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A smectic T phase of 1,4-dialkyl-1,4-diazoniabicyclo[2.2.2]octane dibromides

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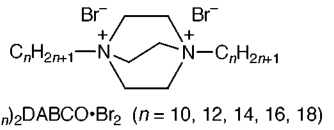
An unidentified phase X of 1,4-dialkyl-1,4-diazoniabicyclo[2.2.2]octane dibromides reported by Nogami *et al.* in 1985 was reinvestigated by differential scanning calorimetry, polarizing microscopy and temperature-dependent X-ray diffraction. The X phase was thus established as a smectic tetragonal (S_T) mesophase which shows spontaneous homeotropic alignment.

I Introduction

A series of 1,4-dialkyl-1,4-diazoniabicyclo[2.2.2]octane dibromides (abbreviated as $(C_n)_2$DABCO·Br_2 in Fig. 1) were synthesized for the first time by Nogami and co-workers in 1985.[1] Each of these salts shows a phase transition from crystal (K) to an unknown phase (X) and the ionic conductivity abruptly decreases by an order of magnitude from 10^{-3}–10^{-4} S cm^{-1} on going from K to X. Furthermore, when the sample between two glass plates was observed under a polarizing microscope under crossed Nicols conditions, the bright transmitted light in the K phase disappeared at the K–X phase transition temperature. The infrared spectra indicated that the alkyl chains in the X phase obviously melt. Since this non-birefringent X phase lacks a spontaneous fluidity, it is not an isotropic liquid. Although the X phase was supposed to be one of the liquid crystalline phases, the phase structure has never been revealed or established up to date.

On the other hand, in 1992 Ujiie and Iimura reported that ionic molecules substituted with a mesogenic moiety show liquid-crystallinity and spontaneous homeotropic alignment.[2] In 1993 Skoulios *et al.* reported that dialkyldimethylammonium bromides exhibit a new smectic mesophase with two dimensional tetragonal symmetry, designated as S_T.[3] This was the first example of the S_T phase.

From these two examples mentioned above, one can recognize that ionic liquid crystals show unique characteristics which cannot be seen in conventional non-ionic liquid crystals. Hence, we supposed that the aforementioned $(C_n)_2$DABCO·Br_2 salts might show spontaneous homeotropic alignment and an S_T mesophase, so we have reinvestigated the unidentified X phase of these $(C_n)_2$DABCO·Br_2 salts.



$(C_n)_2$DABCO·Br_2 (n = 10, 12, 14, 16, 18)

$$K \xrightarrow{°C} X$$

n = 10	64
n = 12	76
n = 14	88
n = 16	92
n = 18	90

Fig. 1 Molecular formula of 1,4-diazoniabicylco[2.2.2]octane dibromides, $(C_n)_2$DABCO·Br_2, and their phase transition temperatures reported by Nogami *et al.*[1]

II Experimental

Synthesis

The synthesis and purification of the present $(C_n)_2$DABCO·Br_2 (n = 12,14,16) salts were carried out by using the method reported by Nogami *et al.*[1] The samples that gave satisfactory elemental analysis data were used for physical measurements.

Elemental analysis (%) found (calc.): $(C_{12})_2$DABCO·Br_2 = $C_{30}H_{62}N_2Br_2$: C, 58.94(59.01); H, 9.99(10.23); N, 4.67(4.59); $(C_{14})_2$DABCO·Br_2 = $C_{34}H_{70}N_2Br_2$: C, 60.77(61.25); H, 10.61 (10.58); N, 3.95(4.20); $(C_{16})_2$DABCO·Br_2 = $C_{38}H_{78}N_2Br_2$: C, 62.86(63.14); H, 10.81(10.88); N, 3.88(3.88).

Measurements

Final products were identified by elemental analysis using a Perkin Elemental Analyzer 240B. The phase transition behavior of these compounds was observed with a polarizing microscope, Olympus BH-2, equipped with a heating plate controlled by a thermoregulator, Mettler FP80 and FP82, and measured with a differential scanning calorimeter, Shimadzu DSC-50. Temperature-dependent X-ray diffraction measurements of the mesophases were performed by using a Rigaku Geigerflex with Cu-Kα radiation equipped with a handmade heating plate controlled by a thermoregulator.[4]

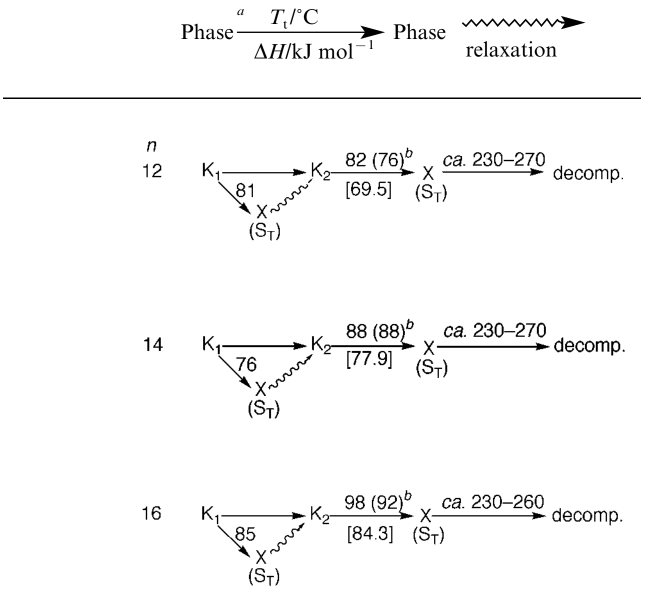
III Results and discussion

III-1 Phase transition behavior

The phase transition sequences of these $(C_n)_2$DABCO·Br_2 (n = 12,14,16) salts established by DSC measurements and polarizing microscopic observations are listed in Table 1. Since each of them shows the same phase transition sequence, a representative C_{16} derivative is described.

When the virgin crystal K_1 prepared by recrystallization from methanol was heated from room temperature at the rate of $\geqslant 2.5$ °C min^{-1}, a phase transition from K_1 to X could be observed at 85 °C. On the other hand, when it was heated at the slower rate of < 2.5 °C min^{-1}, the phase transition from K_1 to X could not be observed because a complete K_1–K_2 phase transition occurred. It only showed the phase transition from K_1 to X at 98 °C. When the virgin crystal K_1 was held at room

Table 1 Phase transition temperatures T_t/°C of $(C_n)_2$DABCO·Br_2



[a] Phase nomenclature; K = crystal and X = mesophase? (S_T = two dimensional tetragonal smectic phase). [b] Values in parentheses are those reported by Nogami *et al.*[1]

temperature for more than four months, it also did not show the phase transition from K_1 to X at 85 °C. This clearly indicates that a slow relaxation from K_1 to K_2 occurred at room temperature. On further heating, the X phase decomposed at *ca.* 230–260 °C. The values in parentheses in Table 1 are the phase transition temperatures from crystal to X phase reported by Nogami *et al.*[1,5] The values coincide with the present ones for $n = 14$ but for $n = 12$ and 16 are a little bit higher than the previous values.

III-2 X-Ray structure analysis of the X phase

As can be seen from Fig. 2, each of the X phases of the $(C_n)_2$DABCO·Br_2 ($n = 12,16$) derivatives at 120 °C gave ten sharp reflections together with a halo at $2\Theta \cong 20°$. The halo corresponds to the melting of long alkyl chains. The spacings of peak nos. 1–7 for $(C_{16})_2$DABCO·Br_2 are in a ratio of $1 : 1/2 : 1/3 : 1/4 : 1/5 : 1/6 : 1/7$, which indicates that this X phase has a lamellar (layered) structure. The distance (c) between the layers could be calculated to be 32.2 Å. For the rest, peak nos. 8–10 could be assigned as reflections from a two dimensional tetragonal lattice. When the spacing of peak no. 8 was assumed as a reflection from the (11) plane of a 2D tetragonal lattice, the lattice constant a could be calculated to be 6.22 Å by using eqn. (1),

$$(1/d_{hk}^2) = (h^2 + k^2)/a^2 \qquad (1)$$

where $d_{11} = 4.40$ Å, $(hk) = (11)$.

In Fig. 3, the corresponding reciprocal lattice plane was drawn and the quarter circles of the inverse values of spacings for peak nos. 8–10 were superimposed. As can be seen from this figure, peak nos. 9 and 10 fit very well to (20) and (21), respectively. This means that the assumption of the 2D tetragonal lattice is correct. Therefore, the present X phase can be identified as a smectic tetragonal (S_T) mesophase. Moreover, the number of molecules in a unit cell (z) could be calculated to be one by using the lattice constants $a = 6.22$ Å, $c = 32.2$ Å and an assumed density $\rho = 1$ g cm^{-3}. It is consistent with the present conclusion that the X phase is an S_T mesophase.

An S_T mesophase was found for the first time for another ionic compound by Skoulios in 1993,[3] but the X phase which had been found previously by Nogami *et al.* in 1985[1] is also an S_T mesophase. Hence, the present S_T mesophase unfortunately becomes the second example.

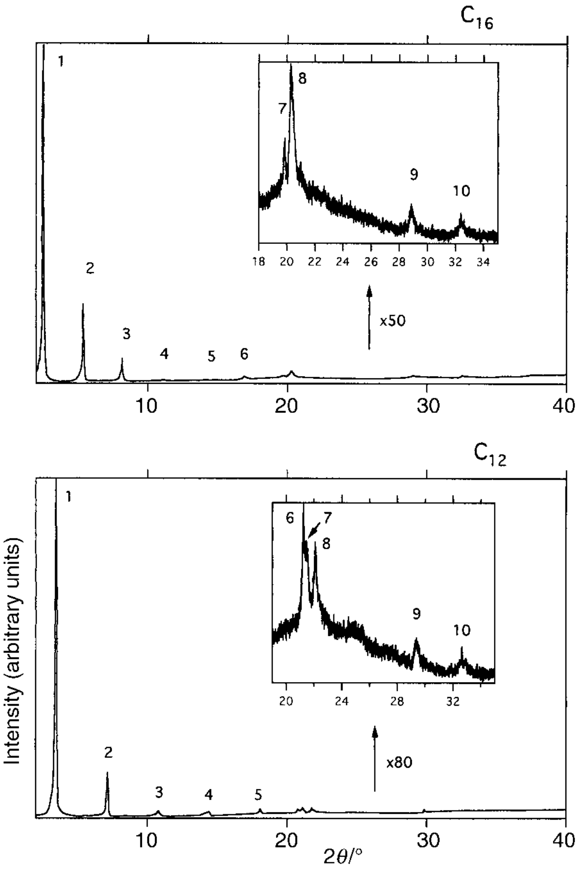


Fig. 2 X-Ray diffraction patterns of $(C_{16})_2$DABCO·Br_2 and $(C_{12})_2$DABCO·Br_2 at 120 °C.

Each of the X phases of the other C_{14}- and C_{12}-substituted derivatives could be also identified as an S_T mesophase. These X-ray diffraction data are summarized in Table 2. As can be seen from Table 2, the lattice constants (a) for these 2D tetragonal lattices remain almost constant on changing the chain lengths from $n = 12$ to $n = 16$. On the other hand, the longer the chain becomes, the longer the layer distance c becomes.

Thus, each of the $(C_n)_2$DABCO·Br_2 derivatives shows an S_T mesophase. However, an interesting small difference between $n = 16$ and $n = 14$, 12 can be seen from the X-ray data. The reflections of the C_{16}-derivative completely divided into one-

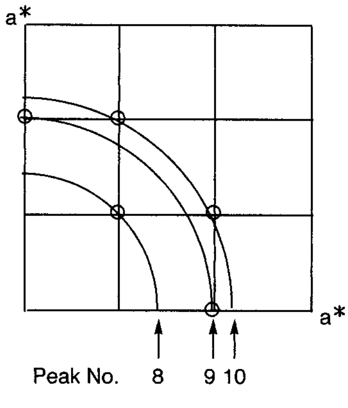


Fig. 3 Reciprocal lattice of two-dimensional tetragonal symmetry calculated from the X-ray data for $(C_{16})_2$DABCO·Br_2 at 120 °C.

Table 2 X-Ray diffraction data of the $(C_n)_2DABCO\cdot Br_2$ salts

Peak no.	d_{obs}/Å	d_{calcd}/Å	Miller indices
$n=16$	$a=6.22$ Å, $c=32.2$ Å at 120 °C		
1	32.9	32.2	(001)
2	16.1	16.1	(002)
3	10.7	10.7	(003)
4	7.97	8.03	(004)
5	6.35	6.43	(005)
6	5.28	5.36	(006)
7	4.51	4.59	(007)
8	4.40	4.40	(110)
9	3.10	3.11	(200)
10	2.77	2.78	(210)
$n=14$	$a=6.21$ Å, $c=28.9$ Å at 120 °C		
1	30.0	28.9	(001)
2	14.6	14.5	(002)
3	9.62	9.62	(003)
4	5.70	5.78	(005)
5	4.75	4.81	(006)
6	4.39	4.39	(110)
7	4.35	4.34	(111)[a]
8	4.06	4.13	(007)
9	3.10	3.11	(200)
10	2.77	2.78	(210)
$n=12$	$a=6.18$ Å, $c=25.1$ Å at 120 °C		
1	25.1	25.1	(001)
2	12.5	12.5	(002)
3	8.33	8.35	(003)
4	6.27	6.26	(004)
5	5.00	5.00	(005)
6	4.35	4.35	(110)
7	4.32	4.29	(111)[a]
8	4.17	4.17	(006)
9	3.08	3.08	(200)
10	2.75	2.75	(210)

[a] Three-dimensional reflection, see the text.

dimensional (00*l*) reflections ($l=1$–7) and two-dimensional (*hk*0) reflections. On the other hand, the C_{14}- and C_{12}-substituted derivatives show an additional three-dimensional (111) reflection (peak no.7). This means that the longer chain C_{16}-substituted derivative does not have such three-dimensionality, whereas the shorter chain C_{14}- and C_{12}-substituted derivatives have slight three-dimensionality. It may be attributable to a bigger thermal fluctuation of the alkyl chains for longer chain-substituted derivatives.

III-3 Model of S_T mesophase

The structure model of this S_T mesophase of the C_{16}-substituted derivative is illustrated in Fig. 4 and 5. Fig. 4 illustrates a top-view of the S_T mesophase. The molecular width of DABCO (1,4-diazabicyclo[2.2.2]octane) could be estimated from Chem 3D to be 6.44 Å, which is almost compatible with the lattice constant $a=6.22$ Å of a 2D tetragonal lattice. Taking account of this lattice constant, bromide anions are located above and below this 2D lattice plane. Fig. 5 illustrates a side-view of the S_T mesophase. The molecular length of the C_{16}-substituted derivative could be estimated from Chem 3D to be 45.4 Å. However, the layer thickness was determined as 32.2 Å from the X-ray diffraction study, as mentioned above. Accordingly, the alkyl chains may interdigitate between layers, as illustrated in this figure.

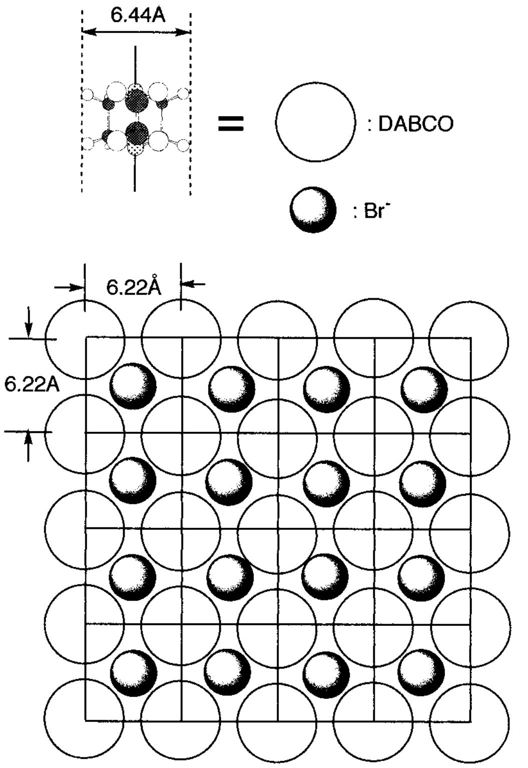


Fig. 4 Top-view of a structure model for the S_T mesophase of $(C_{16})_2DABCO\cdot Br_2$ at 120 °C.

III-4 Spontaneous homeotropic alignment

As mentioned in the introduction, Nogami *et al.* reported no birefringence of this S_T mesophase. We have reconfirmed the non-birefringence in this work. For non-birefringence of materials under crossed Nicols conditions, two reasons could be possible. The first is the isotropy of phases such as a cubic phase and isotropic liquid. However, the present S_T mesophase is neither a cubic phase nor an isotropic liquid as revealed by the X-ray structure analysis. The second reason is homeotropic alignment. As pointed out by Ujiie, ionic liquid crystals themselves work as a surface treatment reagent like a silane coupling reagent.[6] Hence, the present ionic liquid crystal, $(C_n)_2DABCO\cdot Br_2$, may also work as a surface treatment reagent to show spontaneous homeotropic alignment. In order to confirm this hypothesis, two glass plates sandwiching the S_T mesophase were sheared. The sheared sample showed birefringence. Therefore, it clearly indicates that the $(C_n)_2DABCO\cdot Br_2$ salts show spontaneous homeotropic alignment on entering into the S_T mesophase from the crystalline phase.

IV Conclusion

The present $(C_n)_2DABCO\cdot Br_2$ derivatives show a smectic tetragonal (S_T) mesophase, which is the second example in

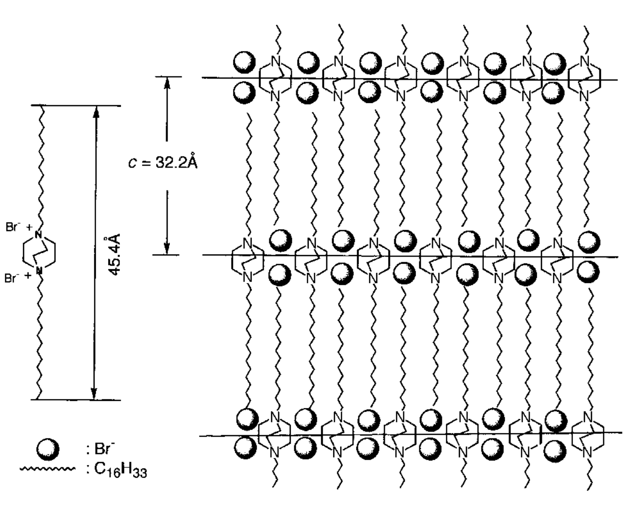


Fig. 5 Side-view of a structure model for the S_T mesophase of $(C_{16})_2DABCO\cdot Br_2$ at 120 °C.

liquid crystals. These ionic $(C_n)_2DABCO\cdot Br_2$ molecules spontaneously homeotropically align in the S_T mesophase. For the S_T mesophase, the shorter chain C_{12}- and C_{14}-substituted derivatives have slight three-dimensionality, whereas the longer chain C_{16}-substituted derivative does not have such three-dimensionality.

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