Phenyl Ring Rotation in Metal Complexes of Tetraphenylporphyrin Derivatives

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Summary Variable-temperature n.m.r. spectra of a series of In, Ru, and Ti complexes of substituted tetraphenylporphyrins show that phenyl ring rotation occurs on the n.m.r. time scale if the phenyl ring *ortho*-substituents are hydrogen.

PAPERS reporting *X*-ray diffraction results on tetraphenylporphyrin complexes commonly emphasize the role of steric repulsion between the phenyl and pyrrole hydrogens in preventing the phenyl rings from becoming even approximately coplanar with the porphyrin ring.[1] In the tetraphenylporphyrin metal complexes in which the axial sites on the metal are not the same, the *ortho* and *meta* hydrogens on the phenyl rings of the tetraphenylporphyrin are nonequivalent and yield an ABCD pattern in the ^{1}H n.m.r. spectrum. In the case of indium tetra-(*p*-tolyl)porphyrin chloride[2] and ruthenium carbonyl tetra-(*p*-isopropylphenyl)-porphyrin[3] we have observed that the nonequivalence can be averaged to yield an apparent AB pattern in the temperature range 30—120 °C. In these reports the averaging of the nonequivalent phenyl proton resonances was attributed to rotation about the porphyrin *meso*-carbon–phenyl-carbon bond, though it was recognized that axial ligand exchange could result in the same net effect on the n.m.r. spectrum. We now report variable-temperature n.m.r.

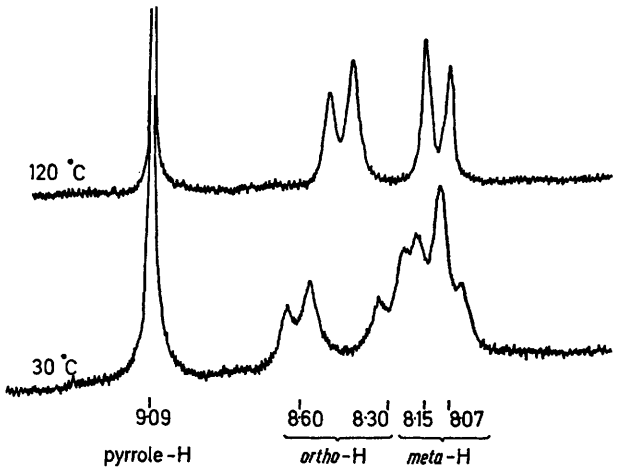

FIGURE. ^{1}H N.m.r. spectra (100 MHz) of indium tetra-(*p*-trifluoromethyl)porphyrin chloride in $Cl_2HCCHCl_2$ at 30 and 120 °C. Slow exchange chemical shifts are in p.p.m. downfield from Me_4Si.

studies of an extensive series of substituted metallotetraphenylporphyrins in which the metal, the axial ligands on the metal, and the substituents on the phenyl rings are varied, to distinguish between the possible mechanisms for the averaging, observed in the n.m.r. spectra.

Averaging of nonequivalent phenyl hydrogen n.m.r. resonances occurs in the temperature range 10—100 °C for indium tetra-(*p*-R-phenyl)porphyrin chloride (R = Me, Pr^i, and CF_3), titanyl tetra-(*p*-R-phenyl)porphyrin (R = Pr^i and CF_3), ruthenium carbonyl tetra-(*p*-isopropylphenyl)-porphyrin with ethanol or 4,5-dimethylpyridazine in the sixth co-ordination position and ruthenium carbonyl tetra-(*p*-trifluoromethylphenyl)porphyrin with tetrahydrofuran in the sixth site. The rate of averaging is independent of concentration. Replacement of the *ortho* hydrogens on the phenyl rings of the tetra-arylporphyrins with fluorine or methyl slows down the rate of averaging so that it cannot be observed by dynamic n.m.r. studies. Thus, no averaging of fluorine resonances in the ^{19}F n.m.r. spectrum of indium tetra(pentafluorophenyl)porphyrin chloride is observed up to 130 °C in tetrachloroethane. Similarly no averaging of methyl hydrogen resonances is seen at temperatures up to 130 °C in indium tetra-(*o*-tolyl)porphyrin chloride, titanyl tetra-(*o*-tolyl)porphyrin, titanyl tetra(mesityl)porphyrin, ruthenium carbonyl tetra-(*o*-tolyl)porphyrin pyridine, and ruthenium carbonyl tetramesitylporphyrin pyridine.

Addition of Bu^n_4NCl to solutions of any of the indium porphyrin chloride complexes results in averaging of the nonequivalent phenyl resonances at room temperature. This process is concentration dependent.

Clearly there are two processes occuring in the indium chloro complexes. In the presence of excess of chloride averaging of nonequivalent phenyl resonances occurs *via* an associative chloride exchange for the indium chloro-complexes. In the absence of excess of chloride the n.m.r. averaging occurs over the same temperature range for the indium complexes as for the titanium and ruthenium complexes when the phenyl *ortho*-substituents are hydrogen and does not occur when the *ortho*-substituents are fluorine or methyl. The similarity of activation energy would not be expected for a concentration-independent ligand exchange, but is fully consistent with phenyl ring rotation.

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[1] See *e.g.*, (a) E. B. Fleischer, *Accounts Chem. Res.*, 1970, **3**, 105; (b) D. M. Collins, R. Countryman, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1972, **94**, 2066.
[2] W. Bhatti, M. Bhatti, S. S. Eaton, and G. R. Eaton, *J. Pharm. Sci.*, 1973, **62**, 1574.
[3] S. S. Eaton, G. R. Eaton, and R. H. Holm, *J. Organometallic Chem.*, 1972, **39**, 179.