รายงานผลการวิจัย
เงินทุนวิจัยรัชดาภิเษกสมโภช

เรื่อง

การศึกษาผลกระทบของโซเดียมไอออนที่มีต่อคอนฟอร์เมชั่นของไกลซีนสวิตเทอร์ไอออนในน้ำ

โดย

ศิริรัตน์ ก๊กผล
สุพจน์ หารหนองบัว
ประยงค์ ดวงดี

2530

จุฬาลงกรณ์ มหาวิทยาลัย

ทุนวิจัยรัชดาภิเษกสมโภช

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ชื่อผู้วิจัย	**ศิริรัตน์ กึกผล**	**สุพจน์ หารหนองบัว**
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เดือนและปีที่ทำวิจัยเสร็จ	พฤษภาคม 2530	

บทคัดย่อ

แรงกระทำระหว่างไกลซีนสวิตเทอร์ไอออนและน้ำคำนวณโดยวิธีแอบอินนิชิโอ และใช้ GLO เบลิสเซทแบบต่ำสุด ทำนายว่า น้ำชั้นแรกที่ล้อมรอบไกลซีนสวิตเทอร์ไอออนประกอบด้วยน้ำ 5 โมเลกุล อิทธิพลของน้ำชั้นแรกที่มีต่อการหมุนภายในของไกลซีนสวิตเทอร์ไอออนและเส้นทางของพลังงานที่เกิดจากการหมุน ได้ถูกนำมาเปรียบเทียบกับโมเลกุลที่อยู่โดดเดี่ยว จากการศึกษาสารประกอบเชิงซ้อนระหว่างไกลซีนสวิตเทอร์ไอออนและโซเดียมไอออนในน้ำ พบว่าน้ำที่ล้อมรอบโซเดียมไอออนจะหลุดไป 2 โมเลกุล และถูกแทนที่ด้วยไกลซีนสวิตเทอร์ไอออน สูตรโมเลกุลของสารประกอบเชิงซ้อนจึงเป็น $[Na(gly)(H_2O)_4]^+$ ระยะระหว่างNa^+ - OH_2 ของสารประกอบเชิงซ้อนในน้ำคำนวณได้ 2.20 Å ในการศึกษาอิทธิพลของโซเดียมไอออนและน้ำที่มีต่อน้ำชั้นแรกที่ล้อมรอบไกลซีนสวิตเทอร์ไอออน ได้อาศัยหลักของทั้งการกระจายของประจุและพลังงานของความเสถียร

Project Title: A Study of the Influence of Na^+ on the Conformation of Glycine Zwitterion in Aqueous Solution .
Name of Investigator: Sirirat Kokpol, Supot Hannongbua, Prayong Doungdee
Year: 1987

ABSTRACT

The interaction of glycine zwitterion and water is calculated using ab initio method with minimized GLO basis set. The first hydration shell of glycine zwitterion is predicted to compose of five water molecules. The influence of the first hydration to the internal rotation of glycine zwitterion is studied and the energy optimized pathway is compared with that of isolated molecule. The investigation of glycine zwitterion - Na^+ complex in water provides that the two coordinated water of aquo complex of Na^+ are dehydrated and replaced by glycine zwitterion. Thus the formula of the complex is described as $[Na(gly)(H_2O)_4]^+$. The Na^+ - OH_2 distances in the complex are 2.20 Å. The effect of Na^+ and its coordinated water on the first hydration shell of glycine zwitterion are discussed on the basis of both charge distribution and stabilization energies.

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CHAPTER 1

INTRODUCTION

Considerable attention has recently been focused on the binding of metal ions and metal complexes (1-15). The presence of the metal ion can influence the electronic and structural arrangement of the protein and so affect its reactivity. The question of the nature and extent of metal ion-protein interaction is therefore a most important one for a vast number of widely differing biological processes It has been the subject of much work using amino acids (10,15), amides (16) and small peptides (5-8,12-13) as model compounds. Increasing knowledge will almost certainly serve to demonstrate this fact more effectively. Some of these processes are quite specific in their metal requirement in that only certain metal ions can fulfill the necessary catalytic or structural requirement, while other processes are much less specific, and it is possible to replace one metal ion by another, although the activity may be reduced.

The complexity of biological macromolecules, and the associated problems in their study, means that it is often worthwhile to examine the behaviour of simpler molecules that contain what appear to be the essential features of the original molecule, uncomplicated by other features of that molecule. The conclusions reached for model compounds may be extrapolated to the parent molecule and some light thrown upon its reactions and functions.

Since biological processes occur almost exclusively in aqueous solution. Knowledge of the aqueous hydration of metal complex is important for the ultimate understanding of metelloprotein hydration and the role of water in biological structure and function. Therefore, theoretical studies on biological relavant molecules should not be restricted to the molecules in the gas phase, but include all relavant interactions with the solvent as well.

In this work, we have investigated the Na$^+$ influence on the conformation of the smallest and simplest amino acid, glycine, in water. Glycine constitutes as the backbone of the protein, namely, polypeptide. Therefore, the electronic structure of glycine is of interest since the general features of the electronic structures of the amino acid and the backbone of protein can be derived from that of glycine.

Glycine is found as a zwitterion $NH_3^+CH_2COO^-$ in the solid state and aqueous solution (17). From our previous work (18), by a semiempirical calculation (CNDO/2), the most stable conformation of glycine zwitterion is predicted to be $(\theta, \phi) = (0, 0)$ as illustrated in Figure 1.

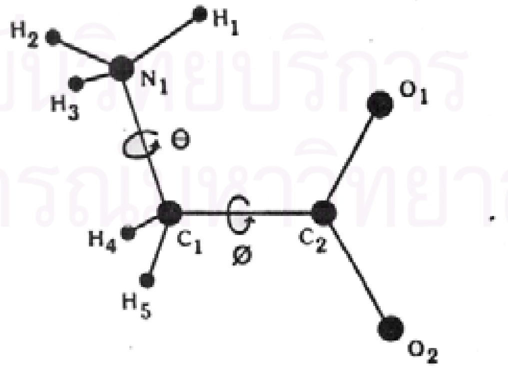


Figure 1. The Glycine Zwitterion with conformation $(\theta, \phi) = (0, 0)$, one H-atom of $-NH_3^+$ and N, C_1, C_2, O atoms are in the same plane.

The small monovalent cation, Na^+ is chosen in this study with two reasons. The first one, Na^+ is involved in certain physiological control and trigger mechanisms. It is present in much greater amounts than the heavy metal ions. In the human body, Na^+, K^+, Mg^{2+} and Ca^{2+} constitute some 99% of the total ion content. The second, the size of Na^+ is small enough for the limiting of computing time we can obtain.

In this study, the effect of solvent on the internal rotation of glycine zwitterion and on the conformation of glycine zwitterion - Na^+ complex in water are investigated by ab initio LCAO-MO-SCF using minimal GLO basis set (19). The procedure will use the supermolecule model to approach the problem. This model is proved (20) to be useful in studying the conformation of molecules in aqueous solution.

CHAPTER 2

SELF CONSISTENT FIELD MOLECULAR ORBITAL THEORY

2.1 The Schrodinger Equation

In principal, all molecular orbital calculations are approximate solutions of the schrodinger equation in the form

$$H^{total}\bar{\Psi} \quad = \quad E\bar{\Psi} \qquad (2.1)$$

where H^{total}, the hamiltonian operator is representative of the sum of the kinetic and potential energy of the system. $\bar{\Psi}$ is an energy eigenfunction for the system and E is the corresponding energy eigenvalue.

Since the masses of the nuclei are about 2000 times larger than the masses of the electrons, so that the nuclei move much more slowly, and we may reasonably suppose the electrons to adjust themselves to new nuclear positions so rapidly that at any one instant their motion is just as it would be if the nuclei were at rest at the position they occupy at the same instant. This simplification is referred to as the Born-Oppenheimer approximation (21). This means the nuclear kinetic energy and nuclear-nuclear repulsion terms can be separated off from the hamiltonian operator, only the part of the hamiltonian which depends on the positions but not the momenta of the nuclei are considered. This is named the electronic hamiltonian operator (H^{el}).

$$H^{el} = -\hbar^2/2m \sum_p \nabla_p^2 - \sum_A \sum_p e^2 Z_A r_{Ap}^{-1} + \sum_{p<q} e^2 r_{pq}^{-1} \quad (2.2)$$

The electronic hamiltonian may be used in a modified Schrodinger equation

$$H^{el} \bar{\Psi}^{el} = \varepsilon \bar{\Psi}^{el} \quad (2.3)$$

for convenience we will adopt H^{el} as H and $\bar{\Psi}^{el}$ as $\bar{\Psi}$

2.2 The Variation Method

For an actual molecule, with given H^{el}, the solution of equation (2.3) is usually attempted by the variation method. In this method, choosing a trial function ϕ dependent on one or more parameters, one minimizes the energy as a function of the parameters. With luck, the ϕ so obtained will be a good approximation to the true ground state wave function; if it is not, it may be improved by further generalization of its functional form. The expectation value of the energy calculated from this function will always be higher than the true energy of the ground state.

2.3 The Orbital Approximation

The usual variation method which is capable of handling many electron systems in molecular quantum mechanics is the molecular orbital (MO) method. Molecular

Orbital theory treats molecules from the same point of view as that which we use for atoms. The basic concept is to find approximate electronic wave function for a molecule by assigning to each electron a one electron wave function.

For n electron system ,

$$\bar{\Psi}(1,2,\ldots n) = \psi_1(1)\ \psi_2(2)\ldots\ \psi_n(n) \qquad (2.4)$$

ψ_i are called orbitals and the product function as such is known as a Hartree product (22)

2.4 The Antisymmetry Principle

If we include spin in one-electron wavefunctions then we have spin orbitals (SO). The total wave function is now a product of spin orbitals, one for each electron.

Even having included spin, the wave function is not yet complete. The Pauli Principle must be applied which resulted the total wave function by antisymmetric with respect to electron permutation.

$$P_{ij}\ \bar{\Psi}(1,2,\ldots,n) = -\ \bar{\Psi}(1,2,\ldots,n) \qquad (2.5)$$

Where P_{ij} is a permutation operator which interchange all the coordinates (including spin coordinates) of electrons i and j.

The general method of constructing the antisymmetric wave function is to build up the determinant by writing the spin orbitals as elements of a square matrix, with the electron labelled as the column index and the orbital labelled as the row index. For closed shell, 2n electron system (n spin orbitals), the antisymmetric wave function will become as:

$$\bar{\Psi}(1,2,\ldots,n) = N \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1)\ldots\ldots\ldots\ldots & \psi_n(1)\beta(1) \\ \psi_1(2)\alpha(2) & \psi_1(2)\beta(2)\ldots\ldots\ldots\ldots & \psi_n(2)\beta(2) \\ & & \\ & & \\ \psi_1(2n)\alpha(2n) & \ldots\ldots\ldots\ldots\ldots\ldots & \psi_n(2n)\beta(2n) \end{vmatrix}$$

(2.6)

N = normalization constant

The abbreviated form of equation (2.6) is written as the product of the diagonal elements of the matrix enclosed in bars.

$$\bar{\Psi}(1,2,\ldots,n) = N \, |\psi_1(1)\alpha(1)\psi_1(2)\beta(2)\ldots\psi_n(2n)\,\beta(2n)|$$

(2.7)

More contracted form,

$$\bar{\Psi}(1,2,\ldots,n) = N \, |\psi_1\bar{\psi}_1\cdots\psi_n\bar{\psi}_n| \tag{2.8}$$

2.5 The Hartree-Fock Equation

Generalizing equation (2.8), the orbital wave function $\bar{\Psi}$ may be written in the form

$$\bar{\Psi} = N \sum_{p} (-1)^{p} P\{\psi_{1}(1)\alpha(1)\psi_{1}(2)\beta(2)\ldots\psi_{n}(2n)\beta(2n)\} \qquad (2.9)$$

where P is permutation of 1,2,.....,2n

$(-1)^p$ is +1 for even permutation

-1 for odd permutation

The hamiltonian operator may be separated into one-electron and two-electron operators,

$$H = H_1 + H_2 \qquad (2.10)$$

H_1 = the one-electron hamiltonian operator

$$= \sum_{p} H^{core}(p) = \sum_{p} \left(-1/2\ \nabla_{p}^{2} - \sum_{A} Z_{A} r_{pA}^{-1}\right) \qquad (2.11)$$

H_2 = the two-electron hamiltonian operator

$$= \sum_{p<q} r_{pq}^{-1} \qquad (2.12)$$

Evaluate the energy expectation value, we obtain

$$\varepsilon = 2\sum_{i}^{n} H_{ii} + \sum_{i}^{n}\sum_{j}^{n} (2J_{ij} - K_{ij}) \qquad (2.13)$$

where H_{ii} is the expectation value of the one-electron core hamiltonian corresponding to the molecular orbital

$$= \int \psi_{i}^{*}(1)\, H^{core}\, \psi_{i}(1)\, d\tau_{1} \qquad (2.14)$$

J_{ij} = coulomb integral

$$= \iint \psi_i^*(1)\,\psi_j^*(2)\,(1/r_{12})\,\psi_i(1)\,\psi_j(2)\,d\tau_1\,d\tau_2 \qquad (2.15)$$

K_{ij} = exchange integral

$$= \iint \psi_i^*(1)\,\psi_j^*(2)\,(1/r_{12})\,\psi_j(1)\,\psi_i(2)\,d\tau_1\,d\tau_2 \qquad (2.16)$$

According to the variational principle, the best molecular orbitals are obtained by varying all the contributing one-electron functions in the determinant (equation 2.6) until the energy reaches its minimum values. Such orbitals are referred to as self-consistent, or Hartree-Fock, molecular obitals. Using the method of undetermined multipliers, the differential equations are obtained. Applying that transformation to the orbitals, the differential equations are brought into the form

$$F_i\,\psi_i = \epsilon_i\,\psi_i \qquad i = 1, 2, \ldots\ldots, n \qquad (2.17)$$

These are known as the Hartree-Fock equations.

where F = Fock operator

$$= H^{core} + \sum_j (2J_j - K_j) \qquad (2.18)$$

with $J_j(1) = \int \psi_j^*(2)\,(1/r_{12})\,\psi_j(2)\,d\tau_2$ (2.19)

$$Kj(1)\,\psi_i(1) = [\int \psi_j^*(2)\,(1/r_{12})\,\psi_i(2)\,d\tau_2]\,\psi_j(1) \tag{2.20}$$

The general procedure for solving the Hartree-Fock equations is essentially a trial-and-error process. The general expression for the eigenvalues of the Hartree-Fock operator is

$$\varepsilon_i = H_{ii}^{core} + \Sigma_j\,(2J_{ij} - K_{ij}) \tag{2.21}$$

ε_i is known as orbital energies

And the total electronic energy,

$$\varepsilon = \sum_i (\varepsilon_i + H_{ii}^{core}) \tag{2.22}$$

2.6 The Roothaan Equation

For molecular systems, the approximate Hartree-Fock orbitals with linear combinations of atomic orbitals (LCAO) are introduced. In this approach, each molecular orbital in Slater determinant is assigned in the form

$$\psi_i = \Sigma_\mu c_{\mu i}\phi_\mu \tag{2.23}$$

ϕ_μ = atomic functions

The requirement that the orbital ψ_i form an orthonormal set will demand that

$$\sum_{\mu\nu} c^{*}_{\mu i} c_{\nu j} S_{\mu\nu} = \delta_{ij} \quad , \quad \delta_{ij} = \text{Kronecker deltar}$$

(2.24)

$$S_{\mu\nu} = \int \phi_{\mu}(1)\, \phi_{\nu}(1)\, d\tau_{1} \tag{2.25}$$

The total electronic energy can be written as

$$\varepsilon = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} + 1/2 \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} [(\mu\nu/\lambda\sigma) - 1/2\, (\mu\lambda/\nu\sigma)]$$

(2.26)

where $P_{\mu\nu}$ = density matrix

$$= 2 \sum_{i}^{occ} c^{*}_{\mu i} c_{\nu i} \tag{2.27}$$

$$H_{\mu\nu} = \int \phi_{\mu}(1)\, H^{core} \phi_{\nu}(1)\, d\tau_{1} \tag{2.28}$$

$$(\mu\nu/\lambda\sigma) = \iint \phi_{\mu}(1)\, \phi_{\nu}(1)\, (1/r_{12})\, \phi_{\lambda}(2) \phi_{\sigma}(2)\, d\tau_{1}\, d\tau_{2}$$

(2.29)

The next important step is to find the optimum value of the coefficient $c_{\mu i}$ by the method similar to the Hartree-Fock procedure , leading to a set of LCAO self-consistent molecular orbitals (LCAO-SCF-MO). The equations obtained in the final form are known as the Roothaan equations (23).

$$\sum_{\nu}(F_{\mu\nu} - \varepsilon_i S_{\mu\nu}) c_{\nu i} = 0 \qquad (2.30)$$

where $$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}[(\mu\nu/\lambda\sigma) - 1/2\ (\mu\lambda/\nu\sigma)] \qquad (2.31)$$

If we write the equations on the matrix form,

$$FC = SCE \qquad (2.32)$$

E is the diagonal metrix of the ε_i

Transforming equation (2.32) to a new matrix by defining

$$F^T = S^{-1/2} FS^{1/2} \qquad (2.33)$$

$$C^T = S^{1/2} C \qquad (2.34)$$

then equation (2.32) becomes

$$F^T C^T = C^T E \qquad (2.35)$$

The elements ε_i of **E** will be roots of the determinantal equation

$$\left| F^T_{\mu\nu} - \varepsilon\ \delta_{\mu\nu} \right| = 0 \qquad (2.36)$$

the lowest root ε_i , the coefficint $c^T_{\mu i}$can be found from the linear equations

$$\sum_{\nu} (F^{T}_{\mu\nu} - \varepsilon_i \delta_{\mu\nu}) \, c^{T}_{\nu i} = 0 \qquad (2.37)$$

and the coefficients then determined from

$$C = S^{-1/2} \, C \qquad (2.38)$$

The Roothaan equations must be solved by an iterative procedure since the matrix elements of the Hartree-Fock hamiltonian operator are dependent on the orbitals through the elements $P_{\mu\nu}$, or another word the unknown coefficient $c_{\mu i}$.

2.7 Population Analysis

A widely used method to analyze LCAO-MO-SCF wave functions is population analysis, introduced by Mulliken (24). The charge density ρ at position R is obtained by

$$\rho(R) = \langle \bar{\Psi} | \rho(R) | \bar{\Psi} \rangle = 2 \sum_{i}^{occ} \psi_i^{*}(R) \, \psi_i(R) \qquad (2.39)$$

substitute $\psi_i = \sum_{\mu} c_{\mu i} \phi_{\mu}$ into equation (2.39), we get

$$\rho(R) = \sum_{\mu\nu} P_{\mu\nu} \, \phi_{\mu}(R) \, \phi_{\nu}(R) \qquad (2.40)$$

where $P_{\mu\nu} = 2 \sum_{i}^{occ} c^{*}_{\mu i} c_{\nu i}$ (2.41)

The integral of $\rho(R)$ over all R should be equivalent to the total number of electrons in the system, i.e.,

$$2n = \int \rho(R) \, dR = \sum_{\mu\nu} P_{\mu\nu} \int \phi_{\mu}(R) \, \phi_{\nu}(R) \, dR = \sum_{\mu\nu} P_{\mu\nu} S_{\mu\nu} \qquad (2.42)$$

A quantity $P_{\mu\nu} S_{\mu\nu}$ may be considered the electronic repulsion of, the atomic overlap distribution $\phi_\mu\phi_\nu$, and diagonal term such as $P_{\mu\mu} S_{\mu\mu}$ may be associated with the net electronic charges residing in orbital ϕ_μ. This is called a Mulliken population analysis (24).

2.8 The Basis Functions

To simplify molecular integral evaluation, Boy (25) proposed in 1950 the use of Gaussian type orbitals (GTO's) instead of Slater type orbitals (STO's) for the atomic orbitals in an LCAO wave function.

A Gaussian function has the form

$$\Psi(r, \zeta) \quad = \quad Ne^{l}e^{-\zeta r^2} Y_l^m(\theta, \phi) \qquad (2.43)$$

which is contrast to Slater functions, whose exponential factor is $\exp(-\zeta r)$.

A modification of the GTO functions is the Gaussian-lobe functions (GLO), which uses 1s Gaussian functions placed at points in space to simulate s, p, d, etc., orbitals.

GLO function is simply given by

$$\Psi(r, \zeta) \quad = \quad Ne^{-\zeta r^2} \qquad \text{(no angular part)}$$

Thus, GLO function for a P_x orbital (which has 2 lobes) can be simulated by 2 Gaussians centered on the X-axis, one on each side of the nucleus.

Although the absolute value of energy is quite poor, the relative energies are reasonable (19,26). The main advantage of the GLO basis function is the decrease of the computing time in the evaluation of the integrals.

The accuracy of the results also depend on the number of basis functions used in the LCAO expansion. Three types of basis sets can be distinguished

(1) minimum basis sets, consist of one STO for each inner-shell and valence-shell atomic orbitals of each atom.

(2) extended basis sets, comprise of a minimal basis set plus any number of atomic orbitals lying outside the valence shell for each atom.

(3) valence basis sets, comprise of just those orbitals of the valence shell of each atom in the system.

CHAPTER 3

QUANTUM CHEMICAL CALCULATIONS AND RESULTS

To study the chemical systems of glycine zwitterion in aqueous solution and the complex of glycine zwitterion - Na^+ in aqueous solution , we have used the super molecule model (20) and calculated by an ab initio LCAO-MO , SCF method with well tested minimal Gaussian basis set (19).

In the SCF approach the interaction energy ΔE between the subsystem A and B was calculated as

$$\Delta E = E_{AB} - E_A - E_B \qquad (3.1)$$

when E_A , E_B denote the SCF energy of the subsystem A and B respectively , calculated using the basis sets for the isolated subsystem,and ΔE is the energy of the supersystem obtained using the basis sets of both A and B. It has been recognized that (27-30) if the insufficient basis sets are used , the energy calculated in the above way suffers from the basis set superposition error and the **overestimated** interaction energy are obtained. The correction of the interaction energy has been tried with many supersystem by using the so called counterpoise method proposed by Boy and Bunardi (28). The correction results improved in some cases (9-10) and yielded destabilization interaction in some studies (31). As mentioned in previous papers (6,8-10), the basis set superposition error leading to an overestimated interaction energy will not influence significantly the relative order of stabilities , and the use of a minimal basis set without counterpoise correction is an acceptable way to reduce the computational effort is therefore used in this present work.

The coordinates of each configuration of molecule were determined by using GEN CORD PROGRAM and testing by KOGEN PROGRAM. The ab initio LCAO-MO-SCF energies were computed by HONDO PROGRAM and the molecular graphics were plotted using the SCHAKAL PROGRAM.

All calculations were performed at the IBM 3031/08 computer center of Chulalongkorn University and the molecular drawings were plotted with the CDC CYBER 835 computer of the University of Innsbrusk.

3.1 Determination of the First Hydration shell and Calculation of the Internal rotation energy of Glycine Zwitterion.

The geometry of glycine zwitterion used in this work is taken from experimental data (32) and listed in table 3.1 . The experimental geometry of water (33) is $H\hat{O}H = 104.5^{\circ}$, O-H distances = 0.9572 Å

Table 3.1 The Geometry Parameters of Glycine Zwitterion.

Bond length (Å)		Bond angle (degrees)	
C_1-C_2	1.52	$H\hat{N}H$	109.47
C_2-O_1	1.27	$H\hat{N}_1C_1$	109.47
C_2-O_2	1.27	$H\hat{C}_1H$	109.47
C_1-N_1	1.47	$N_1\hat{C}_1H$	109.47
C_1-H	1.09	$C_1\hat{C}_2O_1$	119.00
N_1-H	1.03	$O_1\hat{C}_2O_2$	122.00

3.1.1 The Energy Optimized Water Binding Positions at Various Sites of Glycine Zwitterion.

Glycine zwitterion is composed of two hydrophilic groups ($-NH_3^+$ and $-COO^-$) and one hydrophobic ($-CH_2^-$) group, the hydrophilic attraction in the zwitterion is about three times as large as the water-water interaction (34). Therefore, the assumption is made that the solvent interaction can be ignored. In our study, only the first hydration shell is considered as it directly influences on the solute , and has highly ordered structures. The geometrical arrangement of the solvent molecules at larger distance will be resemble very close to the structures of the bulk media .

The presence of amino and carboxyl groups suggests a priori the possibility of formation of two types of association with water :one in which the water molecule acts as a proton donor in a hydrogen bond to the oxygen of the carboxyl group , the other in which the water acts as a proton acceptor in hydrogen bonding to the N-H bonds .

Ten possible hydration sites on glycine zwitterion are illustrated in Figure 3.1 - Figure 3.8 . All of them can not be calculated simultaneously . The total energies of each configuration are reported in tables 3.2 - 3.9.

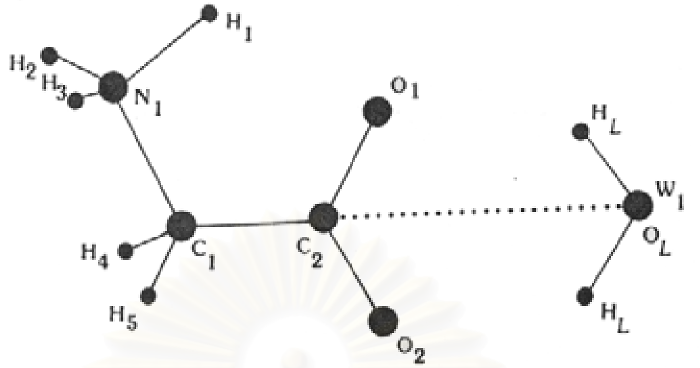


Figure 3.1 Hydration site of glycine zwitterion , water 1 (W1).

Table 3.2 The Total Energies of Glycine Zwitterion and Water 1 . Optimizing $C_2 - O_L$ Distance of the COO^- Group and Water 1 .

$C_2 - O_L$ (Å)	Energies (a.u.)
2.65	-304.57773
2.75	-304.59937
2.85	-304.61468
3.00	-304.62828
3.15	-304.63333
3.20	-304.63358
3.25	-304.63327

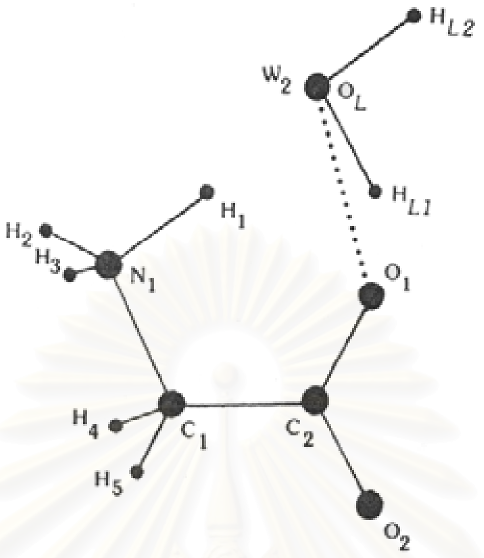


Figure 3.2 Hydration site of glycine zwitterion , water 2 (W2).

Table 3.3 A The Total Energies of Glycine Zwitterion and Water 2 . Optimizing the Angle $C_2\hat{O}_1O_L$ with Fixing the Angle $O_1\hat{O}_LH_{L1}$ = ' 20° and the Distance $O_1 - O_L = 2.60$ Å .

$C_2\hat{O}_1O_L$ (degrees)	Energies (a.u.)
120	-304.62604
125	-304.64252
130	-304.64745
132	-304.64788
140	-304.64382

Table 3.3 B The Total Energies of Glycine Zwitterion and Water 2 . Optimizing the Angle $O_1\hat{O}_LH_{L1}$ with Fixing the Angle $C_2\hat{O}_1O_L$ = 132° and the Distance $O_1 - O_L$ = 2.60 Å .

$O_1\hat{O}_LH_{L1}$ (degrees)	Energies (a.u.)
15	-304.64710
20	-304.64788
25	-304.64781

Table 3.3 C The Total Energies of Glycine Zwitterion and Water 2.Optimizing the Distance $O_1 - O_L$ with Fixing the Angles $O_1\hat{O}_LH_{L1}$ = 20° and $C_2\hat{O}_1O_L$ = 132°.

$O_2 - O_L$ (Å)	**Energies (a.u.)**
2.50	-304.64758
2.55	-304.64795
2.60	-304.64788
2.65	-304.64717
2.75	-304.64480

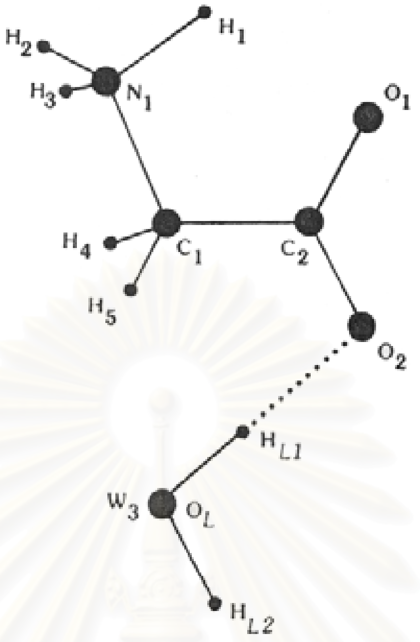


Figure 3.3 Hydration site of glycine zwitterion , water 3 (W3).

Table 3.4 A The Total Energies of Glycine Zwitterion and Water 3. Optimizing the Angle $C_2\hat{O}_2O_L$ with Fixing the Angle $O_2\hat{O}_LH_{L1}$ = 0° and the Distance $O_2 - O_L$ = 2.75 A°.

$C_2\hat{O}_2O_L$ (degrees)	Energies (a.u.)
100	-304.6403
105	-304.64123
108	-304.64135
110	-304.64127
120	-304.64063

Table 3.4 B The Total Energies of Glycine Zwitterion and Water 3. Optimizing the Angle $O_2\hat{O}_LH_{L1}$ with Fixing the Angle $C_2\hat{O}_2O_L$ = 108° and the Distance $O_2 - O_L$ = 2.75 Å .

$O_2\hat{O}_LH_{L1}$ (degrees)	Energies (a.u.)
-10	-304.63813
0	-304.64135
10	-304.64113

Table 3.4 C The Total Energies of Glycine Zwitterion and Water 3 . Optimizing the Distance $O_2 - O_L$ with Fixing the Angles $C_2\hat{O}_2O_L$ = 108° and $O_2\hat{O}_LH_{L1}$ = 0°.

$O_2 - O_L$ (Å)	Energies (a.u.)
2.65	-304.64126
2.70	-304.64156
2.75	-304.64135

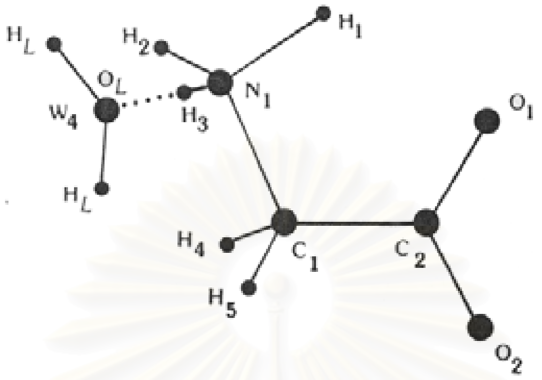


Figure 3.4 Hydration site of glycine zwitterion , water 4 (W4). Water 4 and water 5 are symmetry.

Table 3.5 The Total Energies of Glycine Zwitterion and Water 4 or Water 5. Optimizing the NH − O_L Distance.

NH − O_L (Å)	Energies (a.u.)
2.55	-304.64212
2.60	-304.64275
2.63	-304.64302
2.64	-304.64309
2.65	-304.64306
2.70	-304.59248

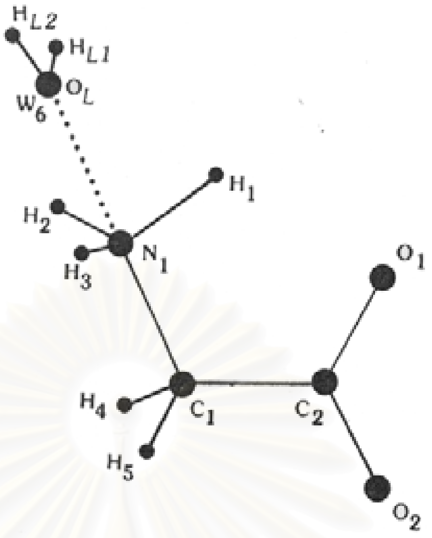


Figure 3.5 Hydration site of glycine zwitterion , water 6 (W6).

Table 3.6 The Total Energies of Glycine Zwitterion and Water 6 . Optimizing the $N - O_LH_{L1}$ Distance.

$N - O_LH_{L1}$ (Å)	Energies (a.u.)
4.12	-304.61700
4.20	-304.61730
4.22	-304.61732
4.25	-304.61730
4.32	-304.61713

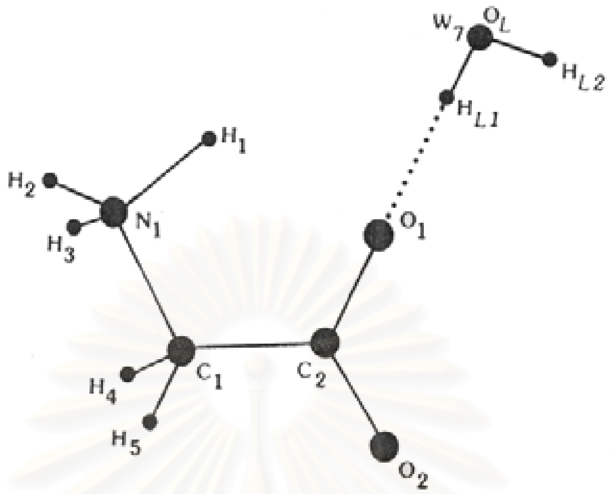


Figure 3.6 Hydration site of glycine zwitterion , water 7 (W7).

Table 3.7 The Total Energies of Glycine Zwitterion and Water 7 . Optimizing the $O_1 - H_{L1}O_L$ Distance.

$O_1 - H_{L1}O_L$ (Å)	Energies (a.u.)
3.87	-304.63381
3.92	-304.63386
3.97	-304.63363

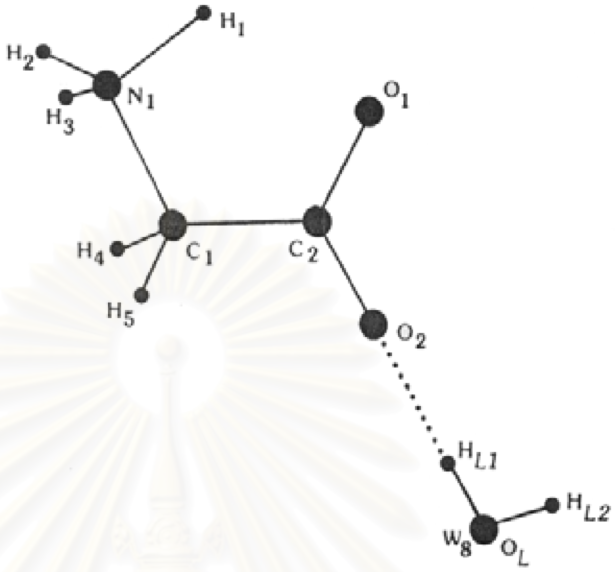


Figure 3.7 Hydration site of glycine zwitterion, water 8 (W8).

Table 3.8 The Total Energies of Glycine Zwitterion and Water 8 . Optimizing the O_2 - $H_{L1}O_L$ Distance.

O_2 - $H_{L1}O_L$ (Å)	Energies (a.u.)
3.87	-304.63206
3.92	-304.63214
3.97	-304.63195
4.02	-304.63151
4.12	-304.63003
4.22	-304.62795

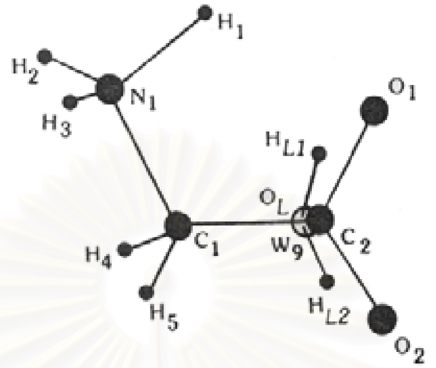


Figure 3.8 Hydration site of glycine zwitterion , water 9 (W9). Water 9 and water 10 are located at the upper and the lower of the molecular plane respectively. Water 9 and water 10 are symmetry .

Table 3.9 The Total Energies of Glycine Zwitterion and Water 9 or Water 10. Optimizing the $O_1 - H_{L1}O_L$ Distance.

$O_1 - H_{L1}O_L$ (Å)	Energies (a.u.)
2.65	-304.62273
2.70	-304.62429
2.75	-304.62440
2.80	-304.62419
2.90	-304.62310
3.00	-304.62156

3.1.2 Calculation of the Interaction Energies of Glycine Zwitterion - Water Systems.

The ten optimized positions for hydration site of glycine zwitterion (Figure 3.9) have been investigated with respect to interaction energies to determine the final hydration structures. The interaction energies are calculated by the equation

$$\Delta E = E_{sup} - E_{gly} - E_{water} \qquad (3.2)$$

where E_{sup} = The energy of supermolecule (glycine zwitterion plus water)

E_{gly} = The energy of glycine zwitterion
= -240.08829 a.u.

E_{water} = The energy of water
= -64.52139 a.u.

All interaction energies are collected together in Table 3.10

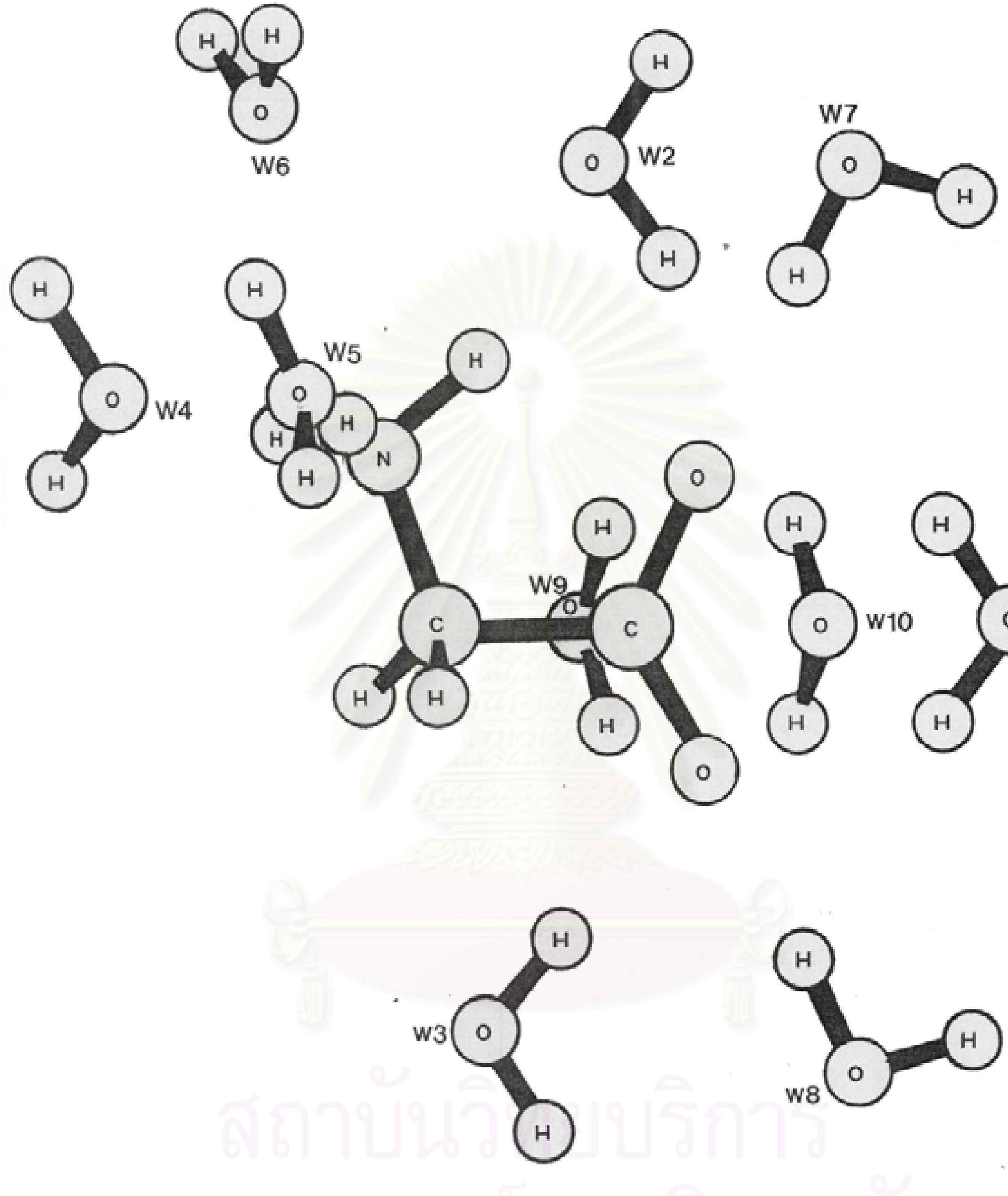


Figure 3.9 The ten optimized water positions for the glycine zwitterion - water system.

Table 3.10 Calculated Interaction Energies of Glycine Zwitterion with One Water at Various Optimized Positions.

position of water (cf. Figure 3.9)	ΔE (kcal /mole)
1	-15.1
2	-24.1
3	-20.1
4	-21.0
5	-21.0
6	-4.9
7	-15.2
8	-14.2
9	-9.3
10	-9.3

1 kcal. = 627.5 a.u.

3.1.3 Calculation of Internal Rotation of Glycine Zwitterion Including the Hydration Shell Effect.

According to the relative interaction energies (Table 3.10) , the first hydration of glycine zwitterion is proposed to consist of 5 water molecules in the orientation illustrated in Figure 3.10 . For this conformation of glycine zwitterion - water , the energy barriers to internal rotation concerning both angles (θ, ϕ) relevant for the conformation have been calculated during the rotation of NH_3^+ or COO^- groups , a corotating hydration shell has been studied as well as of rotation of the hydration remaining fixed. The results for the total energies are shown in Table 3.11 - 3.12 and the energy barriers are reported in Table 3.13 - 3.14 .

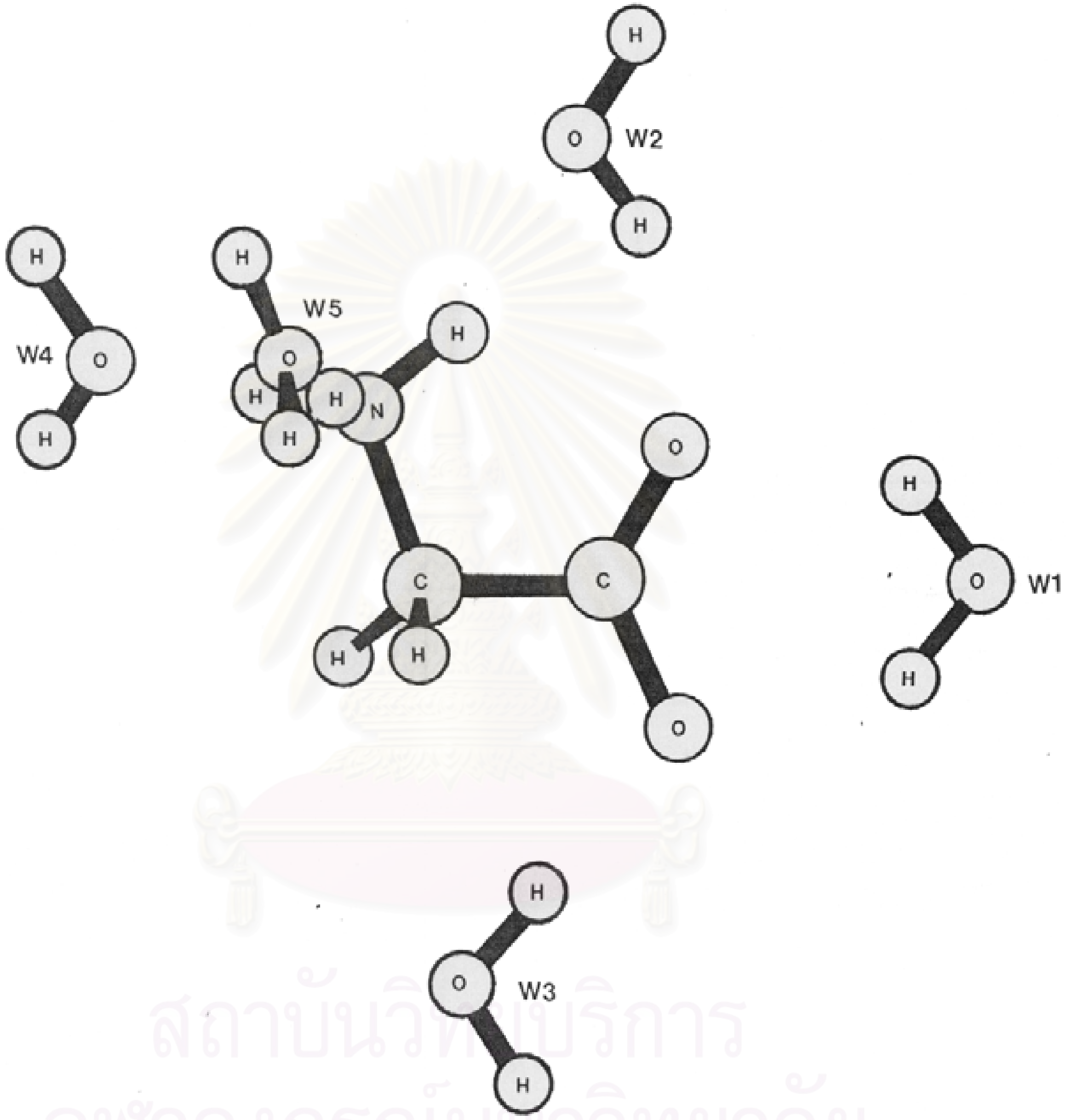


Figure 3.10 The proposed hydration structure of glycine zwitterion.

Table 3.11 The Total Energies (a.u.) of the Isolated Glycine Zwitterion at Various Angles of Rotation.

Angle of rotation (degrees)	System		
	G1	G2	G3
0	-240.08819	-240.08819	-240.07060
5	-	-	-240.07044
10	-240.08684	-240.08628	-240.07000
15	-	-	-240.06917
20	-240.08326	-240.08095	-240.06807
30	-240.07864	-240.07322	-240.06500
40	-240.07439	-240.06445	-240.06091
50	-240.07157	-240.05600	-240.05636
60	-240.07060	-240.04873	-240.05195
70	-	-240.04332	-240.04831
80	-	-240.04000	-240.04592
90	-	-240.03888	-240.04509

Table 3.12 A The Total energies (a.u.) of the Hydrated Glycine Zwitterion at Various Angles of Rotation.

Fixing the $-COO^-$ Group.

Angle of rotation (degrees)	System	
	GW1	GW2
0	-562.85043	-562.85043
5	-562.84970	-562.84992
10	-562.84753	-562.84844
15	-	-562.84607
20	-562.83914	-562.84282
25	-562.83320	-562.83871
30	-562.82640	-562.83397
35	-562.81912	-562.82920
40	-562.81185	-562.82499
45	-562.80518	-562.82177
50	-562.79977	-562.81954
55	-562.79624	-562.81815
60	-562.79501	-562.81738

Table 3.12 B The Total Energies (a.u.) of the Hydrated Glycine Zwitterion at Various Angles of Rotation.

Fixing the $-NH_3^+$ Group.

Angle of rotation (degrees)	System				
	GW3	GW4	GW5	GW6	GW7
0	-562.85043	-562.85043	-562.85043	-562.85043	-562.81738
10	-562.84790	-562.84840	-562.84980	-	-562.81658
20	-562.84017	-562.84216	-562.84558	-562.84772	-562.81540
30	-562.82693	-	-562.83670	-562.83942	-562.81397
40	-562.80897	-562.81668	-562.82722	-	-562.81228
50	-562.78938	-562.80078	-562.81995	-562.82565	-562.81037
60	-562.77215	-562.78716	-562.81486	-562.81241	-562.80854
70	-562.75973	-562.77773	-562.81173	-	-562.80728
80	-562.75254	-562.77250	-562.81028	-	-562.80729
90	-562.75022	-562.77085	-562.81013	-562.80425	-562.81275

Table 3.13 The Energy Barriers (kcal/mol) of the Isolated Glycine Zwitterion at Various Angles of Rotation.

Angle of rotation (degrees)	System G1	G2	G3
0	0.00	0.00	0.00
10	0.85	1.20	0.40
20	3.09	4.54	1.59
30	5.99	9.39	3.54
40	8.66	14.89	6.08
50	10.43	20.22	8.94
60	11.04	24.76	11.70
70	-	28.16	13.99
80	-	30.24	15.49
90	-	30.94	16.01

Table 3.14 A The Energy Barriers (kcal/mol) of the Hydrated Glycine Zwitterion at Various Angles of Rotation

Fixing the $-COO^-$ Group.

Angle of rotation (degrees)	System	
	GW1	GW2
0	0.00	0.00
5	0.46	0.32
10	1.82	1.25
15	-	2.74
20	7.09	4.77
25	10.81	7.36
30	15.08	10.33
35	19.64	13.33
40	24.21	15.96
45	28.40	17.99
50	31.79	19.38
55	34.00	20.26
60	34.78	20.74

Table 3.14 B The Energy Barriers (kcal/mol) of the Hydrated Glycine Zwitterion at Various Angles of Rotation

Fixing the $-NH_3^+$ Group.

Angle of rotation (degrees)	System GW3	GW4	GW5	GW6	GW7
0	0.00	0.00	0.00	0.00	0.00
10	1.58	1.27	0.40	-	0.50
20	6.44	5.19	3.04	1.70	1.24
30	14.74	-	8.01	6.91	2.14
40	26.02	21.18	14.56	-	3.20
50	38.31	31.15	19.13	15.55	4.40
60	49.12	39.70	22.32	23.85	5.54
70	56.92	45.62	24.28	-	6.34
80	61.42	48.90	25.20	-	6.33
90	62.88	49.93	25.29	28.98	2.91

where G represents the isolated glycine zwitterion.

G1 is the rotation of $-NH_3^+$ group alone.

G2 is the rotation of COO^- group alone.

G3 is the rotation of COO^- group, fixing the $-NH_3^+$ groups to 60°.

GW represents the glycine zwitterion - water system.

GW1 is the rotation of $-NH_3^+$ group, fixing the hydration structure.

GW2 is the rotation of $-NH_3^+$ group together with W2, W4, W5 ; fixing the $-COO^-$ group, W1, W3.

GW3 is the rotation of $-COO^-$ group, fixing the hydration structure.

GW4 is the rotation of $-COO^-$ group together with W1; fixing the $-NH_3^+$ group, W2, W3, W4, W5.

GW5 is the rotation of $-COO^-$ group together with W1, W2, W3 ; fixing the $-NH_3^+$ group, W4, W5.

GW6 is the rotation of $-COO^-$ group together with W1, W3 ; fixing the $-NH_3^+$ group, W2, W4, W5.

GW7 is the rotation of $-COO^-$ group together with W1, W3 ; fixing the $-NH_3^+$ group, W2, W4, W5 to 60°.

3.2 Investigation of the Conformation of Glycine Zwitterion - Na^+ Complex.

Glycine zwitterion has the negative charge at the COO^- group, the binding of metal ion will definitely exert to this region. From our previous study on the ion - dipeptide complex formation (6,8), it is found that the most preferential binding site for metal ion is located in the **bisectrix** of the $O_1\hat{C}_2O_2$ angle. Therefore, this position is used to optimize the distance of Na^+

binding simultaneously to O_1 and O_2 of glycine zwitterion. The optimized energies are listed in Table 3.15 and the optimized conformation is shown in Figure 3.11

Table 3.15 The Optimized Distance between Na^+ and Oxygen Atoms of Glycine Zwitterion.

$Na^+ - O_1 = Na^+ - O_2$ (A°)	Energies (a.u.)
2.15	-389.33875
2.20	-389.33995
2.25	-389.33961

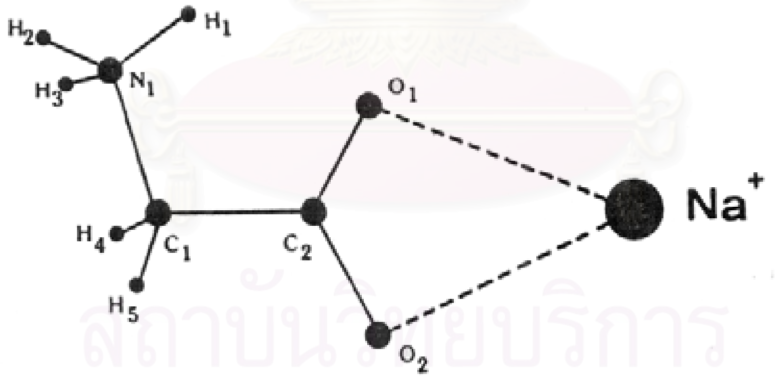


Figure 3.11 The conformation of glycine zwitterion - Na^+ complex.

3.3 Investigation of the Conformation of the Glycine Zwitterion - Na^+ Complex in Aqueous Solution.

3.3.1 Determination of the Effect of Na^+ on the Conformation of the Water Binded to Glycine Zwitterion .

When Na^+ forms a complex with glycine zwitterion at the optimized position , the number of water molecules for the first hydration shell will be left as 4 molecules . To see how the effect of Na^+ will be on the conformation of the remaining water molecules , we reoptimized the orientation of these water molecules (see Figure 3.12 - 3.14 and Tables 3.16 - 3.18).

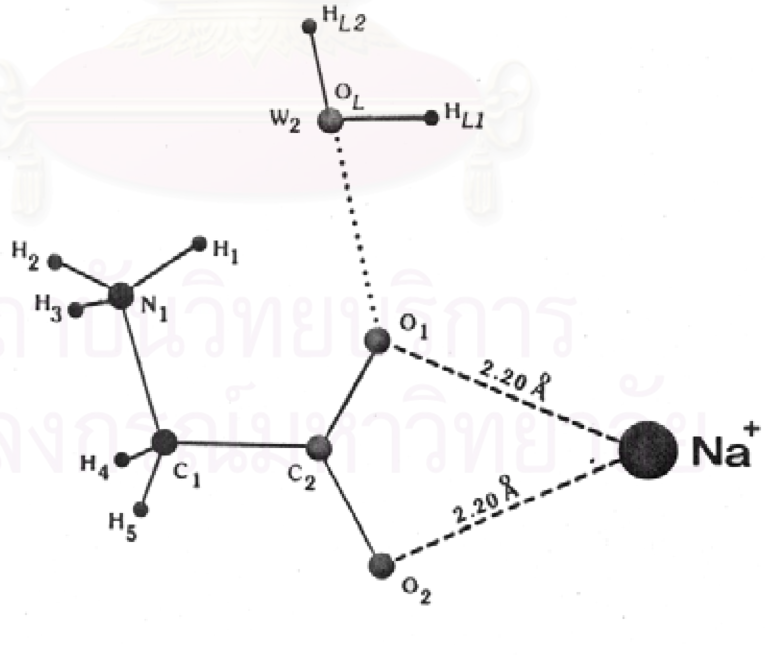


Figure 3.12 Glycine zwitterion - Na^+ complex with W2.

Table 3.16 A The Total Energies of Glycine Zwitterion - Na^+ Complex and Water 2. Optimizing the Angle $C_2\hat{O}_1O_L$ with Fixing the Angle $O_1\hat{O}_LH_{L1}$ = 20° and the Distance $O_1 - O_L$ = 2.65 Å.

$C_2\hat{O}_1O_L$ (degrees)	Energies (a.u.)
124	-453.89072
130	-453.89564
132	-453.89583
140	-453.89028

Table 3.16 B The Total Energies of Glycine Zwitterion - Na^+ Complex and Water 2. Optimizing the Angle $O_1\hat{O}_LH_{L1}$ with Fixing the Angle $C_2\hat{O}_1O_L$ = 132° and the Distance $O_2 - O_L$ = 2.65 Å.

$O_1\hat{O}_LH_{L1}$ (degrees)	Energies (a.u.)
15	-453.89374
25	-453.89713
35	-453.89887
50	-453.90028
60	-453.90093
68	-453.90083
70	-453.90119
80	-453.89905
85	-453.89721

Table 3.16 C The Total Energies of Glycine Zwitterion – Na^+ Complex and Water 2. Optimizing the O_2 – O_L Distance with Fixing the Angles $C_2\hat{O}_1O_L = 132^\circ$ and $O_1O_LH_{L1} = 70^\circ$.

O_2 – O_L (Å)	Energies (a.u.)
2.45	-453.89939
2.53	-453.89950
2.55	-453.90119
2.57	-453.90050
2.65	-453.89900

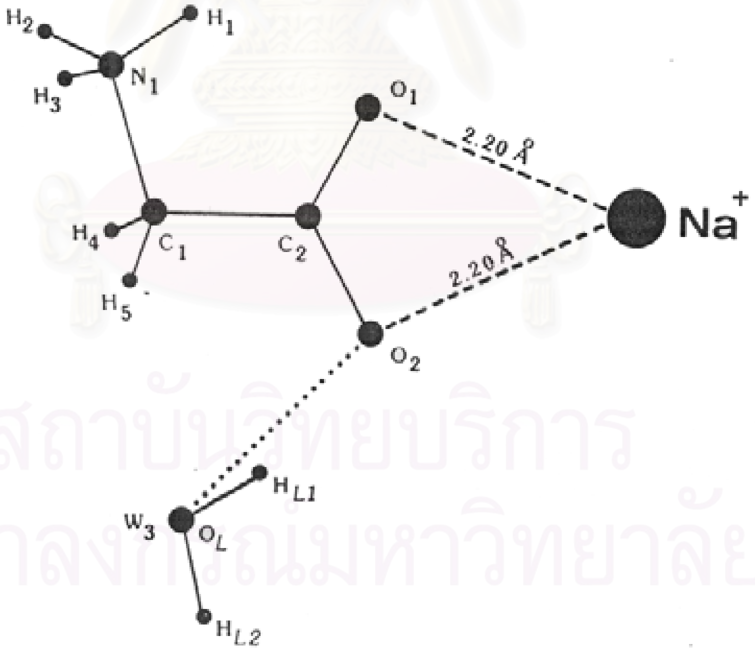


Figure 3.13 Glycine zwitterion – Na^+ complex with W3.

Table 3.17 A The Total Energies of Glycine Zwitterion - Na^+ Complex with Water 3 . Optimizing the Angle $C_2\hat{O}_2O_L$ with Fixing the Angle $O_2\hat{O}_LH_{L1}$ = 0° and the Distance O_2 - O_L = 2.75 Å .

$C_2\hat{O}_2O_L$ (degrees)	Energies (a.u.)
90	-453.87948
100	-453.88488
105	-453.88583
110	-453.88533
120	-453.88412

Table 3.17 B The Total Energies of Glycine Zwitterion - Na^+ Complex and Water 3. Optimizing the Angle $O_1\hat{O}_LH_{L1}$ with Fixing the Angle $C_2\hat{O}_2O_L$ = 105° and the Distance O_2 - O_L = 2.75 Å.

$O_2\hat{O}_LH_{L1}$ (degrees)	Energies (a.u.)
0	-453.88583
10	-453.88712
12	-453.88695
20	-453.88617

Table 3.17 C The Total Energies of Glycine Zwitterion - Na^+ Complex with Water 3. Optimizing the $O_2 - O_L$ Distance with Fixing the Angles $C_2\hat{O}_2O_L = 105°$ and $O_2\hat{O}_LH_{L1} = 10°$.

$O_2 - O_L$ (Å)	Energies (a.u.)
2.55	-453.88426
2.65	-453.88733
2.68	-453.88732
2.70	-453.88722
2.75	-453.88712

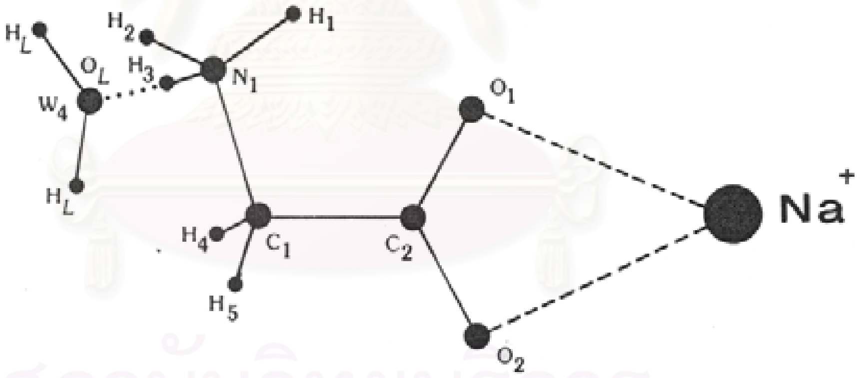


Figure 3.14 Glycine Zwitterion - Na^+ complex with W4.

Table 3.18 The Total Energies of Glycine Zwitterion - Na^+ Complex with Water 4 or Water 5. Optimizing the NH - O_L Distance .

NH - O_L(Å)	Energies (a.u.)
2.60	-453.91111
2.65	-453.91069
2.68	-453.91059
2.70	-453.91135
2.75	-453.90957
2.80	-453.90827

3.3.2 The Energies Optimized Water Binding Positions to Na^+ of Glycine Zwitterion - Na^+ Complex in Aqoues Solution.

As most of metal ions , Na^+ forms an octahedral structure with water molecules (35) . When a ligand is placed into the solution of metal ion , the ion is supposed to bind to the ligand whenever the metal ligand binding energy is greater than its binding to the water . At least one water molecule is then released from the ion's hydration shell. Since Na^+ forms complex with glycine zwitterion in such a way that Na^+ binds to the two oxygen atoms of the COO^- group , therefore Na^+ must release two water molecules from octahedral shell and glycine zwitterion will replace these positions (Figure 3.15). To investigate the orientation of the four water molecules binded to Na^+ , we again optimized the intermolecular parameters with respect to total energy. The results are shown in Table 3.19 .

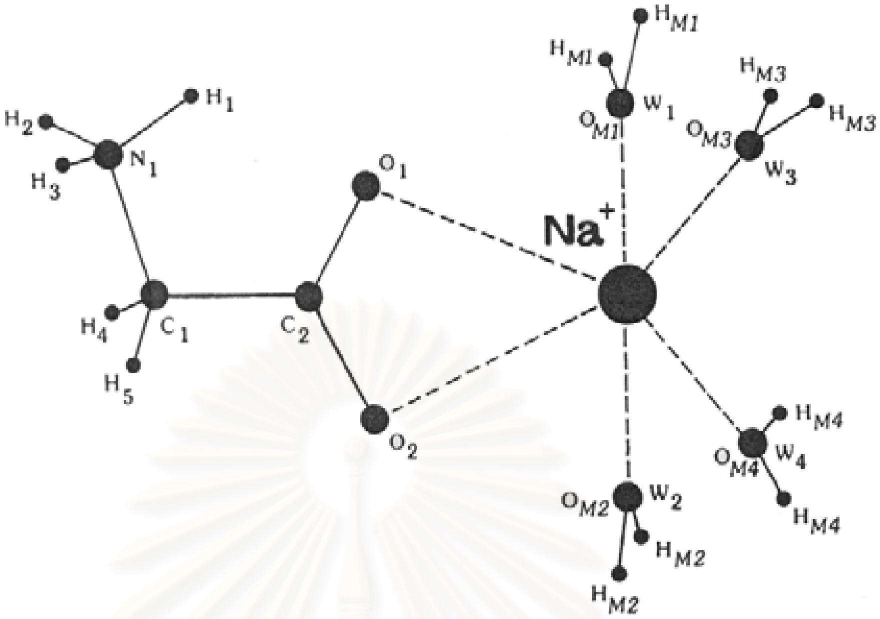


Figure 3.15 Glycine zwitterion-Na^+ complex with **hydration** site on Na^+. (M1 , M2 represent : the axial positions where M3 , M4 represent , the equatorial positions.)

Table 3.19 A The Total Energies of Glycine Zwitterion - Na^+ Complex with Water Binded to Na^+. Optimizing the Angle $O_{M3}\hat{Na}O_{M4}$ with Fixing the Axial Water Molecules Perpendicular to the Molecular Plane , all Distances of $O_M - Na^+ = 2.80 Å$, $O_1 - Na^+ = 2.20 Å$.

$O_{M3}\hat{Na}O_{M4}$ (degrees)	Energies(a.u.)
85.0	-647.48351
90.0	-647.48354
95.0	-647.48339
99.8	-647.48160
110.0	-647.48271
120.0	-647.48198

Table 3.19 B The Total Energies of Glycine Zwitterion-Na^+ Complex with Water Binded to Na^+. Optimizing the Angle $C_2\hat{Na}O_{M1}$ (= $C_2\hat{Na}O_{M2}$) with Fixing the Angle $O_{M3}\hat{Na}O_{M4}$ = 90.0°. The Other Parameters are Kept as in Table 3.19 A.

$C_2\hat{Na}O_{M1}$ (degrees)	Energies (a.u.)
85.0	-647.48298
90.0	-647.48354
95.0	-647.48348

Table 3.19 C The Total Energies of Glycine Zwitterion-Na^+ Complex with Water Binded to Na^+. Optimizing the Distances with Fixing the Axial Water Molecules to Perpendicular to the Molecular Plane.

The Other Parameters are Kept as in Table 3.19 B.

$O_M - Na^+$ (Å)	Energies (a.u.)
2.00	-647.50001
2.15	-647.52471
2.20	-647.52628
2.22	-647.52624
2.25	-647.52565
2.50	-647.50678
2.80	-647.48354

Table 3.19 D The Total Energies of Glycine Zwitterion – Na^+ Complex with Water binded to Na^+. Optimizing the Distances Between the Oxygen of Equatorial Water Molecules and Na^+ with Fixing the Distances Between the Oxygen of Axial Water Molecules and Na^+ = 2.20 Å. The other Parameters are Kept as in Table 3.19 C.

O_{M3} – Na^+ (Å)	Energies (a.u.)
2.10	-647.52627
2.15	-647.52559
2.20	-647.52628
2.25	-647.52592

Table 3.19 E The Total Energies of Glycine Zwitterion – Na^+ Complex with Water Binded to Na^+. Optimizing the Distances Between the Oxygen of Axial Water Molecules and Na^+ with Fixing the Distances Between the Oxygen of Equatorial Water Molecules and Na^+ = 2.20 Å. The Other Parameters are Kept as in Table 3.19 D.

O_{M1} – Na^+ (Å)	Energies (a.u.)
2.15	-647.52572
2.20	-647.52628
2.25	-647.52605

Table 3.19 F The Total Energies of Glycine Zwitterion – Na^+ Complex with Water Binded to Na^+. Reoptimizing the Distance O_1 – Na^+ with Fixing All the Distances Between the Oxygen of Water Molecules and Na^+ = 2.20 Å . The Other Parameters are Kept as in Table 3.19 E.

O_1 – Na^+ (Å)	Energies (a.u.)
2.20	-647.52628
2.29	-647.52775
2.38	-647.52637
2.56	-647.51923

Table 3.19 G The Total Energies of Glycine Zwitterion – Na^+ Complex with Water Binded to Na^+. Reoptimizing All O_M – Na^+ Distances with Fixing the Distances of O_1 – Na^+ = 2.29 Å . The Other Parameters are Kept as in Table 3.19 F.

O_M – Na^+ (Å)	Energies (a.u.)
2.15	-647.52645
2.18	-647.52756
2.20	-647.52779
2.22	-647.52767

Table 3.19 H The Total Energies of Glycine Zwitterion - Na^+ Complex with Water Binded to Na^+. Reoptimizing the Distances Between the Oxygen of Equatorial Molecules and Na^+ with Fixing the Distances Between the Oxygen of Axial Water Molecules and Na^+ = 2.20 Å. The Other Parameters are Kept as in Table 3.19 G.

O_M - Na^+ (Å)	Energies (a.u.)
2.18	-647.52770
2.20	-647.52779
2.22	-647.52771

Table 3.19 I The Total Energies of Glycine Zwitterion - Na^+ - Complex with Water Binded to Na^+.Reoptimizing the Distances Between the Oxygen of Axial Water Molecules and Na^+ with Fixing the Distances between the Oxygen of Equatorial Water Molecules and Na^+ = 2.20 Å .The Other Parameters are Kept as in Table 3.19 H.

O_{M1} - Na^+ (Å)	Energies (a.u.)
2.18	-647.52765
2.20	-647.52779
2.22	-647.52776

3.3.3 Determination of the effect of Na^+ and Its Water on the Water Binded to Glycine Zwitterion .

As in section 3.4.1 , we will reoptimize the orientation of water 2 and water 3 , but this time the water molecules binded to Na^+ are included. The conformations are shown in Figure 3.16 - 3.18 and the total energies are reported in Table 3.20 - 3.22

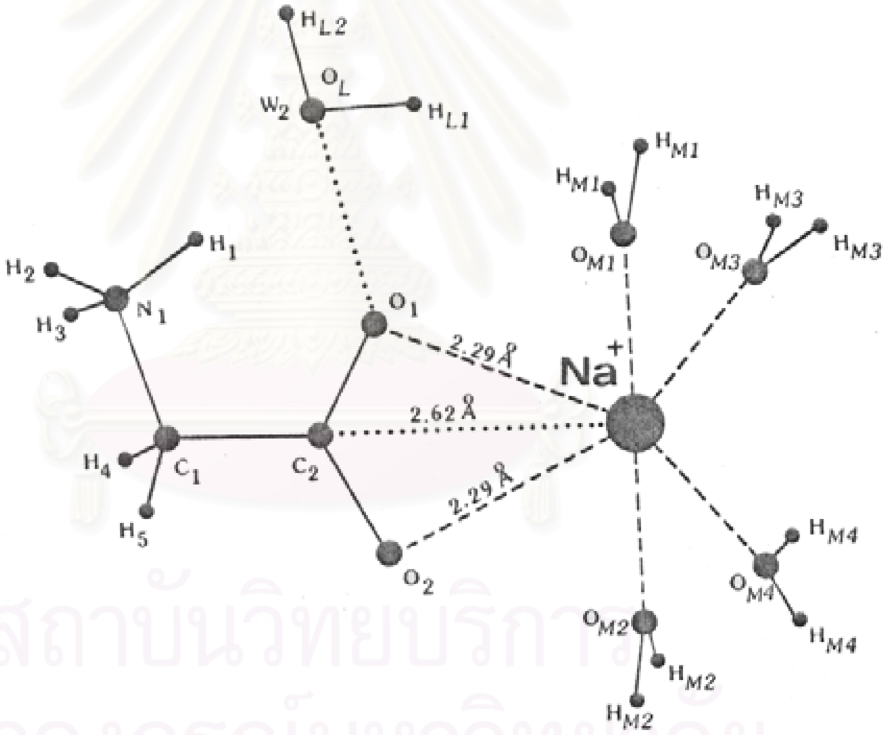


Figure 3.16 Glycine zwitterion - Na^+ complex with water binded to Na^+ and W2.

Table 3.20 A The Total Energies of Glycine Zwitterion - Na^+ Complex with Water Binded to Na^+ Including W2. Optimizing the Angle $C_2\hat{O}_1O_L$ with Fixing the Angle $O_1\hat{O}_LH_{L1}$ =70° and the Distance $O_1 - O_L$ = 2.55 Å .

$C_2\hat{O}_1O_L$ (degrees)	Energies (a.u.)
125	-712.07900
128	-712.08087
130	-712.08080
132	-712.07994

Table 3.20 B The Total Energies of Glycine Zwitterion - Na^+ Complex with Water Binded to Na^+ Including W2. Optimizing the Angle $O_1\hat{O}_LH_{L1}$ with Fixing the Angle $C_2\hat{O}_1O_L$ = 128° and the Distance $O_1 - O_L$ = 2.55 Å .

$O_1\hat{O}_LH_{L1}$ (degrees)	Energies (a.u.)
20	-712.08046
30	-712.08272
35	-712.08305
40	-712.08308
45	-712.08297
50	-712.08269
65	-712.08149
70	-712.08087

Table 3.20 C The Total Energies of Glycine Zwitterion - Na$^+$ Complex with Water Binded to Na$^+$ Including W2 . Optimizing the Distance $O_1 - O_L$ with Fixing the Angles $C_2\hat{O}_1O_L = 128°$ and $O_1\hat{O}_LH_{L1} = 40°$.

$O_1 - O_L$ (Å)	Energies (a.u.)
2.50	-712.08288
2.55	-712.08308
2.60	-712.08285

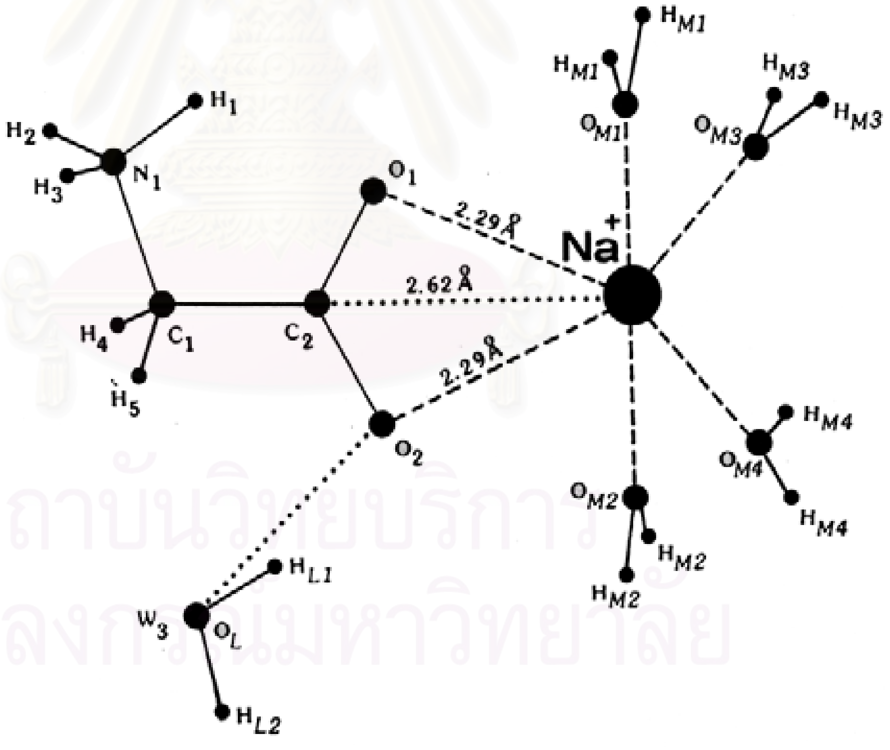


Figure 3.17 Glycine zwitterion - Na$^+$ complex with water binded to Na$^+$ and W3.

Table 3.21 A The Total Energies of Glycine Zwitterion - Na^+ Complex with Water Binded to Na^+ Including W3 . Optimizing the Angle $C_2\hat{O}_2O_L$ with Fixing the Angle $O_2\hat{O}_LH_{L1}$ = 10° and the Distance O_2 - O_L = 2.65 Å .

$C_2\hat{O}_2O_L$ (degrees)	Energies (a.u.)
95	-712.07257
100	-712.07354
102	-712.07347
105	-712.07312

Table 3.21 B The Total Energies of Glycine Zwitterion - Na^+ Complex with Water Binded to Na^+ Including W3 . Optimizing the Angle $O_2\hat{O}_LH_{L1}$ with Fixing the Angle $C_2\hat{O}_2O_L$ = 100 ° and the Distance O_2 - O_L = 2.65 Å .

$O_2\hat{O}_LH_{L1}$ (degrees)	Energies (a.u.)
0	-712.07106
5	-712.07274
10	-712.07354
12	-712.07362
15	-712.07351

Table 3.21 C The Total Energies of Glycine Zwitterion - Na^+ Complex with Water Binded to Na^+ Including W3 . Optimizing the Distance $O_2 - O_L$ with Fixing the Angles $C_2\hat{O}_2O_L = 100^\circ$ and $O_2\hat{O}_LH_{L1} = 12^\circ$.

$O_2 - O_L$ (Å)	Energies (a.u.)
2.65	-712.07362
2.68	-712.07382
2.70	-712.07386
2.72	-712.07382
2.80	-712.07308

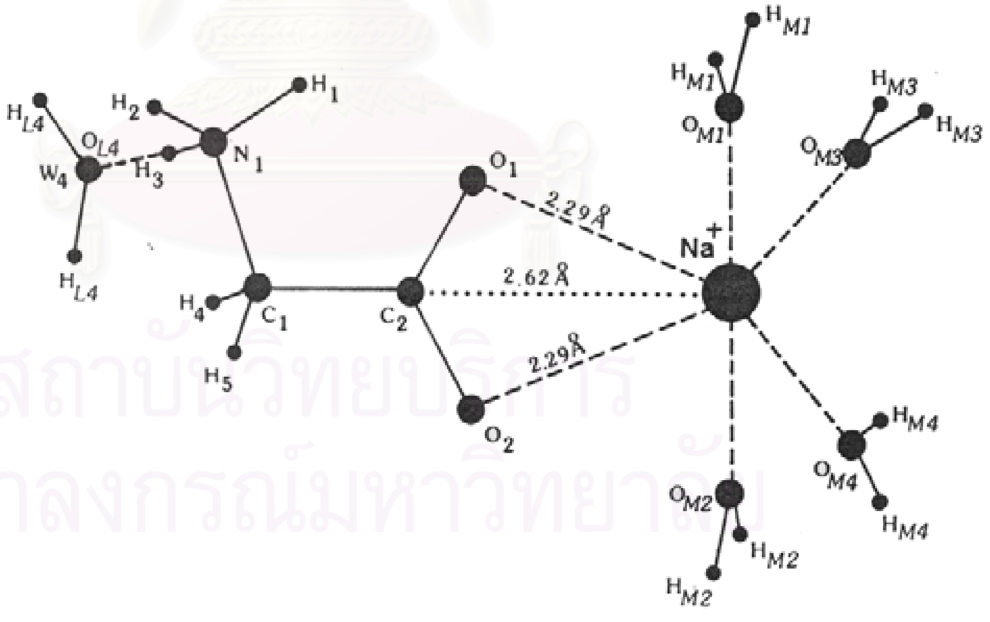


Figure 3.18 Glycine zwitterion - Na^+ complex with water binded to Na^+ and W4

Table 3.22 The Total Energies of Glycine Zwitterion - Na^+ Complex with Binded to Na^+ Including W4. Optimizing the NH...O_L Distance

NH....O_L (Å)	Energies (a.u.)
2.60	-712.09015
2.62	-712.09038
2.65	-712.09031
2.68	-712.09009
2.70	-712.08988
2.72	-712.08961

CHAPTER 4

DISCUSSION AND CONCLUSION

4.1 The System of Glycine Zwitterion in Aqueous Solution

4.1.1 The first Hydration of Glycin Zwitterion in Aqueous Solution

Form our previous study (31) on the determination of the first hydration shell by CNDO/2 method and ab initio method at a fixed hydrogen bond distance 2.75 Å , the conclusion has been drawn that the first hydration shell is composed of 5 water molecules binded to glycine zwitterion (See Figure 4.1). In this work, we try to get a more accurate orientation of water molecules by performing an ab initio calculation and the optimization of each water molecule is taken into account. The interaction energies at the ten possible coordination sites for water on glycine zwitterion (Figure 3.9) obtained from both methods are compared in Table 4.1 . We are not interested in the absolute value but rather a relative order of the interaction energies which are not influenced significantly by the use of minimal basis sets. It is discovered that the order of the interaction energies for both calculations are slightly different. This work which should be more reliable as all the positions are optimized , shows that the most fovourable position is W2 while at a fixed hydrogen bond by ab initio method are W4 and W5. This result is expected due to the formation of hydrogen bonds between NH and W2 as well as O1 and W2 . The relative order of the interaction energies for the rest is almost the same.

The full hydration shell is set up by using a criteria as before (31), the formation of a stable hydration site should occur when the solute-solvent interaction is greater than the solvent-solvent interaction. The calculated binding energy of water dimer, using the same basis set, at the optimized position is -11.8 kcal/mol corresponding to hydrogen bond distance 2.70Å . Our results predicted as our last study that W_2, W_3, W_4 and W_5 form the strongest binding to glycine zwitterion when compare with that of the water dimer, whereas the binding energies for W_6, W_9 and W_{10} are lower. The water W_7 and W_8 are neglected due to solvent-solvent repulsion effect. (see Figure 3.9).

Final decision on the structure of hydration shell is similar to previous conclusion, only the orientation of some water molecules are different (see Table 4.2). The model for the hydration structure is illustrated in Figure 4.1.

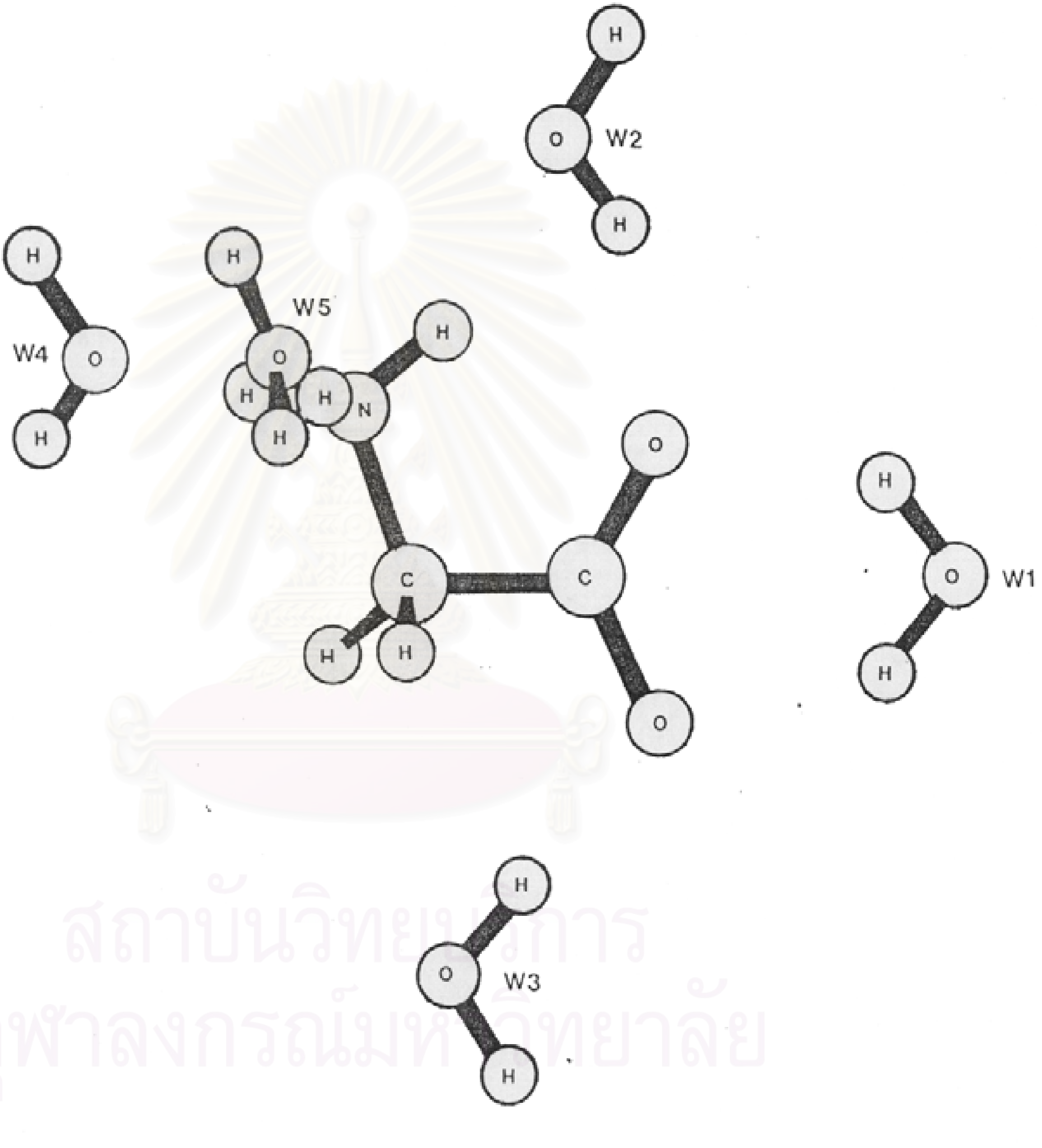


Figure 4.1 The first hydration shell of glycine zwitterion consists of 5 water molecules.

Table 4.1 The Binding Energies (kcal/mol) of Glycine Zwiterrion with One Water Molecule in Ten Different Coordination Sites Calculated by Both CNDO/2 and Ab Initio Methods.

WATER	Fixed H-Bond 2.75 Å		Ab Inition
	Ab Initio	CNDO/2	Optimization
1	-14.8	-10.5	-15.1
2	-20.3	-15.7	-24.1
3	-17.6	-14.7	-20.1
4	-20.8	-11.2	-21.0
5	-20.8	-11.2	-21.0
6	-5.0	-4.5	-4.9
7	-15.2	-9.3	-15.2
8	-14.2	-8.8	-14.2
9	-9.3	-10.1	-9.3
10	-9.3	-10.1	-9.3

Table 4.2 The Conformation of Each Water Molecule in the First Hydration Shell of Glycine Zwitterion in Aqueous Solution.

Water	CNDO/2, H-bond 2.75 Å		Ab Initio, Optimization	
	H-bond (Å)	Angles (degrees)	H-bond (Å)	Angles (degrees)
1	2.75	bridging with O_1 and O_2	2.81	bridging with O_1 and O_2
2	2.75	$C_2\hat{O}_1O_L = 125^\circ$ $O_1\hat{O}_LH_L = 20^\circ$	2.55	$C_2\hat{O}_1O_L = 132^\circ$ $O_1\hat{O}_LH_L = 20^\circ$
3	2.75	$C_2\hat{O}_2O_L = 95^\circ$ $O_1\hat{O}_LH_L = 10^\circ$	2.70	$C_2\hat{O}_2O_L = 108^\circ$ $O_2\hat{O}_LH_L = 0^\circ$
4	2.75	along N-H bond	2.64	along N-H bond
5	2.75	along N-H bond	2.64	along N-H bond

4.1.2 The Influence of Hydration on the Electron-Distribution in Glycine Zwitterion.

The change of electron distribution($\Delta\rho$) by Mulliken population analysis of glycine zwitterion upon hydration is shown in Table 4.3 and illustrated in Figure 4.2

Table 4.3 The Charge of Electron Distribution Calculated by Mulliken Population Analysis.

atom	ρ_{gly-5H_2O}	ρ_{gly}	$\Delta\rho$
H1	0.589	0.603	-0.015
H2	0.583	0.625	-0.041
H3	0.583	0.625	-0.041
N1	7.890	7.708	+0.182
H4	0.757	0.752	+0.005
H5	0.757	0.752	+0.005
C1	6.449	6.502	-0.053
C2	5.594	5.667	+0.074
O1	8.436	8.409	+0.027
O2	8.374	8.356	+0.018

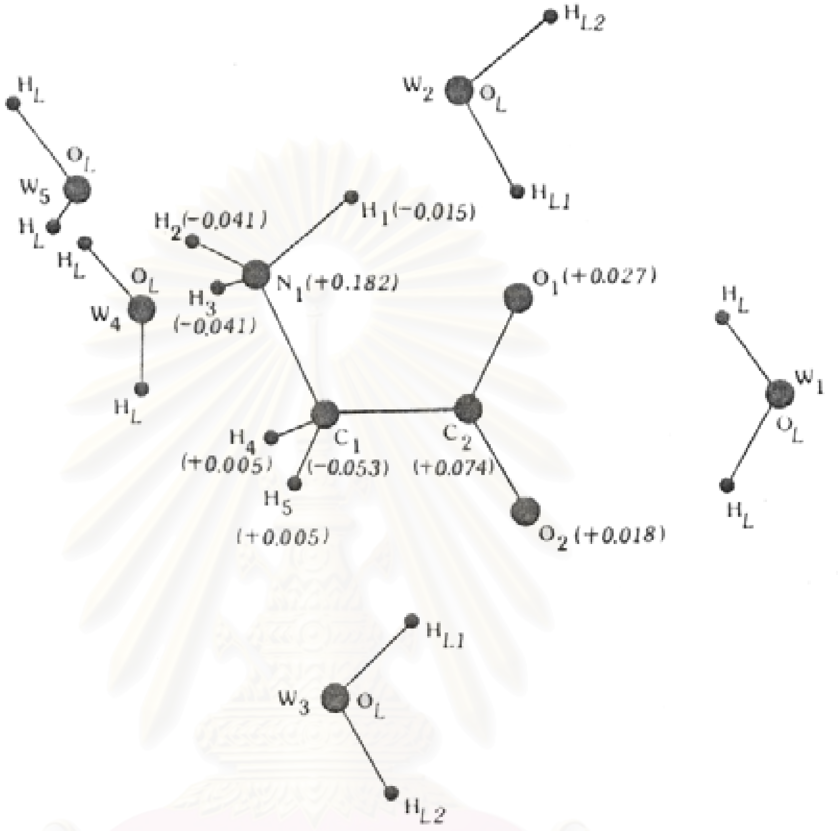


Figure 4.2 The change of electron distribution of each atom in glycine zwitterion due to the hydration effect.

The more pronounced charge transfer is occurred at the polar groups. The decrease of electron density of the NH hydrogens means that the acidity of the NH hydrogens is increased. And the reactivity of the carboxylate oxygen atoms will be enhanced according to the increase of charge distribution in that regions.

4.1.3 The Influence of Hydration on Internal Rotation of Glycine Zwitterion

The rotation of the NH_3^+ (θ) and the COO^- (ϕ) groups of isolated glycine zwitterion has been investigated. Rotation of angle θ from a most stable conformation (0,0) to (60,0) leads to a barrier of 11.0 kcal/mol (graph C, Figure 4.3) and rotation of angle ϕ from angle (0,0) to (0,90) is 30.9 kcal/mol (graph C, Figure 4.4) while a rotation of ϕ starting from (60,0) to (60,90) needs only 16 kcal/mol (graph A, Figure 4.5).

It should be noted that the absolute values of the stabilization energy is quite high as we have mentioned this due to the use of minimum basis set, however the relative order of these results which has been proved to be satisfactory (9,10) agree with that of CNDO/2 method (see Table 4.4)

Table 4.4 The Comparison of the Energy Barrier Corresponding to the Rotation of (θ , ϕ) by Ab Initio with GLO Basis Sets and CNDO/2 Methods.

Rotation Angles (θ , ϕ)	**Ab Initio (kcal/mol)**	**CNDO/2 (kcal/mol)**
(0,0) ⟶ (60,0)	11.0	3.3
(0,0) ⟶ (0,90)	30.9	10.4
(60,0) ⟶ (60,90)	16.0	5.8

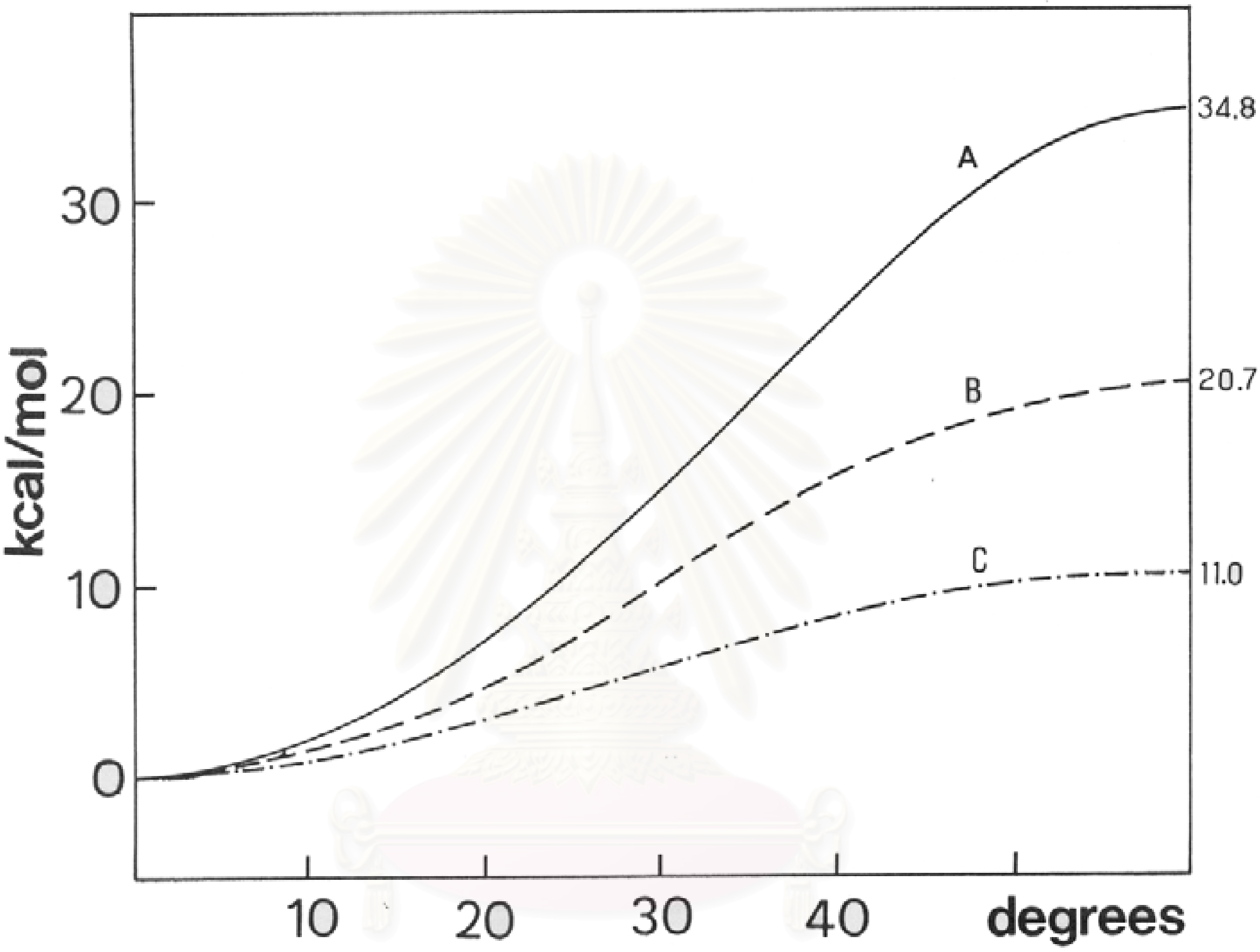


Figure 4.3 The rotation pathways of Glycine Zwitterion . Fixing $-COO^-$ group at Ø = 0 degree.

A. The rotation of $-NH_3^+$ group, fixing the hydration structure.

B. The rotation of $-NH_3^+$ group together with W2, W4, W5, fixing W1, W3.

C. The rotation of $-NH_3^+$ group alone, neglecting the hydration structure.

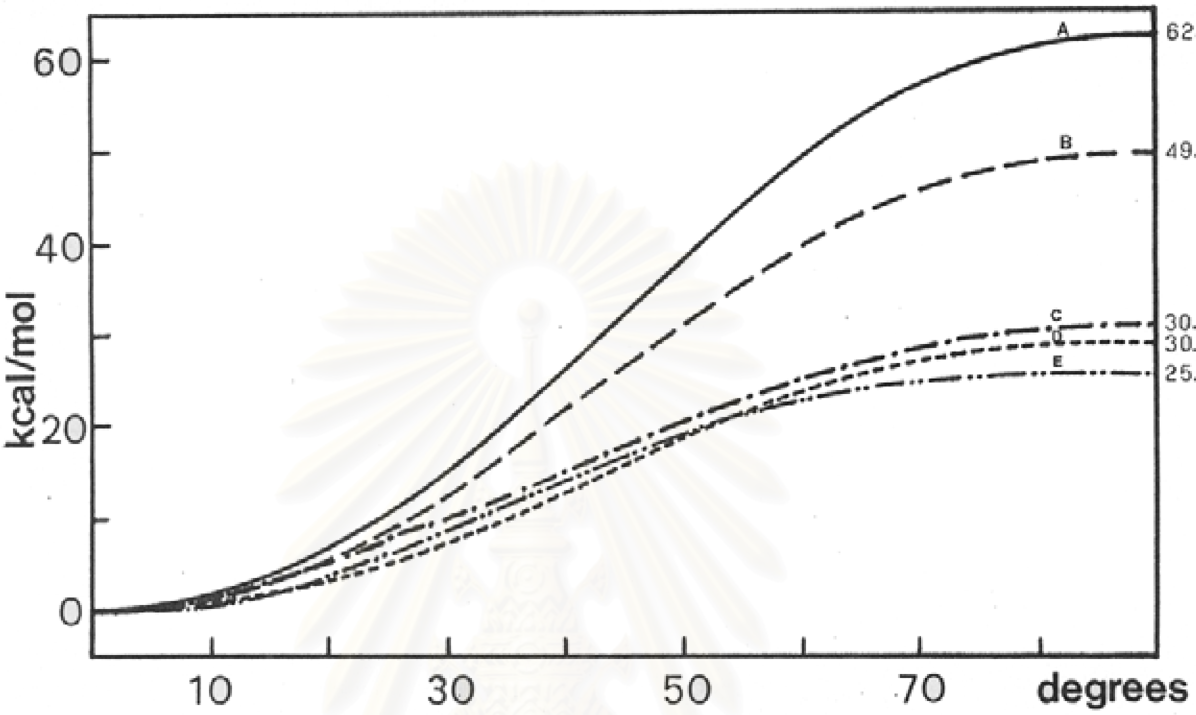


Figure 4.4 The rotation pathways of Glycine Zwitterion . Fixing $-NH_3^+$ group at Θ = 0 degree.

A. The rotation of $-COO^-$ group, fixing the hydration structure.

B. The rotation of $-COO^-$ group together with W1, fixing W2, W3, W4, W5.

C. The rotation of $-COO^-$ group alone, neglecting the hydration structure.

D. The rotation of $-COO^-$ group together with W1, W3, fixing W2, W4, W5.

E. The rotation of $-COO^-$ group together with W1, W2, W3, fixing W4, W5.

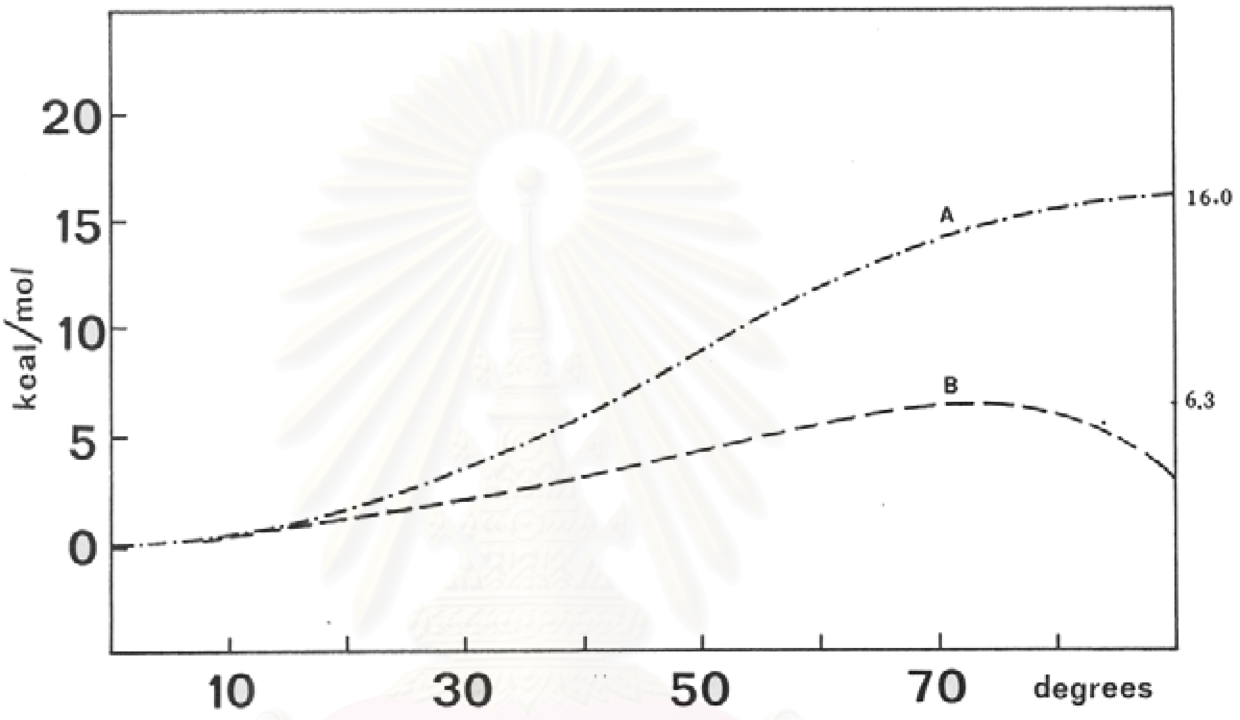


Figure 4.5 The rotation pathways of Glycine Zwitterion . Fixing $-NH_3^+$ group and W2, W4, W5 at Θ = 60 degrees

A. The rotation of $-COO^-$ group, neglecting the hydration structure.

B. The rotation of $-COO^-$ group together with W1, W3.

The rotation of angle θ -is therefore easier than the rotation of angle ϕ . This gives a chance for isolated glycine zwitterion to rotate angle θ first 60° and a subsequent rotation of angle ϕ which needs more 5 kcal, leading to the final conformation (60,90) with an overall barriers of 27.0 kcal/mol.

When the first hydration shell which consists of 5 water molecules is included. The stable conformation of hydrated glycine zwitterion still remains at the conformation (0,0). The rotation of angle θ from conformation (0,0) to (60,0) with fixing the hydration shell (graph A ,Figure 4.3) and corotating its solvation sphere (W2, W4, W5) (graph B, Figure 4.3) utilize the energy barriers of 34.8 kcal/mol and 20.7 kcal/mol respectively.The corotation of the solvated water especially of W2 lower the barrier to 14.1 kcal/mol, this extra energy due to the breaking of the bonds to the hydration water. Thus the relaxation of the solvated molecules has to be considered essential.

The pathways of the rotation of angle ϕ starting from conformation (0,0) to (0,90) of the hydrated glycine zwitterion are presented in Figure 4.4. The results indicate the corotation of the solvated water W1 (graph B) lower the barrier to 13.0 kcal/mol compared to the case of fixing the hydration (graph A). If W3 or both W2, W3 are corotated together with W1 and $-COO^-$ group (graph D, E of Figure 4.4), the barrier are much more decreased (lower to about 34 and 38 kcal/mol respectively) and even lower than in the case of isolated glycine zwitterion (graph C , Figure 4.4). But all the energy barriers either by fixing or corotating the solvation sphere are still higher than the rotation of angle θ (Figure 4.3). Therefore, as in the isolated molecule, the minimum pathway of the hydrated glycine zwitterion should compose of rotation of angle θ follow by a rotation of angle ϕ leading to the conformation (60,90). The barrier shapes of the rotation after rotating the NH_3^+, W2, W4 and W5 to 60° are illustrated in Figure 4.5. The energy barrier for the simultaneously rotation of $-COO^-$, W1, W3 is only 6.3 kcal/mol (graph B, Figure 4.5) , but the peak of the maximum barrier is shifted from 90° to 75° due to the energy gain from interaction between water3 and the $-NH_3^+$ group.

The results obtained from the study of the internal rotation by rotating angle θ and ϕ indicate the hydration increases the barrier, except the corotation of W1, W2, W3 with the angle ϕ ,then the hydration decreases the barrier. All the internal rotations calculated in the work use rigid molecule model because the adjusting the water geometry to every conformation change would require a large of computing times.

4.2 The System of Glycine Zwitterion - Na^+ Complex in Aqueous Solution.

4.2.1 The Conformation of Glycine Zwitterion - Na^+ Complex.

Glycine Zwitterion has only one negative charge group which is almost immediately available for metal binding, especially group I A cations always bind to oxygen donors to form the weak complex. The 4-memberred rings are oftenly formed in which both oxygen atoms are bound to the metal (36). This is agreed to our result, the most preferred binding site for Na^+ to attack glycine zwitterion is along the bisectrix of the $O_1\hat{C}_2O_3$ angle to form $O_1C_2O_3Na^+$ 4-memberred ring, with the optimized distances between the carboxylate oxygen atoms and Na^+ of 2.20 Å (Figure 3.11). The corresponding stabilization energy (Δ E) is -67.1 kcal/mol

where $\Delta E = E_{gly-Na^+} - E_{gly} - E_{Na^+}$

and E_{gly-Na^+} = total energy of glycine zwitterion-Na^+complex
= -389.33995 a.u.

E_{gly} = total energy of glycine zwitterion
= -240.08819 a.u.

E_{Na^+} = total energy of Na^+
= -149.14481 a.u.

4.2.2 The Influence of Na^+ on the First Hydration of Glycine Zwitterion.

In order to predict whether or not a complex is formed in aqueous solution, only the metal ligand interaction energy is not sufficient. One must compare this energy with the hydration energy. The metal ion is supposed to bind to the ligand whenever the metal-ligand binding energy is greater than its binding to the water. The binding of Na^+ to glycine zwitterion has a stabilization energy (Δ E) of -66.4 kcal/mol.

where $$\Delta E = E_{gly-4H_2O-Na^+} - E_{gly-4H_2O} - E_{Na^+}$$

$E_{gly-4H_2O-Na^+}$ = total energy of glycine zwitterion-Na^+ complex with 4 water molecules surrounded glycine zwitterion

= -647.55566 a.u.

E_{gly-4H_2O} = total energy of glycine zwitterion with 4 water molecules surrouned glycine zwitterion

= -498.30507 a.u.

appear more favourable than its binding to W1 with a stabilization energy (Δ E) of -15.0 kcal/mol

$$\Delta E = E_{gly-5H_2O} - E_{gly-4H_2O} - E_{H_2O}$$

E_{gly-5H_2O} = total energy of glycine zwitterion with it's first hydration shell composed of 5 water molecules

= -562.85043 a.u.

E_{H_2O} = total energy of water molecule

= -64.52139 a.u.

The effect of Na^+ on the orientation of the water surrounded glycine zwitterion are investigated. The results are summarized in Table 4.5 and shown in Figure 4.6. The influence of Na^+ seems not to effect the H-bond distance of W2, but the hydrogen of W2 is pushed farther away from O_1 by 50 . This should due to the repulsion between Na^+ and the hydrogen of W2. Although the electron density of

O_1 is increased but the charge of hydrogen of W2 is decreased (Table 4.6). Therefore, the Na^+ stabilizes this H-bond only 0.9 kcal/mol. Contrast to the case of W3, the H-bond distance is shorten by 0.05 Å. The oxygen of W3 is pushed to the region of the hydrophobic group by 3° and the hydrogen is pulled back to the region of Na^+ by 10° due to the increase of the charge at H_S. The electron density of O_2 increased with the increase of the charge at H_{L1} should enhance the stabilization of this H-bond energy. However, our result shows that this H-bond energy is reduced by 3.8 kcal/mol. This could be explained in the basis of the distortion of the H-bond along O_2-H_{L1} O_L upon Na^+ effect. The remarkable increase of the H-bond energies of W4 and W5, 10.3 kcal/mol, also can be rationalized by considering the atomic population of the NH hydrogens and the oxygen of water molecules. The increase of the electron density at O_L of W4, W5 as well as the increase of the charge at NH hydrogens (or the increase of the stability of proton donor)indicates that the Na^+ effect is transferred through the amino group and the water W4, W5.

Table 4.5 The Oreintation of the Solvated Water and the H-bond Energies of Glycine Zwitterion and Glycine Zwitterion - Na^+ Complex in Aqueous Solution.

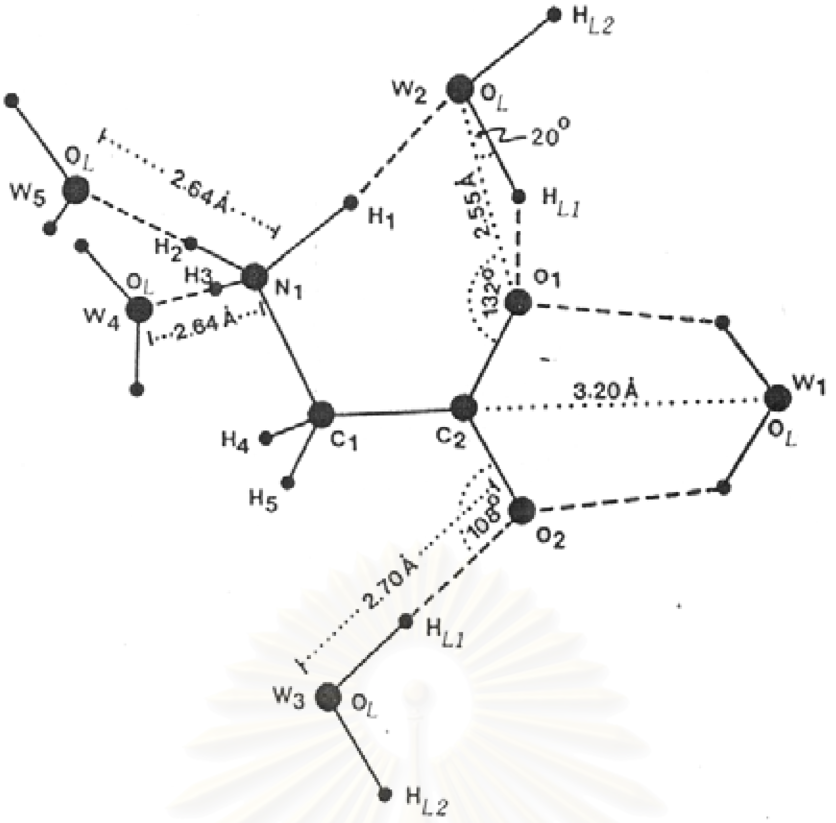
	Glycine Zwitterion	Glycine Zwitterion - Na^+
W2	$O_1 - O_L = 2.55$ Å	$O_1 - O_L = 2.55$ Å
	$C_2\hat{O}_1O_L = 132^\circ$	$C_2\hat{O}_1O_L = 132^\circ$
	$O_1\hat{O}_LH_{L1} = 20^\circ$	$O_1\hat{O}_LH_{L1} = 70^\circ$
	total energy= -304.64795 a.u.	total energy= -453.90119 a.u.
	*H-bond energy= -24.1 kcal/mol	**H-bond energy= -25.0 kcal/mol
W3	$O_1 - O_L = 2.70$ Å	$O_1 - O_L = 2.65$ Å
	$C_2\hat{O}_2O_L = 108^\circ$	$C_2\hat{O}_2O_L = 105^\circ$
	$O_2\hat{O}_LH_{L1} = 0^\circ$	$O_2\hat{O}_LH_{L1} = 10^\circ$
	total energy= -304.64156 a.u	total energy= -453.88733 a.u
	*H-bond energy= -20.1 kcal/mol	**H-bond energy= -16.3 kcal/mol
W4,W5	$NH - O_L = 2.64$ Å	$NH - O_L = 2.70$ Å
	total energy= -304.64309 a.u	total energy= -453.91135 a.u
	*H-bond energy= -21.0 kcal/mol	**H-bond energy= -31.4 kcal/mol

*H-bond energy = $E_{gly+w} - E_{gly} - E_{H_2O}$

**H-bond energy = $E_{gly+Na^++w} - E_{gly-Na^+} - E_{H_2O}$

Table 4.6 The Difference In Electron Density Distribution ($\Delta\rho$) on Glycine Zwitterion - Na^+ Complex with the First Hydration Shell of Glycine Zwitterion Due to Na^+

atom		$\rho_{gly-Na^+-4H_2O}$	ρ_{gly-5H_2O}	$\Delta\rho$
C1		6.417	6.500	-0.032
C2		5.643	5.594	+0.049
O1		8.485	8.436	+0.049
O2		8.470	8.374	+0.096
N1		7.900	7.890	+0.009
H1		0.576	0.588	-0.012
H2		0.578	0.583	-0.005
H3		0.578	0.583	-0.005
H4		0.736	0.757	-0.021
H5		0.736	0.757	-0.021
Na^+		10.055	-	-
O_L		-	8.482	-
H_{L1}	W1	-	0.784	-
H_{L2}		-	0.791	-
O_L		8.397	8.518	-0.121
H_{L1}	W2	0.762	0.732	+0.030
H_{L2}		0.782	0.784	-0.003
O_L		8.484	8.498	-0.014
H_{L1}	W3	0.777	0.773	+0.004
H_{L2}		0.815	0.823	-0.009
O_L		8.416	8.404	+0.012
H_{L1}	W4	0.743	0.747	-0.004
H_{L2}		0.746	0.750	-0.005
O_L		8.416	8.404	+0.012
H_{L1}	W5	0.743	0.747	-0.004
H_{L2}		0.746	0.751	-0.005



Figuer 4.6 a The orientation of solvated water of glycine zwitterion in aqueous solution.

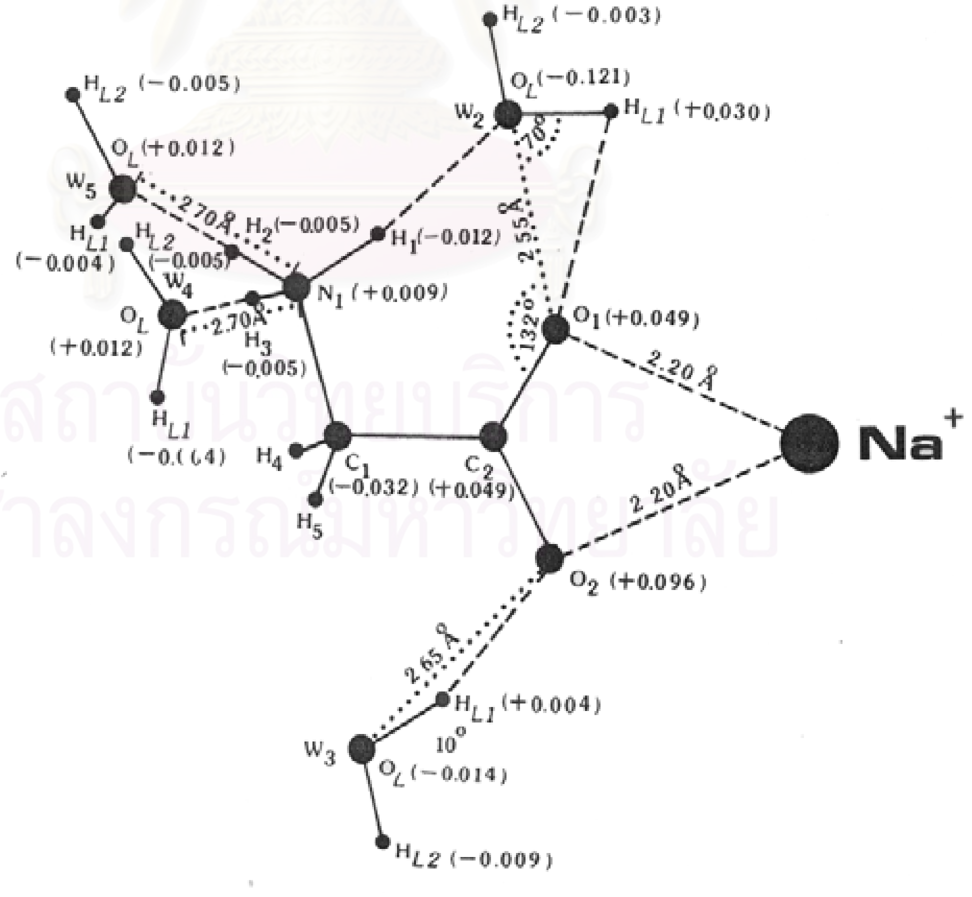


Figure 4.6 b The orientation of solvated water of glycine zwitterion $-Na^+$ complex in aqueous solution.

The value in the parenthesis is the change of charge distribution.

4.2.3 The Structure of Glycine$^-$ Zwitterion – Na^+ Complex in Aqueous Solution.

The replacement of coordinated water by an entering ligand group is a reaction of fundamental importance. For the alkali metals and alkali earth metals, most of their aquo complexes are six coordinate or octahedral structure. The alkali metals usually form complexes faster than any other ions, but the complexes are very weak and so the experimental studies must be carried out at high concentration (36). The glycine zwitterion-Na^+ complex is aqueous solution has not been studied yet. Most stud, concerned the transition metals which interact strongly with ligand (11,15).

In aqueous solution, Na^+ is solvated by 6 water molecules to form an octahedral structure. When glycine zwitterion is placed into this system, partial dehydration is possible to occur resulting from the metal ligand interaction (-40.8 kcal/mol) slightly overcame the hydration energy for 2 coordination sites (-30.8 kcal/mol). Thus it should be considered to be weak interaction. The favourable position for Na^+ to form a complex is already proved to be along the bisectrix of the $O_1C_2O_3$ angle. Therefore, the glycine zwitterion - Na^+ complex in aqueous solution can be described as $[Na(gly)(H_2O)_4]^+$.

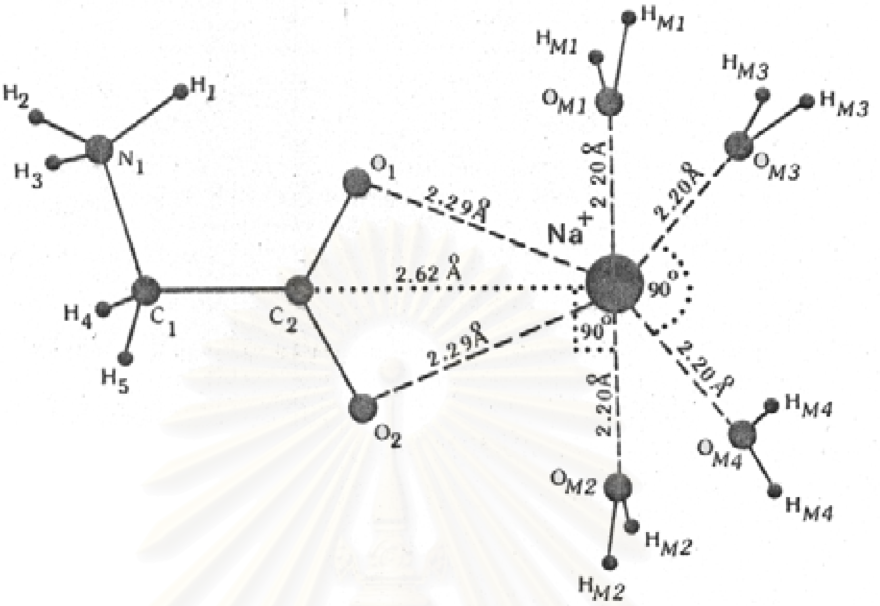


Figure 4.7 **The optimized conformation of $[Na(gly)(H_2O)_4]^+$**

The optimized conformation of $[Na(gly)(H_2O)_4]^+$ is presented in Figure 4.7. The calculated $Na^+...OH_2$ bond lengths are all equal to 2.20 Å. The hydration energy (ΔE_H) per one coordination site in this complex is

$$\Delta E_H = \{E_{[Na(gly)(H_2O)_4]^+} - E_{gly-Na^+} - E_{(H_2O)_4}\}/4$$

$$= \{(-647.52779)-(-389.33995)-(-258.07339)\}/4 \quad \text{a.u.}$$

$$= -18.0 \quad \text{kcal/mol}$$

which is 2.7 kcal/mol weaker than the hydration energy of $Na(H_2O)_6$ (-20.7 kcal/mol)

$$\Delta E_H \text{of } Na(H_2O)_6^+ = \{E_{Na(H_2O)_6^+} - E_{Na^+} - 6E_{H_2O}\}/6$$

$$= \{(-586.47152)-(149.14481)-6(-64.52139)\}/6 \text{ a.u.}$$

$$= -20.7 \quad \text{kcal/mol}$$

the results indicate the ligand did influence the hydration of Na$^+$ by weakening the interaction between Na$^+$ and the water molecules. This is due to the decrease in electron density of all oxygen atoms in water molecule of this complex eventhough the nuclear charge of Na$^+$is increased (see Table 4.7)

Table 4.7 Comparison of the Electron Density Distribution at Na$^+$and at Oxygen Atoms in Water Molecules of the Complexes.

atom		$\rho_{[Na(gly)(H_2O)]^+}$	$\rho_{[Na(H_2O)]^+}$
Na$^+$		10.118	10.123
O		8.445	8.453
H	1	0.770	0.763
H		0.765	0.763
O		8.445	8.453
H	2	0.770	0.763
H		0.765	0.763
O		8.445	8.453
H	3	0.767	0.763
H		0.767	0.763
O		8.446	8.453
H	4	0.767	0.763
H		0.767	0.763
O		-	8.453
H	5	-	0.763
H		-	0.763
O		-	8.453
H	6	-	0.763
H		-	0.763

The optimized distance of carboxylate oxygen atoms to Na^+ is 2.29 Å which is 0.09 Å longer than in the gas phase (2.20 Å). The elongation of this intermolecular distance results a lower of metal - ligand interaction by 26.3 kcal/mol (from -67.1 kcal/mol to -40.8 kcal/mol). This can be explained by considering the change of electron distribution as shown in Table 4.8. The decrease of electron density at O_1, O_2 and the decrease of positive charge of Na^+ due to the influence of hydration of Na^+ reduce the interaction between glycine zwitterion and Na^+ , the distance therefore is increased.

Table 4.8 Calculated Differences in Electron Density Distribution on Glycine Zwitterion - Na^+ Complex Due to the Hydration of Na^+.

atom	$\rho_{[Na(gly)(H_2O)]^+}$	$\rho_{[gly-Na]^+}$	$\Delta\rho$
C1	6.477	6.461	+0.016
C2	5.656	5.665	-0.009
O1	8.457	8.479	-0.002
O2	8.401	8.421	-0.020
N1	7.717	7.721	-0.004
H1	0.592	0.585	+0.007
H2	0.602	0.591	+0.011
H3	0.602	0.591	+0.011
H4	0.730	0.717	+0.013
H5	0.730	0.717	+0.013
Na^+	10.118	10.053	+0.065

4.2.4 The Influence of Na^+ and Its Coordinated Water Molecules on the First Hydration Shell of Glycine Zwitterion

The change of the orientation of W2, W3, W4 and W5 influenced by both Na^+ and the water molecules surrounded Na^+ are investigated. The results are summarized in Table 4.9 and shown in Figure 4.8

The H-bond distances for W2, W3 are not affected but the orientation of W2 and W3 are pushed away from the area of hydrated Na^+ due to the steric hindrance in this region. The H-bond energies for both cases are thus decreased to 2.8 and 4.6 kcal/mol respectively. The H-bond distance between $[Na(gly)(H_2O)_4]^+$ and W4 is not significantly different from that of glycine zwitterion to W4. Increasing of the H-bond energy resulted from the binding of $[Na(gly)(H_2O)_4]^+$ and W4 should be caused by the transferring of the electron density of Na^+ and its surrounded water through the NH hydrogen atoms and make these hydrogen atoms more positive. The interaction is therefore increased to 4.9 kcal/mol.

Table 4.9 The Orientation of the Water W2, W3, W4, W5 and The H-bond Energies in the System of Glycine Zwitterion and of $[Na(gly)(H_2O)_4]^+$ in Aqueous Solution.

	Glycine Zwitterion	$[Na(gly)(H_2O)_4]^+$
W2	$O_1 - O_L = 2.55$ Å	$O_1 - O_L = 2.55$ Å
	$C_2\hat{O}_1O_L = 132^\circ$	$C_2\hat{O}_1O_L = 128^\circ$
	$O_1\hat{O}_LH_{L1} = 20^\circ$	$O_1\hat{O}_LH_{L1} = 40^\circ$
	total energy= -304.64795 a.u.	total energy= -712.08308 a.u.
	*H-bond energy= -24.1 kcal/mol	**H-bond energy= -21.3 kcal/mol
W3	$O_2 - O_L = 2.70$ Å	$O_2 - O_L = 2.70$ Å
	$C_2\hat{O}_2O_L = 108^\circ$	$C_2\hat{O}_2O_L = 100^\circ$
	$O_2O_LH_{L1} = 0^\circ$	$O_2O_LH_{L1} = 12^\circ$
	total energy= -304.64156 a.u.	total energy= -712.07386 a.u.
	*H-bond energy= -20.1 kcal/mol	**H-bond energy= -15.5 kcal/mol
W4,W5	$NH - O_L = 2.64$ Å	$NH - O_L = 2.62$ Å
	total energy= -304.64309 a.u.	total energy= -712.09038 a.u.
	*H-bond energy= -21.0 kcal/mol	**H-bond energy= -25.9 kcal/mol

*H-bond energy $= E_{gly+w} - E_{gly} - E_{H_2O}$

**H-bond energy $= E_{[Na(gly)(H_2O)_4]^{+}+w} - E_{[Na(gly)(H_2O)_4]^{+}} - E_{H_2O}$

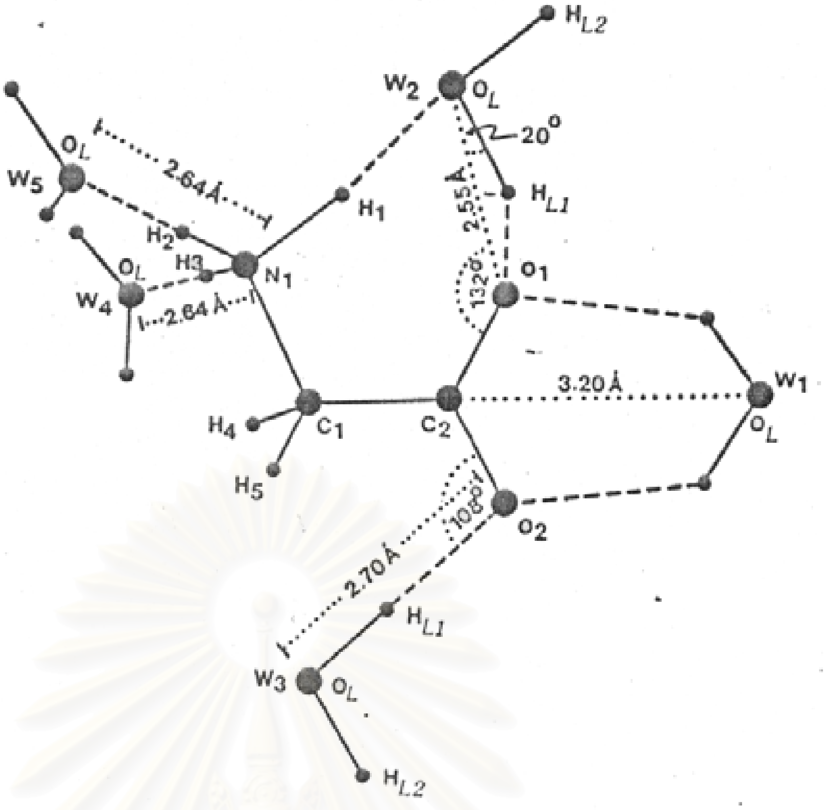


Figure 4.8 a The orientation of W2, W3, W4, W5 of glycine zwitterion in aqueous solution.

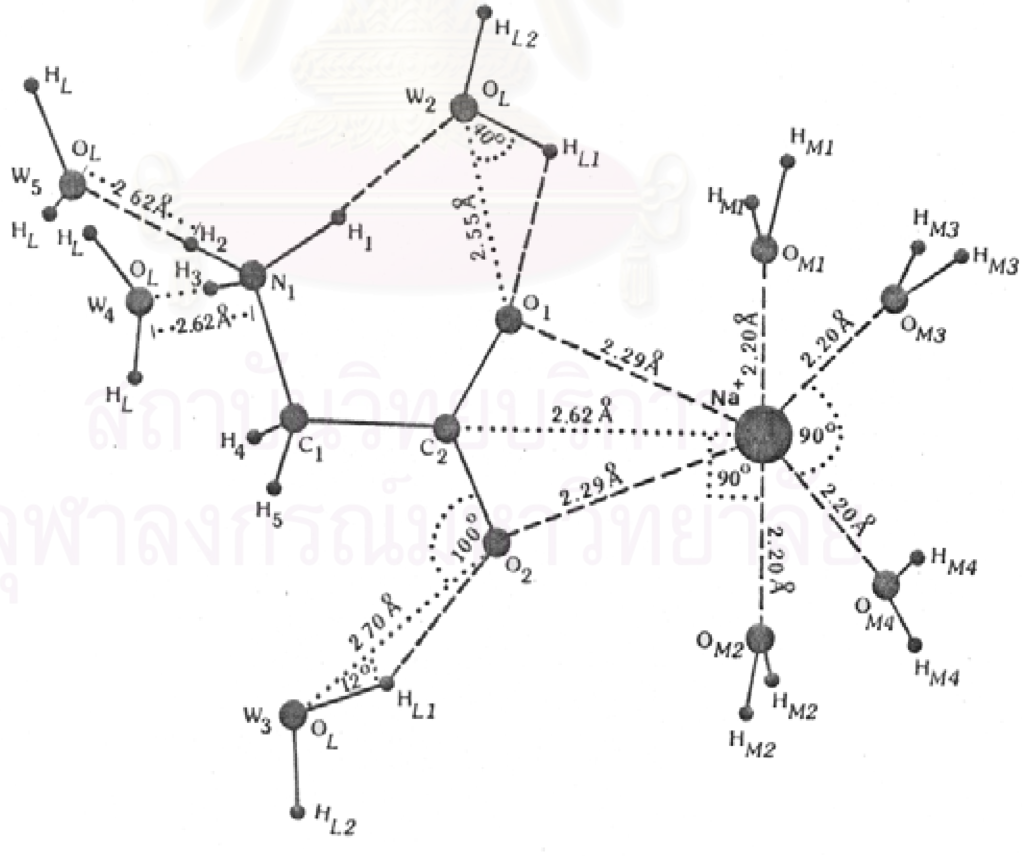


Figure 4.8 b The orientation of W2, W3, W4, W5 in the system of $[Na(gly)(H_2O)_4]^+$.

CONCLUSION

The results calculated by the ab initio with GLO minimal basis set method for the first hydration shell and the influence of the hydration shell on the internal rotation of glycine zwitterion have shown that the CNDO/2 method works quite reliable for the prediction of solvent orientation and solvent influence on the flexibility of the conformation of the amino acid in water. But it should be emphasized that the CNDO/2 can not describe a good hydrogen bonding. Therefore, an average hydrogen bond must be used to investigate the solvent orientation if CNDO/2 is decided to be utilized.

The study of the metal-ligand interaction in aqueous solution compared to the metal-solvent interaction by using glycine zwitterion and Na^+ in water gives a structure as an octahedral arrangement and can be described as $[Na(gly)(H_2O)_4]^+$. The influence of Na^+ and these four water molecules to the water solvated around glycine zwitterion yields the results what we expected.

The significant change of the H-bond energy from the effect of hydrated Na^+ can be explained in terms of electron density distribution through the atoms of ligands and water binded to ligand as well as the distortion of the linearity of the H-bond and the steric hindrance

We hope that the study of glycine zwitterion - Na^+ complex in water which is one of the systematic study of many complexes can contribute to the discovery of the rules which govern the interaction between metal ions and naturally occuring ligands. A metal-amino acid complex may have some properties in common with a metal - protein complex . But we must remember that the simple complex is a model to supply the biological information not a replica.

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