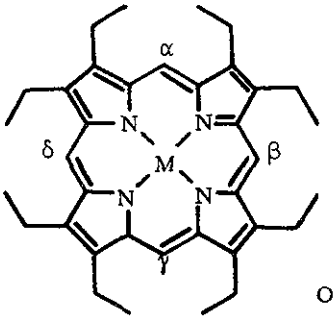
SYNTHESIS AND STRUCTURE OF MESO-SUBSTITUTED PORPHYRIN METAL COMPLEXES

Hisanobu Ogoshi, Ei-ichi Watanabe, Hiroshi Sugimoto,
Satoshi Nishimura, and Zen-ichi Yoshida
Department of Synthetic Chemistry, Faculty of Engineering,
Kyoto University, Yoshida, Kyoto 606

The synthesis of meso-substituted octaethylporphyrin is reported: nitration of octaethylporphyrin with $Zn(NO_3)_2 \cdot 6H_2O$ yields mono-, di-, tri-, and tetranitro-octaethylporphyrinatozinc(II) and formylation of copper, nickel and palladium porphyrin complexes yields monoformyl-(Cu^{II}, Ni^{II}, and Pd^{II}) and diformyl(Cu^{II})octaethylporphyrin metal complexes. The exclusive α,γ-orientation for dinitro- and diformylporphyrins is proved on the basis of n.m.r. spectra of the free bases obtained by demetallation of the complexes. Specific α,γ-orientation of octaethylporphyrin complexes has been interpreted in terms of relative stability of disubstituted porphyrin metal complexes (α,β and α,γ). The strain energy of α,γ-disubstituted complex(D_{2h}) would be less than that of the α,β-disubstituted complex(C_{2v}). The trend of the substitution reaction of porphyrin diacid will be compared with present results.



Octaethylporphyrin - M^{II}