SEMIEXPERIMENTAL EQUILIBRIUM STRUCTURES FOR THE EQUATORIAL CONFORMERS OF N-METHYLPIPERIDONE AND TROPINONE BY THE MIXED ESTIMATION METHOD

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N-methylpiperidone and tropinone, which contain a structural motif found in numerous alkaloids, are too large for determining an accurate equilibrium structure either by ab initio methods or by experiment. However, the ground state rotational constants of the parent species and of all isotopologues with a substituted heavy atom (^{13}C, ^{15}N, ^{18}O) are known from microwave spectroscopy.[a b] These constants have been corrected for the rovibrational contribution calculated from an ab initio cubic force field. These semiexperimental equilibrium rotational constants have been supplemented by carefully chosen structural parameters from medium level ab initio calculations. In the mixed estimation method, the two sets of data have been used in a weighted least-squares fit to determine a reliable equilibrium structure for both molecules. This work shows that it is possible to determine reliable equilibrium structures for large molecules (34 degrees of freedom in the case of tropinone). The method could be applied without too much difficulty to still larger molecules.

[a] L. Evangelisti, A. Lesarri, M. K. Jahn, E. J. Cocinero, W. Caminati, J.-U. Grabow J. Phys. Chem. A 115, 9545-9551 (2011)

[b] E. J. Cocinero, A. Lesarri, P. Écija, J.-U. Grabow, J. A. Fernández, F. Castaño PCCP 12, 6076-6083 (2010)