Analysis of the asymmetric ring puckering potential in 1-oxo-1-chloro-phosphetane and of theoretical vibrational spectra.

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Abstract

The asym. ring puckering potential in 1-oxo-1-chloro-phosphetane (c-C_3H_6POCl) was calcd. using the 6-311+G** basis set and the MP2 as well as the DFT method and fitted as function of the ring puckering coordinate x. It turned out that on MP2 level the potential, is clearly of a double well type with an equatorial and an (higher in energy) axial min., while on DFT level no axial min. exists, just a shoulder in the potential function. Based on our, yet unpublished results on thietane dioxide we conclude that the DFT curve should be the more reliable one. Since we expect that barriers in DFT are somewhat too low, exptl. an axial conformer might still exist, but with an extremely low barrier to ring puckering. Thus with our DFT calcns. we predict the vibrational IR and Raman spectra of the equatorial conformer only, since even if an axial one would exist exptl. its energy would be much higher than that of the equatorial one and thus its contribution to the conformational equil. would be negligible. Thus we consider our prediction based on DFT calcns. as very reliable. The distributions of the potential energies of the different normal modes among the symmetry coordinates (PED) were calcd. and used to assign the lines in the spectra to the different motions of atoms.