Magnesiumphthalocyanine (MgPc) is a near-IR-active photoconductor used for laser printers. Our recent structure analysis revealed that the MgPc molecule is not flat in the solid state, but the central Mg atom is projected upward, forming a pyramidal structure. On top of the Mg atom along the stacking axis, the azamethine nitrogen atom is located with a distance of only 2.70 Å. The present arrangement is quite indicative of an appreciable interaction along the stacking axis through the formation of a five-coordinate Mg-complex. Therefore, the Mg–N interaction along the molecular stack has been investigated by energy partition analysis based on semi-empirical MO calculations. The Mg–N bond energy along the molecular stack is found to be roughly one-third of the Mg–N bond in the molecular plane and approximately one-half of the Mg–O bond of the six-coordinate MgPc-complexes: MgPc/(H2O)2(NMP)2 and MgPc/(2-methoxyethanol)2. These results indicate the formation of five-coordinate MgPc complexes along the stacking axis, showing considerable π–π interactions through the central Mg atom.  

Keywords: PHTHALOCYANINE, ELECTRONIC STRUCTURE, INTERMOLECULAR INTERACTIONS