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Activation Barriers to *meso*-Aryl Group Rotation in Titanyl Tetraaryltetrapyrroles. An Investigation of the Out-of-Plane Flexibility of Hydroporphyrins

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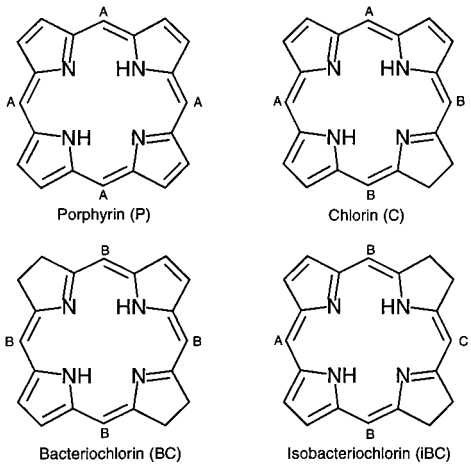
The free-base and titanyl ($Ti^{IV}O$) complexes of *meso*-tetratolyl- and *meso*-tetra(3,5-xylyl)hydroporphyrins were synthesized and characterized. Metalation of the hydroporphyrins with titanium was achieved by reaction of the lithium salts of the hydroporphyrin with $TiCl_4$. Other methods used to metalate porphyrins with titanium required harsher reaction conditions and led to substantial oxidative dehydrogenation of the macrocycle when applied to hydroporphyrins. The titanyl group differentiates the two faces of the macrocycle and consequently the two sides of the *meso*-aryl groups, which are tilted nearly perpendicular to the macrocycle plane. The ^1H NMR signals for the nonequivalent ortho protons and nonequivalent meta protons averaged on the NMR time scale at elevated temperatures due to aryl group rotation. Activation barriers for aryl group rotation in the para-substituted and meta-disubstituted titanyl hydroporphyrin complexes and in related titanyl porphyrin complexes were determined from variable-temperature NMR spectra and ranged from 15.6 to 18.4 kcal/mol. In chlorin compounds, barriers for rotation of aryl groups located between a pyrrole and a pyrroline (reduced) ring are greater than those of aryl groups located between two pyrrole rings. Comparisons of barriers in complexes with different macrocycle saturation levels show that the increased barriers for aryl groups adjacent to pyrroline rings cannot be attributed solely to the increased steric bulk of the pyrroline β-CH_2 group relative to the pyrrole β-CH group. Variations in flexibility and electronic environments at meso carbons in the hydroporphyrins may also contribute. Rotation barriers for meta-disubstituted aryl groups, which are higher than those for para-substituted aryl groups, increase with the size and mass of the substituent.

Introduction

Hydroporphyrins are compounds in which one or more double bonds of a porphyrin have been saturated by the formal addition of hydrogen atoms or alkyl groups across a double bond.[1] Structures of di- and tetrahydroporphyrin compounds are compared with that of the parent porphyrin in Chart 1.

Chart 1



Metal complexes of hydroporphyrins and other non-porphyrin tetrapyrroles play central roles as prosthetic groups in the biochemical pathways of the carbon, nitrogen, and sulfur cycles and in the metabolism of many anaerobic bacteria. Examples include chlorophylls and pheophytins, the magnesium and free-base chlorin and bacteriochlorin pigments of photosynthesis;[2] siroheme, the iron isobacteriochlorin prosthetic group of assimilatory (biosynthetic) nitrite and sulfite reductases;[3−5] and F430, a nickel hydrocorphinoid

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prosthetic group involved in methanogenesis.[6] The absence of enzymes that contain porphyrin prosthetic groups and are competent to catalyze these processes is conspicuous and raises the question of whether non-porphyrin tetrapyrroles are specifically required. Thus, there is considerable interest in delineating the effects of changes in the structure and saturation level of a tetrapyrrole macrocycle on the chemistry of its complexes and in particular on the chemistry of a coordinated metal ion.

Several chemical differences between hydroporphyrins and porphyrins have been observed. Hydroporphyrins have intrinsically larger core sizes and exhibit both a greater tendency to adopt nonplanar conformations and greater displacements from planarity than the corresponding porphyrin complexes that have similar peripheral substitution.[7,8] Standard reduction potentials of ligand-centered redox processes generally decrease with increasing macrocycle saturation.[9−19] Thus, hydroporphyrin macrocycles are easier to oxidize and more difficult to reduce than porphyrins. The resistance of the macrocycle to reduction and the larger core size are reasons that hydroporphyrins can stabilize metal ions in less common, low-valent oxidation states such as Cu^{I} and Ni^{I}, which are not readily accessible in porphyrins.[15,17,18] Other notable differences between hydroporphyrins or porphyrins have been reported or summarized elsewhere.[20,21]

We proposed that hydroporphyrins have shallower conformational energy surfaces than porphyrins and that this could cause significant differences in the chemistries of the complexes of these tetrapyrroles.[17] In other words, hydroporphyrins are more "flexible" than porphyrins. The difference in flexibility could affect both the ease of changing the tetrapyrrole hole size (in-plane flexibility) and the ease of deforming the tetrapyrrole from planarity (out-of-plane flexibility). EXAFS and resonance Raman studies have demonstrated that the metal-centered reductions of the octaethylisobacteriochlorin complexes Cu(OEiBC) and Ni(OEiBC) result in large structural changes that involve in-plane flexibility.[22] Indeed, the four Cu−N distances of 2.00 Å in the Cu^{II} complex increase to 2.06 Å in the Cu^{I} complex, and the four Ni−N distances of 1.94 Å in the Ni^{II} complex change to two Ni−N distances of 1.91 Å and two of 2.07 Å in the Ni^{I} complex.

In an effort to probe the out-of-plane flexibility of tetrapyrroles, we investigated the activation barriers to rotation of *meso*-aryl groups in the previously unknown titanyl (Ti═O) hydroporphyrin complexes. Earlier studies of titanyl porphyrin complexes established that the coordinated titanyl group differentiates the two faces of the porphyrin, that the chemical shift differences in these diamagnetic complexes are substantial between both the nonequivalent ortho protons and the nonequivalent meta protons of the *meso*-aryl group, which is tilted nearly perpendicular to the porphyrin plane and has restricted rotation, and that slow and fast exchange regimes for aryl ring rotation are both accessible at experimentally convenient temperatures.[23−26] In addition, the titanyl group is chemically inert, and its porphyrin complexes are not subject to axial ligand binding or exchange reactions that could lead to complications.[24] The restricted rotation of the *meso*-aryl groups is a consequence of steric interactions between the aryl ortho protons and the porphyrin β-pyrrole protons that occur when the aryl group and porphyrin are nearly coplanar. Although evidence shows that electronic effects from interaction of the aryl group and porphyrin π-systems contribute to the rotation barriers,[25,27] the ability of the porphyrin macrocycle to deform and permit the ortho and β-pyrrole protons to avoid each other is clearly important. As such, changes in macrocycle flexibility in hydroporphyrins could affect the rotation barriers of aryl groups situated adjacent to pyrroline (saturated) rings. Direct comparisons may be complicated by two factors, though. First, the steric environments of the *meso*-aryl groups in hydroporphyrins are not identical to each other or to those in porphyrins. Meso positions adjacent to zero, one, and two pyrroline rings are labeled A, B, and C, respectively, in Chart 1. The two additional β-protons present in a pyrroline ring could increase steric interactions. Second, the symmetry and electronic inequivalence of the hydroporphyrin meso positions could result in different electronic contributions to the rotation barriers. The increased rate of electrophilic reactions at meso positions adjacent to pyrroline rings has been taken as an indication of increased electron density at these sites.[28−31]

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Also, calculated spin densities at the meso positions of hydroporphyrin cation and anion radicals differ within a macrocycle and between the different macrocycles.[32,33] We report in this paper the syntheses of titanyl hydroporphyrin complexes and compare the activation barriers for rotation of *meso*-aryl groups in these complexes with those in titanyl porphyrin complexes.

Experimental Section

All reactions, chromatography, recrystallizations, and sample manipulations involving hydroporphyrins were carried out under subdued lights and under a nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres Co. drybox, unless otherwise noted. Reagents and solvents used in this study were HPLC or reagent grade. Toluene and THF were distilled from sodium benzophenone ketyl. Methylene chloride and chloroform were distilled from CaH_2. Pyridine was distilled from BaO. NMR solvents were treated to remove traces of water and acid immediately before use by passage down a dry column of grade I basic alumina. The initial runnings were discarded.

The *meso*-tetraarylporphyrins H_2(TPP), H_2(TTP), H_2(TXP), H_2(TpClPP), H_2(TpCF$_3$PP), H_2(TpMeOPP), H_2(T3,5FPP), and H_2(T3,5MeOPP) were prepared from pyrrole and the appropriate substituted benzaldehyde by either the Adler−Longo[34] or Lindsey method.[35,36] H_2(T3,5BrPP) and H_2(T3,5tBuPP) were purchased from Strem. H_2(TTC) and H_2(TTiBC) were prepared and purified by literature methods.[37]

Absorption spectra were recorded on a Perkin-Elmer Lambda 6 UV−vis spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL Eclipse 270 spectrometer (270.17 MHz) equipped with a variable-temperature control system.

H_2(TTBC). A mixture of 2.1 g (3.1 mmol) of H_2(TTP), 6.0 g (32.2 mmol) of *p*-toluenesulfonhydrazide, 8.0 g (58 mmol) of anhydrous K_2CO_3, and 250 mL of dry pyridine was placed in a 500 mL three-neck flask that was equipped with a gas inlet atop a reflux condensor, a septum, a stir bar, and a thermocouple probe connected to a J-Kem model 210T temperature controller. The contents of the flask were degassed and placed under nitrogen. The reaction was heated and stirred at 95 °C for 96 h. The warm reaction mixture was filtered anaerobically, and the filtrate was evaporated. The resulting solid was suspended in dry acetone by stirring and then collected on a Schlenk frit. The blue solid was washed with methanol (100 mL) followed by acetone (200 mL) and dried in vacuo to afford 700 mg (1.0 mmol, 32% yield) of H_2(TTBC) that contained roughly 10% of an overreduced impurity presumed to be a hexahydroporphyrin.

H_2(TXC). The compound was prepared from H_2(TXP) and purified by the procedure reported for H_2(TTC).[37] When reacted at 90 °C for 12 h, 1.0 g (1.4 mmol) of H_2(TXP) afforded 0.22 g (22% yield) of isolated product after flash chromatography. UV−vis (CH_2Cl_2): λ_{max}, nm ($10^{-3}\epsilon_M$, M^{-1} cm^{-1}), 420 (64.6), 518 (5.4), 547 (4.2), 597 (2.3), 653 (10.3).

H_2(TXBC). A mixture of 1.0 g (1.4 mmol) of H_2TXP, 1.66 g (8.9 mmol) of *p*-toluenesulfonhydrazide, 4.0 g of anhydrous K_2CO_3, and 250 mL of dry pyridine was reacted at 95 °C for 36 h. After an initial heating period of 2 h, an additional aliquot of 1.0 g of *p*-toluenesulfonhydrazide was added every 4 h (with the exception of one addition during an 8 h overnight period). The reaction was worked up following the procedure for H_2(TTC).[37] The crude product was purified by preparative TLC on silica plates to afford 50 mg (68 μmol, 5% yield). UV−vis (CH_2Cl_2): λ_{max}, nm (rel abs), 355 (0.95), 365 (0.91), 376 (1.00), 522 (0.38), 739 (0.74).

H_2(TXiBC). The compound was prepared from H_2(TXP) and purified by the procedure reported for H_2(TTiBC).[37] When reacted at 100 °C for 24 h, 1.0 g (1.4 mmol) of H_2(TXP) afforded 90 mg (0.12 mmol, 9% yield) of isolated product after flash chromatography. UV−vis (CH_2Cl_2): λ_{max}, nm (rel abs), 370 (sh, 0.66), 391 (0.91), 414 (1.00), 516 (0.10), 553 (0.14), 598.7 (0.20).

Lithium Salts of Tetrapyrroles. The free-base porphyrin or hydroporphyrin was dried overnight in a vacuum oven at 60 °C. A 50 mg sample of the free-base compound was placed in an oven-dried Schlenk flask and dissolved in 5 mL of toluene. The resulting solution was freeze−thaw degassed. A 2.05 equiv sample of butyllithium (2.5 M in hexane) was added by syringe. The mixture was stirred for 5−10 min at room temperature, during which time the solution changed color. The solvent was removed under vacuum to afford a solid that was redissolved in an appropriate solvent for spectroscopy.

(a) Li$_2$(TTP). UV−vis (CH_2Cl_2): λ_{max}, nm (rel abs), 416 (sh, 0.39), 434 (1.00), 576 (0.06), 620 (0.07). ^{1}H NMR (C_7D_8): δ 2.56 (s, 12 H, Ph−CH_3), 7.48 (d, 8 H, meta Ph), 8.28 (br d, 8 H, ortho Ph), 8.92 (s, 8 H, py).

(b) Li$_2$(TTC). UV−vis (CH_2Cl_2): λ_{max}, nm, 407 (sh), 429, 521, 560, 602, 626.

(c) Li$_2$(TTiBC). UV−vis (CH_2Cl_2): λ_{max}, nm (rel abs), 390 (sh, 0.53), 409 (sh, 0.86), 420 (1.00), 503 (0.09), 615 (0.19), 714 (0.01).

(d) Li$_2$(TTBC). A 6.4 equiv sample of butyllithium was required. The solution color changed from red to purple. UV−vis (C_7H_8): λ_{max}, nm (rel abs), 365 (0.96), 390 (1.0), 574 (0.36), 755 (0.77). ^{1}H NMR (C_7D_8): δ 2.42 (s, 12 H, Ph−CH_3), 3.98 (s, 8 H, CH_2-CH_2), 7.33 (d, 8 H, metal Ph), 7.85 (br d, 8 H, ortho Ph), 8.31 (s, 8 H, py).

TiO(TTP). A 2.53 g (3.77 mmol) sample of dried H_2(TPP) and 100 mL of dry toluene were placed in an oven-dried 250 mL Schlenk flask that was stoppered with a septum. The resulting solution was freeze−thaw degassed. The lithium salt was prepared by adding 3.1 mL (7.73 mmol) of butyllithium (2.5 M in hexanes) by syringe. The solution color changed from red to bright forest green while the solution was stirred at room temperature. When the color change was complete after 10 min, 15.0 mL of 1.0 M $TiCl_4$ in toluene solution (15.0 mmol) was added by syringe. The solution was heated to 50 °C and stirred for 2 h, during which time the color changed to dark green. The solution was cooled to room temperature, then exposed to air, and stirred until the color turned bright crimson red due to conversion of the titanium dichloride complex to a titanyl complex. The solution was applied to the top of a column of dry alumina (activity grade I) in a flash chromatography column. Elution with toluene (under gravity flow until the alumina was fully saturated with liquid and then with head pressure applied) gave a band of unreacted H_2(TPP). Chloroform was then used to elute TiO(TTP). The chloroform was removed on a rotary evaporator and the residue recrystallized to afford 2.04

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g of TiO(TTP) (2.78 mmol, 74% yield). UV−vis (CH_2Cl_2): λ_{max}, nm (rel abs), 426 (1.00), 548 (0.06), 586 (0.01).

TiO(TXP). TiO(TXP) (and the titanyl complexes of other substituted tetraphenylporphyrins) was prepared similarly in about 80% yield. UV−vis (CH_2Cl_2): λ_{max}, nm (rel abs), 425 (1.00), 551 (0.08), 590 (0.04).

TiO(TTC). The procedure for TiO(TTP) was modified by decreasing the reaction time at 50 °C to 1.5 h and not exposing the reaction solution to air. Conversion of the titanium dichloride solution to a titanyl complex and initial purification were achieved by applying the reaction solution to the column of dry alumina under a nitrogen atmosphere. The column was run as above. The green chloroform solution of TiO(TTC) was concentrated and brought into a nitrogen-filled glovebag for further purification by preparative TLC on silica. The plates were developed with chloroform. Development was performed in the dark by covering the tank with aluminum foil. Solvent was evaporated from the plates using a heavy stream of nitrogen. The band of silica containing the purified complex was scraped off the plate and the compound recovered by washing the silica with chloroform. A total of 45 mg of TiO(TTC) (61 μmol) was obtained from 70 mg of H_2(TTC) (104 μmol) using corresponding quantities of solvent and reagents, a yield of 59%. UV−vis (CH_2Cl_2): λ_{max}, nm (rel abs), 402 (sh, 0.34), 422 (1.00), 521 (0.15), 593.4 (0.15), 630.8 (0.24).

TiO(TTiBC). The procedure for TiO(TTC) was followed with the exception that the reaction time at 50 °C was 30 min. A total of 70 mg of TiO(TTiBC) (95 μmol) was obtained from 95 mg of H_2(TTiBC) (129 μmol), a yield of 74%. UV−vis (CH_2Cl_2): λ_{max}, nm (rel abs), 385 (0.60), 405 (0.76), 419 (1.00), 567 (0.29), 615 (0.44).

TiO(TTBC). The procedure for TiO(TTC) was modified by using 6.4 equiv of butyllithium and heating at 50 °C for 2.5 h. The solution of the titanium dichloride complex was filtered through a small bed of Celite, which served to convert it to the titanyl complex. The complex was used with no additional purification. UV−vis (CH_2Cl_2): λ_{max}, nm, 359, 402, 556, 790.

TiO(TXC). The procedure for TiO(TTC) was followed. A total of 50 mg of TiO(TXC) (63 μmol) was obtained from 85 mg of H_2(TXC) (116 μmol), a yield of 54%. UV−vis (CH_2Cl_2): λ_{max}, nm (rel abs), 402 (sh, 0.23), 423 (1.00), 522 (0.04), 551 (0.05), 594 (0.05), 633 (0.15).

Variable-Temperature NMR Spectra. ^{1}H NMR spectra were obtained using freshly prepared 1,1,2,2-tetrachloroethane-d_2 solutions of titanyl complexes. The NMR tubes containing the solutions were sealed off with a glassblowing torch under a partial nitrogen atmosphere. Chemical shifts in tetrachloroethane-d_2 are only slightly different (generally within 0.1 ppm) from those reported in Table 3, which are in $CDCl_3$. Solutions were typically $(5-10) \times 10^{-3}$ M in complex. Spectra were recorded at appropriate temperatures over the range from the slow exchange to fast exchange limits. Samples were given adequate time to equilibrate at each temperature before the spectrum was recorded. The reproducibility of the spectra of a particular complex at a given temperature was good, both for repeated measurements of an individual sample cycled over the temperature range and for measurements of independent samples of the complex. Eaton and Eaton have shown that the exchange process is independent of the sample concentration.[23] The probe temperature was calibrated using methanol and ethylene glycol standards and the temperature-dependent shifts of Van Geet, which have errors (rms) of 0.6 and 0.3 °C, respectively.[38] The temperature achieved in the probe was reproducible to ±0.2 °C.

Table 1. Abbreviations for Meso-Substituted Porphyrins

porphyrin	aryl group	porphyrin	aryl group
TPP	phenyl	TpMeOPP	4-methoxyphenyl
TTP	4-methylphenyl (tolyl)	T3,5FPP	3,5-difluorophenyl
TXP	3,5-dimethylphenyl (xylyl)	T3,5BrPP	3,5-dibromophenyl
TpClPP	4-chlorophenyl	T3,5MeOPP	3,5-dimethoxyphenyl
$TpCF_3PP$	4-(trifluoromethyl)phenyl	T3,5tBuPP	3,5-di-*tert*-butylphenyl

Results

Synthesis. The porphyrin and hydroporphyrin complexes used in this study were para-substituted or meta-disubstituted tetraphenylporphyrin complexes. The abbreviations used to specify a particular tetrapyrrole consist of a T (for tetra) followed by a designation for the *meso*-aryl group and then P, C, BC, or iBC to, respectively, indicate porphyrin, chlorin, bacteriochlorin, or isobacteriochlorin. Abbreviations for porphyrin compounds are listed in Table 1 to illustrate the designations for the *meso*-aryl groups.

Replacement of the phenyl para H atom or meta H atoms with groups that do not spin couple with the remaining aryl protons simplifies the latters' resonances from multiplets to doublets or singlets. Given that hydroporphyrins have several inequivalent *meso*-aryl group environments, the greater ease of resolution and assignment of the NMR spectra of phenyl-substituted complexes is a distinct advantage.

Syntheses of the titanyl hydroporphyrin complexes requires two transformations of a parent free-base porphyrin compound: reduction of one or more $\beta-\beta$ double bonds in the porphyrin π-system and metalation of a free-base compound with titanium. In principle, either reduction followed by metalation or metalation followed by reduction could afford the desired complexes. However, the tendency of hydroporphyrin compounds to undergo oxidative dehydrogenation to porphyrins,[10] especially during metalation reactions,[39] and the potential differences in the ease of purification of free-base hydroporphyrin vs metallohydroporphyrin compounds made the most efficient approach to pure samples of the desired complexes less than obvious. Thus, we investigated both approaches.

Several methods have been used for metalation of free-base porphyrins with titanium. The earliest methods reported, reaction with $(C_5H_5)TiCl_2$ in refluxing diethylene glycol[40] and reaction with $TiO(acac)_2$ in refluxing phenol,[41] required harsh conditions and afforded titanyl porphyrin complexes in less than 60% yield. Better yields (90%) of the titanyl complexes were obtained by reaction with $TiCl_4$ in refluxing anhydrous toluene.[24] Mild heating of lithium porphyrin salts $Li_2(THF)_4P$ with $TiCl_4(THF)_2$ in toluene affords titanium porphyrin dihalide complexes.[42] The latter are readily converted to titanyl complexes upon exposure to moisture.

TiO(TTP) and TiO(TXP) were accessible by any of the above methods. Reduction of either complex with diimide,

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N_2H_2, generated in situ from *p*-toluenesulfonhydrazide afforded gross mixtures of the corresponding titanyl porphyrin, chlorin, and isobacteriochlorin complexes that effectively could not be separated. Little, if any, bacteriochlorin was present because reduction of metalloporphyrins results in selective formation of the isobacteriochlorin isomer in the second reduction step.[43] Thus, metalation followed by reduction does not provide ready access to pure samples of all four compounds.

We reported previously the syntheses of the tetratolylhydroporphyrins H_2(TTC), H_2(TTBC), and H_2(TTiBC).[37] These were obtained by diimide reduction of tetratolylporphyrin, H_2(TTP). Consistent with our experience with the diimide reduction of H_2(TPP),[17] the materials obtained directly from the reduction were mixtures of the various compounds that contain at best 80−90% of the target hydroporphyrin. Purities were somewhat lower for the tetratolyl compounds because the rates of reduction are slowed by the electron-donating methyl group. In particular, the reduction step from porphyrin to chlorin is slowed to a greater extent than subsequent steps. Thus, it is harder to both effect complete reduction of the porphyrin and avoid the formation of overreduced compounds. The selective quinone reoxidation and phosphoric acid extration procedures that were reported to afford pure individual tetraphenylhydroporphyrin compounds[43] did not work in our hands.[17] Purified tetratolylhydroporphyrin compounds can be obtained by flash chromatography but only on a 10−100 mg scale. These difficulties were not an issue in the context of the synthesis of *N*-alkyl-substituted hydroporphyrin compounds.[37] It was most efficient to use the 80−90% pure mixtures in the alkylation reactions. Chromatographic separation of the *N*-methylporphyrin and -hydroporphyrin products from each other and from unreacted starting materials was substantially easier and could be conducted on a larger scale than separation of the individual free-base hydroporphyrins. In contrast, chromatographic purification of titanyl hydroporphyrin complexes is relatively difficult. Thus, more highly purified samples of free-base hydroporphyrins had to be employed in the metalation reactions used to prepare complexes for the dynamic NMR experiments reported here. The titanyl complexes generally were further purified by preparative TLC. Unfortunately, TiO(TTBC) is not sufficiently stable to permit its chromatographic separation from TiO(TTC) and TiO(TPP), whose presence interferes with the dynamic NMR experiments. Thus, samples of H_2(TTBC) used in metalation reactions must be free of H_2(TTC) and H_2(TTP). In addition, the metalation reaction must not form TiO(TTC) and TiO(TPP) by oxidation of the bacteriochlorin. The procedure that we reported for H_2(TTBC) is inadequate for our current purposes. Chromatographic purification of H_2(TTBC) leads to great loss of material and does not completely remove H_2(TTC) and H_2(TTP). We report here a modified procedure that eliminates these impurities by extending the reaction time of the diimide reduction and simplifying the workup. In addition, the amount of overreduced, hexahydroporphyrin products produced at extended reaction times is decreased to less than 10% by lowering the temperature of the reduction reaction.

The presence of additional methyl substituents in tetraxylylporphyrin, H_2(TXP), made its reduction even more difficult than that of H_2(TTP). Conditions that forced complete consumption of H_2(TXP) led to substantial conversion of the tetrahydroporphyrins H_2(TXBC) and H_2(TXiBC) to overreduced compounds. Thus, yields of the tetrahydroporphyrins were quite low, and we did not pursue the syntheses of the titanyl complexes of these compounds.

The utility of the various metalation methods (above) when applied to hydroporphyrins was investigated using 80−90% pure free-base compounds. Reaction of H_2(TTC) with either $(C_5H_5)TiCl_2$ in diethylene glycol or $TiO(acac)_2$ in phenol resulted in quantitative conversion to titanyl complex. However, the harsh conditions also led to quantitative conversion of the chlorin to porphyrin. Reactions of hydroporphyrins with 12 equiv of $TiCl_4$ in refluxing toluene for 30 h resulted in near-quantitative conversion to metal complexes and partial oxidation of the hydroporphyrin macrocycle. For H_2(TTC) and H_2(TTiBC), the crude reaction product contained roughly 60% of the respective titanyl complex, which could be substantially purified by repeated chromatography. In contrast, the crude product obtained from H_2(TTBC) contained only about 10% TiO(TTBC), which did not survive chromatography. Reaction of lithium hydroporphyrin salts (see below) with 4 equiv of $TiCl_4$ (or $TiCl_4(THF)_2$) in toluene at 50 °C for a few hours resulted in near-complete metalation accompanied by minimal oxidation of the hydroporphyrin macrocycle. The titanium dichloride complexes of TTC and TTiBC formed in this reaction were converted to titanyl complexes upon contact with the alumina column packing, which served to separate the desired titanyl complex from traces of unreacted free-base and excess titanium compounds. A similar conversion of $Ti(TTBC)Cl_2$ to TiO(TTBC) was effected by rapid filtration through Celite, which, unlike alumina or silica, did not oxidize the bacteriochlorin.

Application of the last metalation method required us to prepare the previously unknown lithium hydroporphyrin salts. The reported procedure for isolation of lithium porphyrin salts involves reaction of free-base porphyrin with 2 equiv of $LiN(SiMe_3)_2$ for 8 h in refluxing THF or DME.[44,45] Spectroscopic monitoring of the reaction showed that hydroporphyrins were incompletely deprotonated and partially oxidized under these conditions. Hence, we chose to rapidly generate the lithium salts in toluene at room temperature with the stronger base butyllithium. Slightly more than 2 equiv of butyllithium was required to deprotonate H_2(TTP), H_2(TTC), or H_2(TTiBC). Complete titration of H_2(TTBC) required roughly 6 equiv. Presumably, some of the protic solvents used to wash the solid during isolation were retained and consumed butyllithium. Organolithium reagents have been reported to add to the meso positions and β-positions

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Table 2. ^{1}H NMR Data for Free-Base Compounds[a]

compd	NH	Ph−CH_3	CH_2CH_2	para H	ortho H	pyrrole H
H_2(TXP)	−2.80 (br s, 2H)	2.60 (s, 24H)		7.40 (s, 4H)	7.83 (s, 8H)	8.87 (s, 8H)
H_2(TXC)	−1.48 (br s, 2H)	2.53 (s, 12H)	4.18 (s, 4H)	7.29 (s, 2H)	7.49 (s, 4H)	8.21 (d, 5.4 Hz, 2H)
		2.56 (s, 12H)		7.34 (s, 2H)	7.76 (s, 4H)	8.46 (s, 2H)
						8.60 (d, 5.4 Hz, 2H)
H_2(TXBC)	−1.37 (br s, 2H)	2.50 (s, 24H)	4.00 (s, 8H)	7.23 (s, 4H)	7.43 (s, 8H)	7.97 (s, 4H)
H_2(TXiBC)	0.82 (br s, 2H)	2.40 (s, 18H)[b]	3.28 (m, 8H)	7.39 (br s, 4H)	7.05 (s, 2H)	6.91 (d, 4.4 Hz, 2H)
		2.42 (s, 6H)			7.10 (s, 2H)	7.42 (d, 4.4 Hz, 2H)
					7.18 (s, 4H)	
H_2(T3,5FPP)	−2.94 (br s, 2H)			7.32 (t,[c] 4H)	7.79 (d,[d] 8H)	8.93 (s, 8H)
H_2(T3,5BrPP)	−2.90 (br s, 2H)			8.14 (br, 4H)	8.29 (br, 8H)	8.88 (s, 8H)
H_2(T3,5MeOPP)	−2.85 (br s, 2H)	3.95 (s, 24H)		6.89 (s, 4H)	7.39 (s, 8H)	8.92 (s, 8H)
H_2(T3,5tBuPP)	−2.72 (br s, 2H)	1.50 (s, 72H)		7.76 (br, 4H)	8.07 (br, 8H)	8.89 (s, 8H)

[a] Parts per million relative to TMS in $CDCl_3$ solution at 20 °C. [b] Two peaks (of 6H and 12H) overlap. [c] Triplet with barely resolved doublet splitting, $^3J_{FH}$ = 8.9 Hz, $^4J_{HH}$ = 2.0 Hz. [d] $^3J_{FH}$ = 6 Hz; peaks too broad to resolve splitting by para H.

of free-base porphyrins and metalloporphyrins.[46−48] We did not observe addition to the hydroporphyrins under the conditions that we employed. Generally, the lithium salts were generated in situ and used in metalation reactions without isolation.

^{1}H NMR Spectra. The ^{1}H NMR spectra of free-base, para-substituted tetraphenylporphyrins consists of a broad singlet near −3 ppm for the NH protons, a singlet near 8.9 ppm for the pyrrole β-protons, a pair of "doublets" (with unequal intensities typical of a four-line AB pattern that has $\Delta\nu \gg J$) between 8.1 and 7.4 ppm for the ortho and meta protons, respectively, and appropriate peaks for the para substituent. The coupling constants between adjacent ortho and meta protons are typically 8 Hz. All other couplings in the phenyl rings are small and unresolved. Spectra for free-base, meta-disubstituted tetraphenylporphyrins are similar with the exceptions that a singlet near 7.4 ppm is present for the para proton, the meta proton peak is absent, and the ortho proton peak is a singlet.

The lower symmetry of hydroporphyrins removes the equivalency of the four *meso*-aryl groups. Chlorins have two aryl environments. Two aryl groups are adjacent to two pyrrole rings (A type), and two are adjacent to one reduced, or pyrroline, ring (B type). Isobacteriochlorins have three environments: one A-type aryl ring, two B-type aryl rings, and one aryl ring between two pyrroline rings (C type). Bacteriochlorins have four equivalent B-type aryl groups. Although the increased saturation of the hydroporphyrins decreases the ring current and in turn moves the NH protons downfield and the aryl group protons upfield, the ranges of chemical shifts of the different aryl groups still overlap each other. The pyrrole β-protons of hydroporphyrins shift upfield relative to their position in porphyrins and can fall in the same chemical shift region as the aryl protons. The pyrrole β-proton peaks are readily distinguished from aryl proton peaks, though, by the integration of singlets or by the characteristic 4.5 Hz coupling of doublets. Finally, new peaks appear for the hydroporphyrin pyrroline β-protons between 4.2 and 3.2 ppm.

^{1}H NMR data for free-base tetratolylporphyrin and -hydroporphyrin compounds were reported previously.[37] Data for free-base tetraxylylporphyrin and -hydroporphyrin compounds and other free-base meta-disubstituted porphyrin compounds are reported in Table 2.

Metalation of the free-base compounds with lithium or titanium results in several changes to the NMR spectra. The upfield NH proton peak disappears due to the replacement of these protons by the metal. Metalation with lithium does not remove the equivalency of the two faces of the tetrapyrrole macrocycles. Hence, the ^{1}H NMR spectra of the lithium complexes have the same multiplicity of peaks as the spectra of the free-base compounds. Small changes in chemical shifts occur, though. In contrast, the titanyl group removes the equivalency of the two faces. Multiplicities of the peaks for pyrrole β-protons, which lie in the macrocycle plane, and para phenyl substituents, which rotate freely, are unchanged relative to those of the spectra of the free-base compounds. However, the peaks for the hydroporphyrin pyrroline β-protons have greater multiplicity due to the additional coupling between the now inequivalent protons. In addition, the spectra of titanyl porphyrin complexes at room or lower temperature show a doubling of peaks for ortho protons and meta protons or substituents. The inequivalence of the faces and the restricted rotation of the *meso*-aryl groups about the meso carbon to aryl carbon bonds cause the AB pattern of the free-base compounds to change to an ABCD pattern in the titanyl complexes. The chemical shift differences between the two doublets for the ortho protons and for the meta protons are both significant. The chemical shift difference between the doublets is 106 Hz for the ortho protons and 26 Hz for the meta protons of TiO(TTP) when the spectra are obtained on a 270 MHz spectrometer. As the temperature is raised, the rate of rotation of the aryl groups increases and the pairs of doublets for the ortho and meta protons broaden and then average to an apparent AB pattern similar to that observed in H_2(TTP). ^{1}H NMR data for metal complexes in the slow exchange limit are reported in Table 3.

The ^{1}H NMR spectra of titanyl hydroporphyrins that have multiple aryl group environments are considerably more complicated than that of TiO(TTP). The slow exchange spectrum of TiO(TTC) has four doublets corresponding to

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Table 3. ^{1}H NMR Data for Titanyl Tetrapyrrole Complexes[a,b]

compd	Ph−CH_3	CH_2CH_2	para H	meta H	ortho H	pyrrole H
TiO(TTP)	2.76 (s, 12H)			7.58 (d, 8.1 Hz, 4H) 7.70 (d, 8.1 Hz, 4H)	8.06 (d, 8.1 Hz, 4H) 8.43 (d, 8.1 Hz, 4H)	9.22 (s, 8H)
TiO(TTC)	2.60 (s, 6H) 2.64 (s, 6H)	4.15−4.40[c] (4H)		7.48 (8H)[d]	7.58 (d, 8.1 Hz, 2H) 7.81 (d, 8.1 Hz, 2H) 7.88 (d, 8.1 Hz, 2H) 8.13 (d, 8.1 Hz, 2H)	8.11 (d, 4.4 Hz, 2H) 8.45 (s, 2H) 8.54 (d, 4.4 Hz, 2H)
TiO(TTBC)	2.57 (s, 12H)	3.95−4.35[c] (8H)		7.42 (d, 7.4 Hz, 4H) 7.48 (d, 7.4 Hz, 4H)	7.56 (d, 7.4 Hz, 4H) 7.84 (d, 7.4 Hz, 4H)	7.96 (s, 8H)
TiO(TTiBC)	2.48 (s, 3H) 2.50 (s, 6H) 2.54 (s, 3H)	3.40−3.60[c] (8H)		*e*	*e*	7.18 (d, 4.3 Hz, 2H) 7.70 (d, 4.3 Hz, 2H)
TiO(TXP)	2.63 (s, 12H) 2.71 (s, 12H)		7.50 (s, 4H)		7.17 (s, 4H) 7.78 (s, 4H)	9.25 (s, 8H)
TiO(TXC)	2.49 (s, 6H) 2.52 (s, 6H) 2.55 (s, 6H) 2.58 (s, 6H)	4.15−4.40[c] (4H)	7.30 (s, 2H) 7.33 (s, 2H)		7.29 (s, 2H) 7.54 (s, 2H) 7.66 (s, 2H) 7.87 (s, 2H)	8.20 (d, 4.4 Hz, 2H) 8.52 (s, 2H) 8.62 (d, 4.4 Hz, 2H)
TiO(TpClPP)				7.76 (d, 8.0 Hz, 4H) 7.85 (d, 8.0 Hz, 4H)	8.06 (d, 8.0 Hz, 4H) 8.40 (d, 8.0 Hz, 4H)	9.14 (s, 8H)
TiO(TpMeOPP)	4.10 (s, 12H)			7.26 (d, 8.0 Hz, 2H) 7.37 (d, 8.0 Hz, 2H)	8.04 (d, 8 Hz, 4H) 8.38 (d, 8 Hz, 4H)	9.15 (s, 8H)
TiO(TpCF$_3$PP)				8.07 (d, 7.7 Hz, 4H) 8.15 (d, 7.7 Hz, 4H)	8.26 (d, 7.7 Hz, 4H) 8.61 (d, 7.7 Hz, 4H)	9.11 (s, 8H)
TiO(T3,5FPP)			7.36 (dt,[f] 4H)		7.67 (d,[g] 4H) 8.03 (d,[g] 4H)	9.19 (s, 8H)
TiO(T3,5BrPP)			8.23[h] (s, 4H)		8.23[h] (s, 4H) 8.60 (s, 4H)	9.21 (s, 8H)
TiO(T3,5MeOPP)	3.95 (s, 12H) 4.00 (s, 12H)		6.96 (s, 4H)		7.33 (s, 4H) 7.66 (s, 4H)	9.23 (s, 8H)
TiO(T3,5tBuPP)	1.53 (s, 36H) 1.57 (s, 36H)		7.85 (s, 4H)		8.05 (s, 4H) 8.34 (s, 4H)	9.21 (s, 8H)

[a] Parts per million relative to TMS in $CDCl_3$ solution. [b] Data are at the slow exchange limit. Typically $T = 0-20$ °C. [c] Multiplet. [d] Multiple unresolved overlapping doublets. [e] Broad, overlapping peaks between 7.30 and 7.55 ppm. [f] Triplet with barely resolved doublet splitting, $^3J_{FH} = 8.9$ Hz, $^4J_{HH} = 2.0$ Hz. [g] $^3J_{FH} = 7.9$ Hz; peaks too broad to resolve splitting by para H. [h] Coincident at the slow exchange limit but resolved at higher temperature.

different ortho protons. The doublets for the ortho protons of the A-type tolyl groups are centered at 7.81 and 8.13 ppm. Those for the B-type tolyl groups are centered at 7.58 and 7.88 ppm. The chemical shifts of the four different meta protons lie in a sufficiently narrow range around 7.45−7.60 ppm that well-resolved doublets are not observed, even at low temperatures. The ortho H doublet at 7.58 overlaps the meta H multiplet. In addition, the ortho H doublet at 8.13 ppm overlaps a doublet for pyrrole β-protons at 8.11 ppm. As the temperature is increased, the ortho H multiplets for the two tolyl groups broaden and shift position through each other at different rates. Consequently, the coalescence temperatures of the ortho protons of the two tolyl groups of TiO(TTC) cannot be judged as precisely as those of TiO(TTP). The situation is even worse for TiO(TTiBC), which has three different tolyl group environments. We were unable to resolve or identify the expected six doublets for the ortho protons that should be observed in the slow exchange limit, even at −60 °C, and were unable to judge the temperatures of coalescence of the related pairs of doublets. It is not clear whether this is due simply to the number of overlapping peaks or this is because exchange is fast at low temperatures. The latter could result from smaller activation barriers and/or smaller frequency differences between the exchanging peaks for this complex.

The inaccessibility of activation parameters for all four of the complexes in the tetratolylporphyrin series led us to investigate the complexes in the tetraxylylporphyrin series. We expected the spectra of the xylyl complexes would be easier to resolve and interpret because ortho H peaks are singlets when meta protons are not present to spin couple. Unfortunately, the electronic effects of the additional methyl substituents in the xylyl group (above) led to the tetrahydroporphyrin complexes being unavailable in the quantities and purity necessary for study. Results are included for TiO(TXP) and TiO(TXC). The activation barriers to rotation of the xylyl groups in these complexes were unexpectedly higher than those for tolyl groups (see below). In an effort to understand the reason for the increase, we expanded the study to include the titanyl complexes of other meta-disubstituted and para-substituted tetraphenylporphyrin complexes that had substituents of varied size and electronic properties.

Analysis of Activation Parameters. Two approaches have been reported to determine the activation parameters for chemical exchange from variable-temperature spectral data. The first approach utilizes the Gutowsky−Holm approximation for coalescence,[49] and obtains $\Delta G^{\ddagger}_{T_c}$ values from $\Delta\nu$ and T_c,[50] where $\Delta\nu$ is the frequency difference and T_c is the coalescence temperature of the exchanging peaks. Coalescence occurs when the valley between the separate, exchanging peaks just disappears. This approach gives only the value of $\Delta G^{\ddagger}$ at a single temperature and hence provides no information about $\Delta H^{\ddagger}$ or $\Delta S^{\ddagger}$. The second approach uses full line shape analysis. Rate constants for exchange, k_r, are

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(50) Shanan-Atidi, H.; Bar-Eli, K. H. *J. Phys. Chem.* **1970**, *74*, 961−963.

determined by comparisons at each temperature of experimental and simulated NMR data for the region containing the exchanging protons. Activation parameters are obtained from weighted least-squares fits of k_r to Arrhenius ($\ln k_r$ vs $1/T$) or Eyring ($\ln(hk_r/kT)$ vs $1/T$) equations over the full temperature range.

The best computer program for full line shape analysis of the NMR spectra of exchanging systems that we were able to locate was DNMR5.[51] The parameters required to simulate the spectrum can be specified as fixed values or variables whose values will be determined by the program. These include chemical shifts, coupling constants, T_2 relaxation times, relative populations of the exchanging configurations, and the rate constants for exchange. The program uses iterative, least-squares fits of a calculated spectrum to the experimental spectrum to model the best values of the varied parameters. Unfortunately, DNMR5 was unable to handle the number of parameters that had to be specified to simulate the hydroporphyrin spectra, which had multiple exchanging spin systems and nonexchanging spin systems whose lines overlapped in the region of interest. Thus, we determined activation parameters by the approximate method.

Absolute errors in $\Delta G^{\ddagger}_{T_c}$ values determined by the approximate method include contributions from experimental errors and from systematic errors introduced as a result of the approximations made to simplify the Bloch equation and the deviations of the actual systems from the idealized system modeled in the approximation. Several studies have shown that the approximate method leads to errors of at worst 0.3 kcal/mol in $\Delta G^{\ddagger}_{T_c}$ compared to full line shape analysis.[52,53] The systematic errors are expected to be of similar size and magnitude for the compounds in this study, which have similar spin systems, populations, T_c values, and $\Delta\nu$ values. We will consider only the relative errors due to experimental measurement errors in making comparisons between compounds.

The main sources of relative error in $\Delta G^{\ddagger}_{T_c}$ are errors in measurement of $\Delta\nu$ and T_c. Given the typical values of activation energies, T_c, and $\Delta\nu$ for the complexes in this study, the error in $\Delta\nu$ would have to be about 15 Hz to change $\Delta G^{\ddagger}_{T_c}$ by ± 0.1 kcal/mol. The accuracy in $\Delta\nu$ measurements in this study was better than 0.5 Hz, which introduces negligible error in $\Delta G^{\ddagger}_{T_c}$. Errors in T_c result both from errors in the actual probe temperature and from errors in judging the temperature at which coalescence occurs. The reproducibility of the probe temperature was about 0.2 °C (although the absolute error is larger). The coalescence point for porphyrin complexes could be judged to ± 1 °C, which introduces an error of roughly ± 0.05 kcal/mol in the systems studied. Thus, relative errors in the values of porphyrin complexes are estimated as 0.1 kcal/mol. The relative errors in $\Delta G^{\ddagger}_{T_c}$ for hydroporphyrin complexes are somewhat larger because the multiple exchanging spin systems made it more difficult to judge coalescence. Values of $\Delta G^{\ddagger}_{T_c}$ and its associated error were estimated by taking the average and half the difference of values calculated for the temperatures at which an observer was certain coalescence had not yet occurred and at which coalescence had definitely occurred.

Table 4. Activation Energies for Aryl Group Rotation[a]

compd	type[b]	T_c, °C	$\Delta G^{\ddagger}$, kcal/mol[c]
TiO(TTP)	A	70	16.1 ± 0.1
TiO(TTC)	A	50	15.6 ± 0.25
	B	60	16.2 ± 0.25
TiO(TTBC)	B	55	15.9 ± 0.25
TiO(TXP)	A	98	17.9 ± 0.1
TiO(TXC)	A	87	17.5 ± 0.15
	B	100	18.0 ± 0.25
TiO(TpClPP)	A	70	16.5 ± 0.1
TiO(TpCF$_3$PP)	A	71	16.5 ± 0.1
TiO(TpMeOPP)	A	58	16.0 ± 0.1
TiO(T3,5FPP)	A	82	17.0 ± 0.1
TiO(T3,5BrPP)	A	108	18.4 ± 0.1
TiO(T3,5MeOPP)	A	105	18.1 ± 0.1
TiO(T3,5tBuPP)	A	110	18.4 ± 0.1

[a] In 1,1,2,2-tetrachloroethane-d_2 solution. [b] A = aryl adjacent to two pyrrole rings, and B = aryl adjacent to one pyrrole and one pyrroline ring. [c] Uncertainty is a relative rather than absolute error.

The $\Delta G^{\ddagger}_{T_c}$ values reported in Table 4 were determined using data for the ortho protons, which have the largest $\Delta\nu$ and therefore are closest to the idealized system modeled in the approximation. The values that we report for TTP, TpClPP, TpCF$_3$PP, and TpMeOPP are in good agreement with literature values that were determined at lower field and referenced to 298 K,[25] especially when the $-\Delta T\Delta S$ correction term is included. (Values of $\Delta S^{\ddagger}$ for phenyl ring rotation in titanyl tetraphenylporphyrin complexes are typically about -10 eu.[25]) In several of the complexes that we studied the ortho protons and meta protons or substituents provided for two independent determinations of $\Delta G^{\ddagger}$. The agreement of these values was reasonable. They will not be identical because the difference in T_c affects $\Delta G^{\ddagger}$.

Discussion

The results in Table 4 establish that reduction of the pyrrole rings in hydroporphyrins affects the barriers for rotation of *meso*-aryl groups. The effects of reduction cannot be explained by simple interpretations. The barriers for B-type aryl groups, which are next to one pyrroline ring, are larger in TiO(TTC) and TiO(TXC) than the barriers for A-type groups in the same compound. Moreover, they may be larger than barriers for the A-type groups in their respective porphyrin complexes. The increased barriers for the B-type groups cannot be attributed solely to the increased steric bulk of the pyrroline β-CH$_2$ group relative to the pyrrole β-CH group. If sterics were the only important factor, then the A-type barriers in porphyrin and chlorin should be identical and the B-type barriers in chlorin and bacteriochlorin should be identical. This is clearly not the case. A-type barriers for chlorins are less than those for parent porphyrins, and the B-type barrier in TiO(TTBC) is smaller than that in TiO(TTC). These observations could be con-

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(52) Kost, D.; Carlson, E. H.; Raban, M. *J. Chem. Soc., Chem. Commun.* **1971**, 656−657.
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sistent with more saturated tetrapyrroles having somewhat increased out-of-plane flexibility. This would make deformation of the macrocycle more facile and in turn permit the ortho H atoms and β-H atoms to avoid each other more readily. However, the observations might also be consequences of electronic effects, which are expected to make variable contributions to the barriers in porphyrins and hydroporphyrins. The aryl group π-system and the tetrapyrrole π-system are coplanar (or nearly so) in the transition state for aryl group rotation. The orbital overlap between these π-systems that occurs at the meso carbon−ipso carbon bond will affect the energy of the transition state. The magnitude of the overlap will differ both for different tetrapyrroles and for the inequivalent aryl groups of chlorins and of bacteriochlorins. Data in Table 4 and the literature[25] clearly show that the electronic nature of the para substituent in titanyl tetraarylporphyrins leads to a variation in barrier that is comparable to or larger than the differences observed here between barriers for the same type (A or B) aryl group in different tetrapyrroles. Barriers are lower for electron-donating substituents than for electron-withdrawing substituents, but were not linearly related to the Hammett−Taft parameters for the substituents.

An interesting observation is that barriers for xylyl group rotation in TiO(TXP) and TiO(TXC) are roughly 1.5 kcal/mol greater than the corresponding barriers for tolyl group rotation in TiO(TTP) and TiO(TTC). These results led us to examine the effects of the size and electronic nature of the meta substituent on barriers to rotation. The data in Table 4 establish that barriers increase from 17.0 kcal/mol for TiO(T3,5FPP) to 18.4 kcal/mol for TiO(T3,5tBuPP). Comparison of the barriers for Br and F meta substituents shows that stronger electron-withdrawing substituents do not have increased barriers, unlike the case for para-substituted aryl groups. A slowing of aryl group rotation for meta-disubstituted groups relative to para-substituted groups had been reported previously and was attributed to the steric bulk of the meta group "buttressing" the ortho hydrogens.[26] Our data lead us to question this suggestion. The van der Waals radius of bromine is comparable to or slightly smaller than that of a methyl group. Yet, the barrier for aryl group rotation in TiO(T3,5BrPP) is larger than that of TiO(TXP) and comparable to that of TiO(T3,5tBuPP). Barriers appear to be related to both the size and mass of the meta substituent. The size effect may be due to a phenomenon analogous to drag, the resistance to movement through a fluid medium. Larger meta substituents, which are off-axis, will sweep out larger volumes of solvent as the aryl group rotates. More massive substituents, on the other hand, will increase the moment of inertia of the aryl group.

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