October, 1987] © *1987 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* ***60,*** *3499—3504 (1987)* 3499

The Phase Transitions of 1-Alkyl-1-azoniabicyclo[2.2.2]octane Bromides, C_n-ABCO-Br ($10 \leqq n \leqq 22$)

Kengo Imamura, Takashi Nogami,* and Yasuhiko Shirota
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565

(Received March 25, 1987)

The phase transitions of a series of 1-alkyl-1-azoniabicyclo[2.2.2]octane bromides were studied on the basis of DSC, the measurements of the ionic conductivities of the bromide anion, and Raman spectroscopy. Most of the materials exhibited three endothermic signals at T_{c1}, T_{c2}, and T_{c3} ($T_{c1}<T_{c2}<T_{c3}$) when they were heated. The temperature dependence of the ionic conductivities of the bromide anion showed conductivity jumps by a factor of 2—4 at around T_{c3}. In order to clarify the phase transition, the temperature dependences of the Raman spectra were measured. It was found that the phase transition at T_{c1} is caused by the molecular rearrangement in the solid, while the transitions at T_{c2} and T_{c3} are caused by both the conformational change in the alkyl chain and the rotational motion of the ABCO portion.

In a series of papers,[1—6] the phase transitions of bis(quaternary alkyl halides) of 1,4-diazabicyclo[2.2.2]octane (DABCO) and mono(quaternary alkyl bromides) of DABCO were studied on the basis of DSC, the measurements of the ionic conductivities of the halide anion, and IR and Raman spectroscopy. All of the symmetric bis(quaternary salts) of DABCO exhibited one transition, which was accompanied by abrupt increases in the ionic conductivities of the halide anion by two to three orders of magnitude.[1,2] The temperature dependence of the IR spectra showed abrupt disappearance of the band progressions at the transition temperature. This fact shows that the motion of the alkyl chain involving conformational change is excited above the transition temperature. On the other hand, unsymmetric bis(quaternary alkyl bromide salts) of DABCO exhibited somewhat different phenomena.[3—5] Although they also showed abrupt increases in the ionic conductivities of the halide anion at the transition temperatures, they were converted to the metastable state after they had been heated above the transition temperature and then cooled to room temperature. The thermodynamic properties of the unsymmetric DABCO salts could be explained on the basis of the free energy-temperature relation. Interesting correlations were found between the difference in the two alkyl-chain lengths of the unsymmetric DABCO salts and the phase transitions, the thermodynamic properties, and the ionic conductivities of the bromide anion.

As an extension of the above studies, we have now studied the phase transitions of a series of 1-alkyl-1-azoniabicyclo[2.2.2]octane bromides, which have only one nitrogen. We have found that most of the salts exhibited three transitions, and that the conductivity jumps of the bromide anion occurred at the highest transition temperature of the three. The phase transition could be analysed on the basis of the temperature dependence of the Raman spectra. In this paper, 1-azabicyclo[2.2.2]octane is abbreviated as ABCO. The materials studied are abbreviated by the numbers of the alkyl-carbons attached to ABCO nitrogen, shown in Fig. 1. For example, 1-decyl-1-azoniabicyclo[2.2.2]octane bromide is abbreviated as C_{10}-ABCO-Br. Thus, the materials in Fig. 1 are generally abbreviated as C_n-ABCO-Br ($10 \leqq n \leqq 22$).

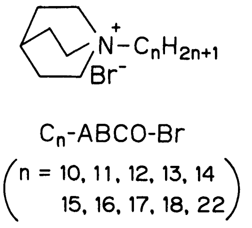

Fig. 1. Quaternary alkyl bromide salts of ABCO.

Experimental

Syntheses of C_n-ABCO-Br. Equimolar amounts (5 mmol) of ABCO and alkyl bromide were dissolved into methanol (20 ml), and the solution was refluxed for 10 h. In the cases of C_n-ABCO-Br (n=10, 11, 12, 13, 15, 17, 22), the methanol was evaporated to dryness, and the white residue was recrystallized three times from a mixed solvent of ethyl acetate and ethanol. In the cases of C_n-ABCO-Br (n=14, 16, 18), the methanol solution of the reaction was poured directly into diethyl ether (300—400 ml), the white precipitate was collected and recrystallized three times from the mixed solvent of ethyl acetate and ethanol. All the products were somewhat hygroscopic, and they were dried under a vacuum after recrystallization. They gave good analytical agreement; the residual solvent and moisture were negligible.

Measurements. A portion of 3—5 mg of the sample, dried beforehand under vacuum, was used for the measurement of the DSC. The details of the DSC and the measurements of the ionic conductivities of the bromide anion were described previously.[1,2] The Raman spectra were measured for the powdered sample by a method which will be reported elsewhere.[6]

Results and Discussion

DSC Measurements. The DSC measurements were

Table 1. Materials, Transition Temperatures, Transition Enthalpies, Transition Entropies, and Conductivity Ratios of the Bromide Anion before and after Transition

Material	T_{c1}	T_{c2}	T_{c3}	ΔH_1	ΔH_2	ΔH_3	ΔS_1	ΔS_2	ΔS_3	σ_h/σ_l
	°C			kJ mol^{-1}			J mol^{-1} K^{-1}			
C_{10}-ABCO-Br[a)]										2.4
C_{11}-ABCO-Br	48	b)	89	16.3	b)	16.4	45	b)	51	4.1
C_{12}-ABCO-Br	61	b)	91	19.9	b)	17.4	48	b)	60	2.5
C_{13}-ABCO-Br	44	72	94	7.1	8.6	17.9	22	25	49	3.0
C_{14}-ABCO-Br	56	63	96	11.9	6.4	23.3	36	19	63	3.0
C_{15}-ABCO-Br	43	83	100	9.8	10.0	24.5	31	28	66	2.6
C_{16}-ABCO-Br	42	66	102	5.6	7.5	26.6	18	22	71	2.6
C_{17}-ABCO-Br	34	87	98	8.5	10.3	25.8	28	29	70	3.4
C_{18}-ABCO-Br	39	75	104	2.7	10.3	34.6	9	30	92	2.4
C_{22}-ABCO-Br	16, 73	83	110	2.2, 3.2	8.7	48.3	9, 24	126	8	2.5

a) Transition temperatures (°C), 13, 54, 71, 131; the corresponding transition enthapies (kJ mol^{-1}), 3.4, 16.8, 2.3, 2.2; the corresponding transition entropies (J mol^{-1} K^{-1}), 12, 51, 7, 5. b) The corresponding endothermic signal was not observed.

made in order to gain insight into the phase transition. Since all samples decomposed above 200 °C, their DSC measurements were made from room temperature to just above the highest transition temperature. Part of Table 1 shows the materials, the transition temperatures, the transition enthalpies, and the transition entropies. The transition temperature was obtained by the onset of the DSC signal. C_n-ABCO-Br (n=13, 14, 15, 16, 17, 18) showed three transitions. C_n-ABCO-Br (n=11, 12) and C_n-ABCO-Br (n=10, 22) showed two and four transitions respectively. Figure 2 shows the DSC thermogram of C_{13}-ABCO-Br as a typical example. When the sample was heated from room temperature, three endothermic signals were observed at T_{c1}, T_{c2}, and T_{c3} ($T_{c1} < T_{c2} < T_{c3}$). The corresponding exothermic signals were observed in the temperature region lower than T_{c1}, T_{c2}, and T_{c3} when the samples were cooled after they had been heated above T_{c3}; the hysteresis between the endothermic and exothermic signals was especially large for the transitions at T_{c1} and T_{c2}. In the second heating cycle, all of the materials showed endothermic signals identical to those of the first cycle. The transition temperatures of C_n-ABCO-Br ($11 \leqq n \leqq 22$) were classified into T_{c1}, T_{c2}, and T_{c3} in Table 1 for the following reasons. Almost iden-

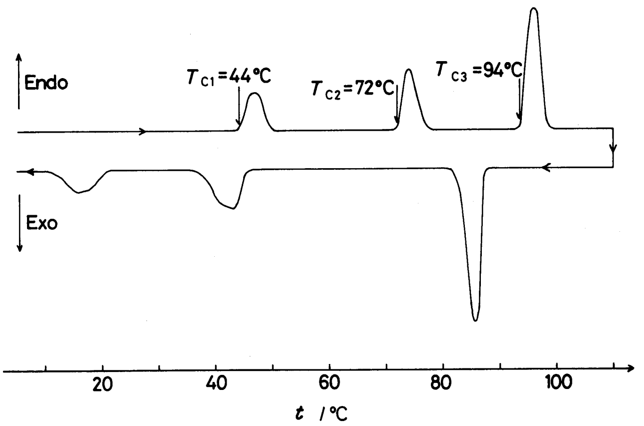

Fig. 2. DSC thermogram of C_{13}-ABCO-Br. Scan speed=5 °C min^{-1}.

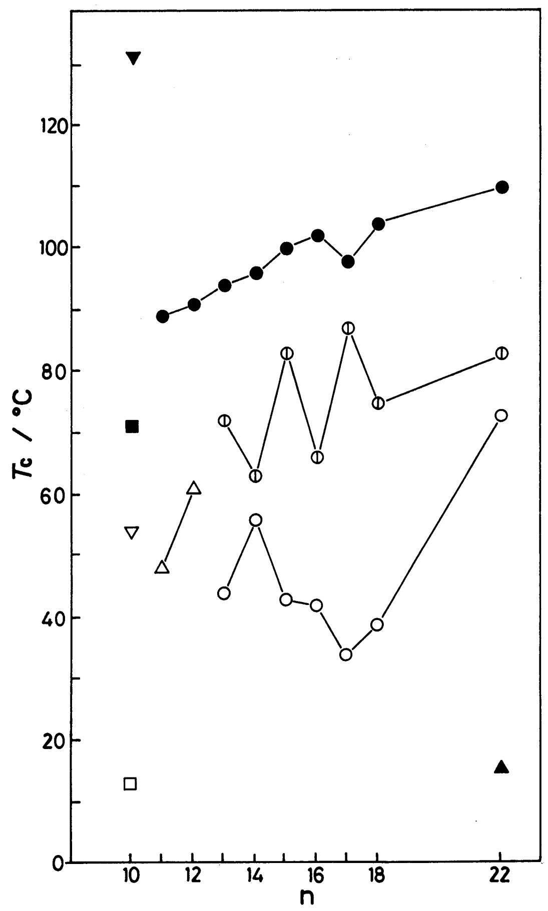

Fig. 3. The plot of the transition temperatures against carbon numbers of alkyl groups in C_n-ABCO-Br.
○ T_{c1}; ⦶ T_{c2}; ● T_{c3}; □▽■▼ transition temperatures of C_{10}-ABCO-Br; △ T_{c1} of C_n-ABCO-Br (n=11, 12); ▲ the lowest transition temperature of C_{22}-ABCO-Br.

tical structural changes seem to occur at T_{c1}, as will be discussed later in connection with the Raman spectroscopy. Regarding the transitions at T_{c2}, another type of structural change, which was also clarified by Raman spectroscopy, occurs for these materials. Since the conductivity jumps of the bromide anion occur at the highest transition temperatures (T_{c3}) for C_n-ABCO-Br ($n \geqq 11$), as will be described later, these transitions seem to be caused by the common structural change in the solid. On the other hand, the transitions of C_{10}-ABCO-Br seem to be different from those of the other ABCO salts.[7] Thus, its thermodynamic data are shown in the footnote of Table 1. The first transition of C_n-ABCO-Br (n=11, 12) is tentatively assigned to T_{c1}, for it has two transition temperatures, in contrast to the three transition temperatures of most of the other salts.

Figure 3 plots the transition temperatures (T_{c1}, T_{c2}, and T_{c3}) of C_n-ABCO-Br ($n \geqq 11$) and the four transition temperatures of C_{10}-ABCO-Br against the carbon numbers of the alkyl group attached to ABCO-nitrogen. Although T_{c1} showed a complex behavior, a distinct even-odd number effect of the alkyl carbons was observed for T_{c2}. T_{c3} increased gradually with the increase in the alkyl-chain lengths except for C_{17}-ABCO-Br. Figure 4 plots the transition enthalpies (ΔH_1, ΔH_2, ΔH_3) against the carbon numbers of the alkyl groups attached to ABCO nitrogen. Here, ΔH_1, ΔH_2, and ΔH_3 correspond to the values of the endothermic heats at T_{c1}, T_{c2}, and T_{c3} respectively. The values of ΔH_1 and ΔH_2 are not so different, being about 10 kJ mol^{-1} or less. An even-odd number effect of the alkyl carbons was observed for ΔH_2 (C_n-ABCO-Br, $n \geqq 13$). On the other hand, ΔH_3 increased with the increase in the alkyl-chain lengths. The transition temperatures (T_{c1} and T_{c2}) for C_n-ABCO-Br ($n \geqq 13$) seem to coalesce to a single transition temperature (T_{c1}) for C_n-ABCO-Br (n=11, 12), because the sum of ΔH_1 and ΔH_2 for the former salts gives values similar to those of ΔH_1 for the latter salts (see Fig. 4). This point will be discussed later in connection with the Raman spectroscopy. The above characteristics of the transition enthalpies were also applicable to the cases of transition entropies ($\Delta S_1 = \Delta H_1 / T_{c1}$, $\Delta S_2 = \Delta H_2 / T_{c2}$, $\Delta S_3 = \Delta H_3 / T_{c3}$).

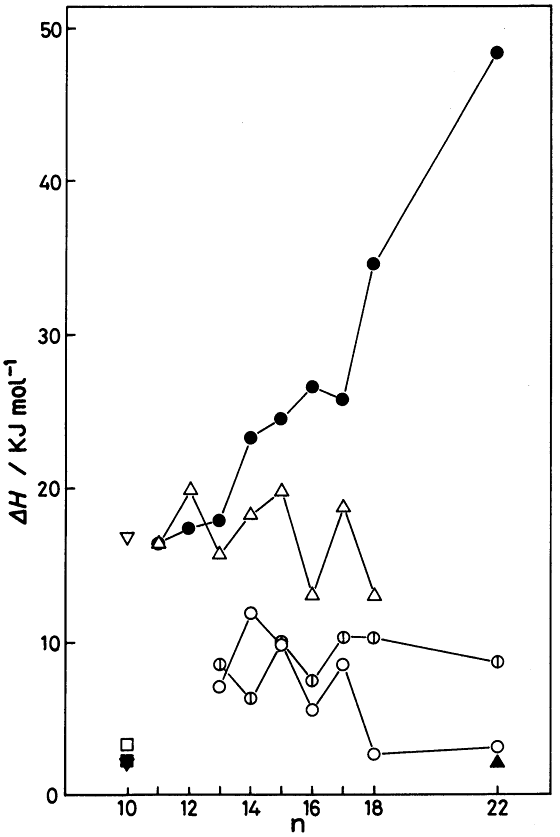

Fig. 4. The plot of the transition enthalpies against carbon numbers of alkyl groups in C_n-ABCO-Br. ○ ΔH_1; ⦶ ΔH_2; ● ΔH_3; △ $\Delta H_1 + \Delta H_2$ and ΔH_1's of C_n-ABCO-Br (n=11, 12); □▽■▼ ΔH of C_{10}-ABCO-Br, corresponding to Fig. 3; ▲ ΔH for the transition of C_{22}-ABCO-Br at 16 °C.

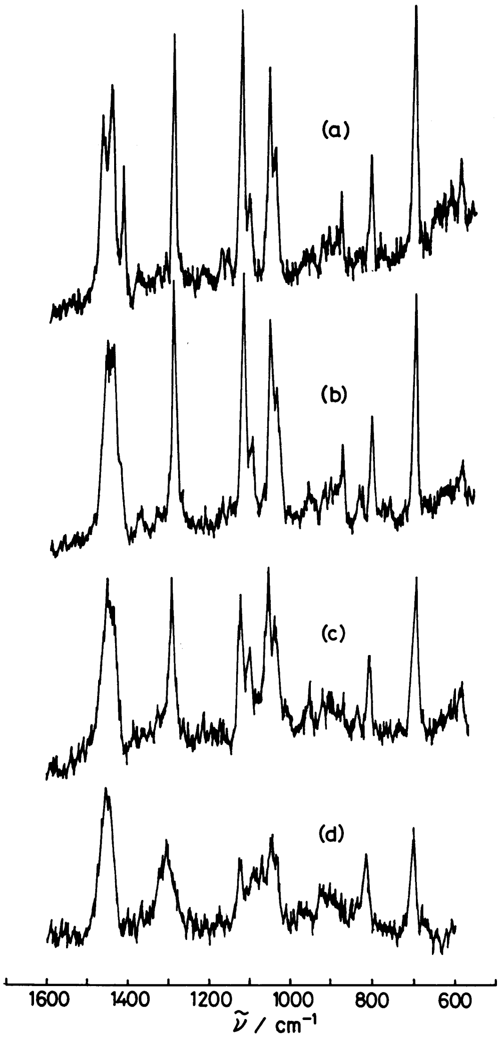

Fig. 5. Temperature dependence of the Raman spectra of C_{18}-ABCO-Br. (a) 17 °C, (b) 50 °C, (c) 80 °C, (d) 110 °C.

Raman Spectroscopy. In order to clarify the phase transitions at T_{c1}, T_{c2}, and T_{c3} in more detail, the temperature dependence of the Raman spectra was measured. Figure 5 shows the result observed for C_{18}-ABCO-Br as a typical example. Below T_{c1} (39 °C), crystal-field splitting[8] was observed at 1419 and 1450 cm^{-1} (see the spectrum at 17 °C). This fact shows that the zigzag planes of the nearest neighboring alkyl chains are packed nearly perpendicular to each other.[8] The crystal-field splitting disappeared above T_{c1} (see the spectrum at 50 °C). In view of the small value of ΔH_1 (2.7 kJ mol^{-1}), the transition at T_{c1} seems not to be caused by the onset of a rotator phase.[9] The lack of the crystal-field splitting above T_{c1} shows that a reorientation of the molecules takes place in the solid. No appreciable decreases in the Raman intensities were observed for the C-C skeletal vibration (1061, 1130 cm^{-1}) and the CH_2 twisting mode (1297 cm^{-1}) in the temperature range of $T_{c1}<T<T_{c2}$. In this context, Kobayashi et al. investigated the correlation between the Raman intensities and the length of the *trans*-zigzag structure in polyethylene.[10] They found that the Raman intensities decreased with the decrease in the length of the *trans*-zigzag portion, and that the Raman bands were broadened by the onset of vigorous reorientational motion of the molecule. Taking these results into account, the present findings suggest that no conformational change of the alkyl group occurs between T_{c1} and T_{c2}.[10] Above T_{c2} (75 °C), the intensities of these vibrational modes decreased significantly (see the spectrum at 80 °C). This fact shows that the conformational change in the alkyl group occurs above T_{c2}. Since the Raman intensities of the NC_4 symmetric stretching mode (706 cm^{-1}) also decreased to some extent above T_{c2}, the rotational motion of ABCO seems to be excited.[10] All of the Raman signals decreased in their intensities and were considerably broadened above T_{c3} (see the spectrum at 110 °C). This fact shows that the alkyl chain seems to be "melt" from the dynamical point of view and that a vigorous rotational motion of ABCO occurs in this temperature range. The coalescence of T_{c1} and T_{c2} observed for C_n-ABCO-Br ($n \geqq 13$) into T_{c1} for C_n-ABCO-Br (n=11, 12) was clearly demonstrated by the fact that both the disappearance of the crystal-field splitting and the decrease in the Raman intensities at 1064, 1130, and 1297 cm^{-1} were simultaneously observed above T_{c1} for the latter materials; the former observation corresponds to the rearrangement of the molecule in the solid, and the latter, to the conformational change in the alkyl group. Thus, the structural changes observed at T_{c1} and T_{c2} for C_n-ABCO-Br ($n \geqq 13$) occurred simultaneously at T_{c1} for C_n-ABCO-Br (n=11, 12).

Ionic Conductivities of the Bromide Anion. The temperature dependences of the ionic conductivities of the bromide anion were measured for the compressed pellet samples by an AC impedance method.[1,2] Figure

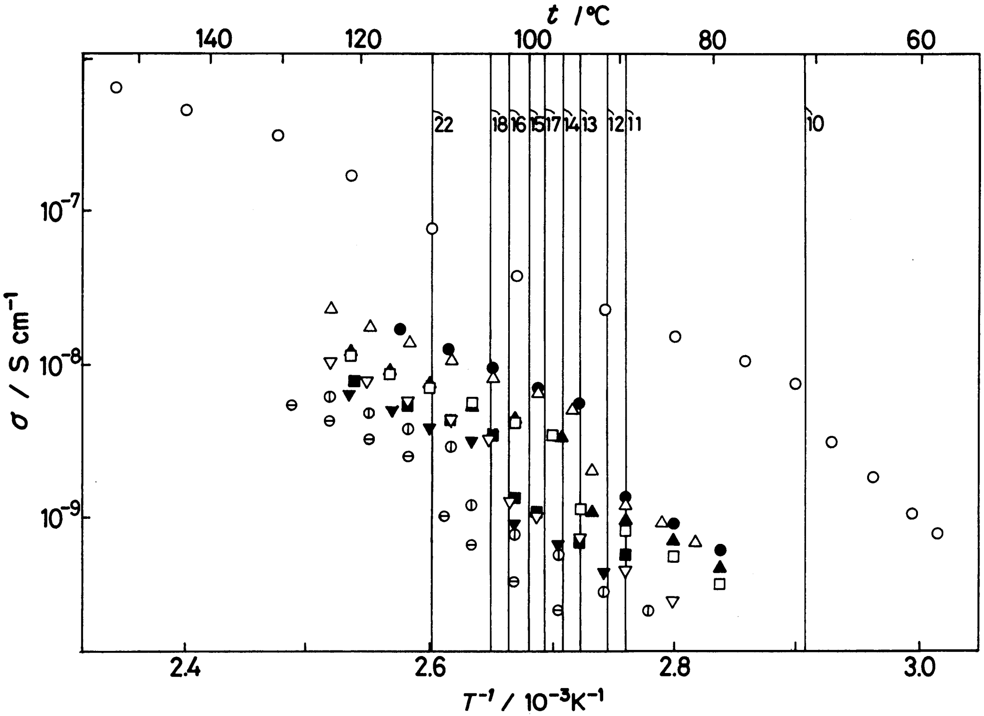

Fig. 6. Temperature dependence of the ionic conductivities of bromide anion of C_n-ABCO-Br. ○ n=10; ● n=11; △ n=12; ▲ n=13; □ n=14; ■ n=15; ▽ n=16; ▼ n=17; ⦶ n=18; ⊖ n=22. The vertical solid lines and the numbers nearby represent T_{c3} and n respectively.

6 shows the observed results. All of the materials exhibited conductivity jumps, and the ratios of the ionic conductivities of the bromide anion before (σ_l) and after (σ_h) the transitions were found to be in the range of 2—4 (see Table 1). These values are much smaller than those of the bis(quaternary alkyl bromide salts) of DABCO,[1-5] but are almost identical with those of the mono(quaternary alkyl bromide salts) of DABCO.[6] In order to correlate the conductivity jumps with the transition temperatures, T_{c3}'s are also shown as vertical solid lines in this figure. The numbers near these lines represent the numbers of the alkyl carbons attached to ABCO nitrogen. From Fig. 6, the following characteristics can be seen: (1) The conductivity jump occurs at around T_{c3} by a factor of 2—4. (2) The shorter the alkyl-chain lengths, the higher the ionic conductivities of the bromide anion. (3) The activation energies of the conduction above T_{c3} are lower than those below T_{c3}.

The first characteristic shows that no appreciable conductivity jump occurs at T_{c1}, where molecular rearrangement takes place, or at T_{c2}, where the conformational motion of the alkyl chain and the rotational motion of ABCO are excited to some extent. Only at T_{c3} where vigorous molecular motion sets in, does the conductivity jump take place. The values of the conductivity jump seem to be related with the degree of the molecular motion for the following reason. The temperature dependence of the Raman spectra of the symmetric bis(quaternary alkyl bromides) of DABCO exhibited an almost complete disappearance of the C-C skeletal modes above the transition temperature.[11] This fact shows that the molecular motion of the alkyl group is too vigorous to be regarded as if it were "liquid." As a result, the conductivity jumps of these materials were large. On the other hand, the molecular motion of the present materials are retarded to some extent, in view of the presence of the C-C skeletal mode even above T_{c3} (see Fig. 6); this gives rise to the small conductivity jump. The second characteristic above can be explained by the fact that the distance between the hopping sites of the bromide anion becomes shorter as the alkyl-chain lengths decrease. The third characteristic above can be explained by the fact that the bromide anion can move more easily in the high-temperature range ($T > T_{c3}$) than in the low temperature range ($T < T_{c3}$) because of the presence of a large number of voids which are produced by the vigorous motion of the alkyl group and the ABCO portion.

Summary. The phase transitions of C_n-ABCO-Br ($10 \leqq n \leqq 22$) were studied on the basis of the DSC, the Raman spectroscopy, and the measurements of the ionic conductivities of the bromide anion. Concluding a series of the studies,[1-6] three characteristic points (the numbers of the transitions, the existence of a metastable state, and the conductivity ratios of the bromide anion before and after the transition) were compared: The results are summarized in Table 2. Here, C_n-DABCO-C_n-Br_2,[1,2] C_n-DABCO-C_m-Br_2,[3-5] and C_n-DABCO-Br[6] denote symmetric bis(quaternary alkyl bromides) of DABCO, unsymmetric bis(quaternary alkyl bromides) of DABCO, and mono(quaternary alkyl bromides) of DABCO respectively; n and m denote the numbers of alkyl carbons. As to the numbers of the transitions, C_n-DABCO-C_n-Br_2, C_n-DABCO-C_m-Br_2, C_n-DABCO-Br, and C_n-ABCO-Br exhibited one, one, two, and three transitions respectively. Regarding the thermodynamic properties, no metastable state was observed for C_n-DABCO-C_n-Br_2, C_n-DABCO-Br, or C_n-ABCO-Br. In the case of the unsymmetric bis(quaternary alkyl bromide salts) of DABCO (C_n-DABCO-C_m-Br_2), however, the low-temperature phase was converted to the metastable state after they had been heated above the transition temperature and then cooled. All of the quaternary salts studied up to now showed conductivity jumps of the bromide anion. The conductivity jumps (the σ_h/σ_l values) are found to be in the range of 100—6000 for the bis(quaternary alkyl bromides) of DABCO. On the other hand, they are small (2—10) for the mono(quaternary alkyl bromides) of DABCO and of ABCO. In the cases of C_n-DABCO-C_n-Cl_2 and C_n-DABCO-C_n-I_2, the conductivity jumps of the chloride anion and iodide anion by a factor of 150—190 and 140—350 respectively were also observed.[2]

We are grateful to Professor Masamichi Kobayashi and Dr. Tsutomu Ishioka, Faculty of Science, Osaka University, for their fruitful discussions with regard to the analysis of the Raman spectra. We are also grateful to Professor Shigekazu Kusabayashi and Dr. Shunsuke

Table 2. Comparison of the Phase Transitions of Quaternary Alkyl Bromides of DABCO and of ABCO

	C_n-DABCO-C_n-Br_2	C_n-DABCO-C_m-Br_2	C_n-DABCO-Br	C_n-ABCO-Br
Number of transition	1	1	2	3
Metastable state	Absent	Present	Absent	Absent
Conductivity jumps of the bromide anion	630—3600[a]	700—3070 ($m=n+2$)[b] 100— 770 ($n=10$)[c] 1500—6000 ($m=n+1$)[d]	2—10[e]	2—4

a) The conductivity jumps of C_n-DABCO-C_n-Cl_2 and C_n-DABCO-C_n-I_2 were found to be in the range of 150—190 and 140—350 respectively (see Ref. 2). b) Ref. 3. c) Ref. 4. d) Ref. 5. e) Ref. 6.

Takenaka, Faculty of Engineering, Osaka University, for the use of the DSC apparatus.

References

1) J. Shimizu, T. Nogami, and H. Mikawa, *Solid State Commun.*, **54**, 1009 (1985).

2) J. Shimizu, K. Imamura, T. Nogami, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, **59**, 1443 (1986).

3) K. Imamura, J. Shimizu, and T. Nogami, *Bull. Chem. Soc. Jpn.*, **59**, 2699 (1986).

4) J. Shimizu, K. Imamura, T. Nogami, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, **59**, 3367 (1986).

5) K. Imamura, T. Nogami, and Y. Shirota, *Bull. Chem. Soc. Jpn.*, **60**, 111 (1987).

6) K. Imamura, T. Nogami, Y. Shirota, T. Ishioka, and M. Kobayashi, *Bull. Chem. Soc. Jpn.*, in press.

7) C_n-ABCO-Br ($n \geqq 11$) were found to be converted to the isotropic phase above T_{c3} by observing their crystals with a polarization microscope under a crossed Nicols condition. On the other hand, C_{10}-ABCO-Br exhibited unusual phenomena; with an elevation of the temperature, the birefringence once disappeared at 62 °C, appeared again at 80 °C, and then disappeared again at 145 °C. Furthermore, the conductivity jump of the bromide anion was observed at around the third transition temperature (71 °C) of the four.

8) R. S. Stein, *J. Chem. Phys.*, **23**, 734 (1955); F. J. Boerio and J. L. Koenig, *ibid.*, **52**, 3425 (1970).

9) The transition enthalpies of *n*-alkanes (C_nH_{2n+2}, $11 \leqq n \leqq 22$) from a low-temperature phase to a rotator phase were found to be in the range of 7—30 kJ mol^{-1}; see M. G. Broadhurst, *J. Res. National Bureau Standards*, **66A**, 241 (1962).

10) Y. Cho, M. Kobayashi, and H. Tadokoro, *Macromolecules*, in press.

11) Unpublished data.