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Amidocrownophanes as Anion Receptor

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Abstract

Crownophanes composed of 28-membered ring atoms having two hydroxy groups, two amide groups, and aromatic parts such as naphthalene rings and either pyridine or benzene ring, can bind anions with high affinity and selectivity. The anion-coordination ability of these species has been observed by ^{1}H NMR techniques. As anion guest molecules, we selected some halides, dihydrogenphosphate and acetate ions. It has been found that amidocrownophanes, **3** and **4**, can recognize anions in the order;$H_2PO_4^- > F^- > CH_3COO^- > Cl^- > > Br^-$ and I^-, while not only **1**, **2**, and **5** having no hydroxy group but also **6** having 27-membered ring have no ability for anion recognition under the same conditions. In order to exhibit the recognition ability for anion receptor, plural amide groups, hydroxy groups, and *m*-phenylene or 1,6-pyridyl rigid part play an important role in this macrocyclic system.

Introduction

One of the interesting areas in host–guest chemistry that continues to attract attention is the recognition of anions. The rapid growth in this area is due to the realization of the many and important roles that anions play in biology, medicine, catalysis and the environment [1, 2]. It is interesting to note that anion binding by proteins is most often achieved by way of neutral amide functions employing the hydrogen-bond accepting properties of the amide NH group [3]. Amide receptor contracted on an organic scaffold most often utilize either solely hydrogen bonding or a combination of hydrogen bonding and electrostatic interactions. The amide binding units are most commonly pre-organized to act cooperatively within some convergent molecular architecture. Complexation properties of macrocyclic receptors depend mainly on the type and arrangement of binding sites, the size and shape of the macroring and its rigidity. Experimental studies on the influence of these factors on anion recognition were focused on highly charged, multiply protonated polyazamacrocycles that bind anions in protic solvents mainly through coulombic interactions [4]. Hydrogen bonding, being more directional, is also more sensitive to geometric constraints. In spite of this aspect, systematic studies on structure/affinity relationships in uncharged macrocyclic receptors are scarce [5, 6, 7].

Recently, we succeeded in synthesizing crownophane type derivatives **3**, **4**, and **6** [8] via ''tandem Claisen rearrangement (TCR)'' [9–14], and have found that **3** and **4**, which consist of 28-membered ring atoms containing cyclophane and oligoethylene glycol unit, two hydroxy and two amide groups, can recognize urea and urea derivatives such as ethyleneurea, propyleneurea, thiourea [8]. One of the most important manners for their recognition might be concluded to be multi-hydrogen bonding between host and guest molecules. On the other hand, it has been reported that plural amide and hydroxy protons could play an important role for anion recognition [15–21]. Therefore, they could be expected to exhibit high affinity and good selectivity not only for neutral guest molecules such as urea and its derivatives but also for anionic guest molecules, because strong proton donating groups, i.e., two hydroxy and two amide groups, exists within the macrocycles which can form hydrogen bonding with the anionic guest molecules. In particular, introduction of amide groups is expected to result in strengthening of hydrogen bonding for the specific anionic guest molecules. Moreover, the aromatic and heteroaromatic ring systems could act to keep the structural spacers to form the complexes [22]. Although there have been reported many macrocycles which exhibit the recognition properties toward anionic guest molecules, there are few reports of macrocyclic receptor having both plural

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hydroxy and amide groups. Using our designed and synthesized macrocycles having hydroxy and amide functional groups, we investigated their molecular recognition properties with some anionic guest molecules such as halides (fluoride, chloride, bromide, and iodide), dihydrogenphosphate, and acetate ions.

Experimental

Reagent grade tetra-*n*-butylammonium salts of fluoride, chloride, bromide, iodide, acetate, and dihydrogenphosphate were purchased from TCI and Aldrich, and used without any further purification. Other commercially available reagents and solvents were also purchased from Wako, Aldrich, TCI, and Cica and were used without further purification.

^{1}H NMR spectra were recorded with a Varian (300 MHz) spectrometer in $CDCl_3$ using tetramethylsilane (TMS, 0.03 wt%) as an internal standard. All chemical shifts are quoted in parts per million (ppm) relative to TMS (δ, 0.00 ppm).

Macrocycles, **3**, **4**, and **6**, were prepared via tandem Claisen rearrangement by the methods which were reported recently [8].

^{1}H NMR of the mixture of crownophanes and tetrabutylammonium salt

^{1}H NMR of crownophane **3** with tetrabutylammonium fluoride ion: δ 3.68 (C*H*$_2$–NH, 4H, t, 5.1 Hz), 3.80 (O–*CH*$_2$CH$_2$–NH, 4H, t, 16.5 Hz), 3.87 (O–*CH*$_2$–CH$_2$–O–Ar, 4H, broad s), 3.87 (=C–CH$_2$–O, 4H, broad s), 4.27 (Ar–O–*CH*$_2$–CH$_2$, 4H, m), 4.58 (C =CH$_2$, 2H, s), 7.04 (Ar–H, 2H, s), 7.19–7.25 (Ar–H, 4H, m), 7.57–7.60 (Ar–H, 2H, m), 7.73–7.76 (Ar–H, 2H, m), 7.83 (Ar–H, 2H, t, 9 Hz), 8.16–8.19 (Ar–H, 2H, dd, 7.8 Hz).

^{1}H NMR of crownophane **3** with tetrabutylammonium chloride ion: δ 3.70 (C*H*$_2$–NH, 4H, t, 5.1 Hz), 3.76 (O–*CH*$_2$–CH$_2$–NH, 4H, m), 3.78 (O–*CH*$_2$–CH$_2$–O–Ar, 4H, broad s), 3.78 (=C–CH$_2$–O, 4H, broad s), 4.31 (Ar–O–*CH*$_2$–CH$_2$, 4H, m), 4.51 (C =CH$_2$, 2H, s), 7.13 (Ar–H, 2H, s), 7.24–7.28 (Ar–H, 4H, m), 7.59–7.67 (Ar–H, 4H, m), 7.82 (OH, 2H, s), 7.85 (Ar–H, 2H, t, 9 Hz), 8.21–8.24 (Ar–H, 2H, dd, 7.8 Hz).

^{1}H NMR of crownophane **3** with tetrabutylammonium dihydrogenphosphate ion: δ 3.71(C*H*$_2$–NH, 4H, t, 4.2 Hz), 3.74 (O–*CH*$_2$–CH$_2$–NH, 4H, m), 3.78 (O–*CH*$_2$–CH$_2$–O–Ar, 4H, broad s), 3.78 (=C–CH$_2$–O, 4H, broad s), 4.30 (Ar–O–*CH*$_2$–CH$_2$, 4H, m), 4.48 (C =CH$_2$, 2H, s), 5.90 (Guest–H + H$_2$O), 7.07 (Ar–H, 2H, s), 7.22–7.25 (Ar–H, 4H, m), 7.56–7.59 (Ar–H, 2H, m), 7.64–7.67 (Ar–H, 2H, m), 7.79 (Ar–H, 2H, t, 7.2 Hz), 8.16 (Ar–H, 2H, d, 7.5 Hz), 9.68 (NH, 2H, broad s).

^{1}H NMR of crownophane **3** with tetrabutylammonium acetate ion: δ 3.68–3.72 (O–*CH*$_2$–C*H*$_2$–NH, 8H, m), 3.73–3.77 (O–*CH*$_2$–CH$_2$–O–Ar, 4H, m), 3.79 (=C–CH$_2$–O, 4H, broad s), 4.32 (Ar–O–*CH*$_2$–CH$_2$, 4H, m), 4.53 (C–CH$_2$, 2H, broad s), 7.14 (Ar–H, 2H, s), 7.24–7.25 (Ar–H, 4H, m), 7.59–7.67 (Ar–H, 4H, m), 7.89 (Ar–H, 2H, t, 7.2 Hz), 8.25 (Ar–H, 2H, d, 7.8 Hz), 9.26 (NH, 2H, broad s).

^{1}H NMR of crownophane **4** with tetrabutylammonium fluoride ion: δ 3.66 (C*H*$_2$–NH, 4H, t, 5.1 Hz), 3.81 (O–*CH*$_2$–CH$_2$–NH, 4H, t, 4.8 Hz), 3.91 (O–*CH*$_2$–CH$_2$–O–Ar, 4H, broad s), 3.91 (=C–CH$_2$–O, 4H, broad s), 4.24 (Ar–O–*CH*$_2$–CH$_2$, 4H, m), 4.52 (C =CH$_2$, 2H, s), 7.03 (Ar–H, 2H, s), 7.19–7.24 (Ar–H, 4H, m), 7.40 (Ar–H, 1H, t, 15.6 Hz), 7.60–7.62 (Ar–H, 2H, dd, 7.2 Hz), 7.72–7.75 (Ar–H, 2H, dd, 7.2 Hz), 7.98–8.01 (Ar–H, 2H, dd, 7.8 Hz), 8.59 (Ar–H, 1H, s).

^{1}H NMR of crownophane **4** with tetrabutylammonium chloride ion: δ 3.70 (C*H*$_2$–NH, 4H, m), 3.79 (O–*CH*$_2$–CH$_2$–NH, 4H, broad s), 3.79 (=C–CH$_2$–O, 4H, broad s), 3.89 (O–*CH*$_2$–CH$_2$–O–Ar, 4H, m), 4.32 (Ar–O–*CH*$_2$–CH$_2$, 4H, m), 4.41 (C =CH$_2$, 2H, broad s), 7.13 (Ar–H, 2H, s), 7.19–7.25 (Ar–H, 4H, m), 7.39 (Ar–H, 1H, t, 8.1 Hz), 7.59 (Ar–H, 4H, m), 7.75 (NH, 2H, broad s), 7.92–7.94 (Ar–H, 2H, m), 7.94 (OH, 2H, broad s), 8.64 (Ar–H, 1H, broad s).

^{1}H NMR of crownophane **4** with tetrabutylammonium dihydrogenphosphate ion: δ 3.66–3.68 (C*H*$_2$–NH, 4H, m), 3.79 (O–*CH*$_2$–CH$_2$–NH, 4H, broad s), 3.79 (=C–CH$_2$–O, 4H, broad s), 3.87 (O–*CH*$_2$–CH$_2$–O–Ar, 4H, m), 4.23 (Ar–O–*CH*$_2$–CH$_2$, 4H, m), 4.42 (C =CH$_2$, 2H, broad s), 5.09 (Guest–H + H$_2$O), 7.03 (Ar–H, 2H, s), 7.21–7.24 (Ar–H, 4H, m), 7.34 (Ar–H, 1H, t, 6.9 Hz), 7.58–7.66 (Ar–H, 4H, m), 7.91–7.94 (Ar–H, 2H, m), 8.51 (NH, 2H, broad s), 8.65 (Ar–H, 1H, s).

^{1}H NMR of crownophane **4** with tetrabutylammonium acetate ion: δ 3.69 (C*H*$_2$–NH, 4H, t, 4.8 Hz), 3.78 (O–*CH*$_2$–CH$_2$–NH, 4H, t, 4.8 Hz), 3.82 (=C–CH$_2$–O, 4H, broad s), 3.84–3.86 (O–*CH*$_2$–CH$_2$–O–Ar, 4H, m), 4.30–4.32 (Ar–O–*CH*$_2$–CH$_2$, 4H, m), 4.42 (C =CH$_2$, 2H, broad s), 7.12 (Ar–H, 2H, s), 7.22–7.25 (Ar–H, 4H, m), 7.38 (Ar–H, 1H, t, 7.5 Hz), 7.61–7.64 (Ar–H, 4H, m), 7.90–7.93 (Ar–H, 2H, dd, 7.55 Hz), 8.24 (NH, 2H, broad s), 8.62 (Ar–H, 1H, s).

Measurement of ^{1}H NMR titration experiment

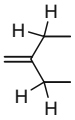
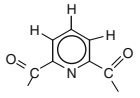
A solution of 0.05 mmol of guest molecules and 0.5 ml of $CDCl_3$ was prepared in a sample vial. A solution of 0.005 mmol of host molecules and 0.5 ml of $CDCl_3$ was prepared in a NMR sample tube. From the solution of the guest molecules, 5 μl of solution, respectively were mixed up with fixed amount (0.005 mmol) of host molecules containing 0.5 ml of $CDCl_3$.

Assuming 1:1 stoichiometry for the complexation of guest (G) with host (H), the complexation can be expressed by the Equation (1).

$$\mathrm{H} + \mathrm{G} \overset{\leftarrow \mathrm{K}}{\Longrightarrow} \mathrm{HG} \tag{1}$$

$$\mathrm{K} = \frac{[\mathrm{HG}]}{[\mathrm{H}][\mathrm{G}]}$$

Table 1. ^{1}H NMR chemical shift values between free ligand (**3**) and ligand (**3**) with guest molecules

Ligand **3**/ ligand **3** with guest molecules			–OH	Ethylene glycol chain Ar–O–CH_2–CH_2–	–NH–CH_2–CH_2–			Chemical shift of guest molecules
3	4.55 (2H, s)	3.68 (4H, s)	7.06 (2H, s)	4.39 (4H, m)	3.64 (12H, m)	8.56 (2H, s)	8.00 (1H, t) 8.38 (2H, d)	
+ $Bu_4N^+F^-$	4.58	3.87	*1	4.26 (m) 3.70 (t)	3.68 (t)	*2	7.83 8.17	
+ $Bu_4N^+Cl^-$	4.51	3.78	7.82	4.31	3.75 3.70 (t)	9.25	7.83 8.23	
+ $Bu_4N^+H_2PO_4^-$	4.48	3.78	*1	4.30	3.74 (m) 3.71 (t)	9.68	7.8 (t) 8.16 (d)	5.90 5.21 (free state)
+ $Bu_4N^+AcO^-$	4.53	3.79	*1	4.32	3.76 (m) 3.71 (d) 3.68 (t)	9.27	7.89 (t) 8.25 (d)	

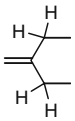
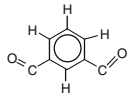
*1 and *2: Peak of hydroxy and amide groups of the ligand **1** disappeared after addition of the guest molecules. This is probably due to the severe broadening of those groups after complexation.

The stability constants (*K*s) of the complex formed can be calculated from the analysis of the sequential changes in chemical shifts ($\Delta\delta$) at varying guest concentration by using a non-linear least squares curve-fitting method.

Association constant determination

General method. A 0.005 mmol of the host molecule was dissolved in 0.5 ml of $CDCl_3$ containing 0.03 wt% of reference standard (Me_4Si) in a NMR tube to be arranged to 0.01 M solution. A 0.05 mmol of the guest molecule was dissolved in 0.5 ml of $CDCl_3$ to be arranged to 0.1 M solution, too. First, the NMR spectrum of the original host solution was recorded on a 300 MHz spectrometer at 298 K. Then 5.0 μl of guest solution was added into the tube of the original host solution, and the NMR spectrum of the solution was recorded after keeping overnight. Adding a portion of each 5.0 μl of the guest solution means that the guest concentration increases each 0.1 M equivalent toward the host concentration. The chemical shifts of the amide NH protons of the host molecules were observed upon the addition of up to 3 equivalent of the guest molecules. The volume of the solution was kept to calculate the binding constant. The variation of the chemical shifts of the amide NH proton ($\Delta\delta_{obs} = \delta_{app} - \delta_{free}$) on the complexation of the free ligand with amines was plotted toward the concentration of anions, where δ_{free} and δ_{app} express the chemical shift of the free ligand and the apparent chemical shift of the ligand in the presence of anions, respectively. The binding constant was determined from the titration curve using curve fitting method by Kaleida Graph.

Table 2. ^{1}H NMR chemical shift values between free ligand (**4**) and ligand (**4**) with guest molecules

Ligand **4**/ ligand **4** with guest molecules			–OH	Ethylene glycol chain Ar–O–CH_2–CH_2–	–NH–CH_2–CH_2–			Chemical shift of Guest Molecules
4	4.41 (2H, s)	3.69 (4H, s)	6.89 (2H, s)	4.38 (m) 3.83 (m)	3.68 (m)	6.87 (2H, s)	8.35 (1H, s) 7.74–7.77 (2H, dd)	
+ $Bu_4N^+F^-$	4.52	3.91	*1	4.24 (m) 3.81 (t)	3.66 (t)	*2	8.59 7.98–8.01 7.40	
+ $Bu_4N^+Cl^-$	4.41	3.79	7.94	4.32 3.88	3.79 (bs) 3.70 (t)	7.75	8.64 7.92–7.94 (m)	
+ $Bu_4N^+H_2PO_4^-$	4.42	3.79	*1	4.23 (m) 3.87 (m)	3.66– 3.68 (m)	8.51	8.65 7.92–7.94	5.09 5.21 (free state)
+ $Bu_4N^+AcO^-$	4.42	3.82	*1	4.30–4.32 (m) 3.84–3.86 (m)	3.77 (t) 3.69 (t)	8.24	8.62 7.91–7.93	

*1 and *2: Chemical shifts of these protons were not possible to detect probably due to the severe broadening after addition of the guest molecules.

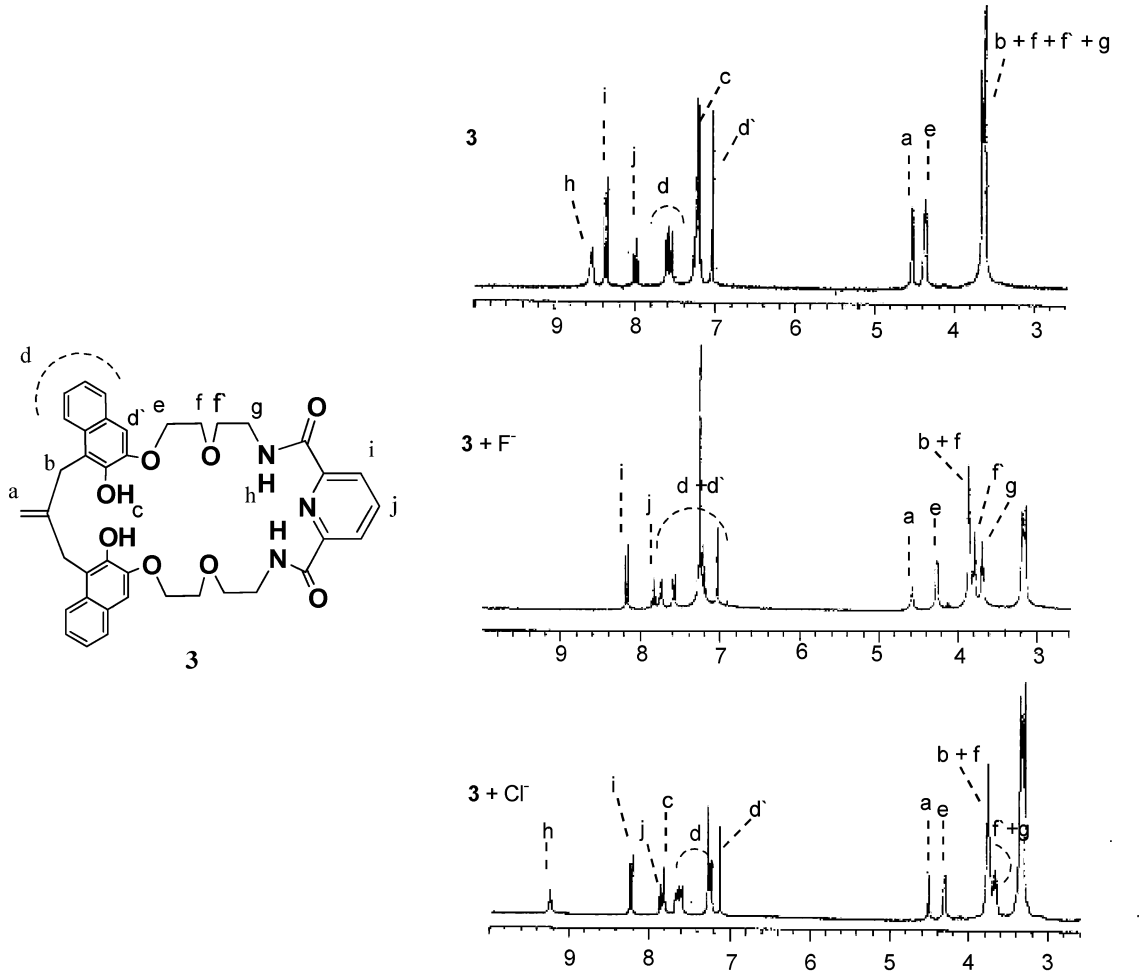


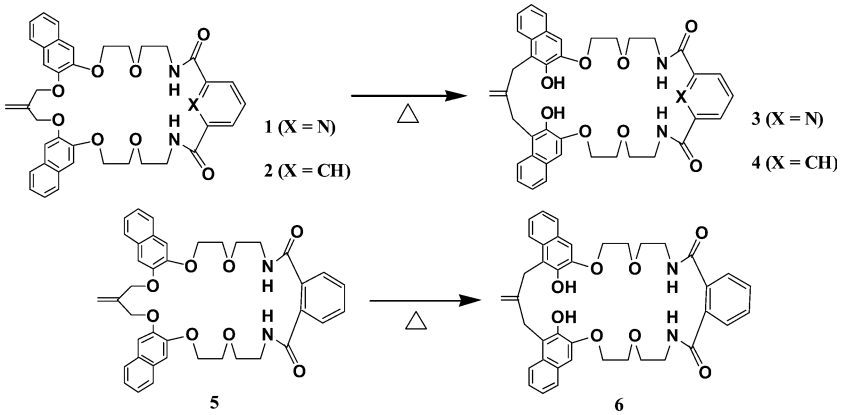
Figure 1. ^{1}H NMR spectra of crownophane **3** and **3** with $Bu_4N^+X^-$ ($X = F^-$, Cl^-).

Results and discussion

In this study, we used three amidocrownophanes **3**, **4**, and **6** in order to compare either the hetero-atom effect or ring size effect, where **3** and **4** have 28-membered ring and **6** has 27-membered ring, all of which were recently prepared in the same manner [8]. For comparison of recognition properties toward anion guest species, the corresponding macrocyclic polyethers, **1**, **2**, and **5** having amide groups before TCR were also used.

Complexation with anions

We carried out complexations of macrocyles **1**–**6** with tetrabutylammonium salts of halides (F^-, Cl^-, Br^- and I^-), $H_2PO_4^-$ and AcO^- using the NMR technique in $CDCl_3$. In order to exclude the influence of cations, tetrabutylammonium ion was used as a counter cation of the guest anions for the investigation of the anion recognition behaviors. In each of the NMR sample tubes, we mixed up the macrocycles and the guest



Scheme 1.

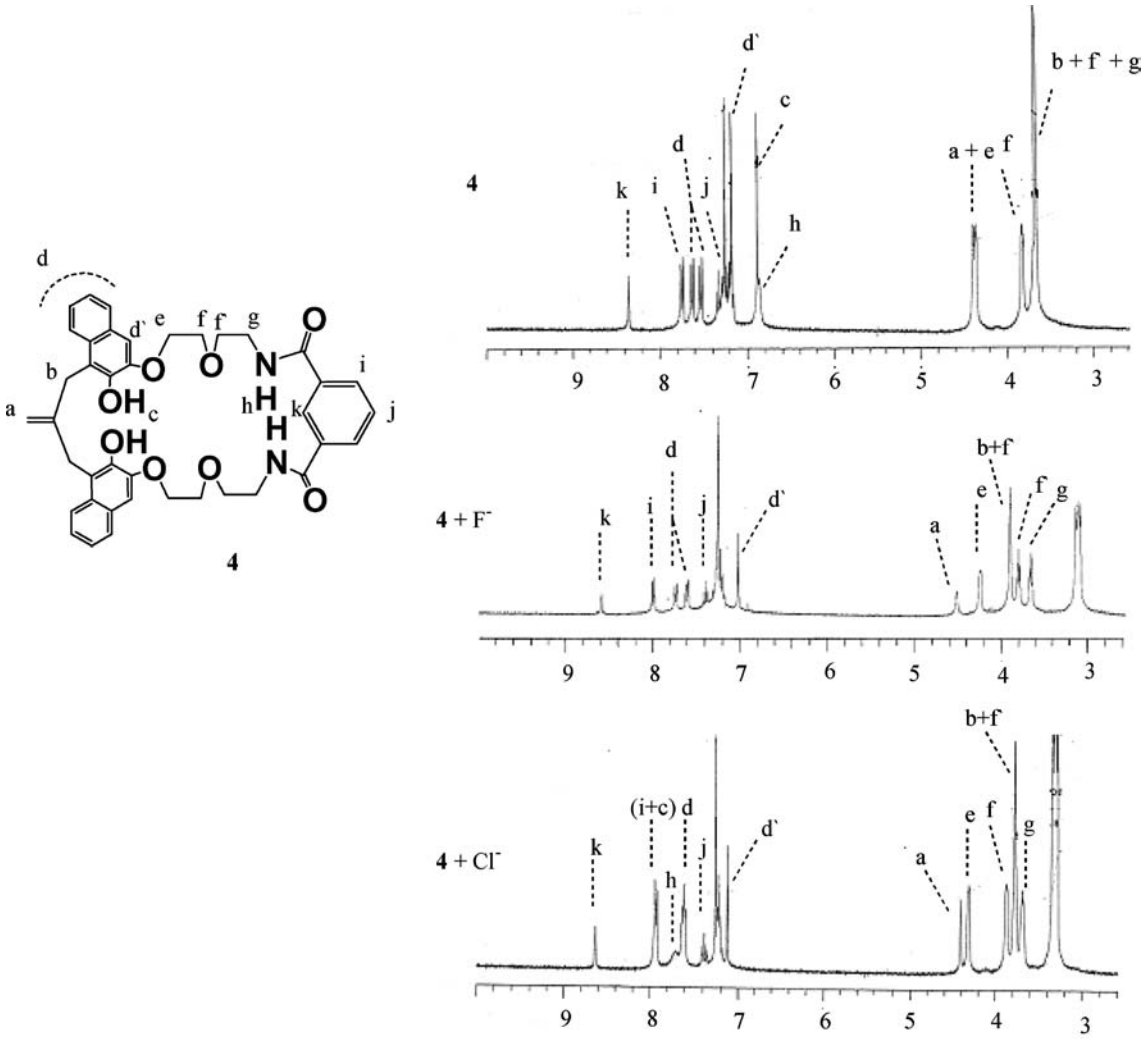


Figure 2. ^{1}H NMR spectra of crownophane **4** and **4** with $Bu_4N^+X^-$ ($X = F^-$, Cl^-).

species in $CDCl_3$, respectively. After sonification of the NMR sample, and keeping the sample tubes for overnight, we measured ^{1}H NMR of them and obtained the following results which have been shown in Tables 1 and 2. Upon addition of anions, downfield shift of the N–H protons, severe broadening of the O–H protons, significant splitting of the NH–CH_2 protons of **3** and **4** were observed clearly. For example, upon addition of chloride ions into the hosts **3** and **4**, significant down field shifts of the amide N–H protons ($\Delta\delta = 0.69$ ppm in the case of **3**; $\Delta\delta = 0.86$ ppm in the case of **4**) were observed. We also observed clear splitting of the NH–CH_2 protons and broadness of the undetected protons of OH, downfield shifts of the aromatic protons of the *o*-phenyl group in the case of host **4** which are shown in Figures 1 and 2. Similarly, in the presence of dihydrogenphosphate and acetate ions with both **3** and **4**, we noticed the large downfield shifts of amide N–H protons {($\Delta\delta = 1.12$ ppm due to $H_2PO_4^-$ in the case of **3**; $\Delta\delta = 1.64$ ppm due to $H_2PO_4^-$ in the case of **4**) ($\Delta\delta = 0.71$ ppm AcO^- in the case of **3**; $\Delta\delta = 1.37$ ppm due to Aco^- in the case of **4**)}, deep broadness of OH protons, significant splitting of NH–CH_2 protons and downfield shifts of the aromatic protons in the case of host **4** which are shown in Figures 3 and 4.

This information from the NMR spectra reveal the unique hydrogen bonding among the amide protons, hydroxy groups and the aromatic protons of the hosts **3** and **4** with the above mentioned anions. From the NMR measurement experiment, large chemical shift values were observed by the complexation of the crownophanes **3** and **4** with $H_2PO_4^-$ anion. Therefore, upon comparison of the complexation abilities of illustrated anions, $H_2PO_4^-$ is more pronounced than the others. In fact, protons of crownophanes (**3** and **4**) after addition of guest species obviously shifted in the ^{1}H NMR spectra which are summarized in Tables 1 and 2.

On the other hand, crownophane **6** did not show any change in the NMR spectrum when adding the selected anions. Therefore, it is assumed that there is some structural effect among them. It should be noted that *m*-substituted phenyl group containing crownophane **4** allows those anions to be incorporated into the cavity,

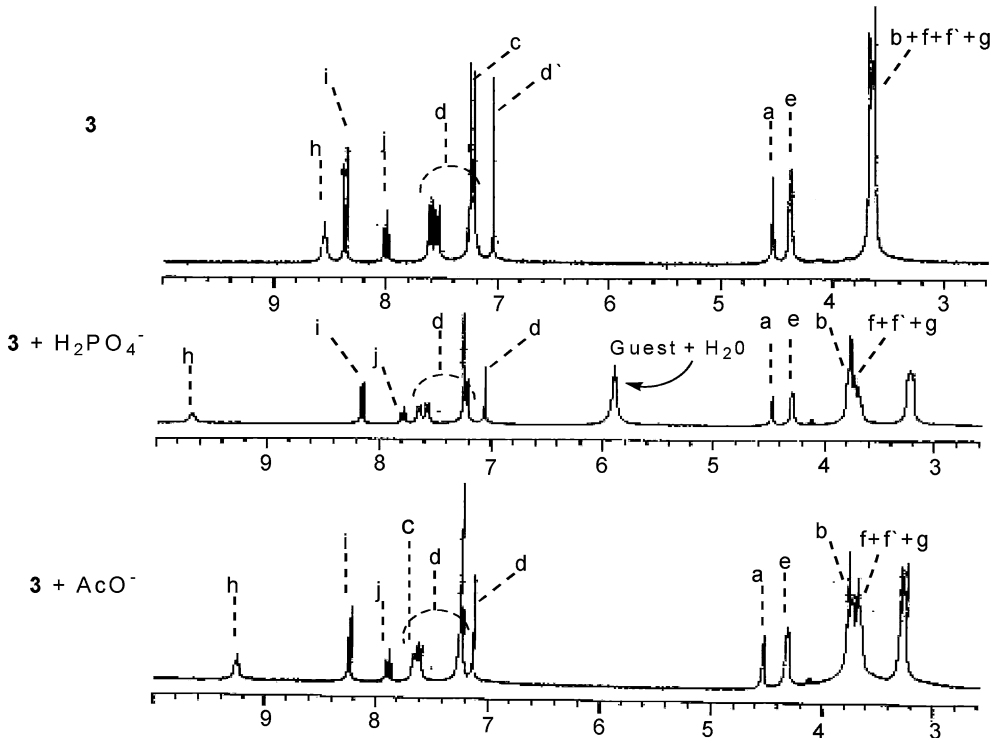


Figure 3. ^{1}H NMR spectra of crownophane **3** and **3** with $Bu_4N^+H_2PO_4^-$ and $Bu_4N^+AcO^-$.

while *o*-substituted phenyl group containing crownophane **6** does not. Crownether derivatives **1**, **2**, and **5** did not show any change in the NMR spectra when adding the anions. This phenomenon projects the lack of strong donating part such as hydroxy groups which are generated by "tandem Claisen rearrangement (TCR)".

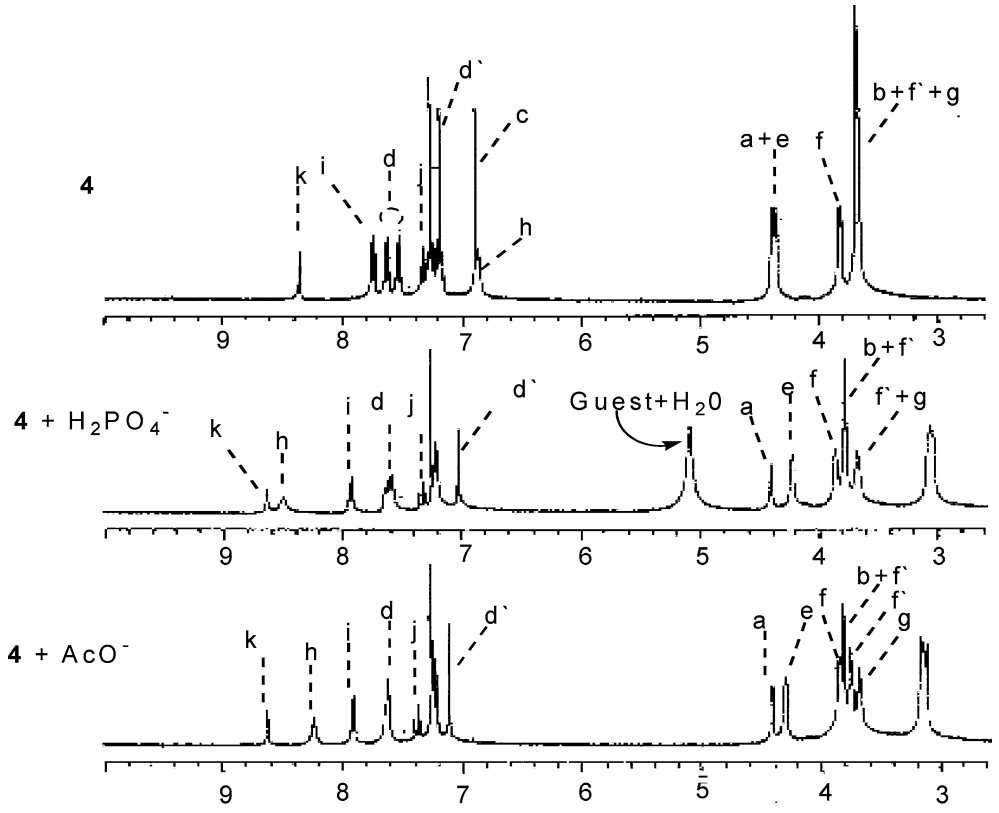


Figure 4. ^{1}H NMR spectra of crownophane **4** and **4** with $Bu_4N^+H_2PO_4^-$ and $Bu_4N^+AcO^-$.

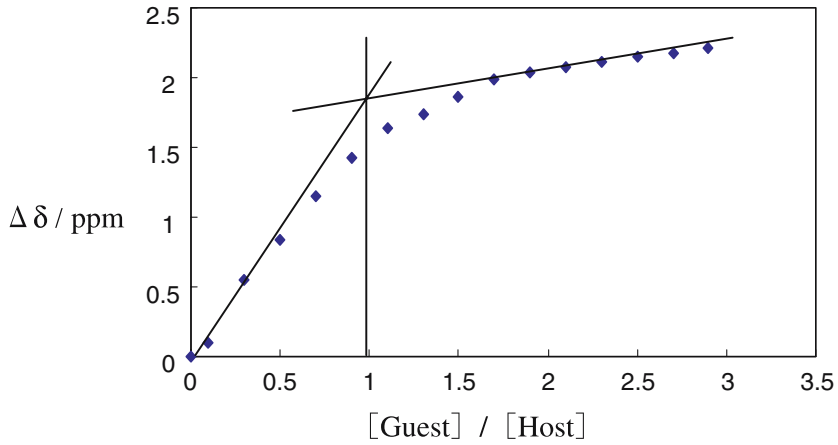


Figure 5. ^{1}H NMR titration experiment between ligand **4** and $H_2PO_4^-$ in $CDCl_3$.

Table 3. Association constants (M^{-1}) of ligand **4** with tetrabutylammonium salts at ambient temperature

Anions	Association constants of crownophane **4**
F^-	2.56×10^2
Cl^-	1.09×10^2
$H_2PO_4^-$	4.42×10^2
AcO^-	1.31×10^2

In order to prove the above hypothesis, crownophane **4** and its anion binding ability using the above mentioned anions were studied by ^{1}H NMR titration experiment. In all cases, the data were indicative of 1:1 (receptor:anion) complex formation. On comparison of the association constants between ligand **4** and the anions, it is found that binding ability of $H_2PO_4^-$ is larger than the others (see Table 3). The ^{1}H NMR titration experimental results in the case of complexation with $H_2PO_4^-$ are shown in Figure 5 and reveal that crownophane **4** selectively bind $H_2PO_4^-$ ion rather than AcO^-, F^-, and Cl^- ions. Besides, the binding constants for bromide and iodide are negligible.

In conclusion, we have demonstrated that 28-membered ring atoms containing novel crownophanes **3** and **4** acting as the receptor for anions such as $H_2PO_4^-$, AcO^- and Cl^- based on the rigid disposition of hydrogen bonding groups in the interior of the macrocyclic scaffold. On the contrary, crownethers **1**, **2**, and **5** have no incorporation ability due to the absence of the hydroxy group indicates that hydroxy group plays an important role to form effective complex. We also showed that crownophane **6** does not have any complexation ability with the selected anions under the same conditions. It is assumed that there is some structural effect among crownophanes **3**, **4**, and **6**. Our synthesized receptors could be active in the case of biologically relevant phosphate, and carboxylate derivatives, and the synthesis of the respective receptors for these anions could be achieved through the design of different structure in the future.

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