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IR and NMR Spectroscopic Correlation of Enterobactin by DFT.

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Abstract.
Emerging and re-emerging epidemic diseases pose an ongoing threat to global health. Currently, Enterobactin and Enterobactin derivates have gained interest, owing to their potential application in the pharmaceutical field. As it is known [J. Am. Chem. Soc *(1979)* 101, 20, 6097-6104], Enterobactin (H_6EB) is an efficient iron carrier synthesized and secreted by many microbial species. In order to facilitate the elucidation of enterobactin and its analogues, here we propose the creation of a H_6EB standard set using Density Functional Theory Infrared (IR) and NMR spectra. We used two exchange-correlation (xc) functionals (PBE including long-range corrections –LC-PBE– and mPW1), 2 basis sets (QZVP and 6-31G(d)) and 2 grids (fine and ultrafine) for most of the H_6EB structures dependent of dihedral angles. The results show a significant difference between the O-H and N-H bands, while the C=O amide and O-(C=O)- IR bands are often found on top of each other. The NMR DFT calculations show a strong dependence on the xc functional, basis set, and grid used for the H_6EB structure. Calculated ^{1}H and ^{13}C NMR spectra enable the effect of the solvent to be understood in the context of the experimental measurements. The good agreement between the experimental and the calculated spectra using LC-PBE/QZVP and ultrafine grid suggest the possibility of the systems reported here to be considered as a standard set. The dependence of electrostatic potential and frontier orbitals with the catecholamide dihedral angles of H_6EB are described. The matrix-assisted laser desorption/ionization time of the flight mass spectrometry (MALDI-TOF MS) of H_6EB is also reported of manner to enrich the knowledge about its reactivity.

Key words: Enterobactin, NMR, FT-IR, DFT and MALDI-TOF MS.