SEMI-EXPERIMENTAL (r_s/r_e) STRUCTURES FOR THE HEAVY ATOM BACKBONES OF TWO MODERATELY LARGE MOLECULES OBTAINED FROM MICROWAVE SPECTROSCOPY AND QUANTUM CHEMICAL CALCULATIONS

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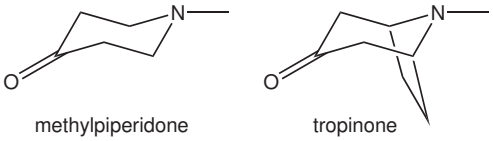

From recent microwave investigations of 1-methyl-4-piperidone[a] and tropinone[b] ground state rotational constants are available for the equatorial conformers of the normal species and the isotopologues with single substitution of all the heavy atoms. Vibration-rotation constants (alphas) were computed with Gaussian 03 (G03) for the B3LYP/cc-pVTZ model and used to convert ground state rotational constants into equilibrium rotational constants. Using the Kraitchman equations (r_s method), the equilibrium (r_e) Cartesian coordinates were determined for all the heavy atoms in the principal axis framework. Equilibrium bond lengths and bond angles are compared with those computed with the B3LYP/cc-pVTZ model. We have compared the ground state rotational constants computed with G03, after scaling by factors based on the normal species, with observed values. The agreement is within 0.1% for the full set of constants (0.04% for methyl-piperidone and 0.1% for tropinone). This agreement between experiment and theory is so good that it seems possible to use calculated ground state rotational constants in place of experimental ones for determining r_s/r_e structures for organic molecules of this size.

[a] L. Evangelisti, A. Lesarri, M. Jahn, E. Cocinero, W. Caminati, J.-U. Grabow J. Phys. Chem. A, submitted.
[b] E. J. Concinero, A. Lesarri, P. Ecija, J.-U. Grabow, J. A. Fernandez, F. Castano PCCP 12, 6076-6083 (2010).