อันตรกิริยาระหว่างอนุพันธ์ของสารประกอบคาลิก[4]ซารีน กับแอนไอออนและโมเลกุลอินทรีย์

นางสาว กมลวรรณ ธรรมเจริญ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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INTERACTION OF CALIX[4]ARENE DERIVATIVES TOWARDS ANIONS AND ORGANIC MOLECULES

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กมลวรรณ ธรรมเจริญ : อันตรกิริยาระหว่างอนุพันธ์ของสารประกอบคาลิก[4]ซารีนกับแอนไอออนและโมเลกุลอินทรีย์ (INTERACTION OF CALIX[4]ARENE DERIVATIVES TOWARDS ANIONS AND ORGANIC MOLECULES) อ. ที่ปรึกษา : ผศ.ดร. ธวัชชัย ตันทุลานิ; 146 หน้า. ISBN 974-332-118-7.

ทำการสังเคราะห์สารใหม่สองชนิดคือ 25,27-*N,N'*-di-((2-ethoxy)benzyl)ethylene diamine-*p-tert*-butylcalix[4]arene (**5a**) และ 25,27-di-(4-pyridylmethoxy)-*p-tert*-butyl calix[4]arene (**6**) การศึกษาอันตรกิริยาพันธะไฮโดรเจนกระทำโดยการไทเทรตด้วยเทคนิคโปรตอนนิวเคลียร์แมกเนติกเรโซแนนซ์ (เอ็นเอ็มอาร์) ในเมธานอล-d_4 หรือคลอโรฟอร์ม-*d* การศึกษาการเกิดสารประกอบเชิงซ้อนกับแอนไอออน เช่น เกลือโซเดียมของคลอไรด์, โบรไมด์, ไอโอไดด์, ไนเตรต, คาร์บอเนต, ซัลเฟต และ ฟอสเฟต กับสารประกอบ ไดเอซา เบนโซ คราวน์ พาราเทอร์เชียลรีบิวทิลคาลิก[4]ซารีนที่ประกอบด้วยสะพานเชื่อมเอธิลีน, โพรพิลีน และ บิวทิลีน เชื่อมระหว่างหมู่เอมีน (ลิแกนด์ (**5a**), (**5b**) และ (**5c**) ตามลำดับ) ไม่สังเกตพบการเปลี่ยนแปลงของสัญญาณในโปรตอนเอ็นเอ็มอาร์ และจากการศึกษาการเกิดสารประกอบเชิงซ้อนกับโมเลกุลอินทรีย์ซึ่งมีหมู่ให้พันธะไฮโดรเจน เช่น 1,3-dialdehyde crown *p-tert*-butyl calix[4]arene (ลิแกนด์ (**2-1**) และ (**2-2**)), acetylacetone, 1,2-diaminoethane, 2,6-diamino pyridine, catechol, resorcinol, hydroquinone, phthalic acid, isophthalic acid และ terephthalic acid กับลิแกนด์ (**6**) ซึ่งมีหมู่รับพันธะไฮโดรเจนในสารละลายคลอโรฟอร์ม-*d* พบว่า ลิแกนด์ (**6**) สามารถเลือกเกิดสารประกอบแบบ 1:4, 1:1 และ 1:1 กับ catechol, resorcinol ($\log K > 22.8$) และ phthalic acid ($\log K = 5.41$) ตามลำดับ จากการทดลองเปรียบเทียบโดยวิธีโปรตอนเอ็นเอ็มอาร์ พบว่า phthalic acid เกิดสารประกอบเชิงซ้อนกับลิแกนด์ (**6**) ได้ดีกว่า catechol นอกจากนี้ยังได้เสนอโครงสร้างที่เป็นไปได้ในสารละลายของสารประกอบเชิงซ้อน (**6**)·catechol, (**6**)·resorcinol และ (**6**)·phthalic acid ทั้งสามชนิดจาก NOESY และ ROESY ด้วย

ภาควิชา...เคมี... ลายมือชื่อนิสิต...กมลวรรณ ธรรมเจริญ...

สาขาวิชา...เคมี... ลายมือชื่ออาจารย์ที่ปรึกษา...ธวัชชัย ตันทุลานิ...

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Two new compounds, 25,27-*N,N'*-di-((2-ethoxy)benzyl)ethylenediamine-*p-tert*-butylcalix[4]arene (**5a**) and 25,27-di-(4-pyridylmethoxy)-*p-tert*-butylcalix[4]arene (**6**) have been synthesized. ^{1}H-NMR titration experiments in chloroform-*d* or methanol-d_4 were used to investigate the hydrogen bonding interaction. Complexation studies of diaza benzo crown *p-tert*-butylcalix[4]arene containing ethylene, propylene and butylene linkages (ligands (**5a**), (**5b**) and (**5c**), respectively) were carried out with various anions such as chloride, bromide, iodide, nitrate, carbonate, sulfate and phosphate. The complexation induced shift could not be observed. Ligand (**6**) containing hydrogen bond acceptors was investigated the hydrogen bonding interaction towards neutral molecules containing a wide varieties of hydrogen bond donors such as 1,3-dialdehyde-crown-*p-tert*-butylcalix[4]arene (ligand (**2-1**) and (**2-2**)), acetylacetone, 1,2-diaminoethane, 2,6-diaminopyridine, catechol, resorcinol, hydroquinone, phthalic acid, isophthalic acid and terephthalic acid. Ligand (**6**) was able to form complexes with catechol, resorcinol (log K > 20.8) and phthalic acid (log K = 5.41) in 1:4, 1:1 and 1:1 fashions, respectively. Comparison studies between catechol and phthalic acid suggested that ligand (**6**) formed a stronger complex with phthalic acid. In addition, the possible structures in the solutions of (**6**)·catechol, (**6**)·resorcinol and (**6**)·phthalic acid were deduced from NOESY and ROESY.

ภาควิชา.....เคมี..... ลายมือชื่อนิสิต.....กมลวรรณ ฌมเจริญ.....

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List of Abbreviations and Signs

Å	Angstrom
K_{ass}	Association constant
^{13}C-NMR	Carbon Nuclear Magnetic Resonance
°C	Celcius
δ	Chemical shift
CIS	Complexation Induced Shift
J	Coupling constant
DEPT	Distortionless Enhancement of NMR signals by Polarization Transfer
g	Gram
Hz	Hertz
MALDI-TOF	Matrix Assistance Laser Desorption /Ionization – Time of Flight
mp	Melting point
mL	Millilit
mmol	Millimol
MM^{+}	Molecular Mechanic Method
NOESY	Nuclear Overhauser Effect Spectroscopy
ppm	Part per million
M^{-1}	Per mole
^{1}H-NMR	Proton Nuclear Magnetic Resonance
RT	Room Temperature
ROESY	Rotation Overhauser Effect Spectroscopy
K_s	Stability constant
2D-NMR	Two-Dimentional Nuclear Magnetic Resonance
VPO	Vapor Pressure Osmometry

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