**Abstract**

We Study The Structural And Energetic Properties Of Binary Ionic Porphyrin Molecular Complexes [H4tpps4]2−∙∙∙Sntp Using Quantum Chemical Techniques. As The Axial Ligands And The Protonation Of Pyridine Sites Highly Influence The Structure And Coordination Of Metal‐Containing Porphyrin, Various Structures Of Sntp In The Presence And Absence Of Axial Ligands And Pyridine Protons Were Considered. The Constructed Porphyrins Were Then Made To Interact Face To Face, And The Formed Complexes Were Optimized At The Hf/Sto‐3g Level Of Theory. The Stability And Stack‐Like Interaction Of The Complexes Were Analyzed Through Interplanar Spacing, Planar Angle, And Edge‐To‐Edge Distance. The Structural Parameters Emphasize The Importance Of Axial Ligands For The Formation Of Stack‐Like Structures. The Complex That Contains Axial Ligands With Pyridine Protons, Namely [H4tpps4]2−∙∙∙[X'snxtph]4+, Shows A Perfectly Stacked Layer With A Reasonable Interplanar Distance, Which Is Confirmed From The Calculated Counterpoise Interaction And Deformation Energies. The Energetic Parameters Were Found To Correlate Well With The Obtained Geometries. The Molecular Electrostatic Potential (Mep) Maps Were Obtained To Infer The Presence Of Nonbonded Interaction Between The Binary Ionic Porphyrins.