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^{1}H NMR and Differential Scanning Calorimetry Studies on Molecular Motions and Phase Transitions in Butylammonium Bromide

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The temperature dependences of the ^{1}H NMR spin-lattice relaxation time and of the second moment of ^{1}H NMR absorptions in the temperature ranges of 90—400 K and 77—456 K, respectively, were studied for butylammonium bromide and its *N*-deuterated analog. There are three known crystalline phases in butylammonium bromide as a result of two phase transitions which are confirmed by the present differential thermal analysis (DTA) experiments. The transition temperatures determined in this study are 200 and 249 K for butylammonium bromide. In the low temperature phase of this salt, CH_3 groups perform the C_3 reorientation with a relatively low activation energy of 11.0 kJ mol^{-1}. The asymmetric T_1 curves observed suggest the existence of some kind of disorder in the crystal structure of this phase. In the intermediate phase, the C_3 reorientation of NH_3^+ groups and the 180° flip motion of butylammonium chains are activated with the activation energies of 23 and 14 kJ mol^{-1}, respectively. The present NMR results for the high temperature phase indicate the occurrence of the conformational melting of the cation chains. The mechanism of the phase transitions is discussed.

It is known that alkylammonium halides involving rather short carbon chains up to C_{10} usually form tetragonal crystals at room temperature.[1-4] In the series of these crystals, the long axis of the carbon chain is located along the crystallographic fourfold axis. Therefore, the presence of dynamical disorder is expected in the arrangement of alkylammonium chains about their long axes.[4] With decreasing temperature, the motion of linear alkylammonium chains should become slow and finally be frozen. This suggests that the tetragonal crystals of these compounds lose their fourfold axis at lower temperatures and are transformed into less symmetric ones. In fact, many of the higher members of the series undergo solid-state phase transitions around or below room temperature,[5] and propyl- and pentylammonium chloride are known to form less symmetric monoclinic crystals at low temperatures.[6,7] Accordingly, it is thought that the molecular motions of alkylammonium chains play an important role in the mechanism of these phase transitions.

Tsau and Gilson[8] studied the wide-line ^{1}H NMR of various alkylammonium chlorides from C_3 to C_{10}, and discussed mainly on the molecular motions of the cations in solid. Recently, the motion of cations in methylammonium halides[9-11] and propylammonium chloride[12] was studied in more detail by use of pulsed and wide-line ^{1}H NMR techniques.

The present investigation of butylammonium bromide by ^{1}H NMR, differential scanning calorimetry (DSC), and differential thermal analysis (DTA) has been undertaken in order to obtain detailed information on the molecular motion of butylammonium cations in solid and also on the mechanism of the successive phase transitions taking place below room temperature.[5]

Experimental

Butylammonium bromide (baBr) was prepared by neutralizing an ethanol solution of butylamine with hydrobromic acid. Colorless crystals separated were purified by recrystallization which was performed twice from a nearly saturated solution of the salt dissolved in a mixed solvent of ethanol and diethyl ether by cooling it very gradually. Vacuum sublimation at *ca.* 80 °C was also employed as another purification method. A partially deuterated analog $C_4H_9ND_3Br$, which is hereafter abbreviated as baBr-d_3, was obtained from the normal salt by repeated recrystallization from heavy water. The deuterated analog thus prepared was finally recrystallized from deuterated ethanol (C_2H_5OD) solution by slowly evaporating the solvent. Since the purified samples were highly hygroscopic, they were carefully dried in vacuum desiccators and sealed in aluminium sample holders for DSC or glass ampouls for NMR and DTA measurements.

The second moment (M_2) of ^{1}H NMR absorptions recorded at 40 MHz were determined at various temperatures between 77 and 456 K by means of a JEOL JNM-MW-40S wide-line NMR spectrometer. The measurements of ^{1}H spin-lattice relaxation time T_1 at the resonance frequency of 20 MHz were carried out by use of a homemade spectrometer[13] and those at 12.6 and 32 MHz were made by another pulsed spectrometer constructed using a transmitter and a receiver from MATEC, Inc.[14] A conventional 180°-τ-90° pulse sequence was used to determine T_1.

A Parkin-Elmer DSC-1B differential scanning calorimeter was employed to determine enthalpy changes at the solid-solid phase transitions and at the melting of the samples. The temperature of the samples was scanned at a rate of 5 K min^{-1}. The values of the transition enthalpies observed at lower temperatures were calibrated against that of succinonitrile observed at 233 K. The melting of indium was also used as a calibration standard for the melting enthalpy. A homemade DTA apparatus was used to determine the phase transition and the melting temperatures.

Results

DTA curves recorded for baBr are shown in Fig. 1. When the sample was cooled from room temperature, two exothermic anomalies appeared at 246 and 195 (±1) K. When it was warmed from *ca.* 80 K, three endothermic ones were observed at 200, 249, and 478 (±1) K. The last one was due to the melting of the sample. The two solid-solid phase transitions showed thermal hysteresis. The samples purified by the two different methods described in the experimental section yielded DTA curves analogous to each other giving the same transition temperatures, T_{tr} as well as the same melting point. Accordingly, it is concluded that baBr undergoes two first-order solid-solid phase transitions at 200 and 249 K. The temperatures of the former transition (200 K) and of the melting agree well with those determined by Tsau and Gilson[5] in their DSC study (198 and 479 K), while the transition temperature

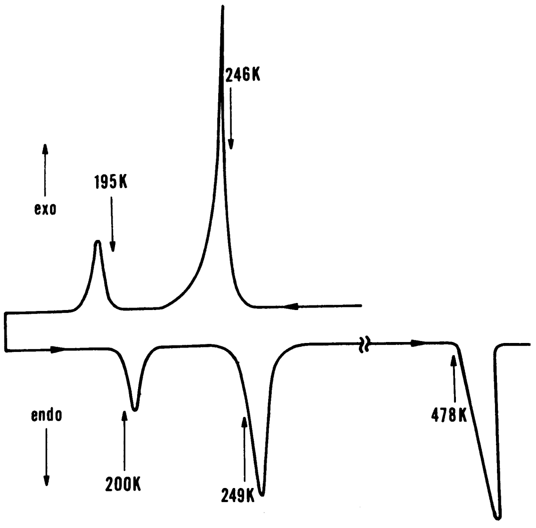

Fig. 1. DTA curves of baBr.

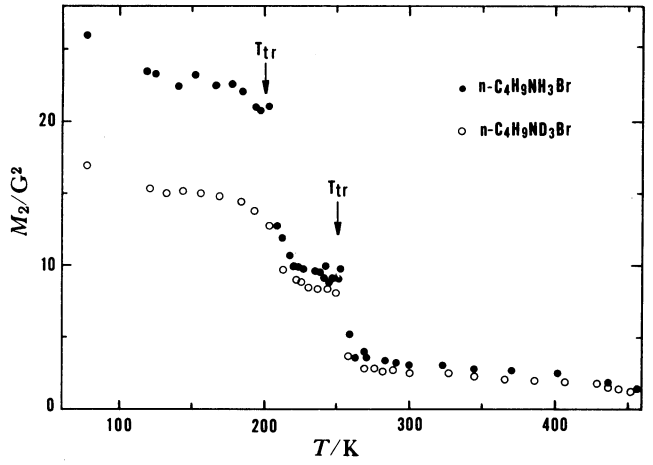

Fig. 2. Temperature dependences of the second moment M_2 of ^{1}H NMR absorptions.

of 249 K is considerably lower than that of 257 K reported by the same authors. For baBr-d_3, two heat anomalies showing quite similar DTA curves to those of baBr were observed at 198 and 249 (±1) K on heating.

The enthalpy changes (ΔH_{tr}) of the phase transitions determined by the DSC measurements of baBr on heating were 1.5_3 and 5.7_4 kJ mol^{-1} for the phase transitions at 200 and 249 K, respectively, and 8.3_0 kJ mol^{-1} for the melting at 478 K. These transition enthalpies in the present study are much larger than the corresponding ones (0.93 and 5.18 kJ mol^{-1} for the low and high transition temperatures, respectively) reported by Tsau and Gilson.[5]

The temperature dependence of M_2 values observed for baBr and baBr-d_3 is indicated in Fig. 2. These values were obtained with increasing the temperature of the sample. From *ca.* 100 K to *ca.* 170 K, baBr yielded an almost constant M_2 value of 23 G^2. In a rather narrow temperature range of 180—200 K, the M_2 value decreased gradually, whereas it decreased discontinuously to 13 G^2 at *ca.* 200 K. This temperature agrees well with the lowest T_{tr} determined by DTA. With increasing temperature above 200 K, the M_2 value gradually decreased until it became 9 G^2 at 250 K. Immediately above this temperature, the M_2 value dropped again discontinuously to 4 G^2 in agreement with the occurrence of the phase transition at 249 K. Between 260 and 320 K, the almost constant M_2 value of 3 G^2 was observed. With increasing temperature further, M_2 gradually decreased to *ca.* 1.5 G^2 at *ca.* 460 K. The partially deuterated analog yielded a temperature dependence curve of M_2 similar to that of baBr although the M_2 value of the latter was expectedly larger than that of the former at the same temperature.

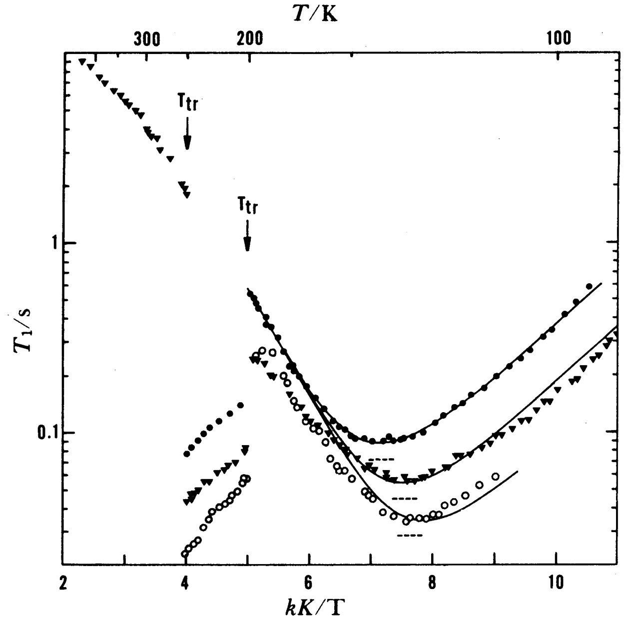

Fig. 3. Temperature dependences of the proton T_1 at 32 (●), 20 (▼), and 12.6 (○) MHz observed for baBr. The solid lines show the theoretical curves fitted by the method of least-squares. The broken lines show the T_1 minima predicted by the BPP theory.

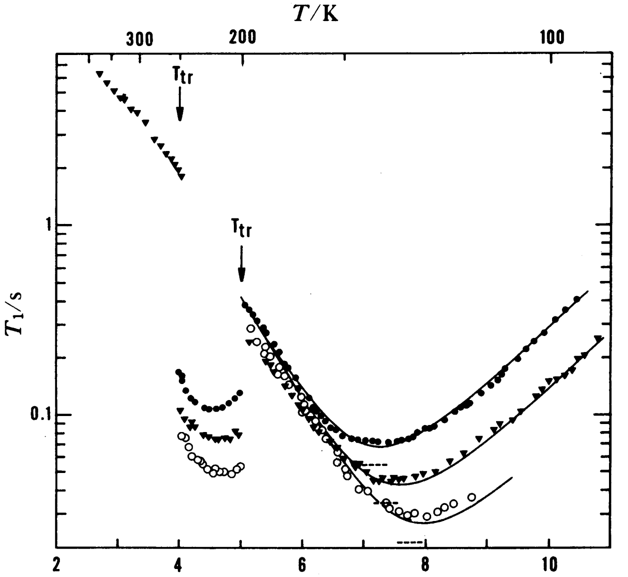

Fig. 4. Temperature dependences of the proton T_1 at 32 (●), 20 (▼), and 12.6 (○) MHz for baBr-d_3. The solid lines show the theoretical curves fitted by the method of least-squares. The broken lines show the T_1 minima predicted by the BPP theory.

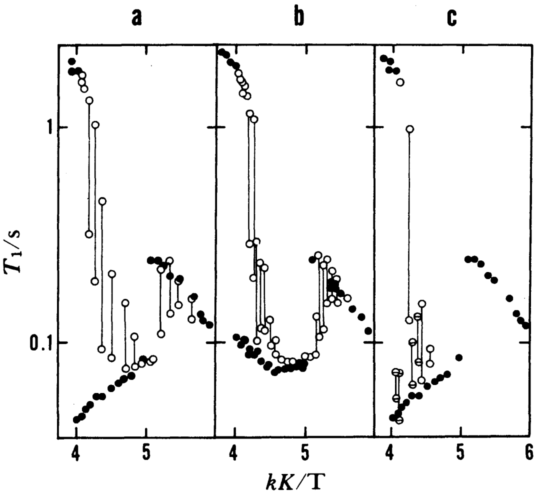

Fig. 5. Proton T_1 values (at 20 MHz) determined for baBr (a, c) and baBr-d_3 (b). Dots indicate the T_1 data obtained with increasing temperature, while open circles are those observed with decreasing temperature. The T_1 interval determined at a given temperature on the cooling run is shown by a vertical line connecting two open circles indicating the longest and shortest T_1 values. The symbols (Θ) indicate the T_1 values obtained with increasing temperature for the sample which had been cooled down to 215 K in advance.

The T_1 values measured at 12.6, 20, and 32 MHz are plotted in Figs. 3 and 4 for baBr and baBr-d_3, respectively. These values were determined at various temperatures between 90 and 400 K. The measurements were made with increasing the temperature of the sample. Each salt yielded a T_1 curve having discontinuities at 200 and 249 K in agreement with the T_{tr}'s determined by DTA. With decreasing temperature, on the other hand, the temperature dependence curve of T_1, which was different from that obtained on the heating run, was observed below each T_{tr} for both salts. In a rather narrow temperature range below each T_{tr}, nonexponential decay of ^{1}H magnetization could be observed for both salts, even though the sample temperature was kept constant for more than half an hour. In these ranges of temperature the longest and shortest T_1 could be approximately determined from the magnetization recovery curve. The results are indicated in Figs. 5a and 5b for the measurements at 20 MHz. It should be noted, here, that the T_1 interval between the longest and shortest values determined at a given temperature varies to some extent at every cooling run of the T_1 measurements.

In the above temperature ranges, another type of anomalous behavior of T_1 was observed. When the sample cooled somewhat below each T_{tr} in advance was warmed, the T_1 values did not reversibly follow those obtained on the cooling run, but decreased roughly along those of the heating run as shown in Fig. 5c. This anomalous behavior is understandable by considering that crystal domains of lower temperature phases newly produced through each phase transition develop gradually with decreasing temperature. Namely, the sample in these temperature ranges is thought to be a mixture of at least two different crystalline phases, the mixing ratio of which is changed with decreasing temperature. The above explanation is compatible with the DTA results that each heat anomaly is accompanied by a long tail only on the low temperature side of the cooling run.

In the low temperature phase, both baBr and baBr-d_3 showed a broad T_1 minimum on the T_1 curve observed at each resonance frequency.

In the intermediate phase, the T_1 value of baBr decreased steadily with increasing temperature to the higher T_{tr}, whereas each of three T_1 curves observed for baBr-d_3 with increasing temperature yielded a shallow minimum. At the T_{tr}, the T_1 values of baBr increased suddenly by about two orders of magnitude. A similar T_1 jump was also observed for baBr-d_3.

In the high temperature phase, long T_1 values were obtained for both salts and they increased monotonously with increasing temperature. No frequency dependence of T_1 was observed in this phase for both baBr and baBr-d_3.

Discussion

The theoretical values of M_2 for four motional states of the cation in solid baBr can be calculated by use of the Van Vleck formula.[15] The results are given in Table 1 along with the total M_2 values of baBr-d_3 calculated in the same way.

In the calculation, all bond angles in the cation were assumed to be tetrahedral and the C–H, N–H, C–C, and C–N bond distances were taken as 1.096, 1.045, 1.540, and 1.470 Å respectively, in accordance with Tsau and Gilson.[8] A trans-zigzag conformation was also assumed for the cation chain.

According to Hendricks,[1] baBr forms tetragonal crys-

TABLE 1. CALCULATED SECOND MOMENTS (M_2/G^2) OF BUTYLAMMONIUM ION IN BUTYLAMMONIUM BROMIDE

Contribution	Rigid lattice	CH_3 rot.	$(CH_3+NH_3^+)$rot.	$(CH_3+NH_3^+)$rot. +Chain 180° flip	$(CH_3+NH_3^+$ +Cation) rot.
Intra CH_3	5.4	1.4	1.4	0.45	0.34
NH_3^+	7.3	7.3	1.8	0.61	0.45
CH_2	5.4	5.4	5.4	5.44	1.36
Other Intra-Ionic	3.8	3.2	2.5	1.44	0.63
Inter Ionic	~5.0	~4.0	~3.2	~2.0	~1.5
Total					
baBr	26.9	21.3	14.3	9.9	4.3
baBr-d_3	(21.2)	(14.2)	(14.2)	(9.6)	(3.6)

tals at room temperature with a=5.02 Å, c=15.23 Å, and Z=2. In the crystal, the cations are packed together between the layers consisting of bromide ions and form a thick layer perpendicular to the c-axis, where the axes of the cationic chains are situated parallel to the c-axis. As to the accurate arrangement of the cations in the layer, no information is available up to date. This is probably because there is a good possibility for the cations in the layer to take highly disordered orientation about their chain axes even at room temperature. Therefore, we estimated the interionic contribution to M_2 by assuming the probable arrangement of the cations in the unit cell as depicted in Fig. 6. The reduction factors of M_2 arising from the averaging of the magnetic dipolar interactions through the molecular motions were evaluated with reference to the methods described in the literature.[16—18)]

The ^{1}H spin-lattice relaxation study also furnishes valuable information concerning the molecular motion of the cation. If magnetic dipolar relaxation is governed by the molecular motion such as the reorientation of CH_3 or NH_3^+ groups in a ba$^+$ cation, T_1 can be written as,[19)]

$$T_1^{-1} = Cf(\tau) = C\{\tau/(1+\omega^2\tau^2) + 4\tau/(1+4\omega^2\tau^2)\}. \qquad (1)$$

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

$$\tau = \tau_\infty \exp (E_a/RT), \qquad (2)$$

where τ_∞ is the correlation time at the limit of infinite temperature.

Low-Temperature Phase. Below 170 K, the nearly constant M_2 values of 23 and 15 (±2) G^2 were obtained for baBr and baBr-d_3, respectively. These values agree fairly well with those calculated under the assumption of the motional model that only the CH_3 group of the cation reorients about its C_3 axis. This means that the CH_3 groups of the cations in this phase reorient more frequently than 10^5 Hz.

The analysis of T_1 gives an analogous conclusion. The broad T_1 minimum($T_{1\,\mathrm{min}}$) observed for each salt is attributable to the C_3 reorientation of the CH_3 groups because of its short minimum value. This indicates that the correlation time of the CH_3 reorientation is *ca.* 10^{-9} s even at about 130 K in agreement with the foregoing discussion of the second moment.

It is noteworthy that the T_1 data observed for both compounds are unexplainable by the BPP theory (Eq. (1)) in the following three respects. First, the $T_{1\,\mathrm{min}}$ values observed for baBr which are 90, 56, and 34 ms at the resonance frequencies of 32, 20, and 12.6 MHz, respectively, and also those for baBr-d_3 which are 72, 45, and 19 ms in the same order of the resonance frequencies are all considerably longer than the theoretical values estimated from Eq. (1). For example, the calculated $T_{1\,\mathrm{min}}$'s at 32 MHz are 72 and 54 ms for baBr and baBr-d_3, respectively, if an isolated CH_3 group with the H···H distance of 1.79 Å is assumed. Secondly, the observed T_1 curves are all highly asymmetric. Namely, the slopes of the T_1 curve on the low and high temperature sides of each minimum are considerably different from each other. Finally, the frequency dependence of T_1 values on the low temperature side of the minimum disagrees with the relationship ($T_1 \propto \omega^2$) derived from Eq. 1.

Conner[20)] showed that shallow and asymmetric T_1 curves similar to those of the present compounds can be explained by introducing continuously distributed correlation times into Eq. 1. We assume a Cole-Davidson type distribution of τ given by [21)]

$$\left.\begin{aligned} g(\tau) &= \frac{\sin \beta\pi}{\pi}\left(\frac{\tau}{\tau_0-\tau}\right)^{\beta} & \tau &\leqq \tau_0 \\ &= 0 & \tau &> \tau_0 \end{aligned}\right\}, \qquad (3)$$

where β represents a width of the distribution and τ_0 is a limit of τ. The value of $\beta(0<\beta\leqq1)$ is a measure of the relative weight of the shorter correlation times than τ_0 and in the limit of β=1, a single correlation time as used in the BPP theory is obtained. Using Eq. 3, T_1 becomes

$$T_1^{-1} = C\left[\frac{\tau_0 \sin(\beta \tan^{-1}\omega\tau_0)}{\omega\tau_0(1+\omega^2\tau_0^2)^{\beta/2}} + \frac{2\tau_0 \sin(\beta \tan^{-1} 2\omega\tau_0)}{\omega\tau_0(1+4\omega^2\tau^2)^{\beta/2}}\right]. \qquad (4)$$

The theoretical T_1 curves expressed by Eqs. 2—4 were fitted to the values observed at 32 MHz for baBr and baBr-d_3 by use of a least mean squares method. The fitted curves (at 32 MHz) are shown in Figs. 3 and 4. The values of the unknown parameters determined from this fitting calculation are given in Table 2. By use of these values of the parameters, the theoretical T_1 curves at 20 and 12.6 MHz are also calculated and exhibited in Figs. 3 and 4. The observed T_1 values agree well with the corresponding calculated curves. The obtained motional constants (see Table 2) also agree well with the values calculated using the geometry of the CH_3 group employed in the calculation of M_2. The values of E_a thus obtained are very close to the average value of E_a for the end CH_3 groups in various kinds of crystalline paraffines,[22)] which is *ca.* 11 kJ mol^{-1}, and also to the potential barrier to the internal rotation of the CH_3 group in gaseous $CH_3CH_2CH_2F$ (12.4 kJ mol^{-1}).[23)] This indicates that the crystal field hindering the CH_3 rotation is quite small in the low temperature phase of the present compounds.

From the β values obtained, we can expect the existence of some kind of disorder in the low temperature phase. As a possible reason for the existence of

TABLE 2. ACTIVATION ENERGIES (E_a), MOTIONAL CONSTANTS (C), PARAMETERS REPRESENTING WIDTH OF τ DISTRIBUTION (β), AND PRE-EXPONENTIAL FACTOR (τ_∞) OBTAINED FROM OBSERVED T_1 CURVES AT 32 MHz FOR THE CH_3 REORIENTATIONS IN baBr AND baBr-d_3

Compound	E_a/kJ mol^{-1}	C×10^{-9}/s^{-2}*	β	τ_∞×10^{13}/s
baBr	11.0	2.2(1.95)	0.51	4.2
baBr-d_3	10.0	2.6(2.60)	0.60	7.6

*The values in parentheses are theoretical ones obtained by use of the BPP equation without distribution of τ.

this disorder, we can presume the following. The disordered structure of the crystal existing in the higher temperature phases, for which we will discuss below may be partly supercooled down to the low temperature phase. To obtain information about this disorder, we measured T_1 of the samples which had been annealed in the following manner; the samples were first cooled gradually from the room temperature phase to the intermediate one and kept at *ca.* 200 K for from several hours to two weeks. After that, they were again cooled slowly to the low temperature phase and, then, one sample was kept at *ca.* 180 K for several hours, and the other was at 77 K for half a day. The observed values of T_1 for the two samples agreed with each other. The values coincide also with those of the normally cooled samples within experimental errors. Accordingly, this disordered structure of the low temperature phase seems to have a very long relaxation time.

At various temperatures between *ca.* 160 and 200 K, the T_1 values of baBr observed at 12.6 and 20 MHz disagree with those at 32 MHz, whereas no such marked disagreement can be observed for baBr-d_3 in the same temperature range. To obtain information about this disagreement, we measured the frequency dependence of T_1 values between 10 and 32 MHz at a fixed temperature of 189 K which is immediately below the low T_{tr}, and obtained a broad T_1 minimum of 19 ms at 18±4 MHz. Since the T_1 of the quadrupolar bromine nuclei in baBr crystals can be expected to decrease near the T_{tr}, the broad T_1 minimum of baBr is considered as resulting from Zeeman-quadrupolar cross relaxation between protons and bromine nuclei,[24] both of which interact through N–H···Br type hydrogen bonds. The above disagreement of the T_1 values may be also explained by the same relaxation mechanism. Although no NQR frequency data are available for baBr, the value of *ca.* 18 MHz seems to be reasonable as an NQR frequency of bromine in baBr crystals because similar frequencies (12—18 MHz) have been reported for analogous alkylammonium bromides.[25]

Intermediate Phase. The shallow T_1 minimum observed for baBr-d_3 clearly indicates the existence of a new relaxation process in the intermediate phase. On the other hand, the sharp decrease of T_1 with increasing temperature obtained for baBr can be attributed to another more effective relaxation process. The shallow T_1 minimum which is also expected to exist in baBr can be thought to be masked by the sharp decrease of T_1 in the case of baBr.

When the T_1 curve of baBr-d_3 was subtracted from that of baBr after a correction for the difference of the number of protons in these two compounds was made, the resultant $\log T_1$ of baBr showed an almost linear decrease against T^{-1} in the nearly whole temperature range of this phase. Although no minimum was observed on the corrected T_1 curve, this linear T_1 decrease can be assigned to the C_3 reorientation of the NH_3^+ groups because this T_1 decrease disappears by *N*-deuteration. From the linear portion of the corrected T_1 curve of baBr, the activation energy for the NH_3^+ reorientation was evaluated as 23 kJ mol^{-1}. It is interesting to note that this E_a value is considerably larger than that for the CH_3 reorientation evaluated above. This means that the NH_3^+ groups are tightly fixed on the layer formed by bromide anions through weak hydrogen bonding, although the CH_3 groups are situated in a weak crystal field produced by the surrounding alkyl chains.

Other alkylammonium bromides having similar crystal structures to that of baBr, such as methylammonium bromide[10] and propylammonium bromide,[26] have fairly close E_a values for the reorientations of the NH_3^+ and CH_3 groups. For propylammonium chloride, strong interactions between the NH_3^+ groups and the Cl^- ions are expected. However, the reorientations of the CH_3 and NH_3^+ groups give rise to their T_1 minima at nearly the same temperature and have the activation energies of 10.0 and 15.5 kJ mol^{-1}, respectively.[12]

From the analysis of the second moment, a conclusion similar to that derived above for the intermediate phase of baBr-d_3 can be obtained. When baBr-d_3 having no NH_3^+ groups was warmed, a marked decrease in M_2 was observed around the low T_{tr}. This clearly indicates that some new motional processes other than the NH_3^+ reorientation are responsible for the reduction of M_2.

Although the M_2 values of baBr and baBr-d_3 obtained for this phase decrease rather sharply at first with increasing temperature, they yield almost the constant values of $9._5$ and $8._5$ (±1) G^2, respectively, at the higher temperatures. Referring to the calculated values of M_2 listed in Table 1, these plateau values observed are too small to be attributed to the motional state of the cations performing only the CH_3 and NH_3^+ reorientations. Furthermore, these values are too large, if one assigns them to the motional model in which the cation rotates as a whole about its long axis while it keeps the rigid conformation of the chain with the end CH_3 and NH_3^+ groups rotating. Therefore, some new motional modes other than the above ones should be adopted in the interpretation of the M_2 values obtained in this phase.

As a possible relaxation process, we take up the 180° flip motion (C_2 reorientation) of the cation about its long axis. This motion is acceptable for the cations shown in Fig. 6, because each NH_3^+ group can form the same type hydrogen bonds with the surrounding Br^- ions even after the 180° flipping. Although the crystal structure of the intermediate phase is necessarily different from that of the high temperature phase, local atomic arrangements around the NH_3^+ groups are expected to be similar for both phases.

As another analogous motional process, the 90° flip motion of the cation about its long axis can be proposed. This type of motion was found to exist in $(n\text{-}C_3H_7NH_3)_2CdCl_4$[27] and $(n\text{-}C_{10}H_{21}NH_3)_2CdCl_4$.[28] The calculated values of M_2 for this motional model, however, are 6.8 and 5.8 G^2 for baBr and baBr-d_3, respectively, these values are too small as compared with the experimental ones. The model of the 180° flip process of the cation together with the independent reorientations of the CH_3 and NH_3^+ groups yielded the M_2 values given in Table 1. These are in good agreement with the observed plateau values of *ca.* 9.5

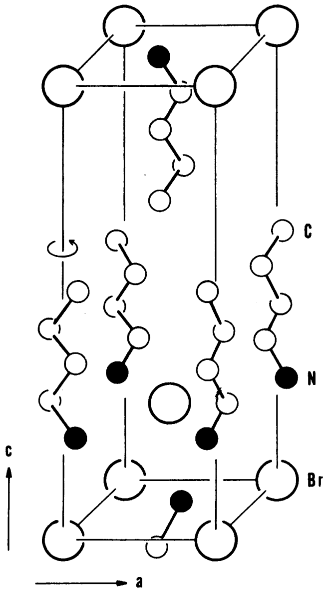

Fig. 6. Predicted crystal structure of baBr at room temperature. The orientations of the cation chains are statistically distributed along the c axis.

and 8.5 G^2 for baBr and baBr-d_3, respectively. Accordingly, it can be concluded that there exists the 180° flip motion of butylammonium chains activated in the intermediate phase of baBr. The E_a value for this motion roughly estimated from the T_1 curves of baBr-d_3 is listed in Table 3.

The entropy change, ΔS_{tr} ($=\Delta H_{tr}/T_{tr}$) at the phase transition of 200 K was determined as 7.6 J mol^{-1}K^{-1} from the present DSC experiments. If we assume that the observed ΔS_{tr} is due only to the orientational freedom obtained by butylammonium ions during the transition, this entropy change can be expressed by $R\ln\Omega$ where R and Ω are the gas constant and the number of the orientations permissible to the cation above T_{tr}, respectively. By use of the observed ΔS_{tr}, we obtain $\Omega=2.5$, which is reasonably explained by our model of the 180° flip process.

Reorientations of the ethyl or the propyl group of the cation, *i.e.*, dynamic *trans-gauche* isomerization can be taken as a new motional process alternative to the 180° flip. Although this isomerization is found to exist in the crystalline paraffine ($C_{19}H_{40}$) by ^{1}H NMR studies,[22] the concentration of the gauche conformation is low (less than 1%). From ^{2}H NMR measurements, a similar result is obtained even for the high temperature rotator phase of the paraffine.[29] Accordingly, it is expected that the gauche isomers generated in this phase of baBr or baBr-d_3 are few and give only a minor contribution to the reduction of M_2 and also to the relaxation time.

TABLE 3. ACTIVATION ENERGIES (E_a) DERIVED FOR THE MOTION OF baBr AND baBr-d_3 FROM SPIN- LATTICE RELAXATION TIMES

Phase Compound	E_a/kJ mol^{-1}	mode
Low temp phase		
baBr	11.0±1	CH_3 reorient.
baBr-d_3	10.0±1	
Intermed. phase		
baBr	23±2	NH_3^+ reorient.
baBr-d_3	14±2	chain 180° flip
High temp phase		
baBr	10.0±0.5(250—300 K)	Whole cationic rotation
	5.8±0.5(310—430 K)	
baBr-d_3	8.2±0.5(250—280 K)	
	6.7±0.5(290—400 K)	

High-Temperature Phase. At the high T_{tr}, each salt of baBr and baBr-d_3 showed a sudden change of M_2. Above the T_{tr}, the M_2 value of the high temperature phase decreased gradually with increasing temperature, suggesting that some motional process governing the M_2 is gradually growing. The M_2 values observed for baBr and baBr-d_3, respectively, at 300 K are 3.2 and 2.3 (±0.5) G^2, and at 435 K, 1.9 and 1.7 (±0.2) G^2. These M_2 values of baBr and baBr-d_3, respectively, are smaller than those of 4.3 and 3.6 G^2 calculated on the basis of a motional model where the cation having its rotating CH_3 and NH_3^+ groups rotates as a whole about its chain axis. This result indicates the existence of some motional processes other than the chain rotation. One of the motions that we can expect to take place in the high temperature phase is the rotation of the cations accompanied by the conformational disorder of the alkyl chain. The observed gradual decrease of M_2 suggests that crystal domains where the cations perform such a motion grow gradually in the crystal with increasing temperature.

The presence of the ba$^+$ cations having such a high degree of movability in the crystal can be proved from the large entropy change (23 J mol^{-1}K^{-1}) observed at the transition to the high temperature phase. This is much larger than that of fusion (17 J mol^{-1}K^{-1}) and is comparable to those reported for various crystals at their transition to a plastic phase.[30] On the other hand, the melting entropy observed is fairly small even though the cation has many allowable conformations in the alkyl chain. Even compounds with no conformational freedom of ions such as NaSCN, KSCN, and KN_3 have the melting entropies of 30—40 J mol^{-1}K^{-1}.[31] These results support our explanation of the second moments and, therefore, it can be concluded that the conformational melting of the cation chains occurs in the high temperature phase.

With increasing temperature, the T_1 value of both salts showed a remarkable increase at the high T_{tr}. This means that the motional time constant of the cations decrease so much at the T_{tr}. In other words, the cations in this phase can move quite freely as compared with those of the intermediate phase. With increasing temperature furthermore the T_1 value increased fairly steeply, although a somewhat nonlinear relation was observed between $\log T_1$ and T^{-1}. The E_a values of baBr determined from the slopes of the T_1 curves are 10.0 and 5.8 kJ mol^{-1} at *ca.* 280 and 380 K, respectively, while those of baBr-d_3 are 8.2 and 6.7 kJ mol^{-1} at the respective temperatures as above. These results suggest that the random chain rotation of the cations mainly contributes to the ^{1}H relaxation at lower temperature in this phase, while contribution from other relaxation process, the dynamic *trans-gauche* isomerization for example, gradually increases with increasing temperature.

Conclusion

From the present study of NMR the low temperature phase can be considered to have a disordered structure, probably of static nature, about the environment of the CH_3 groups. The only motion detected by NMR in this phase was the C_3 reorientation of the CH_3 groups. In the intermediate phase, the 180° flip motion of the cation about its long axis as well as the C_3 reorientation of the NH_3^+ groups are expected to take place. From these motional processes, the intermediate phase is characterized to be a dynamically disordered phase about the orientation of the cations. Above the high temperature transition, the cations obtain much more motional freedom than those in the intermediate phase. The conformational disorder of the cations is considered to develop in the crystals with increasing temperature.

When baBr was cooled through the high T_{tr}, marked nonexponential behavior of T_1 indicating the coexistence of at least two crystalline phases was observed in a fairly wide temperature range. This can be explained by considering that the random axial orientation of the ba^+ chains in the high temperature phase is partially frozen below the T_{tr} and the disordered chains are gradually settled in the stable arrangement with decreasing temperature.

Tsau and Gilson[8] studied the wide-line NMR of butylammonium chloride which is known to show two phase transitions, and assigned the decrease of M_2 at the low T_{tr} to the reorientation of butyl chains with rotating CH_3 and rigid NH_3^+ groups. However, the present study reveals that the NH_3^+ groups of baBr reorient very rapidly even in the intermediate phase. This may be due to the N–H···Br type hydrogen bonds which are weaker than those of the N–H···Cl type.

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