

A THEORETICAL STUDY OF THE INFLUENCE OF SOLVENT  
ON THE INTERNAL ROTATION OF GLYCINE ZWITTERION



Mr. Prayong Doungee

A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Science

Department of Chemistry

Graduate School

Chulalongkorn University

1985

ISBN 974-566-127-9

010114

I 1689365X

Thesis Title A Theoretical Study of the Influence of Solvent  
on the Internal Rotation of Glycine Zwitterion  
By Mr. Prayong Doungdee  
Department Chemistry  
Thesis Advisor Associate Professor Sirirat Kokpol, Ph.D.  
Professor B. M. Rode, Ph.D.



Accepted by the Graduate School, Chulalongkorn University in  
Partial Fulfillment of the Requirements for the Master's Degree.

.....*S. Bunnag*..... Dean of Graduate School  
(Professor Supradit Bunnag, Ph.D.)

Thesis Committee

.....*Padet Sidisunthorn*..... Chairman  
(Professor Padet Sidisunthorn, Ph.D.)

.....*Salag Dhabanandan*..... Member  
(Associate Professor Salag Dhabanandana, Ph.D.)

.....*Waret Veerasai*..... Member  
(Dr. Waret Veerasai)

.....*Sirirat Kokpol*..... Member  
(Associate Professor Sirirat Kokpol, Ph.D.)

หัวข้อวิทยานิพนธ์	การศึกษาทางทฤษฎี ถึงผลกระทบของคว่ำทะเลลายที่มีต่อการหมุนภายในของไกลซีน สวิตเตอร์ไอออน
ชื่อนิสิต	นาย ประยงค์ ดวงดี
อาจารย์ที่ปรึกษา	รองศาสตราจารย์ ดร. ศิริรัตน์ ก๊กผล ศาสตราจารย์ ดร. บี เอ็ม โรเค
ภาควิชา	เคมี
ปีการศึกษา	2528



บทคัดย่อ

ไฮเดรชันเซลล์ของไกลซีน สวิตเตอร์ไอออน ถูกสร้างขึ้นโดย การศึกษาพลังงานอินเทอแรคชันระหว่างไกลซีน สวิตเตอร์ไอออน กับโมเลกุลของน้ำที่ล้อมรอบ โดยใช้วิธีการคำนวณทั้งแบบ เชมิเอ็มไพริกัล และเอ็บอินนิซิโอ พร้อมทั้งได้วิจารณ์ข้อจำกัด และข้อได้เปรียบ เสียเปรียบของวิธีการคำนวณทั้งสอง นอกจากนั้น โดยใช้วิธีการเปรียบเทียบกับไกลซีน สวิตเตอร์ไอออนที่อยู่ในสภาพของโมเลกุลเดี่ยว ทำการศึกษาผลของ ไฮเดรชันเซลล์ ที่มีต่อการหมุนภายในของไกลซีน สวิตเตอร์ไอออน ศึกษาผลของโมเลกุล น้ำที่อยู่ใน ไฮเดรชันเซลล์ ที่มีต่อการเปลี่ยนแปลงคอนฟอร์ เมชัน ทั้งนี้โดยใช้วิธีคำนวณแบบ เชมิเอ็มไพริกัล

ศูนย์วิจัยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย



Thesis Title A Theoretical Study of the Influence of Solvent  
on the Internal Rotation of Glycine Zwitterion

Name Mr. Prayong Doungdee

Thesis Advisor Associate Professor Sirirat Kokpol, Ph.D.  
Professor B. M. Rode, Ph.D.

Department Chemistry

Academic Year 1985



## ABSTRACT

To construct the hydration shell of glycine zwitterion, the interaction of glycine zwitterion with water has been studied. The relative stability of the possible coordination sites has been evaluated using the semiempirical CNDO/2 method and ab initio calculations with minimal Gaussian basis sets. The abilities and limitations of both computational frameworks are critically discussed and a model for the full hydration shell of glycine and the corresponding stabilization energy are given. The influence of a full first hydration shell on the energy barriers related to conformational changes of glycine has been studied by means of approximate molecular orbital calculations. The energy optimized pathway is discussed and compared with that of the isolated molecule, evaluating the possibility of corotation of the hydration shell during conformational changes.



### Acknowledgements

I would like to thank Visiting Professor B. M. Rode and Associate Professor Sirirat Kokpol for the direction and the advice which made the writing of this thesis possible. I am also grateful to the System Analyzers and Operators of the Computer Center of Chulalongkorn University for many helpful suggestions about the programs. A special debt is owed to Bangorn Narmngam, who has given me encouragement and financial support throughout my months of work on this project. Larry Lohmann helped proofread the English version.

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย



## Contents

	Pages
ABSTRACT ( in Thai ).....	iii
ABSTRACT .....	iv
Acknowledgements .....	v
List of Tables .....	ix
List of Figure .....	xvi
Chapter I Self Consistent Field Molecular Orbital Theory ...	4
The Born-Oppenheimer approximation .....	5
The independent electron model .....	8
Molecular orbitals and the linear combination of atomic orbitals (LCAO) approximation .....	9
Self consistent field molecular orbital theory ...	11
1. The Hamiltonian .....	11
2. The Roothaan equation .....	13
The central field approximation and the self consistent field (SCF) procedure .....	15
The basis set (atomic orbitals) .....	16
Chapten II Approximate Molecular Orbital Theories .....	18
SCF equation and transformation properties .....	18
Approximation with complete neglect of differential overlap (CNDO) .....	20
1. The neglect of overlap (NO) .....	21
2. The zero-differential-overlap (ZDO) approximation .....	21



## Contents continued

	Pages
3. The core hamiltonian approximation. ....	22
The CNDO parametrization .....	25
1. The local core matrix element $U_{kk}^A$ .....	25
2. The electron-core potential intergrals $V_B^A$ ..	26
3. The bonding parameters $B_{AB}$ .....	26
The CNDO basis set .....	27
The SCF procedure for CNDO .....	27
 Chapter III Geometry and Conformation of Molecules in	
Aqueous Solution .....	29
The continuous model .....	29
The super molecular approach .....	30
Monte-Carlo simulation .....	31
Determination of the interaction energy in	
the super-molecule approach .....	32
The basis set superposition error .....	32
Determination of interaction energies from	
semi-empirical method (CNDO) .....	35
Population analysis .....	35
 Chapter IV Calculation .....	38
The model .....	38
Methodical steps .....	38
Calculation of the internal rotation of isolated	
glycine zwitterion .....	40

## Contents continued

	Pages
Determination of the hydration shell and calculation of the hydration energy of glycine zwitterion. ....	45
1. Optimization of the water binding sites of the glycine zwitterion. ....	45
2. Calculation of the interaction energy of glycine zwitterion and water (fixing the hydrogen bond distance at 2.75 Å) .....	58
Calculation of the internal rotation of glycine zwitterion including the hydration shell effect. .	67
Chapter V Discussion and Conclusion .....	82
Discussion of the hydration shell of glycine zwitterion in aqueous solution .....	82
Influence of the hydration on the electron distribution in glycine zwitterion .....	88
The influence of hydration on the internal rotation of glycine zwitterion .....	91
REFERENCES .....	106
APPENDIX A Ab Initio Program .....	109
APPENDIX B CNDO Program .....	122
APPENDIX C The Coordinate Program .....	142
About The Author .....	145



## List of Tables

	Pages
Table 4.1 The geometry parameters of glycine zwitterion. All bond lengths and bond angles are reported in Å and degrees respectively.....	39
Table 4.2 The total energy and the rotation barriers of glycine zwitterion (standard geometry), fixing $\psi = 0^\circ$ , rotating $\phi$ from $0^\circ - 90^\circ$ .....	42
Table 4.3 The total energy and the rotation barriers of glycine zwitterion, fixing $\psi = 0^\circ$ , rotating $\phi$ from $0^\circ - 90^\circ$ .....	42
Table 4.4 The total energy and the rotation barriers of glycine zwitterion, fixing $\phi = 0^\circ$ , rotating $\psi$ from $0^\circ - 60^\circ$ .....	44
Table 4.5 The total energy and the rotation barriers of glycine zwitterion, fixing $\psi = 60^\circ$ , rotating $\phi$ from $0^\circ - 90^\circ$ .....	44
Table 4.6 The optimization of energy for glycine zwitterion and water 1. Optimizing C-O distance of the $-\text{COO}^-$ group and water 1 .....	45
Table 4.7A The optimization of energy for glycine zwitterion and water 2, Optimizing O-O distance of the linear hydrogen bond OH-O .....	50
Table 4.7B The optimization of energy for glycine zwitterion and water 2, rotating of water around C=O bond with the OH-O distance 2.40 Å.....	50

## List of tables continued

	Pages
Table 4.7C The optimization of energy for glycine zwitterion and water 2. Fixing $\angle\text{COO} = 130^\circ$ , fixing OH-O distance = 2.40 Å, rotating water around O (of water) center .....	51
Table 4.7D The optimization of energy for glycine zwitterion and water 2, fixing $\angle\text{COO} = 130^\circ$ , fixing $\angle\text{OOH} = 15^\circ$ , optimizing OH-O distance .....	51
Table 4.7E The optimization of energy for glycine zwitterion and water 2, fixing OH-O distance 2.25 Å, fixing $\angle\text{COO} = 130^\circ$ , rotating water around O (of water) center .....	52
Table 4.7F The optimization of energy for glycine zwitterion and water 2, rotating of water around C=O bond with the OH-O distance 2.25 Å, and fixing $\angle\text{OOH} = 20^\circ$ .....	52
Table 4.8A The optimization of energy for glycine zwitterion and water 3, optimizing O-O distance of the linear hydrogen bond OH-O .....	53
Table 4.8B The optimization of energy for glycine zwitterion and water 3, rotating of water around C=O bond with the OH-O distance 2.40 Å.....	53
Table 4.8C The optimization of energy for glycine zwitterion and water 3, fixing OH-O distance 2.40 Å, fixing $\angle\text{COO} = 95^\circ$ , rotating water around O (of water) center. ....	54



## List of tables continued

	Pages
Table 4.8D The optimization of energy for glycine zwitterion and water 3, fixing $\angle\text{COO} = 95^\circ$ fixing $\angle\text{OOH} = 10^\circ$ , and optimizing OH-O distance .....	54
Table 4.8E The optimization of energy for glycine zwitterion and water 3, fixing OH-O distance 2.40 Å, fixing $\angle\text{COO} = 95^\circ$ , rotating water around O (of water) center .....	55
Table 4.8F The optimization of energy for glycine zwitterion and water 3, rotating of water around C=O bond with the OH-O distance 2.40 Å, and fixing $\angle\text{OOH} = 10^\circ$ .....	55
Table 4.9 The optimization of energy for glycine zwitterion and water 4,5, optimizing NH-O distance .....	56
Table 4.10 The optimization of energy for glycine zwitterion and water 6, optimizing HO-O distance .....	56
Table 4.11 The optimization of energy for glycine zwitterion and water 9, optimizing HO-N distance .....	57
Table 4.12 Total energies and interaction energies of glycine zwitterion complexes with one water molecule in nine different conformations (CNDO calculation) .....	60



## List of tables continued

	Pages
Table 4.13 Calculation of the ab initio interaction energy, the stabilization energy, and the corrected interaction energies according to equation 4.4 and 4.6 .....	62
Table 4.14 Mulliken atomic populations (ab initio calculations) .....	63
Table 4.14 continued .....	64
Table 4.15 Mulliken atomic populations (CNDO calculation) ....	65
Table 4.15 continued .....	66
Table 4.16 The change of electron distribution between functional groups due to the influence of hydration in glycine zwitterion .....	66
Table 4.17 The total energy and the rotation barriers of glycine zwitterion plus 5 water molecules, fixing hydrogen bond 2.75 Å, fixing $\psi = 0^\circ$ , and fixing the hydration shell, rotating $-\text{NH}_3^+$ alone .....	67
Table 4.18 The total energy and the rotation barriers of glycine zwitterion plus 5 water molecules, fixing hydrogen bond 2.75 Å, fixing $\psi = 0^\circ$ , and fixing water 1,3, rotating $-\text{NH}_3^+$ and water 2,4,5 .....	68
Table 4.19 The total energy and the rotation barriers of glycine zwitterion plus 5 water molecules, fixing hydrogen bond 2.75 Å, fixing $\psi = 0^\circ$ , and fixing the hydration shell, rotating $-\text{COO}^-$ alone .....	69

## List of tables continued

	Pages
Table 4.20 The total energy and the rotation barriers of glycine zwitterion plus 5 water molecules, fixing hydrogen bond 2.75 Å, fixing $\varphi = 0^\circ$ and fixing the water 2,3,4,5, rotating $-\text{COO}^-$ and water 1 .....	70
Table 4.21 The total energy and the rotation barriers of glycine zwitterion plus 5 water molecules, fixing hydrogen bond 2.75 Å, fixing $\varphi = 0^\circ$ , and fixing the water 3, 4, 5, rotating $-\text{COO}^-$ and water 2 .....	71
Table 4.22 The total energy and the rotation barriers of glycine zwitterion plus 5 water molecules, fixing hydrogen bond 2.75 Å, fixing $\varphi = 0^\circ$ and fixing water 3,4,5, rotating $-\text{COO}^-$ and water 1,2 ...	72
Table 4.23 The total energy and the rotation barriers of glycine zwitterion plus 5 water molecules, fixing hydrogen bond 2.75 Å, fixing $\varphi = 0^\circ$ , and fixing water 2,4,5, rotating $-\text{COO}^-$ and water 1,3 .....	73
Table 4.24 The total energy and the rotation barriers of glycine zwitterion plus 5 water molecules, fixing hydrogen bond 2.75 Å, fixing $\varphi = 0^\circ$ and fixing water 4,5, rotating $-\text{COO}^-$ and water 1,2,3 .....	74



## List of tables continued

Pages

- Table 4.25 The total energy and the rotation barriers of glycine zwitterion plus 5 water molecules, fixing hydrogen bond 2.75 Å, fixing  $\phi = 60^\circ$ , fixing water 2,4,5 (these water molecules have been moved with  $-\text{NH}_3^+$  group to  $60^\circ$ ) and fixing water 1, 3, rotating  $-\text{COO}^-$  alone ..... 75
- Table 4.26 The total energy and the rotation barriers of glycine zwitterion plus 5 water molecules, fixing hydrogen bond 2.75 Å, fixing  $\phi = 60^\circ$ , fixing water 2,4,5 (these water molecules have been moved with  $-\text{NH}_3^+$  group to  $60^\circ$ ) and fixing water 3 rotating  $-\text{NH}_3^+$  and water 1 ..... 76
- Table 4.27 The total energy and the rotation barriers of glycine zwitterion plus 5 water molecules, fixing hydrogen bond 2.75 Å, fixing  $\phi = 60^\circ$  fixing water 2,4,5 (these water molecules have been moved with  $-\text{NH}_3^+$  group to  $60^\circ$ ) rotating  $-\text{COO}^-$  and water 1,3 ..... 77
- Table 4.28 The total energy and the rotation barriers of glycine witterion plus 7 water molecules (4 water molecules are in the first shell, 3 water molecules are in the second shell around  $-\text{NH}_3^+$  group). fixing  $\phi = 0^\circ$ , fixing water 3 and fixing water molecules in the second



## List of tables continued

	Pages
shell, rotating $-\text{NH}_3^+$ and water 2,4,5 .....	78
Table 4.29 The total energy and the rotation barriers of glycine zwitterion plus 4 water molecules (neglecting water 1), fixing hydrogen bond 2.75 Å, fixing $\phi = 0^\circ$ , and fixing water 3 rotating $-\text{NH}_3^+$ and water 2,4,5 .....	79
Table 4.30 The total energy and the rotation barriers of glycine zwitterion plus 5 water molecules, fixing hydrogen bond 2.65 Å, fixing $\phi = 0^\circ$ and fixing water 1,3, rotating $-\text{NH}_3^+$ and water 2,4,5 .....	80
Table 4.31 The total energy and the rotation barriers of glycine zwitterion plus 5 water molecules, fixing hydrogen bond 2.85 Å, fixing $\phi = 0^\circ$ and fixing water 1,3 rotating $-\text{NH}_3^+$ and water 2,4,5 .....	81
Table 5.1 The interaction energies of glycine zwitterion complexes with one water molecule in nine different conformation .....	82
Table 5.1 continued .....	83
Table 5.2 Total energy and hydration energy of hydrated glycine zwitterion, in various hydrogen bond distance .....	84
Table 5.3 The barriers for internal rotation of hydrated glycine zwitterion are a function of Hydrogen bond distance .....	101

## List of Figures

	Pages
Figure A The structure of two different conformation of glycine .....	1
Figure 1.1 The potential energy surface of molecule .....	7
Figure 4.1 The glycine zwitterion, conformation ( $\varphi, \psi$ ) = (0,0) one H atom of $-\text{NH}_3^+$ and N,C1,C2,O atoms are in the same plane .....	40
Figure 4.2 The rotation energy curve of glycine zwitterion, comparison between two sets of geometries. Graph A represents the geometry used in this work. Graph B represents standard geometry .....	41
Figure 4.3 The optimization of glycine zwitterion and water 1 .....	45
Figure 4.4 The optimization of glycine zwitterion and water 2 .....	46
Figure 4.5 The optimization of glycine zwitterion and water 3 .....	47
Figure 4.6 The optimization of glycine zwitterion and water 4 .....	48
Figure 4.7 The optimization of glycine zwitterion and water 6 .....	48
Figure 4.8 The optimization of glycine zwitterion and water 9 .....	49
Figure 4.9 The nine most stabilized water positions around glycine zwitterion with fixed hydrogen bond distance 2.75 Å ..	58



## List of Figures continued

	Pages
Figure 5.1 The glycine zwitterion with 5 water molecules in the hydration shell by CNDO optimization .....	83
Figure 5.2 The most favored water molecules around Formate ion and Ethylamine ion, optimized by ab initio STO-3G (1) .....	84
Figure 5.3 The glycine zwitterion with 5 water molecules in the first hydration shell. All hydrogen bonds are 2.75 Å .....	86
Figure 5.4 The experimental hydration number of glycine zwitterion in aqueous solution. Graph A includes a second hydration shell (26), graph B including only the first hydration shell (27) .....	87
Figure 5.5 The atomic population of glycine zwitterion due to the influence of hydration (the value in brackets are calculated by CNDO) .....	89
Figure 5.6 The charge of electron distribution of groups due to the influence of hydration in glycine zwitterion. The arrows show the direction of the charge transfer between groups of atoms. (The result is taken from table 4.16) .....	90
Figure 5.7 The rotation pathway of glycine zwitterion, changing conformation (0,0) to (60,0) .....	92



## List of Figures continued

	Pages
Figure 5.8 The rotation pathway of glycine zwitterion, changing conformation (60,0) to (60,90) .....	92
Figure 5.9 The predicted most stable conformations of glycine zwitterion, (a) results from this calculation and reference 4, (b) is taken from reference 4. ....	93
Figure 5.10 The glycine zwitterion with 5 water molecules in the first hydration shell .....	95
Figure 5.11 The rotation pathway of glycine zwitterion including 5 water molecules in the hydration shell, fixing $\psi = 0^\circ$ , rotating $\phi$ from 0 to $60^\circ$ .....	96
Figure 5.12 The rotation pathway of glycine zwitterion including 5 water molecules in the hydration shell, fixing $\psi = 0^\circ$ , rotating $\phi$ from 0 to $90^\circ$ . ....	97
Figure 5.13 Glycine zwitterion including 5 water molecules in the hydration shell after rotating $-\text{NH}_3^+$ group together with water molecules 2,4,5 to $60^\circ$ ...	98
Figure 5.14 The rotation pathway of glycine zwitterion including 5 water molecules in the hydration shell, fixing $\psi = 60^\circ$ , rotating $\phi$ from $0^\circ$ to $90^\circ$ (figure 5.13) .....	100

## List of Figures continued

	Pages
Figure 5.15 The comparison of the rotation pathways for hydrated glycine zwitterion rotating $\text{-NH}_3^+$ group and water 2,4,5, at varying hydrogen bond distances, $A = 2.65 \text{ \AA}$ , $B = 2.75 \text{ \AA}$ , $C = 2.85 \text{ \AA}$ .....	102
Figure 5.16 Model of glycine zwitterion including 4 water molecules in first hydration shell and 3 water molecules in the second hydration shell. ....	103
Figure 5.17 The internal rotation pathways of glycine zwitterion including the second shell effect .....	104