

## Ab INITIO STUDY ON THE GLYCINEMETHYLESTER

JA HONG KIM, SUNG HO SOHN, KEE SOO YANG, AND \*SUNG WAN HONG  
 Department of Chemistry Education, Chonbuk National University, Chonju 561-756  
 \*Department of Chemistry, Woosuk University, Wanju 565-701

(Received 26 October 1999; accepted 26 November 1999)

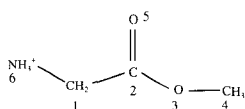
**Abstract** – The conformational studies of glycinemethylester have been carried out by the *ab initio* method. We have optimized the geometries of glycinemethylester at various levels of sophisticated for electron exchange and correlation within MP2 level. The scale factors of glycinemethylester were used to obtain the scaled *ab initio* force field of the minimum energy conformer of it, which was used to predict the vibrational frequencies and their potential energy distribution. The Raman spectra of the glycinemethylester were compared with the observed one and the other calculated with HF/6-31G\*\* level.

Biomolecules are often bulky and therefore can be approached with approximate molecular orbital methods.<sup>1-3</sup> For the purpose of applying the recent *ab initio* calculations based on solving the quantum mechanical problem, this paper describes an evaluation of both the accuracy and practical applicability of correlation method to amino acid in detail. In our previous reports<sup>4,5</sup> the semiempirical methods were used to investigate the electronic structures and reactivities of glycinate and glycineester ligands. The results showed that the bidentate glycinate had a more stable structure with a dihedral angle of the 105.9° between  $\Delta O_4 C_3 C_2$  and  $\Delta C_3 C_2 N_1$  than glycineester.

Herein, the octahedral Co(III) complexes of the glycine-

Table 1. Optimized geometries for the glycinemethylester by *ab initio* calculation (bond lengths in angstroms, bond angles and dihedral angles in degrees)

Geometry	HF/6-31G	HF/6-311G	HF/6-31G**	MP2/6-31G	MP2/6-311G
C2-C1	1.511	1.507	1.522	1.533	1.523
O3-C2	1.336	1.334	1.312	1.386	1.383
C4-O3	1.476	1.472	1.446	1.512	1.507
O5-C2	1.200	1.197	1.176	1.241	1.235
N+6-C1	1.510	1.506	1.501	1.537	1.530
C1-C2-O3	111.368	111.357	111.569	110.041	109.959
C2-O3-C4	120.405	120.161	117.205	116.674	116.709
C1-C2-O5	122.511	122.600	120.889	123.508	123.678
O3-C2-O5	126.097	126.022	127.543	126.408	126.324
C2-C1-N+6	110.094	110.407	111.584	109.716	109.822
O3-C2-C1-N+6	17.159	17.701	0.042	18.492	19.886
O5-C2-C1-N+6	-164.542	-163.861	-179.961	-163.763	-162.257
C4-O3-C2-C1	177.125	177.044	-179.998	176.826	176.495
C4-O3-C2-O5	-1.1004	-1.329	0.005	-0.837	-1.292



methylester have been prepared and characterized by elemental analysis, infrared, and NMR spectra. The photochemical behaviors of the complexes are correlated with theoretical predictions based on the electronic absorption spectra of Co(III) glycineester complexes.<sup>6</sup>

The computational calculations were performed using the Hartree-Fock(HF) wave function with 6-31G basis sets.<sup>7</sup> The contributions of electron correlation to the energy profile were calculated in single point calculations by employing the second-order Møller-(Norwegian letter) Plesset perturbation theory(MP2) at the MP2/6-31G and MP2/6-311G levels.

We have optimized the geometries of glycinemethylester at various levels of sophistication for electron exchange and correlation within MP2 level, and the results are shown in Table 1. The structure that we obtained agrees very well with the results from semiempirical calculation.<sup>4</sup> For example, the angle of  $C_2 O_3 C_4$  is 120° in low level calculation but consistently between 116° and 117° in MP2 level studies. The results show that the expected migration of electron density maxima at coordination towards the center of covalent bonds is distinct from the electron density maxima at coor-

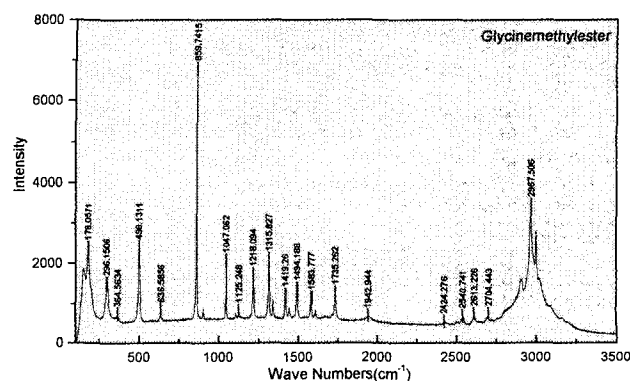


Figure 1. The Raman spectrum of glycine methyl ester.

dination sites predicted on the basis of  $sp^2$  hybridization of the oxygen atoms.

The Raman spectrum of the glycinemethylester is depicted in Figure 1. The observed frequencies and intensities are compared with the values calculated at the HF/6-31G\*\* level for glycinemethylester.

For glycinemethylester we also found a larger discrepancy between the observed and calculated frequency values for N-H stretching vibration. The C-H stretching vibrational modes are calculated in the range 2910 to 3056 $cm^{-1}$  and the C=O stretching vibrational modes are calculated in the range 1718 to 1740 $cm^{-1}$ .

The atomic displacements of the other normal modes are not as localized in a specific chemical functional group. The vibrational frequencies obtained from electronic structure calculations can be as much as 12% above the experimental values due to the use of the harmonic approximation to the vibrational potential energy, and the failure is due to the taking electron correlation fully into account<sup>8</sup>. We investigated this problem further by calculating the frequencies of this mode in the potential energy determined over several points surrounding the minimum values. It has been shown that the accurate Raman intensity calculations require a large basis set including diffuse and polarization functions.

## REFERENCES

1. Stepanian, S. G., Reva, I. D., Radchenko, E. D., and Adamowicz, L. (1998) Conformational Behavior of Alanine. *J. Phys. Chem., A*, **102**, 4623-4629.
2. Kaschner, R., and Hohl, D. (1998) Density Functional Theory and Biomolecules. *J. Phys. Chem., A*, **102**, 5111-5116.
3. Venkateswarlu, D., Leszczynski, J. (1999) *Ab Initio* SCF-MO Studies toward Improved DNA Recognition. *J. Phys. Chem., A*, **103**, 3489-3494.
4. Kim, J. H. (1980) MO Studies on the Electronic Structure and Reactivity of Glycinato, Glycineester Ligands. *J. Kor. Chem. Soc.*, **24**, 15-19.
5. Kim, J. H., Shim, S. C. (1980) Co(III) Complexes of Glycinemethylester(I), Preparation and Characterization. *J. Kor. Chem. Soc.*, **24**, 356-360.
6. Kim, J. H., Lee, K. H., and Shim, S. C. (1984) Photochemistry of Co(III) Complex of Glycinemethylester. *Bull. Kor. Chem. Soc.*, **5**, 262-263.
7. Frisch, M. J., Trucks, G. W., Schlegel, H. B., Gill, P. M. W., Johnson, B. G., Robb, M. A., Cheeseman, J. R., Keith, T., Petersson, G. A., Montgomery, J. A., Raghavachari, K., Al-Laham, M. A., Zakrzewski, V. G., Ortiz, J. V., Foresman, J. B., Cioslowski, J., Stefanov, B. B., Nanayakkara, A., Challacombe, M., Peng, C. Y., Ayala, P. Y., Chen, W., Wong, M. W., Andres, J. L., Replogle, E. S., Gomperts, R., Martin, R. L., Fox, D. J., Binkley, J. S., Defrees, D. J., Baker, J., Stewart, J. P., Head-Gordon, M., Gonzalez, C., Pople, J. A. Gaussian 94 revision E. 2, *Gaussian Inc, Pittsburgh, PA*, 1995.
8. Hehre, W. J., Radam, L., Schleyer, P. V. R., Pople, J.A. (1986) *Ab Initio* Molecular Orbital Theory. *J. Wiley & Sons, N.Y.*

1. Stepanian, S. G., Reva, I. D., Radchenko, E. D., and Adamow-