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Hydrogen Bond Studies

115. A wide-line and pulse proton magnetic resonance study of molecular motion in solid dimethylammonium iodide, bromide and hydrogen oxalate¹

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Abstract

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Second moments and spin-lattice relaxation times are reported for dimethylammonium iodide, bromide and hydrogen oxalate in the temperature range 100-400 K. Relaxation constants, time factors and activation barriers for the different phases of the various compounds are also determined and discussed. It is concluded that the methyl groups as well as the cations as a whole reorient in all compounds.

Introduction

Previous studies have revealed that various types of motion are present in the three phases of dimethylammonium chloride [1, 2, 3]. The low temperature phase is stable below 260 K and exhibits reorientations of the methyl groups only. In the phase stable around room temperature, there is also reorientational motion of the cations about their two-fold pseudo-symmetry axes as well as about axes parallel to the carbon-carbon directions. The latter motion is consistent with the observed rigid X-ray structure [4] only if the reorientations of neighbouring cations are highly correlated so that the translational symmetry is preserved within most of the mosaic blocks [2]. These motions also take place in the disordered phase stable above 313 K [5].

These results have prompted the present investigation of the closely related compounds dimethylammonium iodide, bromide and hydrogen oxalate (which in the following will be denoted by DMAI, DMAB and DMAHOX, respectively).

Experimental

The compounds DMAI, DMAB and DMAHOX were synthesized from dimethylamine and the corresponding acid. Their compositions were checked by X-ray powder analysis and permanganate and hydroxide ion titration. The compounds were purified by repeated recrystallisation. Special care had to be taken in the synthesis of DMAHOX where several substances can be formed:



and



The powdered compounds DMAI, DMAB and DMAHOX were dried for several weeks over silica gel and then sealed into

glass phials under vacuum. The single crystal of DMAHOX was grown from water solution at room temperature.

The registration of spectra and the evaluation of experimental second moments are described previously [2, 6]. A Varian Asc. wide-line NMR spectrometer was used for the measurements on DMAHOX, and a similar but considerably modified instrument at the University of Nottingham for DMAI and DMAB. The relaxation times were also measured in Nottingham on a Bruker B-KR 322s variable frequency pulse NMR spectrometer, as described earlier [7].

The phases

Measurement of relaxation time at various temperatures provides a sensitive tool for determining phase changes since the relaxation time, in general, changes discontinuously at the transition temperature. No phase change was observed for DMAI in the range 150-400 K. DMAB exhibits one phase change in this range, namely at around 180 K. The phases are denoted by α -DMAB and β -DMAB in going from high to low temperature. Both a β -DMAHOX and a γ -DMAHOX can be obtained from a saturated water solution of DMAHOX. It has been observed that a powdered sample of the β -phase slowly transforms to the γ -phase around room temperature (over a period of several weeks). The γ -phase transforms quite readily to the α -phase if heated above about 330 K. When a sample of this phase was cooled to a temperature a few degrees below this transition temperature, it first transformed to the γ -phase, but then, within a few minutes, transformed again to the β -phase. The β -phase was not observed to undergo any rapid phase transition. It thus appears that the γ -phase is stable around and below room temperature, and that the β -phase is stable at some higher temperature. The stability of the α -phase, which appears at the highest temperatures investigated, cannot be ascertained from the present data.

Structural aspects

The crystal structures of DMAI and DMAB are not known. The symmetries and approximate cell parameters were obtained from

Table I. Symmetry and unit cell parameters for DMAI and α -DMAB at 293 K

Compound	Space group	a (Å)	b (Å)	c (Å)	β (°)
DMAI	C2, Cm or C2/m	11.0365 ± 0.0018	9.9911 ± 0.0009	5.5133 ± 0.0006	110.162 ± 0.011
α -DMAB	Cc or C2/c	13.9948 ± 0.0012	5.5352 ± 0.0004	13.5107 ± 0.0012	93.050 ± 0.010

¹ Part 114: *Chemica Scripta* 1976, 9, 127.

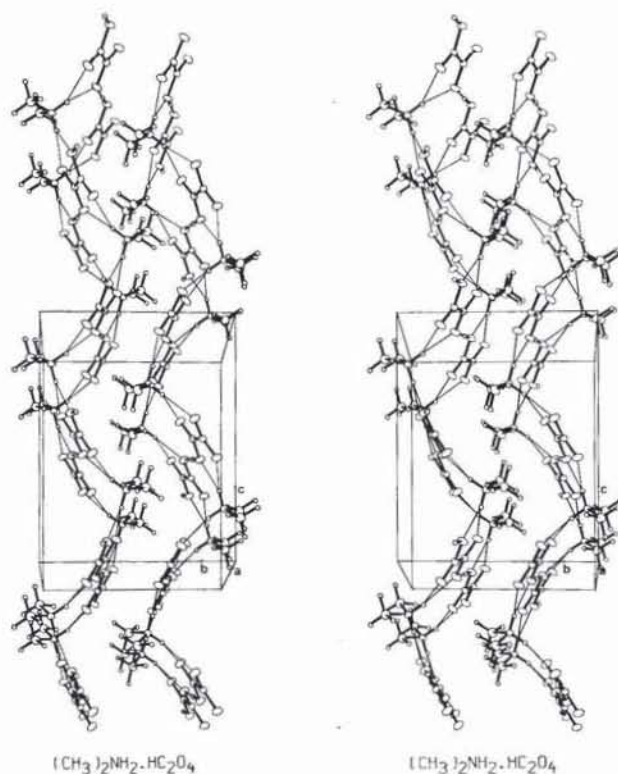


Fig. 1. The stereoscopic view of the crystal structure of γ -DMAHOX at room temperature (8).

Weissenberg films, and the final cell parameters shown in Table I were determined in a least-squares refinement of 13 (DMAI) and 53 (α -DMAB) observed reflexions recorded from powdered samples using a Guinier-Hägg camera. DMAI, α -DMAB, α -DMAC [5] and β -DMAC [4] all exhibit different symmetries as well as large differences in their respective unit cell dimensions.

The crystal structure of γ -DMAHOX has been determined by X-ray diffraction [8] and is shown in Fig. 1. No structural information is available for α - and β -DMAHOX.

Second moments

The experimental second moments are plotted against temperature for powdered samples of DMAI and DMAB in Fig. 2a and 2b, respectively. In view of the close similarity between DMAI, DMAB and DMAC (dimethylammonium chloride), the results of the calculations of the theoretical second moments for DMAC

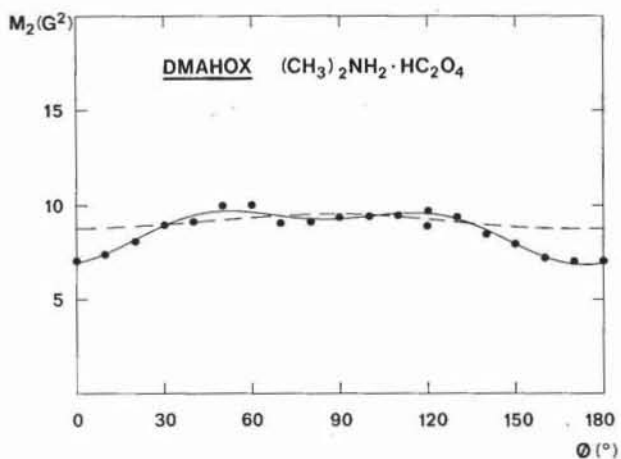
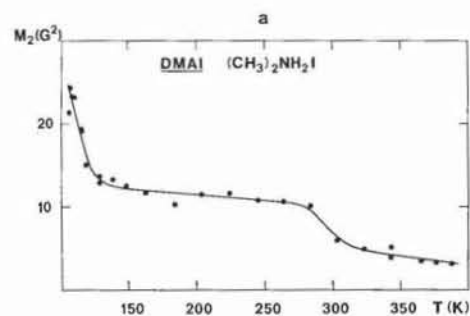


Fig. 3. The experimental second moment vs. orientation angle around the axis $(0.18599, -0.00114, 0.00757)$ for a single crystal of γ -DMAHOX at 230 K. The angle $\phi = 0^\circ$ corresponds to $h = (-0.00931, -0.10151, 0.01108)$ and $\phi = 90^\circ$ to $h = (0.08712, 0.01328, 0.08533)$ where h is a unit vector (expressed in fractional coordinates) parallel to the external magnetic field. The solid curve was obtained directly from the experimental values by a one-dimensional Fourier analysis involving even terms up to and including 4ϕ . The dashed curve shows the theoretical second moment calculated on the assumption that the methyl groups reorient.

given in Ref. [3] will be used here in attempting to determine the motions present. The experimental second moment vs. temperature curves also have the same features. The low temperature plateaus were not observed for DMAI and DMAB, but the highest observed second moments, 24 and 26 G^2 , respectively, lie near the calculated value for a rigid structure: 30.3 G^2 . The experimental intermediate plateaus of 11 and 12 G^2 for DMAI and DMAB, respectively, are in reasonable agreement with the value calculated of 14.2 G^2 which was arrived at on the assumption that the methyl groups reorient rapidly compared with the rate corresponding to the observed line-width. The experimental second moments at the high temperature plateaus of about 3.2 and 3.8 G^2 for DMAI and DMAB, respectively, are close to those determined experimentally for DMAC: 3.7 [1], 3.4 [2] and 3.4 G^2 [3] (the latter value is the trace of the experimental second moment tensor). It was found in the latter study of DMAC that the high temperature second moment is consistent with the value calculated making the assumptions that: (a) the methyl groups reorient, (b) the cations reorient about their two-fold pseudo-symmetry axes, and (c) the cations reorient about essentially four-fold axes parallel to the carbon-carbon directions. The theoretical second moment for DMAC calculated on this assumption is 4.21 G^2 , and those calculated on the basis of assumptions

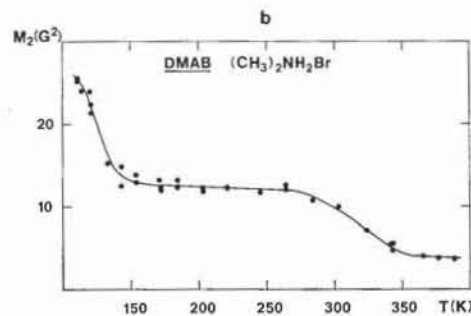


Fig. 2. The experimental second moment vs. temperature for polycrystalline DMAI (2a) and DMAB (2b).

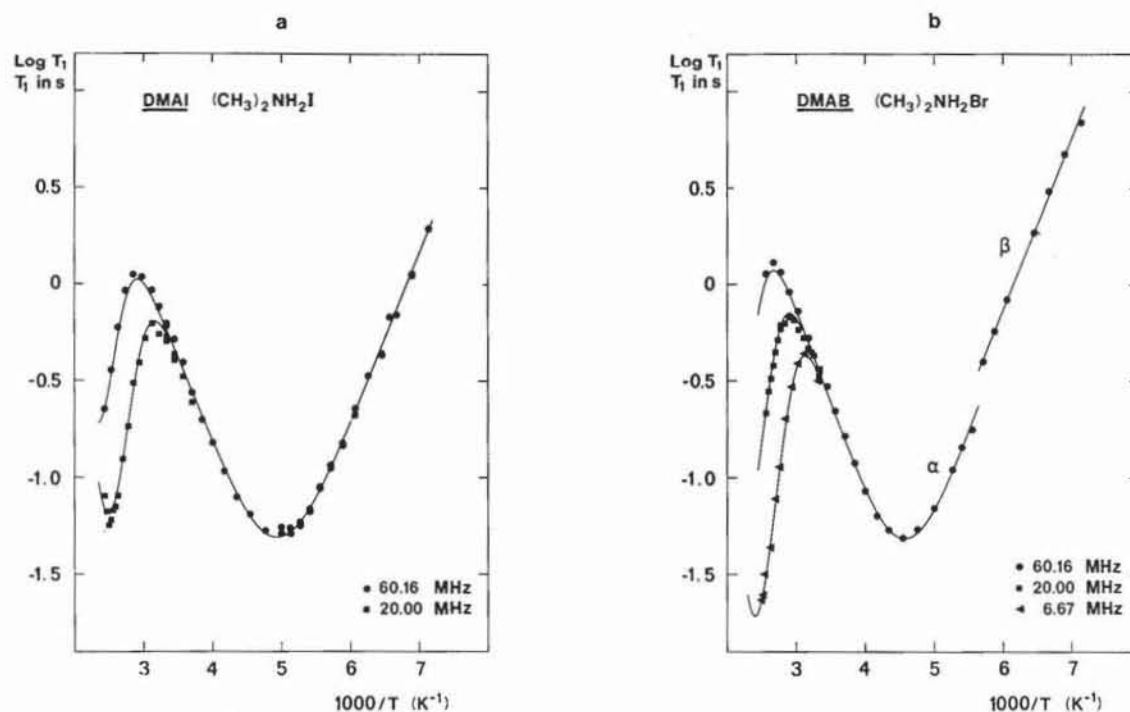


Fig. 4. A plot of $\log_{10} T_1$ (experimental) vs. inverse temperature for polycrystalline DMAI (4a) and DMAB (4b). The solid lines were calculated from the parameters given in Table II.

$a + b$ and $a + c$ are 8.63 and 4.84 G², respectively. The motions in DMAI and DMAB can thus be expected to be rather similar to those in DMAC.

A plot of experimental second moment vs. orientation angle for γ -DMAHOX is given in Fig. 3. The data were recorded at 230 K on a plateau in the second moment vs. temperature curve.

The orientation axis was determined in a least-squares refinement using about 10 reflexions on a four circle X-ray diffractometer: a reference angle in the plane perpendicular to this axis had been determined in previous experiments [3]. Theoretical second moments were calculated from the known X-ray structure of the γ -phase [8] as described earlier [3] and using the procedure

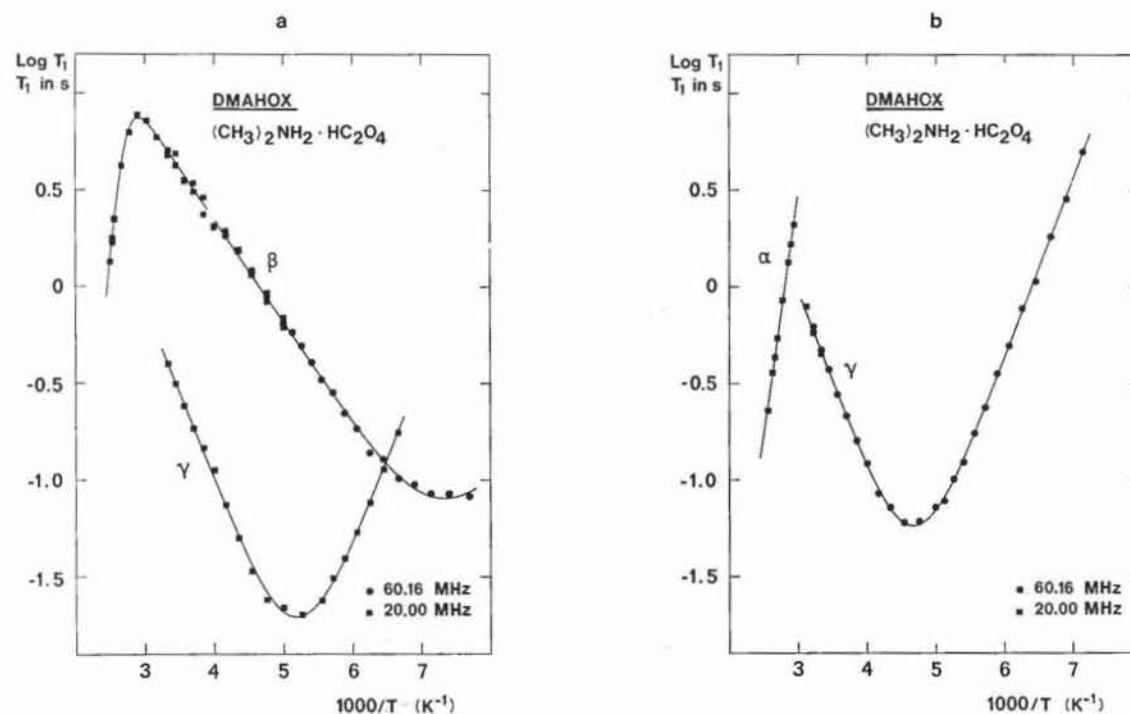


Fig. 5. A plot of $\log_{10} T_1$ (experimental) vs. inverse temperature for polycrystalline DMAHOX (5a) and for an unknown orientation of a single

crystal of γ -DMAHOX (cf. text). The solid lines were calculated from the parameters given in Table II.

Table II. The parameters arising in formula (1) as determined from the experimental relaxation times

The standard deviations are based on the least-squares refinements only

Compound and phase	Motion	RMS (obs.-calc.)/ calc.	C 10 ⁻⁸ s ⁻²	τ_0 10 ⁻¹⁴ s	E kJ/mole
DMAI	-CH ₃ Cation	0.068	54.0 ± 1.1 13.3 ± 0.4	7.2 ± 0.6 0.019 ± 0.010	16.9 ± 0.1 56.9 ± 1.6
β -DMAB	-CH ₃	0.050	—	—	17.0 ± 0.3
α -DMAB	-CH ₃ Cation	0.048	54.8 ± 1.1 15.2 ± 1.4	6.1 ± 0.5 0.026 ± 0.011	18.5 ± 0.2 62 ± 1
γ -DMAHOX (single crystal)	-CH ₃	0.033	46.0 ± 0.6	7.4 ± 0.4	17.8 ± 0.1
γ -DMAHOX (powder)	-CH ₃	0.041	45.5 ± 0.8	11.9 ± 1.1	17.0 ± 0.1
β -DMAHOX	-CH ₃ Cation	0.049	33.1 ± 0.8 —	20.1 ± 0.9 —	10.2 ± 0.1 75 ± 3
α -DMAHOX (cf. text)	Cation	0.027	—	—	48.9 ± 0.6

described in Ref. [9]. The broken line in Fig. 3 shows the theoretical second moment vs. orientation angle calculated on the assumption that the methyl groups reorient. The good agreement strongly supports the assumed nature of the motion (the theoretical second moments for a rigid structure are well outside the range shown in the figure).

Relaxation times

The experimental relaxation times vs. inverse temperature for polycrystalline DMAI and DMAB are shown in Fig. 4a and 4b, respectively. The experimental relaxation times vs. inverse temperature for polycrystalline DMAHOX is shown in Fig. 5a, and for an unknown orientation of a single crystal of γ -DMAHOX in Fig. 5b. The single crystal became opaque on passing through the γ to α phase transition, thus indicating the presence of polycrystallinity in the α -phase.

It has been shown in [9] that, for dynamical processes which have sufficiently different correlation times, the temperature dependence of the relaxation time should follow the formula:

$$T_1^{-1} = \sum_{i=1}^n C_i \left[\frac{\tau_i}{1 + \omega_0^2 \tau_i^2} + \frac{4\tau_i}{1 + 4\omega_0^2 \tau_i^2} \right] \quad (1)$$

together with $\tau_i = \tau_{0i} \exp(E_i/kT)$.

The parameters in this formula have been determined by least-squares refinements using the experimental data. The results are shown in Table II and in Figs. 4 and 5 where the solid curves were calculated from the values given in Table II.

The relaxation constants corresponding to the minima in the relaxation time vs. temperature curve obtained at low temperatures range from 33 to 55 × 10⁸ s⁻². These values are in good agreement with the value obtained experimentally for reorienting methyl groups in DMAC (49 × 10⁸ s⁻²) but are somewhat smaller than the theoretical value (77 × 10⁸ s⁻²) [3]. (The relaxation constant for DMAHOX should actually be multiplied by 1.125 to become comparable with the other values since the formula unit contains an extra acidic proton.) The discrepancy here is probably caused largely by the vibrational motion and the fact that part of the inter-methyl group interactions have smaller correlation times [9]. As expected, the activation barriers fall in the range 10.2–18.5 kJ/mole.

The experimental points deviate slightly but systematically from the calculated curves at and around the high temperature minima for DMAI and DMAB in Fig. 4. This indicates that more than one kind of motion may contribute to the relaxation in this region. The relaxation at the highest temperatures for DMAI, α -DMAB and β -DMAHOX, and at all temperatures for α -DMAHOX is caused by reorientations of the cations as a whole (cf. the discussion in the previous section). The activation barriers range from 49 to 75 kJ/mole.

The detail in these latter motions cannot be extracted from the present data; such an analysis would probably require single crystal X-ray or NMR data. It is interesting to note, however, that the dimethylammonium ion, which has only C_{2v} symmetry, reorients in at least one of the phases in each of the compounds studied.

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