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Effects of Para Substituent and Metal Ion on Rates of Phenyl Ring Rotation in Ruthenium, Indium, and Titanium Complexes of Para-Substituted Tetraphenylporphyrins

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Abstract: Rates of phenyl ring rotation in para-substituted tetraphenylporphyrin complexes with ruthenium carbonyl 4-*tert*-butylpyridine, indium chloro, and titanyl ions were studied by variable temperature ^{1}H NMR of the phenyl resonances. Para substituents examined were trifluoromethyl, chloro, methyl, isopropyl, methoxy, and diethylamino (ruthenium, indium, titanyl) and hydroxy (titanyl). Activation parameters obtained by total line shape analysis are in the ranges $\Delta G^{\ddagger}_{298}$ = 14.3–18.6 kcal/mol, $\Delta H^{\ddagger}$ = 11.2–17.5 kcal/mol, and $\Delta S^{\ddagger}$ = −3.7 to −12.4 eu. Rates as a function of metal ion increase in the order ruthenium < indium < titanyl. Rates are faster for electron-donating substituents than for electron-withdrawing subsituents, but do not give a linear correlation with Hammett σ_p values.

Rotation of phenyl rings in tetraphenylporphyrin complexes of Ru,[1-4] Ge,[5] Ti,[3,4,6] In,[3,4,7] and Fe[8] has been reported. Phenyl ring substituents have recently been shown to influence rates of copper ion incorporation,[9] rates of inversion of ferric porphyrins,[10] rates of axial ligand exchange in ruthenium carbonyl porphyrins,[11] basicity and electronic spectra of free porphyrins,[9,12] equilibrium constants for axial ligation in $(VO)^{2+}$,[13] Fe,[14,15] Co,[16] Ni,[13] and Zn[17] porphyrins, and redox potentials of free porphyrins,[18,19] Co,[16,19] Fe,[20] and Ni[21] porphyrins. A previous paper in this series demonstrated that the dynamic process observed in the ^{1}H NMR of the phenyl resonances of ruthenium carbonyl, indium chloro, and titanyl complexes of para-substituted tetraphenylporphyrins was due to phenyl ring rotation.[4] This report concerns the effect of para substituents and metal ion on the rate of the phenyl ring rotation for an extended series of para substituents for these metals, and includes activation parameters obtained by total line shape analysis.

Experimental Section

Physical Measurements. Infrared spectra were recorded as Nujol or halocarbon mulls on Perkin-Elmer 710 or 337 grating spectrometers. Visible spectra were obtained in chloroform solutions on a Beckman Acta V spectrometer. Data are given below with wavelengths in nanometers and log ϵ in parentheses. ^{1}H NMR spectra were run at power levels well below saturation on a Varian HA-100 spectrometer equipped with a variable-temperature probe. Spectra were obtained with the spectrometer locked on the solvent resonance (1,1,2,2-tetrachloroethane). ^{1}H NMR chemical shifts were measured with respect to 1,1,2,2-tetrachloroethane ($C_2H_2Cl_4$) and are reported below in parts per million downfield of Me_4Si using a correction of 5.96 ppm for the chemical shift of 1,1,2,2-tetrachloroethane at ca. 32 °C.

Preparation of Compounds. The following compounds were prepared and characterized by literature methods: Ru(CO)(*p*-R-TPP)(*t*-Bupy),[22] R = CF_3, Cl, Me, OMe, Et_2N;[11] Ru(CO)(*p*-*i*-Pr-TPP)(*t*-Bupy);[1] TiO(*p*-R-TPP), R = CF_3, *i*-Pr;[4] In(*p*-R-TPP)Cl, R = CF_3, *i*-Pr;[4] In(*p*-R-TPP)Cl, R = Me, OMe;[23] H_2(*p*-CF_3-TPP);[4] H_2(*p*-R-TPP), R = Cl, Me, OMe;[24,25] H_2(*p*-*i*-Pr-TPP);[1] H_2(*p*-Et_2N-TPP).[26] All chromatography was on Baker 0537 alumina.

TiO(*p*-R-TPP), R = Cl, Me, OMe, Et_2N. These compounds were prepared by the method reported for TiO(octaethylporphyrin).[27] Crude complexes were chromatographed on alumina and recrystallized from dichloromethane/hexane. Details of chromatography conditions, yield, and characterization data are given below for individual complexes.

TiO(*p*-Cl-TPP). Chromatography. The crude product was put on a column in benzene. Free porphyrin was eluted with benzene and the complex eluted with 1:1 CH_2Cl_2–benzene: yield 91%; IR $\nu_{Ti=O}$ 840 cm^{-1}; visible spectrum 403 sh (4.62), 424 (5.69), 514 (3.49), 552 (4.40), 590 nm (3.56); ^{1}H NMR (0 °C) pyrrole H, 9.18 (singlet), *o*-H, 8.44, 8.05 (doublets), *m*-H, 7.87, 7.77 ppm (doublets). Anal. Calcd for $C_{44}H_{24}N_4Cl_4TiO$: C, 64.89; H, 2.97; N, 6.88; Cl, 17.41. Found: C, 64.77; H, 3.24; N, 6.88; Cl, 17.21.

TiO(*p*-Me-TPP). Chromatography. The crude complex was put on a column in trichloroethylene (C_2HCl_3). Free porphyrin was eluted with C_2HCl_3 and the complex eluted with 1:1 C_2HCl_3–$CHCl_3$: yield 57%; IR $\nu_{Ti=O}$ 975 cm^{-1}; visible spectrum 406 sh (4.61), 426 (5.70), 516 (3.51), 553 (4.40), 5.92 nm (3.75); ^{1}H NMR (0 °C) pyrrole H, 9.22 (singlet), *o*-H, 8.40, 8.00 (doublets), *m*-H, 7.68, 7.57 (doublets), CH_3, 2.74 ppm (singlet). Anal. Calcd for $C_{48}H_{36}N_4TiO$: C, 78.68; H, 4.95; N, 7.65. Found: C, 78.56; H, 5.08; N, 7.98.

TiO(*p*-OMe-TPP). Chromatography. The crude complex was put on a column in benzene. Free porphyrin was eluted with benzene and the complex eluted with 1:1 CH_2Cl_2–benzene: yield 58%; IR $\nu_{Ti=O}$ 970 cm^{-1}; visible spectrum 408 sh (4.63), 429 (5.62), 517 (3.51), 554 (4.34), 596 nm (3.88); ^{1}H NMR (0 °C) pyrrole H, 9.19 (singlet), *o*-H, 8.42, 8.03 (doublets), *m*-H, 7.39, 7.28 (doublets), CH_3, 4.12 (singlet). These values are in good agreement with those published for an alternate preparation of the compound.[6] Anal. Calcd for $C_{48}H_{36}N_4TiO_5$: C, 72.36; H, 4.55; N, 7.03. Found: C, 72.39; H, 4.26; N, 7.05.

TiO(*p*-Et_2N-TPP). The reaction time was shortened to 1 h and the diethylene glycol was removed by extraction from a chloroform solution of the product into 1:1 methyl ethyl ketone–H_2O. The crude product was put on a column in benzene. Free porphyrin was eluted with benzene and the product eluted with 1:1 $CHCl_3$–benzene: yield 64%; IR $\nu_{Ti=O}$ 975 cm^{-1}; visible spectrum 398 (4.80), 460 (5.17), 568

(4.18), 620 nm (4.41); ^{1}H NMR (0 °C) pyrrole H, 9.29 (singlet), *o*-H, 8.35, 7.99 (doublets), *m*-H, 7.16, 7.06 (doublets), CH_2, 3.66 (quartet), CH_3, 1.42 (triplet). Anal. Calcd for $C_{60}H_{64}N_8TiO$: C, 74.98; H, 6.71; N, 11.66. Found: C, 74.70; H, 6.53; N, 11.53.

TiO(*p*-OH-TPP). TiO(*p*-OMe-TPP) (250 mg) was dissolved in 150 mL of CH_2Cl_2. The solution was cooled in a dry ice–acetone bath and 3 mL of 15% BBr_3 in CH_2Cl_2 was added. The solution was slowly warmed to room temperature and 100 mL of H_2O added. After stirring for 1 h, the green precipitate was filtered off and washed with H_2O. Recrystallization from ethanol–H_2O gave the product as a monohydrate: yield 75%; IR ν_{TiO} 910 cm^{-1}; visible spectrum (1:20 Me_2SO–$CHCl_3$) 431 (5.58), 519 (3.54), 556 (4.31), 597 nm (3.97); ^{1}H NMR (0 °C, 1:10 Me_2SO–tetrachloroethane) pyrrole H, 9.20 (singlet), *o*-H, 8.27, 7.91 (doublets), *m*-H, 7.29, 7.21 (doublets), OH, 9.57 (singlet, disappears when D_2O added). Anal. Calcd for $C_{44}H_{30}N_4O_6Ti$: C, 69.66; H, 3.97; N, 7.39. Found: C, 69.76; H, 3.94; N, 7.65.

In(*p*-Cl-TPP)OH. The complex was prepared by the method reported for In(*p*-CF_3-TPP)Cl.[4] The $CHCl_3$ eluent from the chromatography of the product on alumina was immediately taken to dryness under vacuum and the product was recrystallized from CH_2Cl_2–hexane: yield 85%; visible spectrum 405 sh (4.59), 427 (5.78), 524 (3.52), 562 (4.32), 601 nm (3.95); ^{1}H NMR pyrrole H, 9.07 (singlet), *o*-H, 8.38, 8.02 (doublets), *m*-H, 7.84, 7.74 (doublets). Anal. Calcd for $C_{44}H_{25}N_4InCl_4O$: C, 59.90; H, 2.86; N, 6.35; Cl, 16.07. Found: C, 60.14; H, 2.82; N, 6.18; Cl, 15.81.

In(*p*-Cl-TPP)Cl. In(*p*-Cl-TPP)OH (110 mg) was dissolved in 10 mL of 1,1,2,2-tetrachloroethane and heated in nitrogen atmosphere at 90 °C for 1.5 h. The solvent was removed under vacuum and the product recrystallized from CH_2Cl_2–hexane. Conversion was quantitative: visible spectrum 406 sh (4.63), 427 (5.83), 523 (3.55), 560 (4.38), 599 nm (3.97); ^{1}H NMR pyrrole H, 9.10 (singlet), *o*-H, 8.34, 8.04 (doublets), *m*-H, 7.83, 7.75 (doublets). Anal. Calcd for $C_{44}H_{24}N_4InCl_5$: C, 58.67; H, 2.69; N, 6.22; Cl, 19.68. Found: C, 58.64; H, 2.80; N, 6.18; Cl, 19.60.

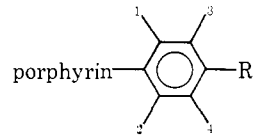
In(*p*-Et_2N-TPP)Cl. The complex was prepared by the method reported for In(*p*-CF_3-TPP)Cl[4] except that the mixture of acetic acid, sodium acetate, and $InCl_3$ was refluxed for 5 min before the free porphyrin was added. Reaction time was 2.5 h. The crude product was put on an alumina column in C_2HCl_3. Free porphyrin was eluted with C_2HCl_3 and the product eluted with $CHCl_3$. Recrystallization was from CH_2Cl_2–heptane: yield 55%; visible spectrum 402 sh (4.81), 460 (5.16), 538 sh (3.77), 5.81 (4.07), 633 nm (4.51); ^{1}H NMR (0 °C) pyrrole H, 9.20 (singlet), *o*-H, 8.24, 7.97 (doublets), *m*-H, 7.12, 7.04 (doublets), CH_2, 3.63 (quartet), CH_3, 1.39 (triplet). Anal. Calcd for $C_{60}H_{64}N_8InCl$: C, 68.80; H, 6.16; N, 10.70; Cl, 3.38. Found: C, 68.84; H, 5.92; N, 10.75; Cl, 3.39.

NMR Spectra. ^{1}H NMR spectra were run on samples freshly prepared in a nitrogen atmosphere. Temperatures were calibrated after each set of data using methanol and ethylene glycol standards and the temperature-dependent shifts of Van Geet.[28] Temperature calibrations were reproducible to ±0.5 °C. Temperatures are considered accurate to ±1.5 °C.

Spectra in the slow exchange limit were analyzed to obtain spin–spin coupling constants and the temperature dependence of nonexchanging chemical shifts and linewidths. Fast-exchange spectra were analyzed to obtain coupling constants and the temperature dependence of chemical shifts and line widths. Slow-exchange chemical shifts were extrapolated through the intermediate exchange region and agreed well with the fast exchange chemical shifts. Line widths were interpolated between slow- and fast-exchange limits. No temperature dependence of the coupling constants was observed.

Simulated spectra were obtained using DNMR3A, a modified version of Binsch's program DNMR3[29] provided by C. H. Bushweller. All spectra were treated as four spin systems. In the complexes with *p*-CF_3 and *p*-Me groups, unresolved long-range coupling of the phenyl ring protons to the nuclei in the substituents caused noticeable line broadening. As noted by Drakenberg and Carter,[30] the neglect of unresolved coupling is a potential source of systematic error in line shape analysis, leading to overestimates of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. The error in $\Delta S^{\ddagger}$ is larger than that in $\Delta H^{\ddagger}$. The errors are less significant, however, for systems with large chemical shift differences where kinetic data can be obtained over a longer temperature interval and data points at the extremes of the kinetic range have less impact on the activation parameters. For the compounds reported here, the chemical shift differences between nonequivalent ortho protons are 20–40 Hz. The effects of unresolved coupling are markedly less than for the 10-Hz shift difference analyzed by Drakenberg and Carter.[30] The weighted least-squares procedure which is used to obtain the activation parameters from the rate constants also takes into account the greater uncertainty of data points near the extremes of the kinetic range. Since the $\Delta S^{\ddagger}$ values for the *p*-CF_3 and *p*-Me complexes are not systematically larger than the $\Delta S^{\ddagger}$ values for complexes without unresolved coupling, it is felt that unresolved coupling is not a significant source of error in the activation parameters for the compounds.

Coupling constants varied with para substituent but were independent of metal ion. The numbering of the nuclei is given in the di-

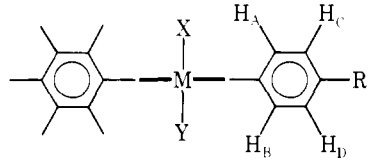


agram. Coupling constants for each para-substituted porphyrin are listed below in the order J_{12}, J_{13}, J_{14}, J_{23}, J_{24}, J_{34}. Values are accurate to ±0.2 Hz; R = CF_3, 1.5, 8.0, 0.5, 0.5, 8.0, 1.5; R = Cl, 2.2, 8.1, 0.5, 0.5, 8.2, 2.3; R = Me, 1.9, 7.9, 0.6, 0.6, 7.9, 1.9; R = *i*-Pr, 1.8, 7.9, 0.6, 0.6, 7.9, 1.8; R = OMe, 2.1, 8.1, 0.6, 0.6, 8.1, 2.2; R = OH, 2.1, 8.2, 0.6, 0.6, 8.2, 2.3; R = Et_2N, 2.0, 8.2, 0.6, 0.6, 8.2, 2.2.

Rate constants were obtained by visual comparison of calculated and observed spectra and are accurate to 8–10% except near the slow- and fast-exchange limits where uncertainties are ca. 20%. Rate constants at 10–16 temperatures were measured over intervals of 65–110 °C for each compound. Activation parameters were determined from weighted least-squares fits to Arrhenius (ln k_r vs. $1/T$) and Eyring (ln (hk_r/kT) vs. $1/T$) equations.

Results and Discussion

^{1}H NMR Spectra. Since the phenyl rings are at an angle to the porphyrin plane in metal complexes of tetraphenylporphyrins,[2] the presence of different ligands on the two sides of the metalloporphyrin plane results in nonequivalence of the ortho protons and of the meta protons on the phenyl ring provided that axial ligand interchange (X ⇌ Y) and phenyl ring



rotation are slow on the NMR time scale. The phenyl protons of MXY complexes of para-substituted tetraphenylporphyrins are thus an ABCD spin system. The slow exchange ^{1}H NMR spectra of MXY(*p*-R-TPP), MXY = Ru(CO)(*t*-Bupy), InCl, and $(TiO)^{2+}$, exhibit typical ABCD spectra. The chemical shift difference between nonequivalent ortho protons (A, B) and meta protons (C, D) range from about 20 and 6 Hz, respectively, in the ruthenium complexes to about 40 and 10 Hz, respectively, in the titanyl complexes. Variable temperature spectra in 1,1,2,2-tetrachloroethane solution were studied for complexes with R = CF_3, Cl, Me, *i*-Pr, OMe, and Et_2N. The spectra of TiO(*p*-Cl-TPP), which are typical of the line shape changes observed in all the complexes, are shown in Figure 1. At fast exchange an AA′BB′ pattern is obtained. All line shape changes were reversible with temperature. We have previously shown that for ruthenium carbonyl (*t*-Bupy), indium chloro, and titanyl complexes of tetraphenylporphyrins, averaging of resonances for nonequivalent phenyl protons is due to rotation of the phenyl rings and not to interchange of the X and Y groups bound to the metal ion.[4] Thus we can use the kinetic data obtained by computer simulation of the variable temperature spectra to determine the effect of both metal ion and para substituents on the barrier to rotation about the bond between the phenyl ring and the porphyrin ring.

Activation Parameters. Activation parameters were obtained by weighted (using the uncertainty of the rate constant)

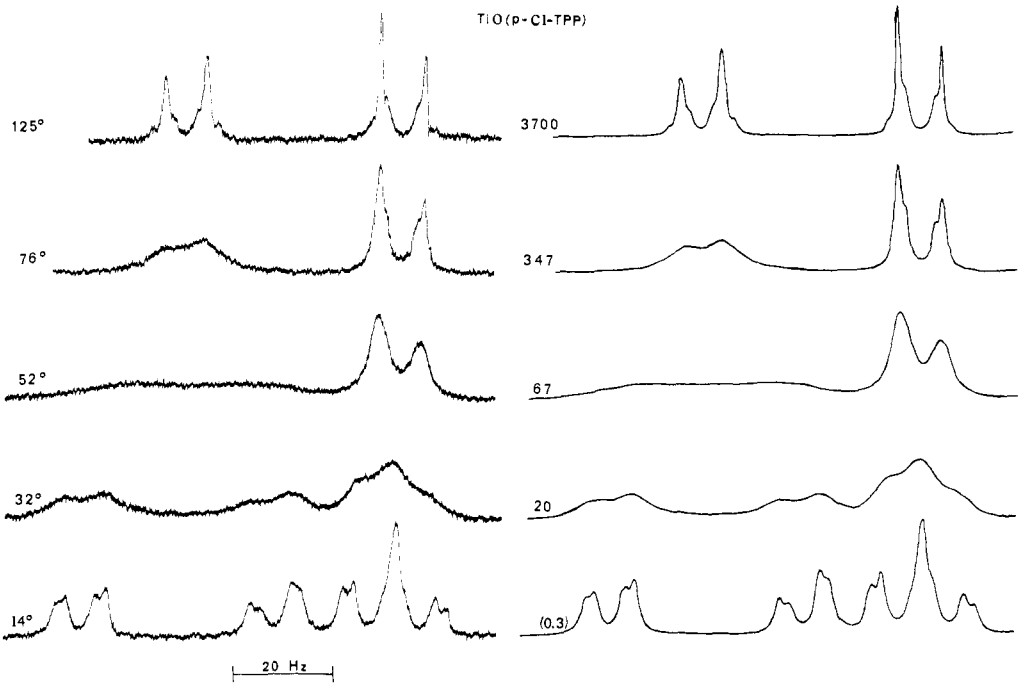


Figure 1. 100-MHz ^1H NMR spectra of the phenyl protons in TiO(*p*-Cl-TPP) in $C_2H_2Cl_4$ at various temperatures compared with spectra calculated by line shape analysis. Rate constants are in s^{-1}.

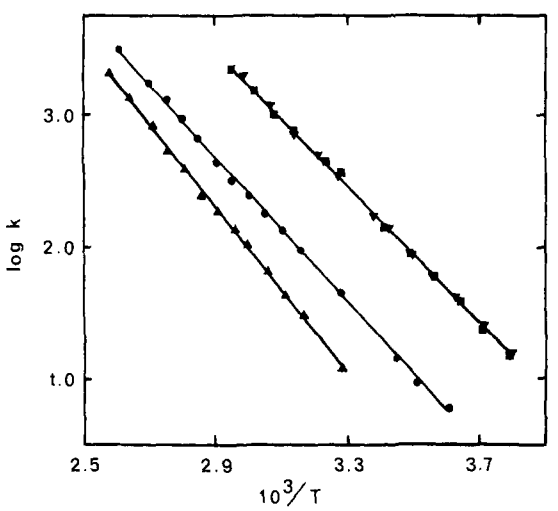


Figure 2. Arrhenius plots for phenyl ring rotation in TiO(*p*-R-TPP): (▲) R = CF_3; (●) R = OMe; (■, ▼) two independent sets of data for R = Et_2N.

least-squares fits of the experimental rate constants to the Arrhenius and Eyring equations. Arrhenius plots for several of the titanyl complexes are shown in Figure 2. In no case was there evidence of deviation from linearity, and correlation coefficients of 0.995 or better were obtained for all cases. Values of the activation parameters are given in Table I. Uncertainties are given as ±3 standard deviations from the weighted least-squares lines. Reproducibility, however, was considerably better than the stated uncertainties. For five of the compounds, variable temperature data were obtained twice, on different preparations of the complexes and on different days, and analyzed independently. In each case the two sets of data agreed very closely. For example, for Ru(CO)(*p*-Et_2N-TPP)(*t*-Bupy), the two sets of data gave $\Delta G^{\ddagger}_{298}$ = 17.3, 17.3; $\Delta H^{\ddagger}$ = 15.9, 15.9; $\Delta S^{\ddagger}$ = −5.0, −4.9; and E_a = 16.6, 16.6 and for In(*p*-Cl-TPP)Cl two sets of data gave $\Delta G^{\ddagger}_{298}$ = 16.7, 16.7; $\Delta H^{\ddagger}$ = 14.1, 14.2; $\Delta S^{\ddagger}$ = −8.8, −8.4; and E_a = 14.8, 14.9 with units as in Table I. The two sets of data for TiO(*p*-Et_2N-TPP) are shown in Figure 2. For the compounds on which duplicate sets of data were obtained, values in Table I are based on least-squares fits for the combined data. Considering the excellent reproducibility of the parameters, it is felt that small differences between the complexes are real and that comparisons are justified. It should also be noted that the uncertainty in $\Delta G^{\ddagger}_{298}$ is based on the uncertainty in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ since some of the kinetic data had to be extrapolated to 298 K for tabulation. Rates at temperatures in the intermediate exchange region are accurate within about 10% uncertainty except near the extremes of the exchange region. Rates of rotation are compared at 323 K since it falls in the intermediate exchange region for the InCl and TiO complexes and necessitates extrapolation over at most 20 K for the ruthenium complexes.

The previously reported values of $\Delta G^{\ddagger}_{T_c}$ obtained from $\Delta\nu$ and the coalescence temperature for TiO(*p*-R-TPP) and In(*p*-R-TPP)Cl, R = *i*-Pr, CF_3[4], agree with the activation parameters obtained by line shape analysis (Table I) within 0.3 kcal. This agreement between values obtained by approximation and by line shape analysis of these ABCD spin systems is consistent with the estimates of uncertainty in approximations of $\Delta G^{\ddagger}_{T_c}$ for AB spin systems reported by Raban and co-workers.[31] We have recently observed that averaging of resonances for nonequivalent phenyl protons in Ru(CO)(*p*-R-TPP)L, L = THF or EtOH, is not reproducible from sample to sample although individually satisfying criteria of reversibility, unless excess axial ligand is present. Parameters for Ru(CO)(*p*-CF_3-TPP)(THF) in Table I were obtained on a sample containing 1:1 Ru(CO)(*p*-CF_3-TPP)(THF)-THF. Values of $\Delta G^{\ddagger}_{T_c}$ previously reported for Ru(CO)(*p*-CF_3-TPP)(THF)[4] and Ru(CO)(*p*-*i*-Pr-TPP)(EtOH)[2] were based on samples which did not contain excess ligand and the $\Delta G^{\ddagger}$ values are lower by ~1 kcal than for samples containing excess ligand. Increased rates of averaging corresponding to a decrease in $\Delta G^{\ddagger}$ of about 2 kcal/mol can also be obtained by excessive heating of the samples, although addition of excess ligand to these samples causes the rates to return to the lower values. Rates of averaging are the same for 1:1 and 1:2

Table I. Activation Parameters for Phenyl Ring Rotation[a]

Porphyrin	$\Delta G^{\ddagger}_{298}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	E_a, kcal/mol	k_{323}[b]
Ru(CO)(*p*-CF_3-TPP)(THF)[c]	18.6 ± 1.5[d]	17.5 ± 1.2	−3.7 ± 3.0	18.3 ± 1.2	1.5
Ru(CO)(*p*-CF_3-TPP)(*t*-Bupy)[e]	18.5 ± 1.0	16.9 ± 0.8	−5.2 ± 2.0	17.7 ± 0.7	1.8
Ru(CO)(*p*-Cl-TPP)(*t*-Bupy)	18.5 ± 1.9	16.8 ± 1.5	−6.0 ± 3.8	17.5 ± 1.5	1.4
Ru(CO)(*p*-Me-TPP)(*t*-Bupy)	18.3 ± 1.3	16.2 ± 1.1	−7.2 ± 2.9	16.9 ± 1.1	2.0
Ru(CO)(*p*-*i*-Pr-TPP)(*t*-Bupy)	18.3 ± 1.4	17.2 ± 1.1	−3.9 ± 3.0	17.9 ± 1.1	2.2
Ru(CO)(*p*-OMe-TPP)(*t*-Bupy)	18.3 ± 1.4	16.5 ± 1.1	−6.1 ± 3.0	17.3 ± 1.1	2.1
Ru(CO)(*p*-Et_2N-TPP)(*t*-Bupy)[e]	17.3 ± 0.7	15.9 ± 0.7	−5.0 ± 1.6	16.5 ± 0.6	9.5
In(*p*-CF_3-TPP)Cl	16.9 ± 1.4	15.0 ± 0.9	−6.2 ± 2.5	15.7 ± 0.9	21.
In(*p*-Cl-TPP)Cl[e]	16.7 ± 0.8	14.2 ± 0.6	−8.5 ± 1.8	14.8 ± 0.6	23.
In(*p*-Me-TPP)Cl	16.4 ± 1.2	13.9 ± 0.9	−8.7 ± 2.7	14.5 ± 0.9	33.
In(*p*-*i*-Pr-TPP)Cl	16.3 ± 1.1	13.9 ± 0.8	−8.1 ± 2.5	14.5 ± 0.8	45.
In(*p*-OMe-TPP)Cl	16.3 ± 1.2	13.8 ± 0.9	−8.3 ± 2.8	14.5 ± 0.9	47.
In(*p*-Et_2N-TPP)Cl[e]	15.0 ± 0.8	11.8 ± 0.6	−10.9 ± 1.9	12.4 ± 0.6	289.
TiO(*p*-CF_3-TPP)	16.2 ± 1.4[f]	13.6 ± 0.8	−8.7 ± 2.6	14.3 ± 0.9	53.
TiO(*p*-CF_3-TPP)[g]	16.4 ± 1.6	13.6 ± 1.2	−9.3 ± 3.6	14.3 ± 1.2	39.
TiO(*p*-CF_3-TPP)[h]	16.3 ± 1.4	13.9 ± 1.0	−8.0 ± 3.0	14.6 ± 1.0	47.
TiO(*p*-CF_3-TPP)[i]	16.4 ± 1.5	14.2 ± 1.0	−7.4 ± 3.0	14.8 ± 1.0	40.
TiO(*p*-CF_3-TPP)[j]	16.6 ± 1.5	13.9 ± 1.2	−9.0 ± 3.6	14.5 ± 1.2	28.
TiO(*p*-Cl-TPP)	16.0 ± 0.7	12.9 ± 0.7	−10.4 ± 1.8	13.6 ± 0.6	67.
TiO(*p*-Me-TPP)	15.6 ± 0.8	11.9 ± 0.6	−12.4 ± 1.8	12.6 ± 0.6	116.
TiO(*p*-*i*-Pr-TPP)	15.5 ± 0.8	11.8 ± 0.7	−12.3 ± 1.5	12.4 ± 0.7	143.
TiO(*p*-OMe-TPP)	15.5 ± 0.8	12.0 ± 0.6	−11.7 ± 1.7	12.7 ± 0.6	141.
TiO(*p*-OH-TPP)[k]	15.4 ± 0.9	11.9 ± 0.7	−11.9 ± 2.1	12.5 ± 0.7	149.
TiO(*p*-Et_2N-TPP)[e]	14.3 ± 0.7	11.2 ± 0.5	−10.3 ± 1.8	11.8 ± 0.5	995.

[a] In 1,1,2,2-tetrachloroethane solutions, unless otherwise noted. [b] Uncertainties in rate constants at 323 K are about 10% for the TiO and InCl complexes. Rates for most of the Ru complexes were extrapolated to 323 K and uncertainties are about 20%. [c] In the presence of 1 equiv of THF. [d] Uncertainties are given as ±3 standard deviations from the least-squares lines. [e] Least-squares fit for two independent data sets combined. [f] The value of $\Delta G^{\ddagger}_{328}$ for TiO(*p*-CF_3-TPP) reported in ref 4 should have been 16.3 kcal/mol. It was reported as 15.6 due to a transcription error. [g] In 1,1,2-trichloroethylene. [h] In 1:1 methyl ethyl ketone–1,1,2,2-tetrachloroethane. [i] In 1,1,2,2-tetrachloroethane with 10:1 1,3,5-trinitrobenzene–TiO(*p*-CF_3-TPP). [j] In 1,2-dimethoxyethane. [k] In 1:10 1,1,2,2-tetrachloroethane–dimethyl sulfoxide.

Ru(CO)(*p*-CF_3-TPP)THF–THF, indicating that the kinetics are not dependent on the concentration of free THF. Free *t*-Bupy is not necessary to obtain reproducible kinetics for Ru(CO)(*p*-R-TPP)(*t*-Bupy). Further study is needed to ascertain the cause of the irreproducible kinetics of phenyl ring resonance averaging for Ru(CO)porphyrin complexes with weakly coordinating axial ligands in the absence of excess ligand.

Effect of Para Substituent. The rate constants at 323 K, which are given in Table I, show that the para substituent has a substantial effect on the rate of rotation of the phenyl rings. For all three metals the rate of rotation is about an order of magnitude faster when R = Et_2N than when R = CF_3. (Differences between the metal ions are discussed below.) The effects of para substituents on the rates of *t*-Bupy exchange in Ru(CO)(*p*-R-TPP)(*t*-Bupy),[11] on the redox potential of free porphyrins and metalloporphyrins,[16,18-21] and on equilibrium constants for axial ligation[13-17] have been observed to correlate well with Hammett σ parameters. Therefore log k for ring rotation is plotted as a function of σ_p[32] in Figure 3, for the three metals studied. The dependence of rate on Hammett σ is clearly not linear, although the pattern of substituent effects is similar for the three metals. Least-squares lines through the data gave correlation coefficients ranging from only 0.87 for the ruthenium data to 0.93 for the titanyl data. Data for the effect of para substituents on the rate of *t*-Bupy exchange in Ru(CO)(*p*-R-TPP)(*t*-Bupy)[11] and for phenyl ring rotation were obtained for the same set of para substituents. For the former, the dependence of log k on σ is linear[11] and for the latter it is not. It therefore appears that the two processes are influenced differently by the interaction between the para-substituted phenyl ring and the porphyrin ring. Comparisons with existing data on redox potentials or equilibrium constants for axial ligation cannot be made satisfactorily because none of the studies included substituents more electron donating

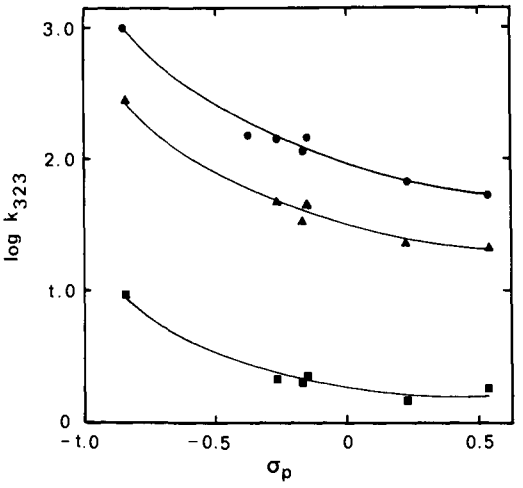


Figure 3. Plots of log (k_{323}) vs. Hammett σ_p for phenyl ring rotation in MXY (*p*-R-TPP): (■) MXY = Ru(CO)(*t*-Bupy); (▲) MXY = InCl; (●) MXY = $(TiO)^{2+}$. The lines are merely visual fits to the data and have no theoretical significance.

than *p*-OH. If the data for the strongly electron-donating *p*-Et_2N were excluded from the present study, the rates of phenyl ring rotation could appear to be a linear function of σ_p. The need to include *p*-Et_2N in future studies is apparent. Adler has noted that the substituent effects on electronic spectra[12] and rates of copper ion incorporation in substituted tetraphenylporphyrins[9] also are not linear functions of σ. Preliminary results indicate that the effects of para substituents on rates of phenyl ring rotation in the compounds reported here are strongly correlated with changes in the energies and oscillator strengths of transitions observed in the visible spectra.[33] The effects of para substituents on other properties of these me-

talloporphyrins are also being examined to obtain a more complete picture of the interaction between the noncoplanar phenyl and porphyrin rings.

Comparison with Biphenyls. Substituents have been observed to have substantial effects on the rates of inversion of biphenyls. In 4,4′-disubstituted 2,2′-diiodobiphenyl the rates of inversion at 25 °C in DMF increase in the order 4,4′ substituent = $CO_2Me \sim CO_2H < H < N(H)C(O)Me < NH_2$.[34] In 4-X,4′-Y, 2-isopropyl-2′-methoxybiphenyls, rates at 86 °C increase in the order X = Y = $NO_2 \sim H < NH_2$ and for X = NO_2, Y = $NO_2 < H < NH_2$.[35] The facilitation of inversion by electron-donating groups was attributed to decreased steric interaction in the transition state owing to easier out-of-plane bending of the 1,1′ bond in accordance with the orbital following theory.[35] When X and Y have substantially different electron-donating or -withdrawing properties, the increased rates of inversion were attributed to resonance stabilization of the transition state.[35] Based on the limited data available, the overall trends in the rates for the biphenyls are very similar to the patterns observed for the tetraphenylporphyrins: (a) rotation is faster when substituents are electron donating and (b) electron-donating groups have a greater impact on the rates than do electron-withdrawing groups.

Effect of Metal Ion. The rate of rotation of the phenyl rings, as given in Table I and Figure 3, are strongly dependent on metal ion. For MXY(*p*-R-TPP) rates of phenyl ring rotation, holding R constant, increase in the order MXY = Ru(CO)(*t*-Bupy) < InCl < $(TiO)^{2+}$, with the rates for the titanyl complexes about 100 times faster than for the ruthenium complexes. Although the effects of the para substituents on the rates of ring rotation and on the electronic spectra of the complexes are strongly correlated,[33] the effect of the metal ion on the rate of ring rotation does not correlate well with the effect of metal ion on the electronic spectra. It therefore seems likely that the metal ions and para substituents affect the rate of ring rotation by different means. Whereas the para substituent effects appear to be largely electronic, it seems reasonable that the effect of the metal ion may be primarily conformational. Although the crystal structures of Ru(CO)(TPP)(EtOH)[2] and Ru(CO)(TPP)(Py)[36] have been reported, no crystallographic results are available for titanyl or indium chloro complexes of tetraphenylporphyrins. Based on molecular models, phenyl ring rotation would appear to be facilitated by distortions of the porphyrin core from planarity. In the ruthenium complex there is very little distortion of the porphyrin core and the phenyl rings are nearly perpendicular to the porphyrin plane.[2,36] Using this concept, the present results suggest that in the five-coordinate TiO and InCl complexes the porphyrin core is more distorted from planarity than in the ruthenium carbonyl complexes.

It is also noteworthy that the metal ion has a considerable impact on the sensitivity of the metalloporphyrin to substituent effects. The ratio of the phenyl ring rotation rates at 323 K for R = Et_2N and R = CF_3 is 5.3 for ruthenium and 19 for titanyl.

Effect of Axial Ligand. The rates of phenyl ring rotation in Ru(CO)(*p*-CF_3-TPP)(THF) and Ru(CO)(*p*-CF_3-TPP)(*t*-Bupy) are identical within experimental error. In the THF complexes, exchange of free and coordinated THF is about 1000 times faster than ring rotation whereas in the *t*-Bupy complex exchange of free and coordinated *t*-Bupy occurs at about the same rate[11] as ring rotation though with rather different activation parameters ($\Delta S^{\ddagger}$ for *t*-Bupy exchange is greater than $\Delta S^{\ddagger}$ for ring rotation). The rate of axial ligand exchange appears to have no effect on the rate of ring rotation in the ruthenium complexes. At five temperatures between 32 and 57 °C the rates of ring rotation in In(*p*-Cl-TPP)OH are systematically about 10% faster than in In(*p*-Cl-TPP)Cl. A complete set of data for In(*p*-Cl-TPP)OH could not be obtained owing to the facile conversion of In(*p*-R-TPP)OH to In(*p*-R-TPP)Cl in tetrachloroethane solution. Thus, the data currently available indicate that the nature of the axial ligand has relatively little impact on the rate of phenyl ring rotation compared with the effects of the phenyl ring substitutents or the metal ion.

Effect of Solvent. The titanyl complexes, particularly TiO(*p*-CF_3-TPP), were found to have sufficient solubility for variable temperature NMR in a greater range of solvents than the other complexes studied. The rate of phenyl ring rotation in TiO(*p*-CF_3-TPP) was studied in $C_2H_2Cl_4$, C_2HCl_3, 1:1 $C_2H_2Cl_4$-methyl ethyl ketone, dimethoxyethane, toluene-d_8, and $C_2H_2Cl_4$ containing a 10:1 ratio of 1,3,5-trinitrobenzene to TiO(*p*-CF_3-TPP). ^1H NMR spectra in the first four solvents were very similar. The chemical shift differences between the nonequivalent ortho protons ranged from 33 Hz in C_2HCl_3 to 40 Hz in $C_2H_2Cl_4$ and the shift differences between nonequivalent meta protons ranged from 8 Hz in C_2HCl_3 to 10 Hz in 1:1 $C_2H_2Cl_4$-methyl ethyl ketone. The chemical shift differences between nonequivalent protons were essentially independent of temperature (extrapolation of chemical shifts as a function of temperature gave less than a 5% change in $\Delta\nu_{ortho}$ or $\Delta\nu_{meta}$ over 100 K). Rates of phenyl ring rotation in these solvents increase in the order dimethoxyethane < C_2HCl_3 < 1:1 $C_2H_2Cl_4$-methyl ethyl ketone $\sim$ $C_2H_2Cl_4$. The total range of rate constants is less than a factor of 2 at any temperature in the intermediate exchange region. Since 1,3,5-trinitrobenzene (TNB) is known to form π complexes with metalloporphyrins,[37] its effect on the rate of phenyl ring rotation was also examined. The ^1H NMR spectra in toluene-d_8 and in the presence of a tenfold molar excess of TNB in $C_2H_2Cl_4$ are markedly different from the spectra in the other solvents studied. The chemical shift differences between nonequivalent protons are smaller than in other solvents and are strongly temperature dependent. In the presence of TNB the chemical shift difference between nonequivalent ortho protons increases from 10 Hz at −16 °C to 23 Hz at 30 °C while the shift difference between the meta protons increases from 1 to 2 Hz. In toluene-d_8 the chemical shift difference between the ortho proton resonances decreases from 12 Hz at −35 °C to 4 Hz at 5 °C while the meta proton nonequivalence decreases from 2.5 to 2.0 Hz. The large temperature dependence of the chemical shift differences in TiO(*p*-CF_3-TPP) in the presence of aromatic molecules suggests a strongly temperature dependent π-complex formation. The observation that the changes are much larger for the ortho protons than for the meta protons suggests that π-complex formation is largely between the aromatic molecules and the porphyrin ring rather than the phenyl rings. In the presence of TNB the rate of phenyl ring rotation falls in the middle of the range of values obtained for the other solvents. In toluene-d_8 the chemical shift differences were too small and too temperature dependent in the intermediate exchange region to permit the determination of accurate activation parameters, but the rates appear to be comparable to those in other solvents. The effects of π-complex formation on the rates of ring rotation are apparently quite small. Although the effects of solvent on the rate of ring rotation are small, compared to the effects of metal ion and para substituents, the differences are not negligible. For this reason all the other comparisons in this study are based on data obtained in the same solvent, 1,1,2,2-tetrachloroethane.

Further work is in progress to answer some of the questions raised by the results presented in this paper. At this point it appears that the large effects of para substituents and metal ions on the rate of phenyl ring rotation result from electronic and conformational changes, respectively. The importance of the strongly electron-donating diethylamino group in ascertaining the degree of linearity of para-substituent effects is also to be noted.

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(22) Abbreviations used throughout: *p*-R-TPP, tetrakis(*p*-R-phenyl)porphyrin dianion; *p*-CF_3-TPP, tetrakis(*p*-trifluoromethylphenyl)porphyrin dianion; *p*-Cl-TPP, tetrakis(*p*-chlorophenyl)porphyrin dianion; *p*-*i*-Pr-TPP, tetrakis(*p*-isopropylphenyl)porphyrin dianion; *p*-OMe-TPP, tetrakis(*p*-methoxyphenyl)porphyrin dianion; *p*-OH-TPP, tetrakis(*p*-hydroxyphenyl)porphyrin dianion; *p*-Et_2N-TPP, tetrakis(*p*-diethylaminophenyl)porphyrin dianion; *t*-Bupy, 4-*tert*-butylpyridine.
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High-Spin Ferrous Porphyrin Complexes as Models for Deoxymyoglobin and -hemoglobin. A Proton Nuclear Magnetic Resonance Study

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Abstract: The ^1H NMR spectra for a variety of high-spin ($S = 2$) ferrous porphyrin complexes have been recorded and analyzed. The five-coordinate high-spin species were generated from the corresponding unligated, intermediate-spin, $S = 1$, complexes by addition of a methyl-α-substituted imidazole or pyridine axial ligand. The isotropic shifts for synthetic porphyrin complexes are consistent with a predominant contact origin, with the high-spin iron(II) exhibiting only very small magnetic anisotropy. The patterns of porphyrin contact shifts in both synthetic and natural porphyrin complexes are very similar and reflect primarily σ spin transfer. Evidence against significant iron $\rightarrow$ porphyrin π back-bonding is presented. The insensitivity of the porphyrin shifts to the nature of the axial base suggests that heme resonances will not be useful probes for detecting histidine–iron tension in deoxyhemoglobins. The shifts for the axial imidazole, on the other hand, are consistent with primarily σ spin transfer and should serve as ideal indicators of such histidine–iron tension. The natural porphyrin resonance positions in the model complexes support earlier heme methyl assignments in deoxymyoglobin and deoxyhemoglobin and facilitate the assignment in the proteins of other single proton heme peaks as well as those of the elusive proximal histidyl imidazole.

Analysis of the ^1H NMR spectra of complexes of paramagnetic iron porphyrins in different oxidation and spin states has proved to be very useful both because the method provides some direct information on the π bonding, thought to be critical in the biological role, and because these complexes serve as models for assigning and interpreting the ^1H NMR spectra of the various paramagnetic forms of hemoproteins.[2,3] Sufficient parallel has been shown to exist between the pattern of proton resonance positions in model complexes[2-5] and hemoproteins[3,6,7] in both the high-spin[4,6] and low-spin[3,5,7] ferric forms, such that the data on the model systems can be used to make probable assignments not only for the isotropically shifted heme resonances[2,3] but also for the coordinated histidine.[5] In the case of the low-spin ferric systems where most of the work has centered, studies on model compounds[3] have provided a basis for interpreting changes in rotational positions and rotational mobility of pyrrole substituents with pH-induced structural changes in the protein.[8]

Although considerable effort has also been expended on the study of the ^1H NMR spectra of the physiologically more important deoxyhemoproteins[3,9-11] (ferrous, high spin, $S = 2$), the isotropic shifts have yielded much more qualitative