

## CHAPTER V

### CONCLUSION

25,27-[*N,N'*-di-((2-ethoxy)benzyl)propylenediamine]-26,28-dimethoxy-*p-tert*-butylcalix[4]arene dihydrochloride (**7**, **L.2HCl**) was synthesized by reducing and protonating its schiffbase derivative **6** in 77%. The compound **7** is lack of intramolecular hydrogen bonding between the phenoxy units and shows intriguing conformational isomerism which depends on solvent polarity and intermolecular hydrogen bonding interactions. In polar aprotic solvents such as CDCl<sub>3</sub> and DMSO-d<sub>6</sub>, <sup>1</sup>H NMR experiments reveal that **7** has mixed conformations. In polar protic solvent, CD<sub>3</sub>OD, the intermolecular hydrogen bonding between CD<sub>3</sub>OH and CH<sub>3</sub>OAr-*t*-C<sub>4</sub>H<sub>9</sub> prohibits rotation of the phenyl ring and thus holds the calix[4]arene compartment in a cone conformation. Variable temperature NMR experiments indicate that one of ROAr-*t*-C<sub>4</sub>H<sub>9</sub> rings must orientate in a pinched cone fashion to avoid the steric congestion.

The basicity constants of 25,27-[*N,N'*-di-((2-ethoxy)benzyl)propylenediamine]-26,28-dimethoxy-*p-tert*-butylcalix[4]arene (**L**) at various temperatures in methanolic solution of 1×10<sup>-2</sup>M Bu<sub>4</sub>NCF<sub>3</sub>SO<sub>3</sub> were determined by potentiometric titration. Calculations by Superquad program suggest two steps in protonation leading to two equilibrium constants which are shown in logarithm (log *K*<sub>1</sub> and log *K*<sub>2</sub>) in Table 4.5.

The relationship of log *K* and  $\frac{1}{T}$  was used to calculate thermodynamic parameters.

The enthalpy energy changes of the first and second protonation, Δ*H*<sub>1</sub> and Δ*H*<sub>2</sub>, are -67 kJ/mol and 3 kJ/mol, respectively. The entropy changes of the first and second protonations, Δ*S*<sub>1</sub> and Δ*S*<sub>2</sub>, are calculated to be -38 kJ/mol·K and 137 kJ/mol·K, respectively. The ligand **L** was also studied its complexation with Cu<sup>2+</sup> and Zn<sup>2+</sup> ions in methanolic solution of 1×10<sup>-2</sup> M Bu<sub>4</sub>NCF<sub>3</sub>SO<sub>3</sub> by the same method. Calculations by Superquad program reveal that **L** does not form complexes with Cu<sup>2+</sup> or Zn<sup>2+</sup>.

## SUGGESTION FOR FURTHER WORK

Further work can be focused on;

1. Synthesize another methyl calix[4]arene derivative which is similar to ligand 7, but has a difference methylene (CH<sub>2</sub>) bridge between ammonium groups and then, study on intermolecular H-bonding in the mixed solvent of CDCl<sub>3</sub> and CD<sub>3</sub>OD by <sup>1</sup>H-NMR spectroscopy.

2. Study complexation ability of the synthesized ligand with divalent transition metal ions such as Cu<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, etc.