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Conformational Preference of Pseudo-Proline Dipeptide in the Gas Phase and SolutionsHae Sook Park¹ and Young Kee Kang²¹Department of Radiotechnology, Cheju-Halla College, ²Department of Chemistry, Chungbuk National University

We report here the results on N-acetyl-N'-methylamide of oxazolidine (Ac-Oxa-NHMe) calculated using the ab initio molecular orbital method with the self-consistent reaction field (SCRF) theory at the HF level of theory with the 6-31+G(d) basis set. The displacement of the α -CH₂ group in proline ring by oxygen atom has affected the structure of proline, cis-trans equilibrium, and rotational barrier. The up-puckered structure is found to be prevalent for the trans conformers of the Oxa amide. The higher cis populations of the Oxa amide can be interpreted due to the longer distance between the acetyl methyl group and the 5-methylene group of the ring for the trans conformer of the Oxa amide than that of the Pro amide. The changes in charge of the prolyl nitrogen and the decrease in electron overlap of the C-N bond for TS structures seem to play a role in lowering rotational barriers of the Oxa amide compared to that of the Pro amide. The calculated preferences for cis conformers in the order of Oxa > Pro amides and for trans-to-cis rotational barriers in the order of Pro > Oxa amide in water are consistent with experimental results on Oxa-containing peptides. The pertinent distance between the prolyl nitrogen and the N-H amide group to form a hydrogen bond might indicate that this intramolecular hydrogen bond could contribute in stabilizing the TS structures of Oxa and Pro amides and play a role in prolyl isomerization.