

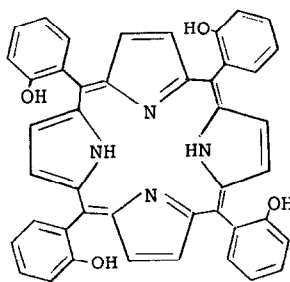
BIPHENYL-TYPE ATROPISOMERISM AS A PROBE FOR
CONFORMATIONAL RIGIDITY OF $\alpha,\beta,\gamma,\delta$ -TETRAARYLPORPHINES.

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The structures of porphines and metalloporphines have been the subject of numerous X-ray studies.¹ The phenyl groups in $\alpha,\beta,\gamma,\delta$ -tetraphenylporphine (TPP) have been found to be tilted out of the molecular plane due to steric effects of the β -CH groups.^{2,3} Deviations from perpendicularity of the porphine and phenyl rings can be correlated with the degree of planarity of the porphine ring. Thus TPP-Ni⁴ and TPP-Zn(H₂O)₂⁵ are nearly planar with perpendicular phenyl groups whereas TPP,^{2,3} TPP-Cu⁵ and TPP·2HCl⁶ have "ruffled" conformations with the phenyl groups, 61° (or 81°), 80°, and 21° out of plane, respectively. These geometrical variations suggest either that the porphine nucleus is intrinsically planar but is easily deformed by crystal packing forces, or that deviations from planarity are due to intramolecular strain effects.⁷ The present work provides chemical confirmation of the geometries and deformability of tetraarylporphines.



THPP

$\alpha, \beta, \gamma, \delta$ -Tetra-o-methoxyphenylporphine^{8,9} was demethylated with 49% hydrobromic acid and the resulting tetra-meso-o-hydroxyphenylporphine¹⁰ (THPP) was purified by silicic acid column chromatography. The analytically pure THPP separated into four components by tlc on silica with 1:1 chloroform-ether as eluant. The absorption spectra of the components were identical. The four components, in the order of increasing probability, were present in a 1:4:2:1 ratio. This is the ratio expected statistically for the four THPP isomers that would result from hindered rotation about the aryl-porphine bonds. The most abundant isomer should have three hydroxyl groups on the same side of the porphine and interconvert by a single rotation with any of the other isomers. In point of fact, on permitting a methanol solution of the most abundant isomer to stand for an hour at 23^o, the three additional components began to reappear in the expected 1:2:1 ratio. This process was monitored by extraction of the components from the tlc plate and spectroscopic determination of the concentrations of the extracts. This technique, while crude, yielded first order plots for approach to the 1:4:2:1 equilibrium ratio. From these data the rate of isomerization about one aryl-porphine bond in methanol was calculated as $k_{23^{\circ}} = 1.5 \pm 0.5 \times 10^{-5} \text{ sec.}^{-1}$ ($\Delta F^{\ddagger} = 24.0 \text{ Kcal/mole}$).

This is the first reported example of atropisomerism in porphines. Models suggest that the porphine ring must distort considerably in the transition state. An increase in the rigidity of the porphine nucleus should thus decrease the isomerization rate. As a test of this conclusion THPP-Cu was studied. This complex was isolated in the anhydrous form after drying at 111^o in vacuo. THPP-Cu also separated into four components by tlc. Although incomplete separation prevented determination of all the isomer ratios, one isomer represented 50% of the total. This component initially approached equilibrium by approximate first order kinetics corresponding to a very approximate rate of isomerization about a single aryl-porphine bond of $k_{23^{\circ}} \approx 10^{-6} - 10^{-7} \text{ sec.}^{-1}$. This rate increased after several hours and appeared to approach the approximate rate of THPP isomerization. Similar results were obtained using ethyl acetate as solvent. However, in 5% aqueous methanol good first order kinetics were obtained. The calculated rate of isomerization, $k_{23^{\circ}} = 1.2 \pm 0.4 \times 10^{-6} \text{ sec.}^{-1}$

($\Delta F^\ddagger = 25.4$ Kcal/mole) was about a tenth the rate in the uncomplexed THPP.

These results are consistent with the formation on the tlc plate of a weak THPP-Cu complex with water which dissociates in anhydrous solvents but is stabilized by the addition of water.¹¹ X-ray data show that metalloporphines and metalloporphyrins with one additional ligand assume shallow bowl-shape conformations.^{12,13} Such a conformation would be expected to be quite rigid since distortions would weaken the metal-ligand bonds in the flattened square pyramidal complex. The unhydrated THPP-Cu probably has a planar geometry which readily distorts to a "ruffled" form with the pyrrol rings alternately tilted upward and downward from the molecular plane.⁵ This should result in a rate of aryl group isomerization in THPP-Cu comparable to that of the metal-free THPP which is capable of a similar type of distortion. On the other hand, the comparative rigidity of THPP-Cu·H₂O would account for the lower rate of isomerization of this compound.

A brief study of THPP-Zn·H₂O was also made. This compound was isolated as the monohydrate. Separation of the isomers by tlc yielded six isomers as would be expected if the rate of exchange of coordinated water to the opposite side of the porphine was sufficiently slow. However the ratios of the THPP-Zn·H₂O isomers were not consistent with statistical prediction, and thus the measured rates could not be related to rates of isomerization about a single center. The reason for the deviations from the statistically expected ratios is not presently understood.

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