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Crystal Structure of *N,N'*-Distearyl-1,4-diazabicyclo[2.2.2]octane Dibromide

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The crystal structure of *N,N'*-distearyl-1,4-diazabicyclo[2.2.2]octane dibromide is orthorhombic (*Pna*2$_1$) with a = 63.851(9), b = 9.156(7), c = 8.366(6) Å and Z = 4.

The molecular mechanism of the ionic conduction of the biomembrane has been ascribed to the function of ion channel proteins embedded in the lipid bilayer. However, the role in ionic conduction of the lipid bilayer itself has not been clearly clarified yet. *N,N'*-distearyl-1,4-diazabicyclo[2.2.2]-octane dibromide (abbreviated as dialkyl-DABCO–Br_2) is a simple model compounds of lipids, and has a first order phase transition from crystal to liquid crystal at 93 °C with an abrupt increase in halide anion conductivity from 10^{-8} to 10^{-5} Sm^{-1}.[1,2] Many numbers of homologous series of the compounds have been synthesized and their transition behavior and the ionic conductivity have been studied.[3—11] In this study, we clarified the crystal structure of dialkyl-DABCO–Br_2 as a typical example of a homologous series member.

The crystal structure of dialkyl-DABCO–Br_2 (Fig. 1) is similar to that of dodecyl ammonium bromide.[12] Adjacent alkyl chains' arrangement along the b axis is 'head-to-tail' fashion. The crystal contains one ethanol and one water solvent per molecule. Each molecule (Fig. 2) consists of three parts: i.e., the alkyl chains, the DABCO ring, and the Br anions. The alkyl chains take almost all-*trans* conformation. The average C–C distance in the chain is 1.517 Å and the average C–C–C angle is 113.5°. The dodecylammonium bromide has a little longer average C–C distance of 1.523 Å, but its average C–C–C angle is almost the same as 113.8°. The average C–N distances of dialkyl-DABCO–Br_2 is 1.511 Å. This is somewhat longer than 1.482 Å of the dodecylammonium bromide. All C–H bond distances were fixed at 1.00 Å and all H–C–H and C–C–H angles were assumed tetrahedral. The two alkyl chains are slightly asymmetric with respect to the C–C bond lengths and the C–C–C bond angles. Both of the chains lie in the ab plane and both axes are tilted 75° from the bc plane. The sub-cell of the alkyl chains is orthorhombic type with c_s = 8.37 and b_s = 4.40 Å. For the DABCO ring, the average N–C and C–C lengths are 1.515 and 1.522 Å. These values are close to 1.513 and 1.528 Å of dimethyl-DABCO,[13] but fairly different from 1.46 and 1.57 Å of DABCO itself,[14] respectively. The average R–N–C, N–C–C, and C–N–C angles are 111.0, 109.2, and 108.0°, where R is the alkyl chain. These angles are also close to 111.0, 109.3, and 107.9° of dimethyl-DABCO but slightly different from N–C–C = 110.0 and C–N–C = 108.9° of DABCO. The average torsion angle N–C–C–N is 21.3°, meaning the distortion of the DABCO ring. Dimethyl-DABCO also has a distortion of 10° but DABCO itself has no distortion, i.e., N–C–C–N = 0°.[15] There are three intermolecular hydrogen bonds of $O_1 \cdots Br_1$ = 3.276(6), $O_2 \cdots Br_1$ = 3.39(1), and $O_2 \cdots Br_2$ = 3.35(1) Å. The typical Br···N distances are $Br_1 \cdots N_1$ is 4.77 Å and $Br_2 \cdots N_2$ 4.12 Å. The latter distance is the shortest one but still somewhat longer than that of usual ionic bonding. It means that Br anion is weakly bonded to N cation and this causes the high mobility of Br anion in the high temperature phase.

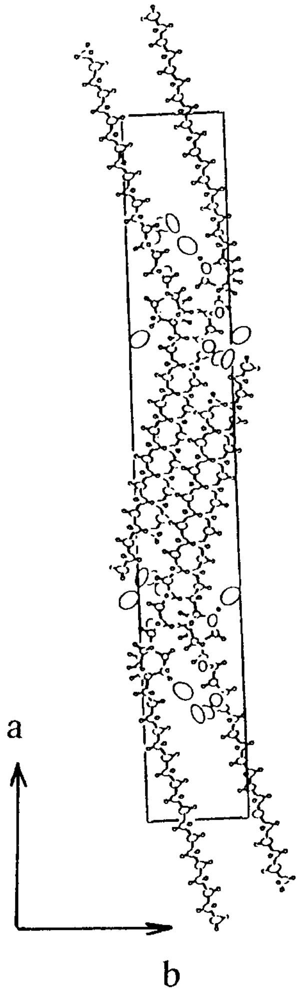

Fig. 1. Molecular packing of dialkyl-DABCO–Br_2 viewed along the c axis.

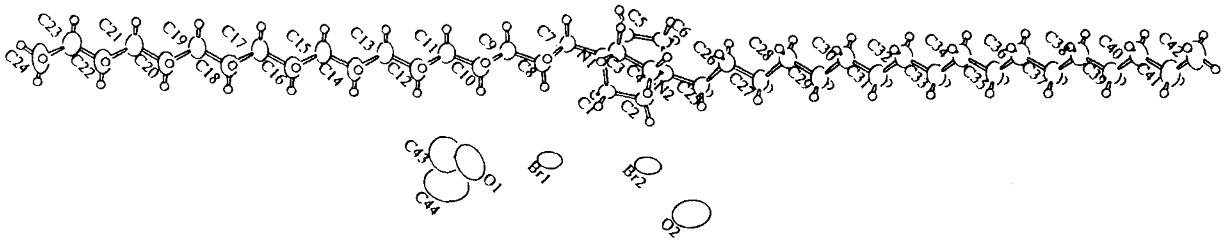

Fig. 2. Molecular packing of dialkyl-DABCO–Br_2 viewed along the c axis.

Experimental

Synthesis. A methanol (50 cm^3) solution of DABCO (2.24 g, 20 mmol) and stearyl bromide (13.37 g, 40 mmol) was refluxed at 81 °C for 48 h. A product was precipitated with diethyl ether (300 ml). This was collected by filtration and recrystallized from ethanol 5 times and dried in vacuo. Anal. Calcd for $C_{42}H_{86}Br_2N_2$: C, 64.17; H, 10.92; N, 3.56%. Found: C, 64.12; H, 11.02; N, 3.56%.

X-ray Crystallography. A single crystal of the sample was obtained by crystallization from dry-ethanol solution and mounted in a glass capillary. Intensity data were collected at 15.0 °C on a Rigaku AFC5R automated four-circle diffractometer equipped with monochromated Cu $K\alpha$ (λ = 1.54178 Å) and ω-2θ scan method, and an empirical absorption correction (ψ scan) was applied. Structure analysis was performed using a program package teXsan.[16] The structure was solved by a direct method and Fourier techniques. Atomic scattering factors were obtained from the literature.[17] Crystal data of $C_{42}H_{86}Br_2N_2$; Mr, 778.97; orthorhombic space group, $Pna2_1$ (No. 33); a = 63.851(9); b = 9.156(7); c = 8.366(6) Å; V = 4890(5) $Å^3$; Z = 4; $\mu(\mathrm{Cu}\ K\alpha)$ = 23.23 cm^{-1}; F(000) = 1752; D_{calcd} = 1.101 g cm^{-3}; Unique reflections ($2\theta \leq 120°$), 3964; Used reflections ($I \geq 2\sigma(I)$), 3961; No. of variables, 451; $R(F_o^2)$, 0.056; $R_w(F_o^2)$, 0.167. The crystallographic results are deposited as Document No. 73063 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication number 150672.

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