A MICROWAVE AND COMPUTATIONAL STUDY OF CARBOXYLIC ACID ANHYDRIDES

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Microwave spectra for a series of carboxylic acid anhydrides derived from acetic acid, pivalic acid, benzoic acid, and trifluoroacetic acid are reported. All semi-rigid rotor spectra, including those of the A states of species with a single methyl rotor, were quickly assigned using the new rotational spectral fitting program, DAPPERS. The observed internal rotor states of the single-rotor anhydrides and the double rotor spectra of parent and D-6 acetic anhydride were fit using XIAM. The aid of closed loops in the assignment of the acetic anhydride spectrum will be briefly discussed along with remaining challenges in the spectral analysis. The heavy atom structure of pivalic anhydride and pivalic trifluoroacetic anhydride were determined through isotopic substitution and Kraitchman analysis. Trends of the dihedral angle between anhydride carbonyls are studied through an analysis of M06-2X/6-311++G(d,p) computational values, which are shown to be in good agreement with those experimentally determined for pivalic and pivalic trifluoroacetic anhydrides. The V_3 barriers measured for acetic anhydride, acetic trifluoroacetic anhydride, and acetic pivalic anhydride are compared with those for a wide variety of molecules exhibiting methyl group internal rotation in an acetate functionality. A straightforward synthesis for mixed carboxylic anhydrides will also be described.