The conformational stability of several vinylhalomethanes, silanes, and germanes using MP Perturbation Theory up to fourth Order and DFT together with a valence triple zeta basis set with polarization functions, compared with experimental results

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Abstract

*In recent literature, it was reported that the valence triple zeta basis set augmented by diffuse and polarization functions is not too reliable for vinylmonohalo and dihalo methanes and silanes, the halogens being either fluorine or chlorine. The major conclusion was that a valence triple zeta basis with polarization functions is too small to be augmented by diffuse functions in a balanced way, at least for vinylmonofluoromethane. Thus, in a previous paper, we had applied the 6-311++G** basis set to the complete series of methanes, silanes and germanes (the latter ones were just added for completeness because no experimental data are available for them) and compared the results to experimental data available in the literature to see whether the failures of this basis set would show up in the complete series of molecules. In the literature we found five such molecules and it was reported which was the most stable conformer. Indeed, we found that predictions on the relative stability of conformers in those systems with this basis set and MP2 as well as DFT have a 60:40 chance, three being correct predictions and two being incorrect.*

*To get an idea whether or not it is really necessary to use the rather large basis sets reported in the literature, we repeated the study using the smaller 6-311G** basis, i.e. a valence triple zeta basis set augmented by polarization functions. Indeed, it turned out in the present study that in the case of this basis set, four out of five experimental results could be qualitatively reproduced. The one that was predicted incorrectly by calculations for the total minimum was also the one in which the relative energy of the higher form is the smallest of all results, hence one should not expect that calculations can predict the result that easily. Furthermore, the calculations cannot be expected to predict whether or not the accuracy of the experimental data in this case is sufficient; it could well be questionable because of the very small relative energy. Moreover, the inclusion of MP3 and MP4 did not improve the results. Note that CPU time consuming oscillations in some optimizations on the MP4 level forced us to use the MP3 optimized geometries for MP4 single-point calculations. Since in our previous study with the larger basis set we have seen that DFT reproduces experimental vibrational spectra rather well even in a case in which the experimental order of the conformers was not reproduced, we also report the vibrational wavenumbers as calculated on DFT level in comparison to the experiments where available, but we do not show plots of the spectra themselves.*

Keywords: MP2, MP3, MP4, DFT, conformational equilibria, vibrational spectra, vinylhalomethanes, vinylhalosilanes, vinylhalogermanes

Résumé

Il a été rapporté dans la littérature récente que la valence triple en base zêta, accrue par les fonctions diffuses et de polarisation, ne semble pas fiable pour les méthanes et silanes vinylmonohalogénés et dihalogénés, dont les halogènes sont soit le fluor ou le chlore. La conclusion principale était qu'une valence triple en base zêta avec fonctions de polarisation, est trop petite

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