Hydrogen Bond Studies

64.* A Proton Magnetic Resonance Study of Molecular Motion in Solid Trimethylammonium Chloride

ROLF SJÖBLOM and JÖRGEN TEGENFELDT

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala 1, Sweden

Proton magnetic resonance data are reported for polycrystalline trimethylammonium chloride. The data were obtained between 110 K and 350 K. Above 200 K the observed second moment plateau is consistent with a rapid reorientation of the methyl groups combined with a reorientation of the whole cation. At 110 K the second moment and the line shape correspond to those of a rigid structure.

A Differential Thermal Analysis indicates a phase transition at 308 K.[1] The two phases of trimethylammonium chloride are denoted by α- and β-TMAC, going from high to low temperature.

The crystal structure of β-TMAC has been determined by X-ray diffraction [2] and is shown in Fig. 1. It is a distorted sodium chloride structure, and each trimethylammonium ion is hydrogen bonded to one chloride ion. The space group is $P2_1/m$.
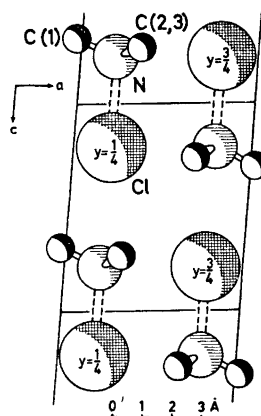
Fig. 1. The crystal structure of β-TMAC.[2] The carbon atoms C(2) and C(3) are related to each other by the mirror plane at $y = \frac{1}{4}$.

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Preliminary X-ray diffraction data on α-TMAC indicate a tetragonal structure with the fourfold axis along the c axis of the β-phase.[3] The fourfold axis is close to, or coincident with the $N-H\cdots Cl$ hydrogen bond. This is inconsistent with the molecular geometry, unless the ion is disordered, statically or dynamically.

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

EXPERIMENTAL

The compound was obtained commercially and recrystallized three times from a mixture of absolute alcohol, chloroform, and carbon tetrachloride. The registration of the spectra, and the evaluation of the second moments are described in previous papers.[4,5] The calculations were performed on a CDC 3600 and an IBM 1800 computer.

CALCULATIONS OF THE SECOND MOMENTS

The calculations of the second moments were based on Van Vleck's formula,[6] and performed as described previously.[4,7] The positions obtained in the X-ray structure determination of β-TMAC were used in all calculations. However, the $H-H$ distances within the methyl groups were given the value 1.79 Å.[8] The calculations were performed including the twelve nearest-neighbour cations. The contribution to the second moments from interactions over larger distances was estimated as described in Ref. 4. The value obtained was 0.32 G^2. Vibrational effects were neglected.

RESULTS AND DISCUSSION

Theoretical second moments have been calculated for three models: (a) a rigid structure, (b) reorientation of the methyl groups around the $N-C$ axis, and (c) reorientation of the methyl groups as in (b) combined with a reorientation of the trimethylammonium ion about the $N-H\cdots Cl$ bond, such that an interchange of the methyl group positions occurs. The motion within a methyl group was assumed to be uncorrelated to all other motions, but the reorientations of neighbouring trimethylammonium ions were assumed to be correlated by a "cog-wheel" effect. The calculated second moments would be approximately the same using other reasonable assumptions about the correlation or assuming no correlation at all. The values thus obtained are given in Table 1.

The experimental second moments are shown in Fig. 2. Below 110 K the experimental value, 30.7 ± 1.5 G^2, corresponds to model (a) (29.4 G^2), and the spectra have the shape expected for a rigid three spin system. Clearly this implies only that any reorientations occurring are too slow to affect the second moment and the line shape, and not necessarily that the structure is actually rigid. Between 110 K and 190 K the second moment drops to a plateau of 2.6 ± 0.3 G^2. This value is much too low to be accounted for by

Table 1. The contributions to the calculated second moments given in G^2. 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 trimethylammonium ions

	a	b	c
Intra CH_3 contribution	19.7	4.9	0.6
Intra cation contribution	25.2	8.0	1.1
Total calculated second moment	29.4	10.6	3.7
Experimental second moment	30.7	—	2.6
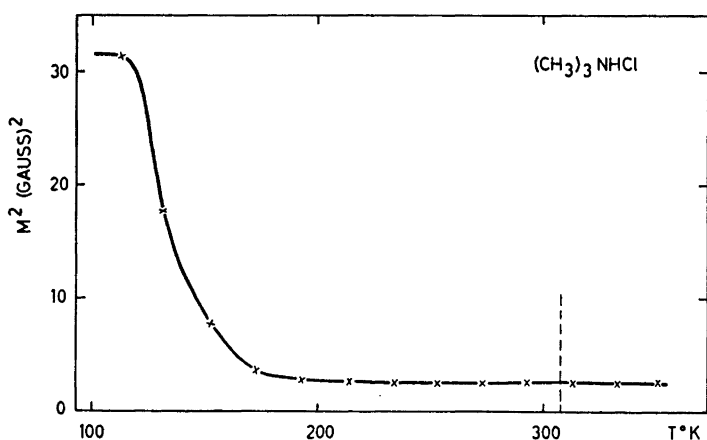
Fig. 2. The second moment for polycrystalline trimethylammonium chloride *versus* temperature. The vertical line indicates the phase transition temperature.

reorientations of the CH_3 groups only. However, it does agree sufficiently well with the value 3.7 G^2 for model (c), and it must be concluded that above 190 K the whole ion, as well as the individual CH_3 groups, reorient rapidly. The fact that no intermediate plateau is observed corresponding to model (b) may suggest that the motions of the whole ion and of the methyl groups are coupled by some "cog-wheel" effect.

The X-ray diffraction study of β-TMAC did not give any evidence of molecular reorientations. However, a reorientation of the whole ion merely interchanges the positions of the methyl groups. Reorientations of this sort have no effect on the X-ray results since the time spent in an ordered state is considerably longer than that taken for the reorientation.

The location of the cation on the fourfold axis of α-TMAC and the three-fold symmetry of a free trimethylammonium ion suggest, that in the α-phase the cation reorients among at least twelve orientations about a direction approximately parallel to the $N - H \cdots Cl$ bond. However, the present investigation cannot distinguish between such a model and model (c) above, since the second moments would be closely the same in both cases.

An estimate of the barrier E restricting the orientations 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.[9] The barrier obtained is 4.0 ± 0.7 kcal/mol.

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