and this could be removed by oxidation with periodate; the binding capacity was thereby reduced considerably. These experiments confirm in a quantitative manner that wall teichoic acids, and presumably also membrane teichoic acids, are responsible for binding bivalent cations, and it is probable that this is a major function of these polymers. It is also possible that the cell can control its binding of cations through control of the amount of alanine ester in its wall.

There are several reasons why it is important for the cell to be able to maintain a high concentration of bivalent cations in the region of its membrane. It is known, for example, that the membrane has bound to it many enzymes,[42] including those required for the synthesis of peptidoglycan, teichoic acids, and capsular polysaccharides and those concerned with electron transport; many of these[13,24,43,45] have been shown to require high concentrations of bivalent cations for optimal activity. The physical integrity[46] of the membrane requires Mg^{2+}, as does the association of membrane and ribosomes during protein synthesis.[47] The membraneous convoluted structures known as mesosomes that are frequently seen in association with the cell membrane also require Mg^{2+} for this association.[48] If the function of teichoic acids is to provide a suitable environment for the correct functioning of the membrane, then it follows that membrane teichoic acid is of fundamental importance to the cell and is thus much more important biologically than is wall teichoic acid. This conclusion is supported by the observation discussed above that in unfavorable circumstances organisms can survive by attaching other acidic polymers to the wall, but nevertheless are obliged to produce

membrane teichoic acid. It is also significant that cells grown under conditions of magnesium deficiency contain exceptionally large amounts of teichoic acid in their walls; this would represent an attempt by the cells to scavenge as much bivalent cation as possible.

Specialized functions have been attributed to specific wall teichoic acids. In the *Pneumococcus* the wall teichoic acid (C substance) is a complex polymer containing sugars, ribitol phosphate, and choline phosphate residues.[9] When the organism is grown in a medium lacking choline but containing ethanolamine, it is possible to substitute the choline residues in the teichoic acid by ethanolamine. Although the cells continue to grow and reproduce under these conditions, the normal characteristic autolysis of older cells is prevented and cell separation is impaired. The bacteria thus grow as long chains of unseparated cells.[49] A relationship between teichoic acid structure and lysis has also been observed in *Streptococcus zymogenes*;[50] the walls of this organism are immune toward the powerful lytic enzymes that it excretes, but if the alanine ester residues of its wall teichoic acid are removed autolysis can occur. The nature of the effect of teichoic acids on these apparently rather specialized aspects of action of autolytic enzymes has not yet been estabished, and it remains possible that their influence on the enzymes might be connected with their cation binding properties. Another obvious property of teichoic acids is associated with their overall negative charge. Their presence in walls should cause mutual repulsion of cells because of their surface charge, thereby ensuring equitable distribution of organisms throughout the nutrient medium. It can be shown experimentally that walls that have had their teichoic acid removed chemically exhibit a marked tendency to aggregate.[44]

(45) P. M. Meadow, J. S. Anderson, and J. L. Strominger, *Biochem. Biophys. Res. Commun.*, 14, 382 (1964).
(46) C. Weibull, *Exp. Cell Res.*, 10, 214 (1956).
(47) G. Coleman, *Biochem. J.*, 112, 533 (1969).
(48) D. A. Reaveley and H. J. Rogers, *ibid.*, 113, 67 (1969).

(49) A. Tomasz, *Proc. Nat. Acad. Sci. U. S.*, 59, 86 (1968).
(50) J. M. Davie and T. D. Brock, *J. Bacteriol.*, 92, 1623 (1966).

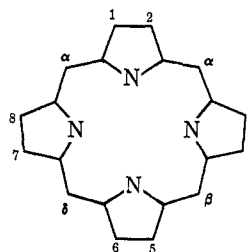# The Structure of Porphyrins and Metalloporphyrins

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Understanding of the porphyrin system has advanced appreciably in recent years;[1] determination of detailed structures for porphyrin and metalloporphyrin molecules by X-ray diffraction has contributed importantly to comprehension of the chemistry and the physical properties of porphyrin molecules. This Account reviews some of these structural studies on porphyrins and discusses their implications.

Porphyrins are a class of tetrapyrrole macrocycles

with a skeleton as shown in 1. The porphine (the parent compound) free base 2 has 11 double bonds and


1, porphyrin skeleton

(1) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier Publishing Co., Amsterdam, 1964.

can be transformed into a metalloporphine (3) by replacement of the two inner pyrrole protons by a metal ion. One can also add two additional protons to the
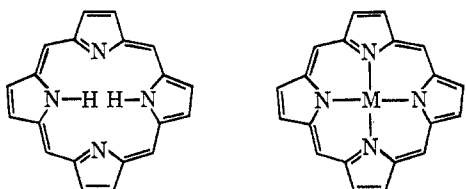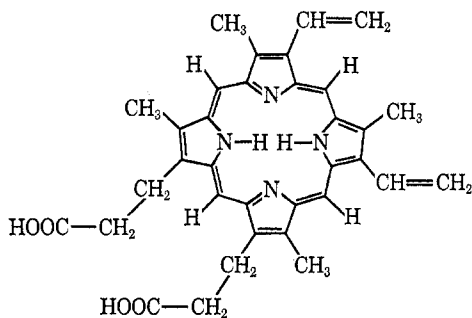

2, porphine free base   3, metalloporphyrin

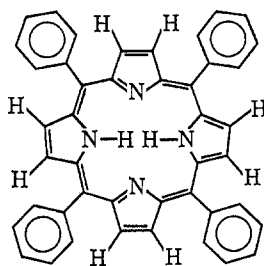free base and obtain the porphyrin diacid species 4 (note that this is a doubly charged species).
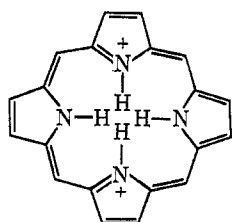
4, porphyrin diacid

Protoporphyrin IX (5) is one of the most abundant naturally occurring porphyrins, while *meso*-tetraphenyl-porphine (6) is a synthetic porphyrin employed as a model for the naturally occurring porphyrins. Three


5, protoporphyrin IX

6, *meso*-tetraphenylporphine

other compounds related to the porphine nucleus are especially important to the overall role played by the porphyrins in chemistry. Replacement of the α, β, γ, δ carbons by nitrogen and fusion of a benzene ring on the pyrroles gives us the well-known dye, phthalocyanine (7). (See ref 2 for an extensive review of phthalo-cyanines.) Two other important naturally occurring compounds related to porphyrins are chlorophyll (8) and vitamin B_{12} (9). A recent symposium on vitamin B_{12} summarizes the structural work carried out in that system.[3]
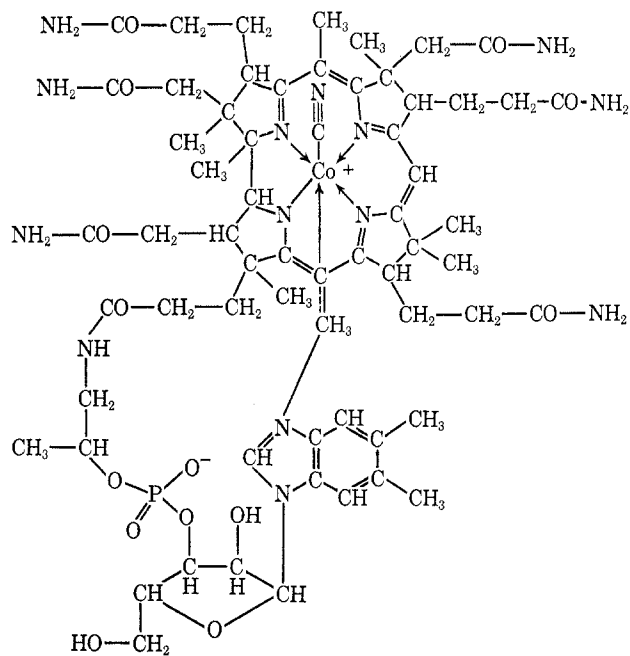
(2) A. B. P. Lever, *Advan. Inorg. Chem. Radiochem.*, 7, 27 (1965).
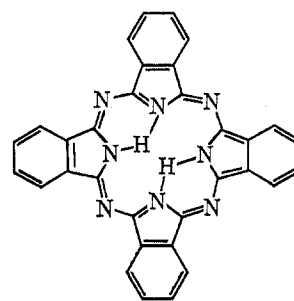
7, phthalocyanine
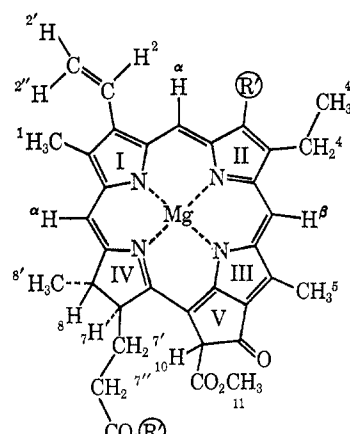
8, chlorophyll
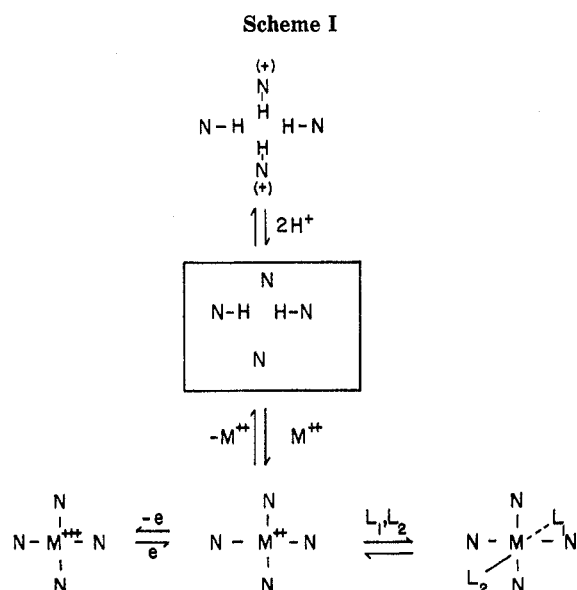

9, vitamin B_{12}

Aspects of the chemistry of porphyrins closely related to their acting as ligands in coordination reactions are summarized in Scheme I; we have approached the chemistry of the porphyrin from this viewpoint.[2,4] The chemistry of porphyrins from synthetic and reactivity aspects has recently been reviewed.[5,6]

(3) Symposium on Vitamin B_{12}, *Proc. Roy. Soc.* (London), **A288**, 294 (1965).

(4) E. B. Fleischer, S. Jacobs, and L. Mestichelli, *J. Am. Chem. Soc.*, **90**, 2527 (1968); E. B. Fleischer and N. Sadasivan, *J. Inorg. Nucl. Chem.*, **30**, 591 (1968); E. B. Fleischer and P. Hambright, *Inorg. Chem.*, **4**, 912 (1965).

Scheme I

the bond distances and angles. A "best" set of these parameters is shown in **10**.

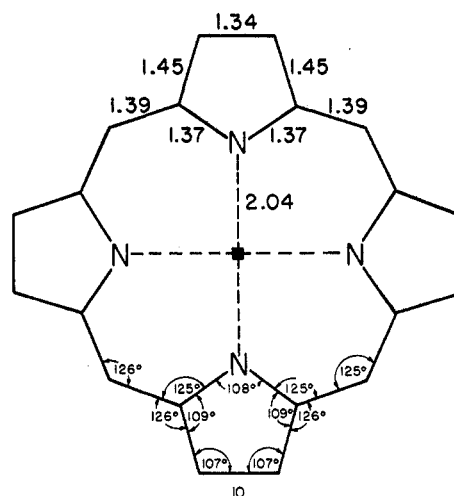"Best" set of parameters for porphyrin skeleton.

The structural properties of the porphyrin molecule described in this article are necessary for understanding its physical properties, such as visible absorption spectra, solubility, and magnetic properties (magnetic susceptibility, nuclear and electron spin magnetic resonance). Knowledge of structure also clarifies chemical features such as the rates and mechanism of metalloporphyrin formation and decomposition, ligand reactions at the metal center of the metalloporphyrins, substitution reactions on the ring system, and oxidation–reduction reactions of the porphyrin and metalloporphyrin system. It is hoped that this review, by showing how structural data can be used in such systems, will assist in achieving broader understanding of the total chemical picture of porphyrins.

Table I lists the known crystallographic data on porphyrin and porphyrin-like molecules. Many of the compounds have been subjected to a complete X-ray diffraction analysis which yields the geometry of these compounds in the *solid state;* some compounds for which only the space group is known are also listed. It should be pointed out that X-ray diffraction gives information only about solid-state structures; although the bond distances are probably the same in solution, it it well known that bond angles and thus conformations of molecules are influenced by solid-state forces and may differ between the solid state and solutions.

Bond Angles and Bond Distances

The bond distances of the porphine skeleton are quite invariant with respect to the porphyrin compound studied. The small differences one might expect due to substituent effects are usually smaller than the estimated errors of the bond parameters of the determined structures, thus not allowing any deductions to be made about variations in these parameters. The porphyrin usually has a fourfold axis of symmetry with respect to

The one bond distance that does change appreciably is the metal–nitrogen bond distance of the metalloporphyrins. The distance can vary from 2.10 Å in the ferric porphyrins to 1.95 Å in the nickel porphyrins. The distance from the pyrrole nitrogen to the center of the ring is 2.05 Å. The trends in these bond distances are not completely understandable in terms of the usual additivities of bond parameters.

Several observations can be made regarding the variations in the metal to pyrrole–nitrogen bond distances. The M–N distance in the phthalocyanine compounds is about 0.05 Å smaller than in the metalloporphyrins.[7] (In copper phthalocyanine the Cu^{II}–N distance is 1.93 Å compared to 1.98 Å in copper tetraphenylporphine.) The macrocyclic nature of the porphyrin ligand might explain some of the metal–nitrogen bond distances in that the nitrogen-to-center-of-ring distance is "fixed" and the macrocycle cannot easily expand and contract to "fit" the metal ion of the metalloporphyrin. Thus the increase in the metal–nitrogen bond distance from 1.96 Å in nickel(II) porphyrins to 2.00 Å in palladium(II) porphyrins is somewhat smaller than might be expected from the differences in their ionic radii of 0.72 and 0.86 Å, respectively. This is also observed in the phthalocyanine compounds where in copper phthalocyanine the Cu^{II}–N distance is 1.94 Å while the platinum phthalocyanine has a Pt^{II}–N distance of 1.98 Å; the ionic radii of these two ions are 0.73 and 0.82 Å, respectively. The larger Fe^{III}–N distance (2.07 Å) in ferric high-spin porphyrins arises from the antibonding d electrons of the ferric ion; the usual Fe^{III}–N bond distance in high-spin ammines is 2.30 Å. The contraction to the 2.07-Å value is probably due to the charge on the pyrrole nitrogens in the metalloporphyrins.

The stability of the second-row divalent metalloporphyrins with respect to metal ion displacement by acids is Ni^{II} > Cu^{II} > Zn^{II}; the metal–nitrogen bond dis-

(5) H. H. Inhoffen, *Pure Appl. Chem.,* **17,** 443 (1968).
(6) H. H. Inhoffen, J. W. Buchler, and P. Jäger, *Fortschr. Chem. Org. Naturstoffe,* **26,** 284 (1968).

(7) J. L. Hoard, S. H. Cohen, and M. D. Glick, *J. Am. Chem. Soc.,* **89,** 1922 (1967).

Table I

Crystal Structure Data for Porphyrins and Phthalocyanines

| Compound	Space group	Z	a^b	b^b	c^b	α^c	β^c	γ^c	Ref
Phthalocyanine[a]	P2₁/a	2	19.85	4.72	14.8		122.3		d
Ni phthalocyanine[a]	P2₁/a	2	19.9	4.71	14.9		121.9		e
Cu phthalocyanine[a]	P2₁/a	2	19.6	4.79	14.6		120.6		f
Pt phthalocyanine[a]	P2₁/a	2	23.9	3.81	16.9		129.6		g
Be phthalocyanine	P2₁/a	2	21.2	4.84	14.7		121.0		h
Co phthalocyanine	P2₁/a	2	20.2	4.77	15.0		121.3		h
Fe phthalocyanine	P2₁/a	2	20.2	4.77	15.0		121.6		h
Mn phthalocyanine	P2₁/a	2	20.2	4.75	15.1		121.7		h
Ni analog of phthalocyanine[a]	I2/a	4	23.5	3.78	21.9		92.8		i
Tetrabenzmonoazoporphine	P2₁/a	2	17.6	6.61	12.5		122.7		j
Tetrabenzporphine	P2₁/a	2	17.2	6.61	12.2		122.5		k
Tetrabenztriazaporphine	P2₁/a	2	19.85	4.72	14.8		122.3		k
Tetramethylhematoporphyrin	R3̄	6	31.3	31.3	19.6				l
Porphine[a]	P2₁/a	4	12.36	12.12	10.27		102.1		m
Tetraphenylporphine[a]	P1̄	1	6.44	10.42	12.41	96.1	99.1	101.1	n
Tetraphenylporphine	P2₁2₁2₁	4	12.0	19.2	14.7				o
Tetraphenylporphine[a]	I4̄2d	4	15.12	15.12	13.94				p
Tetraphenylporphine[a] diacid ([H₄TPP²⁺][FeCl₄⁻,Cl⁻])	I4̄	2	16.45	16.45	7.32				q
Tetrapyridylporphine[a] diacid (H₂TPyP·6HCl·H₂O) (conventional cell)	B2/b	4	19.89	14.31	19.26			133.5	q
	I2/n	4	19.89	19.26	10.34		90.0		q
Cu tetraphenylporphine[a]	I4̄2d	4	15.04	15.04	13.99				r
Cu tetra(p-chloro)phenyl-porphine[a]	P2₁/a	2	15.75	8.64	13.88		96.3		s
Pd tetraphenylporphine[a]	I4̄2d	4	15.09	15.09	13.99				r
Ni tetraphenylporphine[a]	I4̄2d	4	15.04	15.04	13.92				r
Zn tetraphenylporphine	P2₁2₁2₁	4	14.8	17.2	14.6				r
Zn tetraphenylporphine	P1̄	1	6.03	9.89	13.0	101	108	93	r
Zn tetraphenylporphine dihydrate[a]	I4/m	2	13.44	13.44	9.72				r
Fe^III chlorotetraphenylporphine hydrate[a]	I4	2	13.53	13.53	9.82				r
VO tetraphenylporphine	P2₁/a	4	28.9	12.9	11.6		133.8		t
Etioporphyrin I	P2₁/c	2	10.3	19.5	6.75		98		u
Ni etioporphyrin I[a]	I4₁/amd	4	14.61	14.61	12.38				v
Ni etioporphyrin II[a]	I4₁/amd	4	14.68	14.68	12.51				w
Hemin[a]	P1̄	2	11.49	14.10	10.85	98.6	108.5	107.7	x
Methoxyiron(III) meso-porphyrin IX ester[a]	I2/m	4	11.55	24.15	12.51		98.4		y
Ni 2,4-diacetyldeutero-porphyrin IX ester[a]	P1	2	15.62	8.74	13.57	101.8	112.4	86.4	z
FeCl₃–SAT–TPP		4	13.3	17.3	13.3		116		aa
RhCOCl tetraphenylporphine	I4	2	13.48	13.48	9.72				bb
CoCl tetraphenylporphine[a]	I4/m	2	13.41	13.41	9.82				bb
Rh phenylchlorotetraphenyl-porphine[a]	P2₁/a	4	17.33	13.09	23.28			124.8	cc
μ-Oxo-bis(tetraphenylporphine-iron(III))[a]	C2cb	4	15.12	25.06	18.04				dd
Mg phthalocyanine·H₂O·2-pyridine[a]	P2₁/n	4	17.10	16.92	12.45		105.9		ee
Au^III tetraphenylporphine [AuCl₄]	P1̄	1							ff
VO deoxophylloerythroetio-porphyrin[a]	P2₁/a	4	17.96	13.96	14.09		116.9		gg
Co^III corrinoid complex[a]	C2/c	8	24.86	14.33	19.36		113.4		hh
Sn^IV bisphthalocyanine[a]	P2₁2₁2₁	4	10.55	50.74	8.90				ii
μ-Oxo-(bispyridinephthalo-cyaninemanganese(III)) dimer	P2₁2₁2₁	4	22.63	23.85	12.81				jj
Ni^II 1,8,8,13,13-pentamethyl-5-cyano-trans-corrin	PT	2	11.10	12.31	10.69	103	96	78	kk
Vitamin B₁₂	P2₁2₁2₁	4	24.35	21.29	16.02				ll

[a] Indicates that a full structural analysis has been carried out. [b] In ångströms. [c] In degrees. [d] J. M. Robertson, J. Chem. Soc., 1195 (1936). [e] J. M. Robertson and I. Woodward, ibid., 219 (1937). [f] J. M. Robertson, ibid., 615 (1935); C. J. Brown, ibid., 2488 (1968). [g] J. M. Robertson and I. Woodward, ibid., 36 (1940); C. J. Brown, ibid., 2494 (1968). [h] R. P. Linstead and J. M. Robertson, ibid., 1736 (1936). [i] J. C. Speakman, Acta Cryst., 6, 784 (1953). [j] I. Woodward, J. Chem. Soc., 601 (1940). [k] J. M. Robertson, ibid., 1809 (1939).

[l] H. O'Daniel and A. Damasclike, *Z. Krist.*, **104**, 114 (1942). [m] L. E. Webb, Ph.D. Dissertation, The University of Chicago, 1965; L. E. Webb and E. B. Fleischer, *J. Chem. Phys.*, **43**, 3100 (1965). [n] S. Silvers and A. Tulinsky, *J. Am. Chem. Soc.*, **86**, 927 (1964); S. Silvers, Ph.D. Dissertation, Yale University, 1964. [o] J. Goldstein, Ph.D. Dissertation, University of Pennsylvania, 1959. [p] M. J. Hamor, T. A. Hamor, and J. L. Hoard, *J. Am. Chem. Soc.*, **86**, 1938 (1964). [q] E. B. Fleischer and A. L. Stone, *Chem. Commun.*, 332 (1967); *J. Am. Chem. Soc.*, **90**, 2735 (1968). [r] E. Fleischer, C. Miller, and L. Webb, *ibid.*, **86**, 2342 (1964); J. L. Hoard, G. H. Cohen, and M. D. Glick, *ibid.*, **89**, 1992 (1967). [s] E. Fleischer, S. Shapiro, R. Dewar, S. Hawkinson, and A. Stone, submitted for publication. [t] A. Stone, unpublished results. [u] C. L. Clerist and D. Harker, *Am. Mineralogist*, **27**, 219 (1952). [v] E. B. Fleischer, *J. Am. Chem. Soc.*, **85**, 146 (1963). [w] M. B. Crute, *Acta Cryst.*, **12**, 24 (1959). [x] D. F. Koenig, *ibid.*, **18**, 663 (1965). [y] J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *J. Am. Chem. Soc.*, **87**, 2312 (1965). [z] T. A. Hamor, W. S. Caughey, and J. L. Hoard, *ibid.*, **87**, 2305 (1965). [aa] E. B. Fleischer, Ph.D. Dissertation, Yale University, 1961. [bb] Jo Ann Case, private communication. [cc] E. B. Fleischer and D. Lavallee, *J. Am. Chem. Soc.*, **89**, 7132 (1967). [dd] E. B. Fleischer and T. S. Srivastava, *ibid.*, **91**, 2403 (1969). [ee] M. Fischer, D. Templeton, and M. Calvin, American Crystallographic Association Winter Meeting, 1969, Abstracts, p 31. [ff] E. B. Fleischer and A. Laszlo, *Inorg. Nucl. Letters*, **5**, 373 (1969). [gg] R. Peterson and L. Alexander, *J. Am. Chem. Soc.*, **90**, 3873 (1968). [hh] T. J. Shaffner and P. G. Lenhert, American Crystallographic Association, Summer Meeting, 1968, Abstracts, p 64. [ii] W. E. Bennett, D. E. Broberg, and N. C. Baenziger, *Inorg. Chem.*, in press. [jj] L. Vogt, A. Zalkin, and D. Templeton, *ibid.*, **6**, 1725 (1967). [kk] J. D. Dunitz and E. F. Meyer, Jr., *Proc. Roy. Soc.* (London), **A288**, 324 (1965). [ll] J. G. White, *ibid.*, **A266**, 440 (1962); D. C. Hodgkin, J. Lindsey, and M. Mockay, *ibid.*, **A266**, 475 (1962); D. C. Hodgkin, J. Lindsey, R. A. Sparks, K. N. Trueblood, and J. H. White, *ibid.*, **A266**, 494 (1962).

tances in these metalloporphyrins are Ni–N, 1.96 Å; Cu–N, 1.98 Å; Zn–N, 2.05 Å; this suggests that a shorter bond distance indicates a more "stable" metalloporphyrin with respect to demetallization.

It is now well established that the porphyrin molecule is not completely rigid and its geometry can be greatly influenced by intramolecular crystal interactions. The porphyrins range from almost planar in porphine to very ruffled in the tetraphenylporphine series. The tetraphenylporphine free base crystallizes in two different space groups with different conformations of the porphine skeleton in the two forms. The porphyrin in a "free" environment probably exists in a near-planar conformation with low energy barrier with respect to deviations from planarity; this condition makes for the conformational adaptability of the porphyrin skeleton to its surroundings. Because of the small amount of energy necessary to change the conformation of the porphyrin skeleton it is difficult, in general, to predict the structure of a porphyrin under various circumstances; that is, the detailed conformations of porphyrins in solution are not known because solvent–porphyrin interactions are not well enough understood to know the detailed effects they might have on the easily deformed porphyrin skeleton.

An interesting development from the accurate bond distances of the porphyrin skeleton as shown in **10** is a correlation of the observed bond orders with interpretations of electronic structure. Structure **11** shows a

11   12
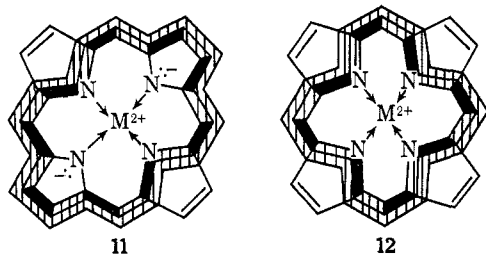
resonance form of the porphyrin in which the "aromatic" ring current of the porphyrin is drawn around the outside of two pyrrole rings and around the inside of the other two; there are several other resonance forms of **11**. From these one would predict the β-pyrrole–β-pyrrole distance (in any pyrrole ring) to be 1.37 Å.[8] The observed bond distance of 1.34 Å is very

close to the carbon–carbon distance in ethylene; thus the β-pyrrole–β-pyrrole bond is nearly a pure double bond.

We have proposed another resonance form that is more consistent with the observed bond data for the porphyrin system; this is shown in **12**. **12** has the outer pyrrole bond as a double bond with the principal ring current now circulating around the 16-membered inner ring. There are two extra electrons in this ring, making it a 16-membered dianion. The conclusion that the main path of conjugation is the inner 16-membered ring as in **12** has been substantiated by the detailed theoretical calculations of Kobayashi and Gouterman.[9-11]

A possible way to a more detailed understanding of the porphyrin ring currents is through the nuclear magnetic resonance spectra of porphyrins. The effects of ring currents on the chemical shifts of substituents can lead to information about the pathways of these ring currents. Some experimental work on the nmr of porphyrins[12,13] and also some theoretical work on their interpretation[14] have been reported, but the work is complicated considerably by the concentration and solvent dependence of the chemical shifts. The best use of nmr in porphyrin chemistry, apart from the usual characterization of compounds, appears to be in studies of the details of the aggregates that porphyrins form, with attention both to thermodynamic stabilities and to structural details of the aggregates.[15] The large chemical shifts that the ring currents of the porphyrins produce are also being employed in the interpretation of the nmr

(8) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959).

(9) M. Zerner and M. Gouterman, *Theor. Chem. Acta.*, **4**, 44 (1966); M. Gouterman and G. Wagmere, *J. Mol. Spectry.*, **11**, 108 (1963).

(10) H. Kobayashi, *J. Chem. Phys.*, **30**, 1362, 1373 (1959).

(11) C. Weiss, H. Kobayashi, and M. Gouterman, *J. Mol. Spectry.*, **16**, 415 (1965).

(12) D. Doughty and C. W. Dwiggins, Jr., *J. Phys. Chem.*, **73**, 423 (1969); W. Caughey and W. S. Koski, *Biochemistry*, **1**, 923 (1962); G. T. Closs, J. J. Katz, F. C. Pennington, M. R. Thomas, and H. H. Strain, *J. Am. Chem. Soc.*, **85**, 3809 (1963).

(13) A. Kane, R. Yalman, and M. Kenney, *Inorg. Chem.*, **7**, 2588 (1968); C. Storm and A. Corwin, *J. Org. Chem.*, **29**, 3700 (1964).

(14) R. J. Abraham, *Mol. Phys.*, **4**, 145 (1961).

(15) R. J. Abraham, P. A. Burbidge, A. H. Jackson, and G. W. Kenner, *Proc. Chem. Soc.*, 134 (1963); E. Berker, R. Bradley, and C. J. Watson, *J. Am. Chem. Soc.*, **83**, 3743 (1961).

spectra of porphyrin-containing proteins.[16] For some theoretical interpretations of porphyrin properties, see the work of Gouterman,[9] Hush,[17] and Chen.[18]

The Inner Hydrogen Problem

X-Ray diffraction studies of porphyrin free bases have now definitely established that the inner pyrrole hydrogens are opposite to each other, as shown in **13**, and


13

hydrogens opposite
free base

14

hydrogens adjacent
to free base

15

16
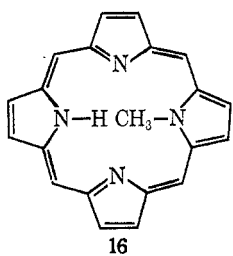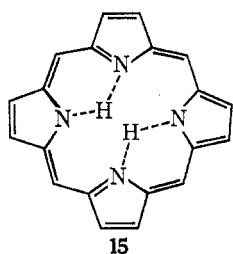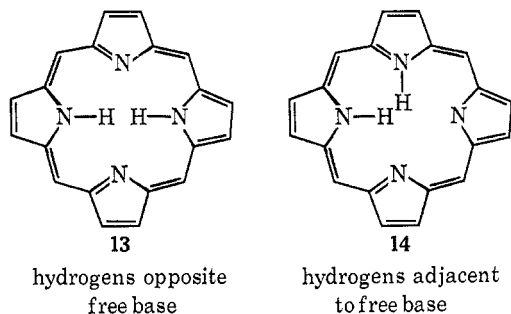
mono-N-methylated porphyrin free base

not adjacent to each other, as in **14**. The possibility of isomer **14** was raised by Rothemund.[19] Another possible structure is shown in **15** where the hydrogen atoms are now equally shared between two nitrogens.

Various physiochemical techniques were used to probe this rather sensitive problem of the position of the hydrogen atoms in porphyrin free bases.[20] Low-temperature visible spectroscopy[21] was interpreted in terms of the existence of the two isomers **13** and **14**. Both ir and nmr studies were carried out without reaching any definitive conclusions. The ir and nmr studies did give evidence for rapid exchangeability of the inner pyrrole hydrogens. Some earlier studies concerned with the synthesis and properties of the N-methylated porphy-

rins[22] **16** established that hydrogen bonding could *not* be important with respect to the electronic properties of the porphyrin molecule. The visible spectra of a free base and a monomethylated free base of a porphyrin were indistinguishable.[23]

The X-ray studies on porphyrins definitely establish that the hydrogen positions are like those in **13**. The triclinic form of tetraphenylporphine shows this most clearly,[24] while the tetragonal forms of tetraphenylporphine[25] and phorphine[26] show this picture with the ambiguity of either a static or dynamic disorder of the hydrogen atoms which causes the X-ray diffraction experiment to see half-hydrogens on each nitrogen.

A refinement of the original Robertson phthalocyanine data[27a] shows that the hydrogens atoms take up positions as in **15**. Hydrogens in these positions may be stabilized by an interaction with the *meso* nitrogens as shown in **17** (but see ref 27b for a contradictory


17
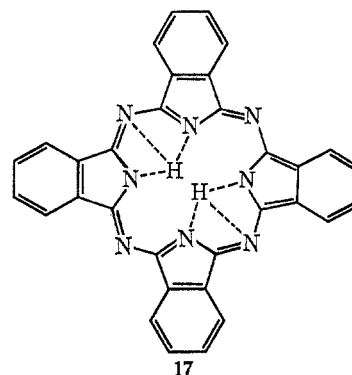
H positions in phthalocyanine

and probably more accurate description of this system). This picture is also consistent with the distance between the hydrogen-bonded pyrrole nitrogens being 2.65 Å while the distance between the nonbonded pyrrole nitrogens is 0.11 Å greater.

Geometry of Metals in Metalloporphyrins

The metalloporphyrins form a set of compounds in which the metal may be four-coordinate with a square-planar geometry, five-coordinate with square-pyramidal geometry, six-coordinate with distorted octahedral geometry, or eight-coordinate to form a sandwich compound with square antiprism geometry. Most metallophthalocyanines and metalloporphyrins form square-planar coordination with the metal ion in the plane of the four pyrrole nitrogens as in **18**.

18
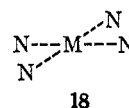
There are several five-coordinate metalloporphyrins with a geometry of a tetragonal pyramid (**19**). The

(16) K. Wüthuch, R. G. Shulman, and J. Pearson, *Proc. Natl. Acad. Sci. U. S.*, **60**, 373 (1968); C. C. McDonald and W. D. Phillips, *J. Am. Chem. Soc.*, **89**, 6332 (1967); A. Kowalsky, *Biochemistry*, **4**, 2382 (1965).

(17) N. S. Hush, *Theor. Chem. Acta*, **4**, 108 (1966).

(18) I. Chen, *J. Mol. Spectry.*, **23**, 131, 144 (1967).

(19) P. Rothemund, *J. Am. Chem. Soc.*, **57**, 2179 (1935).

(20) S. F. Mason, *J. Chem. Soc.*, 976 (1958); G. M. Badger, R. T. N. Harris, R. A. Jones, and J. Sasse, *ibid.*, 4329 (1962); C. S. Vestling and J. R. Downing, *J. Am. Chem. Soc.*, **61**, 3512 (1939).

(21) G. D. Dorough and K. T. Shen, *ibid.*, **72**, 3939 (1950).

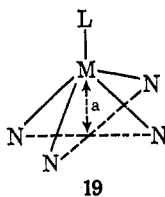(22) J. Erdman and A. H. Corwin, *ibid.*, **68**, 1885 (1946).

(23) W. S. Caughey and P. Iber, *ibid.*, **85**, 269 (1963).

(24) See Table I, footnote *n*.

(25) See Table I, footnote *p*.

(26) See Table I, footnote *m*.

(27) (a) See Table I, footnote *aa*; (b) B. F. Hoskins, S. A. Mason, and J. C. B. White, *Chem. Commun.*, 554 (1969).

19

tetragonal pyramid coordination of five-coordinate metalloporphyrins

high-spin ferric porphyrins assume this geometry with $a \simeq 0.5$ Å; this has been carefully discussed by Hoard and his coworkers.[7,28,29] The prediction by Hoard that a low-spin iron (III) metalloporphyrin would have the iron in the plane of the pyrrole nitrogens has recently been verified by a structural analysis of the bisimidazoleiron(III) tetraphenylporphine complex.[30] The magnesium ion in magnesium phthalocyanine hydrate is 0.495 Å out of the pyrrole nitrogen plane and bonded to a water in the apical position.[31] The vanadium of the vanadyl-substituted etioporphyrin was also noted to be 0.48 Å out of the plane.[32]
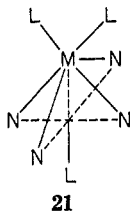
An interesting six-coordinate metalloporphyrin complex is the rhodium carbonyl tetraphenylporphine chloride that has the coordination shown in **20**.[33] This is
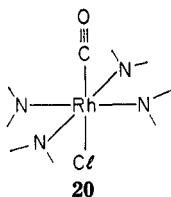
20

six-coordinate metalloporphyrin

a prototype of the coordination that most of the metalloporphyrins assume in nature, as in the hemoprotein and cytochrome systems.

If the metal is out of the porphyrin plane a seven-coordinate species (**21**) is possible; this has not yet been

21

possible seven-coordinate metalloporphyrin

observed in any metalloporphyrin complex.

A very unusual complex is formed between two phthalocyanine rings and a stannic ion. The sandwich complex formed, $Sn(Pc)_2$, has eight-coordination with a square-antiprismatic geometry as shown in **22**.[34]

Two dimeric metalloporphyrin structures have now been determined in systems that have considerable
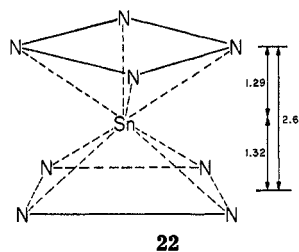
22

square antiprism geometry of eight-coordinate tin phthalocyanine complex

chemical interest. The oxidation of phthalocyaninemanganese(II) with oxygen in pyridine produces a compound that has been shown to be a manganese(III) phthalocyanine dimer with an oxo bridge connecting

$$Mn^{II}Pc \xrightarrow[\text{pyridine}]{O_2} \text{pyridine-PcMn}^{III}\text{-O-Mn}^{III}\text{Pc-pyridine}$$
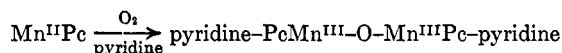
the two manganese(III) phthalocyanines and a pyridine completing the octahedral coordination.[35] The two phthalocyanine rings are staggered by 49° with respect to each other so that the phenyl groups on one ring are approximately between the phenyl groups on the other ring.
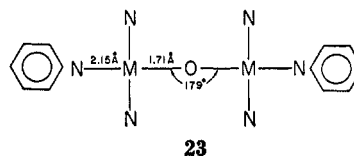
23

manganese(III) phthalocyanine dimer

If one adds base (NaOH) to a solution of a ferric porphyrin or adds oxygen to a ferrous porphyrin a new species occurs that has now definitely been characterized as a μ-oxo-bis(porphyriniron(III)) dimer (**24**).[36,37] The iron in this five-coordinate complex is

24
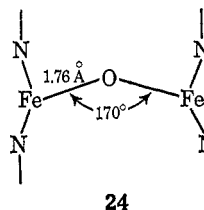
0.5 Å out of the pyrrole nitrogen plane toward the oxygen bridge. The porphyrin skeletons in this iron dimer are staggered. This compound shows interesting magnetic properties with an antiferromagnetic coupling between the iron ions resulting in a diamagnetic ground state at liquid helium temperatures and a magnetic moment at room temperature of 1.85 BM. This compares to the ferric tetraphenylporphine monomer that has a magnetic moment at room temperature of 5.87 BM and follows the Curie–Weiss law in the temperature range from 298 to 77°K.

(28) See Table I, footnote *y*.
(29) J. L. Hoard in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman and Co., San Francisco, Calif., 1968.
(30) J. L. Hoard, private communication.
(31) See Table I, footnote *ee*.
(32) See Table I, footnote *gg*.
(33) E. Fleischer and R. Thorp, *Chem. Commun.*, 475 (1969).
(34) See Table I, footnote *ii*.

(35) See Table I, footnote *jj*.
(36) E. Fleischer and T. S. Srivastava, *J. Am. Chem. Soc.*, **91**, 1969; J. L. Hoard, private communication.
(37) I. A. Cohen, *J. Am. Chem. Soc.*, **91**, 1980 (1969); N. Sadaswan, H. Eberspaecher, W. Fuchman, and W. Caughey, *Biochemistry*, **8**, 534 (1969).

The visible absorption spectra of the monomer and dimer species are quite different. It is hoped that a careful analysis of this system will lead to a better understanding of the electronic configuration of metalloporphyrins and of the way metal ions in complicated systems can interact *via* oxide and other ligand bridging groups. The interaction of two metal ions *via* an oxide bridge is well established in the literature, although the details of the interaction still are not well understood.[38] We have also prepared a dimer of manganese-(III) tetraphenylporphine.

Porphyrin Diacids

The porphyrin diacids that are formed in acidic solution present several interesting problems that were only recently solved by X-ray diffraction.[39] The general geometry of the diacid complexes was unknown. The fact that some porphyrins, in particular, tetrapyridylporphine and tetraphenylporphine, existed in solution only as the free base and diacid but not as the monoacid species (see **25**) was unexplained.[40,41] The

25
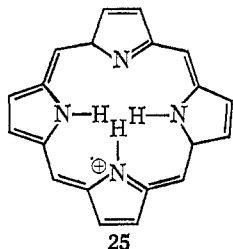
fact that most porphyrin free bases are orange or red in solution while their diacid species are usually violet, except for the tetraphenyl- and tetrapyridylporphine diacid species which are green, can be interpreted in terms of the molecular structures of these diacid compounds.

Both the tetraphenyl- and tetrapyridylporphine diacid species exhibit the remarkable nonplanar conformation of the porphyrin skeleton shown in **26** and **27**. The β-pyrrole carbon atoms are as much as 1.0 Å out of the "plane" of the four pyrrole nitrogen atoms. This highly nonplanar geometry arises from van der Waals and Coulombic repulsions of the four inner hydrogen atoms. The phenyl groups in most tetraphenylporphine compounds are almost perpendicular to the "mean plane" of the porphine ring; this does not allow any π interaction between the benzene π system and the extensive porphyrin π system.

(38) A. Mathieson, D. P. Mellor, and N. C. Stephenson, *Acta Cryst.*, **5**, 185 (1952); J. D. Dunitz and L. E. Orgel, *J. Chem. Soc.*, 2594 (1953); H. Schugar, A. T. Hubbard, F. C. Anson, and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 71 (1969); J. Lewis, F. E. Mabbs, and A. Richards, *J. Chem. Soc.*, *A*, 1014 (1967); W. M. Reiff, G. J. Long, and W. A. Baker, Jr., *J. Am. Chem. Soc.*, **90**, 6347 (1968).
(39) See Table I, footnote *q*.
(40) S. Aronoff and M. Calvin, *J. Org. Chem.*, **8**, 205 (1943).
(41) E. Fleischer and L. Webb, *J. Phys. Chem.*, **67**, 1131 (1963).

26

(a)   (b)
27
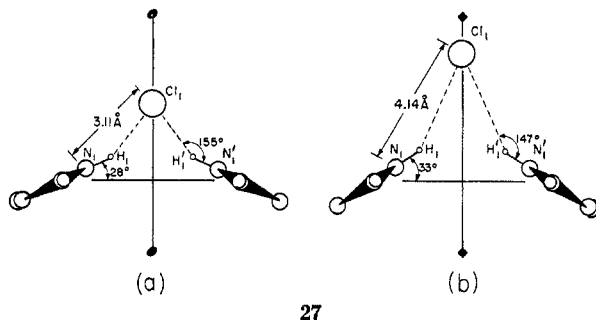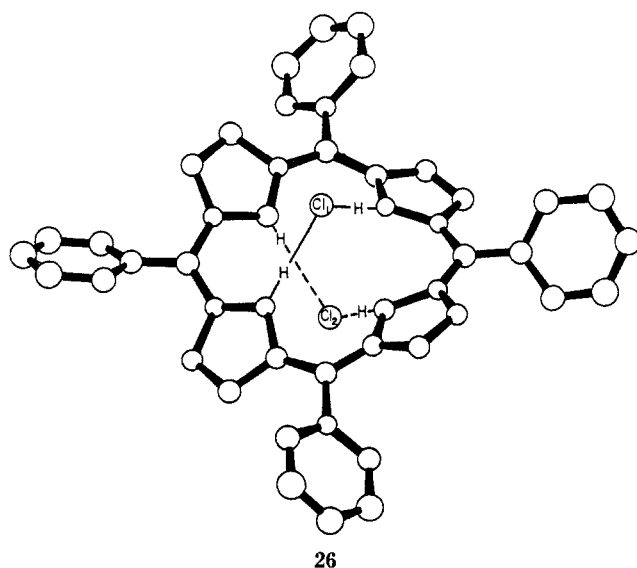
The dihedral angle that the phenyl rings make with the porphyrin ring is required to be greater than 70° because of interactions between the phenyl hydrogens and the outer pyrrole hydrogens. In the diacid of tetraphenylporphine, the tilted porphine skeleton allows the phenyl group to rotate toward the porphine "plane," making an angle of 21° with it; this now allows a strong interaction to occur between the phenyl and porphyrin π system with the resulting green color compared to the usual violet diacid species. All porphyrin diacids would be expected to have the geometry shown in **26** and **27**. For a more extensive discussion of the diacid porphyrin problem see ref 39.

This Account has covered some of the general structural properties of porphyrins and metalloprophyrins. This information can be usefully employed in the interpretation of the chemistry of the porphyrin system and also as an aid to the understanding of the biological action of metalloporphyrins.