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Branching Structures of Alkali Metal Ion Responsive Supramolecules Based on Symmetric Structures of N,N-*Bis*(5-alkyl-2-hydroxybenzyl)methylamine

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This work aimed to design and synthesize the alkali metal responsive supramolecules based on symmetric structures of N,N-*bis*(5-alkyl-2-hydroxybenzyl)methylamine. Novel branching structures of products, such as, N,N-*bis*-[5-methyl-2-(1',3'-diethoxy-2'-propoxy) benzyl]methylamine (**P-I**), N,N-*bis*-[5-ethyl-2-(1',3'-diethoxy-2'-propoxy)benzyl]methyl amine (**P-II**) and N,N-*bis*-[5-methoxy-2-(1',3'-diethoxy-2'-propoxy)benzyl]methylamine (**P-III**) were successfully prepared. The alkali metal ion extraction efficiency of products was studied by Pedersen's technique. The stoichiometric interaction ratios of host compounds (**P-I to P-III**) with alkali metal ion guests determined by UV-visible, ^{1}H NMR and ESI-MS spectroscopic techniques were found to be 2:1, 3:1 and 4:1, respectively.

Key Words: Supramolecules, Pedersen's technique, Stoichiometric interaction ratio.

INTRODUCTION

Supramolecules have received much attention owing to their unique property of molecular recognition at the molecular level which is never achieved in the simple individual molecules. The induced molecular interactions between supramolecules and guests to form host-guest compounds or inclusion compounds are known as noncovalent interactions or secondary forces, such as van der Waals, dipole-dipole interaction, hydrogen bonding, *etc*.[1-5]. Various novel supramolecules with specific functional groups have been, therefore, designed and proposed in both assembly and cyclic structures for the preferred properties[1-5]. For the past few years, our group has focused on the structure of benzoxazines that resemble repeating units of calixarenes (**Scheme-I**)[6-12]. Based on molecular design, the novel controlled structure

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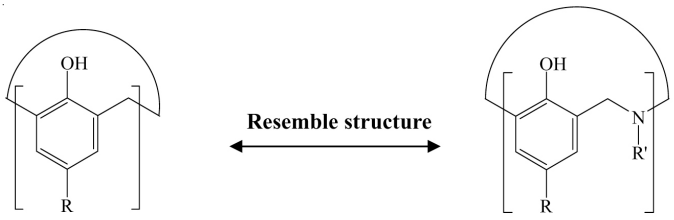
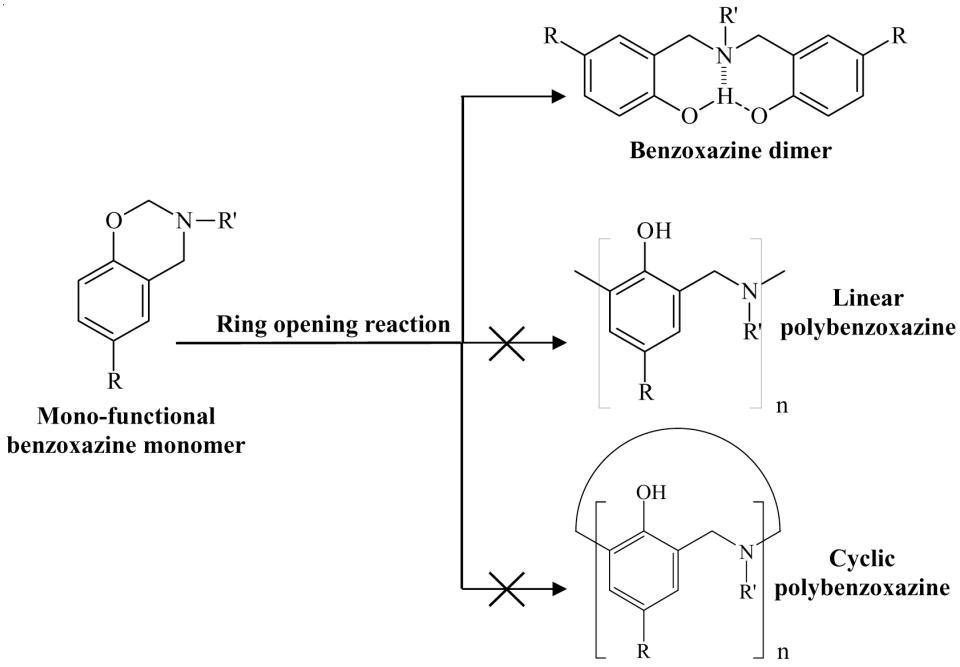


Scheme-I: Resemble repeating units of benzoxazines like structure, calixarenes

of benzoxazine has been proposed and synthesized to obtain a series of supramolecules as ion entrapment materials[6-12].

A series of research works on benzoxazine supramolecule syntheses showed an important point about the reaction of mono-functional benzoxazine monomers. By ring opening reaction, mono-functional benzoxazine monomers were expected to provide products with linear or cyclic structures (**Scheme-II**)[11,12]. The self termination, however, induced during the ring opening reaction, proceeded and only the benzoxazine dimers: N,N-*bis*(5-alkyl-2-hydroxybenzyl)alkylamine consisting of two phenol derivatives with intramolecular hydrogen bonding and azamethylene linkage (**Scheme-II**) was obtained[11,12]. This turned out to be a guideline for our research group to develop the supramolecular structured benzoxazines based on the benzoxazine dimer unit. After carrying out the ion extraction ability of the

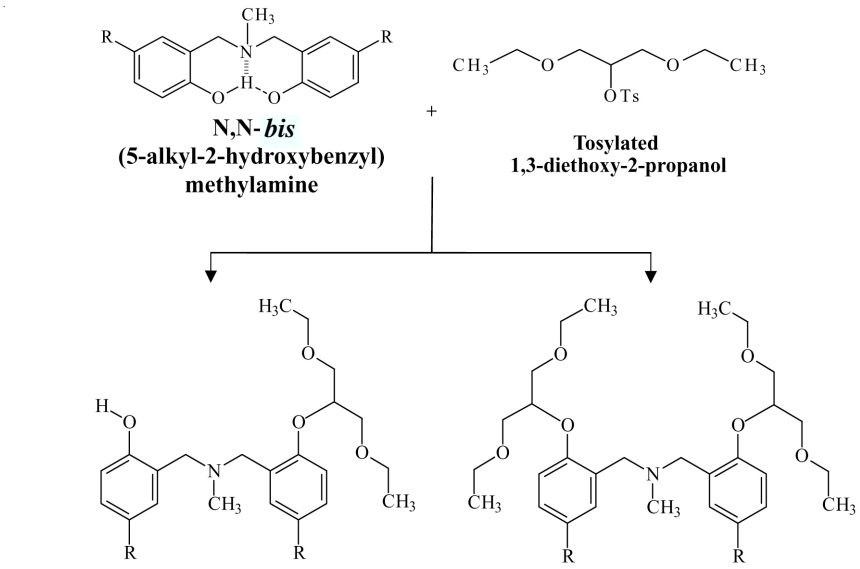


Scheme-II: Self-termination of benzoxazines

benzoxazine dimers, it was surprising to find that benzoxazine dimers performed a specific property as a novel supramolecule responding to metal ions *via* molecular assembly[10,12].

Systematic studies were, therefore, needed to understand the supramolecular assembly at the molecular level and to achieve novel types of high efficiency benzoxazine dimer supramolecules. Benzoxazine dimers also performed as difunctional phenol derivatives, which are possibly functionalized by various chemical reactions, such as, etherification, esterification, Mannich reaction, *etc*.[7-13].

The aim of this present work is to modify benzoxazine dimers based on the molecular design by a simple and effective reaction to enhance their interactions with metal ions (**Scheme-III**). By Pedersen's technique, the stoichiometric interactions between benzoxazine dimer derivatives with alkali metal ions were, additionally, clarified[14,15].



R = -CH_3 (**I** and **P-I**), -C_2H_5 (**II** and **P-II**), and –OCH_3 (**III** and **P-III**)

Scheme-III: Etherification between benzoxazine dimers and tosylated-1,3-diethoxy-2-propanol (A) asymmetric structure and (B) symmetric structure

EXPERIMENTAL

Paraformaldehyde was purchased from Sigma (USA). 4-Methoxyphenol, 4-ethylphenol, *p*-cresol, methylamine (40 % w/v in water), potassium hydroxide,

1,3-diethoxy-2-propanol, tosyl chloride, cesium carbonate and anhydrous sodium sulphate were purchased from Fluka Chemicals (Buchs, Switzerland). Ethanol, methanol, methylene chloride, isopropanol, acetonitrile, sodium hydroxide, picric acid and diethyl ether were the products of Ajax chemicals (Australia). All chemicals were analytical grade and used as received.

Infrared spectra were obtained from Fourier transform infrared spectrophotometer: Bruker Equinox55/S spectrophotometer with 32 scans at a resolution 4 cm^{-1}. NMR data was taken from Fourier transform ^1H NMR spectrometer: ACF 200 MHz of Bruker Switzerland and was used to analyze the products using $CDCl_3$ as a solvent. Mass spectra of precursors were obtained from ESI-MS (Bruker Esquire mass spectrometer).

Syntheses of benzoxazine derivatives (P-I–P-III): Three benzoxazine dimers: (**I**), (**II**) and (**III**), were prepared as reported elsewhere[11-13] and employed as starting materials for synthesizing three respective benzoxazine derivatives: (**P-I**), (**P-II**) and (**P-III**). The procedure is shown in **Scheme-III**.

1.0 mmol of **I** (0.27 g) or **II** (0.30 g) or **III** (0.30 g) was dissolved in 50.0 mL acetonitrile and KOH (0.12 g, 2.00 mmol) was added. The mixture was stirred and refluxed for 0.5 h and a solution of tosylated 1,3-diethoxy-2-propanol (1.21 g, 2.00 mmol) in acetonitrile (50 mL) was added dropwise. After reflux for 3 days, acetonitrile was removed by vacuum distillation. The sticky yellow liquid of product dissolved in methylene chloride was washed several times with distilled water. All products obtained were dried over anhydrous sodium sulphate and the solvent was removed yielding 80-85 % of **P-I**, **P-II** and **P-III**. The final products are clear yellow liquid. The products were characterized by TLC, FTIR, ^1H NMR and ESI-MS.

N,N-*Bis*-[5-methyl-2-(1',3'-diethoxy-2'-propoxy)benzyl]methylamine (P-I): yield 85 %; clear and yellow liquid; $R_f = 0.87$ (10 % MeOH in CH_2Cl_2); FTIR (KBr, ν_{max}, cm^{-1}): 1499 (tri-substituted benzene), 1200 (C-N-C stretching), 1117 (C-O-C). ^1H NMR (200 MHz, $CDCl_3$, ppm): δ_H 1.158 (12H, t, $J_1 = 6.59$ Hz, O-CH_2-CH_3), 2.288 (9H, s, N-CH_3 and Ar-CH_3), 3.501 (8H, q, $J_1 = 6.59$ Hz, O-CH_2-CH_3), 3.618 (8H, d, $J_2 = 4.99$ Hz, -CH_2-CH-CH_2-), 3.660 (4H, s, Ar-CH_2-N), 4.441 (2H, t, $J_2 = 4.99$ Hz, -CH_2-CH-CH_2-), 6.781 (2H, d, $J_3 = 6.59$ Hz, Ar-H), 6.918 (2H, s, Ar-H), 7.022 (2H, d, $J_3 = 6.59$ Hz, Ar-H). ESI-MS (m/z): 532 (M + 1).

N,N-*Bis*-[5-ethyl-2-(1',3'-diethoxy-2'-propoxy)benzyl]methylamine (P-II): yield 80 %; clear and yellow liquid; $R_f = 0.88$ (10 % MeOH in CH_2Cl_2); FTIR (KBr, ν_{max}, cm^{-1}): 1497 (tri-substituted benzene), 1200 (C-N-C stretching), 1114 (C-O-C). ^1H NMR (200 MHz, $CDCl_3$, ppm): δ_H 1.086 (6H, t, $J_2 = 5.19$ Hz, Ar-CH_2-CH_3), 1.140 (12H, t, $J_1 = 6.59$ Hz, O-CH_2-CH_3), 2.252 (3H, s, N-CH_3), 2.515 (4H, q, $J_2 = 4.99$ Hz, Ar-CH_2-CH_3), 3.425 (8H, q, $J_1 = 6.59$ Hz, O-CH_2-CH_3), 3.545 (8H, d, $J_3 = 5.19$ Hz, -CH_2-CH-CH_2-), 3.641 (4H, s, Ar-CH_2-N), 4.377 (2H, t, $J_3 = 4.99$ Hz, -CH_2-CH-CH_2-), 6.665 (2H, d, $J_4 = 6.59$ Hz, Ar-H), 6.869 (2H, s, Ar-H), 6.973 (2H, d, $J_4 = 6.59$ Hz, Ar-H). ESI-MS (m/z): 560 (M + 1).

N,N-*Bis*-[5-methoxy-2-(1',3'-diethoxy-2'-propoxy)benzyl]methylamine (P-III): Yield 80 %; clear and yellow liquid; R_f = 0.84 (10 % MeOH in CH_2Cl_2); FTIR (KBr, ν_{max}, cm^{-1}): 1497 (tri-substituted benzene), 1200 (C-N-C stretching), 1115 (C-O-C). ^1H NMR (200 MHz, $CDCl_3$, ppm): δ_H 1.098 (12H, t, J_1 = 6.58 Hz, O-CH_2-CH_3), 2.204 (3H, s, N-CH_3), 3.435 (8H, q, J_1 = 6.58 Hz, O-CH_2-CH_3), 3.541 (8H, d, J_2 = 4.99 Hz, -CH_2-CH-CH_2-), 3.623 (4H, s, Ar-CH_2-N), 3.684 (6H, s, Ar-O-CH_3), 4.273 (2H, t, J_2 = 4.99 Hz, -CH_2-CH-CH_2-), 6.733 (2H, d, J_3 = 6.59 Hz, Ar-H), 6.888 (2H, s, Ar-H), 7.080 (2H, d, J_3 = 6.59 Hz, Ar-H). ESI-MS (m/z): 564 (M + 1).

Ion extraction property of benzoxazine derivatives: The complexation of benzoxazine derivatives was studied by liquid-liquid extraction *via* Pedersen's technique[14,15]. All dimer derivatives (**P-I** to **P-III**) and 1,3-diethoxy-2-propanol dissolved in methylene chloride and alkali metal picrates aqueous solutions were prepared with the concentration of 7×10^{-5} M. Five mL of each solution were vigorously mixed and left at room temperature until each phase was completely separated. The concentration of metal picrates was determined by the UV-vis spectrophotometer at λ_{max} 355 nm ($\varepsilon = 1.45 \times 10^4$ M^{-1} cm^{-1}). The percentage extraction was calculated by the equation $[(A_0 - A)/A_0] \times 100$ where A_0 = initial absorbance of the picrate solution and A = absorbance of the picrate solution after extraction with the dimer derivative. The molar ratios between dimer derivatives (**P-I** to **P-III**) and metal ions were confirmed by ^1H NMR and ESI-MS.

RESULTS AND DISCUSSION

Molecular design and syntheses: Thin layer chromatography (TLC) with 10 % MeOH in CH_2Cl_2 mobile phase of all products, **P-I**, **P-II** and **P-III** showed only one spot and the R_f values are presented in Table-1. According to our previous works, it is found that due to the intramolecular hydrogen bonding generated in the crystal structures of dimer, the reaction of dimers was either symmetric or asymmetric reaction[10-13]. Therefore, the possible structures of product might be a mono-substituted benzoxazine dimer [structure (A)] or di-substutited benzoxazine dimer [structure (B)], as shown in **Scheme-III**. To prove this, the structures of **P-I**, **P-II** and **P-III** were characterized by ESI-MS, FTIR and ^1H NMR.

TABLE-1
R_f VALUES OF PRODUCTS AND STARTING MATERIALS

Product	R_f	Starting material	R_f
P-I	0.87	**I**	0.49
P-II	0.88	**II**	0.34
P-III	0.84	**III**	0.22

The results of mass/charge determined by ESI mode mass spectrometer for all products are shown in Table-2. Fig. 1 shows the mass spectrum of **P-I**. The protonated **P-I** (m/z = 532) agreed with the calculated molecular weight of 531 in symmetric structure (B) (Table-2).

TABLE-2
MASS/CHARGE (m/z) OF PRODUCTS AND CALCULATED MOLECULAR WEIGHT OF POSSIBLE STRUCTURES

Product	Observed mass/charge	Calculated molecular weight	
		Structure (A)	Structure (B)
P-I	532	401	531
P-II	560	430	559
P-III	564	434	463

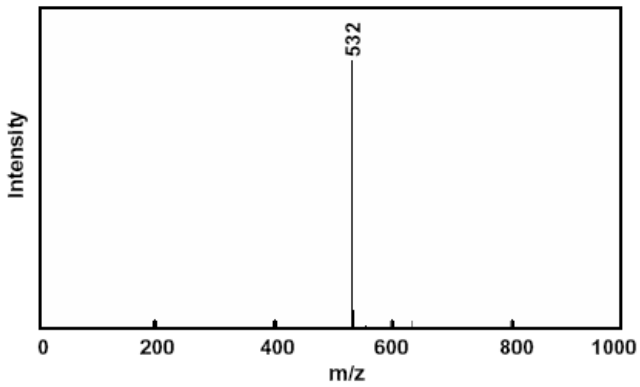


Fig. 1. ESI-MS spectrum of **P-I**

This indicated that the intramolecular hydrogen bonding in the structure of **I** was eliminated by strong base potassium hydroxide to allow the complete etherification on both hydroxyl groups resulting in the symmetric benzoxazine dimer derivative as **P-I**. Similarly, the structures of **P-II** and **P-III** were also symmetric as confirmed by m/z results (**Table-2**) and the corresponding calculated molecular weight of structure (B).

FTIR spectra of **I** and **P-I** in the 4000-500 cm^{-1} range are compared in Fig. 2. From evidence of the crystal structure of **I**[12,13], the peak positions at 3298, 1483 and 1199 cm^{-1} were assigned to be hydroxyl groups, tri-substituted benzene and C-N-C stretching, respectively [Fig. 2(a)]. The peaks referred to hydroxyl groups were not observed in **P-I**. However, the ether functional group at 1117 cm^{-1} was found [Fig. 2(b)], indicating that the etherified dimer had been successfully prepared. There were no significant shifts in tri-substituted benzene (1499 cm^{-1}) or C-N-C stretching vibration (1200 cm^{-1}). This suggested that **I** was only changed in the functional group from the phenol to ether, while the backbone structure of product belonging to that of dimer still remained.

The characteristic FTIR spectra data of **P-II** and **P-III** are given in the experiment section. Similar to **P-I**, **P-II** and **P-III** did not provide the hydroxyl group peaks in FTIR spectra. Both compounds exhibited the peak positions of trisubstituted benzene, C-N-C stretching vibration and C-O-C around 1497, 1200 and 1114 cm^{-1}, respectively. These frequencies are not significantly different from **P-I**.

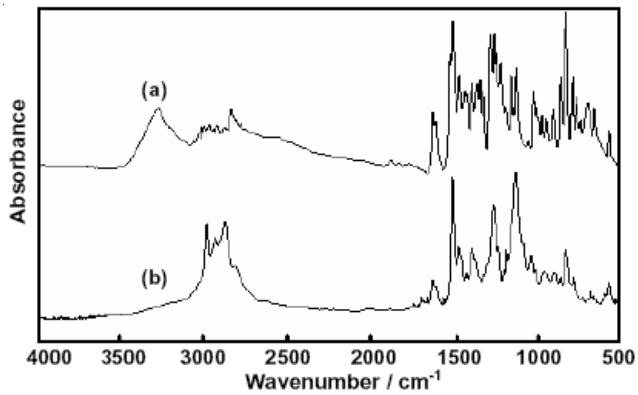


Fig. 2. FT-IR spectra of (a) **I** and (b) **P-I**

^{1}H NMR spectrum (Fig. 3) of **P-I** showed the multiplex peak of methine protons (-CH-) at δ_H = 4.441 ppm which was not observed in **I**. In addition, methylene protons of aza-linkage were singlet at chemical shift of 3.660 ppm, indicating that two symmetric hydroxyl groups of **I** were completely substituted by tosylated-1,3-diethoxy-2-propanol and yielded the symmetrical structure (B) of derivative benzoxazine dimer (**P-I**), **Scheme-III**. The data of the ^{1}H NMR spectra (in $CDCl_3$) obtained for **P-II** and **P-III** are given in the experiment section. Both products, **P-II** and **P-III**, were clarified as products with symmetrical structures as **P-I**.

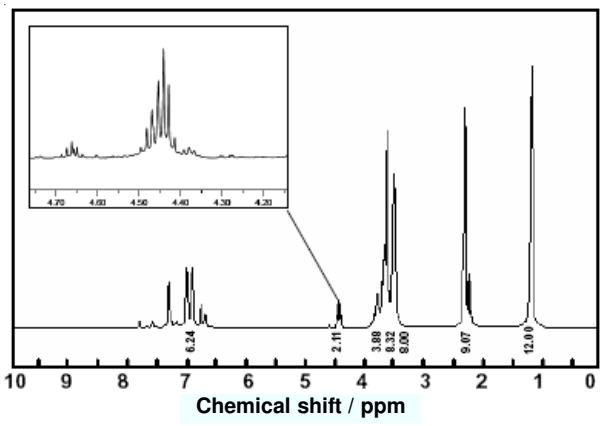


Fig. 3. ^{1}H NMR spectrum of **P-I**

Liquid extraction of alkali metal ions: To identify the ion extraction ability of products (**P-I** to **P-III**), Pedersen's technique was applied by using the equimolar concentrations of benzoxazine derivatives and alkali metal picrates under extraction condition at 25 ºC[10,14,15]. The extracted organic phase was qualitatively collected and measured by UV-Vis. Fig. 4 shows the absorption spectra of Na^+-picrate, **P-I** and Na^+-picrate in **P-I** solution. The peak shift implied the complex formation

between **P-I** and Na^+-picrate. The maximum wavelengths of complexes formed between **P-I**, **P-II** and **P-III** with Na^+, K^+ and Cs^+ picrates are summarized in Table-3.

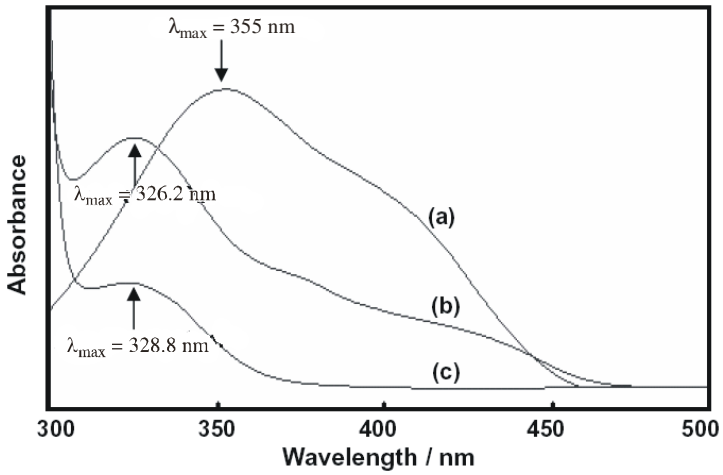


Fig. 4. UV-Vis spectra of (a) Na^+-picrate (b) **P-I** and (c) the complex of **P-I** and Na^+ ion

TABLE-3
PEAK POSITIONS OF MAXIMUM ABSORBANCES OF PRODUCTS AND PRODUCT-ALKALI METAL ION COMPLEXES, λ_{max} OF GUEST (Na^+, K^+ AND Cs^+) IS 355.00 nm

Product	λ_{max} of product (nm)	λ_{max} of complex (nm)		
		Na^+	K^+	Cs^+
P-I	326.20	328.80	328.80	328.40
P-II	326.80	372.20	372.80	372.40
P-III	326.40	360.60	360.40	360.40

Effect of dimer derivative structures on ion extraction ability: Although the original benzoxazine dimers (**I-II**) exhibited a supramolecular property, the ion extraction ability at the equimolar concentrations of dimers and metal ions (7×10^{-5} M) was not significant[10-12]. It is a fact that molecular hydrogen bonds generated in the dimer structure obstruct the ion extraction ability of the original benzoxazine dimers[10-12]. In addition, two other effects on ion extraction ability of the original benzoxazine dimers were found to be the substituted groups on hydroxyl groups or on benzene rings[10-12]. In this present work, by using tosylated-1,3-diethoxy-2-propanol reacted with benzoxazine dimers, the elimination of hydrogen bonds together with an increase in hydrophilicity and lone pair electrons of benzoxazine dimers was carried out. The efficiency of metal ion interaction was evaluated from the aqueous phase by measuring the absorbance before and after extraction to calculate the percentage of ion extraction. Fig. 5 summarizes the ion extraction percentage of benzoxazine derivatives (**P-I** to **P-III**) and alkali metal ions (Na^+, K^+ and Cs^+ picrates). Moreover, the ion extraction ability of 1,3-diethoxy-2-propanol was also

determined. It was found that the structure of 1,3-diethoxy-2-propanol is insufficient to form the molecular assembly with alkali metal ions because only small amount extraction (*ca.* 3 %) was found.

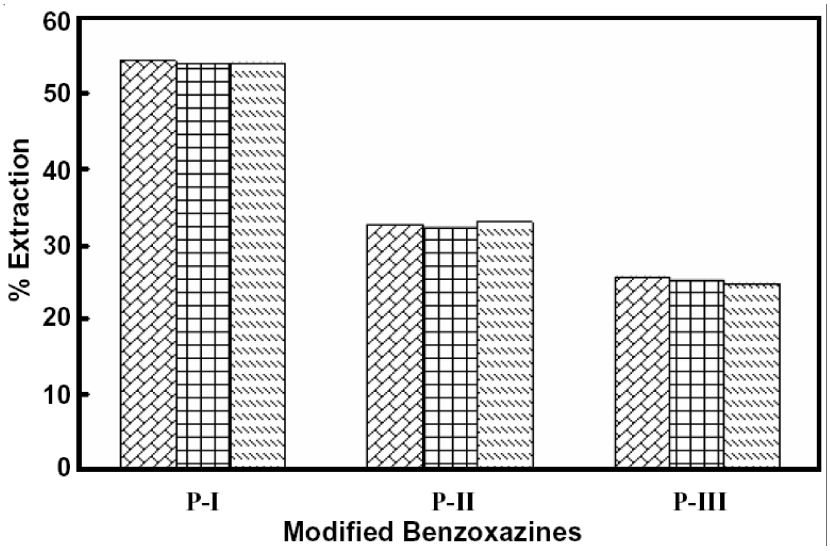


Fig. 5. Extraction percentage of (▨) sodium picrate, (▦) potassium picrate and (▧) cesium picrate at an equimolar concentration of 7×10^{-5} M by **P-I** to **P-III** in CH_2Cl_2 at 25 ºC

Modified benzoxazine derivatives (**P-I–P-III**), consequently, provide high sensitivity and ion extraction ability at equimolar concentration of benzoxazines and ions (7×10^{-5} M) as shown in Fig. 5. However, all modified benzoxazine dimers (**P-I** to **P-III**) showed no selectivity on each alkali ion guest, Na^+, K^+ and Cs^+. It might be the fact that the interaction between dimers and metal ions was induced by the molecular assembly and dimer molecules provide the flexible structure for all types of metal ions to be allowed in the channel[16,17]. These results provide an information about ion extraction ability changes when the hydrogen bond was eliminated and structures of dimers were modified.

It is conceivable that substituted groups in the benzene ring might be one reason for the ion extraction ability of benzoxazine dimer derivatives. Due to the additional lone pair electrons from the oxygen atom belonging to methoxy group, the $-OCH_3$ substituted group at the *para*-position in benzene ring of **P-III** was expected to provide much higher ion extraction ability than that of $-CH_3$ in **P-I** and $-C_2H_5$ in **P-II**. The results, however, are the opposite. The results in Fig. 5 show that **P-I** provided the highest extraction ability to all metal ions (*ca.* 50 %); while that of **P-III** had the lowest efficiency (*ca.* 25 %). **P-I** with a methyl substituted group might form a loosely assembled structure and have a favourable space to interact with metal ions. The results imply that the difference in ion extraction might be due

to the structure of dimer derivatives and the molecular assembly formation, although benzoxazine derivatives (**P-I** to **P-III**) showed no ion selectivity.

Stoichiometry of benzoxazine dimer-ion interaction: As this was the first time to study the interaction of benzoxazines based dimer with metal ions *via* the molecular assembly, the stoichiometric ratio of each derivative benzoxazine dimer (**P-I** to **P-III**) to Na^+, K^+ and Cs^+ was determined. By using the equimolar concentrations (7×10^{-5} M) of dimers and metal species, the percentage of ion extraction determined by Pedersen's technique was used to calculate the molar ratios of benzoxazine dimers to metal ion. The different stoichiometric ratios of each benzoxazine dimer-ion interaction were found and are presented in Table-4.

TABLE-4
HOST-GUEST RATIOS OF PRODUCTS WITH ALKALI METAL IONS

Host	Host-guest ratio		
	Na^+	K^+	Cs^+
P-I	2:1	2:1	2:1
P-II	3:1	3:1	3:1
P-III	4:1	4:1	4:1

Ion interaction studies by ^{1}H NMR and ESI-MS: As **P-I** and **P-III** provided the highest (50 %) and the lowest (25 %) extraction abilities, respectively; their complexations were, therefore, confirmed by ^{1}H NMR spectroscopy. By solid liquid extraction, an excess amount of solid potassium picrate was added into the solutions of **P-I** and **P-III** in $CDCl_3$. Dissolution of picrate salt turns colourless $CDCl_3$ to yellow. The peak shifts in ^{1}H NMR spectra provide useful information of complexation while the integration ratios between picrate protons and protons of modified benzoxazine dimers can be used to evaluate the host-guest ratio.

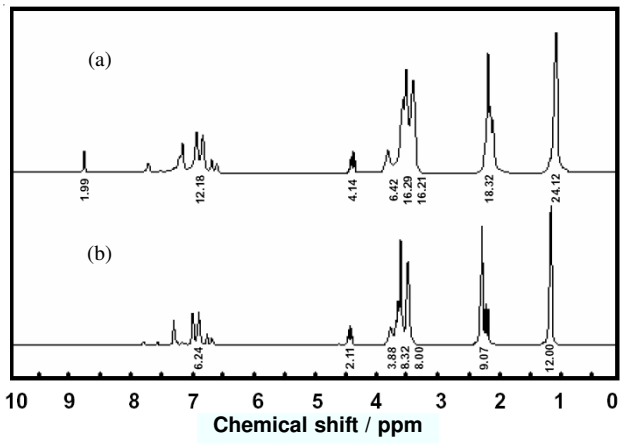


Fig. 6. ^{1}H NMR spectra of (a) **P-I** and (b) the complex between **P-I** and K^+ ion

Figs. 6 and 7(a) clarify that chemical shifts of **P-I** changed after extraction with potassium picrate, especially, methyl protons of aza group (N-CH_3), methylene protons of aza-methylene linkage (-CH_2-N-) and protons of 1,3-diethoxy-2-propoxy groups. This implies that **P-I** interacts with K^+ ion *via* the lone pair electrons of nitrogen and oxygen atoms. In addition, the results indicate that K^+ ion sit in the upper rim of **P-I** on complexation. The intergration ratio of picrate and methine protons was investigated to determine the host-guest ratio. **P-I** showed a host-guest ratio of 2:1 for K^+ ions as corresponded to the results from liquid-liquid extraction.

In case of **P-III**, the peaks of methyl protons belonging to N-CH_3 and methylene linkage (-CH_2-N-) were obviously shifted [Fig. 7(b)] while the protons of 1,3-diethoxy-2-propoxy groups were slightly changed. This hints at the possibility that the interaction between **P-III** and K^+ ion is only induced at nitrogen atom. In addition, it was found that the peak of methoxy protons was insignificantly moved after extraction. This suggests that the methoxy groups at *para*-positions of aromatic rings might not enhance the extraction ability of **P-III**. Thus, **P-III** provides the highest host-guest ratio (4:1) as compared to **P-I** (2:1) and **P-II** (3:1). It is important to note that the ion extraction ability depends on the original structures of benzoxazine dimers (**P-I** to **P-III**) even if the modifications are done with the same procedure. To study the host-guest compounds formation *via* molecular assembly, the electrospray ionization mass spectroscopy (ESI-MS) was applied as seen in the complexation of macrolides[18].

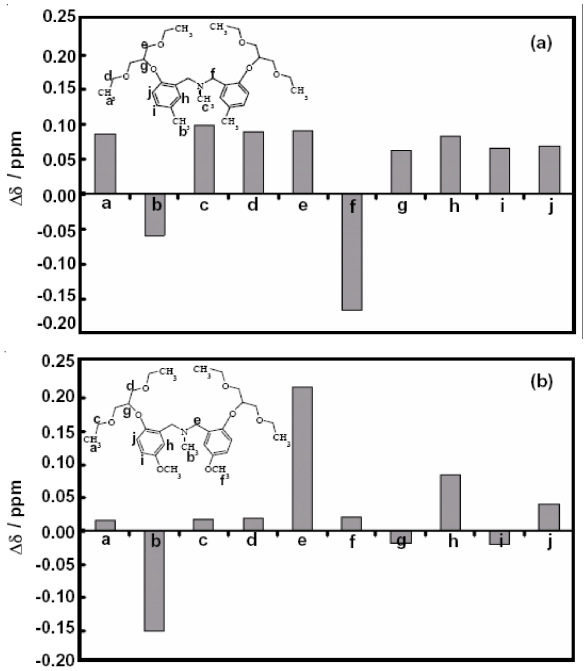


Fig. 7. Δδ of (a) the complex of **P-I** with K^+ picrate and (b) the complex of **P-III** with K^+ picrate

The complex between **P-I** and K^+ was, therefore, elucidated by ESI-MS. Fig. 8 shows the parent peak (M + H) at m/z = 1102 which is equal to the molecular weight of the complex between two molecules of **P-I** and one K^+ ion. The result implies that **P-I** forms an assembly structure with the host-guest ratio of 2:1 as corresponding to the results from liquid-liquid extraction and ^{1}H NMR.

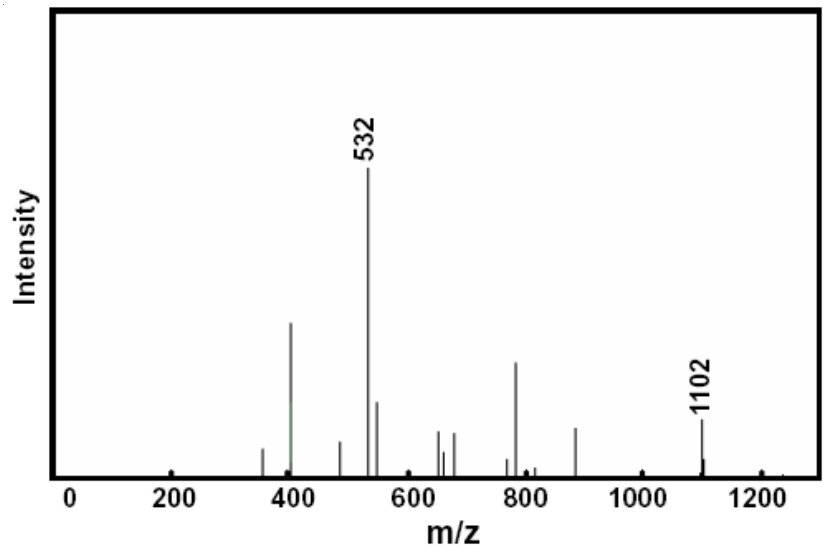


Fig. 8. ESI-MS spectrum of the complex between **P-I** and K^+ ion

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