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The Phase Transition of 1-Alkyl-4-aza-1-azoniabicyclo[2.2.2]octane Bromides, C_n-DABCO-Br ($11 \leqq n \leqq 22$)

Kengo IMAMURA, Takashi NOGAMI,* Yasuhiko SHIROTA, Tsutomu ISHIOKA,† and Masamichi KOBAYASHI*,†

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565

†Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560

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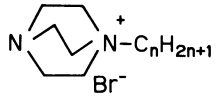
The phase transitions of a series of 1-alkyl-4-aza-1-azoniabicyclo[2.2.2]octane bromides were studied on the basis of DSC, measurements of the ionic conductivities of the bromide anion, and Raman spectroscopy. Two endothermic signals were observed at the temperatures of T_{c1} and T_{c2} ($T_{c1}<T_{c2}$) for most of the materials. The transition enthalpies and transition entropies were not very different for the transitions at T_{c1}, irrespective of the alkyl-chain lengths attached to DABCO nitrogens. On the other hand, these values tended to increase with an increase in the alkyl-chain lengths for the transitions at T_{c2}. The temperature dependences of the ionic conductivities of the bromide anion showed abrupt increases in the conductivities by a factor of 2—10. The conductivity jumps were observed around T_{c2}. The temperature dependences of the Raman spectra gave detailed information on the phase transition; (1) the change in the subcell structure took place at T_{c1}, with the concomitant occurrence of a conformational change in the alkyl group; (2) above T_{c2}, the alkyl chain takes a liquid-like disordered form, and a rotational motion of the DABCO portion sets in.

The solid-solid phase transitions of a series of bis(quaternary alkyl halides) of 1,4-diazabicyclo[2.2.2]-octane (DABCO) have been studied on the basis of DSC, IR absorption spectroscopy, and measurements of the ionic conductivities of the halide anion.[1-5] The phase transitions of quaternary alkyl bromide salts of 1-azabicyclo[2.2.2]octane were also studied.[6] Symmetric bis(quaternary alkyl halide) salts of DABCO showed endothermic signals at the transition temperatures (T_c) when the samples were heated from room temperature.[1,2] They showed exothermic signals around T_c when the samples were cooled after they had been heated above T_c. The absolute values of the endothermic and exothermic heats were equal, within the limits of experimental error. Abrupt increases in the ionic conductivity of the halide anion by a factor of 630—3600 were observed around at T_c. As the temperature was increased, the IR absorption spectra of the symmetric salts showed a sudden disappearance of the band progressions due to the CH_2 rocking-twisting branch at T_c. This fact shows that the trans-zigzag conformation of the long alkyl chains in the low temperature phase is destroyed and changes to a disordered form above T_c. The concomitant formation of voids facilitates the halide-anion transport above the transition temperature, giving rise to the conductivity jump.

The unsymmetric bis(quaternary alkyl bromides) of DABCO showed phenomena different from those of the symmetric salts.[3-5] Endothermic signals were also observed at the transition temperatures (T_c) when the virgin samples[7] were heated from room temperature. However, the exothermic signals were observed at much lower temperatures (T_c') than T_c when the samples were cooled after they had been heated above T_c. The temperature dependence of the IR absorption spectra of the unsymmetric salts revealed that a metastable phase was produced first when the samples had been cooled from a temperature above T_c. For some unsymmetric salts, the metastable phase was converted to the stable phase within a week when the salts were kept at room temperature. The thermodynamic properties of the unsymmetric salts could be explained on the basis of the free energy-temperature relation. Conductivity jumps of the bromide anion by a factor of 100—6000 were also observed around T_c for the virgin samples and around T_c' for the annealed samples.[7]

All of the previous studies were made on the phase transitions of bis(quaternary alkyl halides) of DABCO; it seems that it also be interesting to compare the phase transitions of mono(quaternary alkyl bromides) of DABCO with those of the bis(quaternary salts). Mono(quaternary alkyl bromide salt) of DABCO possesses both a hydrophilic DABCO cation and a hydrophobic alkyl group. Thus, it has a possibility of forming a Langmuir-Blodgett membrane[8] and may be useful in a molecular device by using abrupt changes in the ionic conductivities of the bromide anion and/or the disappearance of the birefringence above the transition temperatures.[2] We have studied the phase transitions of mono(quaternary alkyl bromides) of DABCO on the basis of DSC, the



n= 11,12,13,14,15,16,17,18,22

Fig. 1. Mono(quaternary alkyl bromide) salts of DABCO.

measurements of the ionic conductivities of the bromide anion, and Raman spectroscopy. The materials studied are shown in Fig. 1. The names of the materials are abbreviated by the numbers of the alkyl carbons attached to DABCO nitrogens. For example, 4-dodecyl-1-aza-4-azoniabicyclo[2.2.2]octane bromide is abbreviated as C_{12}-DABCO-Br. Thus, the names of the materials in Fig. 1 are generally abbreviated as C_n-DABCO-Br ($11 \leqq n \leqq 22$). The names of the symmetric bis(quaternary alkyl bromide salts) of DABCO are similarly abbreviated as C_n-DABCO-C_n-Br_2.

Experimental

Syntheses of Mono(quaternary alkyl bromides) of DABCO. The mono(quaternary alkyl bromides) of DABCO were synthesized by the method reported previously.[3]

Measurements. The DSC and the measurements of the ionic conductivities of the bromide anion and the IR spectra were made by the methods reported previously.[1,2] The Raman spectra were measured on a JASCO CT-1000D double monochromator, using the 514.5 nm line (Ar ion laser) as the excitation source. The temperature of the sample was regulated by means of a Thermal Controller E5D (Omron Co., Ltd). In order to quench the fluorescence caused by unknown impurities, the sample held above T_{c2} was irradiated with the excitation beam for several h before the measurement.

Results and Discussion

DSC Measurements. The DSC measurements were made at the heating (or cooling) rate of 5 °C min^{-1}. Figure 2 shows the DSC thermogram of C_{17}-DABCO-Br as a typical example. Most of the samples gave two endothermic signals at the T_{c1} and T_{c2} temperatures ($T_{c1}<T_{c2}$) on heating. As will be shown later, abrupt increases in the ionic conductivities of the bromide anion occurred around T_{c2}. Thus, the phase transitions at T_{c1} and T_{c2} seem to be different in origin. The absolute values of the transition enthalpies at T_{c1} and T_{c2} are denoted as $\Delta H_{en,1}$ and $\Delta H_{en,2}$ respectively. However, C_{13}-DABCO-Br showed three transitions (assigned tentatively as one at T_{c1} and two at T_{c2}).[9] When the samples were cooled after they had once been heated above T_{c2}, exothermic signals were observed. However, the temperatures of the exothermic transitions were usually much lower than the corresponding endothermic temperatures, T_{c1} and T_{c2}. The thermal histories of the samples seem to influence the exothermic transition temperatures and the shapes of the DSC curves. On the other hand, the endothermic transition temperatures (T_{c1} and T_{c2}) were reproducible when the samples were heated after several heating/cooling cycles. $\Delta H_{en,1}$ and $\Delta H_{en,2}$ tend to decrease slightly when the cycles are repeated. Part of Table 1 shows the materials, T_{c1}, $\Delta H_{en,1}$, T_{c2}, $\Delta H_{en,2}$, and the transition entropies ΔS_1 ($=\Delta H_{en,1}/T_{c1}$) and ΔS_2 ($=\Delta H_{en,2}/T_{c2}$).

Figure 3 plots the transition temperatures (T_{c1} and T_{c2}) against the carbon numbers of the alkyl chains. This figure also shows the transition temperatures of the symmetric bis(quaternary alkyl bromide) salts of

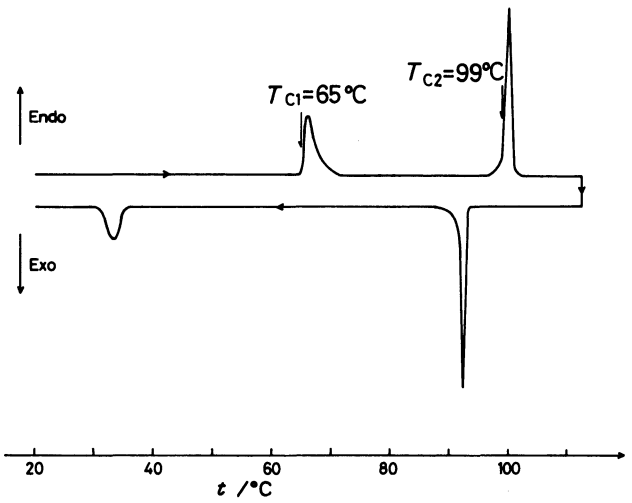


Fig. 2. DSC thermogram of C_{17}-DABCO-Br; scan rate=5 °C min^{-1}.

Table 1. Transition Temperatures (T_{c1} and T_{c2}), Transition Enthalpies ($\Delta H_{en,1}$ and $\Delta H_{en,2}$), Transition Entropies (ΔS_1 and ΔS_2), and Ratios of Ionic Conductivities of Bromide Anion Below (σ_l) and Above (σ_h) Transition Temperatures

Material	T_{c1} / °C	$\Delta H_{en,1}$ / kJ mol^{-1}	ΔS_1 / J mol^{-1} K^{-1}	T_{c2} / °C	$\Delta H_{en,2}$ / kJ mol^{-1}	ΔS_2 / J mol^{-1} K^{-1}	σ_h/σ_l
C_{11}-DABCO-Br	56	32.7	99	64	11.9	35	2
C_{12}-DABCO-Br	55	48.7	148	71	2.3	7	5
C_{13}-DABCO-Br	53	25.4	78	78, 86	3.8, 16.8	11, 47	3
C_{14}-DABCO-Br	60	29.8	89	73	26.4	76	10
C_{15}-DABCO-Br	62	31.1	93	79	31.5	90	5
C_{16}-DABCO-Br	67	31.7	93	85	34.5	96	6
C_{17}-DABCO-Br	65	31.6	93	99	40.6	109	7
C_{18}-DABCO-Br	67	30.4	89	85	25.9	72	3
C_{22}-DABCO-Br	76	33.0	95	107	50.9	134	4

DABCO (C_n-DABCO-C_n-Br_2)[2] for the sake of comparison. T_{c1} tends to increase with the increase in the alkyl-chain lengths for C_n-DABCO-Br ($n \geqq 13$). The variations in T_{c2} with the change in the alkyl-chain lengths were larger than those in T_{c1}. The transition temperatures of most of the symmetric bis(quaternary alkyl bromide) salts of DABCO were higher than T_{c1} and T_{c2}. This is reasonable because the molecular interaction arises mainly from the Coulomb force between N^+ and Br^-. Thus, the molecular interaction between the bis(quaternary salts) is stronger than that between the mono(quaternary salts); this gives rise to the higher transition temperatures for the former materials.

Figure 4 plots the transition enthalpies ($\Delta H_{en,1}$ and $\Delta H_{en,2}$) against the carbon numbers of the alkyl chains. This figure also shows the transition enthalpies of the symmetric bis(quaternary alkyl bromide) salts of DABCO (C_n-DABCO-C_n-Br_2)[2] for the sake of comparison. It is noteworthy that the $\Delta H_{en,1}$'s are close to 30 kJ mol^{-1}, irrespective of the alkyl-chain lengths.[10] On the other hand, the variations in the $\Delta H_{en,2}$'s with the alkyl-chain length are much larger than those in the $\Delta H_{en,1}$'s. These facts suggest that the origin of the phase transition at T_{c1} is common for all of the mono(quaternary salts) of DABCO. This point will be clarified by Raman spectroscopy later in this paper. Both the $\Delta H_{en,1}$ and $\Delta H_{en,2}$ values and their sum are smaller than the transition enthalpies of the symmetric bis(quaternary salts) with the same alkyl chain. This also comes from the fact that the intermolecular interaction of the bis(quaternary salts) is stronger than that of the mono(quaternary salts). No even-odd number effect of the alkyl carbons on the transition enthalpies was observed, unlike the cases of the bis(quaternary salts).[2,3] Similar characteristics described for the transition enthalpies were also applicable to the transition entropies (ΔS_1 and ΔS_2). It is especially noteworthy that the variations in ΔS_1 (78—99 J mol^{-1} K^{-1}) with the change in the alkyl-chain length are much smaller than those in ΔS_2.

Ionic Conductivities of the Bromide Anion. All of the samples were confirmed to be ionic conductors of the bromide anion by the method described previously.[1] The ionic conductivities were measured for sample pellets which had been dried overnight under a dynamic vacuum above T_{c2}. The conductivities less than 10^{-10} S cm^{-1} were below the lower limit of our

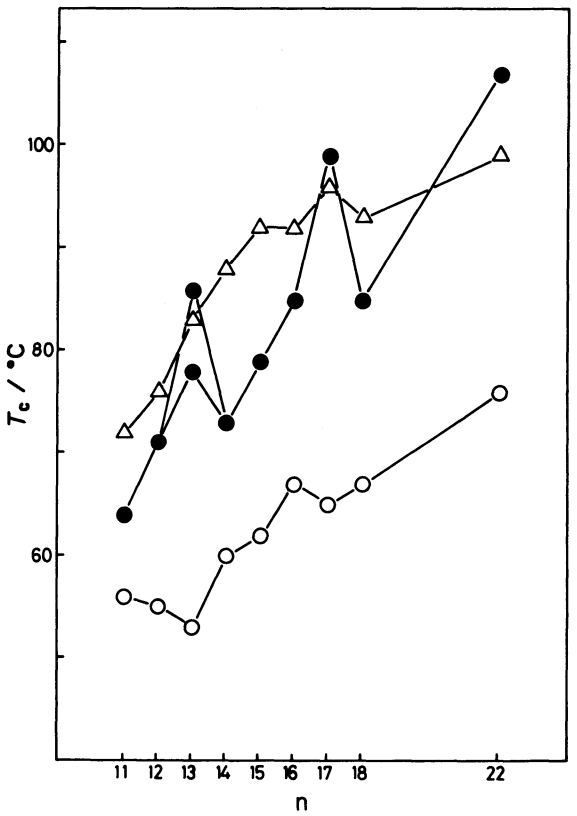


Fig. 3. The plots of the transition temperatures against the carbon numbers of alkyl grops.
○ T_{c1} of C_n-DABCO-Br; ● T_{c2} of C_n-DABCO-Br; △ T_c of C_n-DABCO-C_n-Br_2.

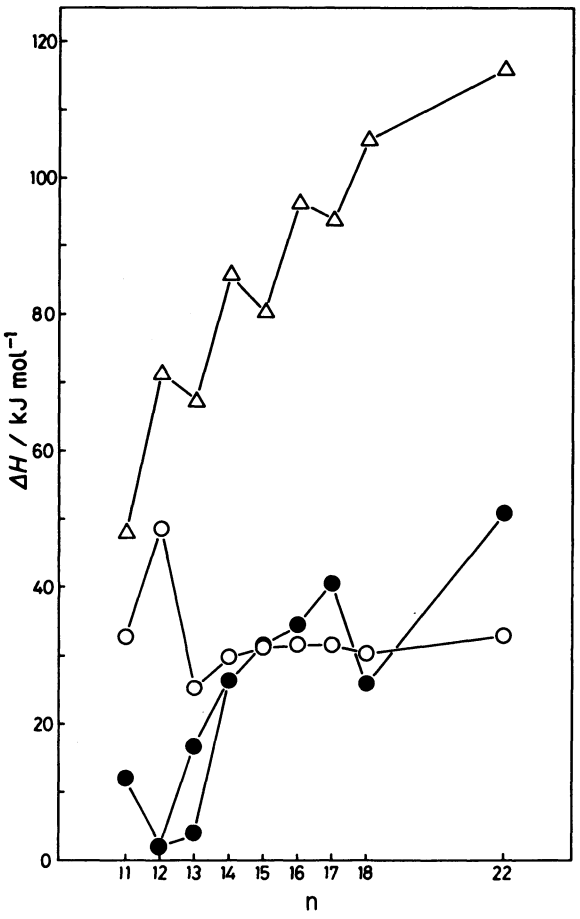


Fig. 4. The plots of the transition enthalpies against the carbon numbers of alkyl group.
○ $\Delta H_{en.1}$ of C_n-DABCO-Br; ● ΔH_{en2} of C_n-DABCO-Br; △ $\Delta\Delta H$ of C_n-DABCO-C_n-Br_2.

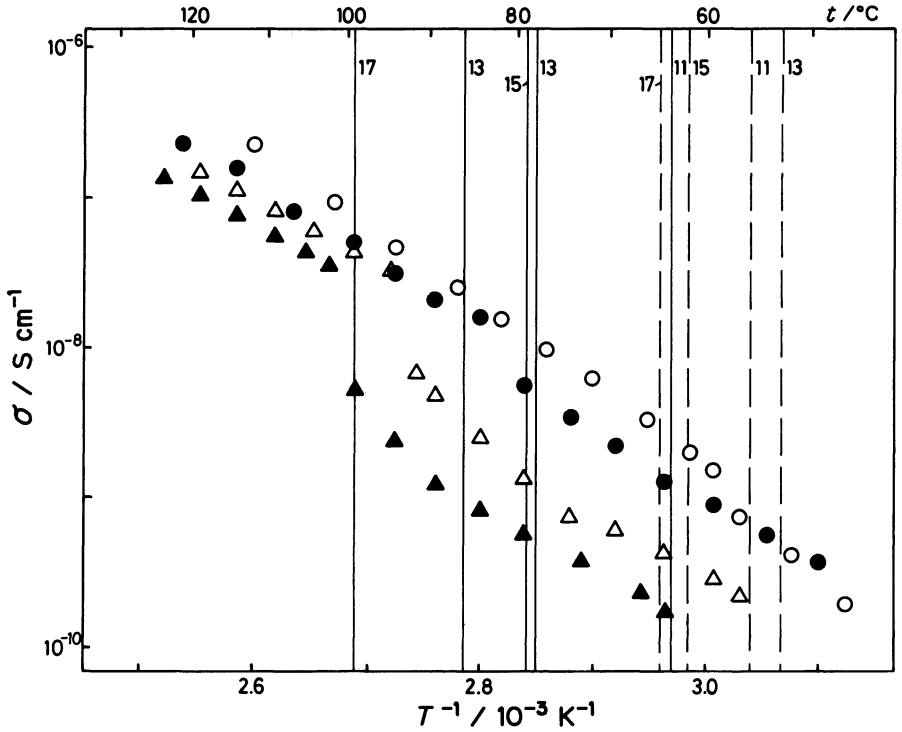


Fig. 5. Temperature dependences of ionic conductivities of bromide anion of monoquaternary DABCO bromide salts possessing odd numbers of alkyl carbons. The broken and solid lines represent T_{c1} and T_{c2} respectively. The numbers near these lines denote the numbers of alkyl carbons attached to DABCO nitrogens.
○ C_{11}-DABCO-Br; ● C_{13}-DABCO-Br; △ C_{15}-DABCO-Br; ▲ C_{17}-DABCO-Br.

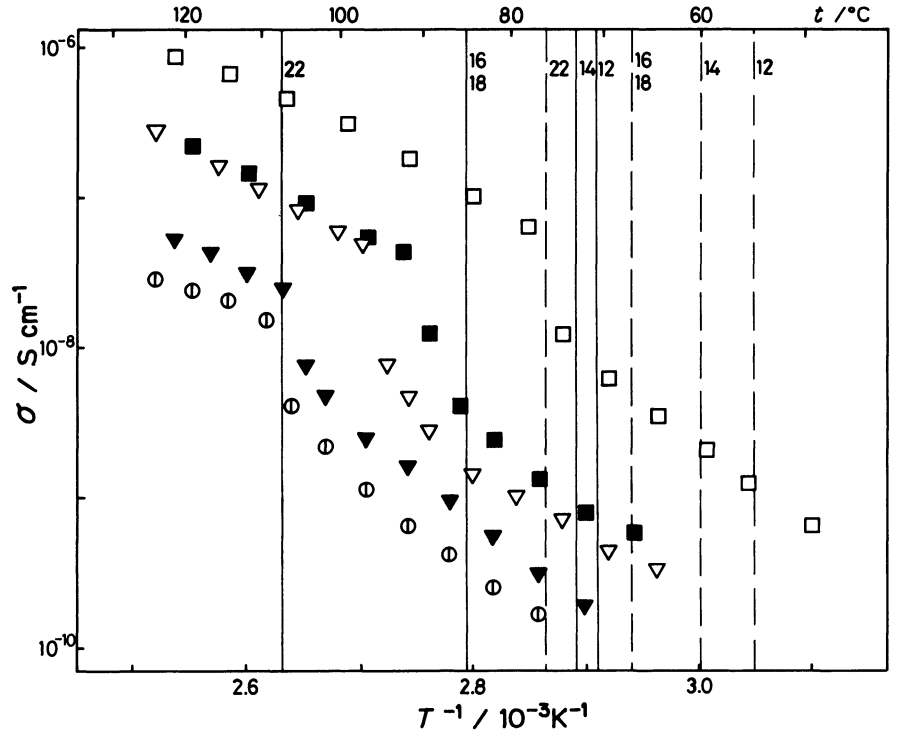


Fig. 6. Temperature dependences of ionic conductivities of bromide anion of monoquaternary DABCO bromide salts possessing even numbers of alkyl carbons. The broken and solid lines represent T_{c1} and T_{c2} respectively. The numbers near these lines denote the numbers of the alkyl carbons attached to DABCO nitrogens.
□ C_{12}-DABCO-Br; ■ C_{14}-DABCO-Br; ▽ C_{16}-DABCO-Br; ▼ C_{18}-DABCO-Br; ⦶ C_{22}-DABCO-Br.

measurement. Figures 5 and 6 show the temperature dependences of the ionic conductivities of the bromide anion of the mono(quaternary alkyl bromide salts) of DABCO, possessing odd and even numbers of alkyl carbons respectively. The broken and solid lines in these figures represent T_{c1} and T_{c2} respectively. The numbers near these lines represent the numbers of the alkyl carbons attached to the DABCO nitrogens.

All of the samples exhibited conductivity jumps. Table 1 shows the ratios of the conductivities below (σ_l) and above (σ_h) the temperature of the conductivity jumps. The σ_h/σ_l values (2—10) were two to three orders of magnitude smaller than those of the bis-(quaternary alkyl bromide salts) of DABCO; the latter salts gave σ_h/σ_l values of about 100—6000.[1-5] Figures 5 and 6 show that the temperatures of the conductivity jumps are much higher than T_{c1}. On the other hand, they are close to T_{c2} for C_n-DABCO-Br (n=12, 13, 16, 17, 22) and are about 10—20 °C higher than T_{c2} for C_n-DABCO-Br (n=14, 15, 18). From the above experimental results, it can be said that the conductivity jump is not caused by the transition at T_{c1}, but is more closely related to the transition at T_{c2}.[10] It can be said that the conductivities become lower with the increase in the alkyl-chain length. It is also noteworthy that the plots of the conductivities against the temperature are nearly parallel with each other for the DABCO salts, possessing even numbers of alkyl carbons both below and above the conductivity jumps (Fig. 6). On the other hand, the conductivities above the conductivity jumps are much closer to each other than are those below the conductivity jumps in the cases of the quaternary DABCO salts possessing odd numbers of alkyl carbons (Fig. 5). In this connection, a series of the bis(quaternary alkyl bromide salts) of DABCO exhibited somewhat different phenomena; their ionic conductivities of the bromide anion above the transition temperatures were very close, irrespective of the alkyl-chain lengths while they were very different below the transition temperatures.[1-5] The reasons for these different phenomena remain to be clarified.

Raman Spectroscopy. The DSC measurements showed that the $\Delta H_{en,1}$'s were close to each other (≈30 kJ mol^{-1}), irrespective of the alkyl-chain length attached to the DABCO nitrogens. The measurements of the ionic conductivities of the bromide anion revealed that the conductivity jump is not caused by the transition at T_{c1}, but is more closely related with the transition at T_{c2}. These results suggest that the transitions at T_{c1} and T_{c2} are different in origin. In order to clarify these two transitions, the temperature dependences of the Raman spectra of C_{17}-DABCO-Br and C_{22}-DABCO-Br were measured for powder samples as typical examples. Since similar changes in the Raman spectra were observed for these materials, only the Raman spectra of C_{17}-DABCO-Br are shown in Fig. 7.

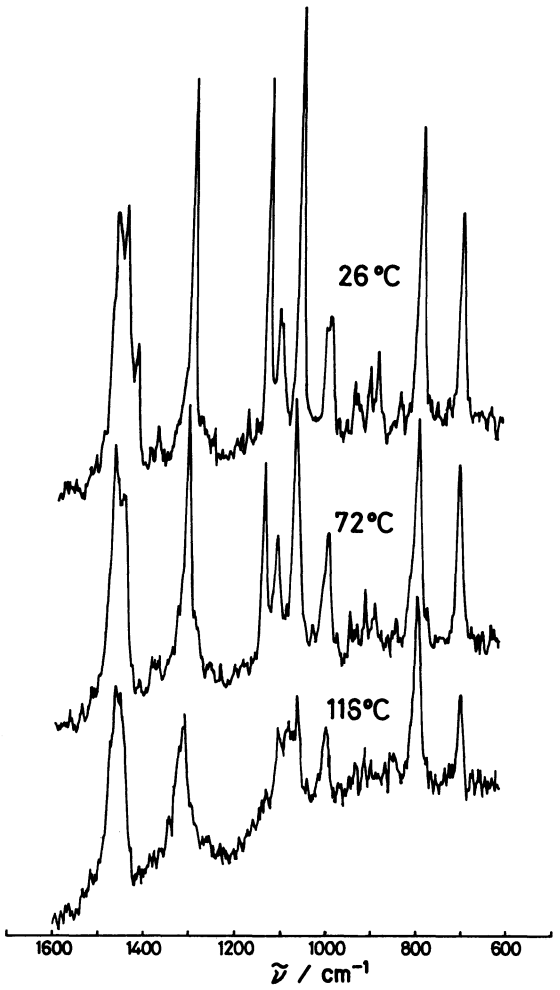


Fig. 7. Temperature dependence of the Raman spectra of C_{17}-DABCO-Br. T_{c1}=65°C, T_{c2}=99°C.

The most conspicuous spectral change at T_{c1} is the disappearance of the 1415 cm^{-1} band above T_{c1}. This band is associated with the A_g split component of the CH_2 scissoring $\delta(CH_2)$ mode,[11-13] and is characteristic of the $O_\perp$-type subcell, where the zigzag planes of the nearest neighboring alkyl chains are packed nearly perpendicular to each other. Therefore, the disappearance of this band means that, at the transition, the subcell structure changes to another type. This is consistent with the change observed in the IR spectrum, i.e., the split pairs due to the $\delta(CH_2)$ [at 1476 and 1463 cm^{-1}] and the CH_2 rocking $r(CH_2)$ modes [at 731 and 720 cm^{-1}] change to the singlets in the temperature range of $T_{c1}<T<T_{c2}$.

As for the subcell structure in the $T_{c1}<T<T_{c2}$ range, there are two possibilities, judging from the infrared and Raman spectra. One is the $T_{//}$-type packing, where the zigzag planes are all parallel to each other, and the other is the hexagonal type with a rotationally disordered orientation of the zigzag planes.[14-17]

When the spectra are measured on powder samples, as in the present case, these two subcells give rise to quite similar spectra and can hardly be distinguished from each other. Judging from the very large value of $\Delta H_{en,1}$, the hexagonal packing may be the more plausible.

The strong Raman bands at 1295 cm^{-1} [the CH_2 twisting $t(CH_2)$ mode], 1131 cm^{-1} [the symmetric CC stretch $\nu_s(CC)$ mode], and 1062 cm^{-1} [the antisymmetric CC stretch $\nu_a(CC)$ mode], which appear in the lowest-temperature phase below T_{c1}, are characteristic of the all-trans conformation of the alkyl chain.[18-20] They decrease in intensity as the amount of conformational disorder accommodated in the chain increases, and smear into very broad bands when the chain takes a disordered form, as in the liquid alkanes.[18-20] In the $T_{c1}<T<T_{c2}$ temperature range, although these bands still exist with a strong intensity and with a narrow band width, the intensities decrease with an increase in the temperature. This indicates that, in this phase, a partial conformational disordering takes place in the alkyl chain. Above T_{c2}, all of these conformational-sensitive Raman bands change to those of the liquid alkanes, indicating that the alkyl chain may be assumed to take a liquid-like disordered form in the highest-temperature phase.

There are sharp Raman bands at 793 and 704 cm^{-1} in the present series of compounds, the positions being independent of the alkyl-chain length. They are associated with the C–C and C–N stretch modes of the bicyclic system.[21] Before and after the T_{c1} transition, these bands show no changes in either intensity or band width. Above T_{c2}, the 704 cm^{-1} band appreciably decreases in intensity. In the case of the bis(quaternary alkyl halides) of DABCO, a strong Raman band [due to the totally symmetric (NC_4) stretch mode] appears in the frequency region of 700—730 cm^{-1}; this band is broadened above the transition point, suggesting the onset of a rotational motion of the bicyclic system in the high temperature phase.[21] The spectral features of the present monosubstituted compounds are somewhat different from those of the disubstituted compounds.[22] The intensity depression of one of the ring bands indicates the occurrence of some disordering, either statically or dynamically, in the ionized bicyclic system above T_{c2}; it may be related to the abrupt increase in the ionic conductivity.

Summary

The phase transitions of a series of mono(quaternary alkyl bromides) of DABCO were studied on the basis of the DSC, the measurements of the ionic conductivities of the bromide anion, and Raman spectroscopy. The comparison of the phase transitions of the present materials with those of the bis(quaternary alkyl bromides) of DABCO will be discussed below. The present materials exhibited two transitions, at T_{c1} and T_{c2}, whereas the bis(quaternary alkyl bromides) or DABCO showed only one transition.[1-5] This comes from the difference in the crystal structure to be described below. The mono(quaternary salts) seem to possess an $O_\perp$-type subcell, judging from the presence of the crystal-field splitting in the Raman and IR spectra. On the other hand, no crystal-field splitting was observed for the bis(quaternary salts); they seem to possess either hexagonal packing or a $T_{/\!/}$-type packing.[23] The mono(quaternary salts) exhibited phase transitions at T_{c1}, probably arising from the conversion from the $O_\perp$-type subcell to hexagonal packing. On the other hand, the bis(quaternary salts) did not show such transitions; this was because of the different packing structures of the alkyl chain from those of the mono(quaternary salts). These facts demonstrate the difference in the number of transitions. As to the thermodynamic properties, no metastable phase was observed for C_n–DABCO–Br and C_n–DABCO–C_n–Br_2. On the other hand, a series of C_m–DABCO–C_n–Br_2 ($m \neq n$) gave rise to the metastable phase when they had been heated above the transition temperature and then cooled. Abrupt increases in the ionic conductivity by a factor of 2—10 were observed for the present materials around T_{c2}. These values were two to three orders of magnitude smaller than those of the bis(quaternary salts). This difference in values arises from the fact that the molecular motion of the bis(quaternary salts) seems to be more vigorous than that of the mono(quaternary salts) above the transition temperature.[22]

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7) The virgin sample and the annealed sample indicate the synthesized sample and the sample heated at least once above T_{c2} respectively.

8) The monolayer of C_{18}–DABCO–Br was found to be formed by the Langmuir method, and its surface pressure became larger than 30 mN m^{-1}. We are grateful to Dr. Masahiro Irie, Institute of Scientific and Industrial Research, Osaka University, for the measurement of the π-A curve.

9) The transitions at 78 and 86 °C of C_{13}-DABCO-Br (Table 1) are tentatively assigned to T_{c2}, because the change in the Raman spectra at these temperatures are similar to those of C_{17}-DABCO-Br at T_{c2} (see the description of the Raman spectra).

10) In the case of C_{11}-DABCO-Br, the temperature of the conductivity jump is, exceptionally, close to T_{c1}. However, the separation between T_{c1} and T_{c2} is small (≈8 °C). Thus, the conclusion that the conductivity jump is related to the transition at T_{c2} can not be drawn for this material.

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22) The temperature dependence of the Raman spectra of the symmetric bis(quaternary salts) of DABCO exhibited an almost complete disappearance of the signal ascribable to the C-C skeltal mode above the transition temperature (unpublished data). This is in sharp contrast to Fig. 7, which shows the presence of this signal even above T_{c2}.

23) In order to determine which of the two possibilities is true, the polarized Raman spectra must be measured for a single crystal. Since the hexagonal packing rarely exists over a wide temperature range, the low temperature phase probably possesses $T_{//}$-type packing.