The Thermodynamic and Kinetic Properties of 2-Hydroxypyridine/2-Pyridone Tautomerization: A Theoretical and Computational Revisit

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Abstract

The gas-phase thermal tautomerization reaction between 2-hydroxypyridine (2-HPY) and 2-pyridone (2-PY) was investigated by applying 6-311++G** and aug-cc-pvdz basis sets incorporated into some density functional theory (DFT) and coupled cluster with singles and doubles (CCSD) methods. The geometrical structures, dipole moments, HOMO-LUMO energy gaps, total hyperpolarizability, kinetics and thermodynamics functions were monitored against the effects of the corrections imposed on these functionals. The small experimental energy difference between the two tautomers of 3.23 kJ/mol; was a real test of the accuracy of the applied levels of theory. M062X and CCSD methods predicted the preference of 2-HPY over 2-PY by 5-9 kJ/mol; while B3LYP functional favoured 2-PY by 1-3 kJ/mol. The CAM-B3LYP and omega B97XD functionals yielded mixed results depending on the basis set used. The source of preference of 2-HPY is the minimal steric hindrance and electrostatic repulsion that subdued the huge hyperconjugation in 2-PY. A 1,3-proton shift intramolecular gas-phase tautomerization yielded a high average activation of 137.152 kJ/mol; while the intermolecular mixed dimer interconversion gave an average barrier height of 30.844 kJ/mol. These findings are boosted by a natural bond orbital (NBO) technique. The low total hyperpolarizabilities of both tautomers mark out their poor nonlinear optical (NLO) behaviour. The enhancement of the total hyperpolarizability of 2-HPY over that of 2-PY is interpreted by the bond length alternation.

Keywords

Author Keywords: 2-hydroxypyridine; 2-pyridone; tautomerization; NBO; NLO

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