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Abbreviations:

- **BChl** bacteriochlorophyll
- **BPheo** bacteriopheophytin
- **Chl** chlorophyll
- **Chlide** chlorophyllide
- **ET** electron transfer
- **NSD** normal structural decomposition
- **OEC** 2,3,7,8,12,13,17,18-octaethylchlorinato
- **Pheo** pheophytin
- **RR** resonance Raman
- **Δ24** deviation of the 24 macrocycle atoms in porphyrins from their least-squares plane [Å]
- **Δ26** deviation of the 26 macrocycle atoms in phytochlorin derivatives from their least-squares plane [Å]
- **ΔC\textsubscript{a}** deviation of the C\textsubscript{a} atoms from the 4N-plane [Å]
- **ΔC\textsubscript{b}** deviation of the C\textsubscript{b} atoms from the 4N-plane [Å]
- **ΔC\textsubscript{m}** deviation of the C\textsubscript{m} atoms from the 4N-plane [Å]
I. Introduction

Chlorophylls are often termed the “pigments of life” and are the primary photosynthetic pigments in nature. They are green colored macrocyclic pigments and the term chlorophyll, coined by Berzelius in 1838, is derived from Greek roots and indicates the green of leaves. Chlorophylls and the related bacteriochlorophylls are the ubiquitous pigments of photosynthetic organisms. As such they share common structural principles and functions. They are responsible for the primary biochemical energy generation in nature through action as reaction center and accessory pigments and give the only indications of life on earth visible from outer space.

Chlorophylls have been studied for over two centuries and, while much of their basic chemistry was established almost 100 years ago, real breakthroughs in their exact biochemical function were only made in the last decades by X-ray crystallographic analysis of both reaction center and antenna complexes. Until the middle of the last century most studies were concerned with the basic structural chemistry of chlorophylls. This was followed by the elucidation of the basic anabolic pathways of Chl in higher plants, photophysical studies on their function in photosynthesis, and more recently their catabolism. Parallel to studies on Chl a/b from Higher Plants, the last decades have seen many efforts to elucidate the structure, function and biosynthesis of photosynthetic pigments from unicellular organisms and photosynthetic bacteria. In applied research chlorophylls are mainly used in solar energy conversion projects or as photosensitizers in photodynamic cancer therapy. Industrially, phytochlorin and rhodochlorin derivatives have found some use as food additives and anti-odor compounds, often in form of simple plant extracts. The best summaries of all chemistry pertinent to chlorophylls are still the monographs by Willstätter and Stoll and Scheer.

Here we will focus on the structural chemistry of isolated Chl derivatives, i.e. small molecule analyses of compounds closely related to chlorophyllides, pheophorbides, phytochlorins and similar compounds.

II. Basic Structure and Reactivity of Chlorophylls

Chls are heteroaromatic compounds, the aromatic character of the underlying tetrapyrrole system and the reactivity of the functional groups in the side chains governing their chemistry. Three different classes of tetrapyrroles, differentiated by their oxidation level, occur in nature (Fig. 1): porphyrins (1, e.g., hemes), chlorins (2, e.g., Chls), and bacteriochlorins (3, e.g., BCHls). As a cyclic tetapyrrole with a fused five-membered ring, the overall reactivity of Chl is that of a standard phytochlorin. Such compounds are capable of coordinating almost any known metal with their nitrogen atoms. Together with the conformational flexibility of the macrocycle and the variability of their side chains, this accounts for their unique role in photosynthesis.
Throughout this contribution the recommendations of the IUPAC commission on the nomenclature of tetrapyrroles\textsuperscript{13} have been followed as much as possible. In this system, the 24 macrocycle atoms are numbered from 1 to 24 (see formula 5 in Figure 2). Four different types of atoms are present in the porphyrin system: the four pyrrole nitrogen atoms, the methine bridge carbons (which are named \textit{meso} carbons or C\textsubscript{m}), and the \(\alpha\)- and \(\beta\)-pyrrole carbons, named C\textsubscript{a} and C\textsubscript{b}, respectively. The latter abbreviations will be later used for the description of geometrical parameters and conformational properties. The practical use of this nomenclature is limited, and its actual use varies with the background of the researchers. Especially in the biological sciences a "derivative nomenclature" is often used. For the bacteriochlorophylls (BChls) a more practical nomenclature has been suggested.\textsuperscript{14,15}

The best known pigment is Chl a\textsuperscript{5} (Fig. 2) which occurs in all organisms that carry out oxygenic photosynthesis. In higher plants it is accompanied in a 3:1 ratio by Chl b\textsuperscript{7}, where the 7-methyl group has been replaced by a formyl group. Both compounds typically consist as the ester of the tetrapyrrole moiety with a C-20 terpenoid alcohol, phytol. Most compounds are magnesium chelates, but the free base of Chl a, Pheo a\textsuperscript{6}, is also active in electron transfer and \textit{in vivo} zinc(II) complexes have been suggested.\textsuperscript{16,17,18}

However, many other similar photosynthetic pigments occur in nature.\textsuperscript{8} All share either a phytochlorin\textsuperscript{8} or 7,8-dihydroporphyrin framework and so far over one hundred related pigments have been isolated. For example, such compounds include Chl d\textsuperscript{9} from \textit{Rhodophytes}, the Bchls c\textsuperscript{10}, d, and e [which are chlorins\textsuperscript{2} (dihydroporphyrins) and show significant variability in their peripheral groups]\textsuperscript{19,20} from \textit{Chlorobiaceae} and \textit{Chloroflexaceae}, and Bchl a\textsuperscript{11} and b (true bacteriochlorins 3, i.e. tetrahydroporphyrins) found in \textit{Rhodospirillales}. Other natural pigments are Chl c, Bchl g and many of these with different esterified isoprenoid alcohols. Chemically related chlorins have also been found in many oxidoreductases, marine sponges, tunicates, and in \textit{Bonella viridis}. A deep-sea dragon fish (\textit{Malacosteus niger}) even utilizes a Chl derivative as a visual pigment.\textsuperscript{21} Most of these are believed to be derived from Chl and then processed by the plant or animal.
Figure 2 Naturally occurring Chls and related systems. Small numbers in the Chl a formula indicate the IUPAC numbering scheme. R groups may vary in different organism or at different developmental stages.

The chemistry of Chls is governed by the aromatic character of the underlying tetrapyrrole moiety and the reactivity of the functional groups in the side chains. As a cyclic tetrapyrrole with a fused five-membered ring, the overall reactivity of Chls is that of a standard heteroaromatic compound. The extended aromatic system, however, which is capable of coordinating almost any known metal with its core nitrogen atoms, together with the variability of its conformation and its side chains, is responsible for its unique role in photosynthesis. The basic aromatic system is susceptible mainly to electrophilic reactions, e.g. halogenations, with a preference for reaction at C20, the meso position closest to the reduced pyrrole ring. The C7-C8 double bond in phytochlorin (next to R1) is not part of the aromatic delocalization pathway and thus is a convenient handle for modification of the Chl macrocycle via addition and oxidation reactions. The side chain substituents undergo standard transformations, e.g. the C3 vinyl group undergoes addition and oxidation reactions, the ester groups at C17 and C13 can be saponified or transesterified, and the reactivity of ring E is generally governed by enolization and subsequent reactions of the β-keto ester system. The latter includes the so-called allomerization reactions, i.e. oxidative degradation reactions involving oxidations, hydroxylation, ring-opening or decarboxylations of the isocyclic pentanone ring. The book by Scheer and a review by Hynninen therein remain the most comprehensive treatises on Chl chemistry and function, while a comprehensive review on side chain transformation has recently been given by Pavlov and Ponomarev. In recent years the group of Tamika has made significant breakthroughs in chemical transformations of chlorophylls (see chapter by Tamiaki and Kunieda in this book). [Editor: reference chapter by Hitoshi Tamiaki and Michio Kunieda in this volume]
III. New chlorophylls

Only few truly new Chl derivatives have been identified \textit{in vivo} in the last decade, esp. in the biological sciences. A new Chl c pigment $\text{12}$ has been isolated from the phytoplankton \textit{Emiliania huxleyi} and characterized both chromatographically and spectroscopically.\textsuperscript{24} Also, the new chlorophylls petasiphyll-a $\text{13}$\textsuperscript{25} and phellophyll-a $\text{14}$\textsuperscript{26} have been isolated from the leaves of \textit{Petasites formosanus} Kitamura and \textit{Phellodendron amurense} var. \textit{wilsonii}, respectively. The HPLC analysis of divinyl Chl a and b and some novel Chl c has been reviewed.\textsuperscript{27} Several new Chl a related compounds have been isolated as antioxidants from the edible parts of the short-necked clam \textit{R. philippinarum} and other bivalve molluscs (and their attached diatoms).\textsuperscript{28} An X-ray crystal structure is available for chlorophyllonic acid a methyl ester $\text{15}$\textsuperscript{29} and stereoselective syntheses of Chl a related chlorins, including some of those isolated from the above species, have been developed.\textsuperscript{30}

In the BChl d series new homologs have been detected in natural populations of green photosynthetic bacteria through HPLC analysis. The structure of the esterifying alcohols were confirmed chemically and via GC-MS.\textsuperscript{31,32}

IV. Biological Relevance of Tetrapyrrole Conformations

One aspect of tetrapyrroles that has received some attention in recent years concerned the conformation of the underlying macrocycle. A critical factor for all biological functions is the close interplay between bound cofactors and the respective apoprotein. In most cases the isolated pigments show physicochemical properties quite distinct from those found in intact pigment-protein complexes \textit{in vivo}. The protein functions as a medium, as a scaffold for the spatial arrangement of the cofactors, it mediates the interaction with other components in a supramolecular biological system, and it acts as a ligand with effects on the configuration and conformation of the cofactors and overwhelming evidence has accumulated for the conformational flexibility of the cofactors \textit{in vivo}.\textsuperscript{33}

Numerous synthetic, structural and spectroscopic studies have established that macrocycle conformation can control the physicochemical properties of the tetrapyrrole to a significant extent.\textsuperscript{12,34,35,36,37,38} For example, it has been shown that increasing nonplanarity with its destabilization of the $\pi$-system leads to bathochromically shifted absorption bands, easier oxidation, lower fluorescence yields, larger Stokes shifts, shorter lifetimes of the lowest excited states and faster intersystem crossing and internal conversion. In natural systems it can be assumed that manipulation of the macrocycle conformation via steric interactions with the surrounding protein side chain in pigment-protein complexes and/or via axial coordination of the central metal can be used to fine-tune the physicochemical properties of the macrocycle. This presents an intriguing rationale for explaining the often
diverse (physico)chemical reactivity of the same chromophore in different protein environments.

A similar rationale can be applied to the (B)Chls. Again, an extended aromatic system such as the one of Chl or BChl must be conformationally flexible and the presence of the reduced pyrrole ring in chlorins and bacteriochlorins should lead to even more conformational flexibility than is observed in porphyrins. For porphyrins the advent of the routine application of X-ray diffraction and vibrational spectroscopy to structural studies has enabled a deeper understanding of the importance of this phenomenon for the functional properties of tetrapyrroles. Despite their biological relevance structural studies on hydroporphyrins are scarce. This is mainly a result of their limited synthetic accessibility, lower chemical stability compared to porphyrins, and problems in obtaining single crystals of suitable quality for crystallographic analyses. A discussion of the available data is the main focus of the present contribution.

V. Conformational Analysis of Porphyrins

A comparative analysis of the structural chemistry of tetrapyrroles requires an analytical framework that allows both qualitative and quantitative comparisons. Even a qualitative look at some representative porphyrin conformations indicates that the macrocycle can adopt quite diverse conformations (Fig. 3). The currently used classification system was suggested by Scheidt and Lee and expanded by Shelnutt et al. The two out-of-plane distortions modes most easily identified are the saddle-shaped and ruffled conformation [named sad ("bending" in Fig. 3) and ruf ("twisting" in Fig. 3) by Scheidt and Lee]. A typical example for the latter is found in metalloporphyrins with small metal ions, such as Ni(II), where metal-nitrogen bond shortening is observed due to ring distortion. The ruffled distortion involves a twisting about the metal-nitrogen bond and is characterized by alternating displacement of the Cm positions above and below the mean plane. A well known example is the S4-ruffled modification of (2,3,7,8,12,13,17,18-octaethylporphyrinato)nickel(II). The saddle distortion involves the alternate displacement of the pyrrole rings above and below the mean plane while the Cm positions remain more or less in plane. Typical examples for this are highly nonplanar, dodecasubstituted porphyrins, e.g. 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrins. Other types of in-plane distortion are wave distortion and doming. The latter is frequently found in five-coordinated complexes, where the axial ligand causes an out-of-plane displacement of the central metal or in metalloporphyrins involving large central metal ions like Tl(III). While these four symmetric distortion modes offer a convenient system of classification for different porphyrin conformations, often deformations occur that do not directly correspond to any of these distortions. In most cases, the conformation of a given macrocycle can be described as a combination of any of these distortion types and includes often significant in-plane distortions (e.g., "stretching in Fig. 3). A detailed description of distortion modes and their energy levels has been given by Jentzen et al.
An analysis of the tetrapyrrole conformation requires determination of specific geometrical parameters and special visual illustrations. This goes beyond the usual analysis of bond lengths and angles. The conformation of a given macrocycle is best described by the displacement parameters of the macrocycle atoms from a mean plane (typically the 4N-or 24-macrocycle atom plane is used here). For example, the deviation of the 24-macrocycle atoms from their least-squares-plane (Δ24) has often been used as a measure for the overall degree of distortion or nonplanarity. As illustrated in Fig. 3, the displacements of the C\textsubscript{m} and C\textsubscript{b} atoms are of notable importance. If axial ligands are present, analysis of the porphyrin core conformation requires determination of the ligand tilt angle (\(\varphi_{\text{ax}}\)) and of the dihedral angle of the axial ligand plane and the N\textsubscript{op}-N\textsubscript{op} axis (\(\Phi\)).\textsuperscript{40} Steric strain often affects not only out-of-plane displacements but the core conformation as well. Here the core size (\(\box it\)) is defined as the average vector length from the pyrrole nitrogen atoms to the geometrical center of the 4N-plane, while the core elongation parameter (\(\Xi\)) gives the average difference between the lengths of the vectors between a nitrogen atom and its two neighboring N-atoms.

Two different graphical representations are used to illustrate the conformation of individual tetrapyroles. One involves a linear display of the skeletal deviations from the 4N-plane in which the macrocycle deviations (to scale) are plotted against a positional parameter (not to scale) when "moving" around the ring system and looking across the 4N- or 24-macrocycle atom plane.\textsuperscript{38,39} The other involves plotting the individual displacement parameters for each distortion mode and illustrates the mix and interplay of the various distortions. This is based on the normal structural decomposition method (NSD) introduced by Shelnutt.\textsuperscript{47,48} This method analyses all out-of-plane and in-plane distortion modes based on experimental or calculated positional atomic data. An example for the use of these different graphical representations is given in Fig. 4 using 5-\textit{tert}-butylporphyrin \textbf{16}.\textsuperscript{49} Naturally, use of these analyses for Chl and phytochlorin derivatives requires modification for the isocyclic ring V, e.g., use of a Δ26 instead of a Δ24 parameter.\textsuperscript{12}
Figure 4 Illustration of a conformational analysis: a) View of the molecular structure of 16 in the crystal. Hydrogen atoms have been omitted for clarity; thermal ellipsoids give 50 % occupancy. b) Skeletal deviation plot with respect to the plane of the 24 macrocycle atoms; ◆ denotes the tert-butyl substituted meso carbon; x-axis not to scale; sequence of pyrrole rings follows the IUPAC nomenclature from left to right (N21, N22, N23, N24). c) Graphical representation of the displacements along the lowest-frequency coordinates that best simulate the structure 16. Adapted from reference 49.

VI. Chlorophyll Complexes in Photosynthesis

As for the porphyrins,\textsuperscript{45} evidence supporting the importance of the chromophore conformation for the biological function has also been established in the past for various chlorophyll protein complexes.\textsuperscript{50} For example, the first crystal structure of such a light harvesting complex, the antenna BChl a protein from Prosthecochloris aestuarii, exhibited a significant range of conformations for the seven bound BChl a molecules.\textsuperscript{51,52,53} The different absorption bands of the individual BChl molecules in this complex were shown to reflect the conformational differences observed in the protein crystal structure.\textsuperscript{54}

An even more intriguing example is the crystal structure of the LH2 complex from Rhodopseudomonas acidophila, one of the most beautiful examples of the special structural engineering used by nature to adapt photosynthetic pigments for light harvesting and storage. Nine B800 BChl and 18 B850 bacteriochlorophyll molecules are each arranged in cyclic arrays and an analysis of the BChl molecules revealed that three different conformational
types of BChl α are present. The B800 BChl and the αB850 chromophores where shown to exhibit a Δ26 of 0.08 to 0.09 Å. In contrast, the βB850 chromophores were significantly more distorted with a Δ26 of 0.15 Å. This was taken as an indication for an influence of the conformation on the spectral properties.

Similarly, the bacterial photosynthetic reaction center pigments exhibit conformational flexibility. Overall the arrangement of the cofactors is roughly C2-symmetric with numerous pigment-protein interactions, which are responsible for the geometrical arrangement of the chromophores. The special pair is characterized by an overlap of the pyrrole rings I. Intriguingly the photochemistry is "asymmetric". Only the L side is photochemically active, although the arrangement of the cofactors (but not the apoproteins) is similar. The symmetry is already broken at the special pair with selective charge-transfer reactivity towards the L side and it has been suggested that the L side molecule has a less distorted macrocycle than the M side chromophore. While other explanations have been brought forward, there is structural evidence for multiple conformations in protein structures from site-directed mutants. Resonance Raman and other vibrational techniques have been used to investigate this situation and have provided supporting information for structural flexibility of the chromophores. This has been reviewed before and an update will be given elsewhere.

RR spectral changes have been observed in PSI after exposure to high light intensities, indicating the extent of photodamage to the Chl α pigments and providing insight into the mechanisms of photoprotection. In a comparative RR and fluorescence line narrowing study of isolated Chl α, β, and γ, specific modes have been assigned to specific parts of the molecule, and the effect of the Mg coordination state has been described. A shift, caused by the photo-oxidation of P700, has been observed in the UVRR spectra of the nearby tryptophan and has potential as a probe for electron transfer in the ETC. Reviews of recent applications and findings of RR spectroscopy regarding pigments photosynthetic complexes and of the application of RR and FTIR to Chls in proteins are available.

Over the past decade, there have been 117 crystal structures of photosynthetic related proteins, containing either (bacterio)chlorophylls or pheophytins, deposited in the PDB. This is a great many more than the 20 deposited in the preceding 10 years and this is a result of the efforts of the crystallographers who have persevered with the challenges associated with the crystallization and X-ray analysis of integral membrane proteins. The culmination of the work on this type of protein crystallization has been reviewed, the latter containing brief descriptions of the structural determination of some photosynthetic pigment-protein complexes. The resolutions of the structures varies from 9.5 Å to 1.3 Å (PDB IDs: 1VCR and 3EOJ, respectively) and thus varying degrees of information are obtainable; proteins have been isolated from plants, algae, dinoflagellates, green bacteria and purple bacteria, totaling 19 distinct species. The structures include super-complexes of entire photosystems; high-resolution studies of individual subunits; wild type and mutated proteins; for reaction centers, charge-neutral and -separated states and structures reconstituted with extrinsic cofactors, all of which bear information regarding the role and nature of the (bacterio)chlorophylls and related cofactors. The following brief summary presents an overview of the up to date findings regarding the structures of PSI, PSII and available structures isolated from Chlorobaculum tepidium, and especially describes the structural information regarding the (bacterio)chlorophylls and related cofactors.

The crystal structure of the integrated PSI super-complex has been determined for the pea plant, Pisum sativum (PDB IDs: 2WSC, 2WSE and 2WSF; 2001; 1QZV), to a maximum resolution of 3.3 Å, and for the thermophilic cyanobacterium Synechococcus elongatus (PDB ID: 1JB0) at 2.5 Å. The 2.5 Å structure provides an atomic model picture
of PSI. Thus, the positions and orientations of the 96 Chl $a$ molecules (90 antenna cofactors and six as part of the ETC) were determined as were the $Q_x$ and $Q_y$ transition dipolar moments. In addition, the ring substituents were modeled for 48 of them. The pigments are coordinated directly or through water molecules to the side chains of subunits PsaA and PsaB for the ETC and 79 of the antenna Chl $a$ cofactors, whilst the rest are borne by other subunits except for one that is bound by the phosphodiester group of lipid (III). The side chain donors are predominantly histidine imidazoles; however some of the antenna pigments are bound by the oxygen atoms of other residues, peptides or waters. Of course there are countless hydrophobic interactions also and, in most cases (notably this excludes the second pair of Chl $a$ molecules in the ETC), significant H-bonding. The 3.3 Å structure of plant PSI (PDB ID: 2WSC$^{79}$) provides the best model from this source to date. Plant PSI consists of 18 protein subunits and 191 photochemical cofactors, of which 173 are chlorophylls (145 of the $Q_x$ and $Q_y$ transition dipolar moments were determined), and shows both the core and LHCI units. The PSI core is made up of 12 subunits with the majority of pigments, including those of the ETC, bound by the symmetry related dimer PsaA and PsaB. Ten of the 12 core subunits are closely related to the cyanobacterial PSI; the remaining two are involved with the LHCI and LHCII complexes, unique to plants. The LHCI peripheral antenna complex consists of four subunits: Lhca-1, -2, -3 and -4, each consisting of 15, 14, 17 and 15 chls respectively. The Chls that constitute the P700 pair appear to be identically positioned to those of the cyanobacterial system and the binding sites of the second and third pairs of the ETC are strictly conserved between the two. In contrast, however, plant PSI contains a number of gap Chls between the core complex and LHCI that mediate excitation energy transfer, and possibly affect binding, between them.$^{79-81}$

The crystal structure of cyanobacterial photosystem II from Thermosynechococcus elongatus (PDB IDs: 3BZ1 and 3BZ2$^{83}$; 2AXT$^{84}$) revealed each monomer as consisting of 20 protein subunits including: RCs D1 and D2; antennas CP47 and CP43 and a heme containing cytochrome b-559. The new model$^{83}$ (2.9 Å) allowed assignment of the phytol chains of all chl$a$ and of two present Pheo molecules, many of these participating in the hydrophobic binding interactions of other chls. The orientations of the chlorin rings were confirmed as had been reported earlier,$^{84}$ except for one that had to be flipped 180°.

The structure of the FMO protein from Chlorobaculum tepidum at 2.2A resolution that was reported in 2003 (PDB ID: 1M50)$^{85}$ has recently been re-refined (PDB ID: 3ENI) resulting in an improved R-value of 0.166 (obs.). Each monomer subunit of the trimer envelopes seven Bchls with two sheets, formed by a series of $\beta$ strands, in what has been termed a “taco shell” arrangement. The positions of the seven Bchls were found to be similar to those of the closely related FMO protein of Prosthecochloris aestuarii (PDB ID: 3EOJ, 1.3 Å) with many of the observed differences accounted for by differing degrees of nonplanarity of the cofactors, rather than translational or rotational displacements. These conformational differences are considered the likely origin of the observed spectral differences between the two proteins.$^{85}$ The reader is referred to the relevant references for complete coverage.

### VII. Structural Analysis of Chlorophyll Derivatives

#### A. Chlorophyll Derivatives

In a sense the title of this contribution is a misnomer as no isolated chlorophyll molecule has ever been characterized by X-ray crystallography. This is due to the amphiphilic character of the molecule with the hydrophilic tetrapyrrole moiety and the hydrophobic phytol chain. Thus, crystallization of an isolated Chl presented a challenge akin to that of the crystallization
of membrane proteins, e.g. the photosynthetic reaction center.\textsuperscript{86,87} None of the early reports on structural investigations of chlorophylls lead to a single crystal X-ray study.\textsuperscript{87,88} Microscopic and electron diffraction studies of microcrystals showed a dependency of the habit on the central metal,\textsuperscript{89,90} Transmission electron microscopy often indicated hexagonal crystal forms.\textsuperscript{91} Liquid crystals of Chl derivatives have found some interest, but are outside the scope of this contribution.\textsuperscript{92}

The following gives an overview of the available single crystal X-ray structures. The ones most closely related to chlorophylls and pheophorbides are compiled with their CCDC deposition numbers in Table 1.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
1. Metallopheophorbides & \\
\hline
\end{tabular}
\end{table}

\begin{center}
17 & 18 & 19 & 20 M = Mg(II) \\
\end{center}

\begin{center}
21 M = Ni(II) & 22 & 23 & 24 & 25 \\
\end{center}

The first small molecule study of a Chl derivative to be analyzed was initiated in 1937 by Ketelaar, who reported the unit cell data of ethyl Chlide a.\textsuperscript{93} The first three dimensional structural analysis of this compound 17 was then reported in 1975 concomitantly by Kratky and Dunitz\textsuperscript{94} and Strouse and coworkers.\textsuperscript{95} Both structure determinations gave almost identical results and the molecular structure in the crystal is shown in Fig. 5. The compound crystallized as the aquo complex with a penta-coordinated magnesium center. At the same time the structure of the closely related Chl b derivative 18 was also reported.
As expected, the structure of methyl Chlide a is almost identical to that of the ethyl ester. Removal of the $13^2$ ester group to yield the pyro-Chlide derivative did not alter the conformation either. All structures of the magnesium chelates have in common the penta-coordinated metal center (with Mg-O$_{ax}$ ~2.03 Å), nonequivalent but typical Mg-N bond lengths (~2.03–2.18 Å). The shorter bonds are to N21 and N23, and the longest is found for Mg-N24, i.e. involving the reduced pyrrole ring. All compounds exhibited an almost planar macrocycle conformation. The $\Delta26$ values for all these derivatives are close and range from 0.04 to 0.062 Å (see Table 1). Note, that the crystal packing in all these structures is very similar.

A very similar structure was found for the related Cd complex. Formally, this is a BChl $d$ derivative where infinite polymeric chains are formed through conjugation of the 3-hydroxymethyl group to the cadmium center. The core and macrocycle conformations are very similar to those of the magnesium complexes described above. A number of related metal complexes have been studied as well, all of them with a penta-coordinated metal center.

The (chloro)iron(III)complex of phytochlorin methyl ester crystallized with two independent molecules mainly distinguished by the orientation of the axial ligand. The macrocycles show significant deviations from planarity larger than those observed in corresponding magnesium($II$) complexes although the overall type of conformation is similar to the Mg complexes. The core of the macrocycle is characterized by the five-coordinated iron(III) center which is ligated by the four pyrrole nitrogen atoms and a chloride atom in the axial position. The axial Fe-Cl bond lengths are 2.230(4) and 2.226(4) Å in the two independent molecules, respectively. The Fe-Cl vector is not orthogonal to the molecular plane, the Cl-Fe-N angles range from 97.8 to 107.2(3)$^\circ$. The averaged bond lengths for the Fe-N$_{pyrrole}$ bonds are 2.045(8) Å in molecule 1 and 2.026(8) Å in molecule 2, respectively. Again, the Fe-N bonds to the reduced pyrrole ring are considerably longer with 2.157(8) Å in molecule 1 and 2.135(9) Å in molecule 2. In general, the core geometry of the present iron(III) chlorin is similar to those found in other iron(III) hydroporphyrins and to those of other high-spin iron(III) porphyrins.
Zinc(II) complexes are expected to be very similar to those of magnesium. However, only very few (phytochlorinato)zinc(II) derivatives have been structurally characterized. One example is compound 24, which was crystallized both as the ethyl formate and chloroform solvate. For the latter it was shown that the compound formed polymeric structures with the zinc center coordinating to the N-OH group. This is not too surprising, zinc(II) likes to form pentacoordinated complexes and in the presence of an intramolecular donor group polymeric or dimeric structures will result. While this has been amply demonstrated for porphyrins a typical example for chlorins involves compounds 26 and 27. Here, 26 forms typical polymeric structures while 27 is monomeric in the crystal.

Two structures of nickel(II) pheophorbides have been reported. The structure of the pyropheophorbide a derivative 21 exhibits a ruffled core conformation, clearly the result of the Ni-N bond contraction (Fig. 6). The severe deformations make it problematic to use Ni-derivatives as model compounds in spectroscopic studies on chlorophylls. A related study investigated the steric influence of the 20-methyl substituent in nickel(II) phytochlorins. The structure of a Ni(II) 20-methylphytochlorin methyl ester 25 exhibited a highly ruffled conformation with a local increase in distortion in the vicinity of the 20-substituent when compared to the reference compound without the meso methyl group. This was indicated by larger C_m displacements and a smaller C_r-C20_m-C_a angle (120.5°) compared to the phytochlorin without the methyl group (123.8°). Such compounds are related to naturally occurring BChl c and d and the results indicate that the larger distortion in the 20-methyl derivative might account for the 10 nm bathochromic shift in the absorption maxima of the BChl c compared to d.

Figure 6 View of the molecular structure of the nickel pyropheophorbide 21 (HAHBAT104) in the crystal. Hydrogen atoms have been omitted for clarity.

The various conformational distortions in the different metal complexes of phytochlorins are clearly shown in Fig. 7. The magnesium derivative exhibits an almost planar macrocycle while a related zinc(II) derivative shows larger out-of-plane displacements mostly involving out-of-plane tilting of the pyrrole rings. These are slightly more pronounced in the iron(III)chloro derivative. In contrast the nickel(II) derivative shows a different conformation more nonplanar than the other ones. Here the largest out-of-plane
displacements are observed for the $C_m$ carbon atoms and a rotation of the pyrrole rings about their $\beta-\beta$ axes indicating a ruf distortion.

![Graphs showing skeletal deviations from the $\Delta 26$ plane in metallopheophorbides.](image)

**Figure 7** View of the skeletal deviations from the $\Delta 26$ plane in metallopheophorbides. The sequence of meso carbon atoms is C20, C5, C10, C15, C20 from left to right; x-axis is not to scale. a) 20 MPCHL10, b) 24 CELRIU, c) 23 YINCAZ, d) 21 HAHBAT.

**2. Pheophorbides**

The first structure of a Pheo a derivative was reported by Calvin and coworkers in 1972. They elucidate the structure of methyl pheophorbide a 28. Overall, the structure exhibited a planar macrocycle with only minimal deviations from planarity. The structure identified the basic characteristics of a chlorophyll derivative, i.e. the characteristic zig-zag conformation of the cyclopentanone ring, differences between the reduced pyrrole ring and the others and conjugation of the vinyl group with the aromatic system. Likewise, methyl mesopyropheophorbide a (methyl phytochlorin) 30 exhibits a planar macrocycle. Only recently, the structure of a pheophorbide b 29 was reported. The four five-membered pyrrole rings are nearly coplanar. Interestingly, for the two N-H units the formation of intramolecular N-H$\cdots$N hydrogen bonds [$N\cdots N = 2.713(5)\cdots 3.033(6)\ \text{Å}$] was reported.
One of the most fundamental studies involved the analysis of several natural Bpheo d derivatives. These include the structures of 31 and 32\textsuperscript{108} and of 33\textsuperscript{109}. Note that these structures differ only in the substituents at C8 and C12, i.e. belong to the homologous series of BCChl d compounds found in nature. A comparative analysis of the structures of these compounds\textsuperscript{110} isolated from \textit{Chlorobium vibrioforme} revealed a series of dimeric and higher aggregates (involving the hydroxyethyl group and the ester carbonyl oxygen atom) that showed significant conformational variations for the same BPheo skeleton depending on the aggregation. Deviation of individual atoms from the N4 plane reached up to 0.5 Å\textsuperscript{110}. This clearly established the conformational flexibility of the basic phytochlorin macrocycle. Fig. 8 illustrates the different conformations observed in chemically closely related macrocycles. While many conformational differences involve ring V the degree of out-of-plane distortion and the type of distortion clearly varies.
Figure 8 View of the skeletal deviations from the $\Delta$26 plane in free base pheophorbides. The sequence of meso carbon atoms is C20, C5, C10, C15, C20 from left to right; x-axis is not to scale. a) 28 MPOPHA, b) 30 ROFVUE, c) 31 (only one of the 2 independent molecules shown) BIPBIL, d) 32 (only one of the 2 independent molecules shown) BIPBOR, e) 33 BIXREF01, f) 35 BAVSUM01.

A related structure of a closely related synthetic derivative is that of the 3-acetyl-8-ethyl)-bacteriopheophorbide $d$ 34 which exhibits structural features similar to the other Bpheo compounds. Note, that the zinc(II) complex of the corresponding porphyrin structure of 32 was reported as well and found to hydrogen-bonded dimers with extended $\pi-\pi$ interactions without the expected ligation of the Zn by the 3-(1-hydroxyethyl) group.

A few bacteriopheophorbide structures, i.e. bacteriochlorin-type tetrahydroporphyrins are available for comparison. One example is that of methyl BPheo a 35. Both a solvated and unsolvated form have been reported. The molecule exhibits a planar macrocycle very similar to that of the respective chlorins (dihydroporphyrins) of the Pheo series in both structures. Thus, at least in a structural sense there are only minor conformational differences between the Chl and BChl pigments based on the limited analytical data.
The different conformations observed here and in the metallo derivatives described above can be compared in more detail using Shelnutt's NSD analysis (vide supra).

**Figure 9** NSD analysis of selected pheophorbide derivatives. Top panel gives out-of-plane distortions, lower panel in-plane distortions. a) 28 MPOPHA, b) 20 MPCHLM10, c) 23 YINCAZ, d) 21 HAHBAT.

One of the striking features of the comparative analysis shown in Figure 9, apparent from the in plane illustrations above, is the large negative in plane **bre** deformation (-0.2914Å) observed for 21 (HAHBAT) which can be attributed as a direct consequence of coordination to Ni(II) by comparison to MPOPHA which is identical in all respects other than coordination to Mg(II). This structure also exhibits a high degree of ruffling, as is mentioned earlier, for the same reason. However, it can also be seen from the NSD that there are significant contributions from the other distortion modes **ruf, dom, wav(x)** and **pro** (all more or less >1Å), that would be less apparent from other conformational analyses due to the overwhelming ruffling. The in plane **rot** mode contribution remains similar to the others whereas the **trn(y)** contribution is greater. The rest of the in plane distortions are all considerably less.
It should be noted that for accurate determination of the magnitude of the in plane distortions, the chosen reference is of great importance. In this case it is the D$_{4h}$ Cu(P) and thus the distortions are comparative to this. For comparative analysis though, this is obviously not a major issue. Also note that the absolute sign of the out of plane distortions is not as significant, because this is determined by the orientation of the macrocycle during analysis, as their within structure phase relationship.

3. Phytochlorins and Related Compounds

Some other phytochlorin-type structures have also been reported. For example, the purpurin 36 and the fused derivative 37 both exhibit planar macrocycles. A similar conformation was found for the simple phytochlorin which forms weak π-stacked aggregates in the crystal 38.

A few other structures of derivatives derived from phytochlorins have been reported which confirm the conclusions made above. Most of these are chlorine 6 or rhodochlorin derivatives. Typically, these compounds show a higher degree of flexibility and one might expect significant deviations from planarity in the "southern half" of the molecule as a result of the presence of the meso substituent in position 15. However, many of these compounds exhibit a more or less planar macrocycle. This is clearly shown in the structure of 39, which has a Δ24 of 0.058 Å and the meso carbons are displaced from this plane by only 0.02, 0.02, 0.05 and 0.09 Å for C5, C10, C15, and C20, respectively. The respective copper(II) complex 40 and 41 indicate the flexibility of these systems. One compound crystallized with two, the other with four independent molecules, all with relatively different conformations.

For the sake of organization the structure of 15 the natural compound chlorophyllonic acid a methyl ester should also be listed here (Fig. 10). Overall, the macrocycle is relatively planar with Δ24 = 0.08 Å and the C$_m$ displacements reach only 0.05 Å.
Figure 10. View of the molecular structure of the aquo complex of 15 (KUBDUB) in the crystal. Hydrogen atoms have been omitted for clarity. Adapted from reference 29.

Other examples are the aspartyl-chlorin $e_6$ 42, 120 and the seleno compound 43. 121 A dimeric structure consisting of a chlorin $e_6$ derivative with an appended etioporphyrin unit was reported as well. 122 Rhodochlorin XV dimethyl ester 44 presents an interesting case as two different crystal forms were found. 123 They form different crystal packing arrangements and overall both show only small deviations from Δ24. Still, the molecular structures of both forms are slightly different indicating the impact of crystal packing and the flexibility of the system. In the triclinic form the β-pyrrole atoms of ring IV deviate by approximately 0.4 Å from the plane of the N atoms, while in the orthorhombic form ring I is located 0.2 Å above, and ring IV 0.15 Å below the plane.
4. Dimers and Other Reaction Center Models

Based on the structural principles outlined above, many attempts have been made to obtain synthetic compounds that mimic the spatial arrangements of the two chromophores in the photosynthetic reaction center, i.e. the "special pair". Typically this involved the preparation of some kind of covalently or noncovalently linked bistetrapyrrole. Due to the difficult chemistry involved many groups have shied away from preparing such compounds with hydroporphyrins. However, a few such examples have been reported.

One of the first structures reported by Senge et al. was that of the ethyl bridged dimer 45.\textsuperscript{124} The compound was obtained in solvated and unsolvated forms, both of which show a similar conformation in the chlorin rings. Notably, due to the presence of a flexible linker group the two macrocycles in both forms form a twisted quasi cofacial arrangement. The twist angles of the two macrocycle planes are 54.4° and 57.3°, respectively. This arrangement is clearly shown in Fig. 11.

![Chemical structures](image-url)
Interesting results were also obtained for the ethene-bridged OEC compounds. These compounds can be prepared as either the trans- or cis-configured dimers. The cis compounds, e.g. 46, have a cofacial arrangement of the two macrocycles with significant π-overlap which can be modulated depending on the central metals (Fig. 12). For example, 47 has a molecular structure more akin to that shown in Fig 11 with an interchlorin angle of 131.8°. Even for the trans-configured dimers different arrangements for the macrocycles were found. The meso compound 48 has an almost orthogonal arrangement of the two macrocycles which form an angle of 88.8° between them. The rac compound 49 shows a much more coplanar arrangement with an angle of 16.2° between the two chlorin planes. A similar structure was also found for the bis nickel(II) complex of a trans-configured octaethylporphyrin octaethylchlorin dimer. McMurry reactions were also used to fuse phytochlorin derivatives. For example, 50 was obtained in the trans configuration. The chlorin macrocycles show Δ26 deviations of 0.10-0.15 Å and the two chlorin planes are almost in plane with each other (≤ 5.7°). A similar arrangement (≤ 4.1°), albeit with larger macrocycle distortions due to the metal center was found in the bischlorin e6 derivative 51.
Cofacial systems can also be prepared through weaker interactions. Thus, the zinc(II) complex of anhydro-mesorhodochlorin methyl ester \(52\) forms a cofacial \(\pi\)-stacked dimer through coordination of the zinc(II) center with the cyclohexanone oxygen atom.\(^{128}\) Other examples for synthetic bischlorins which are structurally distinct from phytochlorins are \(53,\)\(^{129}\) which has a cofacial coplanar structure. The related nickel(II) compound \(54,\) which carries four meso phenyl residues, still has a cofacial structure but the two macrocycles from a more opened angle.\(^{130}\)

\[
\text{\textbullet} \quad \text{52} \\
\text{\textbullet} \quad \text{53} \\
\text{\textbullet} \quad \text{54} \\
\text{\textbullet} \quad \text{55}
\]

Based on phytochlorins derived from Chl a, Smith and coworkers presented the only example of completely conjugated and planar bischlorins \(55.\)\(^{131}\) Fig. 13 clearly shows the overall planar structure and thus the conjugation through the two chromophore units.

**Figure 13** View of the molecular structure of the bisphytochlorin \(55\) (NAHJAH). Hydrogen atoms have been omitted for clarity. Adapted from reference 131.
B. Synthetic Hydroporphyrins

There are about a 100 "nonphytochlorin" or "non-chlorin e_6" type crystal structures. These do give additional information on the conformation and core structure of chlorins. However, their relevance to chlorophyll derivatives is of more theoretical interest. Thus, only a brief overview and survey of related synthetic hydroporphyrin structures will be given here so that the reader can quickly gain access to the literature. A detailed conformational analysis is currently in progress and will be reported in due course.

1. Chlorins

The most accessible chlorins are those derived from 5,10,15,20-tetraphenyl- and 2,3,7,8,12,13,17,18-octaethylporphyrins. Historically, these include some of the earliest structural reports on hydroporphyrins. In the tetraphenylchlorin series a typical example is the structure of pyridine adduct of (5,10,15,20-tetraphenylchlorinato)zinc(II) \( \text{56} \) which was derived through reduction of the related porphyrin.\(^{132} \) Another examples is a hexacoordinated iron(II) species.\(^{133} \)

Many similar systems were obtained through \( \beta \)-addition reactions. 2,3-Dialkylated derivatives such as \( \text{57}^{134} \) and \( \text{58}^{135} \) were described by Senge and coworkers. The free base was characterized both as the unsolvated form and the methylene chloride solvate with almost identical structural features. The respective zinc(II) complex was crystallized as the methanol adduct. Other examples are \( \text{59}^{136} \), \( \text{60}^{137} \) and related species\(^{138} \) derived from carbene reactions, \( \text{61}^{137} \) and \( \text{62}^{139} \) derived from the respective 2,3-dioxspecies, such as the basic framework in \( \text{63}^{140} \). Compound \( \text{64} \), derived from \( \text{63} \) was crystallized in unsolvated and solvated forms while a related 7-oxo-8,8-bis(2-chloroethoxy) free base was characterized as well.\(^{140} \) Related structures are those of the free base and nickel(II) complex of 2-aza-3-oxo-5,10,15,20-tetraphenylechlorin.\(^{141} \) Examples with less residues at the periphery are \( \text{65}^{142} \), \( \text{66}^{143} \) and \( \text{67}^{144} \).
Another example is the structure of N22-methyl-5,10,15,20-tetra(4-methylphenyl)chlorin, which has a very nonplanar conformation due to congestion in the porphyrin core. A number of meso alkylchlorins include (5,10,15,20-tetramethylchlorinato)nickel(II) which exhibited a typical Ni-induced ruf distortion.

One way to stabilize hydroporphyrins against oxidation to the respective porphyrins is substitution of the β-hydrogen atoms with nonhydrogen atoms. Most successful have been derivatives with geminal alkyl residues at the reduced pyrrole ring. A relatively large number of such compounds has been structurally characterized; for example, 68 and 69. An interesting compound is the intramolecularly cyclized chlorin 70. Despite the cyclization the molecule is still relatively planar, an indication of the flexibility of the reduced pyrrole ring to accommodate steric strain. Note that 71 is a natural compound derivative, anhydrobonellin methyl ester. These are physiologically active chlorins from the marine echurian Bonella viridis. The structure shows only moderate distortions. The Δ24 value is 0.12 Å and maximum Cm displacements are 0.2 Å while maximum Cb displacements are 0.55 Å in the vicinity of the fused ring.

Related synthetic compounds are the 132,173-cyclophorphorbide enol (not shown) for which no coordinates are available and the phytoporphyrin derivative 71, which has a planar macrocycle. Other examples are those of compounds derived from pinacol...
rearrangements, such as the iron complexes $^{72}$ and $^{73}$, and the nickel complex.$^{74}$, $^{155,156}$ 

β-Dihydroxy compounds have been characterized as well. Examples include $^{75}$, $^{157}$ and the related 2,3-dihydroxy etiochlorin $^{158}$.

2. Bacteriochlorins and Isobacteriochlorins

In contrast to the chlorins, few tetrahydroporphyrin structures have been reported. This is mainly due to the increasing instability of bacteriochlorins and isobacteriochlorins versus chlorins.

For simple *meso* substituted hydroporphyrins, the structure of 5,10,15,20-tetrabutylbacteriochlorin has been reported, which has a completely planar macrocycle.$^{159}$ The pyridine adduct of the zinc(II) complex of tetraphenylbacteriochlorin shows the typical feature of a five coordinated zinc tetrapyrrole.$^{160}$ Other examples include the carbene adduct $^{76}$, the pyridyl derivative $^{77}$, which formed dimeric structures in the crystal through coordination of the zinc to the nitrogen atom of the pyridyl residues.$^{161}$ For β-substituted systems the structure of $^{78}$ is typical for a nickel complex.$^{162}$ Similar to the chlorins several bacteriochlorins with geminal dialkyl groups have been characterized. A representative tetrapyrrole is $^{79}$.$^{163}$
The most simple isobacteriochlorin structures were derived from octaethylporphyrin. Classic examples are the structures of several different isomers of nickel(II)complex 80 and the related free bases. Most isobacteriochlorin structures include a geminal dialkyl group for stabilization as well. Examples are 81, 82, 83, 84, 85, 86, 87, and 88. Others are those with an exocyclic double bond, e.g. 86. An example for a compound derived from Pheo a is the nickel(II) complex of anhydromesorhodoisobacteriochlorin methyl ester 87, with a typical ruf core conformation.
3. Special cases

Benzochlorins are a special class of hydroporphyrins where the reduced ring is constructed through an intramolecular annelation reaction. While the fused aromatic ring introduces some steric strain it also counteracts to some extent the conformational flexibility found in other hydroporphyrins by making the aromatic system more rigid. A typical example with some resemblance to phytochlorins is the structure of 88, where the overall macrocycle is almost planar due to the fused ring systems. A simpler system is that of free base octaethylbenzo[α]porphyrin which shows only small deviations from planarity with Δ24 = 0.05 Å and maximum C_b displacements reaching 0.21 Å. The corresponding Ni(II) complex is much more distorted and shows a Δ24 value of 0.26 Å. The macrocycle shows an asymmetric ruffled conformation with C_m displacements ranging from 0.28 to 0.51 Å.
Although the concept of the conformational flexibility of porphyrins is now well established, few studies have been performed on specifically designed hydroporphyrins. The first examples are the classic studies on hexahydroporphyrins by Eschenmoser and coworkers. These included compounds such as 89 and 90. Synthetically, most chlorins with peripheral steric interactions are either derived from phytochlorins via subsequent modifications, e.g. ring V ring-opening reactions or from rhodochlorins. Some simple nona- and decasubstituted chlorins are accessible via substitution reactions on octaethylchlorin.

Only a few studies have tried to address the question of the conformational flexibility in hydroporphyrins directly by the synthesis of appropriate compounds; this is the case for compounds closely related to nonplanar porphyrins. One such study was published by Kalisch and Senge and described the structural analysis of tetraphenylchlorin derivatives with an increasing number of β-ethyl groups, and thus an increasing number of peri-interactions. Typical compounds are those of the free bases 91, 92, and 93 and similar ones. Studies on the free bases and zinc(II) complexes clearly identified the impact of the number and regiochemical arrangement of the substituents on the conformation.

Other systems with both meso and β-substituents are 94, 95, 96 and 97. The available structural data of such "highly substituted chlorins" shows a large variability in the conformation of even closely related compounds. Due to the larger conformational flexibility of chlorins the effects of individual substituents on the conformation are difficult to establish.
although larger displacements of substituted meso carbons are frequently observed in metallochlorins. Overall, and only to a rough approximation, it appears that chlorins have a tendency towards more ruf distortion.

Several other compounds, which technically can be termed chlorins have been structurally characterized. These include Osuka's fused systems,\textsuperscript{179,180} iron(III) salt derivatives,\textsuperscript{181,133} Smith's $\beta,\beta$-fused pyrroloporphyrins,\textsuperscript{182} bis(isoxazolo)bacteriochlorins,\textsuperscript{183} purpurins\textsuperscript{184,185} and related compounds.\textsuperscript{186} However, these compounds are structurally too distinct from chlorophyll derivatives to be relevant here.

**VIII. Outlook**

With regard to future structural studies, much attention has recently been given to the self-assembly of porphyrins related to the BChl c and d\textsuperscript{187} and this is currently extended to the hydroporphyrins.\textsuperscript{188,189} Indeed, a recent paper by Wasielewski and coworkers using small- and wide-angle X-ray scattering in solution reveals that Chl trefoils self-assemble in the presence of 1,4-diazabicyclo[2.2.2]octane to yield supramolecular cyclic trimers.\textsuperscript{190} Recent results indicate that fluorophobic effects may be used to construct ordered (B)Chl nanostructures,\textsuperscript{191} and similar strategies are used to construct LHC systems for photovoltaics.\textsuperscript{192} Computational advances will help to predict aggregation structures of chlorophylls,\textsuperscript{193} Most likely any structural chemistry advances in this area will involve completely synthetic hydroporphyrins.\textsuperscript{194} Recent advances made in the synthesis of unsymmetrical porphyrins will now be extended to the respective hydroporphyrins and will allow a definitive analysis of the interrelationship between substituent pattern, conformation, structure and physical properties. In terms of isolated "real" chlorophyll - or at least phytochlorin derivatives - novel structural information will only be slowly forthcoming. At present only few groups are focusing on the advancement of chlorophyll chemistry\textsuperscript{9,195,196,197} and none are active in the area of phytochlorin structural chemistry.

**Acknowledgments**

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**IX. References**


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70. Senge, M. O. *Heterocycles* **2009**, *78*, 1523.
71. Senge, M. O., in preparation.
Table 1. CCDC deposition numbers for small molecule single crystal structure determinations of chlorophyll related hydroporphyrins.

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<td>$\Delta 26_1 = 0.076$, $\Delta 26_2 = 0.067$ Å; 2 independent molecules</td>
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<td>32</td>
<td>Methyl 8,12-diethyl-bacteriopheophorbid e d</td>
<td>$P1$</td>
<td>295</td>
<td>0.048</td>
<td>n.d.</td>
<td>$\Delta 26_1 = 0.071$, $\Delta 26_2 = 0.067$ Å; 2 independent molecules</td>
<td>BIPBOR</td>
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<td>Methyl 8-neopentyl-12-ethyl-bacteriophageophorbid e d</td>
<td>$P2_1\bar{2}_1\bar{2}_1$</td>
<td>120</td>
<td>0.084</td>
<td>n.d.</td>
<td>$\Delta 26 = 0.089$ Å</td>
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<td>34</td>
<td>Methyl (12-acetyl-8-ethyl)-bacteriophageophorbid e d</td>
<td>$P-1$</td>
<td>130</td>
<td>0.129</td>
<td>0.011-0.030</td>
<td>$\Delta 26 = 0.078$ Å</td>
<td>SOSZOP</td>
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<tr>
<td>35</td>
<td>Methyl bacteriophorbid e a•C$_9$H$_6$</td>
<td>$P1$</td>
<td>200</td>
<td>0.045</td>
<td>0.001-0.005</td>
<td>$\Delta 26 = 0.043$ Å</td>
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<td>Methyl bacteriopheophorbid e a</td>
<td>$P1$</td>
<td>200</td>
<td>0.076</td>
<td>0.011-0.030</td>
<td>$\Delta 26 = 0.038$ Å</td>
<td>WIKSEO</td>
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</table>

**Phytochlorins and related compounds:**

<p>| 36 | Benzoimidazolo(2,1-n)purpurin-18 13$^1$-imino-13$^2$-imide methyl ester  | $P2_1\bar{2}_1\bar{2}_1$ | 126     | 0.0603   | 0.006-0.010 | $\Delta 24 = 0.053$ Å                       | FOXTUH | 116  |</p>
<table>
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<th>Number</th>
<th>Reaction Center Model Compound</th>
<th>Space Group</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
<th>Δ241 (Å)</th>
<th>Δ242 (Å)</th>
<th>Δ243 (Å)</th>
<th>Δ244 (Å)</th>
<th>Sample Code</th>
<th>Page</th>
</tr>
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<td>37</td>
<td>Quinoxalino(2,3-n)deoxopyropheophoride a methyl ester</td>
<td>P2₁,2/2</td>
<td>130</td>
<td>0.0577</td>
<td>0.001-0.005</td>
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<td>FOXWIY</td>
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<tr>
<td>38</td>
<td>17-Decarboxyethyl-13¹-deoxo-17-propylphycocyanobilin</td>
<td>P2₁</td>
<td>126</td>
<td>0.0576</td>
<td>0.006-0.010</td>
<td>Δ26₀ = 0.031 Å, 2 independent molecules</td>
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<td>117</td>
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<td>39</td>
<td>3',3'-Didehydrohodochlorin-15-acetic acid trimethyl ester</td>
<td>P2₁</td>
<td>193</td>
<td>0.0891</td>
<td>0.006-0.010</td>
<td>Δ24 = 0.058 Å</td>
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<td>ZUBBIH</td>
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<td>(3',3'-Didehydro-hodochlorinato-15-formic acid trimethyl estercopper(II)•CH₂Cl₂</td>
<td>P1</td>
<td>130</td>
<td>0.0726</td>
<td>0.011-0.030</td>
<td>Δ24₁ = 0.172 Å, Δ24₂ = 0.204 Å, Δ24₃ = 0.055 Å, Δ24₄ = 0.087 Å; 4 independent molecules</td>
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<td>ZAJLUR</td>
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<td>41</td>
<td>(Rhodochlorinato-15-acetic acid trimethyl estercopper(II))</td>
<td>P₂끗</td>
<td>130</td>
<td>0.069</td>
<td>0.006-0.010</td>
<td>Δ24₁ = 0.146 Å, Δ24₂ = 0.148 Å, Δ24₃ = 0.19 Å; Δ24₄ = 0.073 Å, 2 independent molecules</td>
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<td>15²-Mono-(L)-aspartylchlorin-e₈ tetramethyl ester•CH₃OH•H₂O</td>
<td>P₂,2₁,2</td>
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<td>0.105</td>
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<td>Δ24 = 0.103 Å</td>
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<td>Methyl 20-methoxycarbonylmethyl-18-methoxycarbonyl-13-ethyl-3,7,12,17-tetramethyl-8-[2-(ο-nitrophenylselenido)ethyl]chlorin-2-propionic acid</td>
<td>P₂,2₁,2</td>
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<td>0.011-0.030</td>
<td>Δ24 = 0.058 Å</td>
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<td>Rhodochlorin XV dimethyl ester•CH₂Cl₂</td>
<td>P-1</td>
<td>130</td>
<td>0.091</td>
<td>0.006-0.010</td>
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<td>45</td>
<td>Rhodochlorin XV dimethyl ester</td>
<td>P₂,2₁,2</td>
<td>130</td>
<td>0.062</td>
<td>0.006-0.010</td>
<td>Δ24₁ = 0.146 Å, Δ24₂ = 0.148 Å, Δ24₃ = 0.19 Å; Δ24₄ = 0.073 Å, 2 independent molecules</td>
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<td>Meso 1-[2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrinato-5-yl]benzene</td>
<td>nickel(II)•CHCl₃</td>
<td>C2/c</td>
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<td>0.0725</td>
<td>0.006-0.010</td>
<td>Δ24 = 0.07 Å, centrosymmetric</td>
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<td>47</td>
<td>1-[2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrinato-5-yl]benzene</td>
<td>copper(II)•CH₂Cl₂</td>
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<td>Δ24 = 0.11 Å, centrosymmetric</td>
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<td>48</td>
<td>Meso 1,2-Bis[5-(trans-3'-Clorinato-e₈)-trimethyl(2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrinato-5-yl)]copper(II)•CH₂Cl₂•EtOH</td>
<td>P₂/c</td>
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<td>Δ24₁ = 0.10 Å; Δ24₂ = 0.142 Å</td>
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<td>rac 1,2-Bis[5-(trans-3'-Clorinato-e₈)-trimethyl(2,8,12,18-tetraethylporphyrinato-5-yl)]copper(II)•trans-ethene•CH₂Cl₂•EtOH</td>
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</table>

- 5-((E)-1,2-((2,3,7,8,12,13,17,18-Octaethylporphyrinato-5-yl)-nickel(II))ethene)-((trans-2,3,7,8,12,13,17,18-octaethylchlorinato)nickel(II))•CH2Cl2
- 1,2-Bis(20-(1,7,12,18-tetramethyl-2,8-diethyl-13,15-ethano-17-(3-methylpropionate)-17,18-dihydroporphyrinato)-trans-ethene•H2O
- 1,2-Bis(1,7,12,18-tetramethyl-2,8-diethyl-13-(methylmethanoate)-15-(2-methylethanoate)-17-(3-methylpropionate)-17,18-dihydroporphyrinato)-nickel(II)-trans-ethene•H2O
- Bis((anhydro-mesorhodochlorinato-XV methyl ester)zinc(II)
- 10,10',15,15',20,20'-Hexaphenyl-5,7:5',7'-bis(o-phenylene)-7,7'-bichlorin-8,8'-dione•Et2O•CH2Cl2
- 10,10',15,15',20,20'-Hexaphenyl-5,7:5',7'-bis(o-phenylene)-7,7'-bichlorin-8,8'-dione•Et2O•CH2Cl2
- 13',13''-Bis(13'-methoxyphytoporphyrin methyl ester)ylidene•CH2Cl2
- 13',13''-Bis(phytoporphyrin methyl ester)ylidene