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The Phase Transition of 1,4-Dialkyl-1,4-diazoniabicyclo[2.2.2]octane Dibromides, C_n-DABCO-C_{n+2}-Br

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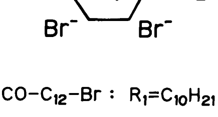
The phase transition of 1,4-dialkyl-1,4-diazoniabicyclo[2.2.2]octane dibromide (diquaternary salt) in which the difference in the carbon numbers of the two alkyl groups is two, was studied by means of differential scanning calorimetry, infrared absorption spectroscopy, and a study of the bromide-anion conductivities. DSC measurements revealed the existence of the metastable phase. The conversion rate from the metastable phase to the stable phase was too slow to be followed. The phase transition could be explained by the free energy-temperature relation. The temperature-dependence of the infrared absorption spectra showed that the band progressions due to two different alkyl chains disappeared at the transition temperature. This shows that the *trans*-zigzag conformation in the low-temperature phase is destroyed by the conformational change of the alkyl chain at the transition temperature. The free energy-temperature relation was also confirmed by the IR spectra. Discontinuous increases in the bromide-anion conductivities were observed at the transition temperatures. The conductivity jump was explained by the voids caused by the conformational change in the alkyl chain.

There have been extensive studies of the solid–solid phase transitions of alkanes and their derivatives[1] and of alkylammonium salts.[2] Especially, IR, Raman, and wide-line NMR spectroscopy have revealed that the transition was caused by the rotation of the alkyl chain. Two types of "rotation" have been recognized: one is the rotation of the whole molecule without changing its conformation,[3] and the other, the rotation involving conformational change.[4] In the cases of alkanes and their derivatives, the rotation of a whole molecule in the solid has long been postulated for the phase transition.[5] However, nonplanar conformers have recently been found for alkanes longer than n-$C_{21}H_{44}$ by IR spectroscopy.[6] These phase transitions have attracted much attention, because they are the best models for such fundamental chemical phenomena as the melting of materials and the glass transition temperatures of polymers.

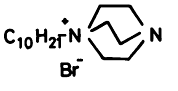
In connection with this, we have found that a series of symmetrical 1,4-dialkyl-1,4-diazoniabicyclo[2.2.2]-octane dibromides (diquaternary salts) exhibited first-order phase transitions, with a concomitant increase in the halide-anion conductivities by two to three orders of magnitude.[7,8] The temperature dependences of the IR spectra showed that the band progressions due to the *trans*-zigzag conformation of the long alkyl chains in the low-temperature phase disappeared completely at the transition temperature.[8] This shows that the conformational change in the alkyl chain occurs at every site of the methylene carbons of the alkyl chain, contrasting with the case of the phase transitions of alkanes; band progressions did not disappear even after the transition in the alkanes. Snyder et al. reported that the conformational change in n-$C_{21}H_{44}$ occurs mainly within four carbons from either end of the molecule; the *trans*-zigzag conformation is almost retained at the central part of the molecule.[9] Thus, the phase transition of the salts of 1,4-diazabicyclo[2.2.2]octane (DABCO) is peculiar case in that the *trans*-zigzag conformation is completely destroyed. Although the transition temperatures of alkanes are a few degrees below their melting points, those of the DABCO salts are more than one hundred degrees lower than the melting points or the decomposition points. Since the phase-transition temperatures and the transition enthalpies tend to increase with the increase in the alkyl-chain length in the symmetric diquaternary salts, it is noteworthy how these properties are modified in the case of the unsymmetric salts. All of the symmetric diquaternary salts exhibited one transition temperature.[7,8] Thus, it is especially interesting to determine whether or not the phase transition takes place at several temperatures, as a result of the difference in the alkyl chains in the unsymmetric diquaternary salts. The effect of the unsymmetric substitution on the halide-anion conductivities and the IR absorption spectra are also noteworthy. As an extension of the previous studies, we have investigated the phase transitions of the unsymmetric diquaternary salts of DABCO on the basis of their differential scanning calorimetry curves, bromide-anion conductivities, and



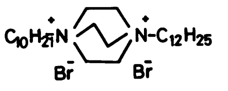
C_{10}-DABCO-C_{12}-Br : $R_1=C_{10}H_{21}$, $R_2=C_{12}H_{25}$
C_{11}-DABCO-C_{13}-Br : $C_{11}H_{23}$, $C_{13}H_{27}$
C_{12}-DABCO-C_{14}-Br : $C_{12}H_{25}$, $C_{14}H_{29}$
C_{13}-DABCO-C_{15}-Br : $C_{13}H_{27}$, $C_{15}H_{31}$
C_{14}-DABCO-C_{16}-Br : $C_{14}H_{29}$, $C_{16}H_{33}$
C_{15}-DABCO-C_{17}-Br : $C_{15}H_{31}$, $C_{17}H_{35}$
C_{16}-DABCO-C_{18}-Br : $C_{16}H_{33}$, $C_{18}H_{37}$

Fig. 1. 1,4-Dialkyl-1,4-diazoniabicyclo[2.2.2]octane dibromides.

infrared-absorption spectra. The materials studied possess two long alkyl chains; the difference in their carbon numbers was fixed at two. The materials studied are shown in Fig. 1. The names of the materials are abbreviated by the numbers of alkyl carbons. For example, 4-Decyl-1-aza-4-azoniabicyclo[2.2.2]octane bromide and 1-decyl-4-dodecyl-1,4-diazoniabicyclo[2.2.2]octane dibromide are abbreviated as C_{10}–DABCO–Br and C_{10}–DABCO–C_{12}–Br respectively. Thus, the materials in Fig. 1 can be described generally as C_n–DABCO–C_{n+2}–Br.



C_{10}-DABCO-Br



C_{10}-DABCO-C_{12}-Br

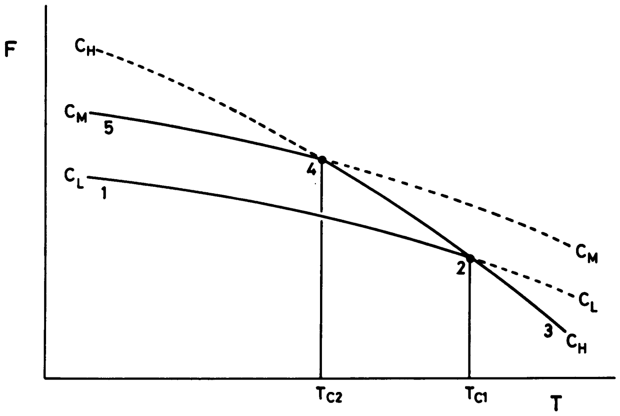


Fig. 2. Free energy (F)-temperature (T) relation of unsymmetric diquaternary salts of DABCO.

Experimental

Materials. The methyl alcohol and acetonitrile were purified as has been described before.[7,8] The ethyl acetate was washed with aqueous sodium hydrogencarbonate, and then aqueous sodium chloride, dried over magnesium sulfate, and distilled. The ethyl alcohol was distilled. The diethyl ether, DABCO, and all of the alkyl bromides were used without purification.

Syntheses of 4-Alkyl-1-aza-4-azoniabicyclo[2.2.2]octane Bromides. The synthesis of 4-alkyl-1-aza-4-azoniabicyclo[2.2.2]octane bromide (monoquaternary salt) will be described for C_{10}–DABCO–Br as a typical example. To the acetonitrile solution (50 ml) of DABCO (5.6 g, 50 mmol) we stirred in, drop by drop, 11.05 g (50 mmol) of decyl bromide for a 30-min period, at room temperature. The solvent was then evaporated, and 500 ml of benzene was added to the residue to obtain a white precipitate. It was recrystallized from a mixed solvent of benzene (1 l) and acetonitrile (50 ml). The same procedures were adopted for the synthesis of C_{11}–DABCO–Br. In the case of C_n–DABCO–Br ($n \geqq 12$), the acetonitrile solution was directly poured into diethyl ether to obtain the crude product. It was recrystallized from ethyl acetate.

Syntheses of Unsymmetric Diquaternary Salts of DABCO. The synthesis of unsymmetric diquaternary salt of DABCO will be described for C_{10}–DABCO–C_{12}–Br as a typical example. A methanol (20 ml) solution of C_{10}–DABCO–Br (2 g, 6 mmol) and dodecyl bromide (1.49 g, 6 mmol) was refluxed for 48 h. After it had then been cooled to room temperature, it was poured into diethyl ether (500 ml) to obtain a white precipitate. The crude product was recrystallized five times from acetonitrile. Essentially the same reaction conditions were adopted for the other materials. The solvents of recrystallization were acetonitrile for C_n–DABCO–C_{n+2}–Br (n=10, 11, 12, 13, 14) and ethyl alcohol for C_n–DABCO–C_{n+2}–Br (n=15, 16).

Measurements. The measurements of the DSC, the IR absorption spectra, and the bromide-anion conductivities were made by the methods described previously.[7,8]

Results and Discussion

Syntheses of Unsymmetric Diquaternary Salts of DABCO. Unsymmetric diquaternary salts of DABCO were synthesized by two-step reactions, i.e., the synthesis of monoquaternary salt, followed by that of the diquaternary salt. In the first step, the reaction of equimolar amounts of DABCO and alkyl bromide readily gave the monoquaternary salt in 30 min at room temperature. Diquaternary salt was not obtained in this case, however, because the reaction rate from the monoquaternary salt to the diquaternary salt is much slower than that from DABCO to the monoquaternary salt. The diquaternary salt was obtained by the reaction with the monoquaternary salt with alkyl bromide under more vigorous reaction conditions in the second step. Since one nitrogen converts to N^+ in the monoquaternary salt, the lone-pair electron at the other nitrogen will be attracted by N^+ by means of Through-bond interaction.[10] This effect causes the lowering of the lone-pair MO level and the decrease in the lone-pair electron density, both of which consequently reduce the rate of the second step of the reaction. MINDO/2 calculation[11] revealed that the former effect is dominant over the latter.[12] In reality, the monoquaternary salt and alkyl bromide did not give the diquaternary salt under the same conditions as in the first step of the reaction. Only after the solution of the reactants had been refluxed for a prolonged period of time (48 h) could the diquaternary salt be obtained.

DSC Measurements. DSC measurements were made while changing the temperature by 5 °C/min. When the virgin samples were heated, single endothermic signals ($\Delta H_{\mathrm{en},1}$) were observed at T_{c1}. However, no reproducible T_{c1} values were obtained; they varied by several degrees in several runs. C_{12}–DABCO–C_{14}–Br and C_{16}–DABCO–C_{18}–Br exhibited three and two transitions respectively. When the samples were

Table 1. Unsymmetric Diquaternary Salts of DABCO, Transition Temperatures (T_{c1} and T_{c2}), Transition Enthalpies ($\Delta H_{en,2}$), Transition Entropies (ΔS), and Ratios of Bromide-anion Conductivities Before (σ_l) and After (σ_h) Transition

Materials	T_{c1} a) / °C	T_{c2} / °C	$\Delta H_{en,2}$ / kJ mol^{-1}	ΔS / J mol^{-1} deg^{-1}	σ_h/σ_l
C_{10}-DABCO-C_{12}-Br	(92)	46	46.9	128	770
C_{11}-DABCO-C_{13}-Br	(95)	60	57.3	173	2170
C_{12}-DABCO-C_{14}-Br	(93, 95, 99)	64	56.8	169	700
C_{13}-DABCO-C_{15}-Br	(96)	74	69.0	199	2070
C_{14}-DABCO-C_{16}-Br	(101)	74	71.6	206	1290
C_{15}-DABCO-C_{17}-Br	(102)	79	86.7	246	3000
C_{16}-DABCO-C_{18}-Br	(90, 103)	84	88.8	249	3070

a) Since the values of T_{c1}'s are not strictly reproducible, they are shown in parentheses as only approximate values.

cooled after they had once been heated above T_{c1}, exothermic signals ($\Delta H_{exo,1}$) were observed at much lower temperatures (T_{c2}) than T_{c1}; $T_{c1}>T_{c2}$. Reproducible T_{c2}'s were obtained. The succeeding heating-cooling cycles showed reproducible endothermic ($\Delta H_{en,2}$) and exothermic ($\Delta H_{exo,1}$) signals at around T_{c2}, but did not show any signal at T_{c1}, even when DSC was measured after the samples had been kept at room temperature for weeks. The absolute values of $\Delta H_{en,1}$, $\Delta H_{en,2}$, and $\Delta H_{exo,1}$ were within the range of experimental error. The annealed sample which gives the phase transition at T_{c2} is designated as C_M; it is assumed to be a metastable phase[13)] on the basis of our related studies of the phase transition of C_{10}-DABCO-C_n-Br ($13 \leqq n \leqq 22$).[14)] For these systems, DSC measurements exhibited phenomena similar to those described above. However, C_M was found to be converted slowly to the stable phase (C_L) when the sample was kept at room temperature. The larger the difference in the carbon numbers of the two alkyl groups attached to DABCO nitrogens, the faster was the conversion rate from C_M to C_L. For example, the conversion rates of C_{10}-DABCO-C_{14}-Br and C_{10}-DABCO-C_{18}-Br were one week and one day respectively. Since the difference in the carbon numbers is only two in the present systems, the conversion rates are too slow to be followed. The above thermodynamic phenomena can be understood by the free energy (F)-temperature (T) relation shown in Fig. 2. In this figure, the virgin sample (C_L) follows the F-T curve from 1 to 2 when the sample is heated. Phase transition takes place at 2 (temperature: T_{c1}), and the sample follows the curve of the high-temperature phase (C_H) from 2 to 3. When the sample is then cooled, it follows the F-T curve of C_H from 3 through 2 to 4. Phase transition takes place at 4 (temperature: T_{c2}), and the sample follows the F-T curve of the metastable phase (C_M) from 4 to 5.

Part of Table 1 shows T_{c1}, T_{c2}, $\Delta H_{en,2}$, and ΔS ($=\Delta H_{en,2}/T_{c2}$). The values of T_{c1} are shown in parentheses, because they are not strictly reproducible.

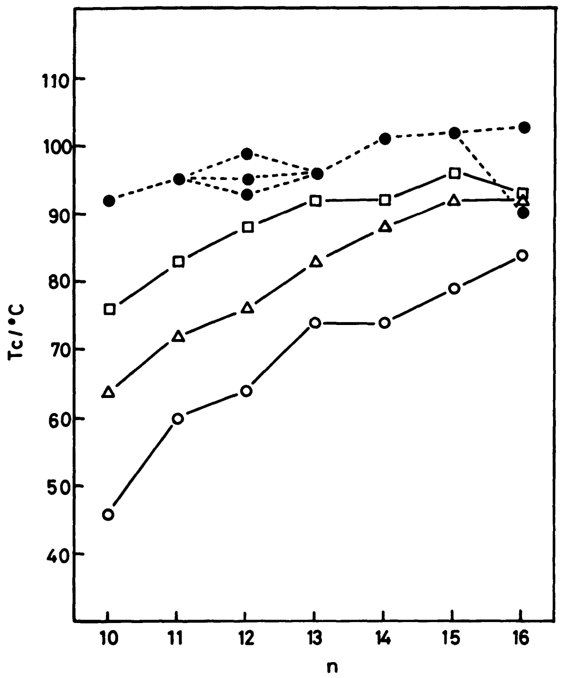


Fig. 3. The plot of the transition temperatures against the carbon numbers of alkyl groups attached to DABCO nitrogens.
○: T_{c2} for C_n-DABCO-C_{n+2}-Br, △: T_c for C_n-DABCO-C_n-Br, □: T_c for C_{n+2}-DABCO-C_{n+2}-Br, ●: T_{c1} for C_n-DABCO-C_{n+2}-Br. Since T_{c1} is not strictly reproducible, the black circles were connected with dotted lines.

They are shown only as approximate values. All of the transition temperatures were obtained from the onsets of the endothermic peaks. The characteristic points of the DSC measurements will be discussed below. Figure 3 plots the T_{c1} and T_{c2} values against the carbon numbers of the alkyl chains. This figure also shows the plots of the transition temperatures of the symmetric diquaternary salts of DABCO[8)] for the sake of comparison. All of the transition temperatures tend to increase with the increase in the alkyl-chain lengths. The order of the transition temperature is as

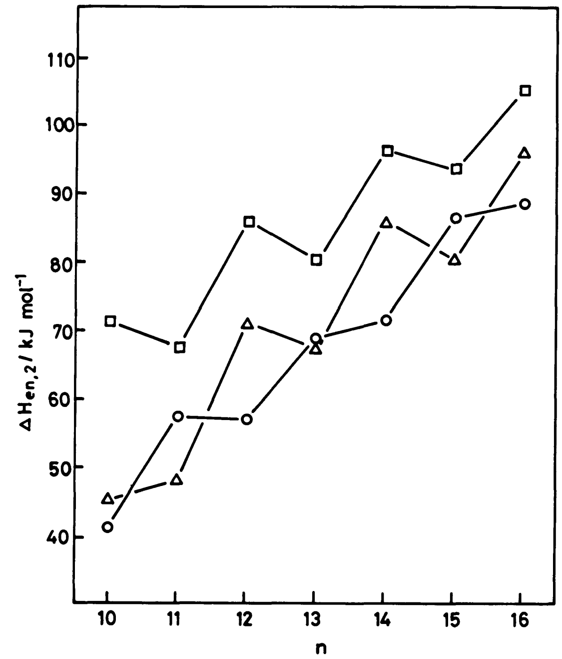


Fig. 4. The plot of the transition enthalpies ($\Delta H_{\mathrm{en},2}$) against the carbon numbers of alkyl groups attached to DABCO nitrogens.
○: C_n–DABCO–C_{n+2}–Br, △: C_n–DABCO–C_n–Br, □: C_{n+2}–DABCO–C_{n+2}–Br.

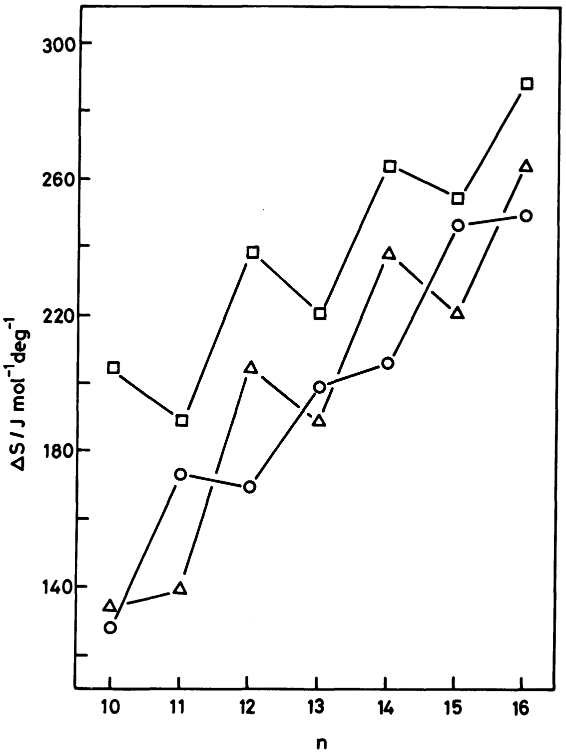


Fig. 5. The plot of the transition entropies ΔS ($=\Delta H_{\mathrm{en},2}/T_{c2}$) against the carbon numbers of alkyl groups attached to DABCO nitrogens.
○: C_n–DABCO–C_{n+2}–Br, △: C_n–DABCO–C_n–Br, □: C_{n+2}–DABCO–C_{n+2}–Br.

follows, if the carbon number of the alkyl group is fixed: $T_{c1}>T_c$ for C_{n+2}–DABCO–C_{n+2}–Br$>T_c$ for C_n–DABCO–C_n–Br$>T_{c2}$. An even-odd number effect of carbon was found for T_{c2}. The difference between T_{c1} and T_{c2} tends to decrease with the increase in the alkyl-chain length, but it is always in the range of 6—50 °C. Since the difference in the alkyl-chain length is only two, the general tendency of the transition temperature with the alkyl-chain length is similar to that of the symmetric diquaternary salts. The great difference in the unsymmetric salts from the symmetric salts is that the metastable phase can be found for the former salts. Figure 4 shows the plots of $\Delta H_{\mathrm{en},2}$ against the carbon numbers of the alkyl chains. This figure also shows the transition enthalpies of the symmetric salts[8] for the sake of comparison. An even-odd number effect of carbon was clearly observed in a reverse manner from the symmetric salts, i.e., up-down for the unsymmetric salts and down-up for the symmetric salts. $\Delta H_{\mathrm{en},2}$ tends to increase with the increase in the alkyl-chain length. The following order of the transition enthalpy is noteworthy, although the reason is as yet not clear; ΔH for C_{2n+2}–DABCO–C_{2n+2}–Br$>\Delta H$ for C_{2n}–DABCO–C_{2n}–Br$>\Delta H$ for C_{2n}–DABCO–C_{2n+2}–Br. ΔH for C_{2n+1}–DABCO–C_{2n+1}–Br$>\Delta H$ for C_{2n-1}–DABCO–C_{2n+1}–Br$>\Delta H$ for C_{2n-1}–DABCO–C_{2n-1}–Br. Figure 5 shows the plots of the transition entropies ($\Delta S=\Delta H_{\mathrm{en},2}/T_{c2}$) against the carbon numbers of the alkyl groups. This figure also shows the plot of the transition entropies of the symmetric salts for the sake of comparison.[15] The ΔS's also tend to increase with the increase in the alkyl-chain lengths. The even-odd number effect of carbon on ΔS was quite similar to that on the $\Delta H_{\mathrm{en},2}$ shown in Fig. 4. The transition entropies also exhibited order similar to that found for $\Delta H_{\mathrm{en},2}$; i.e., ΔS for C_{2n+2}–DABCO–C_{2n+2}–Br$>\Delta S$ for C_{2n}–DABCO–C_{2n}–Br$>\Delta S$ for C_{2n}–DABCO–C_{2n+2}–Br. ΔS for C_{2n+1}–DABCO–C_{2n+1}–Br$>\Delta S$ for C_{2n-1}–DABCO–C_{2n+1}–Br$>\Delta S$ for C_{2n-1}–DABCO–C_{2n-1}–Br. The numbers of sites (W) after phase transition were estimated from the $\Delta S=R\ln W$ relation, and the W's were in the range of 4.9×10^6—9.8×10^{12}.[16] Although T_{c1} could not be obtained correctly, the estimated transition entropies gave the values of W as 10^6—10^{12}. Thus, comparable structural changes seem to occur at T_{c1} and T_{c2}. The large values of W's will be discussed later, together with the IR absorption spectra.

Infrared Absorption Spectroscopy. The temperature dependence of the infrared absorption spectra was measured in order to obtain more information on the phase transition and on the metastable phase. Figure 6 shows the temperature dependence of the IR spectra of C_{14}–DABCO–C_{16}–Br for a KBr disk sample, as a typical example, when the sample is heated from room temperature to 103 °C and then cooled to room

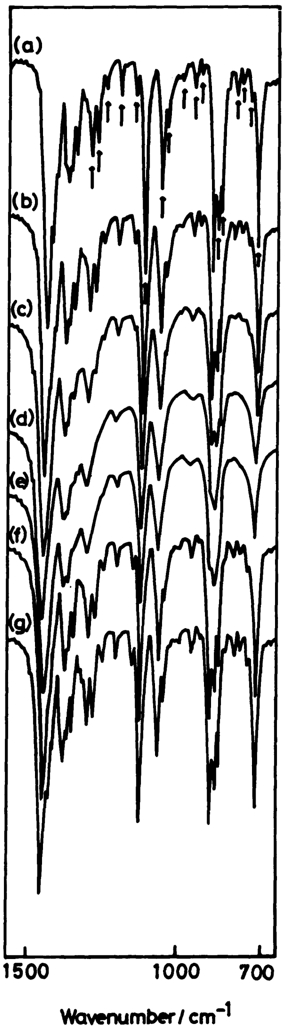


Fig. 6. Temperature dependence of the IR spectra of C_{14}-DABCO-C_{16}-Br for the KBr pellet sample. (a): 29 °C, (b): 79 °C, (c): 98 °C, (d): 103 °C, (e): 80 °C, (f): 61 °C, (g): 33 °C. The virgin sample was heated from (a) to (d), and then cooled from (d) to (g).

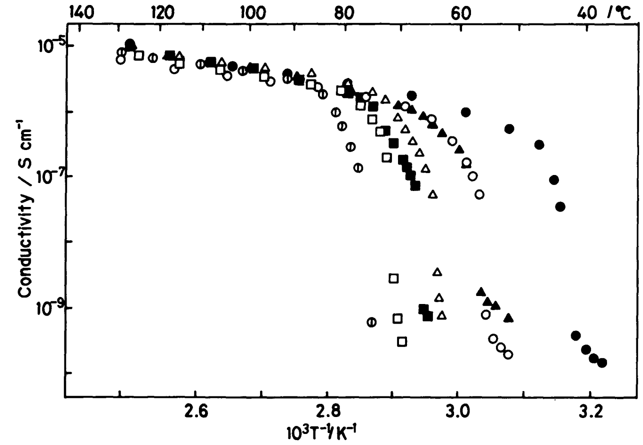


Fig. 7. Temperature dependence of the bromide-anion conductivities of C_n-DABCO-C_{n+2}-Br.
●: $n=10$, ○: $n=11$, ▲: $n=12$, △: $n=13$, ■: $n=14$, □: $n=15$, ⦶: $n=16$.

temperature. The resulting IR spectra are shown sequentially from the top to the bottom in this figure. The IR spectra of the virgin sample (C_L) at 29 °C exhibited several structures, shown by the arrows. The absorption positions of these structures were compared with band progressions of n-$C_{15}H_{32}$ and n-$C_{17}H_{36}$,[17] which have the same numbers of CH_2 units as the alkyl groups of C_{14}-DABCO-C_{16}-Br. The good coincidence[18] leads to the conclusion that the structures in Fig. 6 can be assigned to the band progressions of the two alkyl groups.

The absorption spectra at 29 °C (a) and 79 °C (b) were not so different. When the temperature of the sample approached T_{c1} (101 °C), all of the absorptions were broadened (see Spectrum (c) at 98 °C), but the band progressions could still be seen. However, all of the band progressions disappeared at 103 °C (d). This shows that the *trans*-zigzag conformation of the alkyl groups of the low-temperature phase (C_L) is destroyed at T_{c1}. When the temperature of the sample was lowered after it had once been raised above T_{c1}, the band progression did not appear between T_{c1} and T_{c2}. For example, the absorption spectra (b) and (e) were measured at almost the same temperature, but they are quite different; the Spectrum (b) exhibited the band progressions, but (e) did not show them. This observation is consistent with the DSC result. Since the Spectrum (e) corresponds to the point between 2 and 4 on the F–T curve of the C_H phase in Fig. 2, the *trans*-zigzag conformation of the alkyl chain is still destroyed. Only after the temperature had been lowered below T_{c2} (74 °C) did the band progressions appear again (see Spectrum (f)) to convert to the C_M phase. Since no difference in the spectra was found between (a) and (g) in Fig. 6, the *trans*-zigzag conformation is assumed to be recovered in the C_M phase. However, judging from the broader powdered X-ray diffractions of the C_M phase than the C_L phase,[13] the crystallinity of the C_M phase can be said to be lower than the C_L phase. The high potential barrier between C_M and C_L prevents C_M from going back to C_L.

DSC measurements gave a large numbers of sites (W) above the transition temperature. This is consistent with the results of the IR absorption spectra. Since band progressions disappeared completely above T_{c1} or T_{c2}, the conformational change is assumed to occur at every site of the alkyl carbons. This gives rise to a large numbers of sites. Thus, the conformational changes in the present systems and previous systems[8] are quite different from those in *normal* alkanes,[9] because the *trans*-zigzag conformation still remains above the transition temperature for the latter materials. Although the phase transitions of the diquaternary DABCO salts were ascribed to the conformational change in the alkyl groups, there is some possibility that the portion of DABCO may rotate around the N–N direction.[19] However, the present study could not confirm this possibility.

Bromide-anion Conductivities. All of the samples have already been confirmed as bromide-anion conductors.[7,8] The ionic conductivities were measured for the compressed pellet samples by an AC method. The impedance and a phase shift were measured, and the real and imaginary parts of the impedances were plotted for various frequencies (25 Hz—500 kHz). The resistance of the sample was obtained by a method described previously.[8] The temperature dependences of the bromide-anion conductivities were measured while raising the temperature of the sample slowly (about 0.5 °C min^{-1}) from room temperature; they are shown in Fig. 7. Conductivities less than 10^{-9} S cm^{-1} are below the limit of our measurements. Since the samples were dried overnight under a dynamic vacuum above T_{c1} before the measurements, they were converted to C_M phases. The proton conduction due to moisture was negligible. The following facts are noteworthy from this figure: (1) All of the samples show abrupt increases in the ionic conductivities by two to three orders of magnitude resulting from the phase transitions around T_{c2}. (2) The longer the alkyl chain, the higher the transition temperature. (3) The longer the alkyl chain, the lower the bromide-anion conductivities below T_{c2}. However, the bromide-anion conductivities were close to each other above T_{c2}, with their activation energies of about 30 kJ mol^{-1}.

The second and third characteristics above are also those of the halide-anion conductivities of the symmetric diquaternary salts of DABCO, and they may be explained as before.[8] Table 1 shows the materials and the ratios of the bromide-anion conductivities before (σ_l) and after (σ_h) the phase transition, i.e., σ_h/σ_l. The two steps of the conductivity changes were observed around T_{c2}; the first rapid increase, followed by the slower increase in the conductivities. The changes in the conductivities around T_{c2} were found to be in the range of 770—3070. However, the conductivity jumps in Fig. 7 are slightly broader than those of the symmetric diquaternary salts,[8] because the slower increases in the conductivities were not observed for the latter materials. The virgin samples (C_L) can also be expected to show an abrupt change in the ionic conductivities at T_{c1}. However, no measurement was made for this transition, because DSC measurements did not give reproducible results. Although abrupt increases in the bromide-anion conductivities were observed around T_{c2}, the transition temperatures obtained by DSC were higher than those obtained by the bromide-anion conductivities; the latter transition temperatures were defined as the middle points of the conductivity jumps. This shows that the conductivity jump starts before the considerable structural change sets in. Since ionic conductivities are sensitive to the structure, the conductivity jump takes place at the temperature region of the pre-transition where the local movement of the alkyl groups begins. Since the low-temperature phase possesses a close-packed crystal structure, the conduction pathway of the bromide anion is assumed to be narrow. However, the situation changes considerably at the transition temperature. The conductivity jump can be explained by the formation of voids caused by the onset of the movement of the alkyl chains.

Summary. The phase transitions of the unsymmetric diquaternary salts of DABCO, C_n–DABCO–C_{n+2}–Br ($10 \leqq n \leqq 16$), were studied by means of the DSC, the IR spectra, and the bromide-anion conductivities. The DSC measurements revealed the existence of the metastable phase. The temperature dependence of the IR spectra showed that, with a rise in the temperature, the band progressions in the low-temperature phase disappeared completely at T_{c1} and then appeared again at T_{c2} when the temperature was lowered after it had once been raised above T_{c1}. These results are consistent with the existence of the metastable phase. Abrupt increases in the bromide-anion conductivities by two to three orders of magnitude were found at the transition temperatures (T_{c2}). However, the conductivity jumps were slightly broader than those of the symmetric diquaternary salts. The conductivity jump at the transition temperature was explained by the formation of voids caused by the onset of the conformational change in the alkyl chains.

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References

1) M. G. Taylor, E. C. Kelusky, C. P. Smith, H. L. Casal, and D. G. Cameron, *J. Chem. Phys.*, **78**, 5108 (1983).

2) H. Ishida, R. Ikeda, and D. Nakamura, *Bull. Chem. Soc. Jpn.*, **59**, 915 (1986).

3) D. W. McClure, *J. Chem. Phys.*, **49**, 1830 (1968).

4) M. Maroncelli, S. P. Qi, H. L. Strauss, and R. G. Snyder, *J. Am. Chem. Soc.*, **104**, 6237 (1982).

5) T. Ishinabe, *J. Chem. Phys.*, **72**, 353 (1980).

6) R. G. Snyder, M. Maroncelli, S. P. Qi, and H. L. Strauss, *Science*, **214**, 188 (1981).

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

8) J. Shimizu, K. Imamura, T. Nogami, and H. Mikawa,

Bull. Chem. Soc. Jpn., **59**, 1443 (1986).

9) R. G. Snyder, M. Maroncelli, H. L. Strauss, C. A. Ellinger, D. G. Cameron, H. L. Casal, and H. H. Mantsch, *J. Am. Chem. Soc.*, **105**, 133 (1983).

10) R. Hoffmann, *Acc. Chem. Res.*, **4**, 1 (1971).

11) M. J. S. Dewar and E. Haselbach, *J. Am. Chem. Soc.*, **92**, 590 (1970); N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *J. Am. Chem. Soc.*, **92**, 3854 (1970).

12) MINDO/2 calculation was done for DABCO and the 4-methyl-1-aza-4-azoniabicyclo[2.2.2]octane cation (CH_3-$DABCO^+$) in order to see the quaternization effect on the lone-pair electron density of nitrogen and the orbital energy of the HOMO level. The nitrogen lone-pair electron densities of DABCO and CH_3-$DABCO^+$ are calculated to be 1.75 and 1.72 respectively; those values are not very different. Since the contribution of the nitrogen lone-pair is the largest for HOMO, the large difference in the HOMO levels ($\varepsilon_{\mathrm{DABCO}}=-7.76$ eV, $\varepsilon_{\mathrm{CH_3\text{-}DABCO^+}}=-13.31$ eV) is assumed to cause the large difference in the activation energy of the quaternization reaction.

13) Powdered X-ray diffractions of the virgin samples (C_L) showed several sharp diffractions. On the other hand, the annealed sample (C_M) exhibited somewhat broader diffractions. This suggests that C_M is disordered, possibly by the *gauche* conformation of the alkyl groups. This fact also supports the assumption that C_M is in a metastable phase.

14) J. Shimizu, K. Imamura, T. Nogami, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, in press.

15) From the transition enthalpies and the transition temperatures shown in Ref. 8, the transition entropies (J mol^{-1} deg^{-1}) of the symmetric salts (C_n-DABCO-C_n-Br) were obtained as follows: 134 for $n=10$, 139 for $n=11$, 204 for $n=12$, 189 for $n=13$, 237 for $n=14$, 220 for $n=15$, 263 for $n=16$, 254 for $n=17$, 288 for $n=18$, and 311 for $n=22$.

16) The numbers of sites of the symmetric diquaternary salts of DABCO were estimated from the transition entropies shown in Ref. 15; they are in the range of 1.0×10^{7}—1.9×10^{16}.

17) R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta*, **19**, 85 (1963).

18) Since the difference between the carbon numbers of the two alkyl groups is only two, the band progressions of the two alkyl groups have almost the same absorption positions. Thus, we could not assign the band progressions separately to the individual alkyl group.

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