Chapter IV

Calculation

The model.

To study the influence of solvation to internal rotation of the glycine zwitterion, the supermolecule model was used, calculated by the CNDO method and checked by ab initio calculations for several conformations.

Glycine is present as zwitterion in aqueous solution, according to experimental data (21). Glycine zwitterion has two strongly polar heads, $-NH_3^+$ and $-COO^-$ so that most solute-solvent interactions will occur via these groups. Although there exists possibly more than one hydration shell due to these strongly polar heads, our model will only deal with the first hydration shell and neglect all others, as the first hydration shell exerts the strongest influence on the solute and as a complete investigation of the hydration is beyond the scope of this work and computationally too extensive.

Methodical steps.

According to the aim of this work we also want to study the influence of solvent to internal rotation of glycine zwitterion in aqueous solution. In practice, a comparison between the internal rotation of the isolated glycine zwitterion in the gas phase and the $(Gly)(H_2O)_n$ complex will be performed, for n as the hydration number.

This studying will be separated into 3 steps:

1. Calculation of the internal rotation of isolated glycine

zwitterion.

2. Determination of an increasing hydration shell and calculation of the hydration energy.

3. Calculation of the internal rotation of glycine zwitterion including the optimal hydration shell.

Table 4.1 The geometry parameters of glycine zwitterion. All bond lengths and bond angles are reported in A° and degrees respectively.

Bond length (A°)		Bond angle (degrees)		
C1-C2	1.52 (1.53)	<HNH	109.47	(109.47)
C2-O1	1.27 (1.25)	<HNC1	109.47	(109.47)
C2-O2	1.27 (1.25)	<HC1H	109.47	(109.47)
C1-N	1.47 (1.48)	<NC1H	109.47	(109.47)
C1-H	1.09 (1.10)	<C1C201	119.00	(117.50)
N-H	1.03 (1.03)	<O1C202	122.00	(120.00)

The geometry which is used in this work is taken from experimental data (21). The values in the brackets are standard geometries (22).

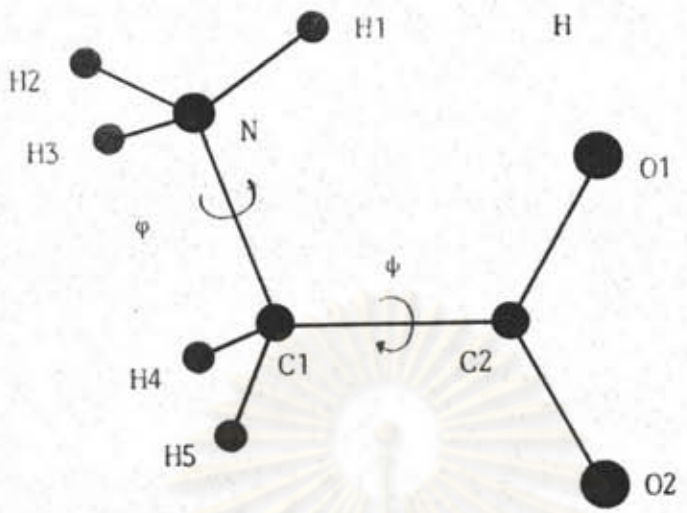

Figure 4.1 The glycine zwitterion, conformation $(\varphi,\psi) = (0,0)$, one H atom of $-NH_3^+$ and N, C1, C2,O atoms are in the same plane.

Calculation of the internal rotation of isolated glycine zwitterion.

According to figure 4.1, the internal rotation potential of glycine zwitterion is defined by two rotation angles φ and ψ in the conformation $(\varphi, \psi) = (0,0)$, one H atom of $-NH_3^+$ and all the other heavier atoms lie on the same plane.

Changes of conformation due to changes of the rotation angles have been performed by a coordinate program for glycine zwitterion (Appendix C) giving the cartesian coordinates as input for the CNDO program (Appendix B).

The results of the calculations are reported in tables 4.2 and 4.3, namely the total energies and the barriers of various comformations with fixed $\varphi = 0^\circ$ and varying ψ from 0° to 90°.

Tables 4.4 and 4.5 report the total energies and the barriers of the conformations with fixed $\psi = 0^\circ$ and varying φ from 0° to

60° , and starting from conformation (60, 0) rotating ψ up to (60, 90).

All barriers (ΔE_{bar}) are calculated by the difference of the total energies of the minimum conformation (E_{min}) and the energy of the respective conformation (E_h)

$$\Delta E_{bar} = E_h - E_{min} \qquad 4.1$$

Barriers(ΔE_{bar}) are reported in kcal/mol (1 hartree = 627.5 kcal/mol)

The plot of the rotation barriers VS rotation angles for the comparison between two sets of geometries is presented in figure 4.2 .

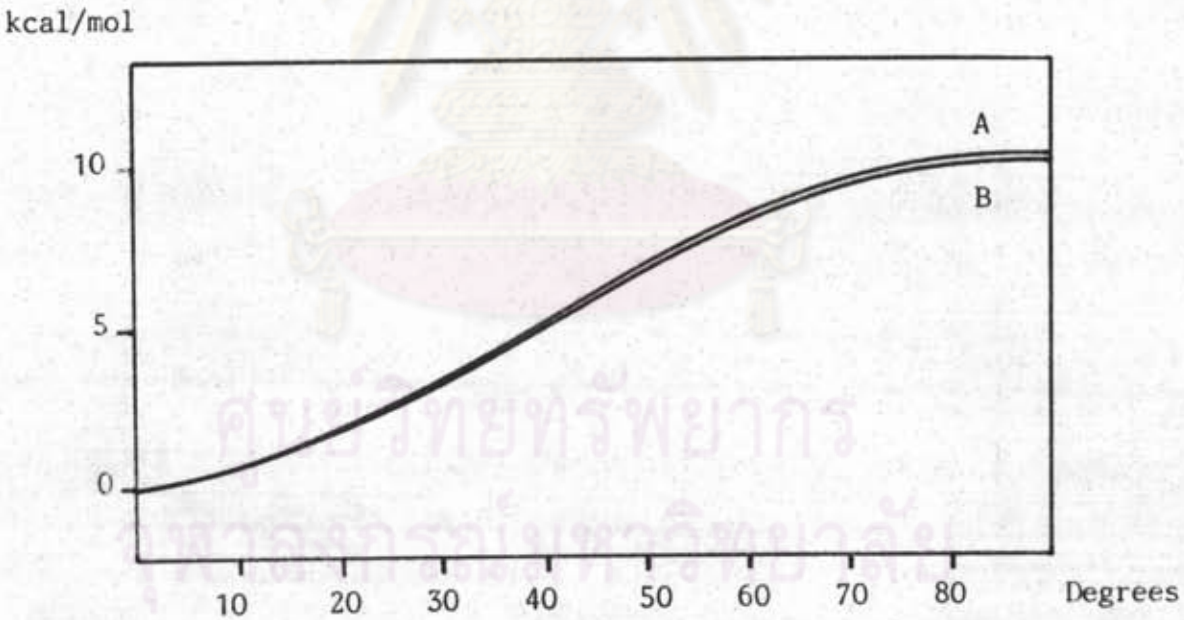

Figure 4.2 The rotation energy curve of glycine zwitterion, comparison between two sets of geometries (fixing φ = 0° , rotating ψ from 0°to 90°). Graph A represents the geometry used in this work. Graph B represents standard geometry.

Table 4.2 The total energy and the rotation barriers of glycine zwitterion (standard geometry), fixing $\varphi = 0^{\circ}$, rotating ϕ from 0° to 90°

Angle (degrees)	Energy (hartrees)	Barrier (kcal/mol)
0.00	-66.3427	0.0
10.00	-66.3421	0.4
20.00	-66.3397	1.9
30.00	-66.3382	2.8
40.00	-66.3343	5.3
50.00	-66.3311	7.3
60.00	-66.3287	8.8
70.00	-66.3274	9.6
80.00	-66.3263	10.3
90.00	-66.3258	10.6

Table 4.3 The total energy and the rotation barriers of glycine zwitterion, fixing $\varphi = 0^{\circ}$, rotating ϕ from 0°- 90°

Angle (degrees)	Energy (hartrees)	Barrier (kcal/mol)
0.00	-66.3491	0.0
10.00	-66.3484	0.4
20.00	-66.3463	1.8
30.00	-66.3449	2.6
40.00	-66.3414	4.8
50.00	-66.3382	6.8
60.00	-66.3358	8.3
70.00	-66.3340	9.5
80.00	-66.3329	10.2
90.00	-66.3325	10.4

Table 4.4 The total energy and the rotation barriers of glycine zwitterion, fixing $\psi = 0^{\circ}$, rotating φ from 0°- 60°

Angle (degrees)	Energy (hartrees)	Barrier (kcal/mol)
0.00	-66.3491	0.0
10.00	-66.3486	0.3
20.00	-66.3473	1.1
30.00	-66.3471	1.3
40.00	-66.3453	2.4
50.00	-66.3442	3.1
60.00	-66.3438	3.3

Table 4.5 The total energy and the rotation barriers of glycine zwitterion, fixing $\varphi = 60^{\circ}$, rotating ψ from 0°- 90° .

Angle (degrees)	Energy (hartrees)	Barrier (kcal/mol)
0.00	-66.3438	0.0
15.00	-66.3433	0.3
30.00	-66.3418	1.3
45.00	-66.3396	2.6
60.00	-66.3371	4.2
75.00	-66.3352	5.4
90.00	-66.3354	5.8

Determination of the hydration shell and calculation of the hydration energy of glycine zwitterion.

1. Optimization of the water binding sites of the glycine zwitterion.

The first polar group ($-NH_3^+$) will act as a proton donor to the water surrounding it, and the second polar group $-COO^-$ will act as a proton acceptor. The optimization has been done by optimizing the total CNDO energy.

The glycine zwitterion geometry is given in table 4.1 . The water geometry was taken from reference (23)(<HOH = 104.5°, O-H = 0.9572 A°). All of these geometrical parameters were fixed during the optimization. Only the intermolecular distance and the orientation of the water molecule was varied.

The optimized conformations are presented in figures 4.3 to 4.8 The total energies and the interaction energies of each configuration are also reported in tables 4.6 to 4.11 .

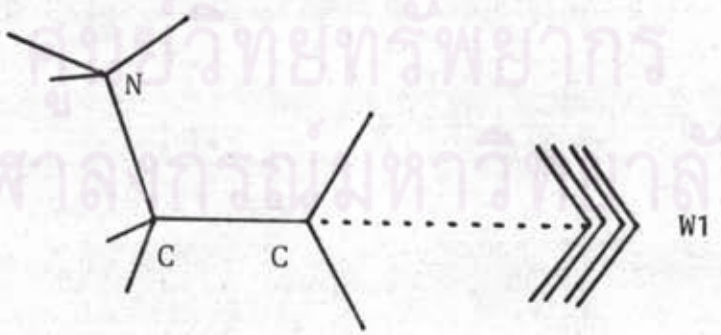

Figure 4.3 The optimization of glycine zwitterion and water 1

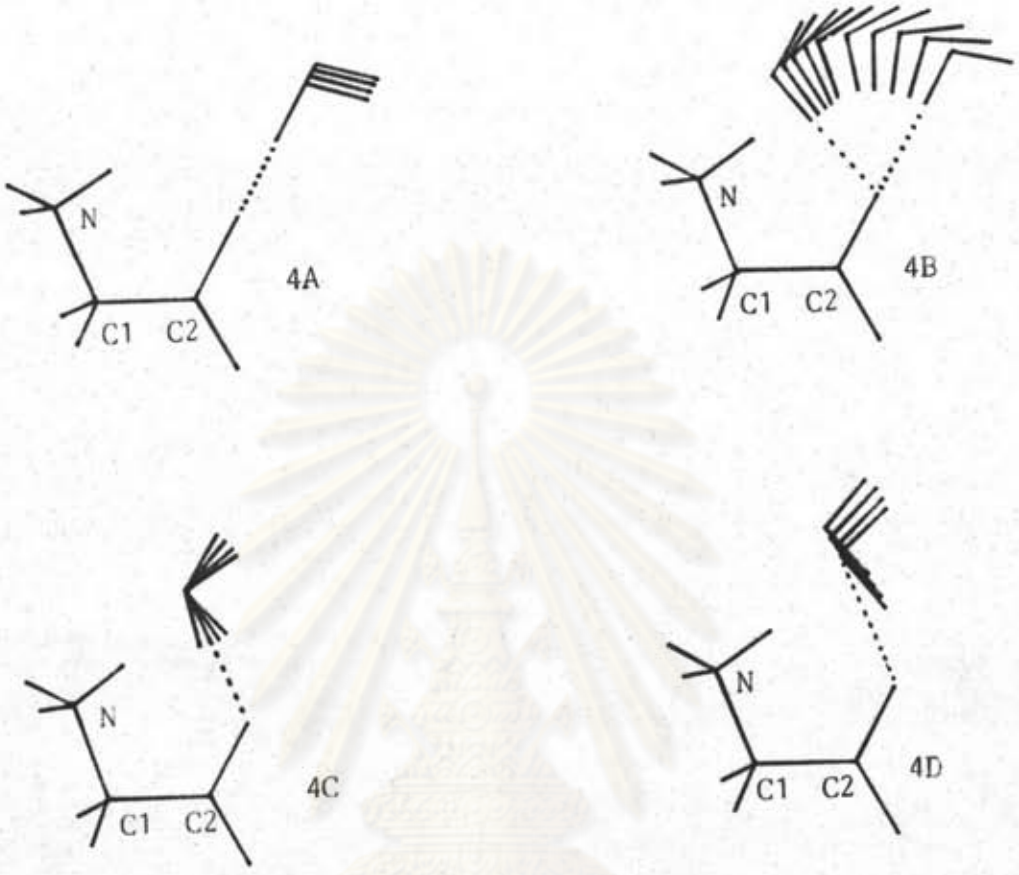

Figure 4.4 The optimization of glycine zwitterion and water 2

4A. Optimizing O-O distance of the linear hydrogen bond OH-O

4B. Rotation of water around C=O bond with the O-O distance obtained from 4A

4C. At the minimum energy of 4B, rotation of water around O (of water) center

4D. Fixing the rotation angle from 4B and the rotation angle from 4C, reoptimizing the O-O distance of the hydrogen bond

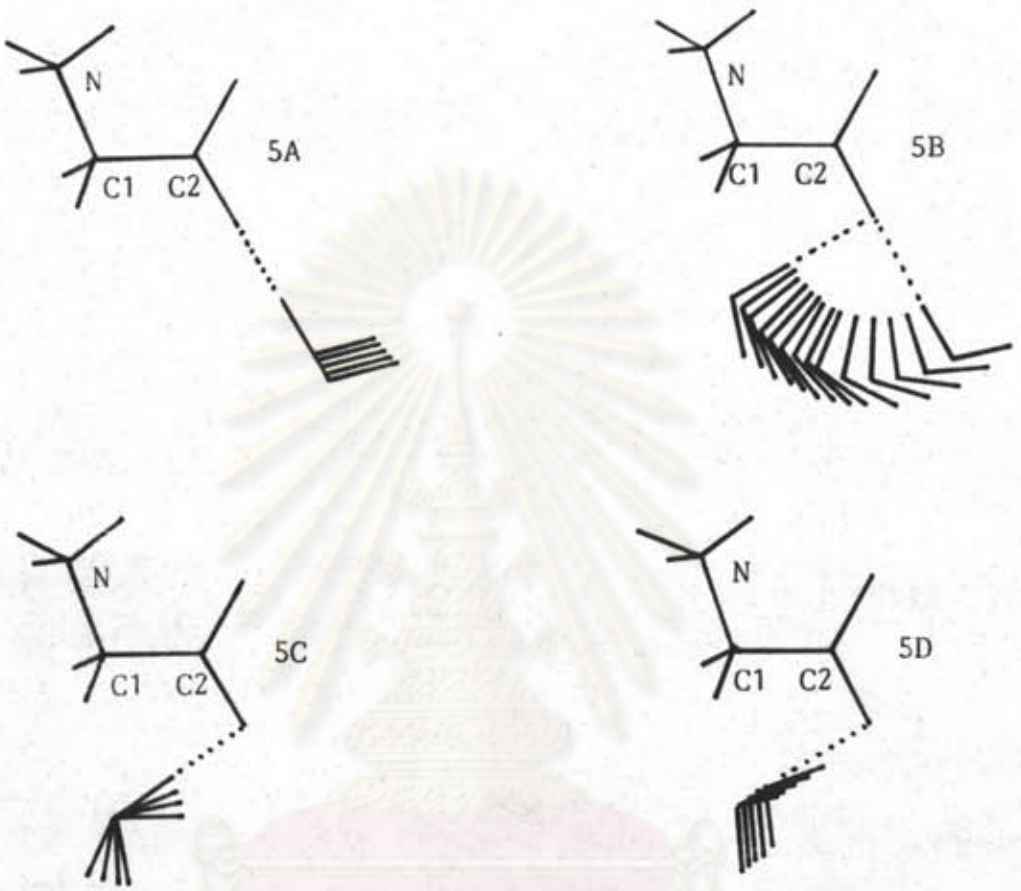

Figure 4.5 The optimization of glycine zwitterion and water 3

5A. Optimizing O-O distance of the linear hydrogen bond OH-O

5B. Rotation of water around C=O bond with the O-O distance obtained from 5A

5C. At the minimum energy of 5B, rotation of water around O (of water) center

5D. Fixing the rotation angle from 5B and the rotation angle from 5C, reoptimizing the O-O distance of the hydrogen bond

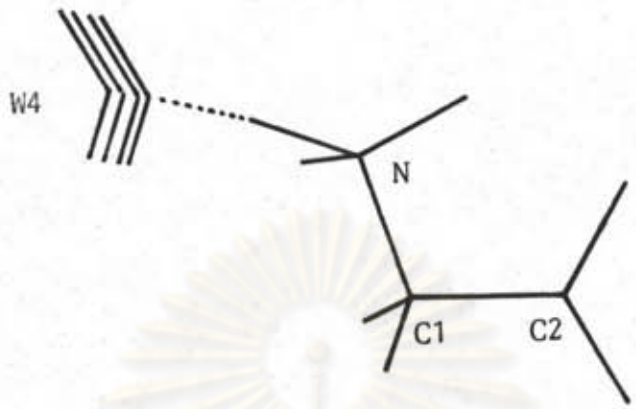

Figure 4.6 The optimization of glycine zwitterion and water 4

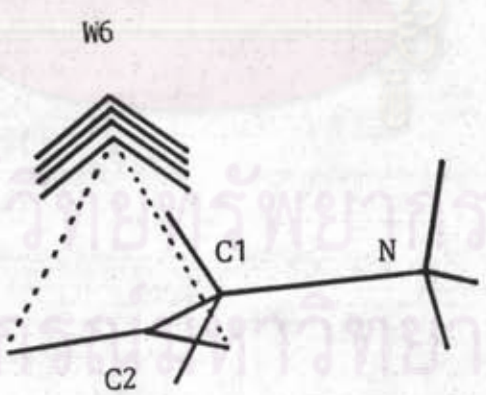

Figure 4.7 The optimization of glycine zwitterion and water 6

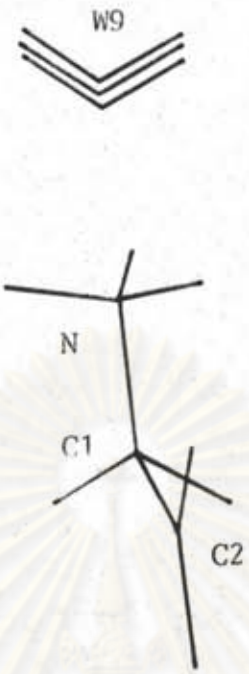

Figure 4.8 The optimization of glycine zwitterion and water 9

Table 4.6 The optimization of energy for glycine zwitterion and water 1 . Optimizing C-O distance of the $-COO^-$ group and water 1

C-O (A°)	Energy (hartrees)
2.65	-86.2424
2.70	-86.2441
2.75	-86.2602
2.80	-86.2442
2.85	-86.2433

Table 4.7A The optimization of energy for glycine zwitterion and water 2, Optimizing O-O distance of the linear hydrogen bond OH-O

O-O (A°)	Energy (hartrees)
2.30	-86.2376
2.35	-86.2393
2.40	-86.2398
2.45	-86.2395
2.50	-86.2387

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 A°

<COO (degrees)	Energy (hartrees)
100	-84.7919
120	-86.2289
125	-86.2489
130	-86.2518
135	-86.2500
140	-86.2475
160	-86.2417
180	-86.2398
200	-86.2395

Table 4.7C The optimization of energy for glycine zwitterion and water 2. Fixing <COO = 130°, fixing OH-O distance = 2.40 A°, rotating water around O (of water) center

<OOH (degrees)	Energy (hartrees)
00	-86.2518
05	-86.2551
10	-86.2569
15	-86.2574
20	-86.2569

Table 4.7D The optimization of energy for glycine zwitterion and water 2, fixing <COO = 130°, fixing <OOH = 15°, optimizing OH-O distance

O-O (A°)	Energy (hartrees)
2.10	-86.2499
2.15	-86.2571
2.20	-86.2600
2.25	-86.2610
2.30	-86.2607
2.35	-86.2594
2.40	-86.2574

Table 4.7E The optimization of energy for glycine zwitterion and water 2, fixing OH-O distance 2.25 A°, fixing <COO = 130° , rotating water around O (of water) center

<OOH (degrees)	Energy (hartrees)
15.00	-86.2610
20.00	-86.2615
25.00	-86.2614

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 A°, and fixing <OOH = 20°

<COO (degrees)	Energy (hartrees)
120	-86.2613
125	-86.2650
130	-86.2615

Table 4.8A The optimization of energy for glycine zwitterion and water 3, optimizing O-O distance of the linear hydrogen bond OH-O

O-O (A°)	Energy (hartrees)
2.30	-86.2359
2.35	-86.2377
2.40	-86.2384
2.45	-86.2383
2.50	-86.2376
2.60	-86.2352

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 A°

<COO(degrees)	Energy (hartrees)
90	-86.2465
95	-86.2488
100	-86.2430
160	-86.2348
180	-86.2384

Table 4.8C The optimization of energy for glycine zwitterion and water 3, fixing OH-O distance 2.40 A° , fixing <COO = 95° , rotating water around O (of water) center.

<OOH(degrees)	Energy (hartrees)
00	-86.2488
05	-86.2502
10	-86.2532
15	-86.2512
20	-86.2486

Table 4.8D The optimization of energy for glycine zwitterion and water 3, fixing <COO = 95° fixing < OOH = 10° , and optimizing OH-O distance

O-O (A°)	Energy (hartrees)
2.25	-86.2463
2.30	-86.2488
2.35	-86.2497
2.40	-86.2532
2.45	-86.2515

Table 4.8E The optimization of energy for glycine zwitterion and water 3, fixing OH-O distance 2.40 A°, fixing <COO = 95° , rotating water around O (of water) center

<OOH (degrees)	Energy (hartrees)
5.00	-86.2502
10.00	-86.2532
15.00	-86.2512

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 A°, and fixing <OOH = 10°

<COO (degrees)	Energy (hartrees)
90	-86.2499
95	-86.2532
100	-86.2497

Table 4.9 The optimization of energy for glycine zwitterion and water 4,5 , optimizing NH-O distance

NH-O (A˚)	Energy (hartrees)
2.35	-86.2354
2.40	-86.2381
2.45	-86.2406
2.50	-86.2407
2.55	-86.2401

Table 4.10 The optimization of energy for glycine zwitterion and water 6, optimizing HO-O distance

O-O (A˚)	Energy (hartrees)
2.40	-86.2318
2.45	-86.2387
2.50	-86.2391
2.55	-86.2370
2.60	-86.2359

Table 4.11 The optimization of energy for glycine zwitterion and water 9, optimizing HO-N distance

HO-N (A˚)	Energy (hartrees)
2.15	-86.2284
2.20	-86.2325
2.25	-86.2329
2.30	-86.2315
2.35	-86.2302
2.40	-86.2291

2. Calculation of the interaction energy of glycine zwitterion and water (fixing the hydrogen bond distance at 2.75 A°)

Since according to the artefact of CNDO calculations in evaluation hydrogen bonds are generally too short, the nine possible positions of water around the glycine zwitterion have been calculated also with fixed hydrogen bond distance of 2.75 A°, which is the average distance of various types of hydrogen bonds (24). These calculations have been done by both CNDO and ab initio methods .

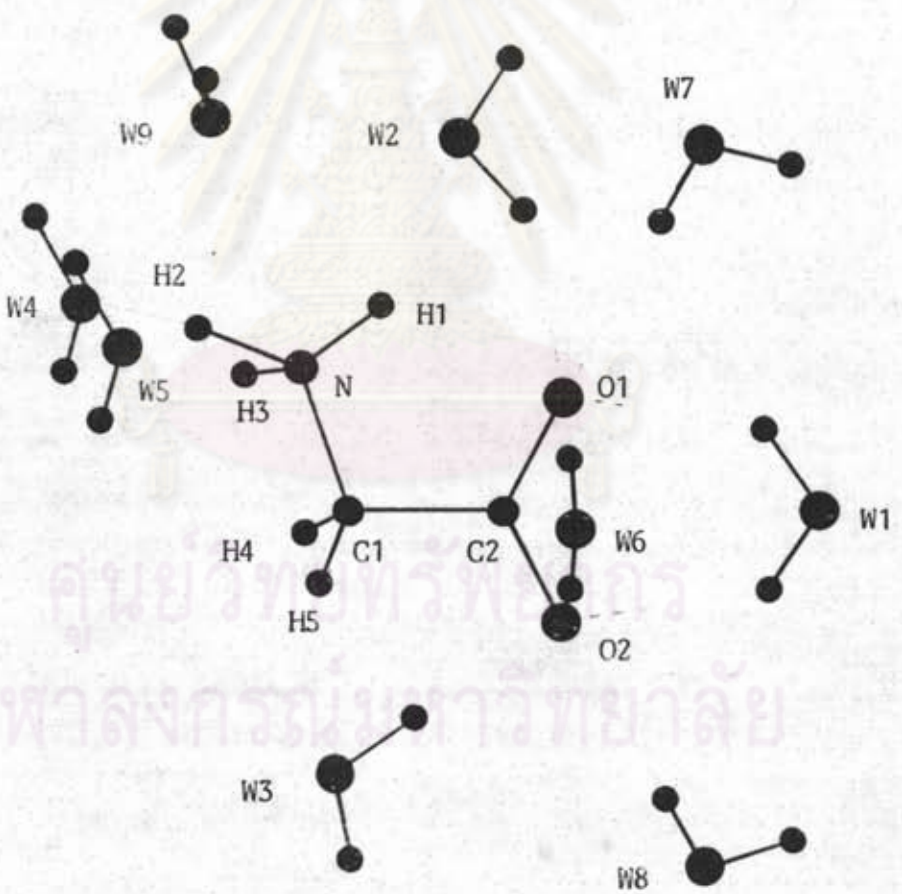

Figure 4.9 The nine most stabilized water positions around glycine zwitterion with fixed hydrogen bond distance 2.75 A°

2.1 Determination of the interaction energy by CNDO calculations

The water-glycine complex in its nine optimized conformations has been investigated with respect to interaction energies, using the extended hydrogen bond of 2.75 A° (figure 4.9) . The evaluation of interaction energies has been performed according to the equation:

$$\Delta E^{CNDO} = E^{CNDO}_{sup} - E^{CNDO}_{gly} - E^{CNDO}_{water} \qquad 4.2$$

where ΔE^{CNDO} is the CNDO interaction energy, E^{CNDO}_{sup} is the supermolecule energy of the complex, E^{CNDO}_{gly} is the energy of glycine zwitterion and E^{CNDO}_{water} is the energy of water. E^{CNDO}_{gly} is -66.3491 hartree and E^{CNDO}_{water} is -19.8679 hartree. All energies are reported in table 4.12 .

Table 4.12 Total energies and interaction energies of glycine zwitterion complexes with one water molecule in nine different conformations (CNDO calculation)

water	CNDO optimization		CNDO fixed H-bond 2.75 A°	
	E_{sup}^{CNDO}	ΔE^{CNDO}	E_{sup}^{CNDO}	ΔE^{CNDO}
1	-86.2602	-27.1	-86.2338	-10.5
2	-86.2650	-30.1	-86.2420	-15.7
3	-86.2532	-22.7	-86.2405	-14.7
4	-86.2407	-14.9	-86.2348	-11.2
5	-86.2407	-14.9	-86.2348	-11.2
6	-86.2329	-10.0	-86.2242	- 4.5
7	-86.2398	-14.3	-86.2318	- 9.3
8	-86.2384	-13.4	-86.2311	- 8.8
9	-86.2391	-13.9	-86.2331	-10.1

Total energies are reported in hartrees and interaction energies are reported in kcal/mol

2.2 Determination of the interaction energy by ab initio calculation.

The nine above mentioned positions of water around the glycine zwitterion with a hydrogen bond distance of approximately 2.75 A° (figure 4.9) have also been calculated with regard to their interaction energies by the ab initio method. The interaction energies are determined analogously to equation 4.3 .

$$\Delta E_{GLO}^{ab} = E_{sup}^{ab} - E_{gly}^{ab} - E_{water}^{ab} \qquad 4.3$$

ΔE^{ab}_{GLO} is ab initio interaction energy E^{ab}_{gly} is -240.0701 hartree, and E^{ab}_{water} is -64.5164 hartree. The ab initio interaction energies of the nine water complexes of glycine zwitterion are reported in table 4.13

2.3 Calculation of the energy correction for ab initio calculation.

Due to the small size of the basis set, which we have used to calculate the interaction energy by ab initio calculations, we have overestimated the absolute values and hence we have to find some procedure to correct this error.

First we have calculated the corrections according to the counterpoise method, which is determined from

$$\Delta E^{cp}_{cor} = \Delta E^{ab}_{GLO} + \Delta e \qquad 4.4$$

where $\Delta e = (E_{gly} - E_{gly(water)}) + (E_{water} - E_{water(gly)})$

and ΔE^{ab}_{GLO} is taken from equation 4.3 . The results are summarized in table 4.13 .

However, only the case of linear water attached to the $-NH3^+$ and $-COO^-$ yields reasonable results, the other case showing destabilized hydrogen bonds. Thus we have calculated a scaling factor f^{HF} which uses water dimer as reference . f^{HF} is determined from equation 4.5

$$f^{HF} = \frac{E^{HF}_{water-dimer}}{E^{GLO}_{water-dimer}} = \frac{-3.67}{-11.50} = 0.32 \qquad 4.5$$

where $\Delta E^{HF}_{water-dimer}$ is taken from reference 25 and $\Delta E^{GLO}_{water-dimer}$ is calculated by the minimal basis set leading to the energy of the water

dimer 2.75 A° of -129.0511 hartree. The Hartree - Fock corrected energy is calculated from

$$\Delta E^{HF}_{cor} = \Delta E^{ab}_{GLO} \times f^{HF} \qquad 4.6$$

and the results are summarized in table 4.13

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

water	E^{ab}_{sup}	$E^{ab}_{gly(w)}$	$E^{ab}_{w(gly)}$	Δe	ΔE^{ab}_{GLO}	ΔE^{cp}_{cor}	ΔE^{HF}_{cor}
1	-304.6101	-240.0921	-64.5245	18.9	-14.8	+4.1	-4.7
2	-304.6188	-240.0921	-64.5270	20.5	-20.3	+0.2	-6.5
3	-304.6146	-240.0947	-64.5209	23.4	-17.6	+5.8	-5.6
4	-304.6196	-240.0732	-64.5304	10.8	-20.8	-10.0	-6.7
5	-304.6196	-240.0732	-64.5304	10.8	-20.8	-10.0	-6.7
6	-304.5945	-	-	-	-5.0	-	-1.6
7	-304.6107	-240.0821	-64.5214	10.7	-15.2	-4.5	-4.9
8	-304.6092	-240.0812	-64.5214	10.1	-14.2	-4.1	-4.5
9	-304.6014	-	-	-	-9.3	-	-3.0

Total energies are reported in hartrees, and interaction energies are reported in kcal/mol

2.4 Calculation of the influence of hydration on electron distribution. If we set the electron distribution of glycine zwitterion in gas phase as reference, the influence of hydration on electron density of each atom (ρ^{atm}) can be calculated by

$$\rho^{atm} = \rho^{gas}_{gly} - \rho^{sol}_{gly} \qquad 4.7$$

and the change of electron distribution of groups (ρ^{group}) due to hydration will be

$$\rho^{group} = \sum_{i}^{n} \rho^{atm}_{i} \qquad 4.8$$

where n is the number of atom in each interesting group. All of the results are reported in tables 4.14, 4.15 and 4.16

Table 4.14 Mulliken atomic populations (ab initio calculations)

atom	gly-W	gly	water	ρ^{atm}
H1	0.586	0.601	-	-0.015
H2	0.586	0.623	-	-0.037
H3	0.586	0.623	-	-0.037
H4	0.747	0.752	-	-0.005
H5	0.747	0.752	-	-0.005
N	7.868	7.716	-	+0.152
C1	6.462	6.500	-	-0.038
C2	5.609	5.663	-	-0.054

Table 4.14 continued

O1	8.436	8.411	-	+0.025
O2	8.382	8.358	-	+0.024
O (W1)	8.497	-	8.382	+0.115
H1(W1)	0.786	-	0.809	-0.023
H2(W1)	0.781	-	0.809	-0.028
O (W2)	8.498	-	8.382	+0.116
H1(W2)	0.747	-	0.809	-0.062
H2(W2)	0.773	-	0.809	-0.036
O (W3)	8.489	-	8.382	+0.107
H1(W3)	0.771	-	0.809	-0.038
H2(W3)	0.814	-	0.809	+0.005
O (W4)	8.407	-	8.382	+0.025
H1(W4)	0.757	-	0.809	-0.052
H2(W4)	0.754	-	0.809	-0.055
O (W5)	8.407	-	8.382	+0.025
H1(W5)	0.757	-	0.809	-0.052
H2(W5)	0.754	-	0.809	-0.055

Table 4.15 Mulliken atomic populations (CNDO calculation)

atom	gly-5W	gly	water	ρ^{atm}
H1	0.756	0.770	-	-0.014
H2	0.795	0.820	-	-0.025
H3	0.795	0.820	-	-0.025
H4	0.964	0.965	-	-0.001
H5	0.964	0.965	-	-0.001
N	5.072	5.000	-	+0.072
C1	4.012	4.013	-	-0.001
C2	3.633	3.646	-	-0.013
O1	6.532	6.525	-	+0.007
O2	6.487	6.474	-	+0.013
O (W1)	6.343	-	6.285	+0.058
H1(W1)	0.840	-	0.858	-0.018
H2(W1)	0.835	-	0.858	-0.023
O (W2)	6.348	-	6.285	+0.063
H1(W2)	0.805	-	0.858	-0.053
H2(W2)	0.844	-	0.858	-0.014
O (W3)	6.344	-	6.285	+0.059
H1(W3)	0.809	-	0.858	-0.049
H2(W3)	0.869	-	0.858	+0.011
O (W4)	6.310	-	6.285	+0.025
H1(W4)	0.836	-	0.858	-0.022
H2(W4)	0.831	-	0.858	-0.027

Table 4.15 continued

O (W5)	6.310	-	6.285	+0.025
H1(W5)	0.836	-	0.858	-0.022
H2(W5)	0.831	-	0.858	-0.027

Table 4.16 The change of electron distribution between functional groups due to the influeuce of hydration in glycine zwitterion

group of atoms	The change of electron distribution of group of atoms (e)	
	ab initio calculation	CNDO calculation
$-NH_3^+$	+0.063	+0.008
$-CH_2$	-0.048	-0.003
$-COO^-$	-0.005	+0.007
W1	+0.064	+0.018
W2	+0.018	-0.003
W3	+0.074	+0.021
W4	-0.082	-0.023
W5	-0.082	-0.023

Calculation of the internal rotation of glycine zwitterion including the hydration shell effect.

Figure 5.10 has proposed the geometry of glycine zwitterion in conformation (0,0) including a first hydration shell consisting of 5 water molecules.

The influencing of hydration shell on the internal rotation of glycine zwitterion are calculated by semi-empirical method (CNDO) and the results are reported in tables 4.17 to 4.31 .

Table 4.17 The total energy and the rotation barriers of glycine zwitterion plus 5 water molecules, fixing hydrogen bond 2.75 A° , fixing ϕ = 0°,and fixing the hydration shell, rotating $-NH_3^+$ alone

Angle (degrees)	Energy (hartrees)	Barrier (kcal/mol)
0.00	-165.7870	0.0
10.00	-165.7848	1.4
20.00	-165.7792	4.9
30.00	-165.7734	8.5
40.00	-165.7665	12.9
50.00	-165.7654	13.6
60.00	-165.7655	13.5

Table 4.18 The total energy and the rotation barriers of glycine zwitterion plus 5 waters, fixing hydrogen bond 2.75 A°, fixing ϕ = 0°, and fixing water 1,3, rotating $-NH_3^+$ and water 2,4,5

Angle (degrees)	Energy (hartree)	Barrier (kcal/mol)
0.00	-165.7870	0.0
10.00	-165.7852	1.1
20.00	-165.7811	3.7
30.00	-165.7790	5.0
40.00	-165.7747	7.7
50.00	-165.7722	9.3
60.00	-165.7711	10.0

Table 4.19 The total energy and the rotation barriers of glycine zwitterion plus 5 waters, fixing hydrogen bond 2.75 A°, fixing φ = 0, and fixing the hydration shell, rotating $-COO^-$ alone

Angle (degrees)	Energy (hartrees)	Barrier (kcal/mol)
0.00	-165.7870	0.0
10.00	-165.7849	1.3
20.00	-165.7792	4.9
30.00	-165.7731	8.7
40.00	-165.7659	13.2
50.00	-165.7634	14.8
60.00	-165.7564	19.2
70.00	-165.7518	22.1
80.00	-165.7491	23.8
90.00	-165.7483	24.3

Table 4.20 The total energy and the rotation barriers of glycine zwitterion plus 5 waters, fixing hydrogen bond 2.75 A°, fixing φ = 0° and fixing the water 2,3,4,5, rotating $-COO^-$ and water 1

Angle (degrees)	Energy (hartrees)	Barrier (kcal/mol)
0.00	-165.7870	0.0
10.00	-165.7852	1.1
20.00	-165.7803	4.2
30.00	-165.7754	7.3
40.00	-165.7696	10.9
50.00	-165.7647	14.0
60.00	-165.7598	17.1
7P.00	-165.7567	19.0
80.00	-165.7549	20.1
90.00	-165.7544	20.5

Table 4.21 The total energy and the rotation barriers of glycine zwitterion plus 5 waters, fixing hydrogen bond 2.75 A°, fixing φ = 0, and fixing the water 3, 4, 5, rotating $-COO^-$ and water 2

Angle (degrees)	Energy (hartrees)	Barrier (kcal/mol)
0.00	-165.7870	0.0
10.00	-165.7848	1.4
20.00	-165.7791	5.0
30.00	-165.7733	8.6
40.00	-165.7659	13.2
50.00	-165.7634	14.8
60.00	-165.7563	19.3
70.00	-165.7517	22.2
80.00	-165.7490	23.9
90.00	-165.7482	24.4

Table 4.22 The total energy and the rotation barriers of glycine zwitterion plus 5 waters, fixing hydrogen bond 2.75 A°, fixing φ = 0° and fixing water 3,4,5, rotating $-COO^-$ and water 1,2

Angle (degrees)	Energy (hartrees)	Barrier (kcal/mol)
0.00	-165.7870	0.0
10.00	-165.7850	1.3
20.00	-165.7795	4.7
30.00	-165.7754	7.3
40.00	-165.7682	11.8
60.00	-165.7594	17.3
70.00	-165.7565	19.1
80.00	-165.7547	20.3
90.00	-165.7540	20.7

Table 4.23 The total energy and the rotation barriers of glycine zwitterion plus 5 waters, fixing hydrogen bond 2.75 A°, fixing $\varphi = 0°$, and fixing water 2,4,5, rotating $-COO^-$ and water 1,3

Angle (degrees)	Energy (hartrees)	Barrier (kcal/mol)
0.00	-165.7870	0.0
10.00	-165.7862	0.5
20.00	-165.7796	4.6
30.00	-165.7746	7.8
40.00	-165.7683	11.7
50.00	-165.7614	16.1
60.00	-165.7573	18.6
70.00	-165.7564	19.2
80.00	-165.7582	18.1
90.00	-165.7621	15.6

Table 4.24 The total energy and the rotation barriers of glycine zwitterion plus 5 waters, fixing hydrogen bond 2.75 A° , fixing φ = 0° and fixing water 4,5, rotating $-COO^-$ and water 1,2,3

Angle (degrees)	Energy (hartrees)	Barrier (kcal/mol)
0.00	-165.7870	0.0
10.00	-165.7860	0.6
20.00	-165.7788	5.1
30.00	-165.7747	7.7
40.00	-165.7669	12.6
50.00	-165.7605	16.6
60.00	-165.7569	18.9
70.00	-165.7562	19.3
80.00	-165.7580	18.2
90.00	-165.7618	15.8

Table 4.25 The total energy and the rotation barriers of glycine zwitterion plus 5 water molecules, fixing hydrogen bond 2.75 A°, fixing φ = 60°, fixing water 2,4,5 (these water molecules have been moved with $-NH_3^+$ groupto 60°) and fixing water 1, 3, rotating $-COO^-$ alone

Angle (degrees)	Energy (hartree)	Barrier (kcal/mol)
0.00	-165.7767	0.0
15.00	-165.7745	1.4
30.00	-165.7691	4.8
45.00	-165.7646	7.6
75.00	-165.7566	12.6
90.00	-165.7551	13.6

Table 4.26 The total energy and the rotation barriers of glycine zwitterion plus 5 water molecules, fixing hydrogen bond 2.75 A° , fixing φ = 60°, fixing water 2,4,5 (these water molecules have been moved with $-NH_3^+$ group to 60°) and fixing water 3 rotating $-NH_3^+$ and water 1

Angle (degrees)	Energy (hartree)	Barrier (kcal/mol)
0.00	-165.7767	0.0
15.00	-165.7751	1.0
30.00	-165.7713	3.4
45.00	-165.7689	4.9
60.00	-165.7645	7.7
75.00	-165.7619	9.3
90.00	-165.7611	9.8

Table 4.27 The total energy and the rotation barriers of glycine zwitterion plus 5 water molecules, fixing hydrogen bond 2.75 A°, fixing φ = 60° fixing water 2,4,5 (these water molecules have been moved with $-NH_3^+$ group to 60°) rotating $-COO^-$ and water 1,3

Angle (degrees)	Energy (hartree)	Barrier (kcal/mol)
0.00	-165.7767	0.0
15.00	-165.7745	1.4
30.00	-165.7706	3.8
45.00	-165.7653	7.2
60.00	-165.7616	9.5
75.00	-165.7625	8.9
90.00	-165.7676	5.7

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 $-NH_3^+$ group). fixing $\phi = 0^\circ$, fixing water 3 and fixing water molecules in the second shell, rotating $-NH_3^+$ and water 2,4,5

Angle (degrees)	Energy (hartree)	Barrier (kcal/mol)
0.00	-205.5214	0.0
15.00	-205.5107	6.7
30.00	-205.5006	13.1
45.00	-205.4934	17.6
60.00	-205.4910	19.1

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 A° , fixing $\phi = 0°$, and fixing water 3 rotating $-NH_3^+$ and water 2,4,5

Angle (degrees)	Energy (hartree)	Barrier (kcal/mol)
0.00	-145.9023	0.0
15.00	-145.8985	2.4
30.00	-145.8940	5.2
45.00	-145.8880	9.0
60.00	-145.8859	10.3

Table 4.30 The total energy and the rotation barriers of glycine zwitterion plus 5 water molecules, fixing hydrogen bond 2.65 A° , fixing ϕ = 0°and fixing water 1,3, rotating $-NH_3^+$ and water 2,4,5

Angle (degrees)	Energy (hartree)	Barrier (kcal/mol)
0.00	-165.8064	0.0
15.00	-165.8021	2.7
30.00	-165.7971	5.8
45.00	-165.7904	10.0
60.00	-165.7881	11.5

Table 4.31 The total energy and the rotation barriers of glycine zwitter ion plus 5 water molecules, fixing hydrogen bond 2.85 A° , fixing ψ = 0° and fixing water 1,3 rotating $-NH_3^+$ and water 2,4,5

Angle (degrees)	Energy (hartree)	Barrier (kcal/mol)
0.00	-165.7663	0.0
15.00	-165.7631	2.0
30.00	-165.7595	4.3
45.00	-165.7545	7.4
60.00	-165.7526	8.6