text{H}_5\cdot\text{Br}^-$. The expected $^{14}\text{N},\text{CH}_3$ cou-

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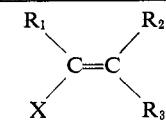
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Table IV. The Selected $J_{X,H}$ Values in Compounds of $XCH=CH_2$ Type (in Hertz)^a

X				$J_{X,H}$			Ref
	R ₁	R ₂	R ₃	<i>trans</i>	<i>cis</i>	<i>gem</i>	
¹ H	H	H	H	+19.1 (0.612)	+11.7 (0.375)	+2.3 (0.074)	33, c
¹³ CH ₃	H	Cl	Cl	+3.2 (0.41)	35
¹⁴ N ⁺ Me ₃	H	H	H	+5.57 (2.47)	+2.53 (1.12)	+3.54 (1.57)	This work
¹⁴ N ⁺ Me ₃	H	Ph	H	...	+2.2 (0.98)	+2.9 (1.29)	This work
¹⁵ NHPh	H	CO ₂ Me	CO ₂ Me	≈0.2 ^b (0.06)	39
¹⁵ NHPh	CO ₂ Me	H	CO ₂ Me	≠3.5 (1.11)	39
¹⁵ NHPh	CO ₂ Me	CO ₂ Me	H	...	≠1.7 (0.54)	...	39
¹⁹ F	H	H	H	+52.4 (1.79)	+20.1 (0.68)	+84.7 (2.89)	d
				+51.60 (1.758)	+19.46 (0.663)	+84.56 (2.881)	e
²⁹ SiMe ₃	Cl	H	H	-10.51 (1.696)	-4.36 (0.704)	...	f
²⁹ SiCl ₃	Cl	H	H	-21.20 (3.421)	-7.48 (1.21)	...	f
³¹ P(CH=CH ₂) ₂	H	H	H	+30.21 (2.392)	+13.62 (1.079)	+11.74 (0.930)	g
³¹ P+Me ₂ Ph	H	H	H	+48.48 (3.839)	+25.29 (2.003)	+23.98 (1.899)	h
³¹ P+Et ₃	H	H	H	+43.80 (3.468)	+21.71 (1.719)	+21.17 (1.676)	h
³¹ P(O)Ph ₂	H	H	Ph	+40.3 (3.191)	...	+19.3 (1.528)	i
³¹ P(O)OEt ₂	H	H	H	+50.52 (4.000)	+25.09 (1.987)	+22.29 (1.765)	h
				+50.175 (3.973)	+24.825 (1.966)	+20.587 (1.630)	j
¹¹⁹ Sn(CH=CH ₂) ₃	H	H	H	-183.1 (15.747)	-90.6 (7.792)	-98.3 (8.454)	k
¹⁹⁹ HgCH=CH ₂	H	H	H	+295.5 (52.98)	+159.6 (28.61)	+128.5 (23.04)	k
¹⁹⁹ HgOAc	H	H	H	±658 (117.97)	±331 (59.34)	±291 (52.17)	l
²⁰⁵ Tl(CH=CH ₂) ClO ₄	H	H	H	±1618 (89.89)	±805 (44.72)	±842 (46.78)	m
²⁰⁵ Tl(ClO ₄) ₂	H	H	H	±3750 (208.33)	±1806 (100.33)	±2004 (111.33)	m

^a ± or ≠ denotes an assumed sign. Values in parentheses are normalized coupling constants, $J'_{X,H}$.⁴⁵ ^b The sign of this value cannot be assumed at present. ^c For other data, see also ref 33. ^d C. N. Banwell, N. Sheppard, and J. J. Turner, *Spectrochim. Acta*, **16**, 794 (1960). ^e V. S. Watts and J. H. Goldstein, *J. Chem. Phys.*, **42**, 228 (1965). ^f S. S. Danyluk, *J. Am. Chem. Soc.*, **87**, 2300 (1965). ^g W. A. Anderson and R. Freeman, *J. Chem. Phys.*, **39**, 1518 (1963). ^h J. E. Lancaster, *Spectrochim. Acta*, **23A**, 1449 (1967). ⁱ R. Freeman, "Varian Technical Instrument Bulletin," Varian Associates, Palo Alto, Calif., summer, 1965. ^j M. P. Williamson, S. Castellano, and C. E. Griffin, *J. Phys. Chem.*, **72**, 175 (1968). ^k D. W. Moore and J. A. Happe, *ibid.*, **65**, 224 (1961). ^l P. R. Wells, W. Kitching, and R. F. Henzell, *Tetrahedron Letters*, 1029 (1964). ^m J. P. Maher and D. F. Evans, *Proc. Chem. Soc.*, 176 (1963).

pling ($J = 1.9$ Hz) in $(CH_3CH_2)_3^{14}N^+C_6H_5 \cdot I^-$ is still washed out by quadrupolar relaxation leading to an upper limit of T_q of about 0.1 sec for the ¹⁴N nucleus in this compound. It thus seems that the vinyl group in I leaves the electrical symmetry at the nitrogen site nearly undistorted as compared to tetramethyl- and tetraethylammonium ions. Although there may also be an effect from the molecular correlation time, the phenyl group apparently induces a much higher dissymmetry than the vinyl group.⁴⁹ Even introduction of a phenyl group

on the β-carbon atom of the vinyl group in I results in somewhat broadenings of the signals of the vinyl protons which are barely split into triplets at 100°, as can be seen in II.

The presence of electronegative substituents on the α-carbon atom of the vinyl group as in III-V introduces a new dissymmetry factor and leads to a shortening of T_q as compared to I rendering the observation of the ¹⁴N,H couplings difficult even at temperatures of 90–100°, where faster molecular reorientations should increase T_q .^{9e,i,50} with respect to measurements at 30°.

(49) Studies of this and similar effects on the quadrupolar relaxation rate of the ¹⁴N nucleus will be published in a separate paper by J. P. Kintzinger and J. M. Lehn.

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Experimental Section

Nmr Measurements. The pmr spectra were taken with a Varian HA-100 and an A-60A (or A-60) spectrometers in about 10% solutions in D₂O containing DSS as an internal reference at various temperatures. The ¹H, ¹H double-resonance experiments were carried out by using the HA-100 spectrometer operating at 100 MHz in the frequency-swept and DSS-locked mode with a Hewlett-Packard HP-200ABR audiooscillator. The peak positions were calibrated by direct readings of frequencies using a Hewlett-Packard HP-5212A electronic counter with accuracies to ±0.1 Hz. The spectra taken with the A-60A (or A-60) spectrometer were calibrated by the usual side-band method.

The ¹H, ¹⁴N double-resonance spectra of I and III at 100 MHz were recorded on the Varian HA-100 spectrometer equipped with an NMR Specialties HD-60B heteronuclear ¹H, ¹⁴N spin decoupler operating at about 7.224 MHz. All the spectra were taken in the frequency-swept and DSS-locked mode. The modulation frequencies were directly read by using the HP-5212A electronic counter.

The ¹H, ¹⁴N double-resonance spectrum of I at 60 MHz was measured with the Varian A-60 spectrometer equipped with an NMR Specialties HD-60A heteronuclear ¹H, ¹⁴N spin decoupler operating at about 4.33 MHz.

The ¹⁴N nmr spectrum of I was determined with a Spectrospin AG (Zürich) HX-3 spectrometer at a frequency of 6.50 MHz (a field of about 21 kG) with simultaneous field-frequency locking on the N⁺(CH₃)₃ proton resonance and ¹H, ¹⁴N decoupling of the CH₃ protons. The spectrometer was operated in the frequency-swept mode. The solution used was 30% in D₂O; the sample tube has 13 mm o.d. Referencing was achieved by inserting a tube containing an acidified aqueous ammonium nitrate solution.

Materials. Trimethylvinylammonium bromide (I) was commercially available.

Trimethyl-(*trans*-β-phenylvinyl)ammonium bromide (II) was prepared according to Truce and Simms.⁵¹

(51) W. E. Truce and J. A. Simms, *J. Org. Chem.*, **22**, 762 (1957).

Trimethyl-(α-bromovinyl)ammonium bromide (III) was prepared according to Klages and Drerup;²⁷ $\nu_{\text{max}}^{\text{KBr}}$ 3000 (m), 1650 (m), 1625 (m), 1470 (m), 1410 (m), 1235 (m), 1145 (m), 1090 (m), 940 (s), 920 (s), and 875 (s) cm⁻¹.

Anal. Calcd for C₈H₁₁NBr₂: C, 24.50; H, 4.49. Found: C, 24.52; H, 4.44.

Trimethyl-(α,β-dichloroethyl)ammonium Bromide. Chlorine gas was bubbled during 3 hr through a solution of I (4.85 g) in chloroform (200 ml). The dichloro addition compound precipitates out during the reaction. After removal of the solvent, the crystals are washed with small quantities of absolute ethanol to obtain 5.49 g of the dichloro product (yield 80%); $\nu_{\text{max}}^{\text{KBr}}$ 3020-2900 (s), 1450-1490 (s), 1420 (m), 1320 (m), 1285 (s), 1240 (m), 1195 (m), 1140 (w), 1055 (w), 965 (s), 955 (s), 935 (m), 880 (s), 790 (s), and 740 (s) cm⁻¹.

Anal. Calcd for C₈H₁₂NBrCl₂: C, 25.40; H, 5.10. Found: C, 25.57; H, 5.24.

Trimethyl-(α-chlorovinyl)ammonium Bromide (IV). Trimethyl-(α,β-dichloroethyl)ammonium bromide was treated with the equivalent quantity of potassium ethoxide in absolute ethanol at room temperature. Potassium chloride precipitates out. After standing 3 hr at room temperature the solution was filtered and concentrated under reduced pressure. The product (IV) was precipitated by an addition of ether and recrystallized from absolute ethanol (yield ca. 30%). The infrared spectrum (KBr) is nearly identical with that of III.

Anal. Calcd for C₈H₁₁NBrCl: C, 29.95; H, 5.53; N, 6.98. Found: C, 29.92; H, 6.42; N, 6.36.

Trimethyl-(α-ethoxyvinyl)ammonium bromide (V) was obtained by the procedure described by Arens, Bouman, and Koerts.²⁸

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Electron Spin Resonance Studies on Neutral Aromatic Hydrocarbon Radicals

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Abstract: Electron spin resonance (esr) spectra have been obtained for the diphenylmethyl, fluorenyl, and perinaphthenyl neutral free radicals. These radicals were generated *via* thermolysis of phosphazine and/or diazo precursors in solvents capable of hydrogen donation and investigated as a function of temperature. The spectra obtained compared favorably with computer-simulated spectra generated from the experimentally determined hyperfine coupling constants. The geometry of these systems is discussed in light of previously developed semiempirical relationships.

The generation of radical species *via* the thermolysis of certain phosphazines and their diazo precursors, in solvents capable of hydrogen donation, has been demonstrated.¹ Analysis of the products obtained on thermolytic decomposition of diphenylmethylenetriphenylphosphazine was in concert with initial fragmentation to triphenylphosphine and the corresponding diaryldiazomethane; the latter undergoing further frag-

mentation to the carbenic species and subsequent hydrogen abstraction.²

When the diazo precursor, as well as azobisdiphenylmethane³ (a known free-radical precursor) were decomposed, respectively, in decalin, bicyclohexyl, or diphenylmethane solvents, the corresponding free radical was detected.

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