

Hydrogen Bond Studies. 107. A Proton Magnetic Resonance Study of Molecular Motion in Solid Trimethylammonium Iodide, Bromide, and Hydrogen Oxalate*

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Proton magnetic resonance data are reported for polycrystalline trimethylammonium iodide and bromide, and for poly and monocrystalline trimethylammonium hydrogen oxalate. The second moments at the lowest temperatures correspond to values calculated for rigid structures. Line narrowings occur in the temperature region 120–220 K; the values of the second moments at higher temperatures are consistent with combined reorientations of the methyl groups and the cations as a whole around their respective threefold pseudo-symmetry axes.

INTRODUCTION

Nuclear magnetic resonance studies of the molecular motion in trimethylammonium chloride (1, 2) (TMAC), trimethylamine (3), and trimethylamine complexes (4–7) have shown that in all cases, the methyl groups as well as the whole molecule or ion reorient around their respective threefold pseudo-symmetry axes. This reorientational behavior is to be expected in view of the well-established reorientational ability of methyl groups (8), and the symmetrical shape of the trimethylamine group, which also suggests a high mobility. It is the purpose of this paper to combine NMR and structural data in the determination and discussion of the molecular motion in trimethylammonium iodide, bromide, and hydrogen oxalate. These compounds will be referred to herein as TMAI, TMAB, and TMAHOX.

STRUCTURAL ASPECTS

The positional parameters for all atoms in TMAHOX were determined in an X ray study (9); the structure is shown in Fig. 1b. However, a similar study of TMAI (10) revealed only the positions of the heavy atoms. Therefore, the following procedure was adopted to provide a reasonable estimate of the hydrogen positions in TMAI. A cation of the form derived for TMAHOX was placed in the cell of TMAI in such a way that the two sets of nonhydrogen atom positions coincided as nearly as possible. The resulting structure is illustrated in Fig. 1a.

Mussgnug (11) compared X ray diffraction data from mono and polycrystalline TMAI and TMAB and concluded that the compounds are isomorphous and belong

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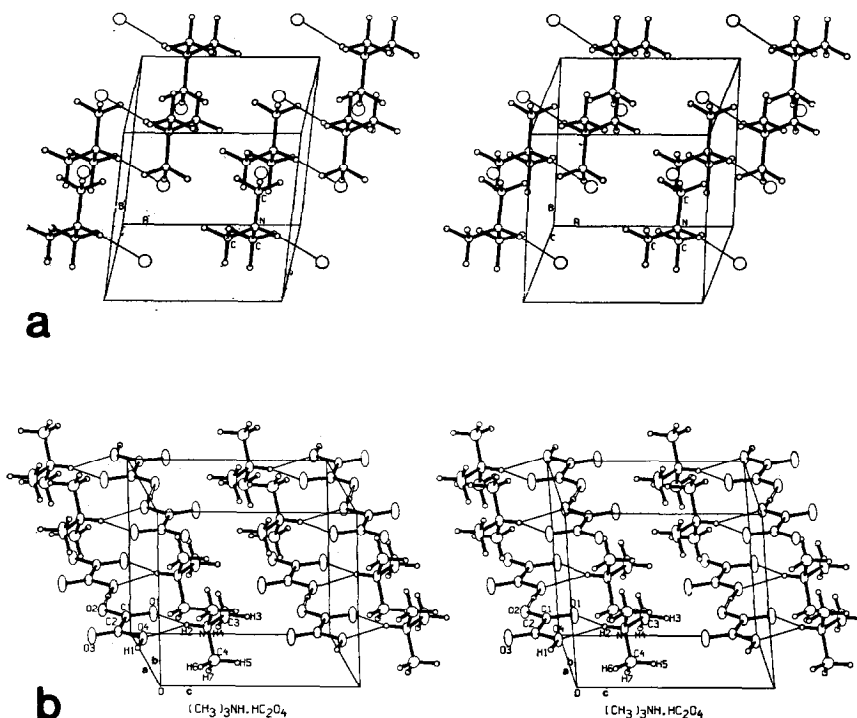


FIG. 1. The crystal structures of (a) TMAI and (b) TMAHOX.

to the space group $C_{2h}^2 (= P2_1/m)$ (12). The centrosymmetric space group was chosen because no piezoelectric effect could be detected in either of the two compounds. The present authors have confirmed Mussgnug's results by determining the Laue symmetry of TMAB from Weissenberg films. Their cell parameters have also been redetermined with an improved precision (cf. Table 1). The Bragg angles for 20 (TMAI) and 39 (TMAB) reflexions were measured from Guinier-Hägg powder films, and the cell parameters were obtained from these angles using a least-squares procedure.

We thus see that Fig. 1a also illustrates the approximate structure of TMAB. Note that TMAI, TMAB, TMAC, and TMAHOX all crystallize in the same space group, $P2_1/m$, but that only TMAI and TMAB have the same packing.

TABLE 1
UNIT CELL PARAMETERS FOR TMAI AND TMAB AT 293 K
(IN ÅNGSTRÖMS AND DEGREES)

	<i>a</i>	<i>b</i>	<i>c</i>	β
TMAI	7.1813	8.3890	5.5617	104.545
	± 0.0011	± 0.0011	± 0.0008	± 0.013
TMAB	6.9386	8.1619	5.4232	107.024
	± 0.0004	± 0.0005	± 0.0003	± 0.005

THEORETICAL CALCULATIONS OF THE SECOND MOMENTS

Theoretical second moments were calculated using a general computer program (PSM), the main features of which have been described in (13). The version currently used has been improved to include a procedure described in (14-16) involving a re-statement of van Vleck's formula in terms of a second moment tensor S (rank two). The program derives the components of this tensor, which depend only on the crystal structure and the assumptions made about the motions of the magnetic nuclei. The second moment, M_2 , for a particular orientation of the magnetic field relative to the crystal can easily be obtained using the formula

$$M_2 = \bar{q} S q$$

where $q_i(\mathbf{h})$ is given in Table 2, and \mathbf{h} is a unit vector along the external magnetic field. Moreover, the second moment averaged over the orientations of the crystallites in a powder is readily obtained as the trace of the second moment tensor (14, 15).

TABLE 2

THE FUNCTIONS q_i USED TO EXTRACT THE ORIENTATIONAL DEPENDENCE OF THE SECOND MOMENT FROM THE SECOND MOMENT TENSOR^a

$q_1 = (5/4)^{1/2} (1 - 3z^2)$	$q_4 = 15^{1/2} xz$
$q_2 = (15/4)^{1/2} (x^2 - y^2)$	$q_5 = 15^{1/2} yz$
$q_3 = 15^{1/2} xy$	

^a The vector $\mathbf{h} = (x, y, z)$ is a unit vector parallel to the magnetic field and given in an orthonormal basis system \mathbf{i} , \mathbf{j} , and \mathbf{k} . These are related to the crystallographic basis vectors \mathbf{a} , \mathbf{b} , and \mathbf{c} in the following way: $\mathbf{i} \parallel \mathbf{a}$, $\mathbf{j} \parallel \mathbf{c}^* \times \mathbf{a}$ and $\mathbf{k} \parallel \mathbf{a} \times \mathbf{b}$.

It is well-known that the positions of covalently bonded hydrogen atoms as determined by X ray diffraction are systematically different from those obtained by neutron diffraction since X rays locate the center of the electron distribution associated with a hydrogen atom while the neutrons locate the average position of the nucleus. The positions of the hydrogen atoms were therefore corrected by increasing the C-H distances by 0.13 Å and the N-H distances by 0.07 Å (17). The distances between the protons within a methyl group were, as earlier (2, 18), constrained to 1.79 Å (18) in all calculations of the intramethyl contributions to the second moments. The 28 nearest neighbor cations were included in all calculations, and the contributions to the second moment from interactions over longer distances were estimated as described in (18).

The following models for the molecular motions were used in the calculations: (a) a rigid structure, (b) reorientations of the methyl groups around their pseudo-symmetry axes, and (c) reorientations of the ions as a whole together with the methyl groups around their respective pseudo-symmetry axes. All motions were assumed to be uncorrelated.

The powder averages of the second moments for TMAI and TMAHOX for the three models are shown in Table 3. The second moment tensor for model (c) for TMAHOX is given in Table 4.

TABLE 3
THE POWDER AVERAGE OF THE THEORETICAL SECOND MOMENTS
FOR TMAI AND TMAHOX IN G²

Compound	Contributing segment	Model ^a		
		a	b	c
TMAI	Intramethyl group	19.7	4.9	0.8
	Intracation	26.5	8.4	1.4
	Total	30.8	11.0	2.6
TMAHOX	Intramethyl group	17.9	4.5	0.7
	Intracation	24.1	7.7	1.3
	Total	28.3	10.3	2.7

^a Three models for the motion have been used in the calculations: (a) rigid structure, (b) reorienting methyl groups, and (c) reorienting methyl groups combined with reorientations of the cations as a whole.

TABLE 4
ONE UNIQUE SET OF THE NONZERO ELEMENTS OF THE SYMMETRIC SECOND MOMENT TENSOR IN G²
FOR TMAHOX^a

Contributing segment	S ₁₁	2S ₁₂	2S ₁₄	S ₂₂	2S ₂₄	S ₃₃	2S ₃₅	S ₄₄	S ₅₅
Intramethyl group	0.406	-0.116	0.703	0.008	-0.100	0.000	0.000	0.305	0.000
Intra cation	0.660	-0.225	1.226	0.029	-0.245	0.000	0.000	0.579	0.001
Total	0.951	-0.163	1.081	0.422	-0.386	0.126	0.098	0.799	0.376

^a Calculated on the assumption that both the methyl groups and the ions as a whole reorient around their respective threefold pseudo-symmetry axes.

EXPERIMENTAL

The compounds were synthesized from the corresponding acid and trimethylamine, which was itself obtained in gaseous form by adding a concentrated water solution of TMAC to partially dissolved sodium hydroxide. The substances were then recrystallized twice from water or ethanol, depending on the compound. Their compositions were checked by powder X ray diffraction (TMAI and TMAB) and by permanganate titration (TMAHOX).

The recording of spectra and the evaluation of experimental second moments were described in a previous paper (20). A Varian wide-line NMR spectrometer (20) was used for the measurements on mono and polycrystalline TMAHOX, and a similar home-built instrument (21) at the University of Nottingham was used for polycrystalline TMAI and TMAB. All calculations were performed on an IBM 1800 and an ICL 1906-A computer.

RESULTS AND DISCUSSION

The experimental second moments versus temperature for polycrystalline TMAI, TMAB, and TMAHOX are shown in Fig. 2. The second moments at the lowest temperatures are much higher than the values expected for Models b and c above (cf. Table 3), but they agree reasonably well with the values obtained for Model a. At higher temperatures, the second moments decrease to 2.2, 2.4, and 2.3 G² for TMAI, TMAB, and TMAHOX, respectively. As may be seen again from comparisons with the values in Table 3, Models a and b must be excluded, but a reasonably good agreement is found for Model c.

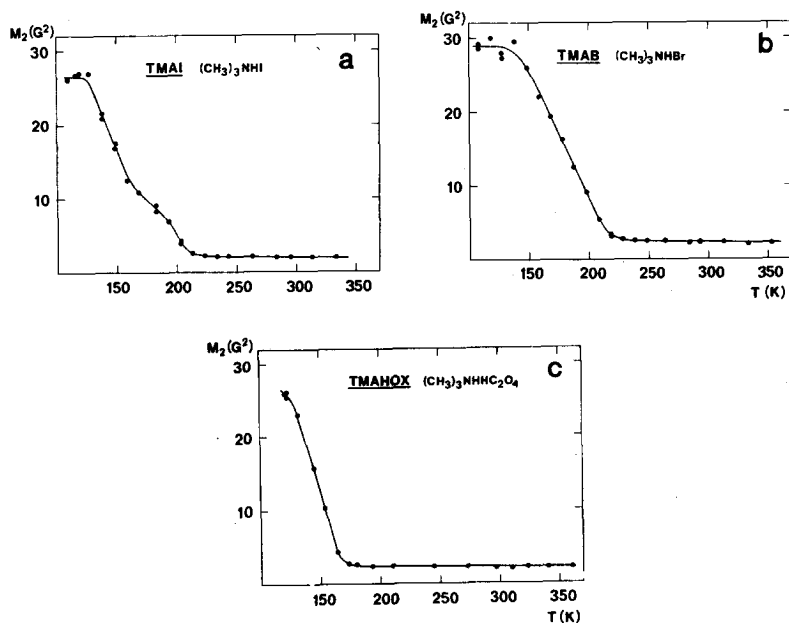


FIG. 2. The experimental second moment versus temperature for (a) TMAI, (b) TMAB, and (c) TMAHOX.

Thus, we conclude that the methyl groups and the ions as a whole both reorient around their respective pseudo-symmetry axes at a rate larger than that corresponding to the linewidth at temperatures above 220, 220, and 180 K for TMAI, TMAB, and TMAHOX, respectively.

To provide further evidence for the dynamical assignments, a single crystal of TMAHOX was studied at 296 K. The second moment was measured for different directions of the magnetic field in a plane of the crystal. The normal to this plane was determined by a least-squares refinement of six reflexions on a four-circle X ray diffractometer. The direction of the magnetic field, which corresponds to $\phi = 0$ in Fig. 3, was determined by a least-squares procedure in which the experimental second moments were compared with those calculated from the theoretical second moment tensor (cf. Table 4) for Model c. The computer program used (ESM) is described briefly elsewhere (15). The experimental points, together with the theoretical curve, are shown in Fig. 3,

and give further support for Model c as describing the reorientations in TMAHOX at high temperatures. The difference between the experimental and calculated curves may be explained partly by imperfections in the single crystal used.

The nearly simultaneous narrowing of the lines due to the two reorientational processes shows that they must have correlation times of about the same order of

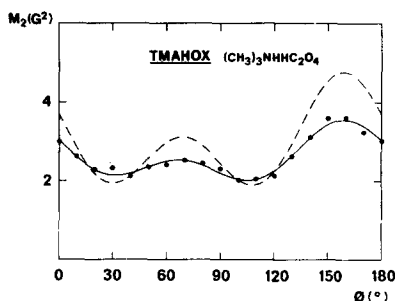


FIG. 3. The experimental second moment versus orientation angle around the axis (0.17831, -0.00335, 0.00015) for a single crystal of TMAHOX at 296 K. The angle $\phi = 0^\circ$ corresponds to $\mathbf{h} = (-0.04917, -0.04075, -0.11474)$ and $\phi = 90^\circ$ to $\mathbf{h} = (0.01257, -0.11178, 0.04183)$. The vectors are expressed in fractional coordinates. The solid curve was determined directly from the experimental values by a one-dimensional Fourier analysis involving the even terms up to and including 4ϕ . The dashed curve shows the theoretical second moment calculated on the assumption that both the methyl groups and the ions as a whole reorient.

magnitude (cf. Fig. 2). This may suggest some form of "cog-wheel" coupling. A similar situation has been observed in TMAC (1, 2). To resolve this situation, a T_1 versus temperature study has been carried out in which two extreme models were used to describe the correlation (22). The two models are: (a) the reorientations of the methyl groups occur completely independently of that of the ion as a whole, and (b) the methyl groups reorient freely during a reorientation of the ion as a whole. However, both models gave almost equally good agreement between experimental and calculated relaxation times. Thus, the totally uncorrelated model was preferred on the grounds of simplicity.

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