MICROWAVE STUDY OF A HYDROGEN-TRANSFER-TRIGGERED METHYL-GROUP INTERNAL ROTATION IN 5-METHYLTROPOLONE

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We present here the first experimental and theoretical study of the microwave spectrum of 5-methyltropolone, which can be visualized as a 7-membered aromatic carbon ring with a five-membered hydrogen-bonded cyclic structure at the top and a methyl group at the bottom. The molecule exhibits two large-amplitude motions, an intramolecular hydrogen transfer and a methyl torsion. The former motion is particularly interesting because transfer of the hydrogen atom from the hydroxyl to the carbonyl group induces a tautomerization in the molecule, which then triggers a 60° internal rotation of the methyl group. Measurements were carried out by Fourier-transform microwave spectroscopy in the 8 to 24 GHz frequency range. Theoretical analysis was carried out using a tunneling-rotational Hamiltonian based on a G_{12}^m extended-group-theory formalism. Our global fit of 1015 transitions to 20 molecular parameters gave a root-mean-square deviation of 1.5 kHz. The tunneling splitting of the two $J = 0$ levels arising from a hypothetical pure hydrogen transfer motion is calculated to be 1310 MHz. The tunneling splitting of the two $J = 0$ levels arising from a hypothetical pure methyl-top internal rotation motion is calculated to be 885 MHz. Some theoretical difficulties in interpreting the low-order tunneling parameters in this and the related molecule 2-methylmalonaldehyde will be discussed.