September, 1989] Bull. Chem. Soc. Jpn., 62, 2793—2797 (1989) 2793

The Phase Transition of Quaternary Fluoroalkyl Halide Salts of 1,4-Diazabicyclo[2.2.2]octane

Tohru TERADA, Takashi NOGAMI,* and Yasuhiko SHIROTA
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565

(Received April 3, 1989)

The solid–solid phase transition of quaternary halide salts of 1,4-diazabicyclo[2.2.2]octane (DABCO) was investigated by DSC, Raman spectroscopies, and the measurements of the ionic conductivity of the halide anions. The DABCO salts studied are classified into two; one is the salt possessing both fluoroalkyl and alkyl groups, and the other the ones possessing the same fluoroalkyl groups at both ends of the molecule. The former molecule exhibited a gradual increase of the ionic conductivity above the transition temperature. The ionic conductivity of the former molecule was higher than that of the latter molecules and the symmetric quaternary alkyl halide salts of DABCO. These facts were explained by a spacer effect of the fluoroalkyl group. The temperature dependence of the Raman spectra of the former salt established that the fluoroalkyl group was much more rigid than the alkyl group, and that the molecular movement took place mainly at the alkyl group and the DABCO portion in the high temperature phase. One of the latter type of molecules exhibited a conductivity jump around the transition temperature.

The phase transition of a series of quaternary alkyl halide salts of 1,4-diazabicyclo[2.2.2]octane (DABCO) was investigated by DSC, IR and Raman spectroscopies, NMR, and the measurements of the ionic conductivities of halide anions.[1–8] The phase transition of the quaternary DABCO salts containing tetrafluoroborate anion has also been reported recently.[9] These materials exhibit conformational change of the alkyl group in the high temperature phase in the solid. A conductivity jump of the halide anion was observed by up to three orders of magnitude around the transition temperature. These materials also showed the disappearance of optical anisotropy in the high temperature phase, and in some cases they remained in a metastable state after having been heated above the transition temperature and then cooled to room temperature. These switching properties of the ionic conductivities[10] and optical and thermodynamic properties may be applicable to some temperature and memory devices.

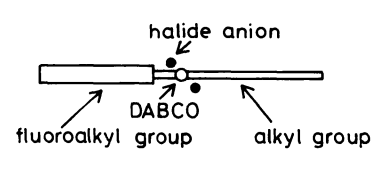

Fig. 1. Schematic drawing of the proposed molecular arrangement, spacer effect, and molecular motion of C_n^F-DABCO-C_n-X_2 in a solid. (a) Low temperature phase, (b) high temperature phase.

A variety of amphipatic materials containing both long alkyl and fluoroalkyl chains as hydrophobic parts were synthesized, and their physicochemical properties investigated.[11] These studies established that the fluoroalkyl and alkyl groups tend to separate from each other in the solid; in other words, the fluoroalkyl chains arrange parallel to one another, and so do the alkyl chains.[12] In general, the fluoroalkyl chain forms a helical structure, and the fluorine atoms surround the C–C backbone.[13] The structural difference of the fluoroalkyl chain from the alkyl chain results in the more rigid structure of the former chain than of the latter. Moreover, the fluoroalkyl group is bulkier than the alkyl group. Thus, the quaternary halide salt of DABCO containing both the fluoroalkyl and the alkyl groups (C_n^F-DABCO-C_n-X_2) may possess the molecular arrangement shown schematically in Fig. 1(a). The bulkier fluoroalkyl groups function as spacers in the solid, so that the less bulky alkyl groups may move relatively freely in the high temperature phase (Fig. 1(b)). On the other hand, the molecular motion of the alkyl group may be retarded in the case

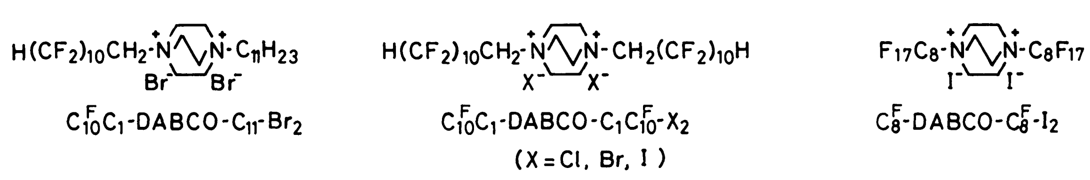

Fig. 2. Quaternary DABCO halide salts.

of the DABCO salts possessing two alkyl groups at both sides of the molecule (C_n-DABCO-C_n-X_2) because of the closed-packed molecular arrangements. Thus, C_n^F-DABCO-C_n-X_2 may show higher halide anion conductivity than C_n-DABCO-C_n-X_2. We are also interested in the difference of the molecular motion between the alkyl and fluoroalkyl groups in the solid. Bearing these assumptions in mind, we have synthesized the two types of quaternary DABCO halide salts shown in Fig. 2; one is a quaternary DABCO bromide salt containing both fluoroalkyl and alkyl groups in the molecule, and the other the symmetric quaternary DABCO halide salts containing two fluoroalkyl groups in the molecule. The names of the molecules in Fig. 2 are abbreviated to $C_{10}^FC_1$-DABCO-C_{11}-Br_2, $C_{10}^FC_1$-DABCO-$C_1C_{10}^F$-X_2 (X=Cl, Br, I), and C_8^F-DABCO-C_8^F-I_2.

Experimental

$C_{10}^FC_1$-DABCO-C_{11}-Br_2. $H(CF_2)_{10}CH_2OH$ (1.2 g, 2.3 mmol) was dissolved in benzene (50 cm^3) containing several drops of pyridine, and thionyl bromide (0.5 g, 2.4 mmol) wad added dropwise to this solution at 0 °C. The solution was heated gradually to 60 °C, stirred for 8 h at this temperature, and allowed to cool to room temperature. The solvent was distilled out using an evaporator, and the residual white powder was recrystallized from a mixed solvent of benzene and hexane to obtain $H(CF_2)_{10}CH_2Br$ (0.54 g, 40%). Quaternary undecylbromide salt of DABCO (C_{11}-DABCO-Br)[3] (0.7 g) and $H(CF_2)_{10}CH_2Br$ (1.2 g) so obtained were dissolved in benzene (50 cm^3) and the solution was stirred for 24 h at 60 °C, and then cooled by ice. The precipitate was collected, and recrystallized from benzene (22% yield, 0.41 g).

$C_{10}^FC_1$-DABCO-$C_1C_{10}^F$-Cl_2. $H(CF_2)_{10}CH_2Cl$ was obtained (62% yield) by the same method as the synthesis of $H(CF_2)_{10}CH_2Br$. Thionyl chloride was used instead of thionyl bromide. DABCO (0.06 g, 0.5 mmol) and $H(CF_2)_{10}$-CH_2Cl (0.6 g, 1.1 mmol) were dissolved in benzene (50 cm^3) and the solution was stirred for 12 h at 60 °C. Subsequently the same procedure as that described for the synthesis of $C_{10}^FC_1$-DABCO-C_{11}-Br_2 was adopted (75% yield, 0.49 g).

$C_{10}^FC_1$-DABCO-$C_1C_{10}^F$-Br_2. This was synthesized by the same method as that described for the corresponding chloride salt (73% yield).

$C_{10}^FC_1$-DABCO-$C_1C_{10}^F$-I_2. $H(CF_2)_{10}CH_2Cl$ (1.2 g, 2.2 mmol), DABCO (0.12 g, 1.1 mmol), and potassium iodide (2 g, 20 mmol) was dissolved in the mixed solvent of ethanol and water (1:1, 50 cm^3), and the solution was refluxed for 12 h. The precipitate was collected, and recrystallized from benzene (68% yield, 1.0 g).

C_8^F-DABCO-C_8^F-I_2. The ethanol solution (50 cm^3) of $C_8F_{17}I$ (1.2 g, 2.2 mmol) and DABCO (0.12 g, 1.1 mmol) was stirred for 6 h at room temperature.[14] The solution was then cooled by ice to yield a white precipitate. It was collected, and recrystallized from benzene (82% yield, 1.08 g).

Measurements. DSC, and ionic conductivities were measured by the methods described previously.[2] The temperature dependence of the Raman spectra was measured by the method described previously.[7] R-500 Laser Spectrometer (Japan Spectroscopic Co., Ltd.) was used as a monochromator, and a GLS/GLG argon ion laser (514.5 nm) (Nippon Electric Co., Ltd.) as an excitation source. Since all of the materials were unstable above ca. 40 °C in air, all of the measurements were made in a sealed cell under nitrogen atmosphere.

Results and Discussion

DSC Measurements of $C_{10}^FC_1$-DABCO-C_{11}-Br_2. Figure 3 shows the DSC curve of $C_{10}^FC_1$-DABCO-C_{11}-Br_2 measured with a scan rate of 5 °C min^{-1}. It showed an endothermic signal at 38 °C (extrapolated onset temperature) when heated from room temperature. When the sample was cooled after having been heated above 50 °C, a much broader exothermic signal was observed. The succeeding heating/cooling cycles gave signals almost identical with those of Fig. 3. Thus, a phase transition occurred at 38 °C, and the initial low temperature phase recovered gradually when the temperature was lowered from the high temperature phase to room temperature. The transition temperature (T_c), transition enthalpy (ΔH), and transition entropy ($\Delta S=\Delta H/T_c$) are shown in Table 1. This material decomposed at 83 °C in an inert atmosphere. This is a much lower decomposition temperature than that of the corresponding C_{11}-DABCO-C_{11}-Br_2.[2] It may be caused by the weak C-N bond energy between DABCO-nitrogen and the fluoroalkyl carbon due to the inductive effect of the fluoroalkyl group.[14]

Ionic Conductivities of $C_{10}^FC_1$-DABCO-C_{11}-Br_2. The temperature dependence of the ionic conductivities of $C_{10}^FC_1$-DABCO-C_{11}-Br_2 was measured for a compressed pellet sample by an AC impedance method,[2] in order to see the effect of the phase transition on the ionic conductivities. This type of quaternary DABCO-halide salt was found to be a halide anion conductor by the fact that the ionic conductivity did not change at all on applying a DC current if the halide anions were injected from the electrode.[1] Figure 4 shows the plot of the ionic conductivity of $C_{10}^FC_1$-DABCO-C_{11}-Br_2 against the

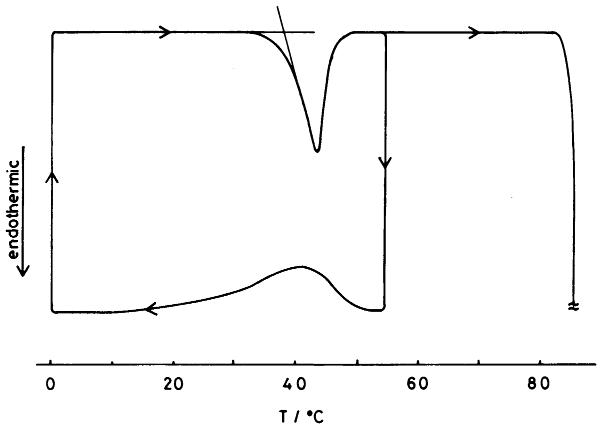

Fig. 3. DSC thermogram of $C_{10}^FC_1$-DABCO-C_{11}-Br_2.

Table 1. Materials, Transition Temperatures (T_c), Transition Enthalpies (ΔH), Transition Entropies (ΔS), and Ratios of Halide Anion Conductivities (σ_h/σ_l) Below and Above Transition Temperatures

Materials	T_c	ΔH	ΔS	σ_h/σ_l
	°C	kJ mol^{-1}	J mol^{-1} K^{-1}	
$C^F_{10}C_1$-DABCO-C_{11}-Br_2	38	38.3	123	a)
$C^F_{10}C_1$-DABCO-$C_1C^F_{10}$-Cl_2	63	109.6	326	120
$C^F_{10}C_1$-DABCO-$C_1C^F_{10}$-Br_2	93	47.5	130	b)
$C^F_{10}C_1$-DABCO-$C_1C^F_{10}$-I_2	96	51.0	138	b)
C^F_8-DABCO-C^F_8-I_2	89	58.3	161	c)

a) Since a gradual increase in the ionic conductivity was observed above the transition temperature, it was difficult to estimate the value of the conductivity jump. b) No conductivity jump was observed. c) Because of the decomposition of the material at a few degrees above the transition temperature, the σ_h/σ_l value could not be estimated.

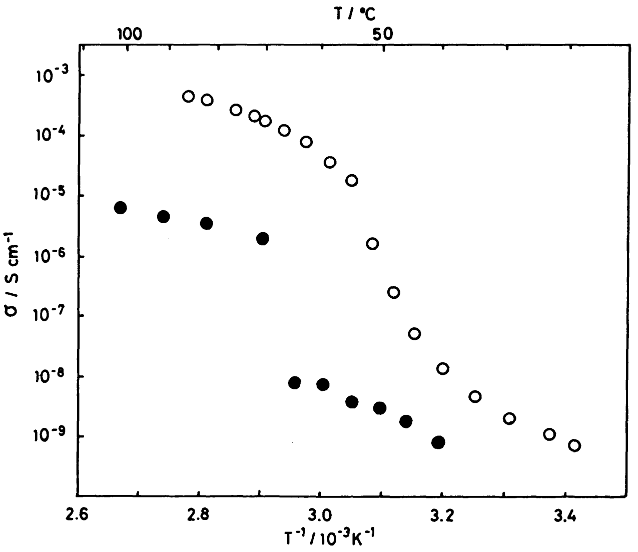

Fig. 4. Temperature dependence of the ionic conductivities of bromide anion. ○ $C^F_{10}C_1$-DABCO-C_{11}-Br_2, ● C_{11}-DABCO-C_{11}-Br_2.

reciprocal temperature. This figure also shows the same plot of C_{11}-DABCO-C_{11}-Br_2 (transition temperature=72 °C[2]) for the sake of comparison. The bromide anion conductivities of $C^F_{10}C_1$-DABCO-C_{11}-Br_2 were always higher than those of C_{11}-DABCO-C_{11}-Br_2, probably due to the spacer effect of the fluoroalkyl group as described in the Introduction (see also Fig. 1). The ionic conductivity of the former material approached to 10^{-3} S cm^{-1} in the high temperature phase, and this value was higher by about two orders of magnitude than those of the symmetric DABCO salts, C_n-DABCO-C_n-Br_2 ($10 \leqq n \leqq 22$).[2] The temperature dependence of the ionic conductivity of $C^F_{10}C_1$-DABCO-C_{11}-Br_2 was different from that of C_{11}-DABCO-C_{11}-Br_2; the latter material showed a conductivity jump by a factor of 630 around the transition temperature.[2] On the other hand, the former material did not show a conductivity jump, but showed a gradual increase of the ionic conductivity in the range of 40—60 °C, which was initiated by the phase transition at 38 °C. These results are explained as follows. In the case of C_{11}-DABCO-C_{11}-Br_2, the alkyl group could not move vigorously due to the closed-packed molecular arrangement in the low temperature phase. When the sample was heated to the transition temperature, the movement of the alkyl chain was released suddenly to give rise to the conductivity jump. On the other hand, the movement of the alkyl chain of $C^F_{10}C_1$-DABCO-C_{11}-Br_2 could be excited more easily due to the spacer effect of the fluoroalkyl group (Fig. 1). Thus, the gradual increase of the ionic conductivity was caused by a facile excitation of the movement of the alkyl group with the elevation of the temperature. This assumption was confirmed by Raman spectroscopy (vide infra).

Raman Spectroscopy of $C^F_{10}C_1$-DABCO-C_{11}-Br_2. Generally, Raman and IR bands broaden as the amount of the thermal motion increases in the solid.[15] In order to clarify the molecular motion in more detail and to relate it to the results of DSC and the measurements of the ionic conductivities, Raman spectra of $C^F_{10}C_1$-DABCO-C_{11}-Br_2 were measured in the low (13 °C) and high (65 °C) temperature phases (Fig. 5). Since the band at 732 cm^{-1} (C–C stretching mode of the fluoroalkyl group)[16] hardly changed at both temperatures, hardly any molecular movement at the fluoroalkyl group accompanied the conformational change. This assumption was confirmed by the almost constant Raman profiles of the CF_2 stretching modes, (1308, 1360, and 1372 cm^{-1}).[16] Slight line broadning was observed at 65 °C for the Raman bands of the CF_2 vibrational modes (306 and 385 cm^{-1}),[16] which indicates that a rotational movement of the fluoroalkyl group was excited to some extent in the high temperature phase.

In contrast to the small change of the Raman bands of the CF_2 vibrational modes, the Raman bands at 1064 and 1132 cm^{-1} (skeltal vibration of the alkyl group[7]) decreased their intensities appreciably in the high temperature phase. This fact suggests that vigorous motions accompany the conformational change occurring at the alkyl group in the high temperature phase.

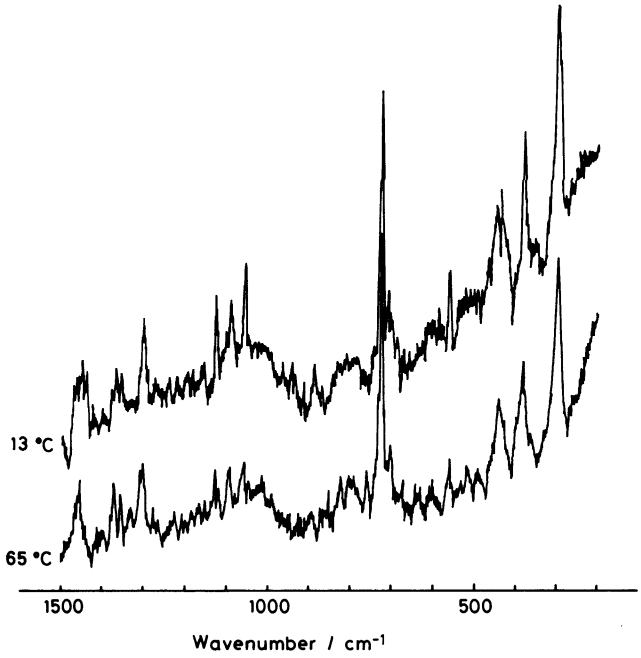

Fig. 5. Raman spectra of $C_{10}^{F}C_1$-DABCO-C_{11}-Br_2 below and above the transition temperature.

As to the Raman bands ascribable to the DABCO portion,[7] the band at 714 cm^{-1} (NC_4 symmetric stretching mode) decreased its intensity at 65 °C, and the band at 890 cm^{-1} (NC_4 degenerate stretching mode) observed in the low temperature phase disappeared almost completely at 65 °C. This suggests that the rotational movement of the DABCO portion was excited in the high temperature phase.

Summarizing the above experimental results, the molecular movement sets in mainly at the alkyl group and DABCO portion at the transition temperature. On the other hand, only a slight rotational movement seems to be excited at the fluoroalkyl group. Thus, the prediction of the molecular motion illustrated in Fig. 1 was confirmed by Raman spectroscopy.

Phase Transition of Symmetric Quaternary Fluoroalkyl Halide Salts of DABCO. The phase transitions of the symmetric quaternary fluoroalkyl halide salts of DABCO, $C_{10}^{F}C_1$-DABCO-$C_1C_{10}^{F}$-X_2 (X=Cl, Br, I), and C_8^F-DABCO-C_8^F-I_2, were also investigated by DSC, Raman spectroscopy, and the measurements of the ionic conductivities of the halide anions in order to compare them with those of $C_{10}^{F}C_1$-DABCO-C_{11}-Br_2 and C_n-DABCO-C_n-X_2. These materials showed reversible DSC signals. Table 1 summarizes the transition temperatures (T_c), transition enthalpies (ΔH), and transition entropies (ΔS) obtained by the DSC measurements in a nitrogen atmosphere. C_8^F-DABCO-C_8^F-I_2 decomposed at 93 °C, just above the transition temperature (89 °C), in an inert atmosphere. The exceptionally instability of C_8^F-DABCO-C_8^F-I_2 may be associated with a weak C–N bond energy caused by an inductive effect of fluorine atoms. Temperature dependences of the halide anion conductivities of $C_{10}^{F}C_1$-DABCO-$C_1C_{10}^{F}$-X_2 (X=Cl, Br, I) were measured, and only the chloride salt showed a conductivity jump (σ_h/σ_l) by a factor of about 120 (Table 1).[17] This value was much smaller than those observed for the corresponding symmetric quaternary alkyl halide salts of DABCO.[2] These facts suggest that the molecular motion of $C_{10}^{F}C_1$-DABCO-$C_1C_{10}^{F}$-X_2 (X=Cl, Br, I) is less vigorous than that of C_{11}-DABCO-C_{11}-X_2 (X=Cl, Br, I) in the high temperature phases. In order to confirm this, the temperature dependence of the Raman spectra of $C_{10}^{F}C_1$-DABCO-$C_1C_{10}^{F}$-Br_2 (not shown here) was measured below and above (16 °C and 103 °C) the transition temperature (93 °C). The Raman band at 732 cm^{-1} (C–C stretching of fluoroalkyl group) hardly changed for the high temperature phase. This suggests that the amount of molecular motion of the fluoroalkyl group is small even for the high temperature phase. Since the Raman intensities ascribable to the -CH_2-DABCO-CH_2- portion were weak, no further detailed analysis could be mode. The phase transition may be caused by the molecular motion of -CH_2-DABCO-CH_2- portion and/or by the change of the molecular packing in the solid. The small σ_h/σ_l values of $C_{10}^{F}C_1$-DABCO-$C_1C_{10}^{F}$-X_2 (X=Cl, Br, I) could be related to the rigid molecular structure of the fluoroalkyl group.

We are grateful to Professor Shigekazu Kusabayashi and Dr. Shunsuke Takeneka, Faculty of Engineering, Osaka University, for allowing us to use the DSC apparatus. The present work was supported by a Grant-in-Aid for Special Project Research on Chemical Sensors (No. 62217014) from the Ministry of Education, Science and Culture.

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, and Y. Shirota, *Bull. Chem. Soc. Jpn.*, **60**, 3499 (1987).

7) K. Imamura, T. Nogami, Y. Shirota, T. Ishioka, and M. Kobayashi, *Bull. Chem. Soc. Jpn.*, **60**, 3879 (1987).

8) H. Nakayama, T. Eguchi, N. Nakamura, H. Chihara, T. Nogami, K. Imamura, and Y. Shirota, *Bull. Chem. Soc. Jpn.*, **62**, 399 (1989).

9) T. Terada, T. Nogami, and Y. Shirota, *Bull. Chem. Soc. Jpn.*, **62**, 5 (1989).

10) Optical switching of ionic conductivities has recently

been reported. K. Kimura, T. Suzuki, and M. Yokoyama, *Chem. Lett.*, **1989**, 227.

11) N. Higashi and T. Kunitake, *Maku* (*Membrane*), **10**, 138 (1985).

12) T. Kunitake and N. Higashi, *J. Am. Chem. Soc.*, **107**, 692 (1985).

13) C. W. Bunn and E. R. Howell, *Nature* (*London*), **174**, 549 (1954).

14) Symmetric quaternary alkyl halide salts of DABCO were usually synthesized by refluxing methanol solution of alkyl halide and DABCO for about 36 h. The much milder condition for the synthesis of C_8^F-DABCO-C_8^F-I_2 exemplifies that a nucleophilic attack of the lone-pair of DABCO nitrogen to the fluoroalkyl carbon takes place more easily than that to the alkyl carbon, due to the inductive effect of fluorine atoms.

15) R. G. Snyder, J. R. Scherer, and B. P. Gaber, *Biochim. Biophys. Acta*, **601**, 47 (1980); Y. Cho, M. Kobayashi, and H. Tadokoro, *J. Chem. Phys.*, **84**, 4643 (1986).

16) C. E. Hathaway and J. R. Nielsen, *J. Chem. Phys.*, **41**, 2203 (1964).

17) This fact corresponds to the largest transition entropy of this material.