SUBSTITUENT EFFECTS ON STRUCTURAL STABILITY OF FORMYL KETENE AND ANALYSIS OF VIBRATIONAL SPECTRA OF FORMYL HALOKETENES AND FORMYL METHYLKETENE

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ABSTRACT

The conformational behavior and the structural stability of formyl fluoroketene, formyl chloroketene and formyl methylketene were investigated by utilizing quantum mechanical DFT calculations at B3LYP/6-311++G** and *ab initio* calculations at MP2/6-311++G** levels. The three molecules were predicted to have a planar s-*cis* ⇔ s-*trans* conformational equilibrium. From the calculations, the direction of the conformational equilibrium 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 calculated to be about 2 kcal mol^{-1} lower in energy than the *cis* form. The calculated *cis-trans* energy barrier was found to be in the order: fluoride (15.3 kcal mol^{-1}) > chloride (13.1 kcal mol^{-1}) > methyl (11.7 kcal mol^{-1}). Full optimization was performed at the ground and the transition states of the molecules. 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 calculated rotational barriers. Complete vibrational assignments were made on the basis of both normal coordinate calculations and comparison with experimental results of similar molecules.

Keywords: Vibrational spectra and assignments; Density functional calculations; Formyl fluoroketene; Formyl chloroketene; Formyl methylketene.