CHAPTER III
EXPERIMENTAL SECTION

3.1 Materials

2,4-Dimethyl phenol (99%), p-cresol and 4-ethyl phenol were purchased from Fluka Chemicals (Buchs, Switzerland). Paraformaldehyde was purchased from Sigma (USA.). Methylamine solution (w/w 40% in water) was purchased from Fluka Chemicals (Buchs, Switzerland). Dichloromethane was purchased from J.T. Baker Inc. (Phillipsburg, USA.). Benzoyl chloride and acetyl chloride were purchased from E. Merck (Germany). All other reagents (dioxane, chloroform i.e;) were purchased from Ajax chemicals (Australia). Picric acid, sodium chloride, magnesium chloride and potassium chloride were from Ajax chemicals (Australia); barium chloride and calcium chloride were from E. Merck (Germany); and lithium chloride was from Fluka Chemicals (Buchs, Switzerland). All chemicals were used without further purification.

3.2 Characterization

3.2.1 Structural Analysis

FTIR spectra were obtained from a Bruker Equinox55 Spectrophotometer with 16 scans at a resolution of 4 cm^{-1} in the frequency range of 4000-400 cm^{-1}. Neat polymer thin films on a KBr plate and sample powder pressed into a KBr pellet were used. ^{1}H-NMR spectra were recorded on Fourier Transform NMR Spectrometer ACF 200MHz of Bruker, Switzerland in $CDCl_3$ with tetramethylsilane as an internal standard. Percent extraction of picrate metal salts was determined by UV absorption spectra

using Perkin-Elmer Lambda-16 Spectrophotometer. Vortex mixer (GENIE-2, Scientific Industries) was used in the procedure of ion extraction.

3.2.2 Metal Ion Extraction and Complexation Studies

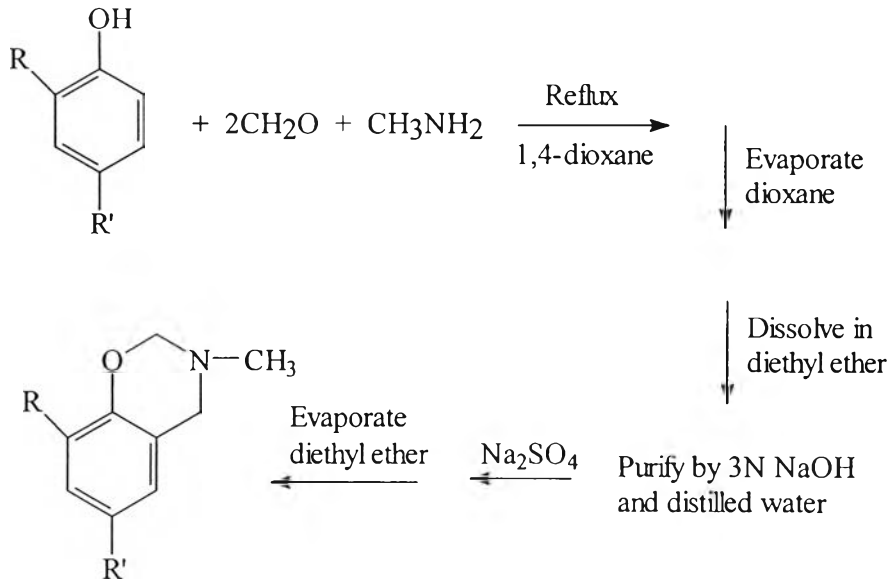
Ion extraction was analyzed by Pedersen's technique. Metal picrate solutions ([Pic] = $7x10^{-5}$M, [MCl] = $[MCl_2]$ = 10^{-1}M) were prepared in deionized water. The benzoxazine dimer derivatives ((4)-(6)) and their ester derivatives ((7)-(12)) were dissolved in chloroform to make the concentration of $7x10^{-4}$M, $3.85x10^{-3}$M, $7x10^{-3}$M, $3.85x10^{-2}$M, $7x10^{-2}$M, $3.85x10^{-1}$M, and $7x10^{-1}$M solution, respectively. The volume of organic and aqueous phase was 5mL each and shaken by Vortex mixer for 2 minutes. The concentration of the picrate in the aqueous phase was determined by the UV spectrum at λ_{max} 354 nm (ε = 14500 $M^{-1}cm^{-1}$) (A. Arduni *et al.*, 1986).

The organic phase was collected and the solvent was evaporated to obtain the complex salt of benzoxazine derivatives and picrates. The obtained product was dissolved in $CDCl_3$ and the complexation was studied by ^{1}H-NMR (D.J. Cram *et al.*, 1986).

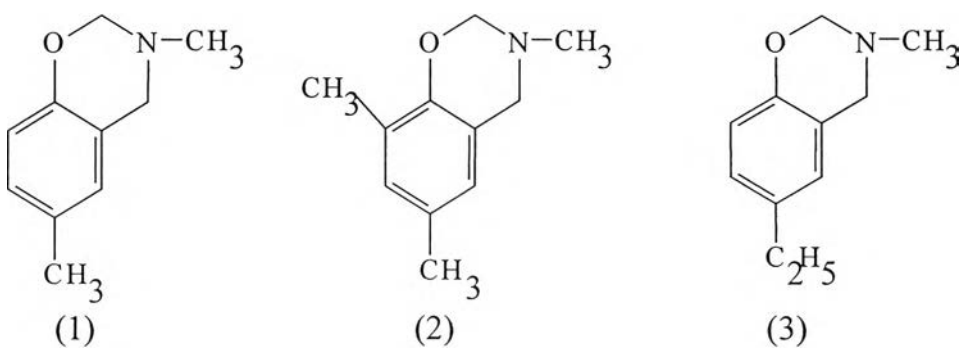
3.3 Methodology

3.3.1 Preparation of Benzoxazine Monomer

3,4-Dihydro-3-methyl-6-methyl-2H-1,3-benzoxazine (1), 3,4-dihydro-3-methyl-6,8-methyl-2H-1,3-benzoxazine (2), and 3,4-dihydro-3-methyl-6-ethyl-2H-1,3-benzoxazine (3) (Scheme 3.2) were synthesized from *p*-cresol, 2,4-dimethylphenol and ethylphenol, respectively, by the reaction with paraformaldehyde and methylamine in the molar ratio of 1:2:1 as reported previously by Ishida *et al.*



Scheme 3.1 Preparation of benzoxazine monomer.

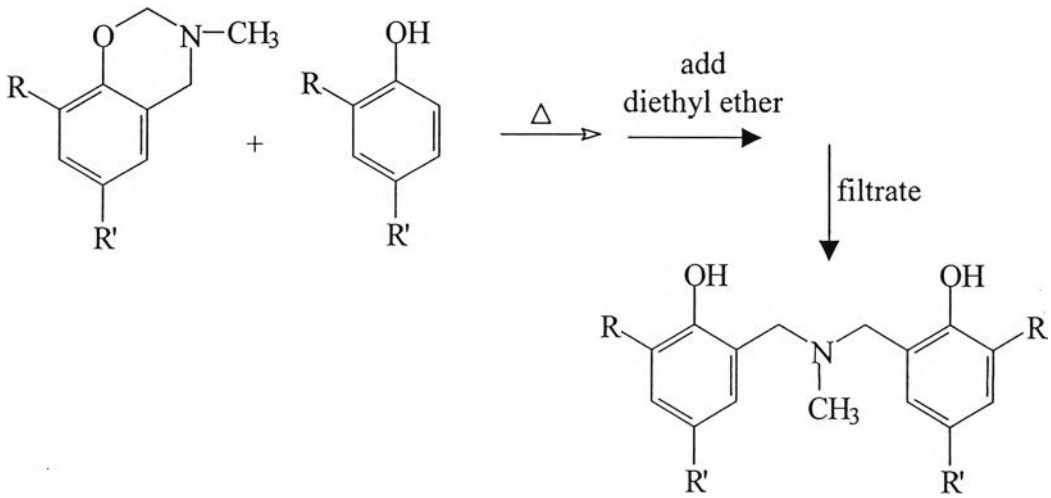


Scheme 3.2 Structure of benzoxazine monomers (1)-(3).

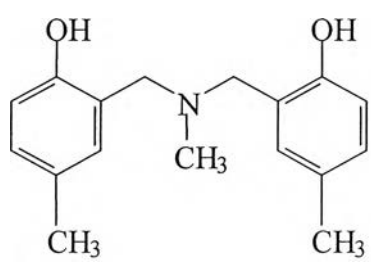
3.3.2 Preparation of Benzoxazine Dimer

The obtained monomers, (1), (2), and (3), were used as the precursors for the reaction with *p*-cresol, 2,4-dimethylphenol, and 4-ethylphenol, respectively, in equimolar ratio without solvent. The reaction was proceeded at 60°C to obtain dimer derivatives (Scheme 3.4). The completion of the reaction was confirmed by thin layer chromatography and was achieved in 1 hour for N,N-Bis (5-methyl-2-hydroxybenzyl) methylamine (4), in 3 hours for

N,N-Bis(3,5-dimethyl-2-hydroxybenzyl)methylamine (5) and 2½ hours for N,N-Bis(5-ethyl-2-hydroxybenzyl)methylamine (6). The crude products were precipitated out from ether and recrystallized in 2-propanol to obtain (4) and in hexane/THF (80/20, V/V) to obtain (5) and (6).



Scheme 3.3 Preparation of benzoxazine dimer.



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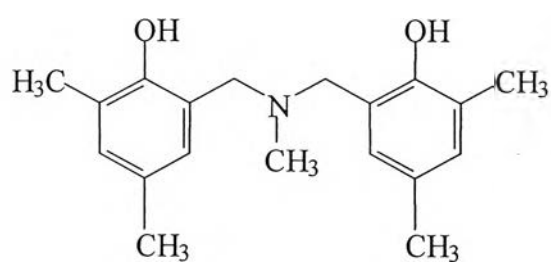

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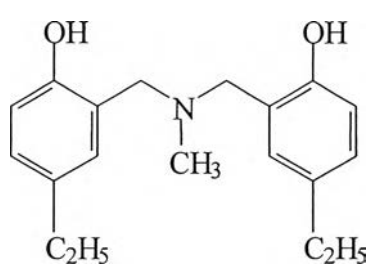
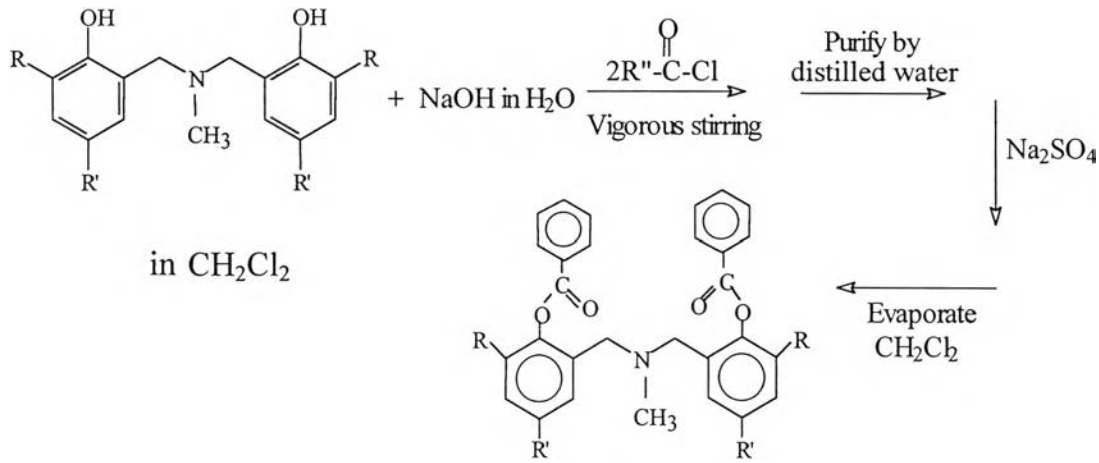


(6)

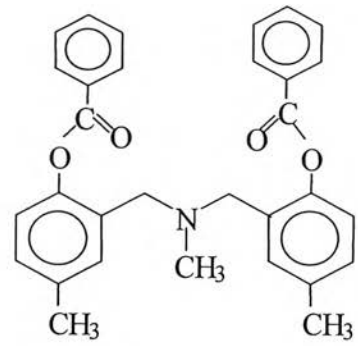
Scheme 3.4 Structure of benzoxazine dimers (4)-(6).

3.3.3 Preparation of Benzoxazine Dimer Derivatives



Scheme 3.5 Preparation of benzoxazine derivatives.

Benzoyl and acetyl chloride were used for the synthesis of benzoxazine dimer derivatives. Five mmol of benzoxazine dimers ((4),(5) and (6)) was dissolved in 50 mL CH_2Cl_2 , followed by adding NaOH (0.82g, 20.5 mmol) in 50 mL H_2O . The mixture was stirred vigorously and 10 mmol of acid chloride (benzoyl or acetyl chloride) in 50 mL of CH_2Cl_2 was slowly added. The reaction was performed at room temperature and the completion was confirmed by TLC. The obtained pale yellow solution was extracted with water to exclude unreacted acid chloride, followed by anhydrous sodium sulphate and was kept overnight. The solvent was removed to obtain white powder of dimer derivatives (Scheme 3.6, (7), (8), (11), and (12)) and syrupy liquid of dimer derivatives (Scheme 3.6, (9), and (10)).



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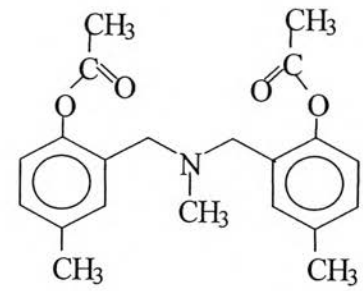

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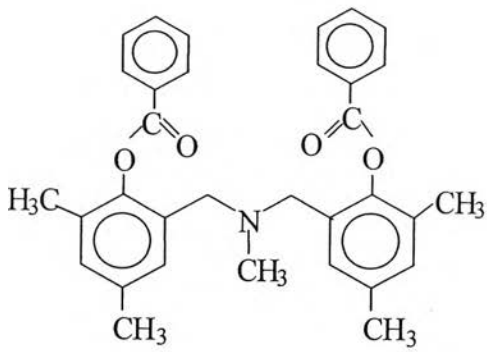

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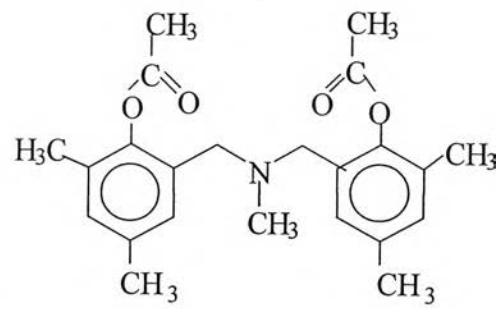

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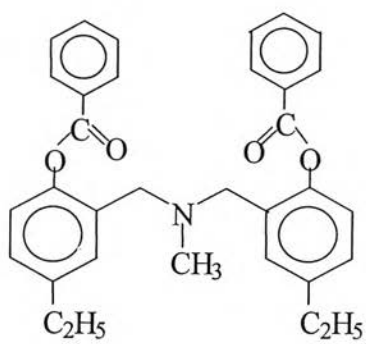

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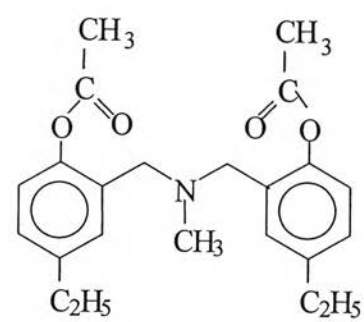

(12)

Scheme 3.6 Structure of benzoxazine dimer derivatives (7)-(12).