

ROTATIONAL SPECTROSCOPIC STUDIES OF *PARA*-NITROBENZOIC ACID, *PARA*-AMINOBENZOIC ACID, *PARA*-CHLOROBENZOIC ACID, AND *PARA*-HYDROXYBENZOIC ACID

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para-substituted benzoic acids, such as *para*-nitrobenzoic acid, *para*-aminobenzoic acid, *para*-chlorobenzoic acid, and *para*-hydroxybenzoic acid, play important roles in atmospheric chemistry and are used as precursors for a wide range industrial products. Surprisingly, there are no high-resolution spectroscopic studies of these compounds, and we describe here their rotational spectroscopic investigations combined with electronic structure calculations. The rotational spectra were recorded using a 2 to 6 GHz chirped-pulse Fourier transform microwave spectrometer, which is based on the design by Pate et al.¹ Experimentally, all four substituted benzoic acids were found to exist in the *cis*-configuration, the global minimum energy configuration, of the carboxylic acid group. In all instances, except *para*-aminobenzoic acid, the global minimum structure is planar. Nudged elastic band calculations² for the wagging motion of the amino group in *para*-aminobenzoic acid suggest that it is a barrierless large amplitude motion and indeed, no tunnelling splittings were observed in the spectra. For *para*-chlorobenzoic acid, the nuclear quadrupole hyperfine structures of the ³⁵Cl and ³⁷Cl isotopologues were measured and analyzed. In the case of *para*-hydroxybenzoic acid two conformers were experimentally and theoretically identified. We noticed in the theoretical structures of the *trans*-conformers that the carboxylic acid group is pushed slightly out of plane, depending on the nature of the *para*-substituent. We were able to correlate the out-of-plane angle with the corresponding Hammett constant³ via the molecular electrostatic potential.⁴ ¹Pérez, C., et al., *Chem. Phys. Lett.* 2013, 571, 1–15. ²Åsgeirsson, V., et al., *J. Chem. Theory Comput.* 2021, 17 (8), 4929–4945. ³Hansch, C., et al., *Chem. Rev.* 1991, 91 (2), 165–195. ⁴Sayed, F. B., et al., *New J. Chem.* 2009, 33 (12), 2465–2471.