
SHORT REPORTS

THE ROTATIONAL BARRIER OF THE HYDRATED GLYCINE ZWITTERION

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ABSTRACT

The influence of the first hydration to the internal rotation of glycine zwitterion is studied by means of ab initio MO-SCF calculations with minimal basis set. The energy optimized pathway of the hydrated structure is compared with CNDO/2 results.

Glycine, one of the simplest amino acids has received considerable attention for its biological interest. As a result, it has been the object of numerous theoretical investigations.

In our previous works on the study of glycine zwitterions^{1,2,3} the first in this series reported the conformation of glycine zwitterion and its hydrated structure. Both CNDO/2¹ and ab initio² procedures predicted the conformation (Θ, ϕ) (0, 0) to be the most stable arrangement. The first hydration shell of glycine zwitterion is proposed to consist of 5 water molecules (W1, W2, W3, W4 and W5) interacting through H-bond². The influence of the hydration on the conformations obtained by CNDO/2 calculation on the rotational barriers of glycine zwitterion has been studied in our second series⁴.

In the current work, we recalculated the rotational barriers of hydrated glycine zwitterion by the more accurate method, the ab initio LCAO-MO-SCF with well tested minimal Gaussian basis sets using the HONDO program,⁵ in order to compare the results predicted by both methods.

The geometries of glycine zwitterion and water are the same as in our previous work¹.

In order to estimate the trends in the rotation barrier change of glycine zwitterion due to the hydration shell, the most stable geometry of hydrated structure have been optimized by ab initio method². The orientation of the first hydration shell, the 5 water

molecules around the glycine zwitterion, is illustrated in Fig. 1. The energy barriers to internal rotation concerning both angles (Θ , ϕ) relevant for the conformation have been calculated during the rotation of $-\text{NH}_3^+$ or $-\text{COO}^-$ group. A corotating hydration shell has been studied as well as of rotation with hydration remaining fixed. The rigid molecule model was used because adjustment of the water geometry to every conformation change would require a large amount of computing time.

In agreement with former study⁴, the ab initio calculations also predict rotation of $-\text{NH}_3^+$ (Θ , ϕ) to be easier than the rotation of $-\text{COO}^-$. (Θ , ϕ) This gives a chance for isolated glycine zwitterion to rotate from a most stable arrangement (0, 0) to the conformation (60, 90) where the molecule experiences the strongest possible conformational change due to internal rotation. The minimum pathway therefore leads to overall barrier of 27.0 kcal/mol. It should be noted that the absolute values of the stabilization energy is quite high due to the use of minimum basis set. However, the relative order of the interaction energies are proved to reproduce correctly⁶⁻⁸.

When the first hydration shell which consists of 5 water molecules is included, the rotation of angle Θ from conformation (0, 0) to (60, 0) with fixed hydration shell (graph A, Fig. 2) and corotating its solvation sphere (W2, W4, W5) (graph B, Fig. 2) utilize the energy barriers of 34.8 kcal/mol and 20.7 kcal/mol respectively. The corotation of the solvated water especially of W2 lowered the barrier 14.1 kcal/mol, this extra energy due to the breaking of the bonds to the hydration water.

The pathway of the rotation of angle ϕ starting from conformation (0, 0) to (0, 90) of the hydrated glycine zwitterion are presented in Fig. 3. The results indicate the corotation of the solvated water W1 (graph B) lowered the barrier 13.0 kcal/mol compared to the case of fixing the hydration (graph A). If W1, W2, W3 are corotated together with $-\text{COO}^-$ (graph E), the barrier is decreased 38 kcal/mol and it is lower than in the case of isolated glycine zwitterion (graph C). But all the energy barriers either by fixing or corotating the solvation sphere are still higher than the rotation of angle Θ (Fig. 2). Therefore, as in the isolated molecule, the minimum pathway of the hydrated glycine zwitterion should compose of rotation of angle Θ followed by a rotation of angle ϕ leading to the conformation (60, 90). The barrier shapes of the rotation after rotating the $-\text{NH}_3^+$, W2, W4 and W5 to 60° are illustrated in Fig. 4. The energy barrier for the simultaneous rotation of $-\text{COO}^-$, Θ , W1, and W3 is only 6.3 kcal/mol (graph B, Fig. 4) but the peak of the maximum barrier is shifted from 90° to 75° due to the energy gain from interaction between W3 and the $-\text{NH}_3^+$ group.

The results obtained from the study of the internal rotation by rotating angle Θ and ϕ indicate that hydration increases the barrier, except the corotation of W1, W2, W3 with the angle, then the hydration decreases the barrier. Therefore, the relaxation process of the solvated molecules in biochemical processes must be considered.

The studies of the rotational barrier of hydrated glycine zwitterion show the influence of the hydration to be of considerable importance because it can change the stability of molecular arrangement.

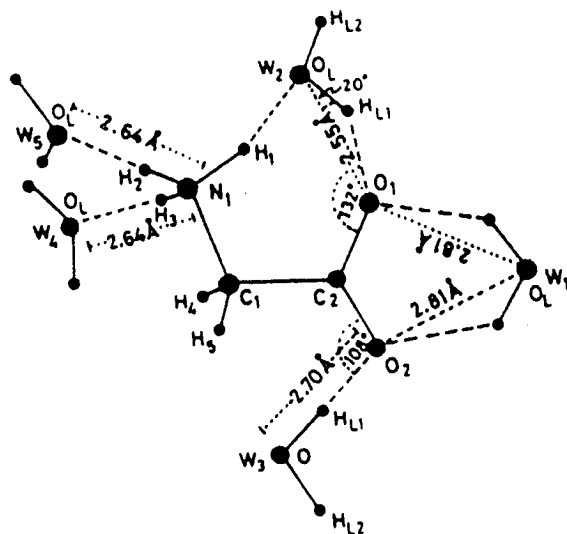


Fig. 1 The orientation of the first hydration shell of glycine zwitterion

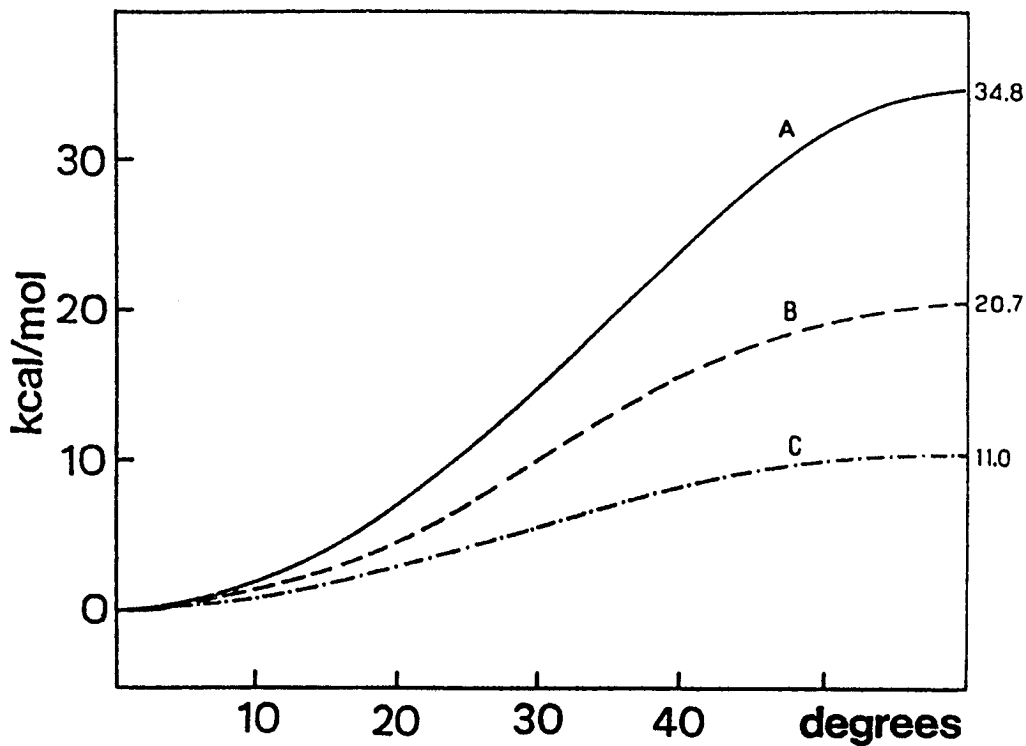


Fig. 2 The rotation pathways of glycine zwitterion

Fixing $-\text{COO}^-$ groups at 0 degree

A. The rotation of $-\text{NH}_3^+$ group, fixing the hydration structure

B. The rotation of $-\text{NH}_3^+$ group together with W2, W4, W5, fixing W1, W3

C. The rotation of $-\text{NH}_3^+$ group alone, neglecting the hydration structure

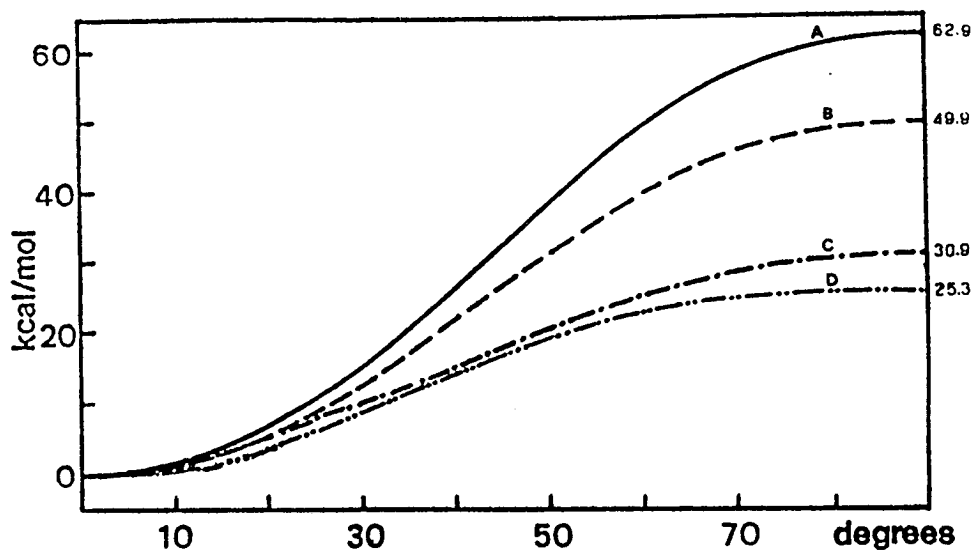


Fig. 3 The rotation pathways of glycine zwitterion

Fixing $-\text{NH}_3^+$ group at 0 degree

- A. The rotation of $-\text{COO}-$ group, fixing the hydration structure
- B. The rotation of $-\text{COO}-$ group together with W1, fixing W2, W3, W4, W5
- C. The rotation of $-\text{COO}-$ group alone, neglecting the hydration structure
- D. The rotation of $-\text{COO}-$ group together with W1, W2, W3 and fixing W4, W5

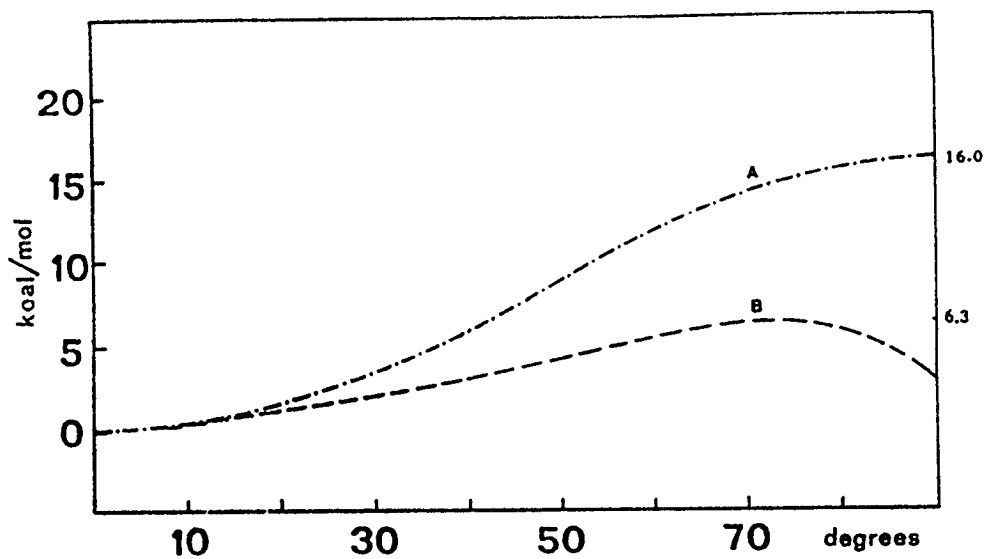


Fig. 4 The rotation pathways of glycine zwitterion

Fixing $-\text{NH}_3^+$ group and W2, W4, W5 at 60 degrees

- A. The rotation of $-\text{COO}-$ group alone, neglecting the hydration structure
- B. The rotation of $-\text{COO}-$ group together with W1, W3

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REFERENCES

1. P.B.Doungdee, S.U.Kokpol and B.M.Rode, *J.Sci.Soc. Thailand*, 1985, **11**, 113
2. S.U.Kokpol, P.B.Doungdee, S.V.Hannonbua and B.M.Rode, *J.Chem.Soc., Faraday Trans. 2*, 1988, **84(11)**, 1789
3. S.U.Kokpol, S.V.Hannongbua and J.P.Limtrakul, *Monatsch Chem.*, 1989, **120**, 491
4. P.B.Doungdee, S.U.Kokpol and B.M.Rode, *Monatsch Chem.*, 1987, *Monatsch Chem.*, **118**, 691
5. M.Dupuis, R.Rys and H.F.King, *J.Chem.Phys.*, 1976, **65**, 111, M.Dupuis, J.J.Wendoloski and D.Spangier. (1980). *Natl. Res. Comput.Chem. Software Cat.* 1, Prog. No.01.
6. M.M.Probst and B.M.Rode, *Inorg Chim Acta*, 1982, **63**, 47
7. B.M.Rode and K.P.Sagarik, *Chem.Phys.Lett.*, 1982, **88**, 337
8. S.U.Kokpol, S.V.Hannongbua, J.P.Limtrakul and B.M.Rode, *Inorg.Chim.Acta*, 1986, **125**, 107

บทคัดย่อ

ได้ทำการศึกษาอิทธิพลของไฮเดรชันแรกที่มีต่อการหมุนภายในของไกลซีนสวิตเทอร์ไอออนโดยวิธี แอบอินนิตีโอเอ็มโอ-เอสซีเอฟ และใช้เบซิสเซทขนาดเล็ก ทำการเปรียบเทียบพลังงานที่ออฟทิมัซของโครงสร้างไฮเดรทเตตรต กับผลที่ได้จากการคำนวณวิธี CNDO/2