

67 Porphyrinoids

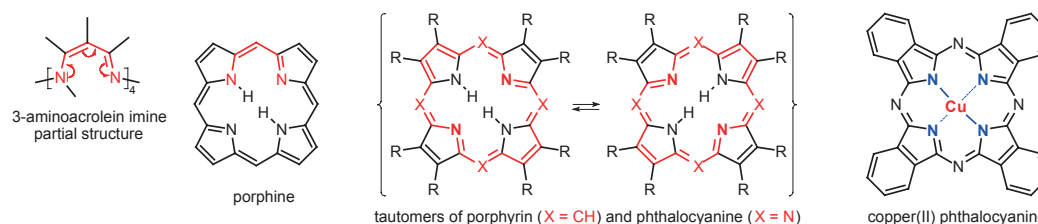
67.1 Porphyrins and Phthalocyanines as Polyaza[18]annulenes

Porphyrids comprise *porphyrins* (from Greek *porphyrus* = purple) of natural origin and synthetically obtained *phthalocyanines* including their metal chelates. They represent *polyaza[18]annulenes*.

Four pyrrole rings linked with methine groups at the α, α' -positions make up the parent macrocyclic porphyrin ring system called *porphine*. Following the red bonds in the tautomers given, porphyrins ($X = \text{CH}$) and their metal chelates turn out to be *diaza[18]annulenes*.

Four imino nitrogen atoms replace the methine fragments in the benzo-fused *phthalocyanine*. Once more tracking the red bonds in the formulas, phthalocyanines ($X = \text{N}$) and their metal chelates can be considered as *hexaaza[18]annulenes*.

To conclude, planar porphyrins and phthalocyanines have 18π electrons and obey HÜCKEL's $(4N + 2)$ rule with $N = 4$ as a criterion for *aromaticity* (Chapters 23.3, 29.1). Metal-free porphyrins exist as tautomers in which diagonal ring nitrogen atoms exchange their hydrogen atoms.



The outstandingly intense SORET band ($\lambda_{\text{max}} \approx 410 \text{ nm}$) in the electronic spectra (Chapter 66.1) of porphyrins and longer-wavelength maxima ($\lambda_{\text{max}} > 500 \text{ nm}$) are attributed to the tetrameric push-pull system of 3-aminoacrolein imine present in the porphyrin ring.

As tetradentate ligands with four nitrogen donors (N_4 ligands), porphyrins and phthalocyanines chelate metal cations with ionic radii of about 70 pm ($1 \text{ pm} = 10^{-12} \text{ m}$). Substituted phthalocyanine metal chelates, industrially prepared from phthalic acid derivatives such as phthalimide and phthalodinitrile in the presence of metal salts, are widely used as dyes, colorants, and pigments. Substituents at the benzenoid rings ($-\text{Cl}$, $-\text{SH}$, $-\text{C}_6\text{H}_5$) change the color from blue to green. Red phthalocyanines contain 1,4-dithiane rings instead of benzene rings.

67.2 Porphyrinoids in Blood and Chloroplasts

67.2.1 Heme

In the protein *hemoglobin* (structure: Fig. 69.2 c and d) of red blood corpuscles, the ferrous chelate (chelated ion: $\text{Fe}^{2\oplus}$) of a substituted porphyrin called *heme* (from Greek *haima* = blood) is the non-protein organic function. It is referred to as the *prosthetic group* of hemoglobin, shown in Fig. 67.1 c, not only giving the red color to the protein but, most importantly, also enabling it to *carry oxygen* in the breathing process. The ferrous ion is coordinated (chelated) to the four pyrrole nitrogens of the porphyrin ring and to an *imidazole* nitrogen of the amino acid *histidine* (Chapter 68.1) in the protein sequence. This fifth coordination to the so-called *proximal histidine* ties heme to the protein (Fig. 67.1 c). *Oxygen* takes the *sixth coordination position of the ferrous ion* of heme protected in a hydrophobic pocket of hemoglobin during transport in the blood flowing from the lungs to the muscles and other tissues where oxygen is needed. *Carbon dioxide* produced by "metabolic burning" of carbohydrates and other tissues reacts with *N-terminal* amino groups of hemoglobin to give carbamate (Chapter 55.3.2); in this state it is carried away by the protein in the blood back to the lungs where it is set free and exhaled. Stronger binding *carbon monoxide* ($^{\ominus}\text{IC}\equiv\text{O}^{\oplus}$) and the isoelectronic *cyanide anion* ($^{\ominus}\text{IC}\equiv\text{N}^{\oplus}$) of hydrogen cyanide displace oxygen in oxygenated hemoglobin, disrupting oxygen transport, causing tachypnea, cyanosis, coma, and death.

Hot acetic acid cleaves hemoglobin. *Hemin* is the ferric chelate (chelated ion: $\text{Fe}^{3\oplus}$) which crystallizes from the solution obtained by pouring blood into hot acetic acid containing some sodium chloride (Fig. 67.1 b). *Protoporphyrin* is the name of the metal-free ligand (Fig. 67.1 a).

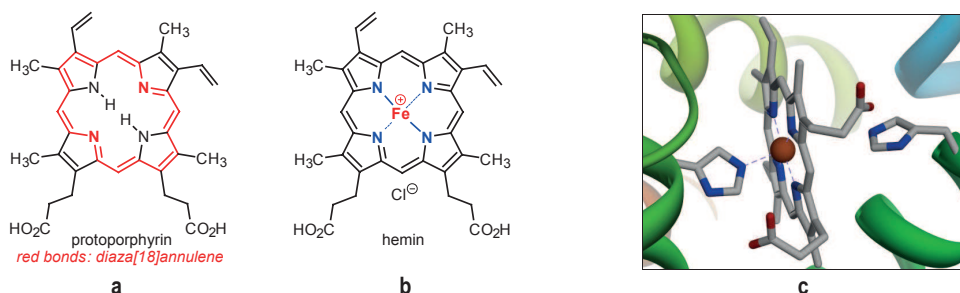
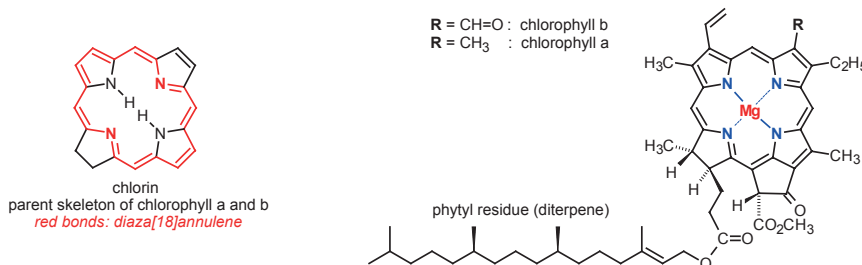


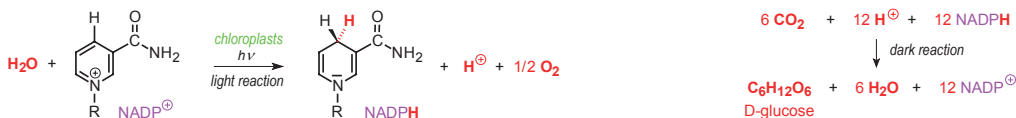
Fig. 67.1. Protoporphyrin (a), hemin (b), and tube model of heme in hemoglobin (c), attached to the helical parts (green) of the protein by coordination of the ferrous ion to the imidazole nitrogen atom of the proximal histidine (left side); oxygen takes the sixth coordination position of the ferrous ion in oxygenated hemoglobin, controlled by the distal histidine (right side)

67.2.2 Chlorophyll

Chlorophyll a (methyl) and *b* (aldehyde) are found in the chloroplasts of plants. They can be extracted from leaves with methanol or acetone, separated by chromatography on silica gel, and isolated as waxy blue-black microcrystals; the waxiness arises from the diterpenoid phytyl ester residue (Chapter 76.3.3). Both chlorophylls are magnesium chelates of a substituted *chlorin*. The parent chlorin derived from porphine contains one partially hydrogenated pyrrole ring; thus, the aromatic diaza[18]annulene system is not disrupted.



The *light reaction of photosynthesis* occurs in the membrane of chloroplasts where chlorophyll-protein complexes collect photons. These excite other chlorophyll molecules, inducing *photolysis of water to oxygen* by the nicotinamide coenzyme NADP^{\oplus} which undergoes reduction to 1,4-dihydropyridine $\text{NADPH} + \text{H}^{\oplus}$. The *dark reaction of photosynthesis* in the stroma of chloroplasts involves *reductive conversion of carbon dioxide into D-glucose via D-glyceraldehyde* (Chapter 71.1) by the reducing coenzyme $\text{NADPH} + \text{H}^{\oplus}$. Without photosynthetically produced oxygen and D-glucose, animal and human life on earth would be impossible.



Chapter 67 permits answers to the following:

- (67.1) How do you account for the outstanding stability of porphyrins and phthalocyanines?
- (67.2) What is the difference between heme and hemin? How is hemin obtained?
- (67.3) What is the difference between porphine and chlorin? Draw formulas.
- (67.4) Briefly outline the biological function of (a) heme and (b) chlorophyll.