

CONFORMERS OF VANILLIC ACID: A ROTATIONAL SPECTROSCOPIC AND THEORETICAL STUDY

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Vanillic acid is produced in significant quantities in forest fires and is used as a biomass burning tracer for softwood and hardwood combustion events. Vanillic acid has also been found in secondary organic aerosol and can be oxidized in aqueous atmospheric processes to humic-like substances. Hydrates of vanillic acid play undoubtedly important roles in the processes involved, and we present here a study of conformers of the vanillic acid monomer to lay the groundwork for subsequent studies of the mono- and di-hydrates.

Computationally, 12 conformers were found within an energy range of 51 kJ/mol using the Conformer–Rotamer Ensemble Sampling Tool (CREST).¹ The two lowest energy conformers could then be identified in the spectrum recorded with a chirped pulse Fourier transform microwave spectrometer in the 2-6 GHz range. The deviation between experimental and theoretical rotational constants determined at the MP2/aug-cc-pVTZ and DFT B3LYP-D3(BJ)/def2-TVPZ levels of theory is less than 1%. No tunnelling splitting was observed which suggests a relatively high barrier to methyl internal rotation, in agreement with other, previously studied vanillin derivatives. Furthermore, no c-type transitions could be observed in agreement with computed zero c-dipole moment component of the lowest energy structures. From the theoretical structures, it is apparent that intra-molecular hydrogen bonds play a significant role in stabilizing the lowest energy conformers. To further explore the intra-molecular interactions in vanillic acid, QTAIM and NCI analyses were performed.

¹P. Pracht, F. Bohle, S. Grimme, *Phys. Chem. Chem. Phys.* 22, 7169-7192 (2020).