

การสังเคราะห์สารประกอบ 25,27-[เอ็น,เอ็น'-ได-((2-เอทอกซี)เบนซิล)โพรพิลีน ไดเอมีน]-  
26,28-ไดเมทอกซี-พารา-เทอร์เชียรี-บิวทิลคาบิก[4]ซารีน ไดไฮโดรคลอไรด์  
และการทดสอบความเป็นเบสและการเกิดสารประกอบเชิงซ้อนกับ  
โลหะแทรนซิชันไอออนบางชนิด



นางสาวสุภารัตน์ วีระวงศ์

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SYNTHESIS OF 25,27-[*N,N'*-DI-((ETHOXY)BENZYL)PROPYLENEDIAMINE]-  
26,28-DIMETHOXY-*p-tert*-BUTYLCALIX[4]ARENE DIHYDROCHLORIDE  
AND INVESTIGATION OF ITS BASICITY AND COMPLEXATION  
WITH SOME TRANSITION METAL IONS

Miss Sudarath Veravong

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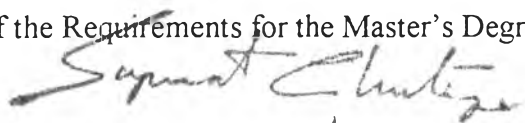
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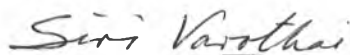
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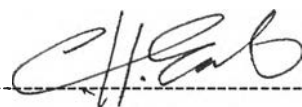
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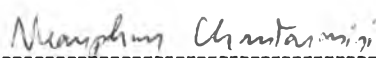
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สุดารัตน์ วีระวงศ์ : การสังเคราะห์สารประกอบ 25,27-[เอีน,เอีน'-ได-((2-เอทอกซี)เบนซิล)โพรพิลีน]ไดเอมีน]-26,28-ไดเมทอกซี-พารา-เทอร์เชียรี-บิวทิลคาลิก[4]ซารีน ไดไฮโดรคลอไรด์และการทดสอบความเป็นเบส และการเกิดสารประกอบเชิงซ้อนกับโลหะทรานซิชันไอออนบางชนิด (SYNTHESIS OF 25,27-[N,N'-DI-((ETHOXY)BENZYL)PROPYLENEDIAMINE]-26,28-DIMETHOXY-*p-tert*-BUTYLCALIX[4]ARENE DIHYDROCHLORIDE AND INVESTIGATION OF ITS BASICITY AND COMPLEXATION WITH SOME TRANSITION METAL IONS) อ.ที่ปรึกษา : รศ.ดร.วิทยาเรืองพรวิสุทธิ, อ.ที่ปรึกษาร่วม : ผศ.ดร.ธวัชชัย ต้นขูลานี; 112 หน้า. ISBN 974-331-216-1.

การสังเคราะห์สารประกอบ 25,27-[เอีน,เอีน'-ได-((2-เอทอกซี)เบนซิล)โพรพิลีนไดเอมีน]-26,28-ไดเมทอกซี-พารา-เทอร์เชียรี-บิวทิลคาลิก[4]ซารีน ไดไฮโดรคลอไรด์ (7, L.2HCl) ซึ่งเป็นอนุพันธ์แอมโมเนียมของสารประกอบไดเอทาคาลิก[4]ซารีนเตรียมโดยการเมทิลเลทฟีนออกซีออกซิเจนของไดอัลดีไฮด์คาลิก[4]ซารีนด้วย  $\text{CH}_3\text{I}$  หลังจากนั้นนำสารประกอบ methylated dialdehyde ไปทำปฏิกิริยากับ 1,3-ไดอะมิโนโพรเพน ได้สารประกอบชิฟเบส ซึ่งนำไปรีดิวซ์ด้วย  $\text{NaBH}_4$  และโปรโตเนทด้วย 2% HCl ใน  $\text{CH}_3\text{OH}$  นำสารประกอบ L.2HCl ไปศึกษา conformational isomerism โดยวิธีโปรตอนเอ็นเอ็มอาร์สเปกโตรสโกปี โปรตอนเอ็นเอ็มอาร์สเปกตรัมของ L.2HCl ใน  $\text{CDCl}_3$  และใน  $\text{DMSO}-d_6$  แสดงให้เห็นว่าคาลิก[4]ซารีนมีการจัดตัวแบบโครงสร้างผสมอย่างใดก็ได้ เอ็นเอ็มอาร์สเปกตรัมใน  $\text{CD}_3\text{OD}$  บ่งบอก ถึงโครงสร้างแบบโคน เมื่อค่อยๆเติม  $\text{CD}_3\text{OD}$  ลงในสารละลาย  $\text{CDCl}_3$  ของ L.2HCl พบว่าพันธะไฮโดรเจนระหว่างโมเลกุลของ  $\text{CD}_3\text{OH}$  กับ  $\text{CH}_3\text{OAr}-t\text{-C}_4\text{H}_9$  ยึดโครงสร้างของคาลิก[4]ซารีนให้อยู่ในรูปโคน การทดลองที่อุณหภูมิต่างๆกันของ L.2HCl ในสารละลายผสม  $\text{CD}_3\text{OD}/\text{CDCl}_3$  แสดงถึงกลไกการเคลื่อนที่ที่อาจเป็นไปได้ของวงเพนนิลและบ่งบอกว่าโครงสร้างแบบ pinched cone จะเกิดขึ้นที่อุณหภูมิ  $-40^\circ\text{C}$

นอกจากนี้ได้มีการศึกษาค่าคงที่ของการรับโปรตอนของ L โดยวิธีโพเทนซิโอเมตริกไทเทรชัน (potentiometric titration) ใน  $1 \times 10^{-2}$  M  $\text{Bu}_4\text{NCF}_3\text{SO}_3$  ในเมทานอล พบว่าค่า  $\text{Log } K_1$ , ( $\text{Log } K_2$ ) ของการรับโปรตอนตัวแรก (ตัวที่สอง) คือ 10.06 (6.67), 9.97 (6.75), 9.61 (6.64), 9.75 (6.77) และ 9.69 (6.68) ที่อุณหภูมิ 20, 23, 25, 27 และ  $30^\circ\text{C}$  ตามลำดับ ค่าฟังก์ชันทางเทอร์โมไดนามิก  $\Delta H_1$ ,  $\Delta H_2$ ,  $\Delta S_1$  และ  $\Delta S_2$  ที่คำนวณได้สำหรับการรับโปรตอนตัวแรกและตัวที่สอง มีค่าเป็น  $-67$  kJ/mol, 3 kJ/mol,  $-38$  kJ/mol·K และ 137 kJ/mol·K ตามลำดับ ในการศึกษาการเกิดสารประกอบเชิงซ้อนของ L กับไอออนของ  $\text{Zn}^{2+}$  และ  $\text{Cu}^{2+}$  ด้วยวิธีเดียวกัน พบว่า L ไม่เกิดสารประกอบเชิงซ้อนกับไอออนทั้งสองชนิด

ภาควิชา.....  
 สาขาวิชา.....  
 ปีการศึกษา.....

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 ลายมือชื่ออาจารย์ที่ปรึกษา.....  
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KEY WORD : BASICITY/CALIX[4]ARENE/DIAZA/METHYLATION/POTENTIOMETRIC TITRATION/PROTONATION CONSTANT/SPECIES/CONFORMATIONAL ISOMERISM  
SUDARATH VERA VONG : SYNTHESIS OF 25,27-[*N,N'*-DI-((ETHOXY)BENZYL) PROPYLENEDIAMINE]-26,28-DIMETHOXY-*p-tert*-BUTYLCALIX[4]ARENE DIHYDROCHLORIDE AND INVESTIGATION OF ITS BASICITY AND COMPLEXATION WITH SOME TRANSITION METAL IONS, THESIS ADVISOR ASSOC. PROF. VITHAYA RUANGPORNVISUTI, Dr. rer. nat., THESIS CO-ADVISOR : ASSIST. PROF. THAWATCHAI TUNTULANI, Ph.D. 112 pp. ISBN 974-331-216-1.

25,27-[*N,N'*-di-((ethoxy)benzyl)propylenediamine]-26,28-dimethoxy-*p-tert*-butylcalix[4]arene dihydrochloride (7, **L.2HCl**), an ammonium derivative of diaza calix[4]arene, was prepared by methylating phenoxy oxygen of dialdehyde calix[4]arene with  $\text{CH}_3\text{I}$ . The methylated dialdehyde was then reacted with 1,3-diaminopropane to give a Schiff base compound which was then reduced with  $\text{NaBH}_4$  and protonated with 2% HCl in  $\text{CH}_3\text{OH}$ . The conformational isomerism of **L.2HCl** was studied by  $^1\text{H}$  NMR spectroscopy.  $^1\text{H}$  NMR spectra of **L.2HCl** in  $\text{CDCl}_3$  and in  $\text{DMSO-d}_6$  showed that the calix[4]arene moiety orientated in mixed conformations. However, the  $^1\text{H}$  NMR spectrum in  $\text{CD}_3\text{OD}$  indicated cone conformation. Gradual additions of  $\text{CD}_3\text{OD}$  into a  $\text{CDCl}_3$  solution of **L.2HCl** revealed that intermolecular hydrogen bonding between methanol and  $\text{CH}_3\text{OAr-}t\text{-C}_4\text{H}_9$  held the calix[4]arene framework in cone conformation. Variable temperature experiments of **L.2HCl** in a mixed solvent of  $\text{CD}_3\text{OD}/\text{CDCl}_3$ , implied a possible mechanism of phenyl ring movement and suggested that a pinched cone conformation was preferred at  $-40^\circ\text{C}$

In addition, protonation constants of **L** were calculated in methanolic solution of  $1 \times 10^{-2} \text{ M Bu}_4\text{NCF}_3\text{SO}_3$  by potentiometric titration.  $\text{Log } K_1$  ( $\text{Log } K_2$ ) values of the first protonation (second protonation) were 10.06 (6.67), 9.97 (6.75), 9.61 (6.64), 9.75 (6.77) and 9.69 (6.68) at 20, 23, 25, 27 and  $30^\circ\text{C}$ , respectively. Calculated thermodynamic functions,  $\Delta H_1$ ,  $\Delta H_2$ ,  $\Delta S_1$  and  $\Delta S_2$  for the first and second protonations were  $-67 \text{ kJ/mol}$ ,  $3 \text{ kJ/mol}$ ,  $-38 \text{ kJ/mol}\cdot\text{K}$  and  $137 \text{ kJ/mol}\cdot\text{K}$ , respectively. Complexation studies of **L** with  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  ions by the same method showed that **L** could not form complexes with both ions.

ภาควิชา..... ๑๗

สาขาวิชา..... ๑๗

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## LIST OF SYMBOLS

$\alpha_c$	degree of formation
$\beta_n$	overall stoichiometric stability constant for $ML_n$
$^{\circ}C$	degree Celcius
$\Delta G$	free energy change
$\Delta H$	enthalpy energy change
$\Delta S$	entropy change
$e_i$	error associated with the $i^{\text{th}}$ component
$E$	observed potential (e.m.f.)
$E^{\circ}$	standard potential
$\phi$	degree of complex formation
$\gamma$	activity coefficient
$\ln$	logarithm to base e
$\log$	logarithm to base 10
$M$	metal
$\mu$	ionic strength
$ML$	mononuclear complex
$n$	(in association with ligand) number of ligands in a complex
$\bar{n}$	complex formation function
$o$	experimental observations
$\Pi$	product
$\bar{p}$	protonation formation function
$pX$	$-\log_{10} [X]$
$\sum$	sum
$T$	absolute temperature
$[ ]$	concentration
$[ ]_T$	total concentration

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