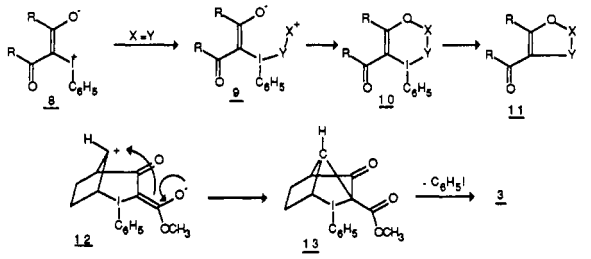
from α-diazo ketones has been shown to follow this pathway.[14,15] This suggests that a keto carbene is not involved in the iodonium ylide reactions.

A mechanism that applies to the cyclopropanation reaction, and the cycloadditions of iodonium ylides with unsaturated compounds (dipolarophiles) in general, may involve addition of the unsaturated molecule to the electrophilic iodine center in **8** (**8** → **9**) to give a zwitterionic intermediate that can undergo ring closure (**9** → **10**) followed by reductive elimination of C_6H_5I to yield the heterocyclic product (**10** → **11**). An equivalent expression using radical and diradical intermediates may be drawn; vide infra.

In the case of **2** → **3**, intermediate **12** is analogous to **9** but a six-membered ring as in **9** → **10** cannot occur (Bredt's rule), so the alternative C–C bond formation occurs (**12** → **13**). Reductive elimination of C_6H_5I yields **3**:[16]



As far as intermolecular cyclopropanation using iodonium ylides is concerned, bis(arylsulfonyl)methylide phenyliodonium ylides $[C_6H_5I^+C^-(SO_2Ar)_2]$ react with olefins to yield *gem*-disulfonyl cyclopropyl derivatives.[17,18] Also, a report exists of the reaction of $C_6H_5I^+C^-(CO_2CH_3)_2$ with cyclohexene to yield the *gem*-dicarbomethoxycyclopropane derivative.[19]

Finally, the role of metal catalysis in these reactions remains obscure. It should be noted that although reaction **2** → **3** occurs in the absence of a catalyst (in lower yield), **2** → **3** does not occur photochemically (in contrast to other iodonium ylide cycloadditions).[11] Both Cu(I) and Cu(II) catalyst **2** → **3**. Beringer and co-workers reported that both Cu(I) and Cu(II) catalyze the decomposition of diaryliodonium salts.[20,21] Roberts et al. attribute the catalytic role of Cu(I) to electron transfer to yield the the iodinanyl radical ArİAr as a reactive intermediate.[22a,b] In the case of nucleophilic addition of aniline to diphenyliodonium-2-carboxylate, Cu(II) catalysis is unique.[23]

In summary, the present method is a viable alternative to the diazo ketone route for intramolecular cyclopropanation, and high yields as well as ease of execution reommend its use.

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A High Precision Structure of a Bacteriochlorophyll Derivative, Methyl Bacteriopheophorbide *a*

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Current X-ray studies of antenna[2,3] and reaction center[4-8] bacteriochlorophyll (BChl) proteins are unveiling the architecture used by photosynthetic bacteria to harvest and transduce light into chemical energy. BChls in antenna complexes funnel incident photons into reaction centers where BChls and bacteriopheophytins (BPheo, demetalated BChls) carry out the primary charge separation that eventually drives the biochemistry of the organisms.[9] Besides the inherent difficulties of refining structures of high molecular weight complexes, X-ray studies of the BChl proteins have been further hampered by a lack of high precision data for BChl derivatives. To date, only three structures of bacteriochlorins have been reported, two synthetic bacteriochlorins[10] and a low precision structure of methyl bacteriopheophorbide *a*,[11] (MeBPheo) in which the phytyl chain of BPheo *a* is replaced by a methyl group (Figure 1a). As a consequence, all BChl protein refinements are based on chlorophyll X-ray data[12] modified to reflect

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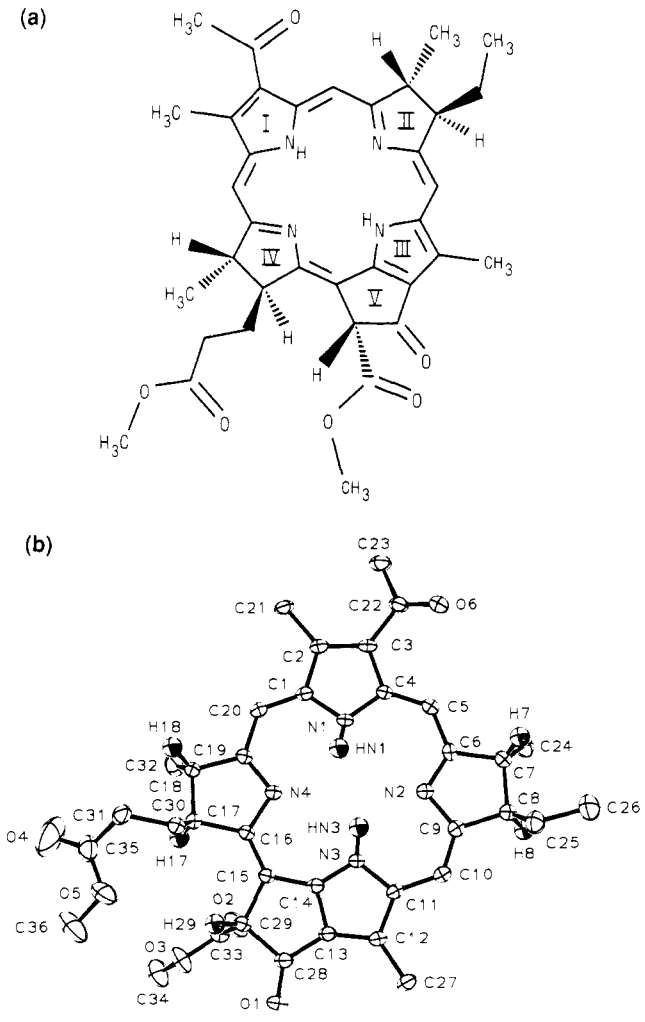

Figure 1. (a) Structural formula of MeBPheo *a*. (b) Molecular structure. Ellipsoids are drawn to enclose 50% probability except for the hydrogens, which are not to scale. Hydrogens at the meso positions and side chains are omitted for clarity.

the saturated ring II and the 2-acetyl group that differentiate BChls from chlorophylls.

The dearth of reliable BChl structural data has also impeded theoretical calculations of optical properties, ESR, Stark effects and vectorial electron transfer of BChls, antennas, and reaction centers.[13]

During an investigation of the Stark effect on crystals of known structure,[14] single crystals of MeBPheo *a* were isolated that diffracted X-rays to the limit of the Cu sphere ($\sin\theta/\lambda = 0.63$ Å). We re-examine here the structure of MeBPheo *a* and present the first high precision structural determination of a BChl derivative.[15]

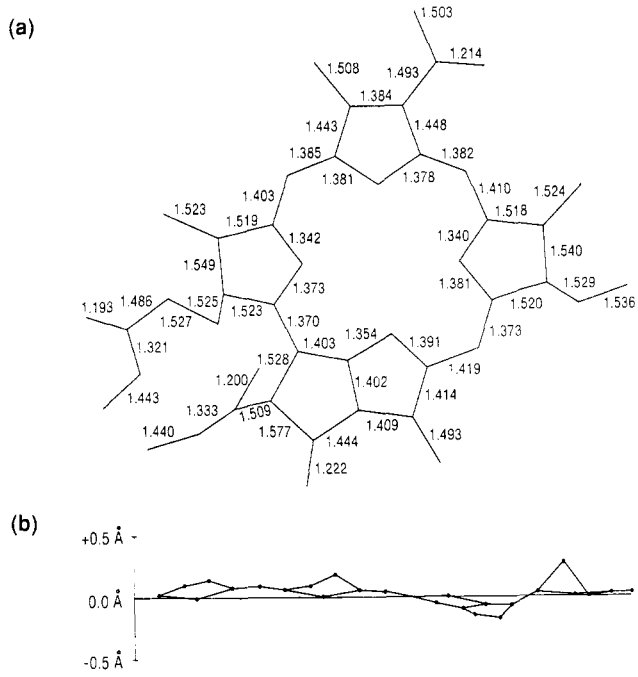

Figure 2. (a) Bond distances for MeBPheo *a*, in Å. The average esd of a typical C–C bond is 0.004 Å. (b) Linear display of the deviations of the 26 atoms of the macrocycle from a plane defined by the four nitrogens. The ring order is I, II, III, V, and IV from left to right (the horizontal axis is not to scale).

The structural formula and the molecular structure of MeBPheo *a* are shown in Figure 1. Bond distances are displayed in Figure 2a. The long Cβ–Cβ and Cα–Cβ bonds of rings II and IV establish that these rings are saturated and that the molecule is indeed a bacteriochlorin derivative. The enlarged core observed in hydroporphyrins,[10a,17] in which center (Ct)–N distances to the reduced rings are longer than those to the pyrroles, is also evident here: Ct–N1 = 2.063 Å, Ct–N3 = 2.002 Å vs Ct–N2 = 2.115 Å and Ct–N4 = 2.170 Å. Noteworthy is the alternating pattern of short and long bonds that best fits the resonance form shown in Figure 1a. The bond distances are also strikingly symmetrical about an axis defined by N1 and N3. This symmetry is only perturbed around ring III and probably reflects steric constraints imposed by the exocyclic ring V. Similar rationales have been invoked for the long C28–C29 bonds of ring V observed in all chlorophyll derivatives studied to date.[12] The asymmetry of C13–C28 (1.444 Å) and C15–C29 (1.528 Å) is also observed in other chlorophylls[12] and suggests partial conjugation of the keto bond C28–O1 with the porphyrin. Analogous reductions in the Cα–Cβ bonds occur in hydroporphyrins bearing exocyclic double bonds at the β carbons (keto[17] or methylene groups[10a]). The C28–O1 distance in MeBPheo *a* is diagnostic of the keto tautomer. In BChl proteins, the oxygen and methyl group of the acetyl substituent on ring I are sometimes hard to distinguish.[2,6] In the present structure, the oxygen points toward ring II and lies above ring I with a torsion angle defined by C2–C3–C22–O6 of 157.2°.

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(15) MeBPheo *a* crystallizes from dichloromethane/benzene with a benzene of solvation[11] in the triclinic space group $P\bar{1}$, with $a = 7.184$ (4) Å, $b = 8.073$ (2) Å, $c = 17.071$ (7) Å, $\alpha = 91.04$ (3)°, $\beta = 93.50$ (4)°, $\gamma = 110.06$ (3)°, $V = 927.43$ Å^3, $Z = 1$. Data collection at 200 K: Enraf-Nonius CAD4 diffractometer with graphite-monochromated Cu Kα radiation; scan range $4 \le 2\theta \le 150°$. 4512 reflections measured, 3794 unique and 3409 with $F_o > 3\sigma(F_o)$. Anisotropic refinement of all non-hydrogen atoms using full-matrix least squares yielded $R_F = 0.045$ and $R_{wF} = 0.049$. The enantiomorph was chosen to be consistent with the previously determined stereochemistry of ring IV.[16] Hydrogens were determined from successive difference maps except for H36 A–C (only two of the three methyl protons were found), H37–H42 (the hydrogens of the benzene), and HN3, which were idealized. A search of the final difference map failed to locate HN3. Additional details of the refinement are given in the Supplementary Material.

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Although the bond distances in rings II and IV are similar, the latter is significantly less planar than ring II, with a dihedral angle about the Cβ–Cβ bond of 14.5 (4)° as compared to 5.4 (4)° in ring II. Deviations of the 26 atoms of the macrocycle from the plane defined by the four nitrogens are presented in Figure 2b; the largest displacement, 0.263 Å, occurs at C17 in the distorted ring IV.

As previously observed,[11] the MeBPheo *a* molecules stack to form one-dimensional chains in which rings I and III of successive molecules overlap with perpendicular separations of 3.59 Å and center-to-center distances of 8.07 Å. The benzene rings sit between rings II in the chains. The chains further associate to form two-dimensional layers with a closest approach of 7.18 Å between the centers of the macrocycles in neighboring layers.

Recent structural data clearly demonstrate the skeletal distortions that crystal packing, steric, or protein constraints can impose on porphyrin derivatives.[2,4,10,12,18] Such conformational variations provide an attractive mechanism for fine-tuning the redox, optical, and charge-transfer properties of the chromophores in vitro and in vivo.[14,18] We are therefore attempting to obtain different crystal forms of MeBPheo in a search for different conformers.

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Supplementary Material Available: Experimental details, tables of bond angles, positional and anisotropic thermal parameters for the non-hydrogen atoms, positional parameters for the hydrogen atoms, contact distances, and some least-square planes and torsion angles, a view of the one-dimensional chains with the benzenes, and a packing diagram (10 pages); table of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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Light-Induced Nicking of DNA by a Synthetic Analogue of Cobalt(III)-Bleomycin

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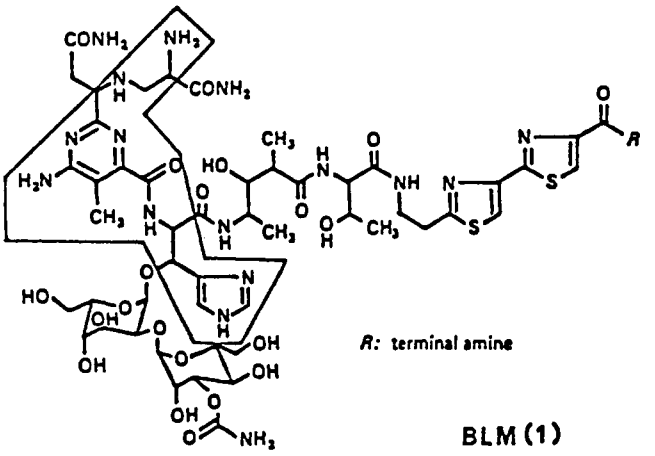
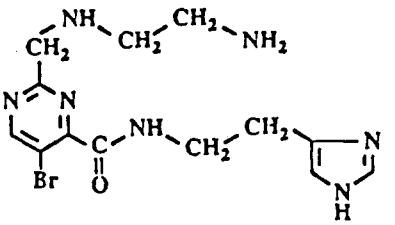
Bleomycins (BLM, **1**) are a family of glycopeptide antitumor drugs that inflict single and double strand breaks in cellular DNA in the presence of metal ions like Fe^{2+} and molecular oxygen.[1] The strand scission reaction is brought about by oxygen-based free radicals like •OH and/or hypervalent metal-oxo species that are formed in the vicinity of the DNA helix. Cobalt(III)–BLMs[2] are however exceptions in this regard—the kinetically inert cobalt(III) chelates of the drug cleave DNA only when illuminated with UV[3,4] or visible[5] light, and this photoinduced cleavage reaction is insensitive to dioxygen.[6] The light-driven DNA degradation reaction of Co^{III}–BLMs has raised renewed interest in the structure(s) and photochemistry of the cobalt(III) complexes of BLM.

Aerobic oxidation of Co^{II}–BLM[7] results in at least three different products two of which appear to contain a superoxide and a hydroperoxide group bound to cobalt(III) (the brown[7,8] and the green[9] Co^{III}–BLM, respectively), while the thermodynamically stable orange Co^{III}–BLM is devoid of any "active" form of dioxygen in the coordination sphere of the metal. More recent



BLM (1)



PMAH
(2)

works have also reported a brown Co^{III}–BLM with water as a ligand on cobalt.[6,9] Unfortunately, no crystallographic information is available on any Co^{III}–BLM at the present time. Spectroscopic studies indicate that in the brown aquo-Co^{III}–BLM as well as in the cobalt(III) complex of pseudotetrapeptide A,[10] BLM employs five nitrogen donor centers located in the primary and secondary amines, pyrimidine and imidazole rings, and the amide moiety (the boxed area in **1**) to bind cobalt(III). The sixth coordination site is filled by a water molecule in both of the *proposed* structures.

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