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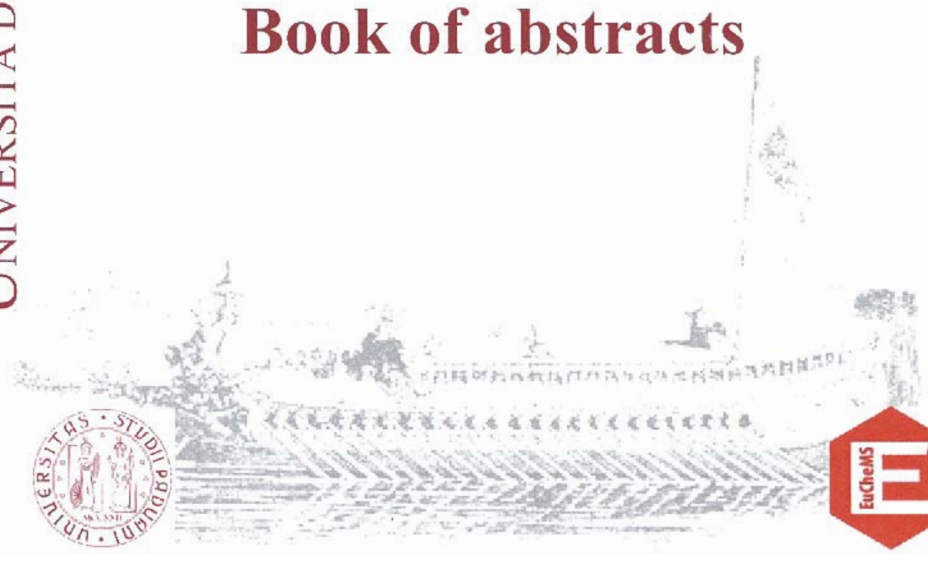
UNIVERSITÀ DEGLI STUDI DI PADOVA

7th European Conference on Computational Chemistry

Book of abstracts



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EXPERIMENTALLY MEASURED, AND *AB INITIO* CALCULATED ^{13}C-NMR SHIFTS FOR POTENTIALLY FLEXIBLE MOLECULES. ON THE CHOICE OF OPTIMAL GROUND-STATE GEOMETRY

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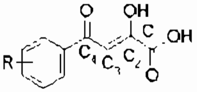
A large number of organic molecules elude the accurate empirical assignment of peaks in ^{13}CNMR spectra. We have studied a series of 13 molecules[1] in enolic form, as depicted on the Scheme 1, where is possible to have a considerable conformational flexibility around C1-C2 and C4-Ar bond.[2] Semiempirical calculations (PM6) [3] revealed a number of ground-state conformations having very close heats of formation – mostly well within the error of calculation method.

NMR shifts were calculated using Gaussian03 on the geometry optimized by PM6. In this kind of molecules, calculated NMR shifts depends heavily on the assumed conformation of molecule, because of different extents of electron delocalisation related to it. This set of values was correlated with experimental values, with little success (Figure 1).

Further study showed the difference in stability order of conformers calculated by various theoretical methods. On the other hand, it is shown that preferred conformations can be assessed by correlation with calculated ^{13}CNMR spectra of series of variably substituted compounds.

Calculated NMR shifts strongly depend on the basis set used for calculation (6-31G, 6-31++G, 6-311++G, 6311++G**), but very little on the Hamiltonian applied (DFT, MP2). For some molecules the objection can be raised on the effect of unrealistic long OH bonds produced by PM6. But their correction didn't change the pattern of ^{13}CNMR signals.



R- = H, 4-Me-, 4-Et, 4-*i*-Pr, 4-*t*-Bu, 4-NO_2, 4-OH, 3-OH, 4-MeO, 4-F-, 4-Cl-, 4-Br.

Scheme 1.

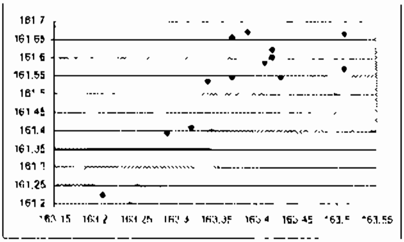


Figure 1. Experimental vs. calculated ^{13}CNMR shifts for carboxyl carbon.

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2. Huang, M.; Richards, W.G.; Grant, G.H. *J. Phys. Chem. A* **2005**, *109*, 5198-5202.
3. Stewart J.J.P., *J. Mol. Mod.* **2007**, 13, 1173-1213.

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