Tautomerization, acidity, basicity, and stability of cyanoform: a computational study

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Abstract

Background: Cyanoform is long known as one of the strongest acid. Cyanoform is only stable below -40 degrees C. The issue of the stability and tautomeric equilibria of cyanoform (CF) are investigated at the DFT and MP2 levels of theory. The present work presents a detailed study of structural tautomer interconversion in three different media, namely, in the gas phase, in a solvent continuum, and in a microhydrated environment where the first solvation layer is described explicitly by one or two water molecule. In all cases, the transition state has been localized and identified. Proton affinities, deprotonation energies and the Raman spectra are reported analyzed and discussed.

Results: The 1 tautomer of cyanoform is shown to be more stable than 2 form by only 1.8 and 14.1 kcal/mol in the gas phase using B3LYP/6-311++G** and MP2/6-311++G** level of theory, respectively. This energy difference is reduced to 0.7 and 13.4 kcal/mol in water as a solvent using CPCM model using B3LYP/6-311++G** and MP2/6-311++G** level of theory, respectively. The potential energy barrier for this proton transfer process in the gas phase is 77.5 kcal/mol at MP2/6-311++G** level of theory. NBO analysis, analysis of the electrostatic potential (ESP) of the charge distribution, donor-acceptor interactions and charge transfer interactions in 1 and 2 are performed and discussed.

Conclusions: Gross solvent continuum effects have but negligible effect on this barrier. Inclusion of one and two water molecules to describe explicitly the first solvation layer, within the supermolecule model, lowers the barrier considerably (29.0 and 7.6 kcal/mol, respectively). Natural bond orbital (NBO) analysis indicated that the stability of the cyanoform arising from charge delocalization. A very good agreement between experimental and theoretical data has been found at MP2/6-311++G** for the energies. On other hand, B3LYP/6-311++G** level of theory has good agreement with experimental spectra for CF compound.

Keywords

Author Keywords: Cyanoform; Tautomerization; Water-assisted proton transfer; B3LYP; MP2; PCM; Raman spectra

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