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 double left right arrows-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.