^{1}H NMR and Differential Scanning Calorimetry Studies of Molecular Motion and Phase Transition in Butylammonium Iodide

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Dedicated to Prof. Dr. Alarich Weiss on the Occasion of his 60th Birthday

The temperature variations of ^{1}H NMR spin-lattice relaxation times and ^{1}H NMR second moments in n-$C_4H_9NH_3I$ and its N-deuterated analog were studied in a wide range of temperatures above 77 K. DTA experiments revealed a solid-solid phase transition between room and low temperature phases taking place at 268 K for the former salt and at 267 K for the latter. For rapidly cooled ($\gtrsim 2$ K min^{-1}) samples, another phase transition possibly between substable low temperature phases was found at ca. 210 K for the former and ca. 205 K for the latter. The transition entropy observed at 268 K was 33 J K^{-1} mol^{-1}. This is much larger than the melting entropy (16 J K^{-1} mol^{-1}), suggesting that butylammonium ions obtain their motional freedom mostly at the phase transition. In the low temperature phase of n-$C_4H_9NH_3I$, the CH_3 and NH_3^+ groups perform C_3 reorientation about their respective symmetry axes with the activation energies $10._4$ and $26._8$ kJ mol^{-1}, respectively. The rapidly cooled sample showed two T_1 components attributable to the stable and substable low temperature phases indicating the coexistence of both phases. In the room temperature phase, the cations rotate rapidly about their long axes and partly conformational disorder of the alkyl chains takes place. The mechanism of the phase transitions is discussed.

Introduction

Recently, we have studied the molecular dynamics of butylammonium cations (ba$^+$) in the three crystalline phases of n-$C_4H_9NH_3Br$ [1]. In the low temperature phase below 200 K, C_3 reorientation of CH_3 groups could be observed while the 180° flip motion of the cation chains and C_3 reorientation of NH_3^+ groups were detected in the intermediate phase between 200 and 249 K. The high temperature phase, having tetragonal crystalline symmetry [2], is characterized by the onset of rapid rotation of the cation chains accompanied by the occurrence of partial conformational melting.

Butylammonium iodide is known to form tetragonal crystals at room temperature, which are isomorphous with the high temperature phase of baBr [2]. Therefore, phase transitions similar to those of baBr are expected to take place for baI at lower temperatures, although no thermal data have been reported as yet. The present investigation of ^{1}H NMR, differential thermal analysis (DTA), and differential scanning calorimetry (DSC) in crystalline baI has been undertaken to locate the expected phase transition and discuss its mechanism as well as to clarify the molecular motion of the cation in such solids.

Experimental

The salt baI was synthesized by neutralizing an ethanol solution of butylamine with hydroiodic acid. The crystals obtained by evaporation were purified by recrystallizing them twice from absolute ethanol. Colorless thin plate crystals were obtained. A partially deuterated salt, n-$C_4H_9ND_3I$ (baI-d$_3$) was prepared by dissolving baI in heavy water and then evaporating the solvent. The above manipulation was done repeatedly in an airtight glass apparatus. Finally, the crystals obtained were purified by recrystallization from deuterated ethanol (C_2H_5OD). Because baI dissolved in water or ethanol is easily decomposed by making contact with air and also it is highly hygroscopic in the crystalline state, the preparative manipulation was performed, at all times, in an atomosphere of dry nitrogen.

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The second moment M_2 of ^{1}H NMR absorption at a resonance frequency of 40 MHz was determined at various temperatures between 77 and 420 K by means of a JEOL JNM-MW-40S wide-line spectrometer. The measurements of the ^{1}H spin-lattice relaxation time T_1 were carried out in the temperature range 100 – 300 K with a frequency-fixed (20 MHz) pulsed spectrometer [3] and a frequency-variable one [4]. A conventional $180° - \tau - 90°$ pulse sequence was used for the determination of T_1.

A homemade DTA apparatus [5] was employed for the observation of phase transitions. A Perkin-Elmer DSC-1B differential scanning calorimeter was used to determine enthalpy changes at the solid-solid phase transition and melting temperatures (hereafter denoted by T_{tr} and T_m, respectively). The temperature of the sample was scanned at a rate of 5 K min^{-1}. The enthalpy changes of transition recorded at T_{tr} and T_m were calibrated by those of adamantane observed at 208.6 K [6] and of metallic indium, respectively.

Temperatures in the above physical measurements were mostly determined by use of a copper-constantan thermocouple and were estimated to be accurate within ± 1 K unless otherwise indicated.

Results

DTA curves recorded in a temperature range 77 – 460 K are shown in Figure 1.

When baI was cooled from room temperature with a slower cooling rate than 0.7 K min^{-1}, an exothermic anomaly was observed at 260 K. With increasing temperature, the sample which had been cooled down to 80 K with the slow cooling rate showed an endothermic peak at 268 K, indicating the occurrence of a first-order phase transition between room and low temperature phases.

When the sample was cooled rapidly ($\gtrsim 2$ K min^{-1}), on the other hand, a new exothermic anomaly appeared additionally at 209 K. This anomaly was much smaller than that at 268 K. With increasing temperature, the sample which had been rapidly cooled down to 77 K yielded a heat anomaly around 210 K. This anomaly had an unusual shape as can be seen in Fig. 1 and in view of its shape one can conclude that three successive phase transitions occur around this temperature showing two endothermic peaks and an exothermic one. When the sample rapidly cooled to 245 ± 5 K was kept (annealed) at this temperature for ca. 1 h, this unusual anomaly disappeared completely, even though the sample temperature was scanned more rapidly than 2 K min^{-1}. Hereafter, we call the rapid temperature change employed above as "rapid-cooling". Conversely, we use "slow cooling" for such cases where the temperature is changed with a rate slower than 0.7 K min^{-1} or the temperature is changed at any rate after it was annealed for ca. 1 h at ca. 245 K.

The DTA curves of baI-d_3 were very similar to those of baI. The slow and rapid cooling methods, respectively, gave a single exothermic peak at 259 K and two exothermic peaks at 259 and 205 K. With increasing temperature, the sample treated by the slow cooling showed an endothermic peak at 269 K while the sample treated by the rapid cooling showed an additional heat anomaly having a structure like that of baI around 205 K. It is interesting to note the low temperature anomaly (ca. 205 K)

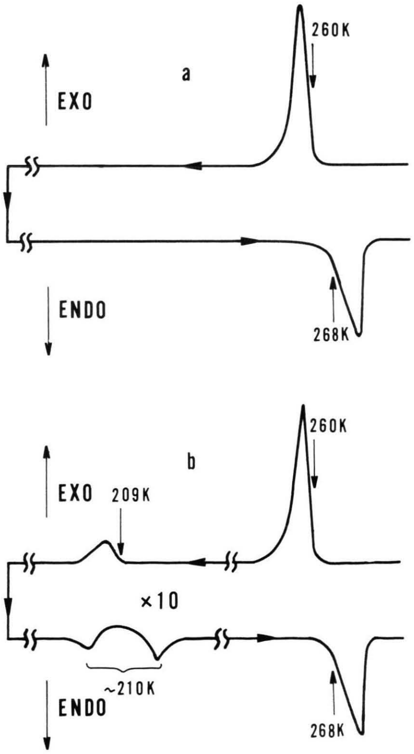

Fig. 1. DTA curves of n-$C_4H_9NH_3I$ recorded on slow (a) and rapid (b) change in temperature. The low temperature anomaly being very small, the intensity scale on the low temperature side of b is ten times enlarged.

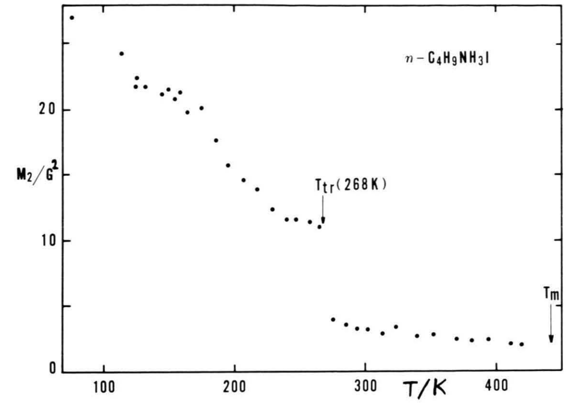

Fig. 2. Temperature variation of the second moment M_2 of ^1H NMR absorptions for n-$C_4H_9NH_3I$.

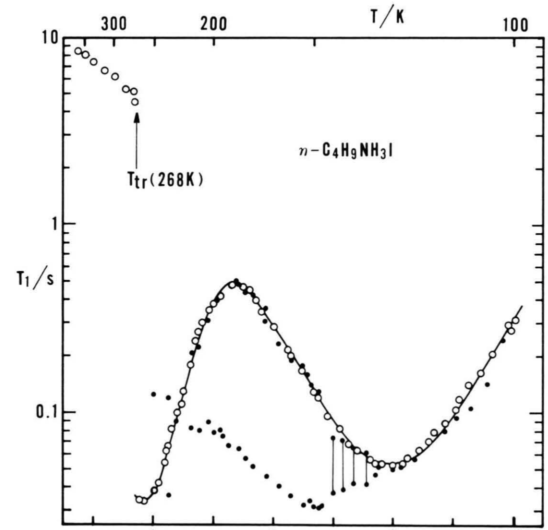

Fig. 3. Temperature dependences of ^1H NMR T_1 observed at 20 MHz for n-$C_4H_9NH_3I$. Circles and dots are the T_1 values described in the text. Vertical lines indicate the uncertainties of T_1 determined at various temperatures where nonexponential ^1H magnetization recovery curves were observed. The solid line shows the theoretical curve fitted by the method of least-squares.

Table 1. Changes in enthalpy ΔH and entropy ΔS at the solid-solid phase transition and melting temperatures of butylammonium iodide. The data for butylammonium bromide are also included for comparison. Data in parentheses are for the partially deuterated analogs (n-$C_4H_9ND_3X$).

Salt	Transition	T/K	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
n-$C_4H_9NH_3I$	solid to	~ 210 (~ 205)	–	–
	solid	268 (269)	8.8	33
	melting	442 (448)	7.2	16
n-$C_4H_9NH_3Br$	solid to	200 (198)	1.5	7.5
	solid	249 (249)	5.7	23
	melting	478	8.3	17

did not easily disappear even when baI-d_3 was treated by the slow cooling. In other words, baI-d_3 gave sometimes two anomalies on warming though it had been treated by the slow cooling. The disappearance of this anomaly in baI-d_3 seems to occur more easily for high purity samples. This is because the sample employed without any purification by recrystallization from deuterated ethanol always yielded the additional anomaly although we tried many runs using several kinds of cooling and annealing processes.

When baI and baI-d_3 were heated above room temperature, no heat anomaly was observed up to 442 and 448 K, respectively, where the samples melted with partial decomposition taking place. This was confirmed from the fact that by repeating the processes of melting and solidifying, T_m gradually decreased and the sample changed its color to yellow or somewhat brown.

From the measurements of DSC, the enthalpy changes observed for the phase transition at 268 K and the melting are given in Table 1. The enthalpy change for the phase transition around 210 K could not be determined, the heat anomaly being too small.

The temperature variation of ^1H M_2 for baI was observed with increasing the temperature after the sample was cooled to 77 K by the slow cooling. The results are shown in Figure 2.

When baI was warmed from 77 K to ca. 270 K, M_2 decreased almost continuously from 27 to 11 G^2, however nearly constant values of 22 and 11.5 G^2 were obtained in two narrow temperature regions around 150 and 250 K, respectively. At ca. 270 K, a discontinuous decrease in M_2 was observed in agreement with the presence of the phase transition revealed by DTA. With increasing the temperature furthermore, M_2 decreased gradually and reached 2 G^2 at 420 K.

Figure 3 shows the temperature dependences of ^1H T_1 at 20 MHz observed for baI. Dots indicate T_1 values measured with increasing temperature after

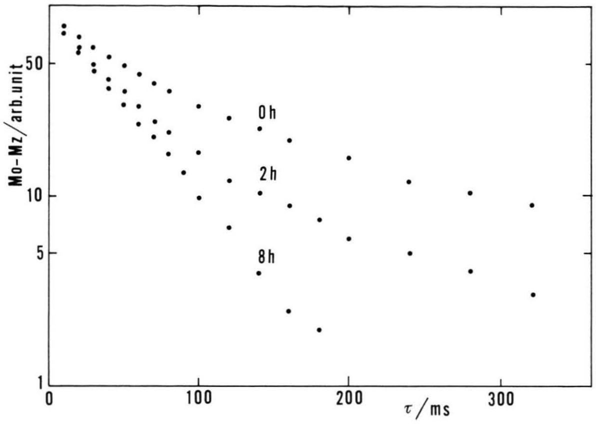

Fig. 4. Time dependence of ^{1}H magnetization recovery at 248 K. Measurements were made immediately (a), 2 h (b), and 8 h (c) after setting the temperature.

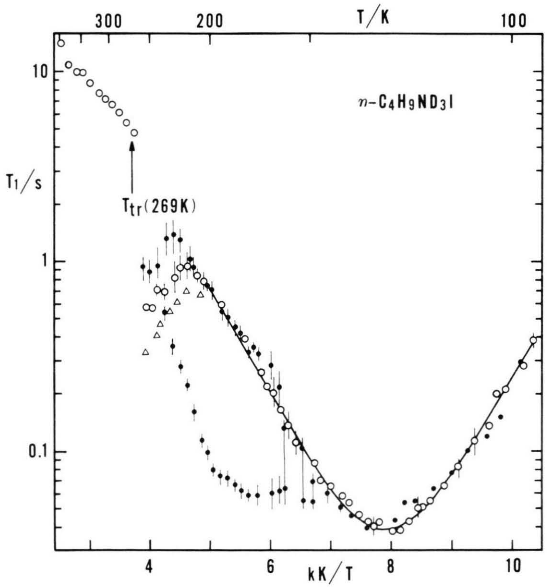

Fig. 5. Temperature dependences of ^{1}H NMR T_1 observed at 12.6 (△) and 20 (○ and ●) MHz for n-$C_4H_9ND_3I$. Dots and circles, respectively, indicate ^{1}H T_1 values determined with increasing temperature after rapid cooling to 77 K and with decreasing the temperature slowly. The meaning of the vertical lines is the same as in Figure 3. The solid line is the least-squares fitted theoretical curve.

cooling rapidly to 77 K while circles show those determined on slow cooling or on warming after slow cooling to 100 K.

The slowly cooled sample yielded, on the warming run, two deep T_1 minima of 51 and 37 ms at 127 and 260 K, respectively, in the low temperature phase. With increasing the temperature T_1 increased discontinuously by two orders of magnitude at 268 K which agreed well with T_{tr} determined by DTA, and increased again monotonously above this temperature.

When baI was slowly cooled from room temperature, nonexponential ^{1}H magnetization recovery curves were observed between 240 and 260 K. At a given temperature in this range, the shape of free induction decay (FID) signals was observed to change gradually over a period of several ten minutes, indicating that the room temperature phase is transformed gradually into the low temperature phase.

To examine the transformation rate of the room temperature phase more in detail, ^{1}H magnetization recovery was measured at 248 K every 1 h by the $180° - \tau - 90°$ pulse sequence. Each measurement was completed within 15 min to avoid complexity arising from a considerable change of the FID signals during our measuring time. The results obtained just after setting the temperature and after 2 and 8 h from that are shown in Figure 4. Two T_1 components, 43 ± 3 and 190 ± 20 ms could be directly obtained by dividing the recovery curves into two parts. The intensity ratios of the divided FID signals giving rise to the long T_1 component and the short one were 1:1 immediately after fixing the temperature, 1:4 after 2 h, and almost zero after 8 h.

The sample baI treated by rapid cooling yielded nonexponential ^{1}H magnetization recovery curves at various temperatures between 145 and 260 K. Therefore, the T_1 values were determined in this temperature range by assuming the presence of two magnetization components having different T_1 values. The roughly estimated ratio of the intensities of these two components was 1:1. Below ca. 130 K, the magnetization showed normal exponential decay curves giving a unique T_1. In the narrow temperature range 130−145 K, the magnetization recovery curves were apparently not due to a single relaxation mechanism. However, it was difficult in the present experiment to determine two T_1 values separately from the recovery curve, because the two magnetization components were too close to each other.

The T_1 values of baI-d_3 determined on both slow and rapid cooling are shown in Figure 5.

When baI-d_3 had been rapidly cooled and then was warmed, nonexponential ^{1}H magnetization recovery curves yielding two different T_1 values were

Table 2. Calculated values of ^{1}H NMR second moment M_2 for various motional states of butylammonium cations in n-$C_4H_9NH_3I$.

Contribution	rigid lattice	CH_3 rot.	(CH_3+NH_3^+) rot.	(CH_3+NH_3^+) rot. + Chain 180° flip	(CH_3+NH_3^+ + Chain) rot.
intra-ionic	21.9	17.3	11.1	7.94	2.78
inter-ionic	~ 4.4	~ 3.5	~ 2.8	~ 1.7	~ 1.3
total	26.3	20.8	13.9	9.6	4.1

observed between 140 and 260 K in the low temperature phase just as in baI. This indicates that some substable phase, probably the same as that of baI is mixed with the low temperature stable phase of baI-d_3. Below 136 K and above T_{tr}, the sample treated by rapid cooling gave the normal exponential recovery curves. A T_1 minimum of 39 ms was located at 130 K, although the short T_1 component showed another T_1 minimum of 60 ms at ca. 180 K.

When baI-d_3 was slowly cooled and warmed, somewhat nonexponential ^{1}H magnetization recovery curves indicating the existence of two T_1 components were observed at all temperatures studied in the low temperature phase. This was always true although the sample was treated by several kinds of annealing processes. These T_1 results are consistent with those of the above DTA experiment: it was not easy to cause the anomaly around 205 K to disappear by annealing whereas the correspondingly anomaly of baI always disappeared by annealing. The foregoing observations of T_1 and DTA suggest that another solid phase of slowly cooled baI-d_3, possibly the same substable phase obtained for rapidly cooled baI-d_3 is always mixed with the low temperature phase. This behavior of the substable phase of baI-d_3 forms a contrast with that of baI. Slowly cooled baI-d_3 yielded a T_1 minimum of 38 ms at 130 K. With increasing temperature, T_1 increased monotonously up to ca. 210 K, above which T_1 decreased. At T_{tr}, T_1 increased discontinuously and in the high temperature phase T_1 again gradually increased with temperature.

Discussion

The theoretical values of ^{1}H M_2 for five motional states of the ba$^+$ cations in baI can be calculated by use of Van Vleck's formula [7] and are given in Table 2. In the calculation of M_2, the intraionic contributions were assumed to be the same as those calculated for a few motional states of the cation in our previous study of baBr [1]. At room temperature, baI forms tetragonal crystals belonging to the space group P4/nmm with $a = 5.18$ Å, $c = 15.30$ Å and $Z = 2$ [2]. Since no data are available for the structure of the low temperature phase, the intercationic contribution to M_2 was estimated by assuming the same crystal structure as that of the room temperature phase.

According to the BPP theory, ^{1}H T_1 due to homonuclear magnetic dipolar interaction can be written as

$$T_1^{-1} = C\,[\tau/(1+\omega^2\tau^2) + 4\tau/(1+4\,\omega^2\tau^2)]\,. \quad (1)$$

Here, C, τ, and ω denote the motional constant, the correlation time of a motion responsible for the relaxation in question, and the angular resonance frequency, respectively. Assuming an Arrhenius relationship between τ and the activation energy E_a of the motional process, one has

$$\tau = \tau_0 \exp(E_a/RT)\,. \quad (2)$$

When two kinds of motions contribute to T_1 without any correlations between them, the resulting relaxation rate $T_1(r)^{-1}$ can be written approximately by the sum of two relaxation rates $T_1(a)^{-1}$ and $T_1(b)^{-1}$:

$$T_1(r)^{-1} = T_1(a)^{-1} + T_1(b)^{-1}\,. \quad (3)$$

The Low Temperature Phase

The M_2 value observed at 77 K was 27 G^2 in good agreement with that calculated for baI by assuming a rigid lattice. This indicates that all molecular motions of the cation given in Table 2 are frozen below 77 K.

The nearly constant M_2 value (22 G^2) obtained around 150 K can be explained by the cation having a reorienting CH_3 group about its C_3 axis. The other plateau value (11.5 G^2) observed just below T_{tr}, however, is somewhat smaller than the value calculated for rotating CH_3 and NH_3^+ groups about their respective C_3 axis. This suggests that some new motion other than those given above also contributes to the decrease of M_2 to 11.5 G^2.

Table 3. Activation energy E_a for each mode of reorientation, the motional constant C, and pre-exponential factor τ_0 determined from NMR T_1 for n-$C_4H_9NH_3I$, n-$C_4H_9ND_3I$, and n-$C_4H_9NH_3Br$ (for comparison).

Compound	E_a/k J mol^{-1}	$C\times10^{-9}$/ s^{-2}*	$\tau_0\times10^{13}$/s	Mode of reorientation
n-$C_4H_9NH_3I$	10.4 ± 1	1.6(1.95)	2.3	CH_3
	26.8 ± 1	2.6(2.59)	2.2	NH_3^+
n-$C_4H_9ND_3I$	10.5 ± 1	2.2(2.60)	2.2	CH_3
	12 ± 2			alkyl chain
n-$C_4H_9NH_3Br$	11.0	2.2(1.95)	4.2	CH_3
	23			NH_3^+

* The values in parentheses are theoretical ones.

As a possible motion which accounts for the additional decrease of M_2, a 180° flip motion or free rotation of the cation as a whole about its long axis can be considered. However, the M_2 values calculated for these motions are much smaller than the observed value. Accordingly, a large amplitude libration or a hindered rotation of the cation as a whole is thought to be excited just below T_{tr} together with the CH_3 and NH_3^+ reorientations.

In the low temprature phase of slowly cooled baI, the T_1 minimum at 127 K is attributable to the random reorientation of CH_3 groups about their respective C_3 axis. This assignment is reasonable in view of the above analysis of M_2. The other deep T_1 minimum at 260 K just below T_{tr} can be assigned to the C_3 reorientation of the NH_3^+ group by taking the foregoing discussion into account. This assignment is strongly confirmed by the fact that baI-d$_3$ never gives such a deep minimum.

Since the log T_1 versus T^{-1} curve observed in the stable low temperature phase of baI can be approximately expressed by the superposition of the above two relaxation processes, a least squares fitting calculation of the T_1 curve according to (1)–(3) was carried out. The best fitted values of the parameters E_a, C, and τ_0 are given in Table 3. The calculated T_1 curve is also shown in Fig. 3 by the solid line. The theoretical values of C given in Table 3 were calculated by employing the same interprotonic distances in the CH_3 and NH_3^+ groups as those used in the preceding calculation of M_2 [1].

The E_a value obtained for the C_3 reorientation of CH_3 groups in baI is nearly the same as that of baBr [1]. This indicates that the intraionic potential barrier hindering the CH_3 reorientation is mainly responsible for E_a, like in the case of baBr. On the other hand, E_a for the NH_3^+ reorientation in baI is somewhat greater than that estimated for baBr. This may be due to greater steric hindrance of the iodide anions.

Immediately below T_{tr}, T_1 of slowly cooled baI-d$_3$ decreases with increasing temperature, indicating that a new relaxation process begins to contribute appreciably to T_1. This agrees well with the additional M_2 decrease found for the plateau near T_{tr}. Therefore, we assign this decrease in T_1 to the large amplitude libration or the hindered rotation of the cation. To estimate E_a for this motional process roughly, we carried out T_1 measurements. The log T_1 versus T^{-1} curve obtained at 12.6 MHz affords an E_a which is given in Table 3 along with the motional parameters for the CH_3 reorientation in slowly cooled baI-d$_3$.

At various temperatures below 130 K, rapidly cooled baI yields a T_1 which can be approximated as being single and nearly the same as that on slow cooling. This indicates that both the stable and substable low temperature phases of baI exhibit almost the same T_1 attributable to CH_3 reorientation and that the local environments of the CH_3 groups are very similar in the two phases.

Above 130 K, rapidly cooled baI gave two quite different log T_1 versus T^{-1} curves attributable to the two phases. The substable phase yielded a broad T_1 minimum of 32 ms at ca. 150 K. The depth of this minimum is almost the same as the T_1 minimum of the stable phase observed at 260 K, which is attributed to NH_3^+ reorientation. Accordingly, the broad T_1 minimum of the substable phase can be assigned to NH_3^+ reorientation, indicating that NH_3^+ groups reorient more easily in the substable phase than in the stable phase, as is to be expected [9, 10]. The broadening of the T_1 curve is thought to be originated partly from the low activation energy of the NH_3^+ reorientation as well as partly from the distributing correlation times of the NH_3^+ reorientation [11]. Such distribution in τ is mostly related to a disordered arrangement of molecules in crystals, which is often found in substable phases similar to the present system [12].

The assignment of the broad T_1 minimum to the NH_3^+ reorientation is confirmed by the following: We measured ^{1}H NMR absorptions of rapidly cooled baI at 155 K, where the NH_3^+ groups should be fixed in the stable phase but reorient rapidly in the substable phase. Because rapidly cooled baI contains both stable and substable phases, the resonance absorption of the substable phase was obtained by estimating difference spectra from the spectra of slowly and rapidly cooled samples observed at the same temperature by adjusting their integrated intensity ratio to 1:2. This is because the abundance ratio of two phases in the rapidly cooled sample is approximately 1:1. The M_2 value of the substable phase calculated based on the difference spectra derived above was ca. 13 G^2. This agrees well with the theoretical value of 13.9 G^2 for the cation having reorienting CH_3 and NH_3^+ groups.

In rapidly cooled baI-d_3, two T_1 components are also observed similarly in baI, which are attributable to the stable and substable low temperature phases. The substable phase yields a shallow T_1 minimum at ca. 180 K in addition to the deep one due to the CH_3 reorientation. The additional minimum can be interpreted as arising from the relaxation process of the large amplitude libration or the hindered rotation of the cation chains. This is because the same motional process detected above 210 K for slowly cooled baI-d_3, namely for the stable low temperature phase, is considered to be activated at lower temperatures in the loosely packed substable phase.

No anomaly in the T_1 curves of the substable phase of rapidly cooled baI and baI-d_3 could be found near 210 K although the DTA curves showed a thermal anomaly. This suggests that the phase transition occurring between the substable phases gives no appreciable effect on the motion of the cation.

The Room Temperature Phase

The value of ^1H M_2 observed for baI at ca. 300 K is (3.4 ± 1.0) G^2, which agrees very well with the one calculated for the model of chain rotation together with CH_3 and NH_3^+ reorientations. Here, the chain rotation means random rotational jumps of the ba^+ cation about its long axis keeping its trans zigzag conformation. With increasing temperature, M_2 decreases gradually suggesting that some other motions of ba^+ chains such as motions of the alkyl chain and local translational motion of the cation as a whole are additionally excited. The $\log T_1$ versus T^{-1} curve of this phase is slightly convex for both baI and baI-d_3. This also indicates the existence of more than one motional mode involved in the relaxation process, in agreement with the above M_2 results.

The change of entropy observed at the phase transition to the room temperature phase is 33 J K^{-1} mol^{-1}. This transition entropy is very large and comparable to those reported for phase transitions to plastic crystals [13]. Such a large transition entropy has been found also in baBr [1]. On the other hand, the entropy of melting is 16 J K^{-1} mol^{-1} which is fairly small in spite of the presence of many allowable conformations in the cation chain. Even ionic crystals having no conformational freedom of the ions such as NaSCN, KSCN, and KN_3 give melting entropies of 30–40 J K^{-1} mol^{-1} [14]. Evidently the cations in baI crystals obtain most of their motional freedom at the phase transition to the room temperature phase. This means that the cations in the room temperature phase are thought to be in a highly dynamically disordered state. With increasing temperature, various motional modes of the cation will be activated successively. This is an explanation of the gradual decrease of M_2 with increasing temperature in the room temperature phase.

Mechanism of Phase Transitions

When baI was slowly cooled and kept at 248 K, it was found from the T_1 measurements that the transition to the low temperature phase, which had started at 260 K required several hours before it was completed. The reproducibility of the starting temperature of the transition was quite good although we checked it by repeating the slow cooling runs of DTA several times.

On these T_1 experiments, we observed two FID components giving rise to long and short T_1 values which are hereafter called $L - T_1$ and $S - T_1$, respectively. The population of protons having $L - T_1$ slowly decreased with time going by at a fixed temperature, whereas that having $S - T_1$ conversely increased . Since the $S - T_1$ value (43 ms at 248 K) is independent of time and is identical with the T_1 value of the stable low temperature phase determined at the same temperature, $S - T_1$ is definitely identified as arising from the stable low temperature phase. However, $L - T_1$ is much shorter than the extrapolated value (2 s) from the T_1 curve of the room temperature phase, altough it is also time independent. This suggests that the cations in the crystal, whose protons yield $L-T_1$, are in a transient state different from both states of the room and low temperature phases.

The crystal structure of the low temperature phase is unknown. However, it can be anticipated to have a lower crystal symmetry than tetragonal because the axial symmetry of the rotating ba^+ chains existing in the room temperature phase is never retained in this phase involving non-rotating cations. Moreover, we can expect that the non-rotating cations are more compactly packed between the layers of iodide ions than the rotating cations of the room temperature phase. In fact, n-$C_{10}H_{21}NH_3Cl$, being an analogous compound to baI, was reported to transform into a new crystalline phase with a disordered structure above room temperature [15, 16], while, below the transition temperature, it forms monoclinic crystals in which the arrangement of the alkyl chains is completely ordered. The cations are compactly packed between the layers of the anions and their long axes are tilted with respect to the normals of the layers. We can expect that the structure of baI in the low temperature phase is similar to that of n-$C_{10}H_{21}NH_3Cl$.

From the foregoing discussion, the following mechanism can be proposed for the phase transition. When baI is slowly cooled from room temperature, the phase transition to the low temperature phase seems to take place in two steps. At first, the room temperature phase is transformed, within a shorter time than several minutes, into an intermediate state having $L-T_1$. In this stage, the cations have lost most of their freedom of motion and, together with the anions fulfil already approximately the symmetry of the low temperature phase. From the T_1 measurements, the relaxation time from the intermediate towards the stable low temperature phase is estimated to be some ten minutes just below T_{tr} and about 4.5 h at 248 K.

When baI is cooled rapidly, the intermediate state may be partly frozen at lower temperatures without changing into the stable low temperature phase because of the long relaxation time of the state. However, this frozen intermediate state is transformed into a substable phase at 209 K which is the additional T_{tr} located on the rapid cooling run of DTA. When this substable phase yielding shorter T_1 values is warmed, it is transformed into another substable phase at ca. 210 K. The new substable phase seems to be different from the intermediate state in two respects: First, the latter gave a different T_1 value from that of the former when T_1 measurements were made at 248 K. Secondly, the time required for the latter to be transformed into the stable phase is much shorter than the time for the former, which is not shorter than 10 h.

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