

Vibrational Spectra of Phenylphosphonic and Phenylthiophosphonic Acid and their Complete Assignment

Wolfgang Förner and Hassan M. Badawi

Department of Chemistry, King Fahd University of Petroleum & Minerals (KFUPM),
Dhahran 31261, Saudi Arabia

Reprint requests to W. Förner. E-mail: forner@kfupm.edu.sa

Z. Naturforsch. **2010**, *65b*, 357–366; received November 1, 2009

Dedicated to Professor Rolf. W. Saalfrank on the occasion of his 70th birthday

The structures and conformational stabilities of phenylphosphonic acid and phenylthiophosphonic acid were investigated using calculations mostly at DFT/6-311G** and *ab initio* MP2/6-311G** level. From the calculations the molecules were predicted to exist in a conformational equilibrium consisting of two conformers which as enantiomers have the same energy, but rather unexpected dihedral angles XPCC (X being O or S) which are not equal to zero. The antisymmetric potential function for the internal rotation was determined for each one of the molecules. In these functions the conformers with zero dihedral angles appear to be stable minima (also optimization converges to this), but the vibrational frequency for the torsion turned out to be imaginary, indicating that they are maxima with respect to this symmetry coordinate. Only optimization without any restrictions and starting from a non-zero torsional angle converged to a real minimum with such a geometry (“non-planar”). For that minimum structure infrared and Raman spectra were calculated, and those for phenylphosphonic acid were compared to experimental data, showing satisfactory agreement. This gives confidence to present the spectra of phenylthiophosphonic acid as a prediction. The rather low intensity of the OH bands in the experimental infrared spectrum (as compared to normal organic acids) indicates rather weak hydrogen bonding. Normal coordinate calculations were carried out, and potential energy distributions were calculated for the molecules in the non (near)-planar conformations providing a complete assignment of the vibrational modes to atomic motions in the molecules. From the rather low rotational barriers we conclude, in agreement with results from the literature (for other P=O compounds) based on localized orbitals that conjugation effects are absent – or at least negligible – as compared to electrostatic and steric ones in determining the structures of the stable conformers in the phenyl derivatives. The P=O (and also the P=S) bond is highly polarized according to our analysis of Mulliken populations. The polarization turned out to be smaller in the thiophosphonic acid due to the smaller electronegativity of sulfur as compared to oxygen.

Key words: DFT and MP2 Calculations, Vibrational Spectra and Assignments, Torsional Potentials, Phenylphosphonic Acid, Phenylthiophosphonic Acid