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

JEAN DEMAISON, *Laboratoire de Physique des Lasers, Atomes et Molécules, Université de Lille I, 59655 Villeneuve d'Ascq Cedex, France*; NORMAN C. CRAIG, *Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH 44074*; EMILIO J. COCINERO, *Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Ap. 644, E-48080 Bilbao, Spain*; JENS-UWE GRABOW, *Institut für Physikalische Chemie and Elektrochemie, Lehrgebiet A, Gottfried-Wilhelm-Leibniz Universität, Callinstrasse 3A, D-30167 Hannover, Germany*; ALBERTO LESARRI, *Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47011 Valladolid, Spain*; H. D. RUDOLPH, *Department of Chemistry, University of Ulm, D-89069 Ulm, Germany*.

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)