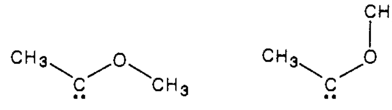
°C.[15] These experiments were monitored at 380 or 400 nm (with comparable results) and afforded bimolecular rate constants in the usual way.[16,17] With 0.002–0.034 M MeOH, curved plots[17] of k versus [MeOH] afforded the rate constant for the reaction of MeCOMe with *oligomeric* MeOH[17] as $7.0 \pm 0.8_2 \times 10^9$ M^{-1} s^{-1}, similar to the quenching of PhCOMe ($\sim 10^{10}$ M^{-1} s^{-1})[13] and much more rapid than the $(MeO)_2C$/MeOH reaction, for which $k = 2.5 \times 10^6$ M^{-1} s^{-1}.[10] Quenching with 0.1–3 M acrylonitrile gave $k = 1.5 \pm 0.1_3 \times 10^6$ M^{-1} s^{-1}, again similar to the analogous PhCOMe rate constant[13] and ~1000 times greater than that of $(MeO)_2C$.[10] With α-chloroacrylonitrile, quenching experiments gave $k \sim 1 \times 10^7$ M^{-1} s^{-1}, about 20 times greater than the comparable $(MeO)_2C$ rate constant.[10] Trimethylethylene did not quench the transient absorption of MeCOMe.

Thermolysis of diazirine **2** at 25 °C in trimethylethylene, isobutene, *trans*-butene, methyl acrylate, acrylonitrile, or α-chloroacrylonitrile gave the anticipated cyclopropanes in low ($\leq 10\%$) isolated yields, based on the acetamidine precursor of **2**. GC analysis showed that the cyclopropanes and methylvinyl ether were the only significant non-azine products.[18] Structures were established by IR and NMR spectroscopy and by exact mass or elemental analysis.

Classical, product based competition reactions,[19] in which binary pairs of olefins were allowed to compete for an insufficiency of thermally generated MeCOMe, gave cyclopropane product mixtures that were analyzed by SE-30 capillary GC, with a calibrated flame ionization detector and an electronic integrator. The resulting relative reactivities, normalized to a *trans*-butene standard, appear in Table I.

The extraordinary nucleophilic selectivity of MeCOMe is obvious and is unsurpassed by previously reported carbenes.[13,20,21] Both the selectivity and spectral properties of MeCOMe are nicely rationalized by theoretical considerations.[22] The carbene should exist as trans and cis ground-state singlets.[23] *trans*-**1** is calculated[22] to be 8.6 kcal/mol more stable than *cis*-**1**. The transition state calculated for their interconversion is 31.3 kcal/mol above *trans*-**1**, so that, if both "isomers" are generated from **2**, cis–trans carbene interconversion would not be expected to occur during the MeCOMe lifetime in solution (<2 μs at 20 °C).



	trans-**1**	*cis*-**1**
ϵ_{LU}, eV[22]	4.04	3.86
ϵ_{HO}, eV[22]	−9.41	−8.96

We calculate[22] S_0–S_1 (σ^2–σ^1p^1) transitions for *trans*- and *cis*-**1** at 376 and 385 nm, respectively, and we do observe two closely spaced UV absorptions for **1** (e.g., 375 and 390 nm) in pentane solution. The IR absorptions of **1** in a nitrogen matrix at 10 K (see above) can be tentatively assigned to isomeric forms of MeCOMe. *trans*-**1** ($\lambda_{\text{calcd}}^{\text{max}}$ 376 nm) is selectively destroyed by irradiation at 335 nm (IR: 1330, 1288, 1160, 1100, 550 cm^{-1}), and *cis*-**1** ($\lambda_{\text{calcd}}^{\text{max}}$ 385 nm) is selectively destroyed by irradiation at 435 nm (IR: 1320, 1275 cm^{-1}).

Qualitatively, the combination of high-lying HOMO and LUMO in either isomer of **1** is precisely what is required for well expressed nucleophilic selectivity.[13] Indeed, the HOMO energies of **1** are comparable to those of PhCOMe,[13] while the LUMO energies are similar to those of $(MeO)_2C$.[10] By using the calculated[22] frontier molecular orbital energies[13,20] of **1** and available experimental orbital energies of the alkenes, we find that differential orbital energies[13,20] for the addition reactions of *both trans*- and *cis*-**1** are dominated by "nucleophilic" HOMO-**1**/LUMO-alkene interactions, in good accord with the experimental results.

The spectroscopic, computational, and kinetic studies of MeCOMe that we have described dramatically illustrate the extraordinary power of the methoxy substituent to alter the properties of an alkylcarbene.

Acknowledgment. We are grateful to the National Science Foundation, the Petroleum Research Fund (R.S.S.), and the A. P. Sloan Foundation (R.S.S.) for financial support. We thank A. Matro and Hong Fan for technical assistance.

---

[15] Appropriate products are formed in the analogous preparative scale bimolecular reactions (i.e., **4** or cyclopropanes). In pentane alone, decomposition of **2**, gave (*E*,*E*)- and (*E*,*Z*)-azines [(Me(MeO)C=N—)$_2$] that are most reasonably derived from the attack of **1** on **2**.

[16] Turro, N. J.; Butcher, J. A., Jr.; Moss, R. A.; Guo, W.; Munjal, R. C.; Fedorynski, M. *J. Am. Chem. Soc.* **1980**, *102*, 7576.

[17] Griller, D.; Liu, M. T. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5549.

[18] The yield of methylvinyl ether formed upon decomposition of **2** in pentane alone was ~8%. The ether was the only non-azine product detected.

[19] Moss, R. A. In *Carbenes*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1973; Vol. I, p 153f.

[20] Moss, R. A. *Acc. Chem. Res.* **1980**, *13*, 58.

[21] For the use of chloroacrylonitrile in carbenic selectivity experiments, see: Moss, R. A.; Fan, H.; Hadel, L. M.; Shen, S.; Włostowska, J.; Włostowski, M.; Krogh-Jespersen, K. *Tetrahedron Lett.* **1987**, *28*, 4779.

[22] Ab initio calculations employed the GAUSSIAN 86 series of programs: Frisch, M.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Martin, R.; Stewart, J. J. P.; Bobrowicz, F.; DeFrees, D.; Seeger, R.; Whiteside, R.; Fox, D.; Fluder, E.; Pople, J. A. GAUSSIAN 86, Release C, Carnegie-Mellon University. Computational procedures included geometries, HF/6-31G*//6-31G*; HOMO/LUMO energies, HF/4-31G//STO-3G (to conform with previous usage);[13,20] S_0–T_1 separations and relative energies, MP3/6-31G*//6-31G*; and S_0–S_1 separations, HF/6-31G* geometries, singly excited configuration interaction, INDO/S model. See ref 10 for more detail and references.

[23] Calculated[22] vertical S_0–T_1 separations are 40.7 (*trans*-**1**) and 32.4 (*cis*-**1**) kcal/mol.

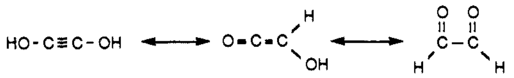
Synthesis and Stabilization of Tantalum-Coordinated Dihydroxyacetylene from Two Reductively Coupled Carbon Monoxide Ligands

Raymond N. Vrtis, Ch. Pulla Rao, Simon G. Bott, and Stephen J. Lippard*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received March 21, 1988

In 1834 Justus Liebig reported the reductive coupling of carbon monoxide by potassium metal to form "potassium carbonyl",[1] later shown to contain the potassium salt of acetylenediolate, $K_2(^-O—C≡C—O^-)$.[2] Many attempts have subsequently been made to obtain useful organic compounds from alkali metal or electrochemical CO reductions, but in general the products are unstable or intractable.[3] Although the conjugate acid of acetylenediolate, dihydroxyacetylene, has been observed in the gas phase by using neutralization–reionization mass spectrometry,[4] solutions of dihydroxyacetylene would presumably be unstable, tautomerizing to hydroxyketene or glyoxal, eq 1.[5] Previously we



(1)

---

[1] Liebig, J. *Ann. Chem. Pharm.* **1834**, *11*, 182. For additional historical background, see: West, R. In *Oxocarbons*; West, R., Ed.; Academic Press: New York, 1980; Chapter 1.

[2] (a) Weiss, E.; Büchner, W. *Helv. Chim. Acta* **1963**, *46*, 1121. (b) Büchner, W. *Ibid.* **1963**, *46*, 2111.

[3] (a) Joannis, A. *C. R. Acad. Sci.* **1893**, *116*, 1518; **1914**, *158*, 874. (b) Pearson, T. G. *Nature (London)* **1933**, *131*, 166. (c) Hackspill, L.; van Altnea, L. A. *Compt. Rend.* **1938**, *206*, 1818. (d) Scott, A. F. *Science (Washington, D.C.)* **1952**, *115*, 118. (e) Weiss, E.; Büchner, W. *Helv. Chim. Acta* **1964**, *47*, 1415. (f) Weiss, E.; Büchner, W. *Z. Anorg. Allg. Chem.* **1964**, *330*, 251. (g) Weiss, E.; Büchner, W. *Chem. Ber.* **1965**, *98*, 126. (h) Büchner, W. *Helv. Chim. Acta* **1965**, *48*, 1229. (i) Silvestri, G.; Gambino, S.; Filardo, G.; Guainazzi, M.; Ercoli, R. *Gazz. Chim. Ital.* **1972**, *102*, 818. (j) Silvestri, G.; Gambino, S.; Filardo, G.; Spadaro, G.; Palmisano, L. *Electrochim. Acta* **1978**, *23*, 413. (k) Bockmair, G.; Fritz, H. P. *Z. Naturforsch. B.* **1975**, *30*, 330. (l) Ellis, J. E.; Fjare, K. L.; Hayes, T. G. *J. Am. Chem. Soc.* **1981**, *103*, 6100. (m) Barber, J. Ph.D. Thesis, Massachusetts Institute of Technology, 1981. (n) Uribe, F. A.; Sharp, P. R.; Bard, A. J. *J. Electroanal. Chem.* **1983**, *152*, 173.

[4] Terlouw, J. K.; Burgers, P. C.; van Baar, B. L. M.; Weiske, T.; Schwarz, H. *Chim.* **1986**, *40*, 357.

0002-7863/88/1510-7564$01.50/0

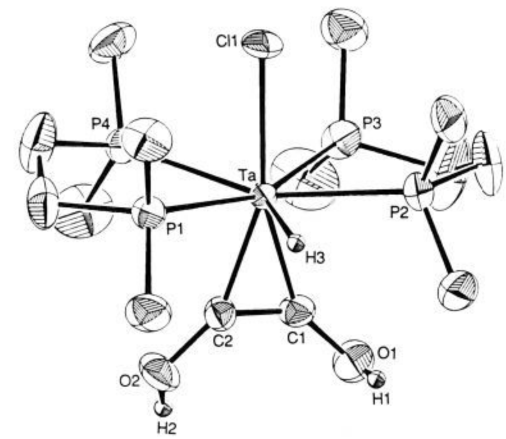


Figure 1. Structure of $[TaH(HOCCOH)(dmpe)_2Cl]^+$ (**2**) showing the 40% thermal ellipsoids and labeling scheme. Selected bond distances (Å) and angles (deg) are as follows: Ta–C1, 2.058 (7); Ta–C2, 2.085 (7); Ta–H3, 1.89 (14); Ta–Cl1, 2.529 (2); Ta–P1, 2.556 (2); Ta–P2, 2.548 (2); Ta–P3, 2.645 (2); Ta–P4, 2.620 (2); C1–O1, 1.361 (9); C2–O2, 1.367 (9); C1–C2, 1.28 (1); O1–H1, 0.94 (9); O2–H2, 0.91 (14); Cl1–Ta–H3, 103 (4); P1–Ta–H3, 65 (4); P2–Ta–H3, 61 (3); P3–Ta–P4, 86.1 (1); P1–Ta–P4, 75.0 (1); P2–Ta–P3, 75.4 (1); Ta–C1–O1, 152.4 (5); Ta–C2–O2, 150.7 (6); O1–C1–C2, 134.4 (7); O2–C2–C1, 138.4 (7); C1–O1–H1, 91 (6); C2–O2–H2, 114 (8).

found that two CO ligands in $[M(CO)_2(dmpe)_2Cl]$ complexes [M = Ta or Nb; dmpe = bis(1,2-dimethylphosphino)ethane] could be reductively coupled by using 40% Na/Hg to give, after addition of R_3SiX, molecules of the type $[M(R_3SiOCCOSiR_3)(dmpe)_2X]$ [e.g., M = Ta, R = Me, X = Cl (**1**)] containing coordinated $R_3Si—O—C{\equiv}C—O—SiR_3$.[6] Mechanistic studies revealed the reaction to proceed via carbonyl/carbyne coupling involving $[M({\equiv}COSiR_3)(CO)(dmpe)_2]$ (M = Ta or Nb) intermediates.[7] Here we report reaction chemistry leading to the formation of the dihydroxyacetylene molecule stabilized by coordination to tantalum in $[TaH(HOCCOH)(dmpe)_2Cl]^+$ (**2**).

When $[Ta(Me_3SiOCCOSiMe_3)(dmpe)_2Cl]$ (**1**) dissolved in THF was allowed to react under nitrogen with 1 equiv of HCl as a 7.6% aqueous solution, there was a rapid color change from dark green to pale yellow. After 30 min white microcrystals of $[TaH(HOCCOH)(dmpe)_2Cl]Cl$ (**2**)[8] formed which were isolated by filtration and washed with THF (yield 94%). This reaction also could be accomplished simply by adding distilled water or methanol to **1** but with significantly lower isolated yields (<50%).

Figure 1 displays the structure of **2**,[9] along with some geometric information. Compound **2** is the first example of a structurally characterized molecule with a dihydroxyacetylene ligand. The coordination geometry of tantalum is pentagonal-bipyramidal, with the chloride atom and the midpoint of the dihydroxyacetylene ligand in axial positions. The equatorial plane contains a hydride and two chelating dmpe ligands. The geometry about the HO—C≡C—OH ligand is similar to that of other four-electron-donating alkyne complexes of tantalum.[10] The hydroxyl protons on the dihydroxyacetylene ligand were located directly from difference Fourier maps and refined. The hydride atom was also located on the difference Fourier maps in what appeared to be two disordered positions. Refinement of the hydrogen at the position of greater electron density resulted in a Ta–H distance of 1.89 (14) Å. This value may be compared with average distances of 1.80 (1) and 1.774 (3) Å reported in neutron diffraction structures of $[TaClH_2(PMe_3)_4]$[11] and $[Cp_2TaH_3]$[12] and 1.94 (11) and 1.85 (11) Å found in the X-ray diffraction structure of $[TaCl_2H_2(PMe_3)_4]$.[13]

A trans influence of the hydride ion results in a 0.08 Å lengthening in the average Ta–P bond length of the *trans*-phosphines [P(3) and P(4), 2.632 (8) Å] versus that for the *cis*-phosphines [P(1) and P(2), 2.552 (4) Å]. This effect can also be seen in the ^{31}P NMR spectrum of **2**. The $^{31}P\{^1H\}$ NMR spectrum of **2** consists of two resonances at 14.55 and 35.45 ppm. When the spectrum is run without proton decoupling, however, the downfield resonance splits into a doublet with a $^2J_{PH}$ = 90 Hz. Similar behavior occurs in the ^{31}P NMR spectrum of $[TaH(CO)_2(dmpe)_2]$ which has a hydride-capped octahedral structure with *trans*-CO ligands.[14]

When a small amount of D_2O is added to a solution of **2** in $CDCl_3$, the hydroxyl protons at 11.0 ppm in the ^1H NMR spectrum disappear, while the hydride resonance, which appears as a triplet of triplets at 5.1 ppm, does not change. The exchangeability of these two protons was also observed in a FAB mass spectrometry experiment in which some D_2O was added to the matrix containing **2**.

Although no mechanistic information is yet available, the reaction is formally comprised of two steps. One is protiolysis by water or HCl to yield the dihydroxyacetylene ligand along with bis(trimethylsilyl)ether, trimethylsilanol, or trimethylsilyl chloride. The other involves reaction with HCl in an oxidative addition step. The sequence of these two steps is currently being investigated. When no HCl is added, it could be formed in situ by hydrolysis of a Ta–Cl bond. Although no hydrolysis products containing a Ta–OH bond have yet been identified, a yellow, THF-soluble compound forms in reactions of **1** with distilled water which may contain such a species. In what may be a similar reaction, the compound $[Fe_2(Me_3SiOC)_4(CO)_3]$, which contains a metallocyclopentadiene fragment, reacts with anhydrous HCl releasing 2 equiv of Me_3SiCl.[15] Partial characterization of the product revealed the presence of –OH functionalities, but further details have not been reported.

In summary, the reaction of aqueous HCl with $[Ta(Me_3SiOCCOSiMe_3)(dmpe)_2Cl]$ (**1**) produces a tantalum complex containing the novel dihydroxyacetylene ligand, $[TaH(HOCCOH)(dmpe)_2Cl]Cl$ (**2**). Since **2** is much more stable than **1** it may be an important precursor for further transformations of the alkyne moiety, studies of which are currently underway.

Acknowledgment. This work was supported by a grant from the National Science Foundation (NSF-CHE-8711212). We thank Dr. W. M. Davis for help with the crystallography of **2**.

---

(5) Serratosa, F. *Acc. Chem. Res.* **1983**, *16*, 170 and references cited therein.

(6) (a) Bianconi, P. A.; Williams, I. D.; Engeler, M. P.; Lippard, S. J. *J. Am. Chem. Soc.* **1986**, *108*, 311. (b) Bianconi, P. A.; Vrtis, R. N.; Rao, Ch. P.; Williams, I. D.; Engeler, M. P.; Lippard, S. J. *Organometallics* **1987**, *6*, 1968.

(7) Vrtis, R. N.; Rao, Ch. P.; Warner, S.; Lippard, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 2669.

(8) Anal. Calcd for $C_{14}H_{35}Cl_2O_2P_4Ta$ (**2**): C, 27.51; H, 5.77; Cl, 11.60. Found: C, 27.01; H, 5.50; Cl, 12.13. Spectroscopic data: FAB mass spectroscopy m/z = 575.1 (M^+); FTIR (KBr) 1604 (ν_{CO} or ν_{CC}) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 10.97 (s, OH), 5.06 (t of t, $^2J_{HPtrans}$ = 90 Hz, $^2J_{HPcis}$ = 5 Hz), 2.60–1.82 (br M, PCH_2), 1.76 (d, PCH_3, $^2J_{PH}$ = 9 Hz), 1.58 (d, PCH_3, $^2J_{PH}$ = 9 Hz), 1.48 (d, PCH_3, $^2J_{PH}$ = 8 Hz), 1.35 (d, PCH_3, $^2J_{PH}$ = 8 Hz) ppm; $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, referenced to external 85% H_3PO_4) δ 35.55, 14.55 ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 204.6 ppm (HOCCOH, by ^{13}C enrichment).

(9) Crystal data for **2**: $C_{14}H_{35}Cl_2O_2P_4Ta$, M_r = 611.18, orthorhombic, space group $P2_12_12_1$, a = 8.777 (2) Å, b = 14.856 (2) Å, c = 18.154 (5) Å, Z = 4, ρ_{calcd} = 1.71 g/cm³. The structure was solved and refined by conventional Patterson, difference Fourier, and full-matrix least-squares techniques. For 2794 unique, observed $[I > 3\sigma(I)]$ reflections measured by diffractometer and 222 variable parameters the current discrepancy indices are R = 0.023, R_w = 0.032. Further attempts to model the possible hydride disorder and to grow crystals large enough for neutron or diffraction study are in progress. Full details will be reported subsequently.

(10) (a) Cotton, F. A.; Hall, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5094. (b) Smith, G.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 387.

(11) Leutkens, M. L., Jr.; Hopkins, M. D.; Schultz, A. J.; Williams, J. M.; Fair, C. K.; Ross, F. K.; Huffman, J. C.; Sattelberger, A. P. *Inorg. Chem.* **1987**, *26*, 2430.

(12) Wilson, R. D.; Koetzle, T. F.; Hart, D. W.; Krick, A.; Tipton, D. L.; Bau, R. *J. Am. Chem. Soc.* **1977**, *99*, 1775.

(13) Luetkens, M. L., Jr.; Huffman, J. C.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1983**, *105*, 4474.

(14) Meakin, P.; Guggenberger, L. J.; Tebbe, F. N.; Jesson, J. P. *Inorg. Chem.* **1974**, *13*, 1025.

(15) Nasta, M. A.; MacDiarmid, A. G.; Saalfeld, F. E. *J. Am. Chem. Soc.* **1972**, *94*, 2449. (b) Bennett, M. J.; Graham, W. A. G.; Smith, R. A.; Stewart, R. P., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 1684.

FAB mass spectra were obtained with the assistance of Dr. C. Costello at the Facility supported by NIH Grant RR 00317 (Principal Investigator, Prof. K. Biemann) from the Biotechnology Resources Branch, Division of Research Resources.

Supplementary Material Available: Tables of atomic positional and thermal parameters for **2** (2 pages). Ordering information is given on any current masthead page.

Structural and Theoretical Models of Photosynthetic Chromophores. Implications for Redox, Light Absorption Properties and Vectorial Electron Flow

K. M. Barkigia,[1a] L. Chantranupong,[1a] K. M. Smith,[1b] and J. Fajer*,[1a]

Department of Applied Science
Brookhaven National Laboratory
Upton, New York 11973
Department of Chemistry, University of California
Davis, California 95616

Received June 9, 1988

Recent structural data for (bacterio)chlorophylls and chlorins as isolated molecules[2-5] and in proteins[6-8] demonstrate the skeletal flexibility of the chromophores that can be imposed by crystal packing and/or protein constraints. We present here single-crystal X-ray data for a homologous series of methyl bacteriopheophorbides *d*, derived from the antenna chlorophylls of the green photosynthetic bacterium *Chlorobium vibrioforme*.[5] The results illustrate the crystallographically significant conformational variations possible for the same chlorophyll skeleton. Comparable variations have also been noted, albeit at lower resolution, for the bacteriochlorophylls *a* (BChl) in the BChl antenna protein of *Prosthecochloris aestuarii*[6] and the BChls *b* that comprise the primary donor (special pair) of the *Rhodopseudomonas viridis* reaction center protein.[7,8]

We thus consider theoretically the possibility that such conformational variations can affect the highest occupied (HOMOS) and lowest unoccupied (LUMOS) molecular orbital levels of the chromophores and thereby modulate their redox potentials and light absorption properties. We test the concept by demonstrating that a sterically distorted porphyrin of known structure exhibits experimental optical and redox properties in solution consonant with theory and extend the calculations, using crystallographic data for the *Rps. viridis* primary donor,[8] to show that a redox asymmetry is possible in the BChl subunits that comprise the special pair of that bacterium.

Smith and Bobe[9] have demonstrated that green bacteria *light-adapt* by sequential alkylation of the antenna chlorophylls to yield a series of homologues with different substituents at position 4 of ring II (see structure in Figure 1). Single-crystal X-ray diffraction of metal-free derivatives (pheophorbides) from *Chlorobium vibrioforme* yield the following results:[5] (a) The substituents range from ethyl to *n*-propyl, isobutyl, and neopentyl. (b) Removal of the magnesium affords a series of dimeric and higher aggregates that are hydrogen bonded via the 2-(1-hydroxyethyl) group to the 9-keto group or to the carbonyl group of the propionic acid side chain of ring IV, depending on the method of crystallization. (c) Significant conformational variations are found for the same pheophorbide skeleton, depending on the

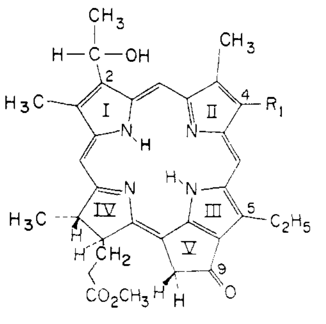


Figure 1. Structural formula of methylbacteriopheophorbide *d*. R_1 can be ethyl, *n*-propyl, isobutyl, or neopentyl.

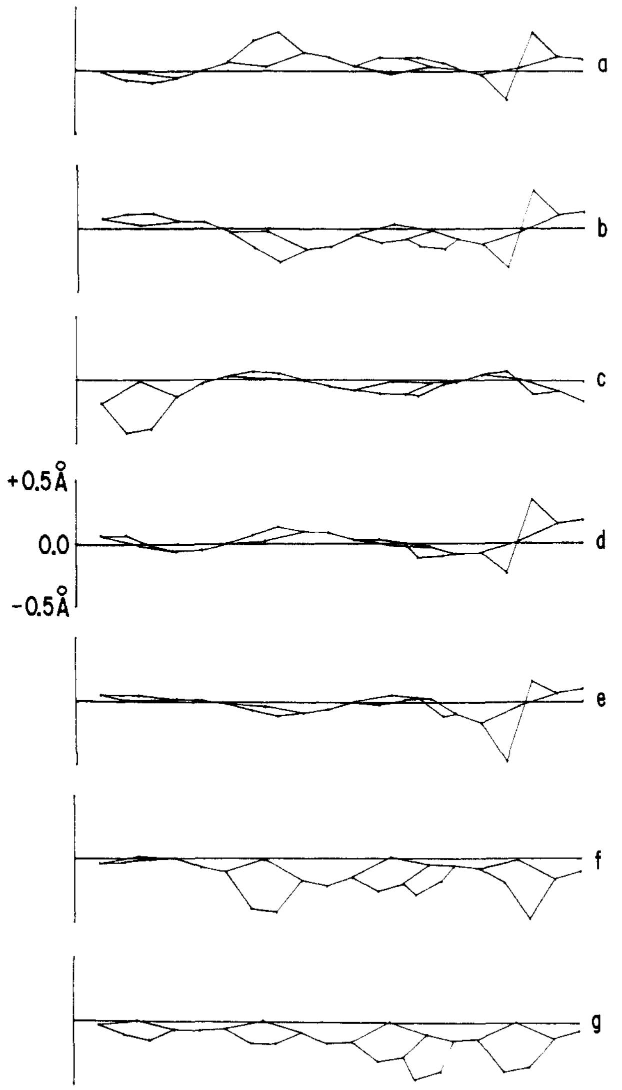


Figure 2. Linear display of the skeletal deviations from the plane defined by the four nitrogens of the bacteriopheophorbides *d*, in Å. Substituents are not shown. Illustrated are: (a) and (b) the two crystallographically independent molecules in the unit cell of 4,5-diethyl-methylbacteriopheophorbide *d*; (c) 4-propyl, 5-ethyl-meBPheo *d*; (d) and (e) the two crystallographically independent molecules in the unit cell of 4-isobutyl,5-ethyl-meBPheo *d*; (f) a different aggregate of 4-isobutyl,5-ethyl-meBPheo *d*; (g) 4-neopentyl,5-ethyl-meBPheo *d*. The order of the rings is I, II, III, V, and IV from left to right. Esd's for the deviations from planarity ≤0.01 Å.

---

(1) (a) Brookhaven National Laboratory. (b) University of California.

(2) Strouse, C. E. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 325. Chow, H. C.; Serlin, R.; Strouse, C. E. *J. Am. Chem. Soc.* **1975**, *97*, 7230. Serlin, R.; Chow, H. C.; Strouse, C. E. *Ibid.* **1975**, *97*, 7237.

(3) Kratky, C.; Dunitz, J. D. *Acta Crystallogr., Sect. B* **1975**, *B32*, 1586; **1977**, *B33*, 545. Kratky, C.; Dunitz, J. D. *J. Mol. Biol.* **1977**, *113*, 431. Kratky, C.; Isenring, H. P.; Dunitz, J. D. *Acta Crystallogr., Sect. B* **1977**, *B33*, 547.

(4) Barkigia, K. M.; Fajer, J.; Smith, K. M.; Williams, G. J. B. *J. Am. Chem. Soc.* **1981**, *103*, 5890. Barkigia, K. M.; Fajer, J.; Chang, C. K.; Young, R. *J. Am. Chem. Soc.* **1984**, *106*, 6457.

(5) Details of the crystal structures will be presented elsewhere. See, also: (a) Smith, K. M.; Goff, D. A.; Fajer, J.; Barkigia, K. M. *J. Am. Chem. Soc.* **1982**, *104*, 3747. (b) *Ibid.* **1983**, *105*, 1674. (c) Fajer, J.; Barkigia, K. M.; Fujita, E.; Goff, D. A.; Hanson, L. K.; Head, J. D.; Horning, T.; Smith, K. M.; Zerner, M. C. In *Antennas and Reaction Centers of Photosynthetic Bacteria*; Michel-Beyerle, M. E., Ed.; Springer-Verlag: Berlin, 1985; p 324.

(6) Tronrud, D. E.; Schmid, M. F.; Matthews, B. W. *J. Mol. Biol.* **1986**, *188*, 443.

(7) Michel, H.; Epp. O.; Deisenhofer, J. *EMBO J.* **1986**, *5*, 2445.

(8) Deisenhofer, J.; Michel, H., private communication.

(9) Smith, K. M.; Bobe, F. W. *J. Chem. Soc., Chem. Commun.* **1987**, 276.

0002-7863/88/1510-7566$01.50/0