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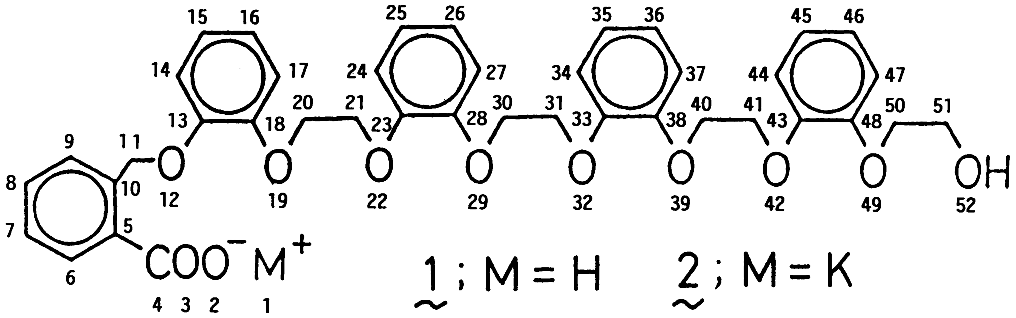
# Crystal Structure of Potassium Salt of Synthetic Carboxylic Ionophore[1]

Hitoshi KUBONIWA, Kazuo YAMAGUCHI, Seiichi NAKAHAMA,
Kayako HORI,[†] and Yuji OHASHI[†]
Department of Polymer Chemistry, Faculty of Engineering,
Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo 152
[†]Department of Chemistry, Faculty of Science,
Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112

Crystal structure of potassium [[2-[2-[2-[2-[2-[2-[2-(2-hydroxyethoxy)phenoxy]ethoxy]phenoxy]ethoxy]phenoxy]ethoxy]phenoxy]-methyl]benzoate (2) has been determined. The backbone forms pseudocycle by head-to-tail hydrogen bonding. Conformations about C-C and C-O bonds are gauche and trans respectively, except for two of the C-O bonds which are gauche to make the pseudocyclic backbone bend like seam of a tennis ball. Ten oxygens except for one of the benzoate group coordinate with the potassium ion.

Naturally ocurring carboxylic ionophores are known to mediate active ion transport through lipophilic biological membranes by formation of hydrophobic complexes with metal cations.[2] It revealed that, in the crystal structures of the ionophores and the complexes with cations, the backbones had pseudo-cyclic conformations secured by head-to-tail hydrogen bonding.[3] We have already reported that the synthetic carboxylic ionophore (1) exhibits high selectivity for



$K^+$ over $Na^+$ in the ion transport experiment across dichloroethane liquid membrane.[4)] This is due to high lipophilicity of potassium salt (2) with a definite coiled conformation in the liquid membrane.[5)] In this letter, we report the X-ray structure determination of 2.

Synthesis of 1 and 2 have been previously described.[4)] Single crystals of 2 were obtained by slow evaporation of a chloroform solution of 2. Crystal data of $C_{40}H_{39}O_{11}K \cdot 2CHCl_3 \cdot H_2O$ are as follows: FW = 991.62, triclinic, space group $P\bar{1}$, $a = 14.517(1)$, $b = 16.380(1)$, $c = 13.315(1)$ Å, $\alpha = 72.313(8)$, $\beta = 117.268(8)$, $\gamma = 120.853(5)°$, $V = 2406.3(4)$ $Å^3$, $Z = 2$, $D_c = 1.37$ g $cm^{-3}$, $\mu(Cu\text{-}K_\alpha) = 25.43$ $cm^{-1}$. Reflection intensities of a selected crystal of size 0.8 x 0.3 x 0.25 $mm^3$, sealed with chloroform in a glass capillary, were measured on a Rigaku automated four-circle diffractometer with graphite monochromated Cu $K_\alpha$ radiation. Corrections were made for Lorentz and polarization, but not for absorption. A total of 7693 independent reflections ( $3° < 2\theta < 125°$ ) were obtained, of which 6351 reflections with $|F_0| > 3\sigma(|F_0|)$ were considered as observed. The structure was solved by direct methods using program MULTAN78,[6)] and refined by repeating full-matrix least-squares methods with program SHELX76.[7)] Anisotropic temperature factors were introduced for all non-hydrogen atoms except those of the disordered chloroform molecule. 16 H-atoms found on a difference map were also included in the refinement. The current R is 0.103 ( $R_w = 0.127$ ).

In the crystal structure, molecules of 2 are stacked on (-1, 1, 0) plane to generate a layer structure of about 10 Å interlayer distance. Interlayer spaces are filled with chloroform and water molecules. One of the two non-equivalent chloroform molecules is highly disordered in a column along the C-axis.

Figure 1 shows the molecular structure of 2, where an intramolecular hydrogen bond is reasonably suggested between terminal carboxylato and hydroxyl groups based on the close O-O distsance of 2.672(7) Å similar to the case of naturally occurring carboxylic ionophores as mentioned above.[3)]

Through the polyether chain, the torsion angles about all of four aliphatic C-C bonds shown in Table 1 are around +60° and -60° alternately. The gauche conformations of 1,2-dioxyethylene moieties of 2 in chloroform solution were also determined from the coupling constants of vicinal protons measured by NMR experiment.[5)] The torsion angles about the C-O bonds are close to ±180° except for C(10)-C(11)-O(12)-C(13) and C(38)-O(39)-C(40)-C(41) frameworks where the main chain makes abrupt turnings. As a result, the thirty one membered pseudocycle tied with hydrogen bond is bent like seam of a tennis ball to wrap the potassium cation inside of the ball. Similar crystal structure was observed by X-ray analysis for a thirty membered polyether ring, dibenzo-30-crown-10.[8)]

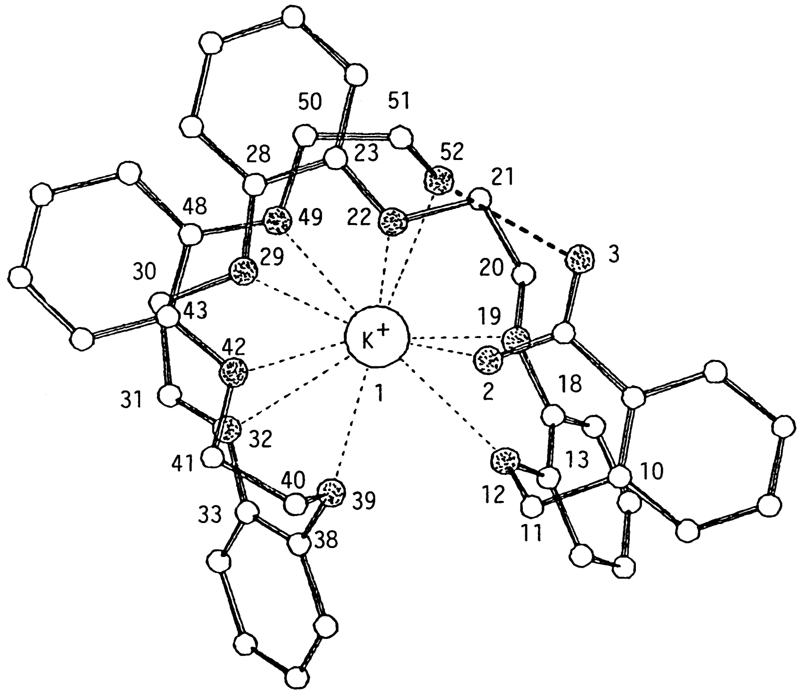


Fig. 1. Molecular structure of **2**.

Table 1. Torsion angles(ϕ/°) in a crystal of **2**

| | |
|---|---|
| C(10)-C(11)-O(12)-C(13) | +71 |
| C(18)-O(19)-C(20)-C(21) | +179 |
| O(19)-C(20)-C(21)-O(22) | -61 |
| C(20)-C(21)-O(22)-C(23) | -168 |
| C(28)-O(29)-C(30)-C(31) | +173 |
| O(29)-C(30)-C(31)-O(32) | +64 |
| C(30)-C(31)-O(32)-C(33) | -177 |
| C(38)-O(39)-C(40)-C(41) | -81 |
| O(39)-C(40)-C(41)-O(42) | -67 |
| C(40)-C(41)-O(42)-C(43) | +173 |
| C(48)-O(49)-C(50)-C(51) | +171 |
| O(49)-C(50)-C(51)-O(52) | +65 |

Table 2. Distances(l/Å) between potassium and oxygens

| | |
|---|---|
| K(1)-O(2) | 2.815(5) |
| K(1)-O(3) | 3.776(5) |
| K(1)-O(12) | 2.883(4) |
| K(1)-O(19) | 3.052(5) |
| K(1)-O(22) | 2.982(5) |
| K(1)-O(29) | 3.034(6) |
| K(1)-O(32) | 3.015(5) |
| K(1)-O(39) | 2.745(4) |
| K(1)-O(42) | 3.155(5) |
| K(1)-O(49) | 3.057(6) |
| K(1)-O(52) | 2.822(5) |

Ten oxygen atoms of the ionophore for which the K-O distances as shown in Table 2 range from 2.745(4) to 3.155(5) Å interact with the potassium ion. The K-O distances are reasonable for coordination numbers of ten.[9)] Only O(3) of the ionophore ( K-O distance = 3.776(5) Å ) does not coordinate with the potassium ion.

The molecular structure established by X-ray analysis here is not completely consistent with the structure in solution estimated by NMR. Further study about the differences between the crystal and solution structures is in progress.

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