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S.E. Filippakis, and R.M. Lemmon

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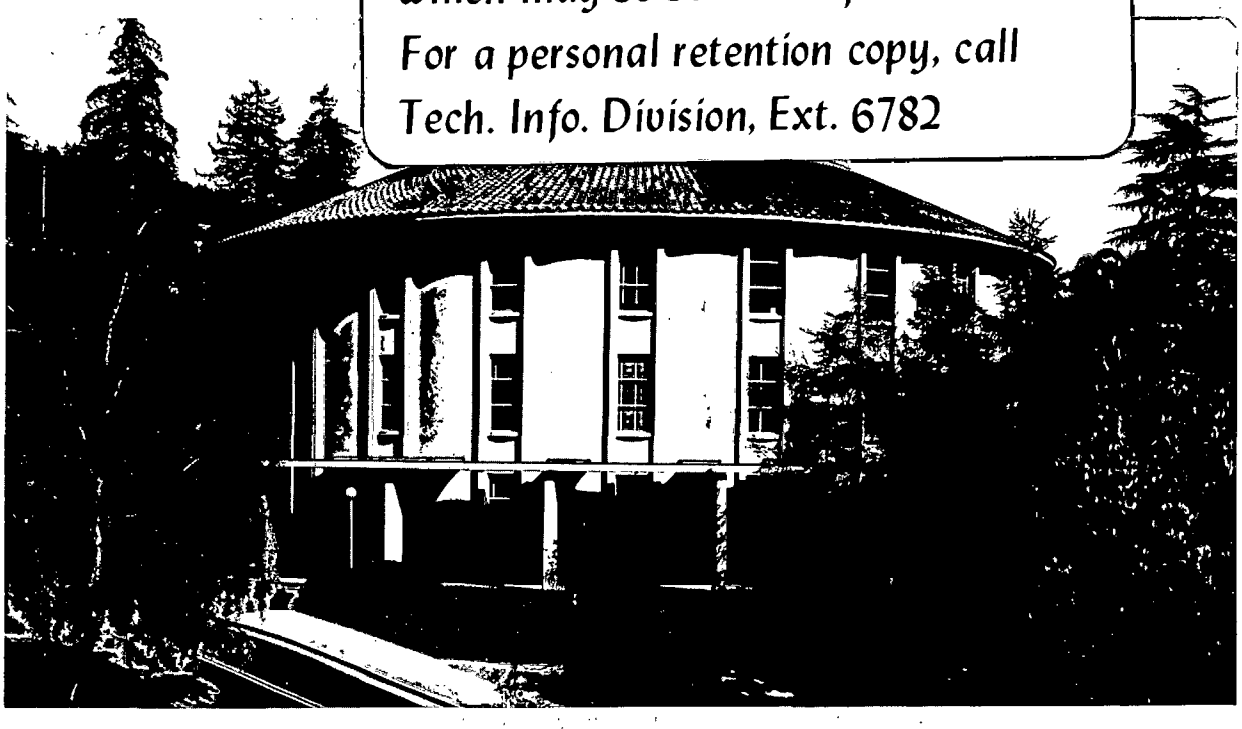

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High Resolution Solid State NMR and X-ray Structure Study of Choline Chloride, Bromide, and Iodide

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^{13}C and ^{2}H high-resolution solid-state NMR studies of choline chloride and bromide in their radiation-sensitive (ambient-temperature) α phases indicate the gradual onset of reorientation motions at temperatures preceding the transition to their respective radiation-stable (higher-temperature) β phases. These motions become isotropic above the α-to-β phase transitions. The early onset of the rotational motion is accompanied by a considerable drop in radiation sensitivity as indicated by previous studies. It is therefore concluded that the extreme difference in radiation sensitivity between the α and β phases is principally due to processes affected by the rotational motions and not to simple crystallographic differences. Choline iodide, which is radiation normal at all temperatures so far studied, shows rotational motions of the two methylene carbons even at room temperature. An x-ray study of the latter compound at ambient temperature indicates the $P2_1/m$ as the possible space group with appreciable disordering motions between the symmetric positions related by the reflection plane defined by the

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O,N, and one of the methyl carbons. The reorientation motion in choline iodide becomes completely isotropic only at temperatures close to its second phase transition (ca. 163°C) accompanied probably by diffusive motions. An analysis of the room temperature spectra shows that in choline chloride and bromide the chemical shift tensor of the N-$^{13}CH_2$ carbon is directed with its smallest principal axis approximately parallel to the N-CH_2 bond. The ^2H spectra (O<u>H</u> position) show that the electric field gradient tensors of all three compounds have similar principal values and are approximately axial.

I. INTRODUCTION

The biologically important choline ion exhibits as a crystalline salt a number of interesting physical properties. Choline chloride $[(CH_3)_3NCH_2CH_2OH]^+Cl^-$ and choline bromide $[(CH_3)_3NCH_2CH_2OH]^+Br^-$ are the most ionizing radiation-sensitive compounds known, while the closely related choline iodide $[CH_3)_3NCH_2CH_2OH]^+I^-$, and a large number of other analogs,are radiation-normal (see Ref. 1 and refs. therein). In addition, the radiation sensitivity of choline chloride and bromide, which is very pronounced at ambient temperature, is limited at higher temperature by phase transitions occurring respectively at ca. 78°C and ca. 89°C.[2]. In addition, the radiation sensitivity is lost at temperatures well below room temperature. Choline iodide, which is radiation normal, shows two crystallographic transitions, one at ca. 95°C and the other at ca. 163°C.[2] Structural data have been available so far only for choline chloride in its α[3] and β[4] phases. The former is characterized by an unusually long N-CH_2 bond of 1.56Å as well as an OH...Cl bond of 3.07Å. Since these are the bonds that dissociate upon γ-irradiation, it has

been suggested that the above features are essential to the unique radiation sensitivity of choline chloride's α form. However, since choline chloride also decomposes upon x-ray irradiation, the above long bonds could be x-ray induced artifacts. Our crystallographic studies of the choline chloride's β form[4] have indicated a highly disordered phase with overall cubic symmetry. As a result, no accurate bond lengths could be obtained from the data. It is not obvious, therefore, whether the large differences in radiation sensitivity between the choline chloride's (and choline bromide's) α and β forms, and those between the choline chloride and choline iodide, are due to simple crystallographic differences or to more complicated molecular mechanisms. In recent studies of the temperature dependence of the radiation sensitivity in choline chloride and bromide[5] we found that with increasing temperature the radiation sensitivity drops well below its maximum value at temperatures close to but clearly lower than the α-to-β phase transition. Apparently, the difference in the radiation sensitivity of the α and β forms should be attributed, at least partially, to mechanisms preceding the α-to-β phase transition. In proton magnetic resonance studies of the linewidth, second moment, and T_1 and T_{1P} relaxation times, Graham and Hannon[6] and McDowell et al.[7] have reported a number of rotational motions in the choline chloride and bromide just below the α-to- β phase transition.

In an effort to obtain direct evidence for the thermally activated rotational motions as well as their possible relations to the temperature dependence of the radiation sensitivity, we have undertaken high resolution solid state ^{13}C and ^{2}H NMR studies of selectively labeled samples of the choline halides. In these studies we have also been

interested in the possibility of determining variations in the structural (e.g., bond lengths) and dynamic (e.g., rotational motions) features of the three salts at the sensitive positions N-$\underline{C}H_2$ and $O\underline{H}$, which could be related to the large differences in radiation sensitivity at room temperature.

In parallel with the NMR studies we have also undertaken an x-ray study of the room temperature phase of the radiation stable choline iodide salt in an effort to locate simple crystallographic differences from the radiation sensitive α phase choline chloride.

II. EXPERIMENTAL

The unlabeled compounds were purchased from Nutritional Biochemicals Corporation and from Sigma Chemical Company. Due to the extreme hygroscopicity, especially apparent in choline chloride (choline bromide is less hygroscopic and choline iodide seems not hygroscopic), the samples were dried by heating under vacuum to ca. 100°C. The dried samples were all handled inside a glove box under dry N_2.

The samples for the NMR measurements were prepared as follows: ^{15}N and ^{13}C labeled samples were prepared from $(CH_3)_3{}^{15}NHCl$ 95% enriched (Stohler) and 90% enriched $Br^{13}CH_2CH_2OH$ (KOR Isotopes). Elemental analyses and mass spectra of the purchased materials gave results in very good agreement with the above specifications. The preparation of the choline halides was effected as follows: $(Me_3)NHCl$ (for simplicity we omit the isotopic mass numbers) was dissolved in a minimum of EtOH, and equivalent KOH was added to 0°C. Then the solution was heated slowly above ambient temperature and the volatile trimethylamine product was transferred gradually over a ca. 2 hour period to a tube containing

the equivalent amount of $BrCH_2CH_2OH$ dissolved in ethanol and cooled at dry ice temperature. The tube containing the bromoethanol-trimethylamine mixture was subsequently sealed under vacuum at -196°C, and then the mixture was allowed to react by heating it slowly to ca. 80°C and maintaining this temperature for ca. 4 hours. The product, $[(CH_3)_3{}^{15}N^{13}CH_2CH_2OH]^+Br^-$, was then collected by evaporating the solution to dryness under vacuum. Part of the product was redissolved in ethanol and converted to the chloride and iodide salts by the following procedure: A small quantity (approx. 5% of the volume) of water was added to the solution, and the choline salt was converted to choline hydroxide, $[(CH_3)_3NCH_2CH_2OH]^+OH^-$, by the addition of a slight excess of Ag_2O (in a darkened flask). The silver products were completely removed by two subsequent filterings through a Celite layer in a fine sintered-glass funnel. Prior to the second filtration, a very small quantity of activated charcoal was added to the solution. (Larger quantities of charcoal adsorb the choline product, in addition to the silver compounds.) The filtrate could be converted to the respective choline halides by the addition of the equivalent amounts of HCl, HBr, or HI. The final products were dried under vacuum at ca. 100°C and kept in a dry box. The above method of preparation was perfected to the point where the yield was better than 80%, and the elemental analysis of C,H, and N before further purification gave results with 1% of the calculated values.

Samples deuterated at the hydroxyl proton were easily obtained by dissolving a small quantity of each choline salt in an excess of D_2O, and drying afterwards under vacuum.

Double resonance NMR experiments were performed with a spectrometer operating at 46.5 MHz freq. for ^{13}C (for a description of this instrument see Ref. 8). Two different probes were used, one for the ^{13}C and the other for the D. The ^{13}C spectra of the natural abundance samples were obtained by enhancing the ^{13}C signal through the protons in a single contact PENIS experiment.[9] The experiments on the enriched samples were simple 90° pulse experiments under pulsed proton decoupling. All samples were in powder form in roughly mmolar quantities, sealed in small pyrex tubes. The temperature was varied by means of a stream of hot or cold nitrogen gas controlled by a feedback system. The stability of the temperature was better than $\pm$ 0.5°. However, the measuring thermocouple (Cu-constantin) was not attached to the sample holder. A correction for the difference in thermocouple reading and sample temperature was made by using a sample (acenapthene) of known melting point. The corrected values are expected to deviate from the real temperature values by 2 deg at most.

Single crystals of choline iodide for the x-ray study were grown by the vapor diffusion method. A small vial filled halfway with a saturated solution of choline iodide in ethanol was placed inside a beaker containing ethyl ether. The breaker was then covered with a watch glass and left overnight at ambient temperature. Due to the much lower solubility of choline iodide in ethyl ether, the salt started precipitating from the solution as the ether vapors diffused into the ethanol. The crystals obtained by this method were plate shaped. The single crystal used in the x-ray measurement was disc shaped with an approximate diameter 0.5 mm and thickness of 0.2 mm.

The crystals of choline iodide are monoclinic with cell constants $a = 5.868(1)\mathring{A}$, $b = 8.178(2)\mathring{A}$, $c = 9.082(2)\mathring{A}$, $\beta = 91.33(2)°$; and unit cell volume $V = 435.7(2)\mathring{A}^3$. The space group, from systematic absences, is either P_{2_1}, or P_{2_1}/m. Data were measured in the 2 θ-θ mode on a P_{2_1} Syntex diffractometer with monochromatic Mo radiation (graphite monochromator). In all, 1143 independence reflections were measured, of which 1089 had amplitudes greater than 2 σ(σ is the standard deviation from counting statistics).

III. NMR RESULTS AND DISCUSSION

In the present studies we center our interest on isolated pairs of nuclei, ^{15}N-^{13}C or D-X (X = chloride, bromide, or iodide). We call the NMR nucleus, I (^{13}C or D), and the pair nucleus, S (^{15}N or X respectively) and we also note that the differences in Zeeman energy of nuclei I and S are large compared to the quadrupolar and dipolar - and consequently all the weaker - interactions. For the study of the NMR spectrum of nucleus I we may therefore apply the following simplified Hamiltonian,

$$\mathcal{H} \simeq -\frac{\gamma_I}{2\pi} H_o I_z (1 - \sigma^I_{zz}) + \frac{\gamma_I \gamma_S \hbar}{2\pi R^3} (1 - 3\cos^2\theta)\, I_z S_z + \frac{eQ}{I(2I-1)} \left\{ 3I_z^2 - I(I+1) \right\} V_{zz} \qquad (1)$$

where, following common practice, we have neglected the nonsecular parts of the non-Zeeman interactions. We did not include in (1) the indirect interaction (J-coupling) because from ^{13}C solution experiments it was estimated that the corresponding splitting is less than 0.15 ppm; i.e., much smaller than the linewidth even in the isotropic phase.

The various quantities in (1) have their usual meanings.

A. ^{13}C NMR Meausrements

For the ^{13}C measurements on the 90-95% enriched $[(CH_3)_3{}^{15}N\ {}^{13}CH_2CH_2OH]^+X^-$ we have the following nuclear spin assignments in equation (1): $I(^{13}C) = 1/2$, $S(^{15}N) = 1/2$. Two possible absorptions occur at frequencies (the energy values have been divided by h):

$$\nu_{\pm} = \frac{-\gamma_I H_o}{2\pi}(1-\sigma^I_{zz}) \pm \frac{1}{2}\left\{\frac{\gamma_I \gamma_S h}{\pi^3}(1 - 3\cos^2\theta)\right\}$$

where $\gamma_I = \gamma(^{13}C) = 0.673 \times 10^4 \frac{\text{rad}}{\text{gauss}\cdot\text{sec}}$ (2a)

and $\gamma_S = \gamma(^{15}N) = 0.271 \times 10^4 \frac{\text{rad}}{\text{gauss}\cdot\text{sec}}$

σ_{zz} is expressed in terms of its principal values as

$$\sigma_{zz} = \sigma_{11}(\cos^2 a \cdot \sin^2 b) + \sigma_{22}(\sin^2 a \cdot \sin^2 b) + \sigma_{33}(\cos^2 b) \quad (2b)$$

where a and b are the polar angles of the magnetic field direction (z axis) with respect to the principal axis system of σ. R in (2a) is the distance between the two nuclei, and θ is the angle between R (bond axis) and H_o. The unknown parameters in (2a) are R, σ_1, σ_2, σ_3, and the Euler angles of the principal axes with respect to a molecular axis system.

Fig. 1 shows the high resolution ^{13}C spectra of unlabeled choline chloride at room temperature and, above the phase transition, at ca. 85°C. No details can be extracted from the room temperature spectrum, which is the sum of contributions from the five carbons of the molecule. The high temperature spectrum verifies the previous assumption[4,6,7] of

an "isotropic" reorientation in this phase. Diffusive motions are unlikely, or at least very limited. The three methyl carbons are approximately equivalent and are expected to give a single line in the spectrum, while the chemically non-equivalent methylene carbons are expected in general to give additional lines. Fig. 1 shows only two lines, with area ratios 4:1. The spectra of the labeled samples, to be presented shortly hereafter, indicate, contrary to what would be implied by the approximate tetrahadral symmetry at the nitrogen atom, that the CH_2-O group carbon has its isotropic absorption line at approximately the same position with the methyl carbons.

Series of representative ^{13}C spectra of ^{15}N and ^{13}C labeled compounds are shown in Figs. 2 through 4. The onset of motional narrowing with rising temperature is clearly demonstrated. Furthermore, the motion leading to the isotropic reorientation starts gradually and clearly below the respective phase transitions. This observation can be combined with our radiation sensitivity-vs-temperature data on choline chloride and bromide[5], which indicate that the decomposition percentage drops well below its maximum value at temepratures below the respective phase transitions. Therefore, the extreme difference in the radiation sensitivity of the α and β forms can be attributed, at least partially, to the rotational motions, and not to simple crystallographic differences[5].

A common feature of the high temperature spectra in Figs. 2-4 is that, besides the main absorption peak, attributed to the ^{15}N-$^{13}CH_2$ carbon, there is a small additional peak in the upfield region. This appears in the same position as the main peak in the non-enriched sample, Fig. 1, and may be attributed partly to the three methyl carbons

at natural abundance (1.1%). Also, in preliminary measurements with samples consisting of a mixture of 50% $[(CH_3)_3{}^{15}N\ {}^{13}CH_2CH_3OH]^+X^-$ and 50% $[(CH_3)_3{}^{15}N\ CH_2{}^{13}CH_2OH]^+X^-$ (X = Cl, Br, I) we obtained at high temperatures two approximately equally intense peaks at the two isotropic positions of Figs. 1-4. We must therefore conclude that the isotropic position of the CH_2-O group carbon approximately coincides with the methyl peaks and, compared to the N-CH_2 carbon, appears in the upfield region.

Some additional features of the high temperature spectra in Figs. 2-4 are the following. The isotropic chemical shift positions of the corresponding methylene carbons practically coincide for choline chloride and bromide; the spearation of the two lines is 14.0$\pm$0.5 ppm in choline chloride and 13.8$\pm$0.5 ppm in choline bromide. In choline iodide one of the methylene carbons is shifted upfield, resulting in a smaller splitting of 11.1$\pm$0.5 ppm. This line shifts back, however, above the second transition to a position close to the one for the other analogs. The new position is 13.4$\pm$0.5 ppm.

The choline chloride and bromide spectra in Figs. 2 and 3 show very strong similarities provided one takes account of the fact that choline bromide has a higher transition temperature. The room temperature spectra of both compounds indicate that motional narrowing mechanisms are frozen out at this temperature except perhaps for indirect effects due, e.g., to C_3 methyl rotations (rotations around the N-CH_2 axis) etc. Choline iodide, Fig. 4, on the contrary, shows distinct characteristics--it should be remembered also that choline iodide is ionizing-radiation stable in contrast to the chloride and bromide. Besides the differences at high temperatures, choline iodide shows appreciable

motional narrowing even at room temperature. The room temperature x-ray results for this compound, Sec. IV, indicate the presence of disordering in the two methylene carbons. It is reasonable, therefore, to assume that these two carbons in choline iodide undergo rotational motions even at ambient temperature.

An approximate simulation of the room temperature spectra in Figs. 2 and 3 employing the Hamiltonian (2) indicated that the dipolar ($N-CH_2$ bond) axis in choline chloride and bromide lies closest (within 30°) to the smallest principal component of the chemical shift tensor. No accurate $N-CH_2$ bond length values could be obtained from this analysis due to the unknown contribution from the other carbon atoms at natural abundance. On the other hand, a similar analysis was not attempted in the R.T. spectrum of choline iodide due to the presence of the motional narrowing.

B. ^2H NMR measurements

For the D measurements I and S in (1) are: I(D) = 1; S(X) = 3/2 for X = ^{35}Cl, ^{37}Cl, ^{79}Br, ^{81}Br, or = 5/2 for X = ^{127}I. In this case the dipolar interaction and the anisotropy of the chemical shift tensor are very small compared to the quadrupole interaction, and they can be neglected in first order. The secular part of the quadrupole interaction will shift the m = $\pm$ 1 Zeeman levels by $(eQ/4)V_{zz}$ each, and the m = 0 level by $(-eQ/2)V_{zz}$. The two absorption lines will appear, therefore, at

$$\nu_{\pm} = \frac{-\gamma_I H_o}{2\pi}(1 - \sigma^I_{zz}) \pm \frac{3eQ}{4h} V_{zz}$$

V_{zz} is expressed in terms of its principal values V_{11}, V_{22}, V_{33} ($|V_{11}| \leq |V_{22}| \leq |V_{33}|$, $V_{11} + V_{22} + V_{33} = 0$) by

$$V_{zz} = \cos^2\theta\, V_{33} + \sin^2\theta \cos^2\phi\, V_{11} + \sin^2\theta \sin^2\phi\, V_{22}$$

where ϕ and θ are the polar angles of the H_0 direction with respect to the principal axis system of the electric field gradient.

The powder line shape will be characterized by intense spikes at the positions

$$\nu_z \pm \nu_1 \left(\nu_z = -\frac{\gamma_I H_0}{2\pi}(1 - \sigma^I_{zz}),\ \nu_i = \frac{3eQ}{4h} V_{ii}\right)$$

and smaller step changes at the position $\nu_z \pm \nu_2$ and $\nu_z \pm \nu_3$.

No evidence of dipolar coupling between deuterons and halogens has been observed, and it is generally assumed that these are quenched by rapid relaxation of the halogens.

The signal-to-noise ratio of the ^2H spectra was not good, but was adequate to permit several conclusions. The similarity of the ambient temperature spectra indicates the presence of the OH...X hydrogen bonding in the bromide and iodide as has been found in the chloride by x-ray crystallography.[3] They also indicate that all three analogs have approximately axially-symmetric electric field gradient tensors, as shown by the values calculated below:

$\nu_1 \simeq 68$ kHz, $\nu_2 \simeq 84$ kHz, $\nu_3 \simeq 152$ kHz and

$$\eta = \frac{\nu_2 - \nu_1}{\nu_3} = \frac{\nu_{11} - \nu_{22}}{\nu_{33}} = 0.1$$

The corresponding values for choline bromide are

$$\nu_1 = 72,\ \nu_2 = 79,\ \nu_3 = 1252 \text{ kHz and } \eta = 0.05$$

and for choline iodide

$$\nu_1 \simeq 69,\ \nu_2 \simeq 86,\ \nu_3 \simeq 155 \text{ kHz and } \eta \simeq 0.1$$

At higher temperatures, but still well below the respective transitions, the apparent ν_3 values for choline chloride and bromide become smaller, while a small isotropic peak appears at the resonance frequency. The latter increases with temperature, and at a few degrees below the transition it becomes the only peak present in the spectrum; above the transition it narrows slightly. These results are in agreement with an early onset (well below the transition) of the isotropic motion evident in the ^{13}C spectra (Figs. 2 and 3). The choline iodide ^{2}H spectrum at 109°C (Fig. 5), representative of the second phase, shows a substantially decreased but not completely quenched quadrupole interaction. Most probably in this phase the rotation for this compound is not perfectly isotropic. This could result from a crystal of less than cubic symmetry. Complete isotropic motion (accompanied probably by diffusive motions, as evidenced from the narrow ^{2}H and ^{13}C lines) set in only at temperatures close to the second phase transition (occurring at ca. 163°C), based on the spectrum at 160°C in Fig. 5.

IV. X-RAY STUDY OF CHOLINE IODIDE

The unit cell volume allows only two molecules in the unit cell, suggesting as a possible space group the P_{2_1} since in the P_{2_1}/m the

molecule, in an ordered structure, would have to lie in a mirror plane. The position of the I, in the space group P_{2_1}, was determined from a Patterson synthesis, and its y coordinate was fixed to y = 1/4. The difference synthesis, calculated with the phases of the I, showed two possible choices for the choline anion, each related to the other with a mirror plane at y = 1/4. The anions shared the N,O and one CH_3(C(1)), all three lying on the y = 1/4 plane, as well as the two other CH_3 groups (C(2)) and C(3)), which lay off the plane and were mirror images of each other. The two remaining carbons, C(4) and C(5), lay above and below the mirror plane, and their mirror images defined the two alternative choices for the choline, Fig. 6.

One of the choline cations was chosen and was refined in the space group P_{2_1}, with an unconstrained least-squares refinement. Gradually, as the structure was being refined the bond distances and angles started to diverge appreciably from the expected values for the choline cation. Repeated attempts to refine an ordered model, in the P_{2_1} space group, failed to converge to a meaningful geometry. This was considered as an indication that the structure might be disordered, and an alternative refinement was attempted in the space group P_{2_1}/m. The atoms I,N,O, and C(1) were restricted to lie on the y = 1/4 mirror plane. The refinement converged to an R_1 = 0.093 and gave a reasonable geometry for the choline molecule. The bond distances were generally larger than those given in Ref. 3 for the choline in choline chloride. The three N-CH_3 distances were larger by 0.04 Å while the C(4)-C(5) and C(5)-O were larger by 0.2 and 0.1 Å.

The constraints imposed on the molecule by the P_{2_1}/m group introduce some distortions to the three angles of C(4)-N-CH_3 and the

C(4)-C(5)-O angle, which is 95°. The C(4) and C(5) carbons show large thermal motions in the direction normal to the mirror plane with rms amplitudes of 2.9 and 3.2 Å respectively. For these atoms, the distances form their mirror images are 0.98 and 1.46 Å. These distances and the large thermal amplitude suggest a disorder in which the molecule converts form the one configuration to its mirror image with large motions of the C(4), C(5) atoms and smaller motions of the rest of the atoms.

These results are in agreement and provide further insight into the rotational motions of choline iodide at room temperature indicated by the NMR measurements (Sec. III A).

V. CONCLUSIONS

We have performed ^{13}C and ^{2}H high-resolution solid-state NMR measurements of the choline halides at the critical positions N-C$\underline{H}_2$ and O$\underline{H}$ (in all crystallographic phases), as well as an x-ray study of the choline iodide at room temperature. The results indicate that with increasing temperature the radiation sensitive choline chloride and bromide undergo rotational motions that become completely isotroic above their respective phase transitions (at ca. 78° and ca. 89°C) to radiation stable phases. The motions leading to the isotropic reorientations start below the phase transitions and this, in conjunction with earlier radiolysis studies[5], indicates the extreme difference in radiation-sensitivity of the two phases should be attributed mainly to mechanisms related to the rotational motions, and not to simple crystallographic differences. The ionizing radiation-stable choline iodide undergoes rotational motions of the methylene carbons even at room temperature.

Furthermore, the reorientation accompanying the first phase transition at ca. 95°C is not perfectly isotropic, but it becomes isotropic accompanied probably by diffusive motions close to the second phase transition (ca. 163°C).

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FIGURE CAPTIONS

Fig. 1. Proton enhanced[9] ^{13}C (46.5 MHz) NMR spectra of choline chloride powder (at natural ^{13}C abundance) in the two crystallographic phases. A single ^{13}C-H contact was employed. The zero of the ppm scale was arbitrarily chosen at the approximate isotropic position of the N-CH_2 ^{13}C absorption.

Fig. 2. Representative FT ^{13}C (46.5 MHz) powder NMR spectra of 90-95% enriched $[(CH_3)_3\ ^{15}N^{13}CH_2CH_2OH]^+Cl^-$. Protons were decoupled. The zero of the ppm scale was chosen at the isotropic position of the ^{15}N-$^{13}CH_2$ peak. The latter appears at approximately the same position for all halogen derivatives.

Fig. 3 As in Fig. 2, but Cl = Br.

Fig. 4. As in Fig. 2, but Cl = I.

Fig. 5. ^2H (28.4 MHz, FT NMR, protons decoupled) spectra of $[(CH_3)_3NCH_2CH_2OD]^+I^-$ above the first transition, and close to the second transition. The zero of the ppm scale was chosen at exact resonance.

Fig. 6. Projection of the two possible conformations of choline ion in choline I on the a,b plane. Dotted line is the mirror plane. Primed atoms represent the alternative configuration of the choline.

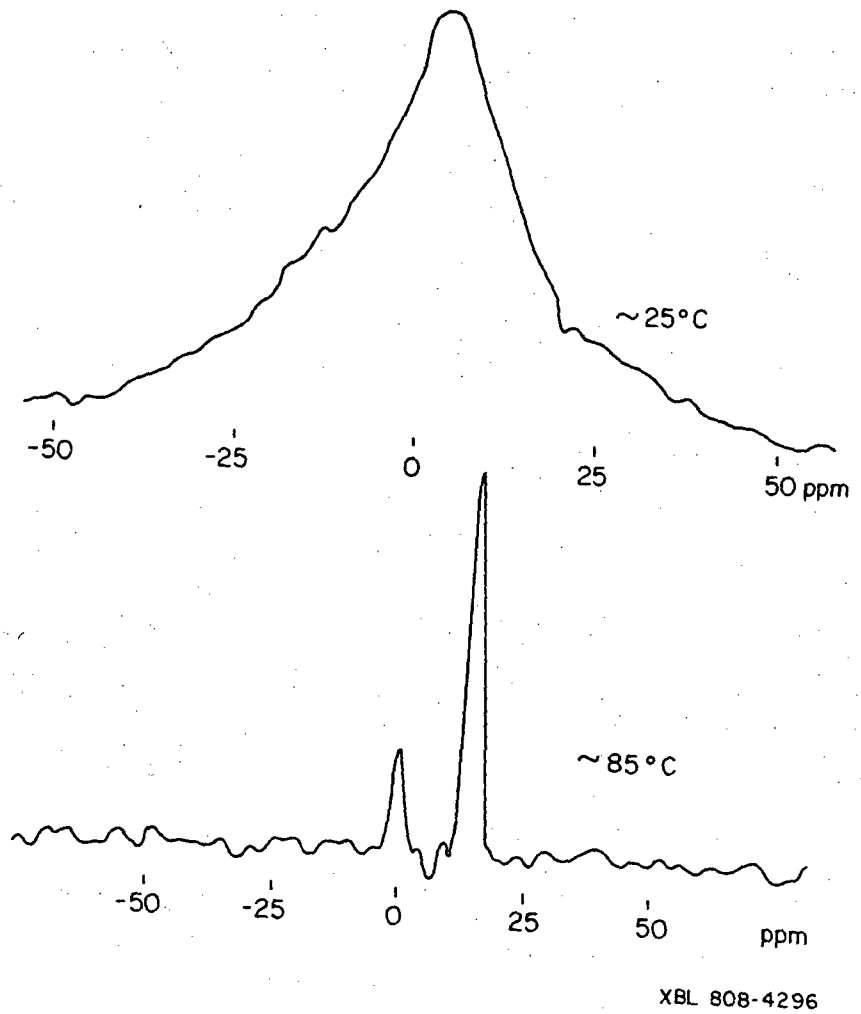

Fig 1
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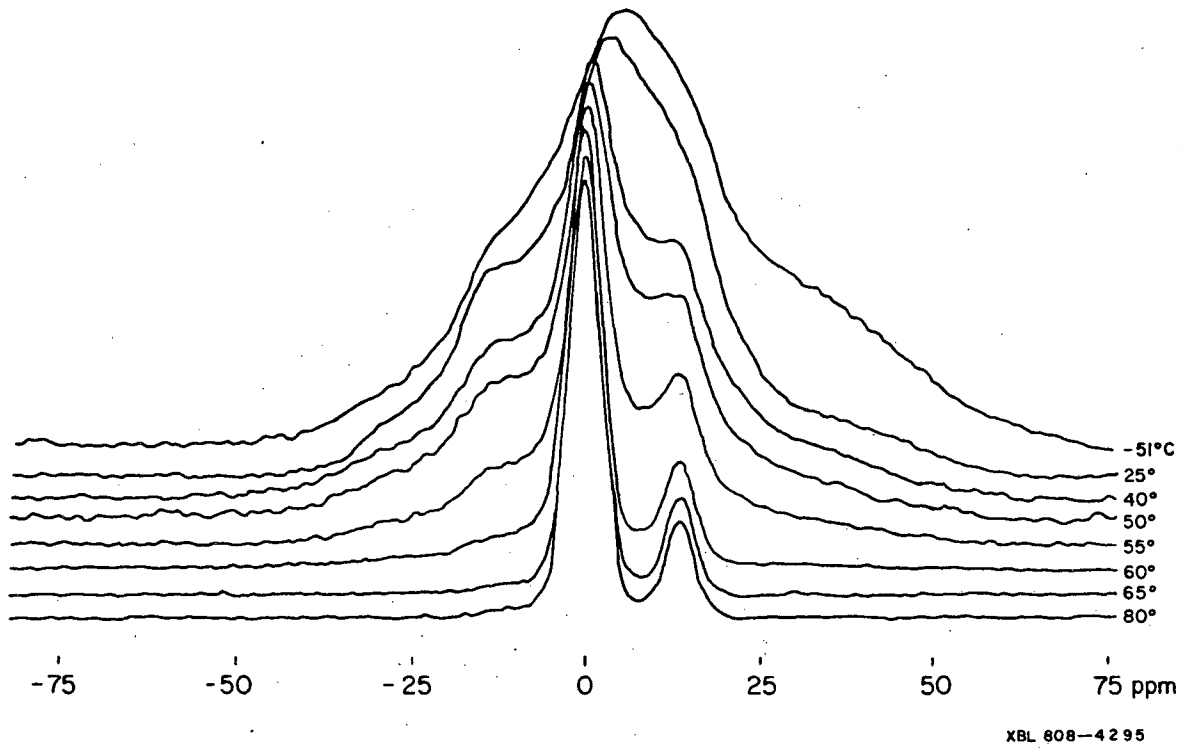

Fig. 2
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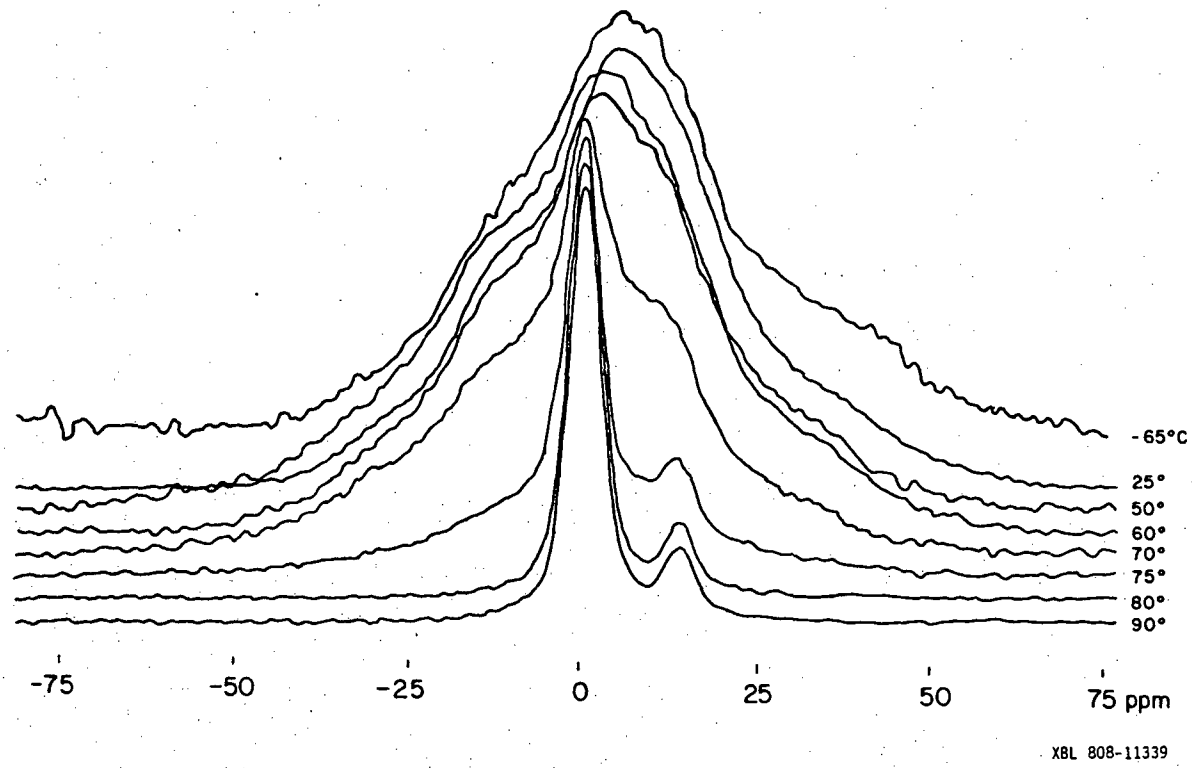

Fig. 3
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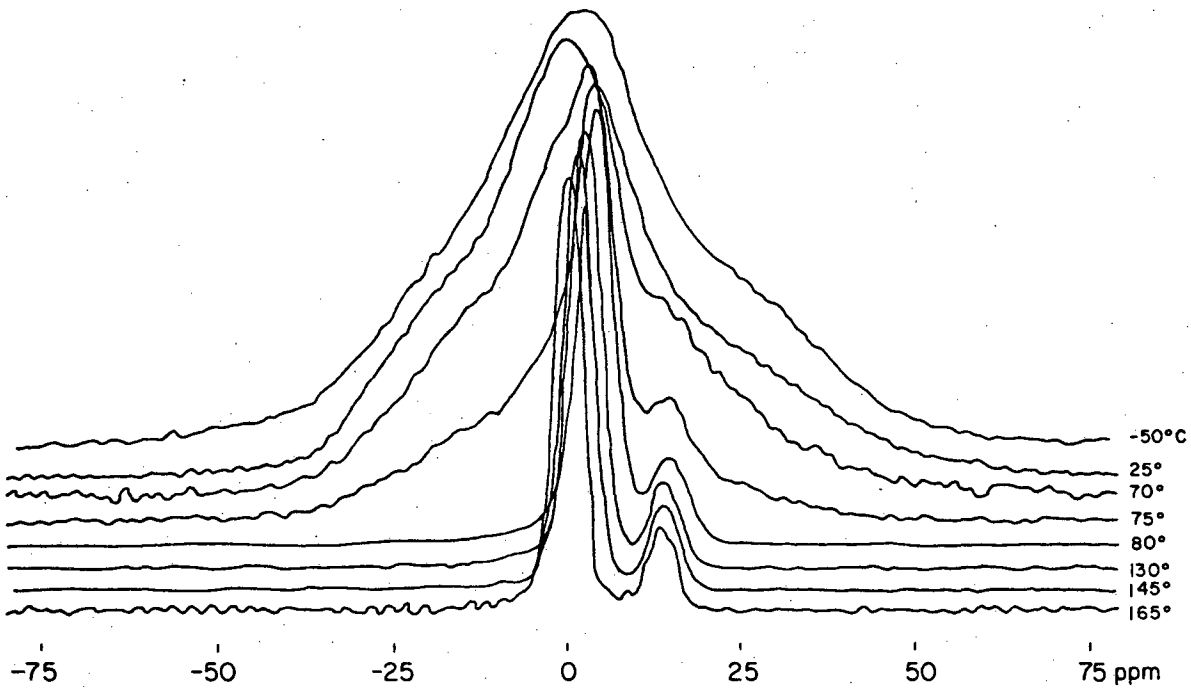


XBL 808-4298

Fig. 4
Wemmer et al.

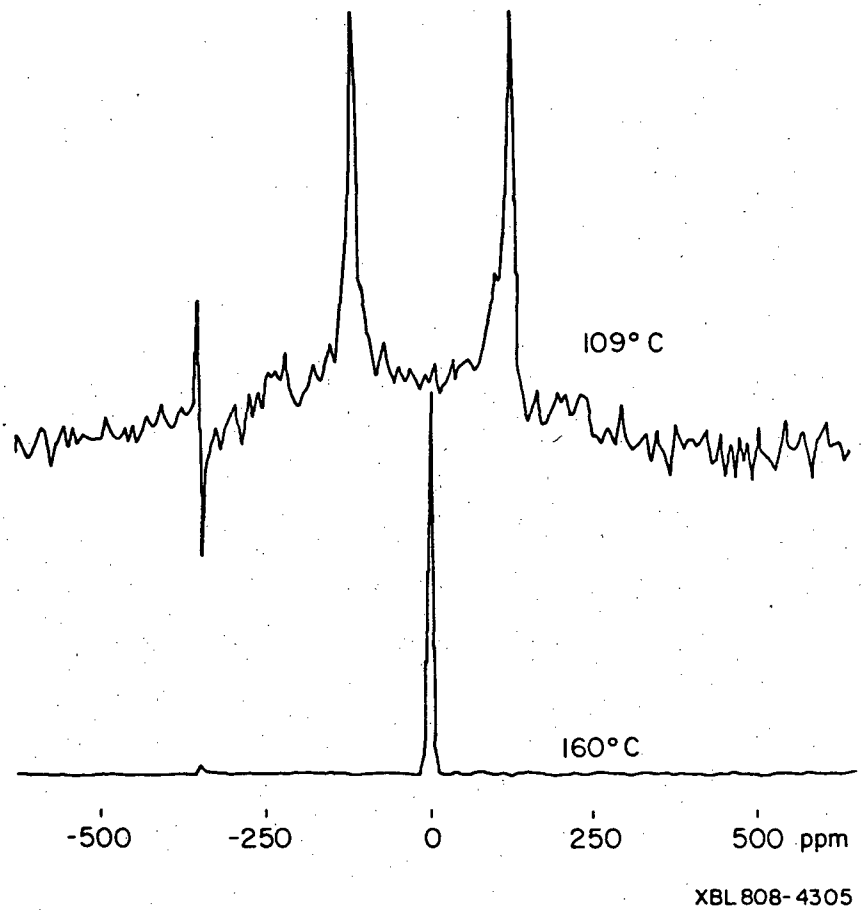
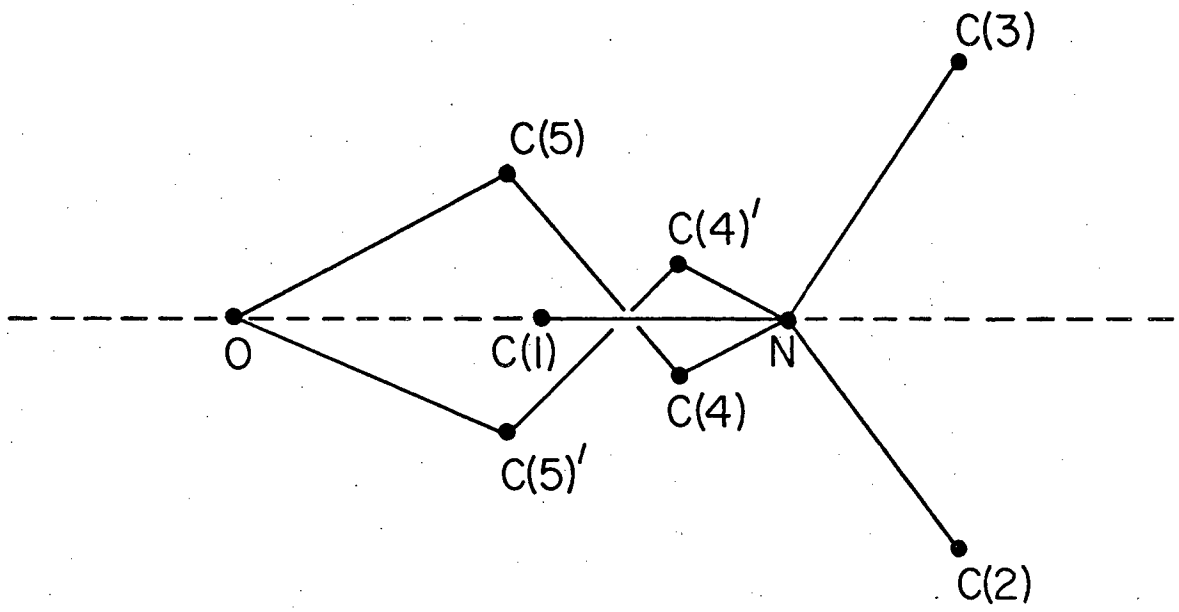


Fig. 5
Wemmer et al.



XBL 808-4306

Fig. 6
Wemmer et al.

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