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Metal Ion Guest Responsive Benzoxazine Dimers and Inclusion Phenomena of Cyclic Derivatives *

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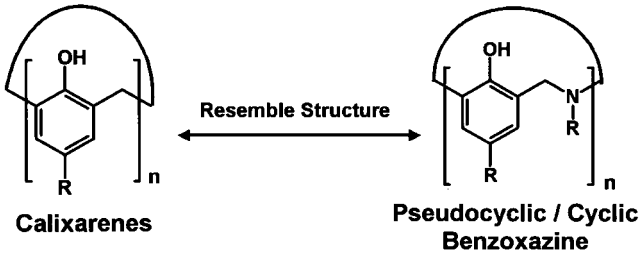
Abstract

A series of benzoxazine dimers (**1–9**), esterified benzoxazine dimers (**10–18**), and benzoxazine dimer based macrocyclic derivatives (**19–22**) are prepared. The metal ion guest responsive properties of the benzoxazine dimers obtained are clarified by using Pedersen's technique. The ion extractions of the benzoxazine dimers are controlled by the bulkiness of the functional group at the aza position. The ones with cyclohexyl bulky groups at the aza position, **7–9**, are two times higher than those with methyl groups, **1–3**. The extractions are close to 100% for esterified dimers (**10–18**). For the macrocyclic derived dimers, the ether cyclic derivatives, **21-22**, interact with sodium, potassium and cesium ions at stoichiometric ratios 2:1 and 1:1 depending on the metal species, as evidenced from ^{1}H-NMR.



Scheme 1.

Introduction

For the past three decades, host–guest compounds or inclusion compounds have received much attention mainly due to the information obtained from interactions at the molecular level [1–2] observed by a variety of characterization techniques. The induced molecular recognition properties are known to be based on non-covalent interactions, or secondary forces, such as van der Waals, dipole–dipole interaction, π–π stacking, and hydrogen bonding between host and guest [1–3]. Many of the host molecules were designed either with specific functional groups to form molecular assemblies or definite macrocyclic structures, in order to achieve novel functional supramolecules.

Polybenzoxazine is a new type of phenolic resin with superb mechanical and thermal properties [4]. Most of the studies on these materials have concentrated on difunctional benzoxazines with the objective of improving the processing conditions of thermosetting materials. In our studies of open-ring benzoxazines [5], we originally proposed that the basic unit is close to that of calixarenes but with an aza methylene linkage in between (Scheme I). Hence, the open-ring benzoxazines can be expected to have properties similar to that of calixarenes. In order to clarify whether the open-ring benzoxazines show inclusion properties and to understand the phenomena related to the structure, a series of the controlled structure benzoxazines dimers were prepared [6–7]. High yield (80%) was obtained from a single step ring opening reaction of benzoxazine monomer. We also extended the work to the [2+2] macrocyclic dimers via esterification and etherification [7–10].

The benzoxazine dimer is an appropriate model to use since there is no complication due to the chain length. Moreover, a series of derivatives can be prepared which enables systematic studies to be done on the inclusion properties related to the chemical structure. The present article is aimed at exploring host–guest interactions of benzoxazine on the basis of the interaction between aza methylenephenol unit and metal ions.

Experimental

Materials

Barium chloride, lithium hydroxide and deuterated chloroform ($CDCl_3$) were purchased from Fluka Chemicals (Buchs, Switzerland). Sodium hydroxide, cesium carbonate, potassium hydroxide, chloroform, magnesium chloride, calcium chloride, and picric acid were the products of Ajax

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chemicals (Australia). All chemicals were analytical grade and used without further purification.

Syntheses

A series of benzoxazine dimers; *N*,*N*-bis(3,5-dimethyl-2-hydroxybenzyl)methylamine **1**, *N*,*N*-bis(5-methyl-2-hydroxybenzyl)methylamine **2**, *N*,*N*-bis(5-ethyl-2-hydroxybenzyl)methylamine **3**, *N*,*N*-bis(3,5-dimethyl-2-hydroxybenzyl)propylamine **4**, *N*,*N*-bis(5-methyl-2-hydroxybenzyl) propylamine **5**, *N*,*N*-bis(5-ethyl-2-hydroxybenzyl)propylamine **6**, *N*,*N*-bis(3,5-dimethyl-2-hydroxybenzyl)cyclohexylamine **7**, *N*,*N*-bis(5-methyl-2-hydroxybenzyl)cyclohexylamine **8**, *N*,*N*-bis(5-ethyl-2-hydroxybenzyl)cyclohexylamine **9**, were prepared as reported elsewhere [6–7] and used as starting materials (Scheme II).

Preparation of
*N,N-bis(2-benzoyl-3,5-dimethylbenzyl)methylamine **10**,*
*N,N-bis(2-benzoyl-5-methylbenzyl)methylamine **11**,*
*N,N-bis(2-benzoyl-5-ethylbenzyl) methylamine **12**,*
*N,N-bis(2-benzoyl-3,5-dimethylbenzyl)propylamine **13**,*
*N,N-bis(2-benzoyl-5-dimethylbenzyl)propylamine **14**,*
*N,N-bis(2-benzoyl-5-ethylbenzyl) propylamine **15**,*
*N,N-bis(2-benzoyl-3,5-dimethylbenzyl)cyclohexylamine **16**,*
*N,N-bis(2-benzoyl-5-ethylbenzyl)cyclohexylamine **17**,*
*N,N-bis(2-benzoyl-5-ethylbenzyl) cyclohexylamine **18***

Benzoxazine dimer **1** (5 mmol) was dissolved in dichloromethane (50 mL) followed by the addition of NaOH (20 mmol) in water (50 mL). The mixture was stirred vigorously at room temperature for 30 min and a solution of benzoyl chloride (10 mmol) in dichloromethane (CH_2Cl_2, 50 mL) was added dropwise for 1 h. The reaction was allowed to proceed at room temperature for 6 h. The CH_2Cl_2 phase was collected and extracted with water several times. The product was dried over sodium sulfate and the solvent removed to obtain a white product of **10**. Similarly, **11–18** were prepared as for **10** with the starting materials **2–9**, respectively. The products obtained were characterized by FTIR, ^{1}H NMR, and EA.

Compound **10**: 95% yield; clear and colorless crystal; mp. 158–159 °C; FTIR (KBr, cm^{-1}): 1737 (vs, C=O), 1484 (s, tetrasubstituted benzene), 1265 (vs, C–N stretching). ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ_H 2.05 (3H, s, N–CH_3), 2.15 (6H, s, Ar–CH_3), 2.30 (6H, s, Ar–CH_3), 3.35 (4H, s, Ar–CH_2–N), 6.98 (2H, s, Ar–H), 7.05 (2H, s, Ar–H), 7.45 (4H, t, Ar–H), 7.62 (2H, t, Ar–H), 8.20 (4H, d, Ar–H). Anal. calcd for $C_{33}H_{33}NO_4$: C, 78.11; H, 6.51; and N, 2.76. Found: C, 77.99; H, 6.54; and N, 2.78.

Compound **11**: 95% yield; clear and colorless crystal; mp.151–152 °C; FTIR (KBr, cm^{-1}): 1738 (vs, C=O), 1499 (s, trisubsubstited benzene), 1266 (vs, C–N stretching). ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ_H 2.05 (3H, s, N–CH_3), 2.30 (6H, s, Ar–CH_3), 3.45 (4H, s, Ar–CH_2–N), 6.98 (2H, d, Ar–H), 7.05 (2H, s, Ar–H), 7.10 (2H, d, Ar–H), 7.45 (4H, t, Ar–H), 7.62 (2H, t, Ar–H), 8.20 (4H, d, Ar–H). Anal. calcd for $C_{31}H_{29}NO_4$: C, 77.66; H, 6.05; and N, 2.92. Found: C, 77.71; H, 6.12; and N, 2.89.

Compound **12**: 95% yield; clear and colorless crystal; mp. 153–154 °C; FTIR (KBr, cm^{-1}): 1738 (vs, C=O), 1498 (s, trisubsubstited benzene), 1264 (vs, C–N stretching). ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ_H 1.25 (6H, t, Ar–CH_2–**CH_3**), 2.05 (3H, s, N–CH_3), 2.65 (4H, q, Ar–**CH_2**–CH_3), 3.45 (4H, s, Ar–CH_2–N), 6.98 (2H, d, Ar–H), 7.05 (2H, s, Ar–H), 7.10 (2H, d, Ar–H), 7.45 (4H, t, Ar–H), 7.62 (2H, t, Ar–H), 8.20 (4H, d, Ar–H). Anal. calcd for $C_{33}H_{33}NO_4$: C, 78.11; H, 6.51; and N, 2.76. Found: C, 78.12; H, 6.48; and N, 2.73.

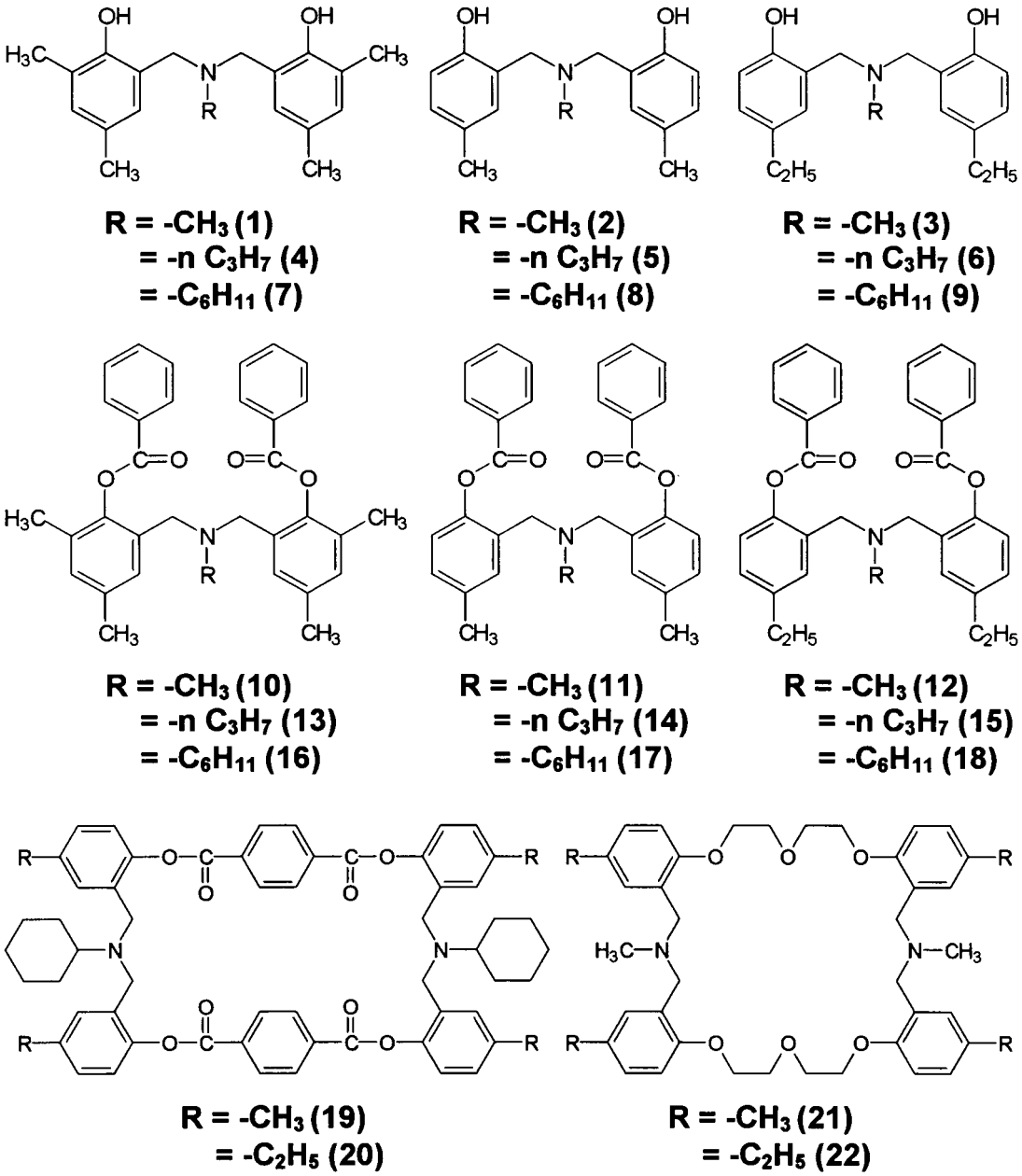
Compound **13**: 95% yield; clear and colorless crystal; mp. 161–162 °C; FTIR (KBr, cm^{-1}): 1734 (vs, C=O), 1498 (m, tetrasubstituted benzene), 1264 (s, C–N stretching). ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ_H 0.75 (3H, t, N–CH_2–CH_2–**CH_3**), 1.45 (2H, m, N–CH_2–**CH_2**-CH_3), 2.10 (6H, s, Ar–CH_3), 2.22 (6H, s, Ar–CH_3), 2.35 (2H, t, N–**CH_2**–CH_2–CH_3), 3.45 (4H, s, Ar–CH_2–N), 6.98 (2H, d, Ar–H), 7.05 (2H, s, Ar–H), 7.10 (2H, d, Ar–H), 7.45 (4H, t, Ar–H), 7.62 (2H, t, Ar–H), 8.20 (4H, d, Ar–H). Anal. calcd for $C_{35}H_{37}NO_4$: C, 78.50; H, 6.92; and N, 2.62. Found: C, 78.48; H, 6.87; and N, 2.65.

Compound **14**: 95% yield; clear and colorless crystal; mp. 154–155 °C; FTIR (KBr, cm^{-1}): 1737 (vs, C=O of ester), 1497 (m, trisubstituted benzene), 1268 (vs, C–N stretching). ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ_H 0.75 (3H, t, N–CH_2–CH_2–**CH_3**), 1.45 (2H, m, N–CH_2–**CH_2**–CH_3), 2.18 (6H, s, Ar–CH_3), 2.35 (2H, t, N–**CH_2**–CH_2–CH_3), 3.45 (4H, s, Ar–CH_2–N), 6.98 (2H, d, Ar–H), 7.05 (2H, s, Ar–H), 7.10 (2H, d, Ar–H), 7.45 (4H, t, Ar–H), 7.62 (2H, t, Ar–H), 8.20 (4H, d, Ar–H). Anal. calcd for $C_{33}H_{33}NO_4$: C, 78.11; H, 6.51; and N, 2.76. Found: C, 78.07; H, 6.46; and N, 2.78.

Compound **15**: 95% yield; clear and colorless crystal; mp. 158–159 °C; FTIR (KBr, cm^{-1}): 1734 (vs, C=O), 1497 (m, trisubstituted benzene), 1267 (vs, C–N stretching). ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ_H 0.75 (3H, t, N–CH_2–CH_2–**CH_3**), 1.25 (6H, t, Ar–CH_2–**CH_3**), 1.45 (2H, m, N–CH_2–**CH_2**–CH_3), 2.35 (2H, t, N–**CH_2**–CH_2–CH_3), 2.65 (4H, q, Ar–**CH_2**–CH_3), 3.45 (4H, s, Ar–CH_2-N), 6.98 (2H, d, Ar–H), 7.05 (2H, s, Ar–H), 7.10 (2H, d, Ar–H), 7.45 (4H, t, Ar–H), 7.62 (2H, t, Ar–H), 8.20 (4H, d, Ar–H). Anal. calcd for $C_{35}H_{37}NO_4$: C, 78.50; H, 6.92; and N, 2.62. Found: C, 78.53; H, 6.90; and N, 2.59.

Compound **16**: 95% yield; clear and colorless crystal; mp. 171–172 °C; FTIR (KBr, cm^{-1}): 1731 (vs, C=O), 1482 (s, tetrasubstituted benzene), 1265 (vs, C–N stretching). ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ_H 1.1 (4H, m, CH2), 1.60 (2H, m, CH_2), 1.82 (4H, dt, CH_2), 2.05 (3H, s, N–CH_3), 2.15 (6H, s, Ar–CH_3), 2.60 (1H, t, CH), 3.35 (4H, s, Ar–CH_2–N), 6.98 (2H, s, Ar–H), 7.05 (2H, s, Ar–H), 7.45 (4H, t, Ar–H), 7.62 (2H, t, Ar–H), 8.20 (4H, d, Ar–H). Anal. calcd for $C_{38}H_{41}NO_4$: C, 79.30; H, 7.13; and N, 2.43. Found: C, 79.28; H, 7.11; and N, 2.47.

Compound **17**: 95% yield; clear and colorless crystal; mp. 163–164 °C; FTIR (KBr, cm^{-1}): 1738 (vs, C=O), 1497 (m, trisubstituted benzene), 1267 (vs, C–N stretching). ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ_H 1.1 (4H, m, CH_2), 1.60 (2H, m, CH_2), 1.82 (4H, dt, CH_2), 2.40 (6H, s, Ar–**CH_3**), 2.50 (1H, t, CH), 3.55 (4H, s, Ar–**CH_2**–N), 6.98 (2H, d, Ar–



Scheme 2.

H), 7.05 (2H, s, Ar–H), 7.10 (2H, d, Ar–H), 7.45 (4H, t, Ar–H), 7.62 (2H, t, Ar–H), 8.20 (4H, d, Ar–H). Anal. calcd for $C_{36}H_{37}NO_4$: C, 78.98; H, 6.76; and N, 2.56. Found: C, 78.88; H, 6.78; and N, 2.55.

Compound **18**: 95% yield; clear and colorless crystal; mp. 166–167 °C; FTIR (KBr, cm^{-1}): 1737 (vs, C=O), 1498 (m, trisubstituted benzene), 1267 (vs, C–N stretching). ^1H NMR (200 MHz, $CDCl_3$, ppm): δ_H 1.1 (4H, m, CH_2), 1.25 (6H, t, Ar–CH_2–**CH_3**), 1.45 (2H, m, N–CH_2–**CH_2**–CH_3), 1.60 (2H, m, CH_2), 1.82 (4H, dt, CH_2), 2.35 (2H, t, N–**CH_2**–CH_2–CH_3), 2.50 (1H, t, CH), 2.65 (4H, q, Ar–CH_2–CH_3), 3.55 (4H, s, Ar–CH_2–N), 6.98 (2H, d, Ar–H), 7.05 (2H, s, Ar–H), 7.10 (2H, d, Ar–H), 7.45 (4H, t, Ar–H), 7.62 (2H, t, Ar–H), 8.20 (4H, d, Ar–H). Anal. calcd for $C_3H_{41}NO_4$: C, 79.30; H, 7.13; and N, 2.43. Found: C, 79.27; H, 7.15; and N, 2.44.

Preparation of cyclic benzoxazines

Benzoxazine dimers based cyclic esters, **19–20**, were prepared as reported elsewhere [7–9] while benzoxazine dimers based cyclic ethers, **21–22** were reported previously [9–10].

Ion extraction property of benzoate benzoxazine dimers

Ion extraction was qualitatively and quantitatively analyzed by Pedersen's technique [1]. Benzoxazine derivatives (**1-22**) were dissolved in chloroform at 7×10^{-3}, 7×10^{-2}, 3.8×10^{-2}, 7×10^{-1}, and 3.8×10^{-1} M. Alkali and alkaline earth metal picrate aqueous solutions were prepared at 7×10^{-5} M. Both solutions were mixed and left for 10 min before determining the concentration of metal picrates. The concentration was determined using a UV-Vis Perkin-Elmer Lambda-16 Spectrophotometer at λ_{max} 354 nm (ϵ =

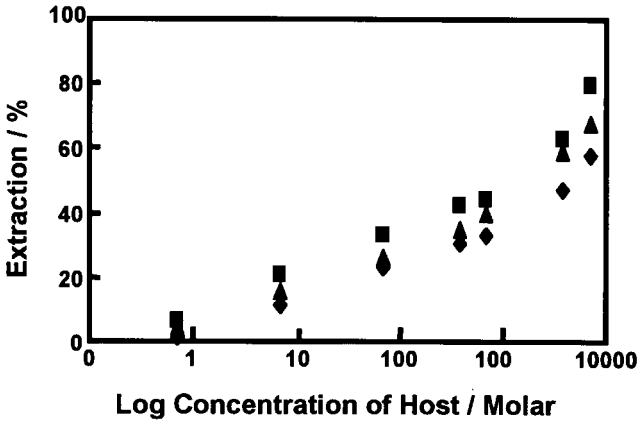


Figure 1. Extraction percentage of potassium picrate at a concentration of 7.5×10^{-5} M by (■) **1**, (♦) **2**, and (▲) **3** with various concentrations in $CHCl_3$ at 25 °.

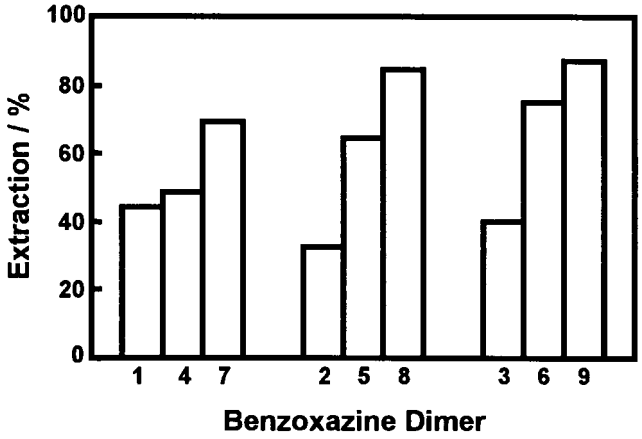


Figure 2. Extraction percentage of potassium picrate at a concentration of 7×10^{-5} M by **1–9** at the concentration of 7×10^{-2} M in $CHCl_3$ at 25 °C.

1.45×10^4 M^{-1} cm^{-1}). For cyclic derivatives, the organic phase was collected and further studied for the host–guest ratio by a ^1H NMR ACF 200 MHz of Bruker, Switzerland, using deuterated chloroform as a solvent with a trace amount of tetramethylsilane (TMS).

Results and discussion

Ion extraction

Figure 1 summarizes the ion extraction of **1–3**. The host molecules have different substituents at the ortho and para positions, while the substituted groups at the nitrogen is the methyl group. When the concentration of **1–3** increases, the extraction of potassium ion increases gradually. At equimolar concentration of host and guest (7×10^{-5} M), the extraction is ~10%. When the concentration of host is increased to 7×10^{-2} M, the extraction accomplished for ~40–50%. Hampton *et al.* [11] reported that a series of hexahomotriazacalix[3]arenes gave ion extraction percentages of less than 0.2% at host and metal picrate concentrations of 5×10^{-3} M, owing to strong intramolecular hydrogen bonding. Recently, our group [7, 12–13] reported a unique inter and intramolecular hydrogen bonded network with the dimers using X-ray structural analysis. The intramolecular hydrogen bond generates a six-membered ring [13–14] via O–H–N and is found to be one of the key factors that provides the asymmetric reaction inevitably [13].

Thus, it is conceivable that intramolecular hydrogen bonding might play an important role for **1–9**. Figure 1 also demonstrates that the ion extraction ability of dimers is achieved for only 20–40% even the host concentration was 1000 times (7×10^{-2} M) higher than that of picrate (7×10^{-5} M). Here, we speculate that the host–guest formation might form a molecular assembly controlled by hydrogen bonding. Here, **1** with two methyl substituted groups at both ortho and para positions might form a loosely assembled structure owing to the steric effect, and consequently, there may be more available space to include the guests.

Sone *et al.* [15] reported that inclusion compounds of phenol-formaldehyde oligomers is enhanced when the phenol unit has a bulky group at the para position as observed that the guest was separated from water phase via the function of oligomers. It is, therefore, reasonable to expect that **3**, which has more bulky group than **2**, shows a higher ion extraction percentage (Figure 1). The electron density of host molecules is another important factor to be considered except the bulkiness of side groups. In terms of the electron donating ability, the order is **1** > **3** > **2**. This directly correlates with the ion extraction percentage. Similarly, it was found that other alkali and alkaline earth metal ions (lithium, sodium, magnesium, calcium, and barium) gave an increase in ion extraction percentage with increasing concentration of **1–3**.

Effect of substituent groups on the aza methylene linkage

Chirachanchai *et al.* [12–13] determined the crystal structures of a series of benzoxazine dimers and found that the hydrogen bonding network and the variation of unit cell are both dependent on the substituted group at the aza linkage. Solid-state NMR studies using dimer crystals by Schnell et al. [16] supported the idea of hydrogen bonded network formation of dimers.

In order to identify the effect of substituent groups on the aza linkage in ion interaction, a series of dimers (**4–9**) were studied. As shown in Figure 2, the ion extraction percentage increased gradually when the functional groups changed from methyl to propyl and cyclohexyl groups. Compounds **4–6** (propyl group on aza linkage) show higher extraction ability than those of **1–3**. In addition, the dimers **7–9**, with cyclohexyl group, show significant extraction percentages up to 70–80%. This suggests that the bulky groups on the aza linkage enhance the ion extraction ability. Comparing **4** with **5** and **7** with **8**, it can be concluded that the substituent group on the aza linkage is more important than any other substituent group in benzoxazine dimers. The extraction ability becomes most significant when both para-substituted groups in phenol and aza units are bulky (**9**).

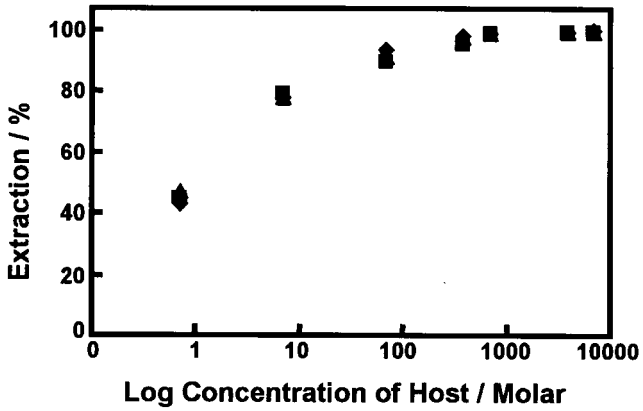


Figure 3. Extraction percentage of potassium picrate at a concentration of 7.5×10^{-5} M by (■), **10**, (♦) **11**, and (▲) **12** with various concentrations in $CHCl_3$ at 25 °C.

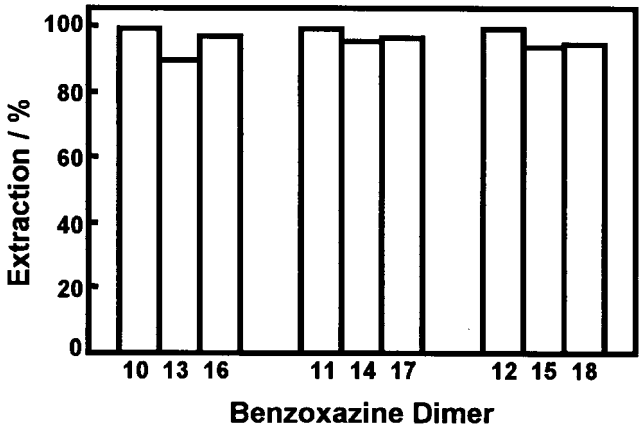


Figure 4. Extraction percentage of potassium picrate at a concentration of 7×10^{-5} M by **10–18** at the concentration of 7×10^{-2} M in $CHCl_3$ at 25 °C.

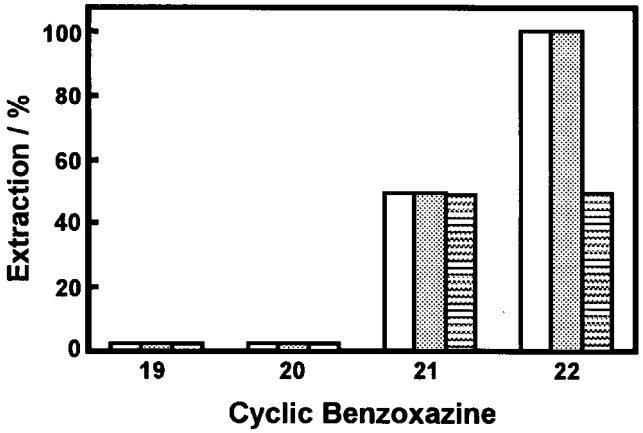


Figure 5. Extraction percentage of (□) sodium picrate, (▨) potassium picrate, and (▤) cesium picrate at a concentration of 7×10^{-5} M by **19-22** in $CHCl_3$ at 25 °C.

Symmetrical products of benzoxazine dimers by esterification

In a previous study, it was reported that the intramolecular hydrogen bond between –OH and –N– generated in each dimer is so strong that asymmetric products were formed due to the Mannich reaction [13]. In the present study, an attempt to obtain symmetric esters was carried out by using a strong base to deprotonate the hydroxyl group and eliminate the intramolecular hydrogen bond between the aza group and the OH of the phenol ring. Compounds **10–18** (Scheme II) were successfully obtained and confirmed by FTIR, ^{1}H-NMR and elemental analysis.

Effect of ester group on phenol unit

A series of compounds, **10–18**, should provide us information on how the ion extraction ability changes when the hydrogen bonded network of the dimer is eliminated. Figure 3 clearly shows that the esterified dimers **10–12** give a two-fold increase in extraction percentage over those of **1–3**. Almost all of the potassium picrate (∼100%) is extracted by **10–12** at a concentration of 7×10^{-2} M. The results suggest that the elimination of hydrogen bonds together with an increase in lone pair electrons produces a strong interaction with metal ions.

Figure 4 shows that the extraction ability of each esterified dimer **10–18** is ∼100%. In other words, the effect of esterification is strong and overcomes that of substituent groups at either the aza or phenol positions.

Speculated ion interaction system

Figures 1–4 show that the ion extraction percentages are in the 30–95% range. In other words, the nearly quantitative extraction proceeds when the concentrations of dimers are higher than those of the metal ions by a factor of 1000. Although the ion extraction ability is clarified, selectivity is rarely observed.

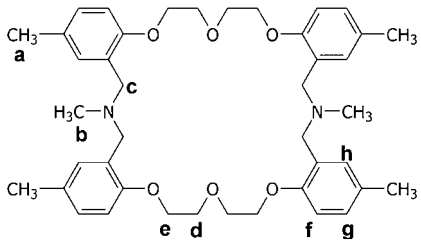
Yamagishi *et al.* [17–18] reported that the metal ion extraction accomplished by acyclic all-ortho *p-tert*-butylphenol-formaldehyde was ∼10–80% when the concentration of host was 1000 times higher than that of the guest. The proposed host–guest formation was expected to be a pseudo-cyclic molecular assembly. In our case, we speculated that the molecular assembly between metal ions and benzoxazine dimers may form and be influenced by (i) the bulky group at nitrogen, (ii) the hydrogen bonding network, and (iii) the lone electron pairs.

Stoichiometry of ion interaction of benzoxazine dimer based cyclic compounds

Figure 5 shows the extraction percentages of sodium, potassium, and cesium ions using benzoxazine dimer based macrocyclic esters (**19–20**) and macrocyclic ethers (**21–22**) determined by Pedersen's technique [1] at equimolar concentration of host and metal species. The metal ion extraction percentages for **19–20** are difficult to observe while those for **21–22** are significant (Figure 5).

Here, the important information is that the extraction percentage for each of **21–22** is either 50 or 100%, which implies a molar ratio basis in integral numbers are 2:1 and 1:1. Thus, the host–guest formations are in stoichiometric ratio.

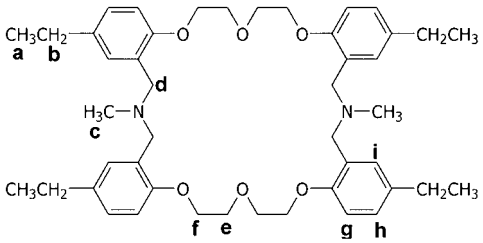
Table 1. ^{1}H NMR data of **21** and **21**-metal ion complexes



21

Position	Chemical Shift/ppm			
	21	**21**-Na^+ complex	**21**-K^+ complex	**21**-Cs^+ complex
a	2.27	2.32	2.32	2.30
b	2.21	2.25	2.25	2.25
c	3.60	3.78	3.78	3.78
d	3.87	3.85	3.78	3.78
e	4.05	3.98	3.98	4.01
f	6.95	7.02	7.02	7.01
g	6.70	6.68	6.68	6.68
h	7.21	7.15	7.18	7.18

Table 2. ^{1}H NMR data of **22** and **22**-metal ion complexes



22

Position	Chemical Shift/ppm			
	22	**22**-Na^+ complex	**22**-K^+ complex	**22**-Cs^+ complex
a	1.21	1.15	1.15	1.16
b	2.58	2.52	2.52	2.52
c	2.22	2.44	2.42	2.37
d	3.65	4.15	4.18	3.92
e	3.89	3.69	3.69	3.75
f	4.05	3.91	3.91	3.92
g	6.72	6.68	6.68	6.69
h	6.98	7.11	7.11	7.08
i	7.25	7.21	7.21	7.21

Further, ^{1}H NMR was applied to qualitatively and quantitatively study the host–guest ratio [19]. Since our studies were achieved using a liquid-liquid extraction system with picrate salt, the picrate peak at 8.8 ppm would be observed if host-metal complexes formed. In addition, the peak shifts indicate the changes of electron density in the host structure. Tables 1 and 2 clarify that δ_H values of **21–22** are shifted after extraction with picrate salts, especially the ones belonging to the methylene linkage and diethylene oxide unit. This implies that the host interacts with the metal guest via the lone pair electrons of nitrogen and oxygen atoms. It is important to note that even the type of metal ion changed; the chemical shifts for hosts (either **21** or **22**) appear at nearly the same position. This implies that the inclusion structure does not depend on the type of metal ion for both hosts (**21** and **22**).

To evaluate the molar ratio of host–guest, the peaks of picrate and aromatic protons were investigated. Compound **21** showed host–guest ratio of 2:1 for all studied ions while **22** has a ratio of 1:1 for Na^+ and K^+, and 2:1 for Cs^+ (Figures 6–7). This indicates that the macrocyclic structure affects the host-metal formation significantly. In other words, **22** with more bulky group in the para position might preferentially form 1:1 type. It was unexpected that **19** and **20** did not show any ion extraction ability. It is speculated that the unpreferable cavity in the host compound could be the reason for the lack of extraction ability; future studies are being carried out to investigate this hypothesis.

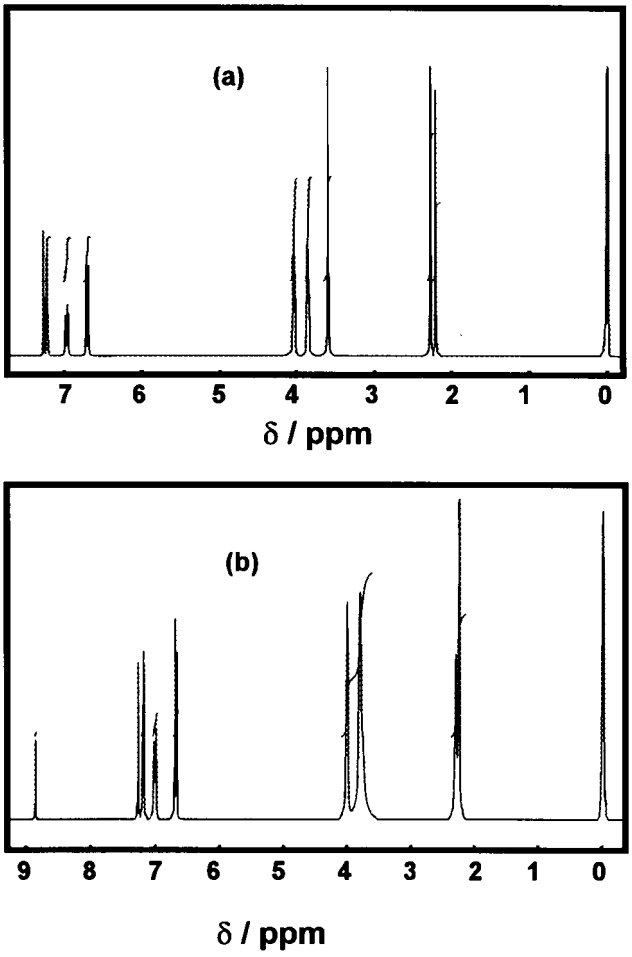


Figure 6. ^{1}H NMR spectra of (a) **21** and (b) complex of **21** and cesium ion.

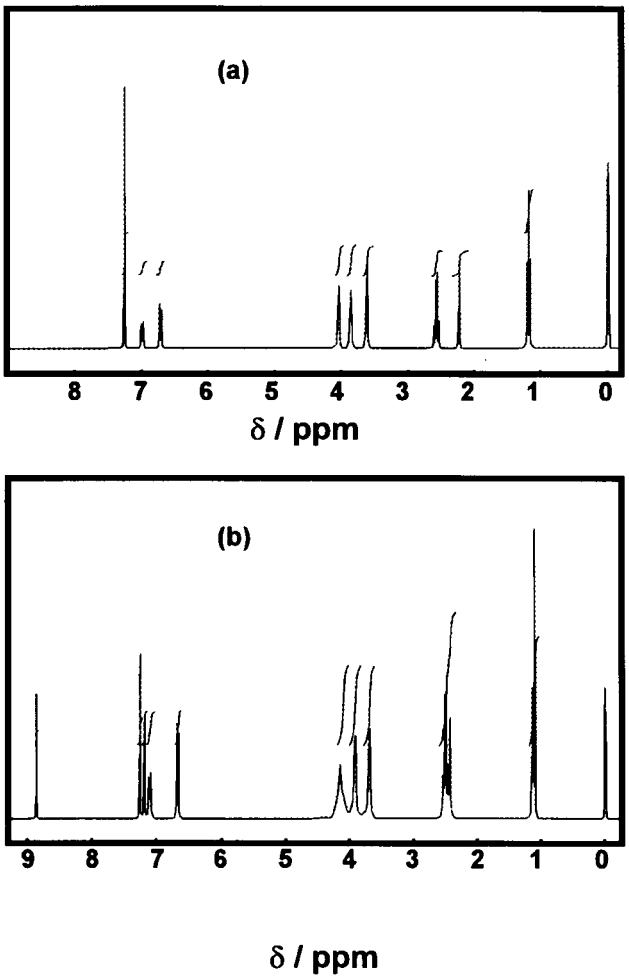


Figure 7. ^{1}H NMR spectra of (a) **22** and (b) complex of **22** and potassium ion.

Conclusions

Ion extraction studies using a series of benzoxazine dimers (**1–9**) and their esterified derivatives (**10–18**) verified that the ion interaction ability was related to (i) the inter and intramolecular hydrogen bond network (ii) the bulky group at the aza position and (iii) the number of electron lone pairs. A stoichiometric ratio between host-metal ions was observed when benzoxazine dimers were modified to be cyclic compounds. Studies on macrocyclic types (**19–22**) showed that ion interactions were involved with (i) the preferable structure of cyclic molecules, and (ii) the size of metal ions.

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