

Hydrogen Bond Studies

63.* A Nuclear Magnetic Resonance Study of Molecular Motion in Solid Dimethylammonium Chloride

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Proton magnetic resonance data is reported for polycrystalline $(\text{CH}_3)_2\text{NH}_2\text{Cl}$ and $(\text{CH}_3)_2\text{ND}_2\text{Cl}$. The data were obtained in the temperature region 110 to 350 K. The second moment plateau observed at high temperature is consistent with a rapid reorientation of the methyl groups combined with a reorientation of the whole dimethylammonium ion. At the lowest temperature reached, the second moment has a value corresponding to that of a rigid structure. There is an additional intermediate plateau, the height of which corresponds well with that expected for methyl group reorientation only. The barrier to reorientation of the methyl group has been estimated to be 3.3 kcal/mol.

An independent confirmation of the reorientation of the dimethylammonium ion is provided by deuteron magnetic resonance data for $(\text{CH}_3)_2\text{ND}_2\text{Cl}$, giving a quadrupole coupling constant of 72.9 kHz at 303 K.

Differential Thermal Analysis of dimethylammonium chloride indicates two phase transitions,¹ one at 313 K and another at 260 K. The three phases of dimethylammonium chloride are denoted by α -, β -, and γ -DMAC, going from high to low temperature in accordance with Ref. 2.

The crystal structures of α -DMAC² and β -DMAC³ have been determined by X-ray diffraction. β -DMAC has an orthorhombic structure built up of layers, one of which is shown in Fig. 1. The $(\text{CH}_3)_2\text{NH}_2^+$ and Cl^- ions are arranged in a distorted sodium chloride structure. The space group is *Ibam*. The structure of α -DMAC is tetragonal, built up of layers similar to those of the β phase and perpendicular to the *c* axis. The ions are statically or dynamically disordered around the fourfold symmetry axis (*c* axis). The fourfold axis passes through the $(\text{CH}_3)_2\text{NH}_2^+$ ion of one layer and close to the Cl^- ion in the layer below. It is shown in the preceding paper that the short range structure is almost the same in α -DMAC as in β -DMAC.²

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The purpose of the present nuclear magnetic resonance study is to obtain additional information concerning the phase transitions and the dynamical behaviour of the dimethylammonium ion.

EXPERIMENTAL

The compound was obtained commercially and recrystallized three times from a mixture of absolute alcohol, chloroform, and carbon tetrachloride. Deuteration of the NH_2 group was achieved by dissolving the substance in heavy water and allowing the water to evaporate completely *in vacuo*. This was repeated until infrared measurements indicated a degree of deuteration better than 95 %.

Much of the experimental detail dealing with the registration of spectra and the evaluation of second moments is described in a previous paper.⁴ The radio frequency used was 16 MHz for the hydrogen, and 6.5 MHz for the deuterium resonance. The signal-to-noise ratio was improved by using a time-averaging computer (Varian Assoc. C-1024). A CDC 3600 and an IBM 1800 computer were used for the calculations.

The sample had to be kept for a considerable time around 240 K and 110 K to give reproducible spectra in these regions. The temperature was always *increased* between two spectra in a series of measurements in order to avoid supercooling.

CALCULATIONS OF THE SECOND MOMENTS

The theoretical second moments are based on Van Vleck's formula.⁵ The interatomic vectors were based on the atomic coordinates reported in Ref. 3. The only exceptions were the H-H distances within the NH_2 group and within the methyl groups. These were given values of 1.68 Å and 1.79 Å, respectively.⁶ For other pairs of atoms the contribution to the second moment is smaller and less sensitive to the values of the distances used. The hydrogen coordinates of Ref. 3 are therefore sufficient.

A program for the calculation of the reduction of second moments produced by molecular motion has been written.⁷ The motions considered in this program are jumps of atoms and molecules between the possible equilibrium positions, whereas vibrational effects are neglected. These jumps may be considered as correlated or uncorrelated with respect to the motions of other atoms or groups of atoms. For single crystal second moments, the average of the factor $b = (1 - 3 \cos^2 \theta)/r^3$ is taken over the various equilibrium positions of the pair of atoms involved. In this expression, θ is the angle between the external magnetic field and the interatomic vector considered and r is the distance between the atoms. In the case of a powder an additional average of b^2 over all possible crystal orientations is taken using an expression given in Ref. 4.

The calculations as described above included only the dipole-dipole interactions within one cation and between the ion and its twelve nearest-neighbour cations. The quantity $\Delta M_2 = M_2'' + M_2''' - M_2'$ was used as an estimate of the contribution from interactions acting over longer distances. M_2' is the moment obtained for the rigid case when calculations are performed for the twelve nearest-neighbour cations. M_2'' is obtained similarly, but including *all* interatomic distances $r \leq 7$ Å. For $r > 7$ Å, a uniform distribution of protons was assumed, and the second moment contribution, M_2''' , was obtained by integration to infinite r . For normal and deuterated DMAC the corrections, ΔM_2 , were 0.17 G² and 0.12 G², respectively.

RESULTS AND DISCUSSION

Proton resonance data. The experimentally obtained second moments are shown in Fig. 2. The theoretical second moments have been calculated for three main models: (a) rigid structure, (b) reorientation of the methyl groups around the N—C axis, and (c) reorientation of the methyl groups combined with a reorientation of the whole ion among the eight orientations possible for the ion in the α -phase as described in Ref. 2. The axis of the latter reorientation coincides with the fourfold symmetry axis of the α -phase (c axis in the β -phase, *cf.* Fig. 1). Hence the reorientation axis is parallel to the vector between the two carbon atoms of the ion. The values thus computed are given in Table 1.

Table 1. The contributions to the calculated second moments for the proton resonance. The moments are given in G². The corresponding experimental second moments are also shown. The models (*cf.* text) used are: (a) rigid structure, (b) reorienting methyl groups, (c) reorienting methyl groups and dimethylammonium ions.

	$(\text{CH}_3)_2\text{ND}_2\text{Cl}$		$(\text{CH}_3)_2\text{NH}_2\text{Cl}$		
	b	c	a	b	c
Intra CH_3 contribution	5.5	1.4	16.4	4.1	1.0
Intra NH_2 contribution	—	—	4.2	4.2	1.1
Intra cation contribution	6.3	2.2	27.0	11.8	2.9
Total calculated second moment	8.1	3.6	30.3	14.1	4.7
Experimental second moment	8.1	3.0	29.8	13.0	3.4

For each methyl group the reorientation is assumed to be independent of all other motions. In model (c) the reorientations of any two different ions are assumed to be correlated in such a way that these ions at any instant may be described by the arrangement in Fig. 1. The calculated second moments would be approximately the same using other reasonable assumptions about the correlation.

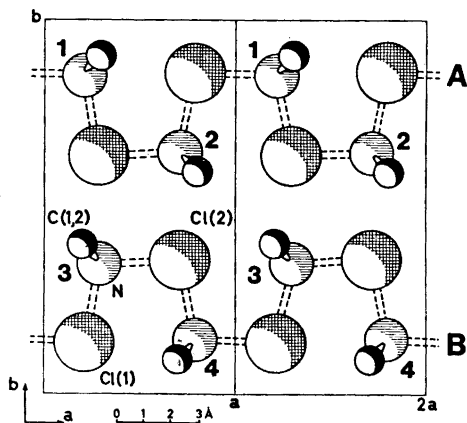


Fig. 1. The crystal structure of β -DMAC.³ A projection on the mirror plane $z=0$ of atoms in and close to this plane.

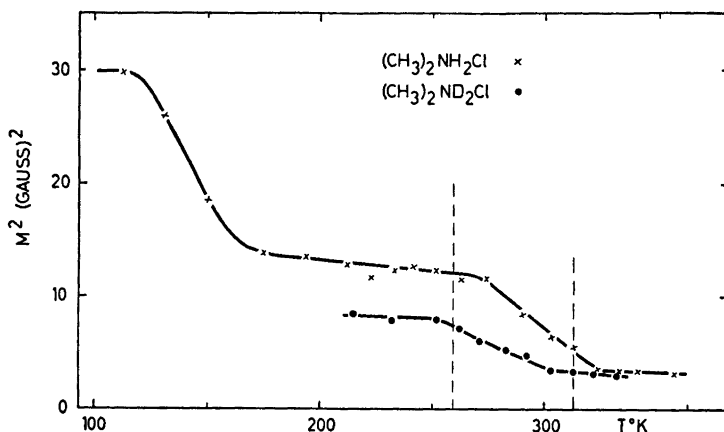


Fig. 2. The second moment for polycrystalline dimethylammonium chloride, normal and deuterated, versus temperature. Vertical lines indicate the phase transition temperatures.

For $(\text{CH}_3)_2\text{NH}_2\text{Cl}$ the experimental second moment below about 110 K is $29.8 \pm 1.0 \text{ G}^2$ and the calculated rigid structure second moment is 30.3 G^2 . This agreement indicates a structure in which all molecular reorientations are too slow (average reorientation frequency $\ll 10^5 \text{ Hz}$) to reduce the observed second moment appreciably. As shown in Fig. 2, on increasing the temperature the experimental second moment passes through two plateaus at about $13.0 \pm 0.6 \text{ G}^2$ and $3.4 \pm 0.3 \text{ G}^2$. These values agree well with those for models (b) and (c), respectively. Data were also obtained for $(\text{CH}_3)_2\text{ND}_2\text{Cl}$ covering only the two high temperature plateau regions. Here the experimental second moments, $8.1 \pm 0.6 \text{ G}^2$ and $3.0 \pm 0.3 \text{ G}^2$, at the plateaus again agree well with models (b) and (c).

An estimate of the barrier E restricting the reorientations has been made assuming: (a) that the reorientation is a thermally activated, random process characterized by a single activation energy E and a single correlation time τ given by

$$\tau = \tau_0 \exp(E/RT)$$

(b) that the second moment reduction as a function of τ follows the relation of Gutowsky and Pake.⁸ An energy barrier of $3.3 \pm 0.3 \text{ kcal/mol}$ was obtained for the methyl group reorientation. This value is reasonable, falling within the range previously observed for methyl groups in solids. Since two phase transitions occur in the temperature range between the two plateaus of 13.0 G^2 and 3.4 G^2 , a calculation of the barrier for reorientation of the whole ion would be rather meaningless.

Deuterium resonance data. The deuterium resonance spectrum of polycrystalline $(\text{CH}_3)_2\text{ND}_2\text{Cl}$ was recorded at 303 K and is shown in Fig. 3. A computer calculated least-squares line shape analysis⁹ gave a quadrupole coupling constant $K = e^2qQ/h = 72.9 \pm 0.7 \text{ kHz}$ and an asymmetry parameter $\eta = 0.83 \pm 0.02$.

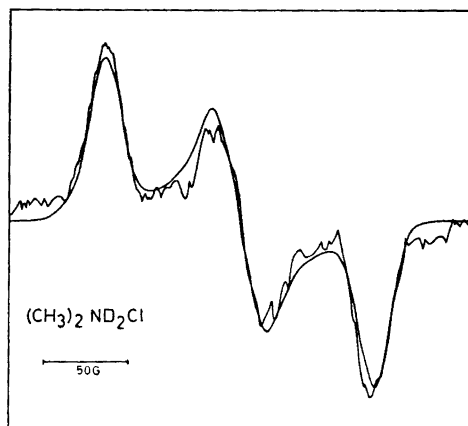


Fig. 3. The deuterium resonance spectrum for $(\text{CH}_3)_2\text{ND}_2\text{Cl}$, and the curve obtained from the least squares refinement.

The parameter η is defined as $(V_{xx} - V_{yy})/V_{zz}$, where $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$ are the components along the principal axes of the electric field gradient tensor at the deuterium atoms, and $eq = V_{zz}$. The line shape obtained from the least-squares analysis is also shown in Fig. 3. Judging from the infrared N-H stretching frequencies (2985 and 2793 cm^{-1})² a quadrupole coupling constant of about 170 kHz would be expected for a stationary deuterium.^{10,11} The asymmetry parameter for a stationary deuterium in a N-D...X hydrogen bond is normally approximately zero. On the other hand, if the molecule is flipping

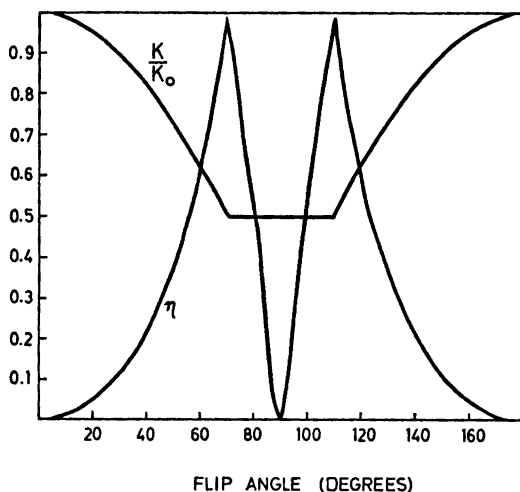


Fig. 4. The asymmetry parameter η and the relative reduction K/K_0 of the quadrupole coupling constant as a function of the flip angle for a deuterium atom jumping between two sites. The electric field gradients at the two sites are assumed to be identical except for the orientation and to have axial symmetry. The flip angle is the angle between the largest principal axes of the two field gradient tensors.

rapidly about an axis normal to the plane of the ND_2 group between equilibrium positions approximately 90° apart, then one would expect the quadrupole coupling constant to be reduced by about 50 %. The asymmetry parameter and the reduction of the quadrupole coupling constant have been calculated as a function of the flipping angle. The results are shown in Fig. 4. The deuteron has been assumed to jump between two sites with $\eta=0$ field gradients and with their largest principal component normal to the rotation axis. This should correspond closely to the situation for the reorienting NH_2 group. The observed value for η corresponds to flip angles of 67, 74, 106, or 113° . An estimate of the flip angle from structural parameters should be the angle between the N–D directions for a particular deuterium atom before and after a jump. However, the deuterium positions are not well known in the present case. Still, an approximate flip angle may be obtained from the N...Cl directions of the hydrogen bonds in which the deuterium atom is involved. For the models described below of the motion in the β -phase of the $(\text{CH}_3)_2\text{NH}_2$ ion, the angle between two successive flips would be 82 or 98° using the N...Cl directions. It must be emphasized that this is a very crude estimate of the N–D flip angle since the hydrogen bonds may be considerably bent. Furthermore, the amount of nonlinearity may be different before and after the jump, since the two bonds involved are structurally nonequivalent.

The essential point, however, is that the deuteron magnetic resonance data apparently rule out the possibility of a stationary NH_2 group, and indicate that some kind of rapid reorientation must occur at 303 K.

Comparison with structural data

1. β -Phase. The structure of the β -phase is shown in Fig. 1. The NMR data clearly show that the dimethylammonium ion reorients rapidly and yet an ordered structure is obtained from the X-ray diffraction data. Uncorrelated jumps of the ions are accordingly ruled out as such motions would imply a disordered structure at any instant. It is therefore necessary to find a model involving a co-operative reorientation of the dimethylammonium ion, and which at the same time gives the diffraction pattern of the ordered structure. Structural features which suggest possible models are the following (*cf.* Fig. 1). The structure is built up of two sets of parallel chains which are equivalent but not identical. The chains are denoted by A and B in Fig. 1. Ions 1 and 2 of chain A may be rotated about 82° to become oriented in the same way as ions 3 and 4 of chain B. In this way the A chain becomes a chain oriented as B and similarly the B chain becomes oriented as A. If at the same time the chlorine atoms are slightly displaced, a structure is obtained which is identical to the original except that it has been translated half a unit cell along the b axis. It would therefore be indistinguishable from the original structure using diffraction methods. Alternatively, the ions may reorient in such a way that the structure is displaced $1/4$ of a unit cell along b and $1/2$ of a unit cell along a . This would be accomplished by letting the molecules 1,2,3 and 4 rotate to the orientations of the molecules 4, 1, 2, and 3, (or alternatively 2, 3, 4, and 1), respectively. If the latter (or both) of the reorientation models suggested above

occur sufficiently often ($\geq 10^5 \text{ sec}^{-1}$), then the NMR spectra will be narrowed as observed. On the other hand, an ordered structure may be observed using X-ray diffraction technique, provided that the time spent in an ordered state is considerably longer than that taken for the reorientation. Clearly the reorientations causing the translations as described above do not have to occur simultaneously in the whole crystal. The mosaic blocks of a crystal may be considered to contribute independently to the *intensity* of the diffracted beam. Consequently it is only necessary to consider what happens within domains of the approximate size of an average mosaic block.¹² To summarize, the model suggested is the following. Molecular flips are excited somewhere in the crystal. These propagate as a dislocation through a domain of the crystal in an average time τ_1 , so transforming it to a "displaced" structure. The process is repeated, on the average, within a time $\tau_2 \gg \tau_1$ and yet short enough to cause the observed NMR line narrowing. On increasing the temperature, τ_2 is expected to shorten, so causing an increased number of dislocations per unit volume of the crystal. This might in fact induce the transformation to the α -phase.

2. α -Phase. On basis of X-ray diffraction and infrared spectroscopic data a description of the structure of the α -phase is given in Ref. 2 in terms of planar domains each with a structure very nearly the same as in the β -phase.

For the reorientation of each $(\text{CH}_3)_2\text{NH}_2^+$ ion, required by the NMR data, eight orientations are available within the structural description of Ref. 2. Four new orientations must be added to the four described above for the β -phase. Each of these new orientations is related to one of the old ones by a 90° rotation of the $(\text{CH}_3)_2\text{NH}_2^+$ ion. The close similarity of the α -structure within one domain to the structure of the β -phase suggests that the reorientations occurring in the α -phase are correlated in a similar way as in the β -phase. However, a correlation between different layers is no longer necessary.

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