

DFT and MP2 ring puckering potential functions, vibrational analysis and comparison with experiment for 3-chloro-1,3-thiaphosphetane 3-oxide, 3-sulfide and 1,3-dithietane 1,1-dioxide. Badawi, Hassan M.; Foerner, Wolfgang; Al-Suwaiyan, Abdul-Aziz. Department of Chemistry, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia. *Journal of Molecular Structure* (2008), 875(1-3), 189-197.

Abstract

The ring puckering in the four-membered 3-chloro-1,3-thiaphosphetane 3-oxide, its 3-sulfide deriv. and 1,3-dithietane 1,1-dioxide hetero rings were investigated by DFT and ab initio MP2 calcns. using a 6-311+G** basis set. From the calcns. at both levels of theory the asym. ring puckering potential energy curves in the two phosphetanes were consistent with an almost single min. that corresponds to a pseudo-axial configuration (P[σ]-Cl bond is in axial position) with a puckering angle of about 15-20°. In the case of the dithietane dioxide the sym. ring puckering potential was consistent at the B3LYP level with a flat min. that corresponds to a planar ring but at the MP2 level with a double min. with a very low barrier of about 185 cal/mol to ring planarity. The potential functions that describe the ring puckering in the three mols. were derived at the B3LYP/6-311+G** and the MP2/6-311+G** levels of calcns. The vibrational wavenumbers were calcd. and the potential energy distributions PED among the symmetry coordinates of the normal modes were computed for the stable conformers of each of the mols. Complete vibrational assignments were provided on the basis of the calcd. PED values. The exptl. IR and Raman spectra of the two phosphetane mols. were simulated and compared to the calcd. ones.