MICROWAVE SPECTROSCOPY OF ALKALOIDS: THE CONFORMATIONAL SHAPES OF NICOTINE

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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 heteoaromatic 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 perperdicular 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.

[a]Lavrich, R. J.; Suenram, R. D.; Plusquellic, D. F.; Davis, S. 58th International Symposium on Molecular Spectroscopy, Columbus, OH 2003, RH13.