Molecular Motion and Crystal Structure of Solid Tetrapentylammonium Iodide

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The proton NMR spectra and spin-lattice relaxation times of tetrapentylammonium iodide have been measured between 100 K and the melting point. The room temperature crystal structure has been determined by X-ray diffraction as orthorhombic, space group Ccca, $Z = 4$ with $a = 10.811(2)$, $b = 22.771(5)$ and $c = 9.500(2)$ Å with fully ordered tetrapentylammonium cations. The existence of a solid-solid phase transition at 400 K has been confirmed by DTA. The onset of C_3 methyl group reorientations characterized by Arrhenius activation parameters has been evidenced. The intracation conformational motions in the pentyl chains start to manifest themselves already at lower temperatures. The appearence of an ionic plastic phase with coexisting liquid-like and solid-like cations has been discovered.

Key words: Nuclear Magnetic Resonance; Crystal Structure.

Introduction

In our NMR study of the molecular dynamics of the symmetrical tetraalkylammonium cations we have revealed the onset of methyl group reorientation at lower temperatures and quasi-isotropic reorientation of the whole cations around their center of gravity (molecular tumbling) at higher temperatures [1 - 4]. The crystal structure of tetraethyl-, tetrapropyl-, and tetrabutylammonium bromides and iodides is different, however the extended cation conformation is the same [5]. The increase in the length of n-alkyl chains may suggest additional motions due to the appearence of new intracation degrees of freedom. In the case of tetraethyl- and tetrapropylammonium cations we have detected reorientations of their ethyl groups [1, 2]. However, for tetrabutylammonium cations it was not possible to separate this motion from the complicated chain reorientations manifested as a continuous diminishing of the proton second moment with increase in temperature [3, 4]. The investigated salts at higher temperatures undergo phase transitions related with conformational disorder and molecular tumbling. Studying the NMR proton spectra for tetrabutylammonium bromide we have detected solid-like and liquid-like cations representing a conformationally disordered phase (condis phase) coexisting with an ionic plastic phase.

It seemed interesting to extend our study to tetra-n-pentylammonium iodide $(C_5H_{11})_4NI$ in order to examine the expected molecular motions between 100 and 407 K – the melting point of the compound. Therefore, we have undertaken an NMR study of proton second moment, spin-lattice relaxation time, an X-ray crystal structure determination at room temperature and differential thermal analysis (DTA).

Experimental

The polycrystalline sample of tetrapentylammonium iodide (purum, Fluka AG) was recrystallized from anhydrous ethanol, evacuated for several hours and sealed under vacuum in a glass tube. Using a home-made wide-line spectrometer operating at a Larmor frequency of 28 MHz, proton NMR spectra were recorded over a wide range of temperatures. The second moments M_2 were calculated by numerical integration from the first derivative of the absorption lines. Proton spin-lattice relaxation times were measured with a home-made pulse spectrometer operating at 60 MHz, using a saturation method. The temperature of the sample was controlled by means

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Table 1. Crystal data and structure refinement results for tetrapentylammonium iodide.

Empirical formula	$C_{20}H_{44}IN$
Formula weight	212.73
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	orthorhombic, Ccca
Unit cell dimensions	$a = 10.811(2)$, $b = 22.771(5)$, $c = 9.500(2)$ Å
Volume	2338.7(8) Å^3
Z	4
Calculated density	1.208 Mg/m^3
Absorption coefficient	1.369 mm^{-1}
$F(000)$	896
Crystal size	0.4×0.4×0.2 mm
Θ Range for data collection	2.99 to 25.05°
Limiting indices	$-12 \le h \le 12, 0 \le k \le 27, 0 \le l \le 11$
Reflections collected / unique	4712 / 1043 [R(int) = 0.0871]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1043 / 0 / 52
Goodness-of-fit on F^2	0.963
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0511$, $wR2 = 0.1529$
R indices (all data)	$R1 = 0.1109$, $wR2 = 0.1867$
Largest diff. peak and hole	0.558 and –0.511 e·Å^{-3}

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for tetrapentylammonium iodide. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
I	5000	2500	2500	64(1)
N	0	2500	2500	41(2)
C(1)	795(8)	2119(3)	3466(8)	47(2)
C(2)	1609(8)	1673(4)	2756(8)	51(2)
C(3)	2362(8)	1340(4)	3820(9)	52(2)
C(4)	3143(9)	868(4)	3188(11)	65(2)
C(5)	3977(9)	553(4)	4262(12)	76(3)

of a gas-flow cryostat and monitored to an accuracy of 1 K.

After recrystallization from anhydrous ethanol, the transparent crystals of tetrapentylammonium iodide were selected for X-ray investigation. The data collection was performed on a KM4-KUMA diffractometer using MoK_α ($\lambda = 0.71073$ Å, graphite monochromator, and $\omega - 2\Theta$ scan mode). Two control reflections measured after each of 100 reflections showed no significant intensity change throughout the data collection. Lattice parameters were refined from setting angles of 40 reflections in the $15° < 2\Theta < 25°$ range. 4712 reflections were measured, of which 1043 reflections were independent R(int) =0.087 and used in the calculations. The structure was solved by the heavy atom method SHELXS-86 [6] and refined by SHELXL-93 [7]. The H atom positions were calculated assuming C-H = 1.09 Å.

Table 3. Bond lengths [Å] and angles [deg] for tetrapentylammonium iodide.

N-C(1)	1.527(7)	C(1)-C(2)	1.504(11)
C(2)-C(3)	1.503(11)	C(3)-C(4)	1.493(12)
C(4)-C(5)	1.539(13)		
C(1)$^{\#1}$-N-C(1)	110.8(6)	C(1)$^{\#1}$-N-C(1)$^{\#2}$	111.5(6)
C(1)-N-C(1)$^{\#2}$	106.1(6)	C(1)$^{\#1}$-N-C(1)$^{\#3}$	106.1(6)
C(1)-N-C(1)$^{\#3}$	111.5(6)	C(1)$^{\#2}$-N-C(1)$^{\#3}$	110.8(6)
N-C(1)-C(2)	116.4(6)	C(1)-C(2)-C(3)	110.9(6)
C(4)-C(3)-C(2)	113.5(7)	C(3)-C(4)-C(5)	113.6(9)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x, y, -z + 1/2$; $^{\#2}$ $-x, -y + 1/2, z$; $^{\#3}$ $x, -y + 1/2, -z + 1/2$.

The differential thermal analysis (DTA) was made using a home-made apparatus with a heating rate of 2.5 K min^{-1}.

Results

Our DTA study, performed to verify the existence of phase transitions in tetrapentylammonium iodide, shows two heat capacity anomalies at 400 and 406 K (see Fig. 1) in full accordance with the previous investigation [5]. The crystal data, experimental and refinement details are given in Table 1, the atomic parameters of the final model in Table 2 and bond lengths and bond angles in Table 3. Hydrogen atoms coordinates and torsion angles are given in Tables 4 and 5.

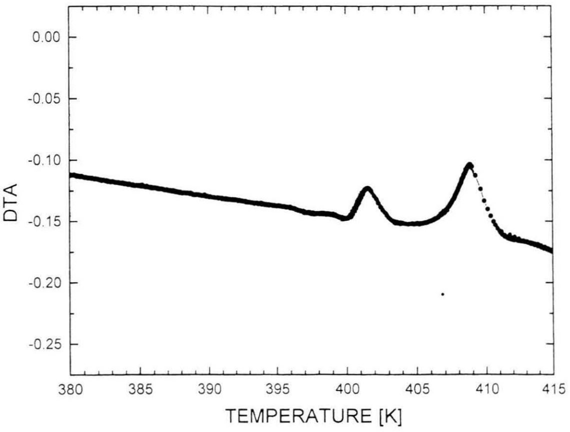

Fig. 1. DTA curve of tetrapentylammonium iodide.

Table 4. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for tetrapentylammonium iodide.

	x	y	z	U_{eq}
H(1A)	188	1883	4186	60
H(1B)	1382	2408	4092	60
H(2A)	2237	1900	2042	60
H(2B)	1040	1371	2145	60
H(3A)	1726	1141	4572	60
H(3B)	2962	1642	4391	60
H(4A)	3725	1063	2375	60
H(4B)	2540	546	2689	60
H(5A)	4530	213	3754	60
H(5B)	4587	875	4749	60
H(5C)	3392	354	5065	60

Table 5. Torsion angles [deg] for tetrapentylammonium iodide.

$C(1)^{\#1}$-N-C(1)-C(2)	54.9(6)	$C(1)^{\#2}$-N-C(1)-C(2)	176.1(8)
$C(1)^{\#3}$-N-C(1)-C(2)	–63.1(6)	N-C(1)-C(2)-C(3)	178.6(6)
C(1)-C(2)-C(3)-C(4)	177.0(7)	C(2)-C(3)-C(4)-C(5)	176.3(8)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x, y, -z + 1/2$; $^{\#2}$ $-x, -y + 1/2, z$; $^{\#3}$ $x, -y + 1/2, -z + 1/2$.

The temperature dependence of the second moment of the proton magnetic resonance lines is shown in Figure 2. In phase II, between 100 and 398 K the plot exhibits a continuous diminishing of M_2 from 20.6 to 17.2 G^2. In phase I M_2 changes from about 13.7 G^2 to 12.2 G^2. At about 407 K it jumps to a value smaller than 0.1 G^2, determined only by the nonhomogeneity of the magnetic field. The temperature variation of the spin-lattice relaxation time T_1 in phase II shows a minimum of 110 ms at 154 K (Figure 3). At 400 K a sudden jump to higher T_1 values was observed. It was not possible, however, to obtain reliable data in the very narrow phase I.

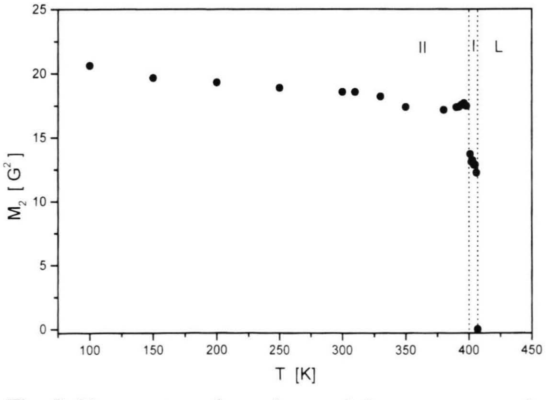

Fig. 2. Temperature dependence of the proton second moment.

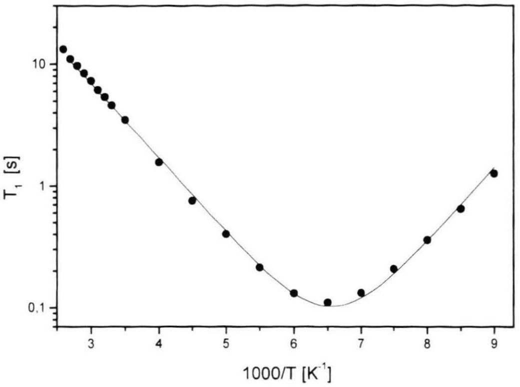

Fig. 3. Temperature dependence of the proton spin-lattice relaxation time in phase II. The solid line is a theoretical fit.

Discussion

Unlike in other tetra-n-alkylammonium halide crystal structures, such as tetraethylammonium iodide, tetrapropylammonium bromide and iodide and tetrabutylammonium bromide and iodide [8], the tetrapentylammonium cation presented in Fig. 4 as an ORTEP drawing at 50% probability is well ordered with an all-trans zig-zag fully extended conformation

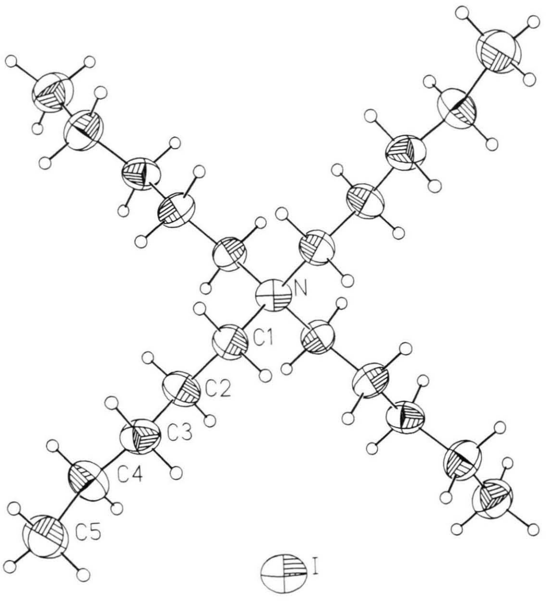

Fig. 4. ORTEP drawing at 50% probability level of tetrapentylammonium iodide.

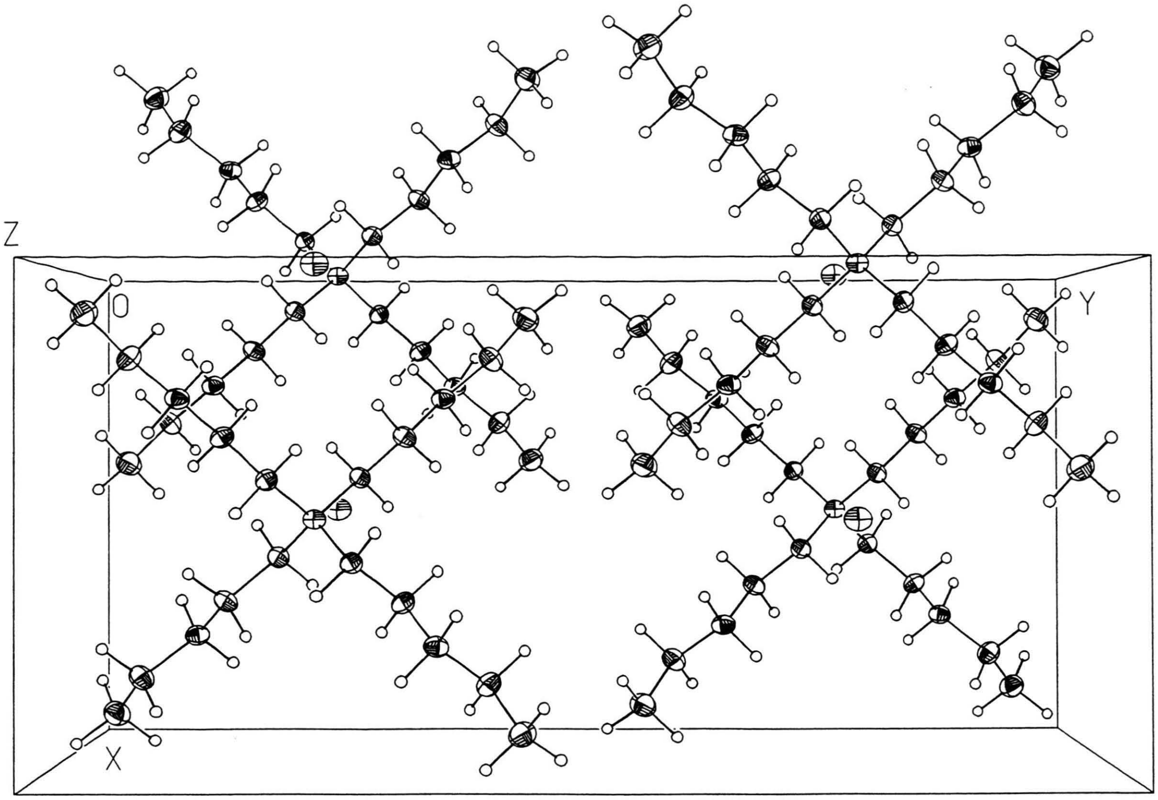

Fig. 5. Packing in the crystal structure of tetrapentylammonium iodide along [001].

of pentyl chains. The bond lengths and valency angles agree with their expected values, but relatively large thermal motions and lack of other strong intermolecular interactions prevent a further discussion of the geometry of the cation. The temperature factors of carbon atoms in the pentyl chain and the distorsions from 180° of the torsion angles at C-C bonds increase with the number of alkyl groups in the chains. This is commonly observed in similar crystal structures. There are four molecular formula units in the unit cell (presented in Figure 5). The N atoms occupy site *a* while the I atoms site *b*, which are the intersections of three perpendicular to each other two fold axes. Using the structural data obtained in our X-ray study we were able to calculate exactly the rigid lattice second moment of the compound. The calculations, performed for 27 unit cells, yield an intracation contribution equal to 23.90 G^2 (H-H interaction 23.39 G^2, H-N interaction 0.51 G^2) and an intercation contribution equal to 5.11 G^2 (H-H interaction 5.09 G^2, H-N interaction 0.02 G^2). The total rigid lattice M_2 value equals 29.04 G^2 being the sum of 23.90 G^2, 5.11 G^2 and 0.03 G^2 (H-I interaction). The observed low temperature M_2 value, equal to 20.6 G^2, indicates the onset of a motion still below 100 K. Its reasonable interpretation is reorientation of the methyl groups about their C_3 symmetry axes. A similar behaviour was observed for all tetraalkylammonium salts investigated. Our observation of a distinct minimum of T_1 confirms the character of the C_3 motion of the methyl groups. The best fitted Arrhenius activation parameters for the C_3 reorientation of the methyl groups are E_a = 11.7 kJ/mol and $\tau_0 = 1.6 \cdot 10^{-13}$ s, (see the fitted solid line in Figure 3). From the know relation $1/T_1^{\min} = \frac{2}{3}\gamma^2 \Delta M_2 g(\omega, \tau)$, one gets $\Delta M_2 = 5.4$ G^2, corresponding to the reduction of the second moment due to reorientation of the methyl groups. Hence the reduced second moment should be about 23.6 G^2. M_2 observed at 100 K equals to 20.6 G^2. This means that even below 100 K the onset of consecutive conformational motions in all n-pentyl chains takes place, leading to further diminishing of M_2 observed up to the

II→I phase transition. It is interesting to note that over the whole temperature range one can observe a narrow component of the spectrum. The intensity of this component increases with the temperature, similarly as it was observed for tetrabutylammonium bromide [4] or tetradecylammonium bromide [9].

This effect can be interpreted as the appearence of liquid-like cations, the mobility of which seems to be thermally activated. The increasing number of such species at still higher temperatures leads to a transition to a new ionic plastic phase with coexisting liquid-like and solid-like cations.

Conclusions

Our NMR and DTA results corroborate the existence of a solid-solid phase transition in tetrapentylammonium iodide at 400 K. The Arrhenius activation parameters characterize the methyl groups reorientation around their triad symmetry axes. Simultaneous conformational motions in the pentyl chains are observed already at lower temperatures. The gradual increase in the number of disordered liquid-like cations observed even at lower temperatures leads to the appearence of an ionic plastic phase I.

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