

Rotation of Phenyl Rings in Metal Complexes of Substituted Tetraphenylporphyrins

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Abstract: ^1H NMR signals for nonequivalent ortho protons and nonequivalent meta protons on the phenyl rings in indium tetrakis(*p*-isopropylphenyl)porphyrin chloride, indium tetrakis(*p*-trifluoromethylphenyl)porphyrin chloride, titanyl tetrakis(*p*-isopropylphenyl)porphyrin, titanyl tetrakis(*p*-trifluoromethylphenyl)porphyrin, and ruthenium carbonyl tetrakis(*p*-trifluoromethylphenyl)porphyrin tetrahydrofuran adduct are observed to average on the NMR time scale between 10 and 140° by a concentration independent pathway. In the same temperature range there is no evidence of averaging of nonequivalent methyl ^1H NMR signals in indium tetrakis(*o*-tolyl)porphyrin chloride, indium tetrakis(mesityl)porphyrin chloride, titanyl tetrakis(*o*-tolyl)porphyrin, titanyl tetrakis(mesityl)porphyrin, ruthenium carbonyl tetrakis(*o*-tolyl)porphyrin pyridinate, or ruthenium carbonyl tetrakis(mesityl)porphyrin pyridinate. In the ^{19}F spectrum of indium tetrakis(pentafluorophenyl)porphyrin chloride, signals for nonequivalent ortho and meta fluorines do not average up to 130° on the NMR time scale. The averaging of ^1H NMR peaks, in the compounds in which both ortho substituents on each phenyl ring are hydrogen, is attributed to rotation of the phenyl rings. Addition of *n*-Bu₄NCl to the indium complexes causes a concentration dependent averaging attributed to chloride exchange. Addition of CO to the ruthenium complexes also effects averaging of nonequivalent resonances.

Restricted rotation of phenyl rings resulting from steric interactions with neighboring groups has been the subject of considerable investigation since the early work on optically active biphenyls.¹ The use of dynamic NMR has permitted the study of molecules with rotational barriers too low to allow separation of isomers.² Some recent examples include measurements of activation energies for rotational processes in tertiary benzylic metal compounds,³ mono(tricarbonyl)chromium complexes of diarylmethanes,⁴ trimesitylmethane and related compounds,⁵ arylboranes,⁶ and arylsilanes.⁷

Although maximum conjugation between the porphyrin ring and the phenyl rings in tetra-*meso*-phenylporphyrins would be achieved through coplanarity of the rings, steric interaction between pyrrole hydrogens and ortho hydrogens on the phenyl rings has been estimated to require a dihedral angle of 44.5,⁸ 60,⁹ or 70°.¹⁰ X-Ray diffraction results on tetra-*meso*-arylporphyrins and their metal complexes indicate that the phenyl rings are tilted at an angle to the "mean plane" of the porphyrin ring.¹⁰ The dihedral angle is 61–63° in H₂TPP,^{11,12} and almost 90° in most metal complexes of TPP¹⁰ although angles as small as 69,¹³ 71,¹⁴ 73,¹⁵ and 76°⁹ have been found. The phenyl rings are "nearly perpendicular" to the porphyrin plane in Ru(CO)(TPP)-(EtOH)¹⁶ and Ru(CO)(TPP).py.¹⁷ The angle is ca. 21° in the highly nonplanar H₄TPP²⁺¹⁸ and 50–68° in ZnTPP⁺ClO₄.¹⁹

In view of these observations it is of interest to determine the barrier to rotation of phenyl groups in substituted tetraphenylporphyrins. Preliminary results have been reported.^{16,20–22} This paper concerns the effect of ortho substituents on the rate of phenyl ring rotation in substituted ruthenium carbonyl tetraphenylporphyrins, indium chlorotetraphenylporphyrins, and titanyl tetraphenylporphyrins. The effect of axial ligand exchange on the averaging of nonequivalent phenyl resonances is also discussed.

Experimental Section

Physical Measurements. Infrared spectra were recorded as Nujol or halocarbon mulls on a Perkin-Elmer 710 grating spectrometer. Visible spectra were obtained in chloroform solution on a Beckman Acta V spectrometer. Data are given below with wavelengths in nanometers and log ϵ in parentheses. ^1H NMR spectra were run at power levels well below saturation on a Varian HA-

100 spectrometer equipped with a variable temperature probe. Temperatures were calibrated with methanol and ethylene glycol. Spectra were obtained with the spectrometer locked on the solvent resonance. Unless otherwise noted, ^1H chemical shifts are reported in parts per million downfield of tetramethylsilane for 1,1,2,2-tetrachloroethane solutions at ambient temperature. ^{19}F spectra were recorded on a JEOL C-60 HL spectrometer. All variable temperature line shape changes were reversible with temperature.

Preparation of Compounds. Octaethylporphyrin,²³ tetrakis(*o*-tolyl)porphyrin,²⁴ tetrakis(*p*-isopropylphenyl)porphyrin,²⁰ and tetrakis(pentafluorophenyl)porphyrin²⁵ were prepared by reported methods. Baker 0537 alumina and reagent solvents were used for all chromatography. All products were dried to constant weight in vacuo at ethanol reflux. 1,1,2,2-Tetrachloroethane (C₂H₂Cl₄) was purified by distillation from P₄O₁₀ under nitrogen.

Tetrakis(*p*-trifluoromethylphenyl)porphyrin, H₂(*p*-CF₃TPP). The porphyrin was prepared from *p*-trifluoromethylbenzaldehyde and pyrrole using a procedure analogous to that reported for tetraphenylporphyrin.²⁶ The crude product was chromatographed on alumina in CHCl₃ and recrystallized from dichloromethane–heptane. Visible spectrum: 402 sh (4.97), 418 (5.64), 480 sh (3.55), 514 (4.30), 547 (3.81), 590 (3.77), 646 (3.48). ^1H NMR: N-H, –2.85 singlet; *m*-H, 8.03 doublet; *o*-H, 8.35 doublet; pyrrole-H, 8.82 singlet. Anal. Calcd for C₄₈H₂₆N₄F₁₂: C, 64.99; H, 2.75; N, 6.25; F, 25.77. Found: C, 65.02; H, 2.96; N, 6.32; F, 25.71.

Tetrakis(mesityl)porphyrin, H₂(Me₃TPP). The porphyrin was prepared as the zinc complex by the method of Badger et al.²⁷ The zinc complex was purified by chromatography on alumina in benzene solution and the metal removed by shaking a benzene solution with concentrated HCl. The free porphyrin was recrystallized from benzene–methanol. Visible spectrum: 403 sh (4.92), 419 (5.72), 483 sh (3.57), 514 (4.34), 548 (3.81), 590 (3.81), 646 (3.47). ^1H NMR (CDCl₃ with C₂H₂Cl₄ added as lock signal): N-H, –1.52 broad singlet; *o*-CH₃, 1.86 singlet; *p*-CH₃, 2.62 singlet; *m*-H, 7.28 singlet, slightly to low field of CHCl₃ in the CDCl₃, and partially superimposed; pyrrole-H, 8.61 singlet (lit. (CDCl₃),²⁷ N-H, –1.5; *o*-CH₃, 1.85; *p*-CH₃, 2.63; *m*-H, 7.79; pyrrole-H, 8.62). Anal. Calcd for C₅₆H₅₄N₄: C, 85.89; H, 6.95; N, 7.16. Found: C, 85.94; H, 6.81; N, 7.07. (Lit.²⁷ C, 83.1; H, 7.9; N, 6.6.)

Indium Complexes. The procedure used to synthesize the indium complexes was analogous to that reported by Bhatti and coworkers.²⁸ Porphyrin (0.5 mmol) and InCl₃ (1.0 mmol) were refluxed in 250 ml of acetic acid containing excess anhydrous sodium acetate (0.13 mol). The reaction was monitored by the disappearance of the free porphyrin band at ca. 515 nm in the visible spectrum. When the reaction had ceased, the acetic acid was removed in vacuo and the product was extracted into chloroform. Purification was effected by chromatography on alumina in chloroform solu-

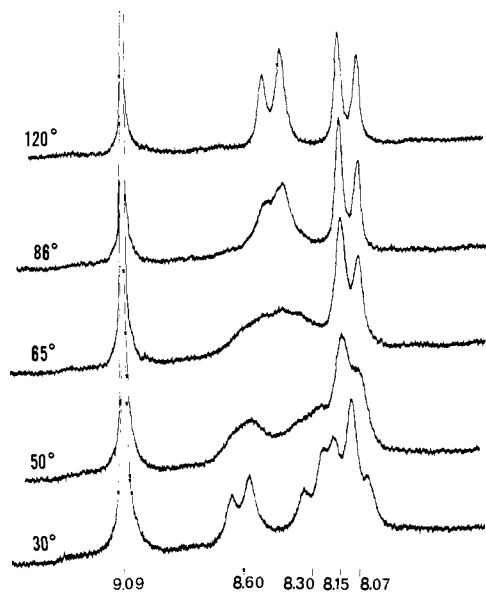


Figure 1. ^1H NMR spectra (100 MHz) of $\text{In}(p\text{-CF}_3\text{TPP})\text{Cl}$ in 1,1,2,2-tetrachloroethane at various temperatures. Slow-exchange chemical shifts are in parts per million downfield of tetramethylsilane: pyrrole-H, 9.09; *o*-H, 8.09; *o*-H, doublets centered at 8.60, 8.30; *m*-H, doublets centered at 8.15, 8.07.

tion, followed by recrystallization. Crystals are purple, except as noted. Reaction times, recrystallization solvents, yields of pure complexes, and characterization data are given below for individual complexes.

Indium Tetrakis(*p*-isopropylphenyl)porphyrin Chloride, $\text{In}(p\text{-i-PrTPP})\text{Cl}$. Reaction time, 48 hr. Recrystallization, trichloroethylene-hexane. Yield 48%. Visible spectrum: 408 (4.66), 428 (5.84), 522 (3.63), 562 (4.37), 602 (4.13). ^1H NMR: CH_3 , 1.57 doublet; methine-H, 3.29 septet; *m*-H, 7.61, 7.67 doublets; *o*-H, 8.02, 8.34 doublets; pyrrole-H, 9.13 singlet. Anal. Calcd for $\text{C}_{56}\text{H}_{52}\text{N}_4\text{InCl}$: C, 72.22; H, 5.63; N, 6.02; Cl, 3.81. Found: C, 71.82; H, 5.83; N, 6.14; Cl, 3.91.

Indium Tetrakis(*p*-trifluoromethylphenyl)porphyrin Chloride, $\text{In}(p\text{-CF}_3\text{TPP})\text{Cl}$. Reaction time, 2 hr. Recrystallization, CHCl_3 -hexane. Yield 93%. Visible spectrum: 405 (4.60), 424 (5.84), 520 (3.53), 558 (4.39), 597 (3.80). ^1H NMR (Figure 1): *m*-H, 8.07, 8.15 doublets; *o*-H, 8.30, 8.60 doublets; pyrrole-H, 9.09 singlet. Anal. Calcd for $\text{C}_{48}\text{H}_{24}\text{N}_4\text{F}_{12}\text{InCl}$: C, 55.70; H, 2.34; N, 5.41; F, 22.03; Cl, 3.42. Found: C, 55.98; H, 2.46; N, 5.46; F, 21.80; Cl, 3.37. An identical product was obtained whether InCl_3 , InBr_3 , or InI_3 was used as starting material provided that chloroform was used as the solvent for chromatography.

Indium Tetrakis(pentafluorophenyl)porphyrin Chloride, $\text{In}(\text{F}_5\text{TPP})\text{Cl}$. Reaction time, 4 days. Recrystallization, CHCl_3 -hexane. Yield 80%, red-purple crystals. Visible spectrum: 400 (4.67), 421 (5.75), 517 (3.46), 554 (4.39), 588 (3.37). ^{19}F NMR (Figure 2), chemical shifts in $\text{C}_2\text{H}_2\text{Cl}_4$ solutions in parts per million downfield of external neat C_6F_6 : *m*-F, 4.2, 6.5 multiplets; *p*-F, 17.0 apparent triplet; *o*-F, 32.7, 33.5 multiplets. Anal. Calcd for $\text{C}_{44}\text{H}_8\text{N}_4\text{F}_{20}\text{InCl}$: C, 47.07; H, 0.72; N, 4.99; F, 33.84; Cl, 3.16. Found: C, 47.06; H, 0.92; N, 5.01; F, 33.96; Cl, 3.19.

Indium Tetrakis(*o*-tolyl)porphyrin Chloride, $\text{In}(o\text{-CH}_3\text{TPP})\text{Cl}$. Reaction time, 20 hr. Recrystallization, dichloromethane-heptane. Yield 69%. Visible spectrum: 404 (4.62), 425 (5.87), 521 (3.54), 559 (4.39), 597 (3.82), 630 (3.19). ^1H NMR: CH_3 , 1.79, 1.82, 1.85, 1.89, 2.17, 2.20 apparent singlets; phenyl-H, 7.68, 7.98, 8.28, multiplets; pyrrole-H, 8.91 multiplet. Anal. Calcd for $\text{C}_{48}\text{H}_{36}\text{N}_4\text{InCl}$: C, 70.39; H, 4.42; N, 6.84; Cl, 4.33. Found: C, 70.18; H, 4.66; N, 6.72; Cl, 4.34.

Indium Tetrakis(mesityl)porphyrin Chloride, $\text{In}(\text{Me}_3\text{TPP})\text{Cl}$. Reaction time, 20 hr. Recrystallization, dichloromethane-heptane. Yield 79%. Visible spectrum: 404 (4.67), 427 (5.90), 523 (3.56), 561 (4.41), 600 (3.91). ^1H NMR: *o*- CH_3 , 1.77, 1.90 singlets; *p*- CH_3 , 2.61 singlet; *m*-H, 7.28 broad singlet; pyrrole-H, 8.81 sin-

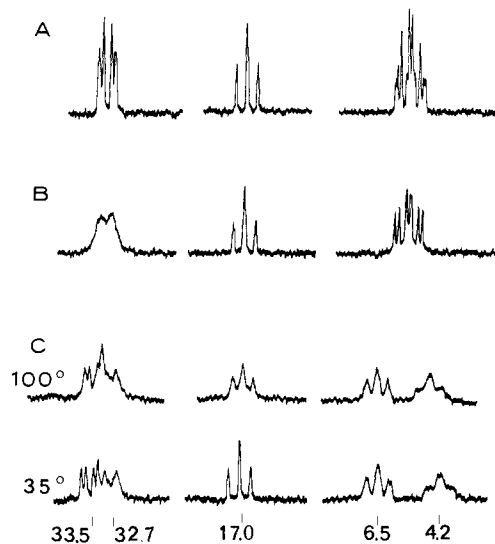


Figure 2. ^{19}F NMR spectra (56 MHz) of 1,1,2,2-tetrachloroethane solutions of: A, $\text{H}_2(\text{F}_5\text{TPP})$ at 30° ; B, $\text{In}(\text{F}_5\text{TPP})\text{Cl}$ in the presence of excess $n\text{-Bu}_4\text{NCl}$ at 35° ; C, $\text{In}(\text{F}_5\text{TPP})\text{Cl}$ at 35° and 100° . Chemical shifts are in parts per million downfield of external neat C_6F_6 : *o*-F, 33.5, 32.7; *p*-F, 17.0; *m*-F, 6.5, 4.2.

glet. Anal. Calcd for $\text{C}_{56}\text{H}_{52}\text{N}_4\text{InCl}$: C, 72.22; H, 5.63; N, 6.02; Cl, 3.81. Found: C, 72.34; H, 5.85; N, 5.86; Cl, 3.77.

Indium Octaethylporphyrin Chloride, $\text{In}(\text{OEP})\text{Cl}$. Reaction time, 1 hr. Recrystallization by CHCl_3 -heptane. Yield 94%, magenta needles. Visible spectrum: 385 (4.77), 407 (5.74), 505 (3.39), 540 (4.31), 576 (4.37). ^1H NMR: CH_3 , 1.97 triplet; CH_2 , 4.18 quartet; meso-H 10.36. Anal. Calcd for $\text{C}_{36}\text{H}_{44}\text{N}_4\text{InCl}$: C, 63.30; H, 6.49; N, 8.20; Cl, 5.19. Found: C, 63.12; H, 6.43; N, 8.25; Cl, 5.21.

Titanyl Complexes. Titanyl complexes were prepared by the method reported for titanyl octaethylporphyrin.²⁹ Porphyrin (0.37 mmol) and excess dicyclopentadienyltitanium dichloride (4.0 mmol) were refluxed in 100 ml of 2,2'-oxydiethanol for 2 hr. Crude products were put on alumina columns in benzene. Unreacted porphyrin was eluted with benzene and the product was eluted with CHCl_3 . Details for individual complexes are given below.

Titanyl Tetrakis(*p*-trifluoromethylphenyl)porphyrin, $\text{TiO}(p\text{-CF}_3\text{TPP})$. Recrystallization, dichloromethane-heptane. Yield 51%, purple crystals. Visible spectrum: 403 sh (4.69), 4.22 (5.71), 512 (3.50), 550 (4.42), 585 (3.39). Ir: $\nu_{\text{Ti-O}}$ 975 cm^{-1} . ^1H NMR (Figure 3): *m*-H, 8.09, 8.18 doublets; *o*-H, 8.29, 8.68 doublets; pyrrole-H, 9.15 singlet. Anal. Calcd for $\text{C}_{48}\text{H}_{24}\text{N}_4\text{F}_{12}\text{TiO}$: C, 60.77; H, 2.55; N, 5.91. Found: C, 61.07; H, 2.66; N, 5.91.

Titanyl Tetrakis(*p*-isopropylphenyl)porphyrin, $\text{TiO}(p\text{-i-PrTPP})$. Recrystallization, trichloroethylene-heptane. Yield 50%, red-purple crystals. Visible spectrum: 404 sh (4.62), 4.26 (5.69), 515 (3.54), 553 (4.41), 592 (3.80). Ir: $\nu_{\text{Ti-O}}$ 980 cm^{-1} . ^1H NMR: CH_3 , 1.59 doublet; methine-H, 3.39 septet; *m*-H, 7.68 broad doublet; *o*-H, 8.08, 8.43 broadened doublets; pyrrole-H, 9.23 singlet. Anal. Calcd for $\text{C}_{56}\text{H}_{52}\text{N}_4\text{TiO}$: C, 79.60; H, 6.20; N, 6.63. Found: C, 79.51; H, 6.13; N, 6.44.

Titanyl Tetrakis(*o*-tolyl)porphyrin, $\text{TiO}(o\text{-CH}_3\text{TPP})$. Recrystallization, dichloromethane-heptane. Yield 69%, purple crystals. Visible spectrum: 402 sh (4.51), 422 (5.75), 511 (3.48), 550 (4.41), 586 (3.32), 631 (2.97). Ir: $\nu_{\text{Ti-O}}$ 980 cm^{-1} . ^1H NMR: *o*- CH_3 , 1.70, 1.72, 1.83, 1.93, 2.07, 2.20, 2.26, 2.40, 2.60 singlets; phenyl-H, multiple signals in region 7.53-8.70; pyrrole-H, 9.02 multiplet. Anal. Calcd for $\text{C}_{48}\text{H}_{36}\text{N}_4\text{TiO}$: C, 78.69; H, 4.94; N, 7.65. Found: C, 78.97; H, 5.14; N, 7.58.

Titanyl Tetrakis(mesityl)porphyrin, $\text{TiO}(\text{Me}_3\text{TPP})$. Recrystallization, dichloromethane-heptane. Yield 54%, red-purple crystals. Visible spectrum: 406 sh (4.65), 424 (5.74), 512 (3.49), 552 (4.42), 588 (3.35), 633 (2.81). Ir: $\nu_{\text{Ti-O}}$ 980 cm^{-1} . ^1H NMR: *o*- CH_3 , 1.71, 2.02 singlets; *p*- CH_3 , 2.62; *m*-H, 7.26, 7.32 pyrrole-H, 8.88. Anal. Calcd for $\text{C}_{56}\text{H}_{52}\text{N}_4\text{TiO}$: C, 79.60; H, 6.20; N, 6.63. Found: C, 79.45; H, 6.26; N, 6.35.

Ruthenium Complexes. Ruthenium complexes were prepared by the method reported for ruthenium carbonyl tetrakis(*p*-isopropyl-

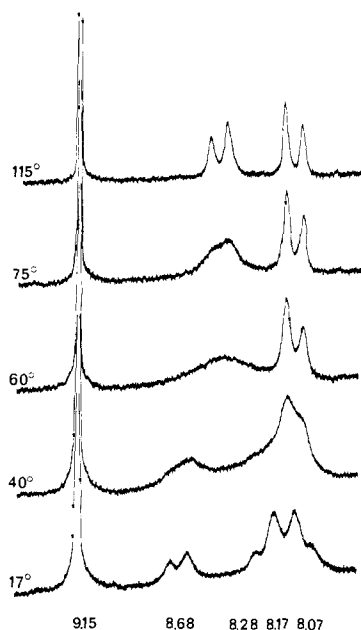


Figure 3. ^1H NMR spectra (100 MHz) of $\text{TiO}(p\text{-CF}_3\text{TPP})$ in 1,1,2,2-tetrachloroethane at various temperatures. Slow-exchange chemical shifts are in parts per million downfield of tetramethylsilane: pyrrole-H, 9.15; *o*-H, doublets centered at 8.68, 8.28; *m*-H, doublets centered at 8.17, 8.07.

phenyl)porphyrin.²⁰ The crude product was put on an alumina column in trichloroethylene and the complex eluted with tetrahydrofuran (THF). Recrystallization from THF-hexane gave brick red crystals of the THF adduct.

Ruthenium Carbonyl Tetrakis(*p*-trifluoromethylphenyl)porphyrin Tetrahydrofuran, $\text{Ru}(\text{CO})(p\text{-CF}_3\text{TPP})\cdot\text{THF}$. Yield 90%. Visible spectrum: 410 (5.46), 529 (4.37), 560 sh (3.49), 604 (3.18). Ir: ν_{CO} 1950 cm^{-1} . ^1H NMR (Figure 4): THF, -1.64, -0.56 broad multiplets; *m*-H, 7.98, 8.01 broad doublets; *o*-H, 8.25, 8.41 doublets; pyrrole-H, 8.64 singlet. Anal. Calcd for $\text{C}_{53}\text{H}_{32}\text{N}_4\text{F}_{12}\text{O}_2\text{Ru}$: C, 58.62; H, 2.97; N, 5.16; F, 20.99. Found: C, 58.39; H, 2.88; N, 5.09; F, 21.18.

Ruthenium Carbonyl Tetrakis(*o*-tolyl)porphyrin Tetrahydrofuran, $\text{Ru}(\text{CO})(o\text{-CH}_3\text{TPP})\cdot\text{THF}$. Yield 33%. Visible spectrum: 411 (5.43), 530 (4.36), 562 sh (3.39). Ir: ν_{CO} 1940 cm^{-1} . ^1H NMR: THF, -1.39, -0.52; CH_3 , 1.86, 1.91, 1.94, 1.97, 2.07, 2.09 overlapping singlets; phenyl-H, multiple resonances in region 7.39–8.18; pyrrole-H, 8.46. Anal. Calcd for $\text{C}_{53}\text{H}_{44}\text{N}_4\text{O}_2\text{Ru}$: C, 73.17; H, 5.10; N, 6.44. Found: C, 73.11; H, 5.01; N, 6.40.

Ruthenium Carbonyl Tetrakis(mesityl)porphyrin Tetrahydrofuran, $\text{Ru}(\text{CO})(\text{Me}_3\text{TPP})\cdot 2\text{THF}$. Based on integration of the ^1H NMR spectrum, the isolated product contained THF of crystallization in addition to coordinated THF. The second mole of THF was not removed by drying in vacuo at ethanol reflux temperature, yield 14%. Visible spectrum: 412 (5.44), 530 (4.42), 560 sh (3.36). Ir: ν_{CO} 1930 cm^{-1} . ^1H NMR (pyridine added to ^1H NMR sample to displace THF): *o*- CH_3 , 1.54, 1.99 singlets; *p*- CH_3 , 2.55 singlet; *m*-H, 7.13, 7.23 singlets; pyrrole-H, 8.32 singlet. Anal. Calcd for $\text{C}_{65}\text{H}_{48}\text{N}_4\text{O}_3\text{Ru}$: C, 74.05; H, 6.50; N, 5.31. Found: C, 73.63; H, 6.50; N, 5.31.

Assignment of Spectra. NMR. The assignment of signals for the ortho and meta protons on the phenyl rings in the complexes of $\text{H}_2(p\text{-}i\text{-PrTPP})$ have been discussed previously.^{20,30} The chemical shifts in the complexes of $\text{H}_2(p\text{-CF}_3\text{TPP})$ are similar but with the signal for the meta protons shifted downfield, closer to the signal for the ortho protons, due to the electron-withdrawing effect of the *p*-trifluoromethyl group. The resonances for the ortho and para methyls in the complexes of $\text{H}_2(\text{Me}_3\text{TPP})$ were assigned by comparison with the spectrum of the free porphyrin. No attempt was made to assign signals due to phenyl protons in the complexes of $\text{H}_2(o\text{-CH}_3\text{TPP})$ because of the large numbers of isomers present in solution. Signals in the ^{19}F spectra of $\text{H}_2(o\text{-CH}_3\text{TPP})$ and $\text{In}(\text{F}_5\text{TPP})\text{Cl}$ were tentatively assigned by analogy with spectra of substituted pentafluorobenzenes.³¹

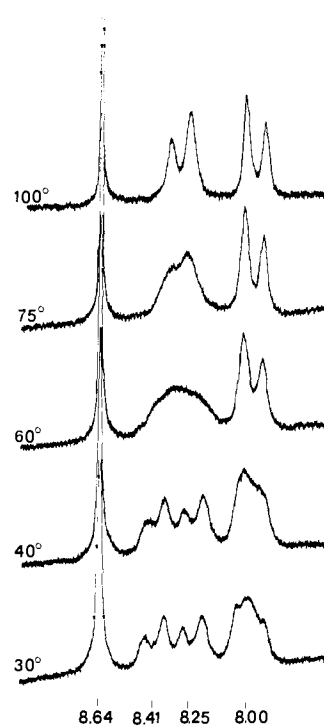


Figure 4. ^1H NMR spectra (100 MHz) of $\text{Ru}(\text{CO})(p\text{-CF}_3\text{TPP})\cdot\text{THF}$ in 1,1,2,2-tetrachloroethane at various temperatures. Slow-exchange chemical shifts are in parts per million downfield of tetramethylsilane: pyrrole-H, 8.64; *o*-H, doublets centered at 8.41, 8.25; *m*-H, overlapping doublets at 8.00.

Ir. For each porphyrin ligand the ir spectra of the ruthenium carbonyl, indium chloro, and titanyl complexes from 4000 to 600 cm^{-1} were very similar with the exception of two features. A single strong band between 1930 and 1950 cm^{-1} was observed only in the ruthenium carbonyl complexes and is assigned to the C–O stretch. Similar bands have been observed for other ruthenium carbonyl porphyrins.^{16,20} A band between 975 and 980 cm^{-1} was observed only in the titanyl complexes and is assigned to the Ti–O stretch. A similar band at 1038 cm^{-1} was found in the ir of $\text{TiO}(\text{OEP})$.³²

Analysis of NMR Spectra. The four protons on the para-substituted phenyl rings in the metalloporphyrins with different ligands on the two sides of the porphyrin plane comprise an ABCD spin system. The predominant coupling constant is the 7 Hz coupling between adjacent *o*-H and *m*-H protons. All other couplings are small and unresolved. The chemical shift differences between *o*-H and *m*-H are sufficiently large that the signal for each proton is clearly a doublet although with the unequal intensities characteristic of AB patterns with $\Delta\nu \gg J$.

Since the cross-ring coupling constants are unresolvably small, the spectra consist approximately of two overlapping AB patterns of equal intensity and the exchange process averages A with A' and B with B'. Raban and coworkers^{33a} analyzed the validity of the calculation of $\Delta G^\ddagger_{T_c}$ from $\Delta\nu$ and T_c ^{33b} for the case of coalescing doublets of equal intensity and concluded that the approximate treatment caused, at worst, an error of 0.3 kcal/mol in $\Delta G^\ddagger_{T_c}$.^{33a} Mislow and coworkers compared approximate methods with full line shape analysis and concluded that approximations of $\Delta G^\ddagger_{T_c}$ were relatively accurate even for complex spin systems.^{33c} Potter and Sutherland examined the rate of rotation of benzene rings in paracyclophanes and found no significant difference between $\Delta G^\ddagger_{T_c}$ obtained by approximate and full line shape methods.^{33d} St-Jacques and coworkers reported that the rates and activation parameters calculated by approximate methods and those calculated using Binsch's DNMR program were within the accepted error limit, and the ΔG^\ddagger values were within 0.2 kcal/mol.^{33e} Therefore the $\Delta G^\ddagger_{T_c}$ values quoted below were obtained by the Gutowsky-Holm approximation^{33b} with errors estimated as ± 0.5 kcal/mol.

Discussion

^1H NMR of $\text{H}_2(p\text{-}i\text{-PrTPP})$ Complexes. In 1,1,2,2-tetrachloroethane solution the ^1H NMR spectrum of $\text{H}_2(p\text{-}i\text{-PrTPP})$ contains a doublet for the isopropyl methyls, a septet for the methine protons, a singlet for pyrrole protons, and an apparent AB pattern for the ortho and meta protons on the phenyl rings. Upon formation of the indium chloro, titanyl, or ruthenium carbonyl porphyrin complexes, the ^1H NMR spectrum of the isopropyl and pyrrole protons retains the same multiplicity of signals as in the free porphyrin with some changes in chemical shifts. However, the room temperature spectra of the phenyl protons change from a single doublet for the ortho protons to two doublets and similarly for the meta protons. The doubling of signals for the phenyl protons while the remainder of the spectrum is unchanged is attributed to nonequivalence of the two sides of each phenyl ring due to restricted rotation about the meso-carbon to phenyl-carbon bond and the presence of an axial ligand on only one side of the porphyrin plane in the indium chloro and titanyl complexes or two dissimilar axial ligands in the ruthenium carbonyl complexes.

At room temperature the chemical shift difference between the two doublets for the ortho protons in $\text{In}(p\text{-}i\text{-PrTPP})\text{Cl}$ is 32 Hz and the difference between the doublets for the meta protons is 6 Hz. As the temperature is raised from 30 to 110° the pairs of signals for the ortho- and meta-protons broaden and average to an apparent AB pattern, closely resembling the spectrum obtained at room temperature for the phenyl resonances in the free porphyrin. Based on the slow exchange chemical shift difference and coalescence temperature of ca. 50° for the resonances of the ortho protons, $\Delta G_{323}^\ddagger \sim 16.2$ kcal/mol for the averaging process.³³ When the concentration of the solution is varied by a factor of four there is no observable change in the rate of averaging (Figure 5A).³⁴ If tetrabutylammonium chloride ($n\text{-Bu}_4\text{NCl}$) is added in the ratio of 0.23 mol of $n\text{-Bu}_4\text{NCl}$ to 1.0 mol of $\text{In}(p\text{-}i\text{-PrTPP})\text{Cl}$, the coalescence temperature for the signals of the ortho protons is decreased to ca. 20°. A mole ratio of $n\text{-Bu}_4\text{NCl}$ to $\text{In}(p\text{-}i\text{-PrTPP})\text{Cl}$ of 4.3 causes fast exchange at room temperature (Figure 5A). At a constant mole ratio of $n\text{-Bu}_4\text{NCl}$ to $\text{In}(p\text{-}i\text{-PrTPP})\text{Cl}$ the rate of averaging is strongly dependent on the overall concentration of the solution (Figure 5B). For a mole ratio of $n\text{-Bu}_4\text{NCl}$ to $\text{In}(p\text{-}i\text{-PrTPP})\text{Cl}$ of 0.23 and an initial concentration of complex of 2.2×10^{-3} M, dilution by factors of two and four increases the coalescence temperature for the signals of the ortho protons from ca. 20° to ca. 30° and ca. 40°, respectively. Addition of comparable mole ratios of $n\text{-Bu}_4\text{NClO}_4$ causes no apparent change in rates indicating a specific effect by chloride ion and not simply an effect of ionic strength.

The room temperature spectrum of $\text{TiO}(p\text{-}i\text{-PrTPP})$ is similar to that of $\text{In}(p\text{-}i\text{-PrTPP})\text{Cl}$, but partially exchange broadened. A slow exchange spectrum, obtained at 9°, shows a 41 Hz splitting between the two doublets for the ortho protons and ca. 6 Hz between the doublets for the meta protons. Based on a coalescence temperature of ca. 40° for the ortho-proton signals, $\Delta G_{313}^\ddagger \sim 15.6$ kcal/mol.

Averaging of nonequivalent phenyl resonances has been reported for $\text{Ru}(\text{CO})(p\text{-}i\text{-PrTPP})(\text{EtOH})$ ¹⁶ and $\text{Ru}(\text{CO})(p\text{-}i\text{-PrTPP})(4,5\text{-dimethylpyridazine})$ ²⁰ and activation energies estimated on the basis of slow exchange chemical shifts and coalescence temperatures for the signals of the ortho protons are $\Delta G_{343}^\ddagger \sim 17.9$ kcal/mol¹⁶ and $\Delta G_{367}^\ddagger \sim 18.6$ kcal/mol,²⁰ respectively.

^1H NMR of $\text{H}_2(p\text{-CF}_3\text{TTPP})$ Complexes. The ^1H NMR spectrum of $\text{H}_2(p\text{-CF}_3\text{TTPP})$ contains a singlet for the pyrrole protons and one doublet each for the ortho and meta

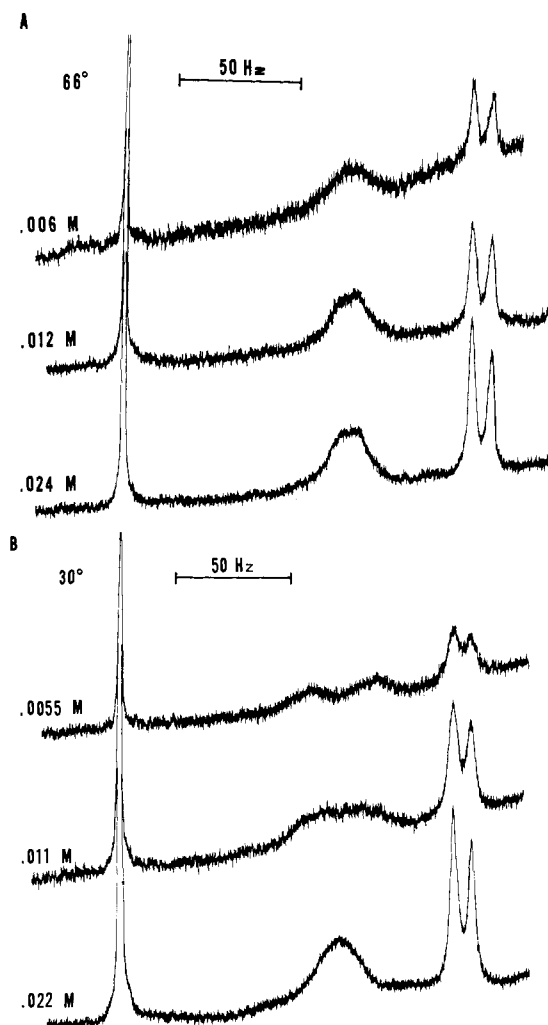


Figure 5. (A) ^1H NMR spectra (100 MHz) of phenyl region for $\text{In}(p\text{-}i\text{-PrTPP})\text{Cl}$ in 1,1,2,2-tetrachloroethane at various concentrations.³⁴ (B) ^1H NMR spectra (100 MHz) of $\text{In}(p\text{-}i\text{-PrTPP})\text{Cl}$ in the presence of $n\text{-Bu}_4\text{NCl}$ at 30°. The ratio of $n\text{-Bu}_4\text{NCl}$ to $\text{In}(p\text{-}i\text{-PrTPP})\text{Cl}$ is constant at 0.23. The concentration of $\text{In}(p\text{-}i\text{-PrTPP})\text{Cl}$ is given to the left of each spectrum.

protons on the phenyl rings. Formation of indium chloro, titanyl, or ruthenium complexes doubles the multiplicity of the signals for the ortho and meta protons, similar to the changes that are observed upon complex formation with $\text{H}_2(p\text{-}i\text{-PrTPP})$. Figure 1 shows the ^1H NMR spectrum of $\text{In}(p\text{-CF}_3\text{TTPP})\text{Cl}$ from 30 to 120°. The smaller chemical shift difference of 8 Hz between the two doublets for the meta protons coalesces at a lower temperature (ca. 45°) than the 30 Hz chemical shift difference between the two signals for the ortho protons which coalesces at ca. 65°. Based on the coalescence of the signals for the ortho protons ΔG_{338}^\ddagger is estimated as 17.0 kcal/mol. Very similar behavior has also been observed for $\text{In}(p\text{-MeTTPP})\text{Cl}$.²¹

The slow exchange chemical shift difference of 40 Hz at 17° for the two ortho-proton signals in $\text{TiO}(p\text{-CF}_3\text{TTPP})$ is fully averaged at 115° (Figure 3). Based on a coalescence temperature of 55° for the ortho-proton signals, $\Delta G_{328}^\ddagger \sim 15.6$ kcal/mol. Similarly a chemical shift difference of 16 Hz at 30° between the signals for the ortho protons on the phenyl rings in $\text{Ru}(\text{CO})(p\text{-CF}_3\text{TTPP})(\text{THF})$ coalesces at 65°. ΔG_{338}^\ddagger is estimated as 17.5 kcal/mol.

Complexes of $\text{H}_2(\text{F}_5\text{TTPP})$. The electronegativity of the pentafluorophenyl groups greatly decreases the reactivity of $\text{H}_2(\text{F}_5\text{TTPP})$ relative to the other porphyrins examined in

this study. For most of the porphyrins the reaction between InCl_3 and free porphyrin in refluxing acetic acid went to completion in 2–24 hr. The reaction with $\text{H}_2(\text{F}_5\text{TPP})$ required 4 days. Attempts to prepare titanyl and ruthenium carbonyl complexes of $\text{H}_2(\text{F}_5\text{TPP})$ by the methods used with the other porphyrins, afforded very low yields of impure products.

The fluorine signals in the ^{19}F NMR of $\text{H}_2(\text{F}_5\text{TPP})$ (Figure 2A) have been assigned by analogy with pentafluorobenzenes.³¹ The spin-spin coupling patterns observed for the ortho and meta fluorines in the free porphyrin (Figure 2A) are approximately doubled for the ortho and meta fluorines in the ^{19}F spectrum of $\text{In}(\text{F}_5\text{TPP})\text{Cl}$ (Figure 2C) indicating nonequivalence of the two sides of each phenyl ring similar to the behavior of the indium chloro complexes discussed above. The signals for the para fluorine are similar in the ligand and the complex. Averaging of nonequivalent fluorines is not observed up to 130° in 1,1,2,2-tetrachloroethane. Rapid averaging can be achieved by addition of excess *n*- Bu_4NCl to $\text{In}(\text{F}_5\text{TPP})\text{Cl}$ yielding a spectrum (Figure 2B) similar to that of $\text{H}_2(\text{F}_5\text{TPP})$.

^1H NMR of $\text{H}_2(\text{Me}_3\text{TPP})$ Complexes. The methyl region of the ^1H NMR spectrum of $\text{H}_2(\text{Me}_3\text{TPP})$ in 1,1,2,2-tetrachloroethane shows two singlets with a 2 to 1 ratio of intensities at 1.86 and 2.62 ppm downfield of tetramethylsilane. Based on relative populations the former is assigned to the ortho-methyl protons and the latter to the para-methyl protons. Upon formation of indium chloro, titanyl, or ruthenium carbonyl complexes, the signal for the ortho-methyl protons is split into two singlets of equal intensity consistent with nonequivalent sides of each phenyl ring. The signal for the para-methyl protons remains a singlet. The two singlets for the ortho-methyl protons in $\text{In}(\text{Me}_3\text{TPP})\text{Cl}$ are separated by 13 Hz at room temperature in 1,1,2,2-tetrachloroethane. The chemical shift difference between the two signals decreases as temperature increases. Up to 100° no averaging is observed, but above 100° the chemical shift difference is too small to provide any information concerning averaging of nonequivalent sites. If *n*- Bu_4NCl is added to $\text{In}(\text{Me}_3\text{TPP})\text{Cl}$ in 1,1,2,2-tetrachloroethane in large (5:1) molar excess a single *o*- CH_3 signal is observed at room temperature.

The methyl region of the ^1H NMR spectrum of $\text{TiO}(\text{Me}_3\text{TPP})$ contains a pair of equal intensity signals 21 Hz apart for the ortho-methyl protons in addition to the singlet for the para-methyl protons. No averaging is observed up to 135° indicating that ΔG^\ddagger is greater than 20 kcal/mol for averaging of nonequivalent ortho-methyl sites. Similarly no averaging is observed up to 135° for nonequivalent methyl resonances in $\text{Ru}(\text{CO})(\text{Me}_3\text{TPP})(\text{pyridinate})$. (The isolated THF adduct was converted to the more soluble pyridine adduct by addition of equimolar pyridine to the NMR sample. Free THF was observed in the spectrum.)

^1H NMR of $\text{H}_2(o\text{-CH}_3\text{TPP})$ Complexes. Due to restricted rotation of the unsymmetrically substituted phenyl rings, $\text{H}_2(o\text{-CH}_3\text{TPP})$ can exist as a mixture of four isomers with six different environments for the methyl groups.³⁰ When the porphyrin is coordinated to a metal with different groups in the fifth and sixth coordination sites, the number of possible methyl environments is doubled from 6 to 12. We assume that at room temperature the phenyl rings rapidly oscillate about a position perpendicular to the mean plane of the porphyrin. The approximate calculations of Wolberg⁸ indicate an energy minimum at ca. 45° , but the estimated barrier between 45° and 90° is not inconsistent with rapid torsional oscillations. This assumption is consistent with the absence of detectable torsional isomers in the NMR spectra of porphyrins in prior work.^{20–22,30} In the room temperature ^1H NMR spectrum of $\text{In}(o\text{-CH}_3\text{TPP})\text{Cl}$

in 1,1,2,2-tetrachloroethane solution, the methyl region includes two groupings of signals about 40 Hz apart. The downfield group appears to be a superposition of two peaks and the upfield group includes four partially resolved signals. As the temperature is raised the peaks remain sharp and relative chemical shifts change slightly, such that at 140° seven signals are observed. In nitrobenzene solution no averaging is observed up to 150° at which point the chemical shift differences become too small to distinguish averaging from temperature dependence of chemical shifts. Addition of *n*- Bu_4NCl in a mole ratio of 4.5 mol of *n*- Bu_4NCl to 1.0 mol of $\text{In}(o\text{-CH}_3\text{TPP})\text{Cl}$ (concentration = $5.6 \times 10^{-2} M$) caused averaging of the six methyl signals spread over a 40 Hz range to three signals within a 5 Hz range at 70° .

In a tetrachloroethane solution of $\text{TiO}(o\text{-CH}_3\text{TPP})$ at ambient temperature nine methyl signals are observed over a range of 90 Hz. At 135° nine sharp signals are still clearly resolved. In nitrobenzene solution there is no evidence of averaging up to 180° , indicating $\Delta G^\ddagger > 23$ kcal/mol. Similarly, averaging of nonequivalent methyl signals is not observed up to 135° in $\text{Ru}(\text{CO})(o\text{-CH}_3\text{TPP})(\text{pyridinate})$.

Comparison of Complexes. In the ^1H NMR spectra of indium chloro, titanyl, and ruthenium carbonyl complexes of $\text{H}_2(p\text{-}i\text{-PrTPP})$ and $\text{H}_2(p\text{-CF}_3\text{TPP})$, resonances are observed for nonequivalent ortho and nonequivalent meta protons in 1,1,2,2-tetrachloroethane solution at or slightly below room temperature. As the temperature is raised to ca. 120° the signals for nonequivalent phenyl protons broaden and coalesce to an apparent AB pattern by a concentration independent pathway. The observed averaging on the NMR time scale could in principle be effected by any process which makes the two sides of each phenyl ring equivalent. Rotation of the phenyl rings with respect to the plane of the porphyrin ring or exchange of axial ligands from one side of the porphyrin plane to the other by a dissociative pathway could cause such averaging. Since the activation energies are similar for such different combinations of metal and axial ligands as $\text{In}-\text{Cl}$, $\text{Ti}-\text{O}$, and $\text{Ru}-\text{CO}$ it seemed unlikely that ligand exchange was responsible for the observed averaging.

Since it was expected that the size of the ortho substituent would have considerably more influence on the rate of ring rotation than on the rate of a dissociative axial ligand exchange, complexes were prepared with methyls or fluorines in the ortho positions of the phenyl rings. In 1,1,2,2-tetrachloroethane solutions of the indium chloro, titanyl, and ruthenium carbonyl complexes of $\text{H}_2(o\text{-CH}_3\text{TPP})$ and $\text{H}_2(\text{Me}_3\text{TPP})$ and in $\text{In}(\text{F}_5\text{TPP})\text{Cl}$, no averaging of resonances for nonequivalent phenyl substituents was observed in the temperature range where averaging was fast for complexes with only protons in the ortho positions of the phenyl rings. Thus the process observed in the absence of excess axial ligand for complexes with ortho protons is attributed to rapid rotation on the NMR scale around the meso-carbon to phenyl-carbon bond. The presence of larger ortho substituents, either methyls or fluorines, increases the steric interaction with the pyrrole hydrogens and greatly increases the activation energy for rotation.

A concentration dependent process was observed in the presence of added chloride ion, for all of the indium complexes studied. The spectra of $\text{In}(o\text{-CH}_3\text{TPP})\text{Cl}$ are particularly informative concerning the nature of this process. Twelve methyl environments are theoretically possible considering the various isomers of this compound if both chloride exchange and phenyl ring rotation are slow. Chloride exchange would average the 12 environments to 6 and phenyl ring rotation would cause averaging to a single methyl environment. In $\text{In}(o\text{-CH}_3\text{TPP})\text{Cl}$ at 140° in 1,1,2,2-tetra-

chloroethane solution, 7 methyl signals are observed, indicating both processes are slow on the ^1H NMR time scale. Addition of $n\text{-Bu}_4\text{NCl}$ causes collapse to three closely spaced signals at 70° . The observation of more than one signal indicates that chloride exchange is occurring and not phenyl ring rotation, under these conditions.

The addition of CO to solutions of ruthenium carbonyl porphyrins has been observed to cause averaging of signals due to nonequivalent phenyl protons. The averaging is attributed to rapid CO exchange in the presence of excess CO.³⁵ The details of the CO exchange are currently under investigation.

Coordination of Additional Ligands. The coordination of bases in the sixth position of the ruthenium carbonyl complexes has been discussed.²⁰ Addition of equimolar EtOH or 4-*tert*-butylpyridine (*t*-Bu(py)) to solutions of $\text{In}(p\text{-}i\text{-PrTPP})\text{Cl}$ caused no detectable shift in the ^1H NMR resonances for the ethyl group in EtOH or the *t*-butyl group in *t*-Bu(py), indicating little or no interaction between the metalloporphyrin and the potential donor atoms. Similar results were obtained with $\text{TiO}(p\text{-}i\text{-PrTPP})$ and EtOH or *t*-Bu(py). However, it appears that $\text{TiO}(p\text{-}i\text{-PrTPP})$ and $\text{TiO}(\text{Me}_3\text{TPP})$ readily pick up a half mole of water per mole of complex in the solid state. Samples dried at EtOH reflux under vacuum were observed to gain weight during subsequent weighing in air. Analyses of dried samples handled in air were consistently low in carbon relative to the value for $\text{TiO}(\text{porphyrin})$ but correct for $\text{TiO}(\text{porphyrin}) \cdot \frac{1}{2}\text{H}_2\text{O}$. Samples dried in vacuo and subsequently handled in inert atmosphere analyzed correctly for the anhydrous complex. No evidence for water of hydration was found in the ^1H NMR spectra, but other investigators have commented on the difficulty of observing axial water and hydroxy ligands.³⁶⁻³⁸ For example, in thalium(hydroxy)(aquo)(OEP) no ^1H NMR signal could be found for either the hydroxy group or the water.³⁶

Comparison with Prior Results. Both phenyl ring rotation and concentration dependent chloride exchange processes have been reported for $\text{Fe}(\text{TPP})\text{Cl}$ and $\text{Fe}(p\text{-CH}_3\text{TPP})\text{Cl}$.^{39,40} However, in $\text{Fe}(p\text{-CH}_3\text{TPP})\text{I}$, iodide exchange occurs even in the absence of added iodide ion.³⁹ Averaging of nonequivalent phenyl ring proton resonances attributed to ring rotation was observed for (*cis*-4-*tert*-butylcyclohexoxy)(OH)GeTPP.⁴¹ Thus, temperature dependent NMR spectra attributable to phenyl ring rotation have been observed for Ge, Fe, In, Ru, and Ti complexes of tetraphenylporphyrins with protons in the ortho positions of the phenyl rings. The temperature at which rotation is fast on the NMR time scale depends on the metal. Estimated activation energies increase in the order $\text{Ge}(\text{OH})\text{L}^{41} \sim \text{TiO} \sim \text{FeCl}^{42} < \text{InCl} < \text{Ru}(\text{CO})$. ΔG^\ddagger values range from 15.6 kcal/mol for $\text{TiO}(p\text{-}i\text{-PrTPP})$ to 18.6 kcal/mol for $\text{Ru}(\text{CO})(p\text{-}i\text{-PrTPP})(4,5\text{-dimethylpyridazine})$.²⁰ Based on the steric interactions discussed below, it appears reasonable to assume that phenyl ring rotation requires substantial distortion of the porphyrin. Presumably the differences in rates are due to differences in the degree of nonplanarity of the porphyrin planes and/or to differences in the ease of distortion of the complexes. Further studies are currently in progress to understand this variation.

The NMR of $\text{Ni}(o\text{-CH}_3\text{TPP})$ shows nonequivalent methyls up to 180° ³⁰ ($\Delta G^\ddagger > 26$ kcal/mol). Isomers of $\text{H}_2(o\text{-OHTPP})$ have been separated, and the rate constant for rotation in methanol at 23° is $1.5 \times 10^{-5} \text{ sec}^{-1}$ ($\Delta G^\ddagger_{296} = 24$ kcal/mol).⁴³ Rotation was about ten times slower for $\text{Cu}(o\text{-OHTPP})(\text{H}_2\text{O})$ in aqueous methanol ($\Delta G^\ddagger = 25$ kcal/mol).⁴³ The difference in rates is interpreted as indicating the $\text{H}_2(o\text{-OHTPP})$ must distort considerably in the transition state and that the more rigid $\text{Cu}(\text{II})$ complex is

less able to undergo such distortions.⁴³ Including the rates observed in this work, the data indicate that the rate of rotation about the meso-carbon to phenyl-carbon bond in metal complexes of ortho-substituted tetraphenylporphyrins varies in the order $\text{CH}_3 < \text{OH} \ll \text{H} \gg \text{F}$, which is consistent with the steric requirements of the ortho substituents. Isomers of $\text{H}_2(o\text{-NH}_2\text{TPP})$ have been separated and interconversion achieved by refluxing in toluene for 20 min.⁴⁴ Since data have not been reported for metal complexes of $\text{H}_2(o\text{-NH}_2\text{TPP})$ and the reported information on the ligand is not quantitative, it is not possible to include it in the series of relative rates above. However, it would appear to fall somewhere in the vicinity of the CH_3 or OH substituents.

Wolberg used Lennard-Jones potentials and resonance energies as a function of phenyl-ring rotation angle in tetraphenylporphyrins to calculate that the minimum energy configuration occurs when the angle between the phenyl ring and the plane of the porphyrin is 44° .⁸ This angle is considerably smaller than the angles of $69\text{--}90^\circ$ ^{9,10,13-15} found in X-ray crystallographic structures of metal complexes of tetraphenylporphyrins. The calculations suggest that in solution a considerable range of orientations of the phenyl rings relative to the porphyrin plane are energetically accessible with rapid motion through angles as varied as 44 to 136° . Such motion is presumably much faster than rotation through the plane of the porphyrin.

Several recent studies have indicated that resonance effects of phenyl ring substituents influence behavior at the metal center. Variation of X groups in $\text{Ni}(p\text{-XTPP})$ affects the coordination of donor ligands in accordance with Hammett correlations.⁴⁵ Rate constants and optical absorption maxima also correlate with phenyl ring substituent variation.⁴⁶ These results are more readily understood in light of the mobility of the phenyl rings and the range of orientations available to them.

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Stereochemical Consequences of Orbital Symmetry Control in the Reversible Combining of Sulfur Dioxide with Conjugated Systems (Sulfolene Reactions)

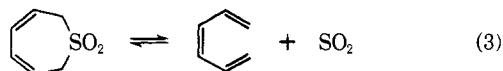
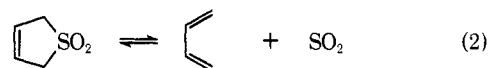
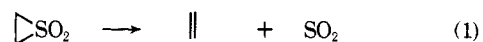
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Abstract: The syntheses of the cis and trans stereoisomers of 2,5-dimethyl-2,5-dihydrothiophene 1,1-dioxide (**1** and **2**) and 2,7-dimethyl-2,7-dihydrothiepin 1,1-dioxide (**3** and **4**), the latter pair via a novel ring expansion, are recorded. Thermolysis of these two heterocycles into sulfur dioxide plus 2,4-hexadienes and 2,4,6-octatrienes, respectively, was observed to occur stereospecifically: **1** \rightarrow (*E,E*)-C₆H₁₀; **2** \rightarrow (*Z,E*)-C₆H₁₀; **3** \rightarrow (*Z,Z,E*)-C₈H₁₂; **4** \rightarrow (*E,Z,E*)-C₈H₁₂. The chelotropic cycloreversion proceeded suprafacially in the smaller ring (>99.9%) and antarafacially in the larger ring (>97%) with respect to the hydrocarbon product. Some mechanistic implications regarding these apparently concerted transformations are discussed.

The well known, reversible formation of the sulfolene (2,5-dihydrothiophene 1,1-dioxide) structure from sulfur dioxide plus a conjugated diene comprises a reaction which has occasionally been exploited for synthetic purposes and which also offers challenges of a mechanistic nature having to do with valence shell expansion of sulfur. We attempt here and in the following paper in this issue² to summarize our recent and continuing inquiry into the mechanistic details of the chemical interaction of sulfur dioxide with conjugated systems, with specific and especial consideration of orbital symmetry concepts. In this connection, the sulfolene cycloadditions are to be considered as members of a family of chelotropic reactions (eq 1-3). It is from a comparison of structure-reactivity relationships within this sequence that mechanistic inferences may be drawn.

At the inception of this inquiry, episulfone fragmentation (eq 1) had received some study³ and the sulfolene reaction (eq 2) considerably more thorough examination.⁴ The 1,6 addition (eq 3) was found in the course of this investigation.⁵ There was for the second and third reactions, how-



ever, lack of definitive stereochemical evidence regarding the mode of sulfur dioxide addition and elimination. In this article, we shall describe and comment upon the stereochemical course of fragmentation in the latter set of transformations (eq 2,3). In the following paper in this issue,² we describe additional evidence of a kinetic and thermodynamic nature which has bearing on the mechanisms of these reactions.

Adequate documentation exists to establish that fragmentation of the three-membered ring episulfones (eq 1) proceeds cleanly suprafacially with respect to the alkene