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42. Kazuo Tori, Tatsuo Iwata, Katsutoshi Aono, Masako Ohtsuru, and Toshio Nakagawa : Proton Magnetic Resonance Spectra of Several Types of Substituted Ammonium Ions.*1

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Proton magnetic resonance spectra of substituted ammonium ions were studied in deuterium oxide, being classified in methylammonium, ethylammonium, β-substituted ethylammonium, and vinylammonium ions. The chemical shifts of the methyl groups are discussed in terms of inductive effects of other substituents on nitrogen atoms. From the internal chemical shifts of ethyl groups, the electronegativity of $(Alkyl)_3N^+$ were derived to be 3.16 according to Cavanaugh and Dailey's equation. Spin-coupling constants between ^{14}N and protons were usually observed in the cases where the electric field at the ^{14}N nucleus is thought to be homogeneous.

We suggest that the sign of $J_{^{14}N-C-CH_3}$ in ethyltrialkylammonium ions might be positive. Interestingly, spin-couplings between ^{14}N and the vinyl protons in trimethylvinylammonium bromide were evidently observed even at room temperature.

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In general, the nuclear magnetic resonance signal of a proton capable of interacting with an ^{14}N nucleus ($I=1$) is broadened by quadrupole relaxation of the ^{14}N nucleus unless the nitrogen atom is symmetrically substituted as in ammonium ions, in which the very homogeneous electric field at the ^{14}N nucleus gives the triplet structure to the proton signal, or unless proton exchange is very rapid.[1] Grunwald and coworkers[2] reported the triplet structure of the methyl signal in tetramethylammonium ions ($J_{^{14}N-CH_3}=0.5_4$ c.p.s.). When the electric field at the ^{14}N nucleus is very inhomogeneous as in N-substituted amides, ^{14}N-H proton signal is narrow and split by the α-CH proton(s).[1,3,4] Hertz and Spalthoff[5] firstly reported an interesting indirect spin-coupling between ^{14}N and methyl protons in aqueous solutions of tetraethylammonium ions. The triplet signal of the methyl group is further split to triplets of equal heights ($J_{^{14}N-C-CH_3}=1.5$ c.p.s.). In a previous paper[6] dealing with some proton magnetic resonance spectral features of substituted methylammonium salts, we described substituent effects on the chemical shift of the methyl group attached to the ^{14}N atom and also the interesting indirect spin-coupling in trimethylethylammonium bromide, in which the absolute value of $J_{^{14}N-C-CH_3}$ (2.2 c.p.s.) is larger than that of $J_{^{14}N-CH_2-C}$ (<0.3 c.p.s.).

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*1 This paper constitutes Part Ⅵ of the series of "NMR Studies of Aliphatic Nitrogen-containing Compounds." For earlier papers of this series, see Refs. (3, 6, and 4) (Part Ⅰ, Ⅱ and Ⅲ, respectively), J. Shoji, K. Tori, H. Ōtsuka : J. Org. Chem., **30**, 2772 (1965) (Part Ⅳ), and K. Tori, M. Ohtsuru, T. Kubota : Bull. Chem. Soc. Japan, **39**, 1089 (1966) (Part Ⅴ).

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1) For a leading reference, see G. V. D. Tiers, F. A. Bovey : J. Phys. Chem., **63**, 302 (1959).
2) E. Grunwald, A. Loewenstein, S. Meiboom : J. Chem. Phys., **27**, 630 (1957).
3) K. Tori : Ann. Rept. Shionogi Res. Lab., **12**, 114 (1962).
4) K. Tori, K. Aono, K. Hirai, A. Takamizawa : *Ibid.*, **14**, 198 (1964).
5) H. G. Hertz, W. Spalthoff : Z. Elektrochem., **63**, 1096 (1959).
6) T. Nakagawa, K. Tori : Ann. Rept. Shionogi Res. Lab., **12**, 217 (1962).

Thereafter, several workers[7~14] have reported and discussed this unusual coupling, $J_{^{14}N,H}$, in various quaternary ammonium ions. The confirmation of the assignments of the proton spectra of these ammonium ions was made by ^{14}N spin-decoupling experiments.[7,11] The appearence of triplet of triplets signal of a methyl group was revealed to depend upon the field gradient at the ^{14}N nucleus[12,13] and temperature.[7,13] Several authors have discussed with considerable interest in the magnitudes and in the relative signs of J_{M-CH_2} and J_{M-C-CH_3} in compounds of the type $(CH_3CH_2)_nM$.[14~26] However, so far as we are aware, any discussions on the sign of the coupling constant, $J_{^{14}N-C-CH_3}$, have not yet been reported except for the case of a few alkylisonitriles,[15] in which $J_{^{14}N-C-H}$ was determined to be opposite in sign to $J_{^{14}N-C-C-H}$ and $J_{H-C-C-H}$ (absolutely positive).[27]

In this paper we report the proton magnetic resonance spectra of various types of substituted ammonium ions and discuss the chemical shifts and coupling constants obtained in connection with the nature of substituents attached to the ^{14}N nucleus. Further, interesting spin-couplings between ^{14}N and the vinyl protons observed in trimethylvinylammonium bromide are presented.

We feel that since several ammonium ions treated in this report are biologically active, studies of their physical properties such as proton magnetic resonance spectra are necessary.

Experimental

Proton magnetic resonance spectra were taken with a Varian A-60 spectrometer, the calibration of which was checked by the usual audio side-band method by using a Hewlett-Packard 200CD audio-oscillator and 521C electronic counter, and/or a Varian HA-100 spectrometer operating at 100 Mc.p.s. and in the frequency sweep and DSS locked mode. Proton spin-decoupling experiments were performed by using the HA-100 spectrometer with a Hewlett-Packard 200ABR audio-oscillator. The samples were dissolved into heavy water (about 5%) containing about 1% DSS as internal reference to measure respective proton signals at successively diluted concentrations and at ordinary probe temperature unless otherwise noted. The reproducibility of the chemical shifts was about 0.01 τ. The chemical shifts obtained at several concentrations were extrapolated to infinite dilution. Most of the solutions showed no significant dilution shift in this concentration range, but somewhat larger dilution shifts (about 0.5 p.p.m.) were observed in the compounds XII~XXI and XXXIII~XXXIX. The reproducibility of the coupling constants was about 0.1 c.p.s. or less. The chemical shifts and coupling constants were obtained by the first-order approximation.

The compounds examined were commercially available and were purified in necessary cases.

7) J.M. Anderson, J.D. Baldeschwieler, D.C. Dittmer, W.D. Phillips : J. Chem. Phys., **38**, 1260 (1963).
8) E. Bullock, D.G. Tuck, E.J. Woodhouse : *Ibid.*, **38**, 2318 (1963).
9) M. Franck-Neumann, J.M. Lehn : Mol. Phys., **7**, 197 (1963).
10) E.A. LaLancette, R.E. Berson : J. Am. Chem. Soc., **85**, 2853 (1963).
11) R.S. Milner, D.W. Turner : Chem. Commun., **1965**, 31.
12) P.G. Gassman, D.C. Heckert : J. Org. Chem., **30**, 2859 (1965).
13) J.M. Lehn, M. Franck-Neumann : J. Chem. Phys., **43**, 1421 (1965).
14) A.G. Massey, E.W. Randall, D. Shaw : Spectrochim. Acta, **20**, 379 (1964); *Idem* : *Ibid.*, **21**, 263 (1965).
15) I.D. Kuntz, P. von R. Schleyer, A. Allerhand : J. Chem. Phys., **35**, 1533 (1961).
16) E.B. Baker : J. Chem. Phys., **26**, 960 (1957).
17) P.T. Narashimhan, M.T. Rogers : *Ibid.*, **31**, 1430 (1959).
18) R.E. Dessey, T.J. Flautt, H.H. Jaffé, G.F. Reynolds : *Ibid.*, **30**, 1422 (1959).
19) P.T. Narashimhan, M.T. Rogers : J. Am. Chem. Soc., **82**, 34 (1960).
20) *Idem* : J. Chem. Phys., **34**, 1049 (1961).
21) J.P. Maher, D.F. Evans : Proc. Chem. Soc., **1961**, 208.
22) S.L. Stafford, J.D. Baldeschwieler : J. Am. Chem. Soc., **83**, 4473 (1961).
23) G.J. Karabatsos : *Ibid.*, **83**, 1230 (1961).
24) G.J. Karabatsos, J.D. Graham, F.M. Vane : *Ibid.*, **83**, 2778 (1961); *Idem* : *Ibid.*, **84**, 37 (1962).
25) G. Binsch, J.B. Lambert, B.W. Roberts, J.D. Roberts : *Ibid.*, **86**, 5564 (1964).
26) S.L. Manatt, G.L. Juvinall, D.D. Elleman : *Ibid.*, **85**, 2664 (1963).
27) See the footnote (12) in Ref. (26), and also refer to A.J.R. Bourn, D.G. Gillies, E.W. Randall : "Nuclear Magnetic Resonance in Chemistry," ed. by B. Pesce, p. 277 (1965). Academic Press, New York.

Results and Discussion

Methylammonium Ions——The proton magnetic resonance spectral data on the methyl group in the methylammonium ion derivatives examined are listed in Table I. Changes in the halogen anion, X^-, had no effect upon the chemical shifts, since no ion-pair formation occurs in aqueous solutions.[14] Infinite dilutions used in this study remove the effect even for the aromatic ammonium ions examined which were reported to show this effect owing to the large polarisabilities of aromatic substituents.[14] As discussed in the previous paper,[6] the change in the chemical shifts of the methyl groups in a series of $(CH_3)_3N^+R$ is correlated with the inductive effect of the substituent R. The τ-value decreases in the following order of R (see Table I);

$$C_2H_5>CH_2C_6H_5>CH_3>CH_2CH_2Br\geq CH_2CH_2OH\geq CH_2CH_2OCOCH_3$$
$$>CH_2CH_2Cl>CH_2COO^->CH_2COOH>CH=CH_2>CH=CHC_6H_5>C_6H_5$$

The inductive effect of a substituent R can be expressed in terms of a polar substituent constant σ^*.[28,29] Kan[29] attempted to correlate the chemical shift of the

Table I. Proton Magnetic Resonance Spectral Data on Compounds $CH_3N^+RR'R''\cdot X^-$ Type in D_2O

No.	Compound				Chemical shift of CH_3 (τ)	Coupling constant, $\lvert J_{^{14}N-CH_3}\rvert$ (c.p.s.)
	R	R′	R″	X^-		
I	H	H	H	Cl^-	7.40	*a*)
II	CH_3	H	H	〃	7.28	0.6
III	〃	CH_3	H	〃	7.11	*a*)
IV	〃	〃	CH_3	〃	6.81	0.6_0
V	〃	〃	〃	Br^-	6.81	0.6_0
VI	〃	〃	〃	I^-	6.82	0.5_5 0.5_5 *b*)
VII	〃	〃	C_2H_5	〃	6.91	0.6_0
VIII	〃	〃	CH_2CH_2Cl	Cl^-	6.78	*a*)
IX	〃	〃	CH_2CH_2Br	Br^-	6.81	〃
X	〃	〃	CH_2CH_2OH	Cl^-	6.80	0.4_7
XI	〃	〃	$CH_2CH_2OCOCH_3$	Br^-	6.79	*a*)
XII	〃	〃	CH_2COO^-		6.74	〃
XIII	〃	〃	CH_2COOH	Cl^-	6.70	〃
XIV	〃	〃	$CH_2C_6H_5$	〃	6.89	〃
XV	〃	〃	$H\rangle C=C\langle {}^{H}_{H}$	Br^-	6.68	0.5_0
XVI	〃	〃	$H\rangle C=C\langle {}^{H}_{C_6H_5}$	〃	6.60	*a*)
XVII	〃	〃	C_6H_5	〃	6.36	〃
XVIII	〃	〃	〃	I^-	6.36	〃
XIX	〃	$CH_2C_6H_5$	〃	Cl^-	6.37	〃
XX	Pyridinium			I^-	5.59	〃
XXI	Quinolinium			〃	5.32	〃

a) Not observable. *b*) Ref. (5).

acetic acid and succinic acid protons of acetates and succinates with σ^* values of the alcohol group of the esters. He found that aromatic substituents are responsible for deviations from linearity owing to their magnetic anisotropy. Having attemted to correlate the chemical shifts of the methyl group with the σ^* values of R,[28] we also

28) R. W. Taft, Jr. : "Steric Effects in Organic Chemistry," ed. by M. S. Newman, p. 619 (1956). John Wiley and Sons Inc., New York.

found that the plots for the benzyl, phenyl, and vinyl groups deviate from linearity. Examination of molecular models shows that the benzyl group shifts the methyl signals upfield and that the phenyl and vinyl groups do the signals downfield by their magnetic anisotropies. Another exceptional case is the amine hydrohalides, in which the chemical shift of the methyl group becomes higher with a decrease of the number of the methyl group attached to the nitrogen atom. However, in this case the circumstances are somewhat complicated by the acid-base equilibria as already studied by Grunwald and coworkers.[30]

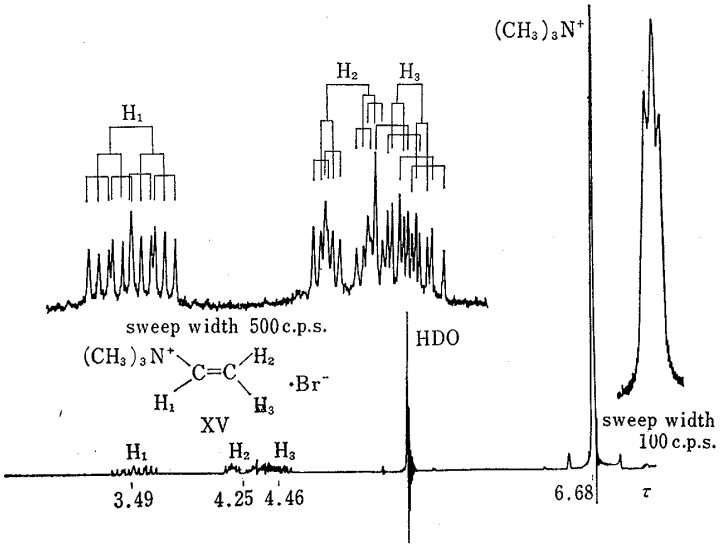


Fig. 1. Proton Magnetic Resonance Spectrum of Trimethylvinylammonium Bromide (XV) in Deuterium Oxide at 100 Mc.p.s. (sweep width 1000 c.p.s.)

The triplet structure with the small splittings of about 0.5~0.6 c.p.s. is always observed in the spectra of tetraalkylammonium ions in which the electric field at the ^{14}N nucleus is very homogeneous. Trimethylvinylammonium bromide (XV) shows a clear triplet for its methyl signal as shown in Fig. 1. This is an exceptional case. No splitting in methyl signals at room temperature was observed in ammonium ions having substituents other than alkyl groups. Dimethylammonium chloride (II) and choline chloride (X) (see Fig. 2) show not well-resolved triplets for their methyl signals.

Ethylammonium Ions——In Table II are listed the proton magnetic resonance spectral data on the ethylammonium ion derivatives examined. The internal chemical shift between the CH_3 and CH_2 groups in ethyl derivatives, $\Delta\delta$, has been used to study the nature of the substituent attached to the ethyl group. Several workers[16,31~33] have discussed correlations between $\Delta\delta$ and the electronegativity of the substituent and found reasonable linear correlations. Massey and coworkers[14] found that $\Delta\delta$ is larger for the cationic species $(CH_3CH_2)_4M^+$ than for the corresponding compounds $(CH_3CH_2)_3M$ where M = N, P, As, and Sb, and ascribed the change in $\Delta\delta$ to the larger electronegativity of the cation M^+, ignoring the magnetic anisotropy

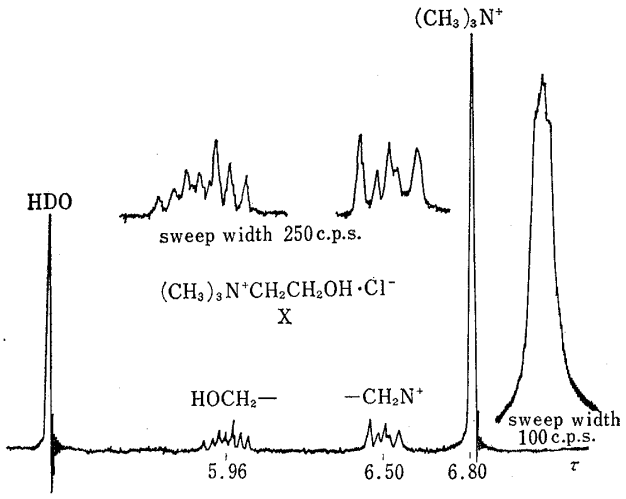


Fig. 2. Proton Magnetic Resonance Spectrum of Choline Chloride (X) in Deuterium Oxide at 100 Mc.p.s. (sweep width 500 c.p.s.)

29) For a leading reference, see R. O. Kan : J. Am. Chem. Soc., **86**, 5180 (1964).
30) E. Grunwald, A. Loewenstein, S. Meiboom : J. Chem. Phys., **27**, 641 (1957).
31) B. P. Dailey, J. N. Shoolery : J. Am. Chem. Soc., **77**, 3977 (1955).
32) H. Spiesecke, W. G. Schneider : J. Chem. Phys., **35**, 722 (1961).
33) J. R. Cavanaugh, B. P. Dailey : *Ibid.*, **34**, 1099 (1961).

TABLE II. Proton Magnetic Resonance Spectral Data on Compounds $C_2H_5N^+RR'R''\cdot X^-$ Type in D_2O

No.	Compound R	R′	R″	X^-	Chemical shift (τ) CH_3	CH_2	$\Delta\delta_{CH_3-CH_2}$ (c.p.s. at 60 Mc.p.s.)	Coupling constant, $\lvert J_{^{14}N-C-CH_3}\rvert$ [a] (c.p.s.)
XXII	H	H	H	Cl^-	8.75	6.96	107.2	[b]
XXIII	C_2H_5	H	H	〃	8.73	6.90	109.9	〃
XXIV	〃	C_2H_5	H	〃	8.73	6.79	116.7	〃
XXV	〃	CH_2CH_2OH	H	〃	8.70	6.72	119.0	〃
VII	CH_3	CH_3	CH_3	I^-	8.64	6.60	122.0	2.2_0 2.1_5 [c]
XXVI	〃	〃	C_2H_5	〃				2.0_1 [c] 1.9 [d]
XXVII	〃	C_2H_5	〃	〃				1.8_5 [c]
XXVIII	C_2H_5	〃	〃	Cl^-	8.75	6.75	120.3	1.8_5
XXIX	〃	〃	〃	Br^-	8.75	6.76	119.4	1.8_5 1.8 [d]
							122.1 [e]	1.8 [e]
XXX	〃	〃	〃	I^-	8.75	6.76	119.4 120 [g]	1.8_0 1.8_0 [c] 1.6_5 [f] 1.7 [g]
XXXI	〃	〃	$(CH_2)_2CH_3$	〃				1.7_8 [c]
XXXII	〃	〃	$(CH_2)_3CH_3$	〃				1.8_0 [c]
XXXIII	〃	〃	$CH_2-CH=CH_2$	〃				1.5_0 [c]
XXXIV	〃	〃	$CH_2C_6H_5$	Cl^-				[b] [d]
XXXV	〃	〃	〃	I^-	8.62	6.77	111.0	1.5_0 [h]
XXXVI	〃	〃	C_6H_5	〃	8.86	6.14	163.1	[b]
XXXVII	$(CH_2)_2CH_3$	$(CH_2)_2CH_3$	$(CH_2)_2CH_3$	〃	8.74	6.72	121.0	1.8_5
XXXVIII	Pyridinium			Br^-	8.36	5.36	181.3	[b]
XXXIX	Quinolinium			I^-	8.26	4.88	202.5	〃

a) The values of $\lvert J_{^{14}N-CH_2}\rvert$ are usually less than 0.5 c.p.s. and not clearly observed.
b) Not observable. c) Ref (12). d) Ref. (13). e) Ref. (7). f) Ref. (8). g) Ref. (14).
h) Observed at elevated temperature (100°).

effect of M in the neutral compounds. Also in this case, changes in the halogen ions for aqueous solutions had no effect upon $\Delta\delta$. The amine hydrohalides are also exceptional. The $\Delta\delta$ values are almost constant for $CH_3CH_2N^+(Alkyl)_3$, although slight difference was observed owing to the kinds of the alkyl group. The averaged value is 121 c.p.s. at 60 Mc.p.s. in deuterium oxide. However, the large differences from the above $\Delta\delta$ value were observed when a phenyl or a benzyl group is attached to the nitrogen atom or in the case of aromatic ammonium ions. These can be ascribed to their ring-current anisotropy effect. From Cavanaugh and Dailey's equation (1),[33] we obtained the electronegativity of $N^+(Alkyl)_3$ to be 3.16, by using the $\Delta\delta$ value of 121 c.p.s.

$$\text{Electronegativity} = 0.0114\Delta\delta\,(\text{in c.p.s. at } 60\,\text{Mc.p.s.}) + 1.78 \qquad (1)$$

As stated earlier, the fact that the value of $\lvert J_{^{14}N-C-CH_3}\rvert$ is larger than that of $\lvert J_{^{14}N-CH_2}\rvert$ is very interesting. In some other molecules of the CH_3CH_2M type, it was recognized that J_{M-CH_2} and J_{M-C-CH_3} are of opposite sign.[14,19~21,27] Among these, the data on tetraalkylphosphonium ions shown in Table III are the most useful for inferring the sign of $J_{^{14}N-C-CH_3}$. The determination of relative signs of $J_{^{14}N-CH_2}$ and $J_{^{14}N-C-CH_3}$ is difficult because of very small value of $\lvert J_{^{14}N-CH_2}\rvert$ (about $\leq$ 0.5 c.p.s.). We can see from Table III that the absolute value of J_{P-C-CH_3} decreases with an increase of the number of the ethyl group. The similarity is seen for the tetraalkylammonium ions examined

Table III. ^{31}P–^{1}H Coupling Constants in Phosphonium Ions (c.p.s.)[a]

Compound	J_{P^+-Me}	$J_{P^+-CH_2-C}$	$J_{P^+-C-CH_3}$
P^+Me_4	14.6	—	—
P^+Me_3Et	14.5	±14.0	∓20.6
$P^+Me_2Et_2$	14.0	±13.3	∓19.5
P^+MeEt_3	13.5	±13.4	∓18.8
P^+Et_4	—	±12.8	∓18.5

a) Taken from Ref. (14). Me=CH_3 and Et=C_2H_5.

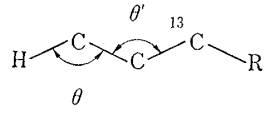
Table IV. ^{13}C–^{1}H Coupling Constants in Some ^{13}C-Enriched Compounds (c.p.s.)[a]

Compound	$\lvert J_{^{13}C-Me}\rvert$	$\lvert J_{^{13}C-CH_2-C}\rvert$	$\lvert J_{^{13}C-C-CH_3}\rvert$
$Et\,^{13}CD_2OH$	—	~4	6.4±0.2
$Et_2\,^{13}CDOH$	—	4.0±0.1	5.3±0.2
$Et_3\,^{13}COH$	—	3.8±0.2	4.5±0.2
$Et\,^{13}CMe_2OH$	4.1±0.1	4.0±0.1	4.0±0.2
$(Me_3)_3C\,^{13}CH_2OH$	—	—	4.48
$[(Me_3)_3C]_2\,^{13}CHOH$	—	—	3.80
$[(Me_3)_3C]_3\,^{13}COH$	—	—	3.80
$(Me_3)_3C\,^{13}CMe_2OH$	—	—	3.59

a) Taken from Refs. (24 and 34). Me=CH_3 and Et=C_2H_5.

in Table II. Therefore, the sign of $J_{^{14}N-C-CH_3}$ would be suggested to be negative, if the sign of J_{P-C-CH_3} would be negative as assumed.[14] The positive shift of the J_{P-C-CH_3} value with increasing ethyl groups was attributed to the less electronegativity of the ethyl group than that of the methyl group.[14]

On the other hand, Karabatsos and coworkers[23,24,34] have found a similar trend about $|J_{^{13}C-C-CH_3}|$ as shown in Table IV, although no determination of the sign of the coupling constant has been made so far. They reported that the absolute value of $J_{^{13}C-C-CH_3}$ increases with an increase of *s*-character of the ^{13}C atom, but it decreases with an increase of the size of substituents attached to the ^{13}C atom. As a substituent R increases in size, angles θ and θ' should increase on account of nonbonded repulsions (see below).



These increases in the angles are responsible for the decrease in $|J_{^{13}C-C-CH_3}|$.[34] This is also thought to be the case with $J_{^{14}N-C-CH_3}$ and J_{P-C-CH_3}. On this assumption the data on the coupling constants listed in Tables II and III, and those reported by Gassman and Heckert[12] can be qualitatively accounted for.

It has also been known that the sign of $J_{^{13}C-C-H}$ is changed from negative to positive with increasing *s*-character of the C atom.[35] Manatt and coworkers[26] also expected the change in signs of J_{P-C-H} from examination of a number of data on relative signs of J's relating to the ^{31}P nuclear spin, considering J_{P-H} and $J_{P-C-C-H}$ as positive. Recently, Cullingworth and coworkers[36] presented clear evidence for the reverse in the sign of J_{P-C-H} by the process of complex formation between trimethylphosphine and some organoaluminum compounds. In methylphosphines, J_{P-H} and J_{P-C-H} are like signs,[37] and

34) G. J. Karabatsos, C. E. Orzech, Jr. : J. Am. Chem. Soc., **87**, 560 (1965).
35) R. M. Lynden-Bell, N. Sheppard : Proc. Roy. Soc. (London), **269A**, 385 (1962); K. A. McLauchlan, T. Schaefer : Can. J. Chem., **44**, 321 (1966) and references therein.
36) A. R. Cullingworth, A. Pidcock, J. D. Smith : Chem. Commun., **1966**, 89.
37) G. M. Whitesides, J. L. Beauchamp, J. D. Roberts : J. Am. Chem. Soc., **85**, 2665 (1963).

may be positive.[26] Thus, J_{P-C-H} shows a negative trend with rising *s*-character of the ^{31}P atom like $J_{^{13}C-C-H}$. It is highly possible that the signs of J_{P^+-C-H} and $J_{P^+-C-CH_3}$ listed in Table III are negative and positive, respectively. We would like to suggest that $J_{P^+-C-C-H}$, $J_{^{13}C-C-C-H}$, and $J_{^{14}N^+-C-C-H}$ have all the positive sign. However, it seems to us that the angular dependence of these coupling constants should be fully revealed in future to discuss their signs exactly (*vide infra*).

β-Substituted Ethylammonium Ions——Table V lists the spectral data on the β-substituted ethylammonium ions examined. The $RCH_2CH_2N^+$ proton signals always appear as AA'BB' types. The AA' parts RCH_2 are further split to triplets by the ^{14}N nucleus, but the BB' parts CH_2N^+ show no further splittings. For example, the spectrum of choline chloride (X) is shown in Fig. 2. The value of $|J_{^{14}N-C-CH_2}|$ in these compounds were obtained by comparing the signal of the AA' part with that of the

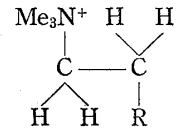
Table V. Proton Magnetic Resonance Spectral Data on Compounds of $RCH_2CH_2N^+R'_3 \cdot X^-$ Type in D_2O

No.	Compound			Chemical shifts (τ)		Coupling constant, $\lvert J_{^{14}N-C-CH_2}\rvert$[a] (c.p.s.)
	R	R'	X^-	α-CH_2	β-CH_2	
XI	$OCOCH_3$	CH_3	Br^-	6.27	5.45	2.6
X	OH	〃	Cl^-	6.50	5.96	2.8
IX	Br	〃	Br^-	5.37	5.37	[b]
VIII	Cl	〃	Cl^-	~6.21[c]	~5.98[c]	~1.7[c]
XL	CH_3	$(CH_2)_2CH_3$	I^-	6.85	8.31	≲0.3[d]

a) The values of $|J_{^{14}N-CH_2}|$ are always less than 0.5 c.p.s. and not exactly measured.
b) The signals of α- and β-CH_2 protons coincide even at 100 Mc.p.s. field.
c) The small difference in the chemical shifts of α- and β-CH_2 protons gave the approximate values.
d) Obtained by proton spin-decoupling on the α-CH_2 protons at 100 Mc.p.s. field.

BB' part because the shapes of these two signals should be symmetrical. The value of $|J_{^{14}N-C-CH_2}|$ in β-bromoethyltrimethylammonium bromide (IX) cannot be obtained because of the coincidence of the signals of the two CH_2 groups even at 100 Mc.p.s. field. The reason why only the ^{14}N-C-C-H spin-couplings can be observed in this type of compounds, whereas no couplings between ^{14}N and methyl groups is observable because of the broadening of the methyl signal, is not apparent at present. To obtain the value of $|J_{^{14}N-C-CH_2}|$ in tetra-*n*-propylammonium iodide (XL), we performed the proton spin-decoupling experiments at 100 Mc.p.s. field. Double irradiation at the frequency of the α-CH_2 protons reduces a complicated multiplet of the β-CH_2 proton signal to a clear quartet split only by the γ-CH_3 protons. The value of $|J_{^{14}N-C-CH_2}|$ in this compound is equal to or less than 0.3 c.p.s.

The proton-proton spin coupling constant in $H-C-C\langle^{H}_{R}$ system is known to show a negative shift with increasing the electronegativity of the substituent R.[38] If this is also the case with the present $N^+-C-C\langle^{H}_{R}$ system, the sign of $|J_{^{14}N-C-CH_2}|$ can be inferred from the present data in Table V. The compounds under discussion may have the following conformation at room temperature, where the dihedral angle between the α-C-N^+ and β-C-H bonds is always about 60° (*gauche*). This assumption is believed true because the AA'BB' type spectra appear in all cases. Thus, as seen from Table V, the value of $|J_{^{14}N-C-CH_2}|$ increased



38) For a leading reference, see K. L. Williamson : J. Am. Chem. Soc., **85**, 516 (1963); A. D. Cohen, T. Schaefer : Mol. Phys., **10**, 209 (1966).

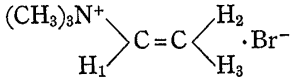
(negative shift) with an increase of the electronegativity of the substituent R. This fact suggests that the sign of $J_{^{14}N-C-CH_2}$ (*gauche*) is negative at least in Ⅷ~Ⅺ. The large value of $J_{^{14}N-C-CH_3}$ (2.2_0 c.p.s.) in trimethylethylammonium ions (Ⅶ) might be due to the contribution of the *trans* (dihedral angle $=180°$) coupling constant between N^+-CH_2 and CH_2-H which may be absolutely larger than the *gauche* coupling constant,[39] because the methyl group can be freely rotated around N^+CH_2-CH_3 bond in this case.*3 More detailed experiments and more elaborate discussions on the spectra of this type of compounds will be presented in our subsequent paper of this series.*4

Vinylammonium Ions——Interestingly, we have found that the olefinic proton signals as well as the methyl signal in trimethylvinylammonium bromide (XV) are evidently split by ^{14}N nucleus even at room temperature as shown in Fig. 1. These splittings are quite broadened in trimethyl-(*trans*-β-phenylvinyl)ammonium bromide (XVI) in which the electric field at the ^{14}N nucleus may become inhomogeneous owing to introduction of the phenyl group.

From the electronegativity of N^+Me_3 obtained in the second section, we can assume the order of the proton-proton spin coupling constants between vinyl protons as follows;[40,41]

$$J_{H_1,H_2\,(trans)} > J_{H_1,H_3\,(cis)} > |J_{H_2,H_3\,(gem)}| \text{ (may be negative).}$$

Table Ⅵ. Proton Magnetic Resonance Spectral Data on Trimethylvinylammonium Bromide in Deuterium Oxide



	Chemical shift (τ)	Coupling constant (c.p.s.)	
CH_3	6.68	$J_{H_1,H_2\,(trans)}$	+14.8
H_1	3.49	$J_{H_1,H_3\,(cis)}$	+ 8.3
H_2	4.25	$J_{H_2,H_3\,(gem)}$	− 4.1
H_3	4.46	$\lvert J_{^{14}N,H_1\,(gem)}\rvert$	3.5
		$\lvert J_{^{14}N,H_2\,(cis)}\rvert$	2.6
		$\lvert J_{^{14}N,H_3\,(trans)}\rvert$	5.5
		$\lvert J_{^{14}N-CH_3}\rvert$	0.5_0

On this assumption we assigned the signals of the olefinic protons and measured the coupling constants as shown in Fig. 1 and Table Ⅵ. The values of $J_{H,H}$ are very similar to those obtained from vinyl halides.[42] The order of the $J_{^{14}N,H}$ values is different from that of the $J_{F,H}$ values in vinylfluoride[42] and that of the $J_{P,H}$ value in trivinylphosphine.[43] The determination of the relative signs of $J_{^{14}N,H}$ in XV and more detailed discussions will be presented in our subsequent paper.[44]

*3 The angular dependence of the vicinal $J_{^{13}C-C-C-H}$ was recently reported by G. J. Karabatsos, C. E. Orzech, Jr., N. Hsi : J. Am. Chem. Soc., **88**, 1817 (1966).

*4 *Note Added in Proof.*——After submitting the manuscript of this paper, a communication has been published by Culvenor and Ham (Chem. Commun., **1966**, 537), who revealed that the compound Ⅺ in D_2O at room temperature is dominantly of the *gauche* conformation. We will report our further results on this type of compounds with our revised and more elaborate discussion soon.

39) M. Karplus : J. Am. Chem. Soc., **85**, 2870 (1963), and references therein.

40) For example, see T. Schaefer : Can. J. Chem., **40**, 1 (1962); F. Hruska, G. Kotowycz, T. Schaefer : *Ibid.*, **43**, 2827 (1965).

41) Also refer to J. A. Pople, A. A. Bothner-By : J. Chem. Phys., **42**, 1339 (1965).

42) R. E. Mayo, J. H. Goldstein : J. Mol. Spectry., **14**, 173 (1964).

43) W. A. Anderson, R. Freeman, C. A. Reilly : J. Chem. Phys., **39**, 1518 (1963).

44) M. Ohtsuru, K. Tori : Chem. Commun., **1966**, 750.