

**Table 4.** Comparison of Analytical Results on Tap Water<sup>a</sup>

Running No.	Concentration of Cl <sup>-</sup> (ppm)		
	Orion-ISE method	Spectrophotometric method <sup>b</sup>	Present work
1	13.0	12.7	13.2
2	13.3	13.1	13.4
3	13.1	13.0	13.1
4	13.2	13.0	13.0
5	13.0	12.9	13.1
Mean	13.12(a)	12.94(b)	13.16(c)
S.D.	± 0.13	± 0.15	± 0.13
C.V.(%)	0.99	1.17	0.98
Relative error(%)	0.30	1.70	
	(c-a)/a × 100	(c-b)/b × 100	

<sup>a</sup>Tap water sample were taken from Yonsei Univ. in 9th Feb., 1988.<sup>b</sup>Mercuric thiocyanate method.

chloride-CWE was much greater than those for either solid state epoxy body chloride electrodes or liquid membrane chloride electrodes.

Analysis of water samples. Carbon chloride-CWE was ap-

plied to the determination of chloride ion in tap and ground water. The analytical results are given in Table 3 and 4 along with those obtained by other methods. The results were in excellent agreement (RSD, 3.0%) with those by other established methods such as spectrophotometric or other chloride selective electrode method.

**Acknowledgement.** The work was supported by the Korea Research Foundation under grant in 1987.

### References

1. C. J. Coetzee and H. Freiser, *Anal. Chem.*, **41**, 1128 (1969).
2. K. Suzuki, H. Ishibashi, T. Shirai and S. Yamagisawa, *Japan Analyst*, **30**, 751 (1981).
3. H. Ishiwada, K. Suzuki and T. Shirai, *ibid.*, **31**, 71 (1982).
4. A. Ansaldi, S. I. and Epstein, *Anal. Chem.*, **45**, 595 (1973).
5. S. Mesaric and E. A. M. F. Dahmen, *Anal. Chim. Acta.*, **64**, 431 (1973).
6. Y. K. Lee, J. T. Park, C. K. Kim and K. J. Whang, *Anal. Chem.*, **58**, 2101 (1986).
7. H. James, G. Carmack and H. Freiser, *ibid.*, **44**, 856 (1972).

## Theoretical Studies on the Potential Energy Profiles for Proton Transfer Reaction in Formamide Dimer

Young Shik Kong

*Institute of Basic Science, Chonbuk National University, Chonju 560-756*

Mu Shik Jhon\*

*Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 130-650.*

*Received January 19, 1989*

Theoretical studies on the proton transfer reaction in a formamide dimer have been done by Ab initio SCF calculation. In this study, we have shown several effects on the potential energy profile of the proton transfer in a formamide dimer, such as the effect of a basis set, the effect of a geometry optimization, and the effect of a distance between proton-donor and proton-acceptor.

### Introduction

There are many studies on the hydrogen bonding<sup>1-8</sup>. Especially, proton transfer reactions in biomolecules are very important to understand many biological phenomena<sup>9</sup>. Precise potential energy profiles of proton transfer reactions may give many informations to deduce the possibility of the proton transfer. Therefore, in this study, we have chosen a formamide dimer as the model of an asymmetric double proton transfer reaction and obtained potential energy profiles for the proton transfer reaction by ab initio SCF calculations. Several effects on the proton transfer reaction have been tested in order to know how the potential energy profiles

have been changed according to the conditions. The effect of a basis set on the potential energy profile of the proton transfer reaction has been checked by varying the basis set, such as STO-3G, 3-21G, and 4-31G. The effect of a geometry optimization and that of a distance between proton-donor and proton-acceptor have been also checked by adopting the geometry optimization or not and varying the distance between proton-donor and proton-acceptor respectively.

### Method of Calculations

Ab initio SCF calculations have been performed to obtain the potential energy profiles for the proton transfer in a for-

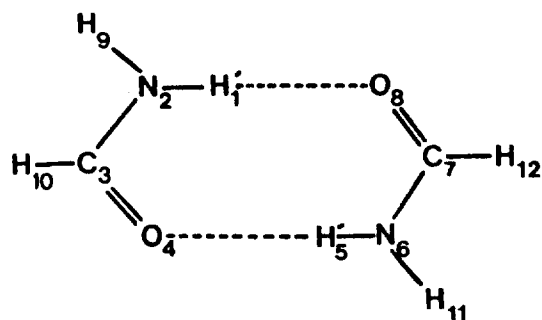


Figure 1. Structure of a formamide dimer.

mamide dimer. All calculations in this study have been done on an IBM 3083 computer using a version of the Gaussian 82 system of programs. The structure of a formamide dimer is shown in Figure 1. The initial bond lengths, angles, and intermolecular distance are taken from Ottersen *et al.*<sup>10</sup>. In a formamide dimer, the distance between  $N_2$  and  $H_1$  and that between  $N_6$  and  $H_5$  have been elongated in steps by 0.1 Å along the lines  $N_2-O_8$  and  $N_6-O_4$ , respectively and energies for the double proton transfer have been calculated [See Figure 1]. In this study, several effects on the proton transfer in a formamide dimer have been tested. The effect of a basis set on the double proton transfer in a formamide dimer has been performed by varying basis sets, such as STO-3G, 3-21G, and 4-31G, where the distance between proton-donor and proton-acceptor has been fixed at 2.85 Å, and the geometry optimization has been adopted. The effect of a geometry optimization, except the distances between proton-donor and proton-acceptor which have been fixed at 2.85 Å, has been also performed by adopting the geometry optimization or not, where STO-3G basis set has been used and  $C_{2h}$  symmetry has been maintained. Finally the effect of a distance between proton-donor and proton-acceptor has been shown by varying distances, such as 2.35 Å, 2.55 Å, 2.85 Å, and 3.05 Å, where STO-3G basis set has been used and the geometry optimization has been also adopted. The calculated results have been discussed in the next section.

## Results and Discussions

**The Effect of a Basis Set.** The calculated results for the

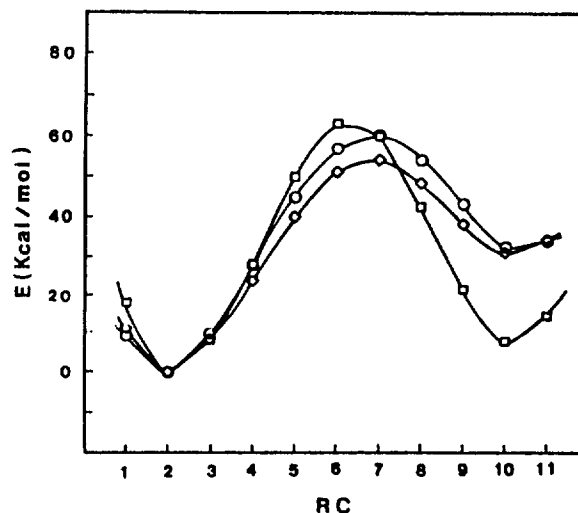


Figure 2. Potential energy profiles for the double proton transfer in a formamide dimer (The effect of basis sets) (□): STO-3G, (◇): 3-21G, (○): 4-31G.

Table 2. Energies for the Double Proton Transfer in a Formamide Dimer with and without the Geometry Optimization<sup>a</sup>

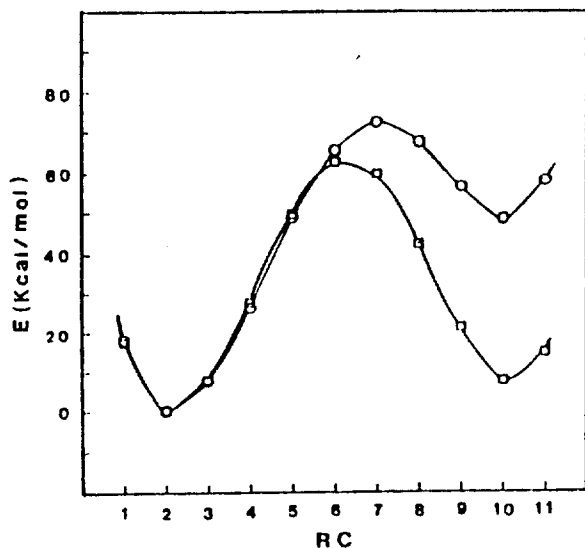
RC	d(N-H) (Å)	E(Hartree)		E(Kcal/mol) <sup>b</sup>	
		without Opt.	with Opt.	without Opt.	with Opt.
1	0.92	-333.3589846	-333.368091	18.57	17.77
2	1.02	-333.3885792	-333.3964061	0.00	0.00
3	1.12	-333.377402	-333.3838151	7.01	7.90
4	1.22	-333.3465926	-333.3518387	26.35	27.97
5	1.32	-333.3113263	-333.317187	48.48	49.71
6	1.42	-333.2838504	-333.2960428	65.72	62.98
7	1.52	-333.2731248	-333.301149	72.45	59.77
8	1.62	-333.2808279	-333.3287193	67.62	42.47
9	1.72	-333.2987643	-333.3624649	56.36	21.30
10	1.82	-333.311176	-333.3843881	48.57	7.54
11	1.92	-333.2959817	-333.3732577	58.11	14.53

<sup>a</sup>The energy calculations have been performed with STO-36 basis set and the distance between proton-donor and proton-acceptor has been fixed at 2.85 Å. <sup>b</sup>Energy difference when compared with the energy (RC = 2).

Table 1. Energies for the Double Proton Transfer in a Formamide Dimer with Different Basis Sets<sup>a</sup>

RC	d(N-H) (Å)	E(Hartree)			E(Kcal/mol) <sup>b</sup>		
		STO-36	3-216	4-316	STO-36	3-216	4-316
1	0.95	-333.368091	-335.987221	-337.3734715	17.77	10.93	9.34
2	1.02	-333.3964061	-336.0046337	-337.3883528	0.00	0.00	0.00
3	1.12	-333.3838151	-335.9916974	-337.3728439	7.90	8.12	9.73
4	1.22	-333.3518387	-335.9665006	-337.3450981	27.97	23.93	27.14
5	1.32	-333.317187	-335.9408397	-337.3171277	49.71	40.03	44.69
6	1.42	-333.2960428	-335.9231865	-337.2977114	62.98	51.11	56.88
7	1.52	-333.301149	-335.9187306	-337.2924369	59.77	53.91	60.19
8	1.62	-333.3287193	-335.9274407	-337.3017244	42.47	48.44	54.36
9	1.72	-333.3624649	-335.9434448	-337.3199433	21.30	38.40	42.93
10	1.82	-333.3843881	-335.9560582	-337.3363347	7.54	30.48	32.64
11	1.92	-333.3732577	-335.9488128	-337.3343013	14.53	35.03	33.92

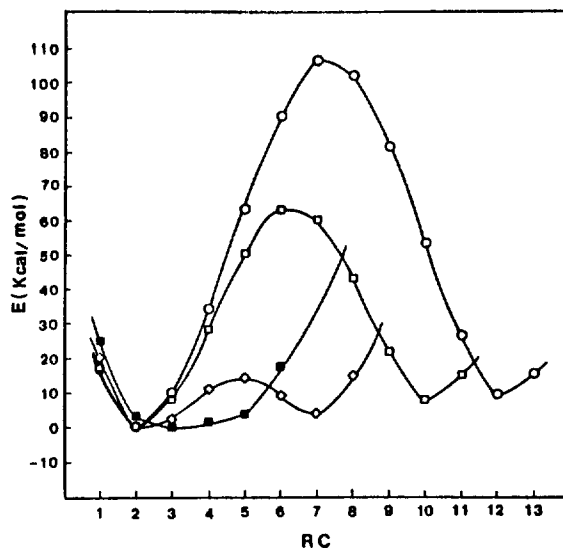
<sup>a</sup>The energy calculations have been performed with the geometry optimization and the distance between proton-donor and proton-acceptor has been fixed at 2.85 Å. <sup>b</sup>Energy difference when compared with the energy (RC = 2).



**Figure 3.** Potential energy profiles for the double proton transfer in a formamide dimer (The effect of a geometry optimization) (○): without geometry optimization, (□): with geometry optimization.

effect of a basis set have been summarized in Table 1 and Figure 2. The shapes of potential energy profiles have been affected by basis sets. The potential energy profile using STO-3G is different from the potential energy profiles using 3-21G and 4-31G, whereas the potential energy profile using 3-21G is similar to that using 4-31G. STO-3G basis set has more stabilized the energy of a tautomer, which has been made by the double proton transfer, compared with the results using 3-21G and 4-31G basis sets. Therefore, the potential energy profile using STO-3G has been less asymmetric than the potential energy profiles using 3-21G and 4-31G.

**The Effect of a Geometry Optimization.** The calculated results for the effect of a geometry optimization have been summarized in Table 2 and Figure 3. The geometry op-



**Figure 4.** Potential energy profiles for the double proton transfer in a formamide dimer (The effect of the distance between proton-donor and proton-acceptor) (■): 2.35Å, (◇): 2.55Å, (□): 2.85Å, (○): 3.05Å.

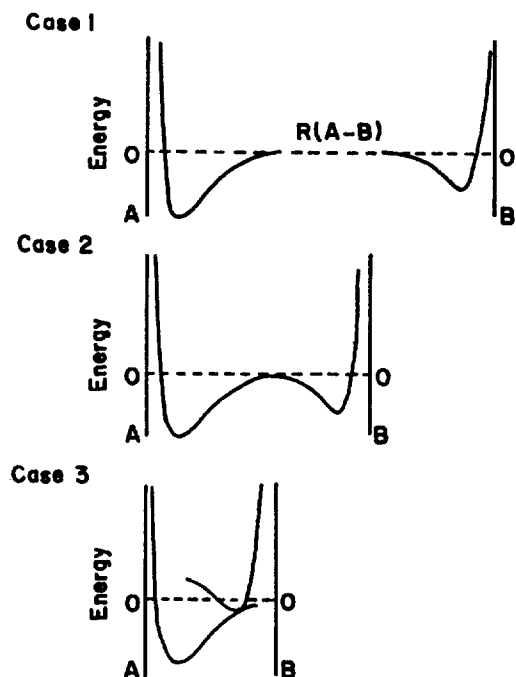
timization has brought about not only lowering the reaction barrier height but also deepening the second well of a double-well potential energy profile.

**The Effect of a Distance between Proton-Donor and Proton-acceptor.** The calculated results for the effect of a distance have been summarized in Table 3 and Figure 4. When the distance between proton-donor and proton-acceptor has been shortened, the double-well potential energy profile has been changed to the single-well potential energy profile. The schematic feature for the effect of a distance between proton-donor and proton-acceptor has been shown in Figure 5<sup>11</sup>. Conclusively, the potential energy profile of the proton transfer reaction has been effected by several factors. Therefore, it is not easy to obtain the reliable potential

**Table 3.** Energies for the double Proton Transfer in a Formamide dimer Varying the Distance between Proton-donor and Proton-acceptor<sup>a</sup>

RC	d(N-H) (Å)	E(Hartree)				E(Kcal/mol)			
		2.35Å <sup>d</sup>	2.55Å <sup>d</sup>	2.85Å <sup>d</sup>	3.05Å <sup>d</sup>	2.35Å <sup>c,d</sup>	2.55Å <sup>b,d</sup>	2.85Å <sup>b,d</sup>	3.05Å <sup>b,d</sup>
1	0.92	-333.3476857	-333.3658843	-333.368091	-333.3650311	24.79	19.93	17.77	16.78
2	1.02	-333.3823851	-333.3976527	-333.3964061	-333.3917699	3.01	0.00	0.00	0.00
3	1.12	-333.3871882	-333.3938611	-333.3838151	-333.3761058	0.00	2.38	7.90	9.83
4	1.22	-333.3856015	-333.3801214	-333.3518387	-333.3380065	1.00	11.00	27.97	33.74
5	1.32	-333.3822593	-333.3749997	-333.317187	-333.2912987	3.09	14.21	49.71	63.05
6	1.42	-333.3595966	-333.3833696	-333.2960428	-333.2480301	17.31	8.96	62.98	90.20
7	1.52	—	-333.3915677	-333.301149	-333.2224264	—	3.82	59.77	106.26
8	1.62	—	-333.3746571	-333.3287193	-333.2287242	—	14.43	42.47	102.31
9	1.72	—	—	-333.3624649	-333.2626558	—	—	21.30	81.02
10	1.82	—	—	-333.3843881	-333.3079945	—	—	7.54	52.57
11	1.92	—	—	-333.3732577	-333.3508883	—	—	14.53	25.65
12	2.02	—	—	—	-333.3772382	—	—	—	9.12
13	2.12	—	—	—	-333.3681194	—	—	—	14.84

<sup>a</sup>The energy calculations have been performed with a STO-36 basis set and with the geometry optimization. <sup>b</sup>Energy difference when compared with the energy (RC = 2). <sup>c</sup>Energy difference when compared with the energy (RC = 3). <sup>d</sup>The distance between proton-donor and proton-acceptor.



**Figure 5.** Schematic representation of potential energy profiles for three limiting cases as a function of the distance between proton-donor and proton-acceptor.

energy profile of a proton transfer reaction theoretically, and much careful attention must be paid to the interpretation of

the potential energy profiles.

**Acknowledgement.** This work was supported by the Basic Science Research Grant from the Ministry of Education of Korea and the Research Grant from Korea Science and Engineering Foundation.

### References

1. E. Caldin and V. Gold, Eds., "Proton Transfer Reactions", Wiley, New York, 1975.
2. P. Schuster, G. Zundel and C. Sandorfy, Eds., "The Hydrogen Bond—Recent Developments in Theory and Experiments", North-Holland Publishing Co., Amsterdam, 1978.
3. Š. Scheiner, *J. Am. Chem. Soc.* **103**, 315 (1981).
4. M. D. Newton, *J. Chem. Phys.* **67**, 5535 (1978).
5. S. Scheiner and C. W. Kern, *J. Am. Chem. Soc.* **101**, 4081 (1978).
6. J. E. Del Bene and W. L. Kochenour, *J. Am. Chem. Soc.* **98**, 2041 (1976).
7. S. Scheiner, P. Redfern, and M. M. Szczesniak, *J. Phys. Chem.* **89**, 262 (1985).
8. Y. S. Kong, M. S. Jhon, and P. O. Löwdin, *Int. J. Quantum Chem., Quantum Biology Symp.* **14**, 189 (1987).
9. P. O. Löwdin, *Adv. Quantum Chem.* **2**, 212 (1965).
10. T. Ottersen and H. H. Jensen, *J. Mol. Struct.* **26**, 355 (1975).
11. E. Clementi and J. Mehi, and W. V. Niessen, *J. Chem. Phys.* **54**, 508 (1971).

## Optical Resolution of Dansyl Amino Acids with Addition of Benzyl-L-Hydroxyproline Copper(II) Chelate by High Performance Liquid Chromatography

Sun Haing Lee\*, Tae Sub Oh, and Sang Hyun Bak

Department of Chemistry, Kyungpook National University, Taegu 702-701. Received March 4, 1989

Resolution of enantiomers of DNS-amino acids has been achieved by a reversed phase liquid chromatography with an addition of a copper(II) complex of N-benzyl-L-hydroxyproline to the mobile phase. N-Benzyl-L-hydroxyproline was prepared and used as a chiral ligand of copper(II) chelate for the optical resolution. The pH and the concentration of copper(II) chelate, organic solvent, and buffer agent in the mobile phase all affect the optical resolutions of dansyl amino acids. The elution orders between D and L-DNS-amino acids were different depending on the structure of the side chain of the amino acids. The retention mechanism for the chiral separation of the dansyl amino acids can be illustrated by the equilibrium of ligand exchange and by hydrophobic interaction with  $C_{18}$  stationary phase. The chiral separation can be illustrated with cis and trans effect of the ligand exchange reaction.

### Introduction

Methods for separating free or derivatized amino acids by reversed phase high performance liquid chromatography (HPLC) consisting of mixed chelate complexes of amino acids have been well described. They are based upon addition of a chiral chelate to the mobile phase<sup>1-15</sup>.

The resolution of enantiomers of amino acids by HPLC has been interested especially in the synthesis of peptides and the determination of the chemical structure. Many different kinds of chiral chelate have been developed for the resolution of  $\alpha$ -amino acids and dansyl- $\alpha$ -amino acids<sup>1</sup>. Copper (II) chelates have been used as the chiral eluents for the optical resolution. Proline and its derivatives have been used