

The Structure of the Methylammonium Ion in Lyotropic Nematic Solution

L. W. Reeves*¹ and A. S. Tracey

Contribution from the Instituto de Química, Universidade de São Paulo, Cidade Universitária, São Paulo, Brazil. Received September 22, 1973

Abstract: Recently described techniques from this laboratory have been applied to study the structure of the methylammonium ion. The ion in a lyotropic medium participates in an equilibrium involving the oriented electrical double layers of a nematic phase and this leads to proton magnetic resonance spectra typical of oriented solute species. The preparation of several middle soap nematic phases using methylammonium decyl sulfate, decanol, water (acidified), and sodium sulfate is described according to two different and general procedures. The proton magnetic resonance spectra of the C-13 enriched, N-15 enriched, and naturally occurring isotopic abundance methylammonium ion have been studied in aqueous isotropic and orienting lyotropic solvents. The scalar coupling constants between all nuclei but the equivalent protons in the CH₃ and NH₃⁺ groups have been carefully re-determined. The partially averaged dipole-dipole coupling constants obtained from the spectra of the oriented ions have been used to determine the complete structure for the ion in solution. The proton-proton dipole couplings between CH₃ and NH₃⁺ groups depend on the internal rotation about the C-C bond and they correspond to a situation between the extremes of free and independent rotation and a fixed staggered conformation. The bond distances and angles are referenced to a proton-proton distance in the CH₃ group of 1.796 Å.

The ordered superstructures of middle soap phases² cause the ordering of some small solute molecules³⁻⁶ but more important they orient their mobile ionic constituents.^{7,8} This latter quality has led this laboratory to investigate in detail and for the first time the structure of ions in aqueous solution by nuclear magnetic resonance (nmr) spectroscopy. The orientation of relatively small counterions in phases containing both cationic and anionic detergents derives from an exchange process between the surface of a static component of an electrical double layer and the free ion in the interstitial water.^{9,10}

In this study, we shall report an investigation of the methylammonium ion oriented in a lyotropic middle phase. Nuclear magnetic resonance (nmr) studies of the methylammonium ion in isotropic aqueous solution give information with respect to protolysis and proton exchange.¹¹ Pertinent to this present study is a literature, now quite extensive, on measurements and calculations of hindered rotation barriers in ethane-like

derivatives.¹²⁻¹⁶ Ethane and its derivatives have been investigated in thermotropic nematic solvents.¹⁷ The structure of the methylammonium ion has been studied by X-ray diffraction methods¹⁸ as the chloride salt, but proton positions are not known. The C-N distance was reported as 1.465 ± 0.010 Å. No recent structural studies of this ion are available and questions regarding the proton positions on CH₃ and NH₃⁺ groups and the internal rotation are unanswered.

Experimental Section

Nmr spectra were recorded on a Perkin-Elmer R10 spectrometer with a probe temperature of 33.3° or on Varian T60 and HA100 spectrometers with probe temperatures of 34.0° and 31.5°, respectively. The spectra were analyzed by using the computer program UEA¹⁹ modified to include dipole-dipole couplings and to iterate on some or all input parameters. All spectrometer sweep ranges used were carefully calibrated with standard samples and by use of the sideband technique.²⁰

Methylammonium decyl sulfate was prepared by two methods, the first of which is applicable to any stable positively charged ions in aqueous solution.

Method 1. A dilute aqueous methylammonium hydrochloride (~2 g/100 ml) solution was passed through a chromatographic column containing Dowex 50-H⁺ solution until the effluent was neutral to pH paper. The column was washed with 50 ml of distilled water, then an aqueous solution (5 g/30 ml) of sodium decyl sulfate which was allowed to pass slowly through the column. This fraction together with a final wash of 40 ml of distilled water were collected, then evaporated *in vacuo* to dryness at room temperature. The crystalline product was recrystallized from chloroform-petroleum ether (65-110°) to yield 4.7 g of purified methylammonium decyl sulfate.

Method 2. Sodium decyl sulfate (1.70 g) was mixed with methylammonium hydrochloride (0.5 g) in chloroform (50 ml). Water

(1) Visiting Professor, 1967-present. Address correspondence to the Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada. Research supported by the National Research Council of Canada (NRCC) and the Defense Research Board of Canada (DRB). Travel and local expenses provided by NRCC, the Conselho Nacional de Pesquisas do Brasil (CNPq), and the Banco Nacional de Desenvolvimento Economico (BNDE).

(2) G. H. Brown, J. W. Doane, and V. D. Neff, "The Structure and Physical Properties of Liquid Crystals," Chemical Rubber Co., Cleveland, Ohio, 1971.

(3) K. D. Lawson and T. J. Flautt, *J. Amer. Chem. Soc.*, **89**, 5489 (1967).

(4) P. J. Black, K. D. Lawson, and T. J. Flautt, *Mol. Cryst. Liquid Cryst.*, **7**, 201 (1969).

(5) L. W. Reeves, J. M. Riveros, R. A. Spragg, and J. Atilio Vanin, *Mol. Phys.*, **25**, 9 (1973).

(6) (a) S. A. Barton, M. A. Raza, and L. W. Reeves, *J. Magn. Resonance*, **9**, 45 (1973). (b) R. C. Long Jr., S. L. Baugham, and J. H. Goldstein, *J. Mag. Resonance*, **7**, 253 (1972).

(7) L. W. Reeves, J. Sanches de Cara, M. Suzuki, and A. S. Tracey, *Mol. Phys.*, **25**, 1481 (1973).

(8) L. W. Reeves, A. S. Tracey, and M. M. Tracey, *J. Amer. Chem. Soc.*, **95**, 3799 (1973).

(9) L. W. Reeves, J. A. Vanin, and V. Vanin, *An. Acad. Brasil. Cienc.*, in press.

(10) D. M. Chen and L. W. Reeves, *J. Amer. Chem. Soc.*, **94**, 4384 (1972).

(11) E. Grunwald, A. Loewenstein, and S. Meiboom, *J. Chem. Phys.*, **27**, 630 (1957).

(12) S. Weiss and G. E. Leroi, *J. Chem. Phys.*, **48**, 962 (1968).

(13) A. Veillard, *Theor. Chim. Acta*, **18**, 21 (1970).

(14) U. Wahlgren and K. H. Johnson, *J. Chem. Phys.*, **56**, 3715 (1972).

(15) W. E. Palke, *J. Chem. Phys.*, **56**, 5308 (1972).

(16) R. M. Stevens, *J. Chem. Phys.*, **52**, 1397 (1970).

(17) D. N. Silverman and B. P. Dailey, *J. Chem. Phys.*, **51**, 655 (1969).

(18) E. W. Hughes and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **68**, 1970 (1946).

(19) J. A. Ferritti, R. K. Harris, and R. B. Johannesen, *J. Magn. Resonance*, **3**, 84 (1970).

(20) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959.

Table I. Percentage by Weight of Components Used to Make the Quaternary Middle Soap Nematic Phases Used in This Study^a

Component	—Weight % of components—		
	MADS	¹⁵ N-	¹³ C-
MADS	34.8	35.2	34.9
Na ₂ SO ₄	5.8	5.6	5.7
Decanol	5.3	5.5	5.2
H ₂ O ^b (pH 1.5)	54.1	53.7	54.2

^a ¹⁵N-MADS and ¹³C-MADS are abbreviations for the respective isotopically enriched methylammonium decyl sulfates. ^b The acidity of the water was adjusted by use of sulfuric acid previous to preparing the phase.

Table II. The "Spin-Spin" Scalar Couplings (in Hz) in the Methylammonium Ion Determined from Isotropic and Oriented Solutions

	Roberts, <i>et al.</i> ²²	—Present work isotropic solution—		—Present work oriented—	
		¹⁵ NH ₃ CH ₃	¹³ CH ₃ NH ₃	¹⁴ NH ₃ CH ₃ ⁺	¹⁵ NH ₃ CH ₃ ⁺
J_{vicinal}	6.2 ± 0.2	6.16 ± 0.01	6.15 ± 0.02	+6.15 ± 0.31 ^a (6.25 ± 0.19) ^b	6.08 ± 0.08
$J_{^{15}\text{N}-\text{H}}$	75.6 ± 0.2	-74.92 ± 0.03			
$J_{^{15}\text{N}-\text{CH}_3}$	0.8 ± 0.2	0.79 ± 0.02 ^c			
$J_{^{13}\text{C}-\text{H}_3}$	145.0 ± 0.2 ^d		143.61 ± 0.04 ^d		
$J_{^{13}\text{C}-\text{NH}_3}$	3.5 ± 0.2				

^a Determined from ¹⁵N-methylammonium. ^b Determined from ¹³C-methylammonium. ^c Absolute sign not known. ^d A factor 1.01 between the results in isotropic solution and those of ref 22 suggests a small calibration error in their results.

(0.5 ml) was added and removed by codistillation with chloroform. The solution was filtered and then evaporated. The product was crystallized from chloroform-petroleum ether (65–110°) to yield the purified product (1.5 g).

Experiments were carried out with isotopically labeled methylammonium decyl sulfate. For this purpose, the starting products for method 2 were Stohler Isotope Chemical Co. 95% enriched nitrogen-15 methylammonium chloride and in a second preparation a sample 90% enriched in carbon-13 from the same source. These isotopically labeled methylammonium ions introduce in each case a spin half nucleus ¹³C or ¹⁵N which enables the spectral determination of the nitrogen and carbon positions in the ions.

The analysis of oriented molecule spectra differs in no regard from that for oriented ions and has been described in a recent review article.²¹ The general method, recently introduced by this laboratory, for the study of nuclear positions in both positive⁷ and negative⁸ complex ions has been followed. The successful nematic lyotropic middle soap phases for the present study have compositions given in Table I. The final phases were prepared by weighing into test tubes mixing the components alternately with centrifugation until a homogeneous nematic phase appeared. This process took about 5 min. Purity of all components is critical. Ultimate recognition of the correct phase is proven by the correct nmr spectrum but useful indications of a successful phase can be achieved. The phase should be quite fluid, indicating nematic rather than the neighboring smectic or viscous isotropic phase,² and also should be birefringent. This last property is easily verified by constructing a fairly light tight box with crossed polaroid sheets placed at each end. Insertion of the nmr tube between the polaroid sheets must lead to an illuminated sample when held up to a light source. The sample is allowed to spin in the nmr probe for up to 16 hr to achieve homogeneity of ordering. The kinetics of ordering follow the velocity of ordering of the middle soap phase, which depends on the particular viscosity of the sample being investigated. The solute ion achieves its order as part of an exchange process between the interstitial water and the static oriented wall of the negative component in an electrical double layer. The homogeneous orientation of the cylindrical superstructure of the middle soap phase² is necessary before high resolution is evident in the wings of the spectrum.

The spectra of methylammonium hydrochloride solution have

been extensively studied by Meiboom, Loewenstein, and Grunwald,¹¹ but in order to determine the activities necessary to prevent rapid proton exchanges in the nematic phases the spectra have been re-examined in the presence of sodium sulfate in the same proportions as in the phase. The weighings used were 90 mg of ¹⁵N-methylammonium hydrochloride, 58 mg of Na₂SO₄, and 546 mg of acidified water (pH 1.5). Spectra of methylammonium hydrochloride were highly resolved and gave all coupling constants to the ¹⁵N spin in the slow exchange limits.

Results

Methylammonium Hydrochloride in Isotropic Solution. The analysis of the spectrum of the ordered methylammonium ion yields an independent value of

³J_{HH} within the ion. As an independent check of this and other values of *J* the nmr spectrum of both the N-15 and C-13 methylammonium ions have been examined in acidic isotropic solution (see Experimental Section for concentrations). Previous studies of methylammonium in aqueous solution have been made by Roberts, *et al.*,²² and in almost all cases the absolute signs of these scalar couplings can be related to the positive absolute sign of the C–H coupling. In making comparisons the negative magnetogyric ratio of N-15 must be taken into account. The spectra of N-15 methylammonium consist of two quadruplet signals, designated at low field as ¹⁵NH₃⁺ protons, which couple to the CH₃ protons and the ¹⁵N nucleus. The high field CH₃ signals are a quadruplet also but under the highest resolution conditions a doubling of each feature can be ascribed to a ²J_{N–H} spin-spin coupling of 0.79 Hz. The proton spectra of the carbon-13 enriched methylammonium ion gives the ¹J_{CH} coupling as well as checks on the ³J_{HH}. All isotropic aqueous solution spectra were repeated four times with audio side-band modulation and careful calibration of each peak position. The present measurements are compared with the previous measurements of Roberts, *et al.*,²² in Table II. Further columns in this table list the independent determination of the scalar coupling ³J_{HH} from the analysis of oriented methylammonium ions in the present work. The study of oriented species by nmr has been regarded as an indirect means of determining the absolute signs of the scalar couplings based on reasonable assumptions about the orientation,²¹ but the reverse is more useful in the present case. A secure set of absolute sign determinations of scalar couplings cannot only aid the spectral analysis but determine absolute signs of the dipolar couplings in some cases.

(22) G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 5564 (1964).

(21) P. Deihl and C. L. Khetrapal, "NMR of Oriented Molecules," Chapter 1, p 1. "NMR Basic Principles and Progress," Volume 1, P. Deihl, E. Fluck and R. Kosfeld, Ed., Springer-Verlag Inc., New York, N. Y., 1969.

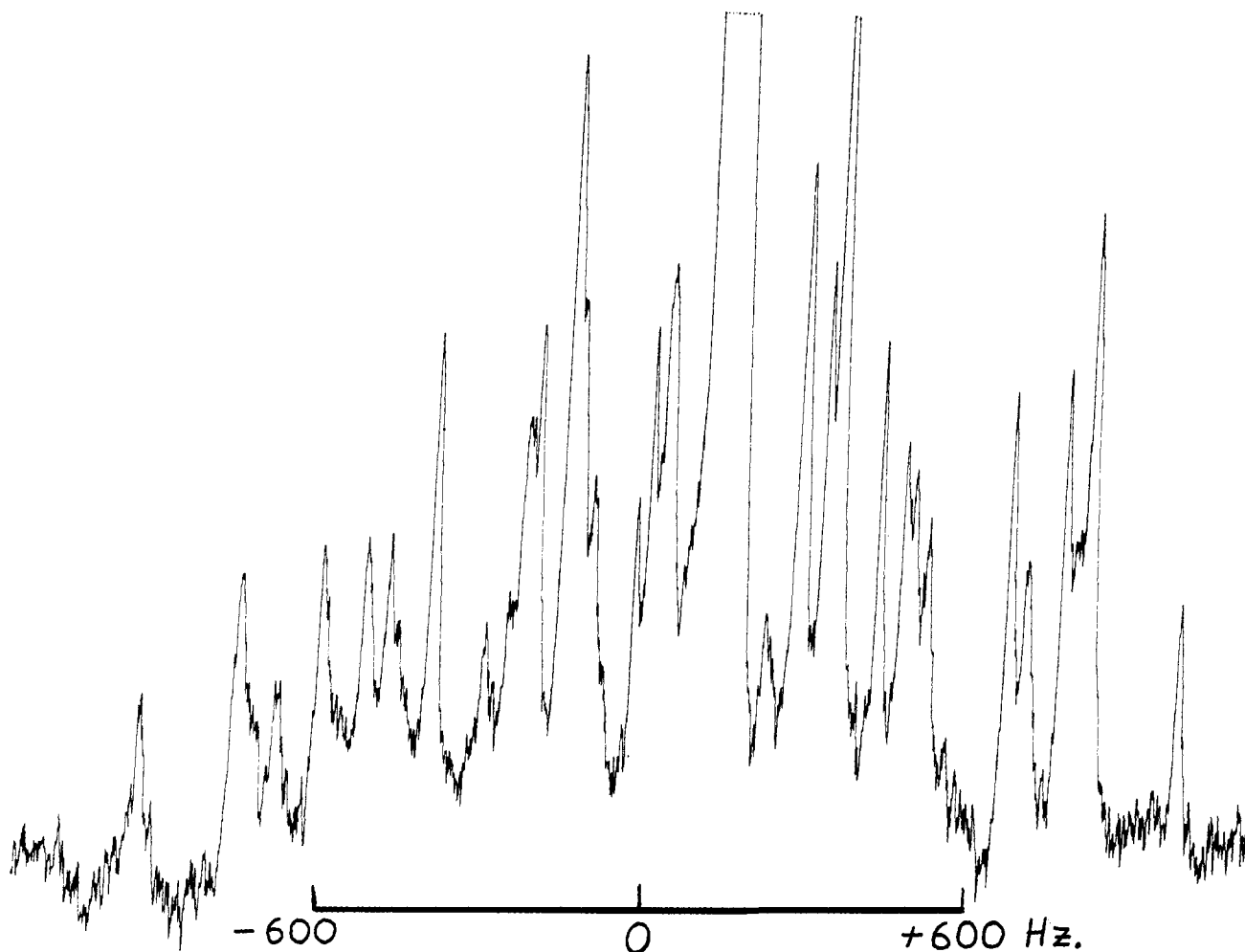


Figure 1. The spectrum of $\text{CH}_3^{14}\text{NH}_3^+$ ion oriented in a lyotropic nematic phase. The strongest peak which exceeds the limit of the recorder is the water peak from the phase. Considerable variation in line widths of individual transitions derives from the influence of the relatively rapidly relaxing N-14 nuclear spin. This relaxation preferentially broadens the NH_3^+ proton transitions. The analyses of spectra are presented in Tables II and III with indicated error limits.

Spectra of Ordered Methylammonium. The spectrum of methylammonium in the lyotropic phase is highly dependent on the pH since the rate of exchange of the NH_3^+ protons can be in the slow, intermediate, or fast exchange limit with respect to the inverse frequency differences defined by scalar and dipolar couplings to the CH_3 protons.²³ Although these exchange rates may be quite different to those obtained by Meiboom and coworkers¹¹ in isotropic solutions the purpose of the present work is purely structural and the question of exchange rates is left for future studies.^{24, 25} In the fast limit of proton exchange the spectrum of ordered methylammonium is a typical triplet from intramethyl dipole-dipole coupling²¹ and no structural information is available. In acidified phases the coupling constants between methyl and NH_3^+ protons are not lost because of exchange with water and the much more complex spectrum presented in Figure 1 is obtained. The peaks arising from NH_3^+ protons are readily recognized as being much broader than those from CH_3 protons. This can be ascribed to modulation of couplings to the ^{14}N nucleus (spin = 1) at a rate

(23) L. W. Reeves, *Advan. Phys. Org. Chem.*, **8**, 187 (1965).

(24) S. O. Chan and L. W. Reeves, *J. Amer. Chem. Soc.*, **95**, 670 (1973).

(25) S. O. Chan and L. W. Reeves, *J. Amer. Chem. Soc.*, **95**, 673 (1973).

close to the fast exchange limit. The relaxation rate of the N-14 nucleus by fluctuating electric field gradients almost completely decouples the N-14 spin.⁴ The accurate analysis of the spectrum is somewhat impeded by these larger line widths which obscure fine structures in some cases. Thirty-five transitions were used for the analysis, and on iteration the refined couplings quoted in Tables II and III give a theoretical spectrum with an RMS deviation of 1.4 Hz on the 35 transitions. This error limit is much better than is usually achieved in thermotropic phases but proved to be about a factor of 3 worse than the analysis with the N-15 ion. All spectra must necessarily be observed with a large water signal, since a slow chemical exchange with deuterium oxide removes the spectrum in a D_2O phase.

Molecules with $\text{A}_3\text{A}_3'$ nuclear spin systems in ordered phases lead to symmetric spectra.^{7, 17, 26-28} A_3B_3 spectra such as for the methylammonium ion reflect the lack of symmetry plane perpendicular to the C_3 axis in the unsymmetric ion (see Figure 1).

Spectra of Ordered N-15 Methylammonium Ion.

(26) A. D. Buckingham, E. E. Burnell, and C. A. Le Lange, *Mol. Phys.*, **15**, 285 (1968).

(27) G. Englert, *Z. Naturforsch.*, **249**, 1074 (1969).

(28) G. Englert, A. Saupe, and T. P. Weber, *Z. Naturforsch.*, **239**, 152 (1968).

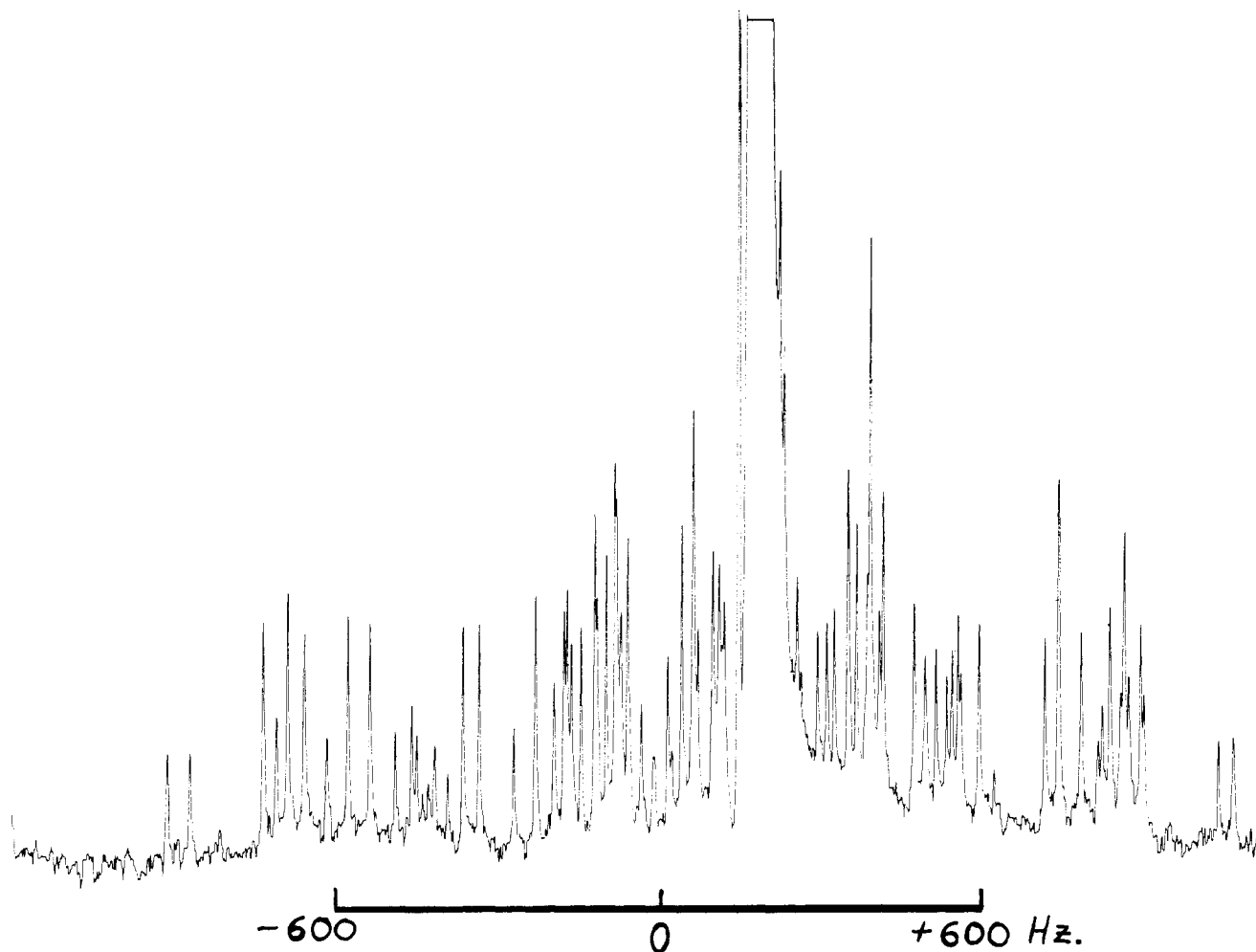


Figure 2. The proton magnetic resonance spectrum of oriented $\text{CH}_3^{15}\text{NH}_3^+$ in a lyotropic nematic phase. The strong peak exceeding the recorder limit is the water signal from the phase. All transitions in the spectrum have a line width of ~ 1.5 Hz which is typical of the high resolution obtainable with spinning lyotropic phases. The analyses of spectra are presented in Tables II and III with indicated error limits.

Table III. Analysis Results for the Spectra of the Methylammonium Ions Oriented in the Lyotropic Nematic Phases^{a, b}

	$^{14}\text{NH}_3\text{CH}_3^+$ ^(a) ^c	$^{14}\text{NH}_3\text{CH}_3^+$ ^(b)	$^{15}\text{NH}_3\text{CH}_3^+$	$^{13}\text{CH}_3\text{NH}_3^+$
$D_{13} = D_{14}$				-253.10 ± 1.5
$D_{15} = D_{16}$				68.00 ± 1.3 or 75.00 ± 1.3^d
$D_{23} = D_{24}$			-27.23 ± 0.13 or -25.65 ± 0.13	
$D_{25} = D_{26}$			114.19 ± 0.13	
D_{34}	-181.21 ± 0.10	-341.15 ± 0.18	-342.65 ± 0.05	-331.88 ± 0.35
D_{vic}	85.10 ± 0.22	160.68 ± 0.32	160.93 ± 0.09	155.47 ± 0.6
D_{is}	-223.64 ± 0.11	-418.28 ± 0.18	-421.37 ± 0.05	-408.49 ± 0.31
δ	277.8 ± 0.3	274.3 ± 0.5	275.0 ± 0.3	
RMS error (no. transitions)	0.83 (34)	1.46 (35)	0.57 (77)	4.6 (48)

^a The nuclei are numbered according to the designations in Figure 3. " D_{ij} " represents the partially averaged dipole-dipole coupling between nuclei enumerated as i and j . The separate phases correspond to slightly different compositions and hence different dipole-dipole couplings. (a) and (b) in the table refer to two different phases, (a) with a higher water content. The degree of orientation in phase (b) for the ion is much higher, but ratios of dipole-dipole coupling constants are the same (see Table IV). ^b Errors reported are those given by the computer program and are probable errors derived only from the input parameters. Attempts to minimize errors in input parameters were made by averaging line positions from separate spectra. ^c Made with slightly more water and less decanol than the phases reported in the Experimental Section. These values are included for comparative purposes. ^d Ambiguity in values of $D_{15} = D_{16}$ arise because of lack of a sign for $J_{16} = J_{15}$.

The spectrum of the oriented N-15 methylammonium ion is presented as Figure 2. The spin half N-15 nucleus introduces an X spin in the system giving a spectrum of the type A_3B_3X . The removal of the N-14 spin and replacement by a spin half nucleus lead to sharp transitions of half-width in the order 1.5 Hz; thus a

somewhat more precise analysis is possible. Seventy-seven transitions were carefully measured and were fitted in the final iteration with an RMS error of 0.5 Hz. The dipolar and scalar coupling constants are listed in Tables II and III. The analysis was aided by assigning dipole couplings obtained from the outer transitions of

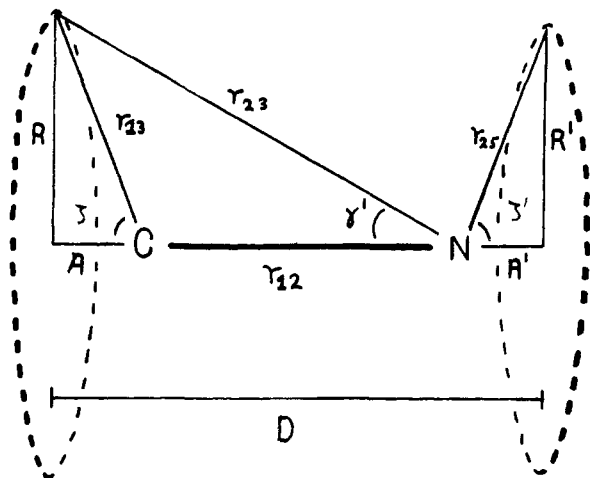


Figure 3. Geometric parameters of CH_3NH_3^+ used in the analysis. The C-methyl protons move on a circle of radius R and the NH_3^+ protons move on a circle of radius R' . The C-N distance is labeled r_{12} , the C-H distance r_{13} , the NH distance r_{25} , and the N- CH_3 , nitrogen proton distance r_{25} . The perpendicular distance between the two circles of rotation of the CH_3 and NH_3^+ protons is designated D . Angles of interest are ζ between the C_3 axis and the CH bonds, ζ' between the C_3 axis and the NH bonds, and γ' between the C_3 axis and the vector joining the carbon to the CH protons. The perpendicular distance between the carbon atom and the circle of rotation of the CH_3 protons along the C_3 axis is labeled A and the corresponding distance of the nitrogen nucleus from the circle of rotation of the NH_3^+ protons is assigned A' . Note that $D = (A + A' + r_{12})$.

the spectrum. The two transitions to low field have the spacing $|D_{15\text{N-H}} + J_{15\text{N-H}}|$ while those at high field have the spacing $|D_{15\text{N-CH}_3} + J_{15\text{N-CH}_3}|$. Since the splitting at low field is less than $J_{15\text{N-H}}$ it was immediately obvious that $D_{15\text{N-H}}$ and $J_{15\text{N-H}}$ had opposite signs.

Spectra of Ordered C-13 Methylammonium Ion. The spectrum of the 90% enriched C-13 methylammonium ion in the partially oriented state was examined and analyzed so as to define the position of the carbon atom in the overall structure. The spectrum corresponded to the acid region where proton exchange is slow. The A_3B_3X spectrum is characterized by broader or sharper transitions corresponding to protons attached to the nitrogen-14 or carbon-13 centers, respectively. The important part of the analysis is linked to the $^{13}\text{CH}_3$ group; 48 transitions were measured and fitted with an RMS error of 4.6 Hz. Scalar and dipolar coupling constants are listed in Tables II and III.

Discussion

The Structure of Methylammonium Ion. The methylammonium ion has C_{3v} symmetry and therefore requires only one parameter to describe the anisotropic motion.²¹ The dipole-dipole coupling constants between methyl and ammonium protons are sensitive to any internal rotation about the C-N bond, but it is possible to avoid this particular dipole-dipole coupling in determining the structure. The internal rotation independent couplings can therefore be used to determine the ionic structure and the value of the dependent coupling gives some information about the state of internal rotation. The spectra are pH dependent in both isotropic and anisotropic media and removal of couplings to exchanging NH_3^+ protons at higher pH can be an aid in assigning dipole-dipole couplings in the methyl

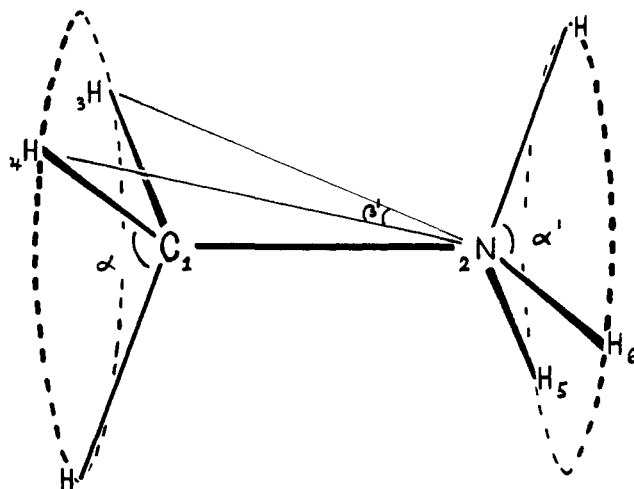


Figure 4. Further geometric parameters of CH_3NH_3^+ used in the analysis of the structure. The angle HNH is labeled α' and the geminal angle HCH is called α . The angle HNH between remote CH_3 protons and the nitrogen atom, which is also independent of the internal rotation about the C-N bond, has been labeled β' .

group. In the N-14 methylammonium ion the hetero spin is almost completely decoupled by the relaxation rate of the spin 1 nucleus, which interrupts the dipolar and scalar couplings. Considerable line broadening of the NH_3^+ proton signals and lack of resolved couplings compel the use of the N-15 labeled ion, if information about the position of the nitrogen nucleus is required. In this detailed study we have sought the position of all atoms so that a separate series of experiments with C-13 labeled ion have been carried out. The N-15 and C-13 substitution is especially helpful to the analysis because both atoms lie on the C_3 symmetry axis and dipolar couplings to the protons are independent of the internal rotation.

Two diagrams describing the geometric problem are presented as Figures 3 and 4. Using the distance parameters described in these figures and equations already derived for the ratios of dipole-dipole coupling constants^{21, 29} we can write eq 1-5. The gyromagnetic ratios

$$\frac{D_{34}}{D_{56}} = \left(\frac{r_{56}}{r_{34}}\right)^3 \quad (1)$$

$$\frac{D_{13}}{D_{34}} = \frac{\gamma_{13\text{C}}}{\gamma_{\text{p}}} \left(\frac{r_{34}}{r_{13}}\right)^3 \left[\left(\frac{r_{34}}{r_{13}}\right)^2 - 2 \right] \quad (2)$$

$$\frac{D_{25}}{D_{56}} = \frac{\gamma_{15\text{N}}}{\gamma_{\text{p}}} \left(\frac{r_{56}}{r_{25}}\right)^3 \left[\left(\frac{r_{56}}{r_{25}}\right)^2 - 2 \right] \quad (3)$$

$$\frac{D_{15}}{D_{56}} = \frac{\gamma_{13\text{C}}}{\gamma_{\text{p}}} \left(\frac{r_{56}}{r_{15}}\right)^3 \left[\left(\frac{r_{56}}{r_{15}}\right)^2 - 2 \right] \quad (4)$$

$$\frac{D_{23}}{D_{34}} = \frac{\gamma_{15\text{N}}}{\gamma_{\text{p}}} \left(\frac{r_{34}}{r_{23}}\right)^3 \left[\left(\frac{r_{34}}{r_{23}}\right)^2 - 2 \right] \quad (5)$$

$\gamma_{15\text{N}}$, $\gamma_{13\text{C}}$, and γ_{p} are those for N-15, C-13, and protons, respectively. From the ratios of the measured D 's listed in Table IV, a table of interatomic distance ratios for the ion can be presented (Table V). The angles, which appear in Figures 3 and 4, can also be determined from these distance ratios in terms of simple trigonometric formulas. The relevant angles denoted in the figures are also listed in Table V.

(29) H. Spiesscke, *Z. Naturforsch. A*, **23**, 407 (1968).

Table IV. Ratios of Partially Averaged Dipole–Dipole Coupling Constants Derived from the Experimental Values in Table III^{a,b}

	¹⁴ NH ₃ CH ₃ ^{+(a)}	¹⁴ NH ₃ CH ₃ ^{+(b)}	¹⁵ NH ₃ CH ₃ ⁺	¹³ CH ₃ NH ₃ ⁺
D_{34}/D_{vic}	-2.1294 ± 0.0067	-2.1232 ± 0.0053	-2.1292 ± 0.0015	-2.1210 ± 0.010
D_{56}/D_{vic}	-2.6280 ± 0.0081	-2.6000 ± 0.0063	-2.6183 ± 0.0018	-2.6107 ± 0.012
D_{56}/D_{34}	1.2341 ± 0.0013	1.2261 ± 0.0012	1.2297 ± 0.00033	1.2308 ± 0.0030
D_{23}/D_{56}			-0.27100 ± 0.00034	
D_{23}/D_{34}			0.07947 ± 0.00039 or 0.07486 ± 0.00039	
D_{13}/D_{34}				0.7626 ± 0.0054
D_{15}/D_{56}				-0.16665 ± 0.0033 or -0.1836 ± 0.0033^c

^a (a) and (b) refer to two different phases as reported in the legend to Table III. The subscripts for D_{ij} are referred to Figure 4. ^b See footnotes in Table III. ^c See same footnotes in Table III.

Table V. Tables of Internuclear Distance Ratios Derived Using Equations 1–5 from Experimental Dipole–Dipole Couplings^a

$r_{34}/r_{56} = 1.0714 \pm 0.0001$	$r_{56}/r_{25} = 1.6210 \pm 0.0002$
$r_{34}/r_{13} = 1.6395 \pm 0.0011$	$r_{56}/r_{15} = \begin{cases} 0.781 \pm 0.007^b \\ 0.819 \pm 0.007 \end{cases}$
$r_{34}/r_{23} = \begin{cases} 0.8497 \pm 0.0022^c \\ 0.8237 \pm 0.0022 \end{cases}$	$\alpha = 110.12 \pm 0.11$
$\zeta = 71.18 \pm 0.11$	$\alpha' = 108.29 \pm 0.02$
$\zeta' = 69.37 \pm 0.02$	$\beta = \begin{cases} 45.97 \pm 0.44^b \\ 48.35 \pm 0.44 \end{cases}$
$\gamma = \begin{cases} 26.80 \pm 0.26^b \\ 28.22 \pm 0.26 \end{cases}$	$\beta' = \begin{cases} 50.28 \pm 0.14^c \\ 48.64 \pm 0.14 \end{cases}$
$\gamma' = \begin{cases} 29.38 \pm 0.08^c \\ 28.40 \pm 0.08 \end{cases}$	

^a Ambiguities arise because the sign of the scalar coupling ${}^2J_{15\text{N}-\text{CH}_3}$ is not determined from spectral analysis. The two possible signs of $|0.79|$ lead to slightly different values of D between corresponding nuclei and all bracketed values in the table correspond to the two signs of the scalar coupling. The ambiguity can be resolved by other arguments presented in the text. All values not directly involved with the ¹³C nucleus were taken from the coupling from the CH₃¹⁵NH₃ spectrum. ^b Ambiguity in distances and angles connected with ${}^2J_{\text{C}-\text{N}-\text{H}}$, which is not given a sign. ^c Ambiguity in distances and angles connected with ${}^2J_{\text{N}-\text{C}-\text{H}}$, which is not given a sign.

In Table V the ambiguity of the sign of the scalar coupling ${}^2J_{15\text{N}-\text{CH}_3} = |0.79|$ leaves uncertain the bracketed angles and distances. The internuclear distance ratios where possible are preferably derived from dipole–dipole couplings involving the ¹⁵N nucleus rather than the ¹³C. The spectrum of acidified and oriented ¹³CH₃NH₃⁺ has many broadened transitions, which derive from the protons attached to the ¹⁴N nucleus. This makes the spectral analysis less precise. Table V can be converted into absolute distances and angles assuming that r_{HH} , the interproton distance within the CH₃ group, is 1.796 Å. The resultant bond distances referred to Figures 3 and 4 are provided in Table VI. Bracketed distances give two separate values derived from the ambiguity in the sign of ${}^2J_{15\text{N}-\text{CH}_3}$. A reasonable decision with respect to this ambiguity may be derived from the value of r_{12} , the C–N bond length, by comparing the two possible values with the early X-ray diffraction study¹⁸ (1.465 ± 0.01 Å) and that derived for similar ions.³⁰ The comparison with X-ray diffraction data suggests strongly that the correct value of $r_{12} = 1.488$ Å. This decision, which can, in principle, be further substantiated, determines the absolute value of the scalar coupling by the following argument.

Table VI. Internuclear Distances in the Methylammonium Ion Referred to the Distance, $r_{34} = 1.796$ Å^a

$r_{34}^b = 1.796$ Å	$r_{56} = 1.6764 \pm 0.0002$
$r_{13} = 1.0955 \pm 0.0007$	$r_{25} = 1.0342 \pm 0.0003$
$R^b = 1.0369$	$R' = 0.9679 \pm 0.0001$
$A = 0.3534 \pm 0.0018$	$A' = 0.3644 \pm 0.0003$
$r_{15} = \begin{cases} 2.146 \pm 0.019 \\ 2.0471 \pm 0.018^c \end{cases}$	$r_{23} = \begin{cases} 2.1136 \pm 0.0055 \\ 2.1804 \pm 0.0058^d \end{cases}$
$r_{12}^e = \begin{cases} 1.552 \pm 0.020 \\ 1.439 \pm 0.020^c \end{cases}$	$r_{12}^f = \begin{cases} 1.488 \pm 0.009^d \\ 1.564 \pm 0.009 \end{cases}$

^a Ambiguity in the distances are bracketed and for the correct choice of these see arguments presented in the text. Actual experimental errors derived from spectral analysis are always of the order ±0.001 Å, but these are considerably smaller than the systematic errors of the experiment arising from a neglect of vibrational corrections.²¹ All distances measured in Å. All values not directly involved with the ¹³C nucleus were taken from the couplings obtained from the CH₃¹⁵NH₃ spectrum. ^b Standard reference distance $R = (r_{34}/\sqrt{3}) = (1.7960/\sqrt{3})$ Å. ^c Ambiguity in distances connected with value of ${}^2J_{\text{C}-\text{N}-\text{H}}$, which is not given a sign. ^d Ambiguity in distances connected with value of ${}^2J_{\text{N}-\text{C}-\text{H}}$, which is not given a sign. ^e Value from $r_{12} = \sin [180 - \{\gamma' + (180 - \zeta')\}]r_{13}/\sin \gamma'$. ^f Value from $r_{12} = \sin [180 - \{\gamma + (180 - \zeta)\}]r_{25}/\sin \gamma$.

Both couplings $D_{32} = D_{34}$ and $D_{15} = D_{16}$ are involved in sign ambiguities in the scalar couplings $J_{32} = J_{34}$ and $J_{15} = J_{16}$ since the overall couplings derived from spectral analysis involve only $|D + J|$.

The resolution of the ambiguity in structure and the absolute signs of geminal scalar couplings. The analysis of the proton magnetic resonance spectrum of oriented ¹³CH₃NH₃⁺ and CH₃¹⁵NH₃⁺ gives values of the $|D + J|$, dipolar plus scalar couplings, for geminal ¹⁵N–C–H and ¹³C–N–H. The values obtained from the spectral analysis are $|(D + J)_{15\text{N}-\text{C}-\text{H}}| = 26.44 \pm 0.13$ Hz and $|(D + J)_{13\text{C}-\text{N}-\text{H}}| = 71.5 \pm 1.3$ Hz. The magnitude of the scalar couplings, determined in separate experiments in isotropic acidified aqueous solution, are $|{}^2J_{13\text{C}-\text{N}-\text{H}}| = 3.5 \pm 0.2$ Hz and $|{}^2J_{15\text{N}-\text{C}-\text{H}}| = 0.79 \pm 0.02$ Hz; see Table II. In arguments regarding absolute signs it is important to recognize that the magnetogyric ratio of ¹⁵N is negative while that of ¹³C is positive. The only reasonable value of $|(D + J)_{15\text{N}-\text{C}-\text{H}}|$ is an absolutely negative one, for reasons that the positive absolute value leads to a completely erroneous structure for the ion. We are left with a small ambiguity in structure because $D_{23} \gg J_{23}$ and J can in principle have either sign. By a similar argument, derived from the necessity of a reasonable structure for the ion, $|(D + J)_{13\text{C}-\text{N}-\text{H}}|$ must be absolutely positive. Again $D_{15} \gg J_{15}$ and a small ambiguity in structure remains since J can have either sign. In this case the error bound from the spectral analysis of oriented

(30) (a) J. Lindgren and I. Olovsson, *Acta Crystallogr., Sect. B*, **24**, 554 (1968); (b) *ibid.*, **24**, 549 (1968).

$^{13}\text{CH}_3\text{NH}_3^+$ is much higher because of the larger line widths in the spectrum.

The two possible dipole-dipole coupling constants derived for $D_{23} = D_{24}$ between ^{15}N and the methyl protons with the sign uncertainty in J can both be used to compute the distance r_{12} . The two computations give 1.56 ± 0.009 and 1.488 ± 0.009 Å (Table VI). The corresponding dipole-dipole coupling constants derived for $D_{15} = D_{16}$ lead to $r_{12} = 1.439 \pm 0.016$ or 1.553 ± 0.018 Å (Table VI). The more acceptable figures are those which have the best agreement between the two independent sets of calculations and also which are closest to previously determined C-N distances in similar species.^{18,30} This in principle determines the correct absolute sign of J and the best value of r_{12} . Because of the larger errors in spectral analysis for the $^{13}\text{CH}_3\text{NH}_3^+$ ion, the value of r_{12} derived from these data must be considered inferior in precision. The error bounds of the mean square deviation between theoretical and experimental frequencies is an inadequate description of the total error, most of which, in the case of the ion $^{13}\text{CH}_3\text{NH}_3^+$, is from systematic sources. The experimental frequencies cannot be adequately defined because of spectral broadening and consequent overlap of peaks which belong to separate transitions. The value of $^2J_{^{15}\text{N}-\text{C}-\text{H}}$ is thus determined as -0.79 ± 0.02 Hz and $J_{^{13}\text{C}-\text{N}-\text{H}}$ as $+3.5 \pm 0.2$ Hz. This decision is based on comparison with similar species which have a C-N bond, rather than the values of r_{12} which are not distinguished by the independent calculations. The value preferred for the C-N bond distance r_{12} is 1.488 ± 0.009 Å because the spectral analysis has negligible systematic error and the distance $r_{12} = 1.564 \pm 0.009$ is unreasonably large compared to other similar ions. It must be noted that this distance derives from the first assumption that the methyl proton-proton distance is 1.746 Å.

The final refined structure for the methylammonium ion is presented as Table VII.

Table VII. Final Structure of the Methylammonium Ion Based on the Geminal HCH²⁶ Distance, 1.796 Å

$r_{\text{C}-\text{N}}$	1.488 ± 0.009 Å
$r_{\text{C}-\text{H}}$	1.096 ± 0.001 Å
$r_{\text{N}-\text{H}}$	1.034 ± 0.001 Å
$\angle^+\text{NCH}$	$108.82 \pm 0.11^\circ$
$\angle\text{C}^+\text{NH}$	$110.63 \pm 0.02^\circ$

Hindered Rotation in the Methylammonium Ion. Considerable efforts have been made to obtain the hindered rotation barrier about the C-C bond in ethane, which is isoelectronic with the ion studied here. The principle methods used have been thermodynamic functions,³¹ spectroscopic methods,¹² and calculations of varied sophistication.¹³⁻¹⁶ The best experimental value from spectroscopy gives a barrier of 2928 cal mol⁻¹ and a torsional potential function appropriate to a purely threefold barrier.¹² Calculated barriers depend on optimization procedures in orbitals and molecular geometry but good agreement is often obtained with minimum basis set. Reported values in calculations

vary between 2.5 and 3.5 kcal mol⁻¹.¹³⁻¹⁶ In the absence of experimental values the rotation barrier has been computed for the isoelectronic molecule BH_3NH_3 .¹⁵ The assumptions of the calculation in this case do not depart from a known molecular geometry. The N-H and B-H bond lengths are taken from NH_3 and BH_3 and angles are assumed to be tetrahedral. Without any geometric optimization the calculated barrier is 2.93 kcal mol⁻¹, while the inclusion of geometric optimization during the rotation as previously reported by Stevens¹⁶ for ethane gives a barrier of 2.77 kcal mol⁻¹.

The proton magnetic resonance spectra of ethane and 1,1,1-trifluoroethane oriented in a thermotropic nematic phase is affected by the internal rotation.¹⁷ We shall use here a similar formulation for the rotationally dependent dipole-dipole coupling constant ratio. Silverman and Dailey¹⁷ have derived the intermethyl and intramethyl dipole-dipole coupling constant ratio assuming free and independent rotation for the molecule 1,1,1-trifluoroethane. The derived equation (eq 6) is entirely appropriate for the methylammonium

$$\frac{D_{35}}{D_{56}} = -\frac{3\sqrt{3}}{2\pi} \int_0^{2\pi} \frac{Q_N(n^2 + 1 - 2n \cos \phi) d\phi}{(Q_N + (n^2 + 1 - 2n \cos \phi))^{5/2}} \quad (6)$$

ion in which the methyl and ammonium protons move on circles of different radius. D_{56} is the intra-ammonium proton dipole coupling and D_{35} is the inter-methyl to ammonium proton dipole coupling (see Figure 4). Q_N is the value $[R'^2/D^2]$ from Figure 3. " n " is the ratio of the distances (r_{34}/r_{56}) from Figure 4. A corresponding ratio of dipole-dipole couplings (D_{35}/D_{34}) can also be expressed by replacing in eq 6 Q_N by Q_0 where $Q_0 = [R^2/D^2]$ from Figure 3. The angle ϕ is an angle of relative rotation about the C-N axis of the methyl and ammonium protons. A small computer program was prepared to evaluate the integral in eq 6 using the distances derived from rotationally independent couplings.

Using the bond distances and angles in Table VII the ratio D_{56}/D_{35} computed from eq 6 using steps of 0.5° in the integration of ϕ gives -2.573 . The measured ratio is -2.618 . In a calculation for the fixed staggered form of CH_3NH_3^+ the ratio $D_{56}/D_{35} = -4.272$ while in the fixed eclipsed form the ratio is -1.996 . Changing the C-N bond length according to the other possible length derived here, namely 1.564 Å, leads to a ratio $D_{56}/D_{35} = -2.747$ for free rotation according to eq 6. The C-N bond distance taken from the previous X-ray study¹⁸ of 1.465 Å gives the ratio $D_{56}/D_{35} = -2.521$ also for free rotation.

The ratio of the rotationally dependent dipole-dipole couplings D_{56}/D_{35} is relatively insensitive to C-N bond length. The restricted rotation, which we assume exists, will define an experimental value in the ion for the ratio of dipole couplings between that of free rotation and the fixed staggered conformation. The values of the C-N bond length derived from the X-ray structure, 1.465 Å, and from this work, 1.488 Å, are both acceptable, since the experimental ratio of dipole couplings is properly bracketed by the freely rotating and the fixed staggered conformational models. The alternate C-N bond length of 1.564 Å corresponding to $^2J_{\text{N}-\text{C}-\text{H}}$ is not acceptable because the experimental

(31) K. S. Pitzer, *J. Chem. Phys.*, **4**, 749 (1936); *Discuss. Faraday Soc.*, No. 10, 66 (1951).

ratio D_{56}/D_{35} is bracketed by the free and the eclipsed ratios. A preferentially eclipsed conformer would be indicated rather than staggered. The experimental ratio

is much closer to the free rotation model than the fixed staggered model for a C–N bond length of 1.488 Å, suggesting a low barrier to internal rotation in the ion.

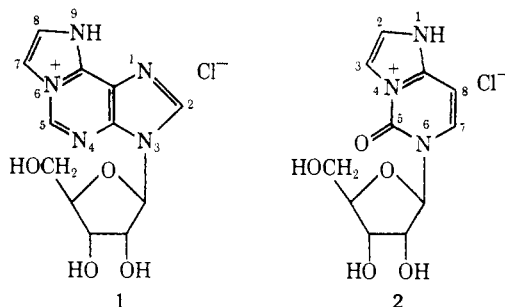
The Crystal and Molecular Structure of a Derivative of 1,*N*⁶-Ethenoadenosine Hydrochloride. Dimensions and Molecular Interactions of the Fluorescent ϵ -Adenosine (ϵ Ado) System

Andrew H.-J. Wang, Laurence G. Dammann, Jorge R. Barrio, and Iain C. Paul*

Contribution from the Department of Chemistry, School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801. Received September 14, 1973

Abstract: The crystal structure of 7-ethyl-3- β -D-ribofuranosylimidazo[2,1-*i*]purine hydrochloride monohydrate (**3**) has been determined both to establish the direction of addition of chloroacetaldehyde to adenosine in the preparation of ϵ -adenine derivatives and to probe the molecular interactions of the highly fluorescent ϵ -adenosine derivative. The crystals of **3** are monoclinic, with $a = 12.952$ (3), $b = 6.667$ (2), and $c = 9.679$ (2) Å, and $\beta = 101^\circ 34'$ (1'). There are two molecules of $C_{14}H_{18}N_5O_4 \cdot Cl^- \cdot H_2O$ in the space group $P2_1$. The structure has been refined to an R factor of 0.043 in 1373 nonzero reflections. The entire ϵ -adenine moiety is near-planar with a maximum deviation of 0.028 Å among the ring atoms. There are some minor differences in bond lengths in the adenine residue in **3** when compared to unbridged adenine rings, but the greatest differences involve the exocyclic angles at C(6). The arrangement about the glycosyl bond is syn ($\chi_{CN} = -109.1^\circ$) and the ribose ring exists in the C(2') endo-C(1') exo conformation. The C(4')–C(5') exocyclic bond is in the trans-gauche arrangement. The N–H bond in the base, all three O–H bonds in the sugar, and the water molecules are involved in hydrogen bonding in the monohydrate. The crystal can be divided into successive regions (in the a direction) of polar and nonpolar character. In the nonpolar regions, there are infinite stacks (in the b direction) of ϵ -adenine rings, each of which overlap considerably with their neighbors with alternate ring–ring separations of 3.344 and 3.324 Å. These overlaps are compared with those found in related molecules.

The reaction of chloroacetaldehyde with adenosine and cytidine to produce fluorescent derivatives^{1,2} is claiming increasing biochemical interest.³ Two compounds that have been particularly useful as fluorescent probes in biochemical systems are 3- β -D-ribofuranosylimidazo[2,1-*i*]purine (1,*N*⁶-ethenoadenosine or ϵ Ado) and 5,6-dihydro-5-oxo-6- β -D-ribofuranosylimidazo[1,2-*c*]pyrimidine (3,*N*⁴-ethenocytidine or ϵ Cyd), each shown as the hydrochlorides, **1** and **2**,



respectively. As an aid to understanding the fluorescent behavior of these compounds, in order to provide detailed molecular dimensions, and to explore

their capability for intermolecular interactions, we have carried out single crystal X-ray studies on a derivative of ϵ Ado, and on ϵ Cyd, both as hydrochloride salts. For the formation of ϵ Ado as the hydrochloride salt from chloroacetaldehyde and adenosine, a logical mechanistic sequence was suggested that first involved alkylation at N(1) (according to convention for numbering in adenine) of the adenosine followed by ring closure of the aldehyde and 6-NH₂ groups with elimination of water.² A test of the direction of introduction of the etheno bridge can be made by utilizing the higher homologs, such as α -chloropropionaldehyde⁴ or α -chloro-*n*-butyraldehyde. It has now been found that the latter reacts with adenosine more slowly than does chloroacetaldehyde but yields a pure ethyl-substituted ϵ -adenosine that exhibits a fluorescent emission maximum at 440 nm with a quantum yield of 0.33 and a lifetime of 17 nsec under neutral conditions. In order to gain the additional information required, we chose the product of the reaction of adenosine with α -chloro-*n*-butyraldehyde for the X-ray study of an example of an ϵ -adenosine derivative. The X-ray analysis establishes the product as 7-ethyl-3- β -D-ribofuranosylimidazo[2,1-*i*]purine hydrochloride monohydrate ($E\epsilon$ Ado·HCl·H₂O) (**3**), thereby proving that N(1) (rather than N(6)) of adenosine reacts with the α carbon of the aldehyde.

(1) J. R. Barrio, J. A. Secrist III, and N. J. Leonard, *Biochem. Biophys. Res. Commun.*, **46**, 597 (1972).

(2) J. A. Secrist III, J. R. Barrio, N. J. Leonard, and G. Weber, *Biochemistry*, **11**, 3499 (1972).

(3) J. R. Barrio, L. G. Dammann, L. H. Kirkegaard, R. L. Switzer, and N. J. Leonard, *J. Amer. Chem. Soc.*, **95**, 961 (1973).

(4) N. K. Kochetkov, V. N. Shibaev, and A. A. Kost, *Dokl. Akad. Nauk. SSSR*, **205**, 100 (1972). These authors did not establish the structure of the product.