

Substituent effects on structural stability of formyl ketene and analysis of vibrational spectra of formyl haloketenes and formyl methylketene. Badawi, H. M.; Al-Saadi, A.; Forner, W

Abstract

The conformational behavior and the structural stability of formyl fluoroketene, formyl chloroketene and formyl methylketene were investigated by utilizing quantum mech. DFT c93

calcs. at B3LYP/6-311++G** and ab initio calcs. at MP2/6-311++G** levels. The three mols. were predicted to have a planar s-cis.tautm.ns conformational equil. From the calcs., the direction of the conformational equil. was found to be dependent on the nature of the substituting group. In formyl haloketenes, the cis conformation, where the C:O group eclipses the ketenic group, was expected to be of lower energy than the trans conformer. In the case of formyl methylketene the conformational stability was reversed and the trans form (the aldehydic hydrogen eclipsing the ketenic group) was calcd. to be about 2 kcal mol⁻¹ lower in energy than the cis form. The calcd. cis-trans energy barrier was found to be in the order: fluoride (15.3 kcal mol⁻¹) > chloride (13.1 kcal mol⁻¹) > Me (11.7 kcal mol⁻¹). Full optimization was performed at the ground and the transition states of the mols. The vibrational frequencies for the stable conformers of the three ketenic systems were computed at the DFT-B3LYP level, and the zero-point corrections were included into the calcd. rotational barriers. Complete vibrational assignments were made on the basis of both normal coordinate calcs. and comparison with exptl. results of similar mols.