

MICROWAVE SPECTROSCOPY OF ALKALOIDS: THE CONFORMATIONAL SHAPES OF NICOTINE

JENS-UWE GRABOW, *Gottfried-Wilhelm-Leibniz-Universität, Institut für Physikalische Chemie und Elektrochemie, Lehrgebiet A, Callinstraße 3A, D-30167 Hannover, Germany*; S. MATA, J. C. LÓPEZ, I. PEÑA, C. CABEZAS, S. BLANCO, J. L. ALONSO, *Departamento de Química-Física y Química-Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47005 Valladolid, Spain*.

Nicotinoid alkaloids consist of two ring systems connected via a $C - C$ σ -bond: Joining pyridine either with a (substituted) pyrrolidine or piperidine ring system, pyrrolidinic or piperidinic nicotinoids are formed. Nicotine itself, consisting of pyridine and N-methylpyrrolidine, is the prototype pyrrolidinic nicotinoid. Its coupled heteroaromatic and heteroaliphatic ring systems exhibit three sites that allow for conformational flexibility: (I) puckering of the pyrrolidine ring (Eq./Ax. positions of the pyridine), (II) inversion of the N-methyl group (Eq./Ax. positions of the hydrogen), and (III) relative orientation of the two rings (Syn-Anti).

Two conformations of nicotine have been observed using the In-phase/quadrature-phase-Modulation Passage-Acquired-Coherence Technique (IMPACT) Fourier Transform Microwave (FTMW) spectrometer in Valladolid. The preferred conformations^a are characterized by an equatorial (Eq.) pyridine moiety and equatorial (Eq.) $N - CH_3$ stereochemistry. The planes of two rings are almost perpendicular with respect to each other while exhibiting two low energy conformations, Syn and Anti, that differ by a 180° rotation about the $C - C$ σ -bond. The Eq.-Eq. conformational preference is likely due to a weak hydrogen bond interaction between the nitrogen lone pair at the N-methylpyrroline and the closest hydrogen in pyridine. Supporting quantum-chemical calculations are also provided.

^aLavrich, R. J.; Suenram, R. D.; Plusquellic, D. F.; Davis, S. 58th International Symposium on Molecular Spectroscopy, Columbus, OH 2003, RH13.