BARRIER TO INTERNAL-ROTATION IN 2,3-DIFLUOROPROPENAL AND 3,3-DIFLUOROPROPENAL AND THEIR METHYL-DERIVATIVES

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Summary

The conformational stability and structure of 2,3-dimethylpropenal, 2,3-difluoropropenal and their 3,3-dimethyl and 3,3-difluoro derivatives were investigated utilizing ab initio calculations with 3-21G and 6-31G basis sets. For 2,3-dimethylpropenal and 3,3-difluoropropenal the s-trans was predicted to be the low-energy form. In the case of 3,3-dimethylpropenal and 2,3-difluoropropenal the s-cis was predicted by both levels of calculation to be the more stable conformer. Full optimization was performed at the transition states and the barriers to internal rotation were calculated. Methyl and fluorine substitution were found to significantly increase the barrier to interconversion in propenal. The relative change in the barrier depends on the position and the type of the substituent. The trans to cis barrier in 2,3-dimethylpropenal was calculated to be about 3 kcal mol(-1) greater than that in 3,3-dimethylpropenal, while the cis to trans barrier in 2,3-difluoropropenal was predicted to be about 7 kcal mol(-1) higher than the corresponding one in 3,3-difluoropropenal.

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