The spontaneous formation of azetidione groups in crystalline MDI thus appears to provide what is at present a rare example of a *thermal* reaction that proceeds in the solid because of the proper alignment of the reacting functional groups by the solid matrix.[16]

Acknowledgment. We are indebted to the National Science Foundation (CHE-79-05-04871 and CHE 82-09-393) for support of this work. We would like to thank Dr. David Chadwick for calling this problem to our attention and to Dr. Chadwick and Dr. Ronald Taylor of the Mobay Chemical Corp. for samples of MDI.

Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, and observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

---

[16] Preliminary examination of the reaction of single crystals of MDI with the nucleophilic reagents methanol, ammonia, and pyridine has shown evidence of gas–solid reactions whose anisotropic behavior can be correlated with the internal structure of the crystal.

Isolation and Characterization of Two New Bacteriochlorophylls *d* Bearing Neopentyl Substituents

Kevin M. Smith* and Dane A. Goff

Department of Chemistry, University of California
Davis, California 95616

Jack Fajer and Kathleen M. Barkigia*[1]

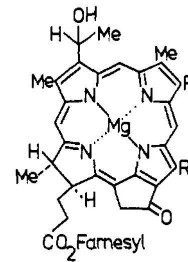
Department of Energy and Environment
Brookhaven National Laboratory, Upton, New York 11973

Received December 6, 1982

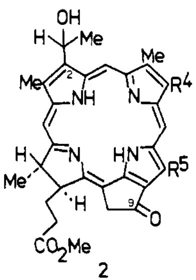
The bacteriochlorophylls *c* and *d* are found in a variety of photosynthetic green sulfur bacteria. They differ structurally from the plant chlorophylls in several ways, a remarkable feature of which is the presence of ethyl, *n*-propyl, or isobutyl substituents at position 4 (where chlorophyll *a* bears ethyl), and either methyl or ethyl at position 5 (in place of methyl); the source of the additional methyl groups has been shown to be methionine.[2] Intriguingly, the bacteriochlorophylls *c* exhibit[3] a further variance in the chirality of the 2-(1-hydroxyethyl) substituent, which changes from *R* to *S* as the size of the 4-substituent increases upon successive additions of methyl groups to a presently undefined precursor related to chlorophyll a. The chirality of the 2-substituents of the bacteriochlorophylls *d* (Table I, **1**) extracted from *Chlorobium vibrioforme* forma *thiosulfatophilum* (NCIB No. 8327) varies similarly:[4] it is *R* for the 4-Et,5-Me, 4-Et,5-Et, 4-*n*-Pr,5-Me, and 4-*n*-Pr,5-Et pigments (**1a–d**), but *S* for the 4-*i*-Bu,5-Me and 4-*i*-Bu,5-Et compounds (**1e** and **1f**, respectively). We describe here the isolation and characterization of two additional pigments from the same organism. The new bacteriochlorophylls possess a neopentyl substituent at position 4, and the *S* stereochemistry at the 2-(1-hydroxyethyl) group.

Figure 1A shows the reverse-phase HPLC[4] trace of an intact mixture of methyl bacteriopheophorbides *d* (**2**) from *C. vibrioforme*; these were obtained from the corresponding bacteriochlorophylls (**1**) by treatment with sulfuric acid in methanol.[2] The traces in Figure 1, B and C, show the 5-methyl (**2a,c,e**) and 5-ethyl (**2b,d,f**) series, respectively, after a preliminary separation using a silica gel column.[4,5] Two additional pigments, not previously reported, are apparent in the chromatograms (arrows in Figure 1, B and C). After isolation by preparative HPLC,[6] the new pigments (one from the 5-methyl and one from the 5-ethyl series) were subjected to spectroscopic analysis.

Table I



1



2

	R^4	R^5	confign at position 2
a	Et	Me	*R*
b	Et	Et	*R*
c	*n*-Pr	Me	*R*
d	*n*-Pr	Et	*R*
e	*i*-Bu	Me	*S*
f	*i*-Bu	Et	*S*
g	neoPn	Me	*S*
h	neoPn	Et	*S*

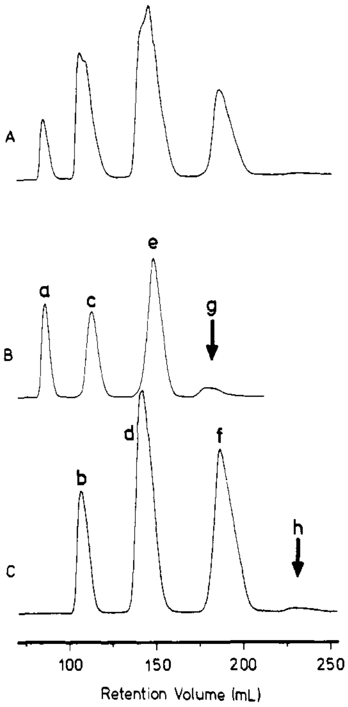


Figure 1. HPLC traces[4] of the methyl bacteriopheophorbides *d*: (A) complete mixture from *C. vibrioforme*; (B) the 5-methyl series, after preliminary separation by chromatography on silica; (C) the 5-ethyl series, after preliminary separation by chromatography on silica. The neopentyl derivatives are indicated by the arrows in B and C.

The methyl series bacteriopheophorbide (mp 181°C) showed a molecular ion at m/e 608 (100%) in its mass spectrum, together with a large ion (m/e 551, 65%) indicating cleavage of a fragment of mass 57 Daltons. Assuming normal benzylic cleavage,[7] this suggested the presence of a neopentyl substituent in the molecule. Likewise, the ethyl series bacteriopheophorbide (mp 218°C)

---

[1] Address correspondence concerning the X-ray structure to this author.

[2] Kenner, G. W.; Rimmer, J.; Smith, K. M.; Unsworth, J. F. *J. Chem. Soc., Perkin Trans. 1* **1978**, 845–852.

[3] Smith, K. M.; Kehres, L. A.; Tabba, H. D. *J. Am. Chem. Soc.* **1980**, *102*, 7149–7151.

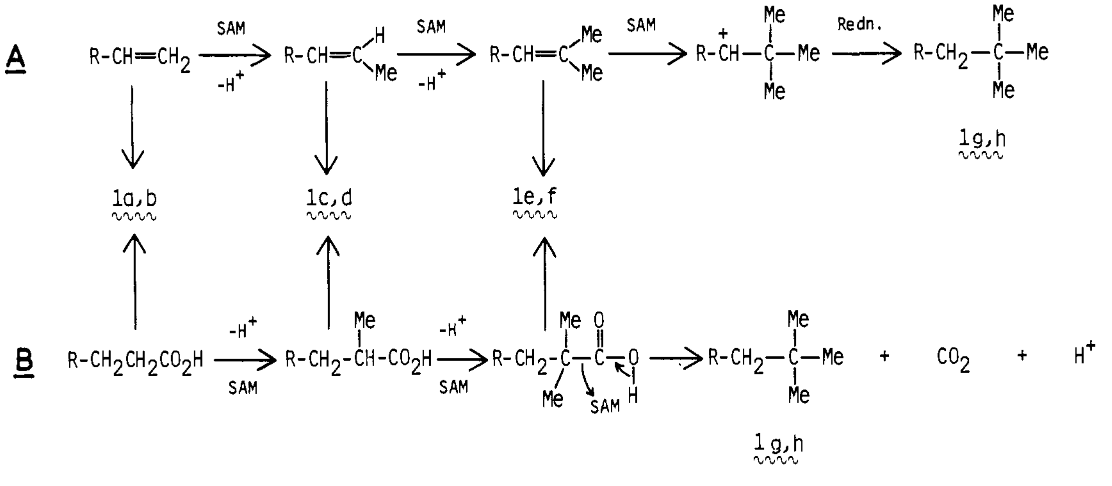
[4] Smith, K. M.; Goff, D. A.; Fajer, J.; Barkigia, K. M. *J. Am. Chem. Soc.* **1982**, *104*, 3747–3749.

[5] Kemmer, T.; Brockmann, H., Jr.; Risch, H. *Z. Naturforsch., B* **1979**, *34B*, 633–637.

[6] A Waters Associates Prep 500A chromatograph equipped with an ISCO 1840 variable-wavelength detector set at 650 nm was used. Reverse-phase cartridges were used, and the solvent was 15% water in methanol (flow rate 150 mL/min, with recycling).

[7] Jackson, A. H.; Kenner, G. W.; Smith, K. M.; Aplin, R. T.; Budzikiewicz, H.; Djerassi, C. *Tetrahedron* **1965**, *21*, 2913–2924.

Scheme I. Proposed Schemes for the Methylation of Vinyl (A) or Propionic Acid (B) Precursors in the Biosynthesis of Bacteriochlorophylls *d* (SAM = *S*-Adenosylmethionine)



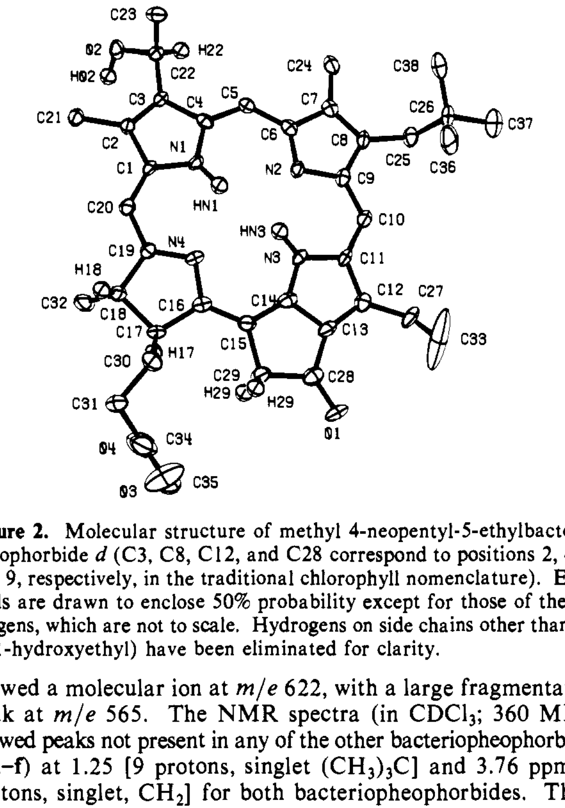


Figure 2. Molecular structure of methyl 4-neopentyl-5-ethylbacteriopheophorbide *d* (C3, C8, C12, and C28 correspond to positions 2, 4, 5, and 9, respectively, in the traditional chlorophyll nomenclature). Ellipsoids are drawn to enclose 50% probability except for those of the hydrogens, which are not to scale. Hydrogens on side chains other than the 2-(1-hydroxyethyl) have been eliminated for clarity.

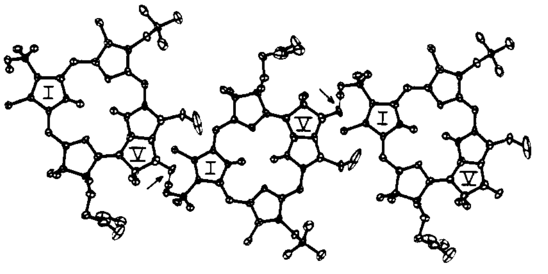


Figure 3. Aggregation of methyl 4-neopentyl-5-ethylbacteriopheophorbide *d*. The arrows indicate the hydrogen bonds between the protons of the hydroxyl groups and the oxygens of the 9-keto groups. The distance of 2.81 (1) Å between the two oxygen atoms is typical of that found for O-H- - -O.[10]

showed a molecular ion at *m/e* 622, with a large fragmentation peak at *m/e* 565. The NMR spectra (in $CDCl_3$; 360 MHz) showed peaks not present in any of the other bacteriopheophorbides (**2a–f**) at 1.25 [9 protons, singlet $(CH_3)_3C$] and 3.76 ppm [2 protons, singlet, CH_2] for both bacteriopheophorbides. These resonances are clearly indicative of a neopentyl group in both cases, therefore the new pigments were assigned the structures (**2g,h**; methyl bacteriopheophorbides) or (**1g,h**; bacteriochlorophylls, prior to acidic methanolysis). To confirm the neopentyl assignment and the expected (*S*) chirality of the 2-(1-hydroxyethyl) group, the ethyl series bacteriopheophorbide (**2h**) was crystallized from methanol and subjected to single crystal X-ray analysis.

The neopentyl group at position-4 and the (*S*) chirality of the 2-substituent are obvious from the structure of compound (**2h**) illustrated in Figure 2. The compound crystallized[8] from methanol in chains connected by hydrogen bonds between the hydroxyls of the 2-side chains and the 9-keto groups, an architecture unique to this compound, so far (Figure 3). Of particular interest is the fact that the molecule is very nearly planar, unlike the bacteriopheophorbides **2b,f**, which crystallized as dimers from dichloromethane/hexane and showed considerable deviations from planarity in the reduced ring.[4,11] These differences typify the wide range of conformations that packing forces can induce in the chlorophylls and, by extrapolation, may exemplify the structural effects that protein environments can impose on the chromophores. Such protein-induced conformational differences have previously been invoked to rationalize the varying paramagnetic characteristics of chlorophyll radicals in photosynthetic bacteria.[12]

Our results also shed light on the biosynthetic mechanisms that transform the vinyl or propionic acid side chains of a precursor into *n*-propyl, isobutyl, or neopentyl in these bacteria. Addition of the final methyl group to a vinylic precursor (isobutenyl) would require concomitant reduction of the resulting carbocation (Scheme IA). On the other hand, methylation of a propionic acid precursor, as previously suggested,[2,13] would demand a simultaneous decarboxylation (Scheme IB). Biosynthetic studies of these chlorophylls are in progress.

The studies described here should be relevant not only for green bacteria but also for the chlorophyll variants found in purple

---

(8) The compound crystallizes from methanol with $Z = 4$ in the space group $P2_12_12_1$ in a cell of dimensions $a = 6.414$ (2) Å, $b = 21.814$ (7) Å, $c = 23.412$ (6) Å, $V = 3275.7$ Å^3. Data were collected at 120 K, on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Cu Kα radiation in the scan range $0 \le 2\theta \le 144°$. Of the 3982 reflections measured, 3697 were unique and 3065 had $F_o > 2\sigma(F_o)$. Current values of R_F and R_{wF} are 0.088 and 0.084. The enantiomorph was chosen such that the orientation of the substituents in ring IV was consistent with the previously determined absolute stereochemistry of that ring.[9] The absolute configuration of the chiral centers was not determined by the present analysis. Hydrogens were idealized 0.95 Å from their respective carbons or nitrogens. Details of the structure will be presented elsewhere.

(9) Brockmann, H., Jr. *Philos. Trans. R. Soc. London, Ser. B* **1976**, *273*, 277–285.

(10) Hamilton, W. C.; Ibers, J. A. "Hydrogen Bonding in Solids"; W. A. Benjamin: New York, 1968; p 17.

(11) Bacteriopheophorbides **2b,f** crystallized from dichloromethane/hexane in the space group $P1$ with $Z = 2$ and formed cofacial dimers linked by two hydrogen bonds between the sets of hydroxy and keto functions.[4]

(12) Davis, M. S.; Forman, A.; Hanson, L. K.; Thornber, J. P.; Fajer, J. *J. Phys. Chem.* **1979**, *83*, 3325–3332.

(13) Kenner, G. W.; Rimmer, J.; Smith, K. M.; Unsworth, J. F. *Philos. Trans. R. Soc. London, Ser. B* **1976**, *273*, 255–276.

bacteria[12] (BChl *b*) and in green plants. Several new chlorophylls have been reported in the latter.[14,15] One of these has been proposed[15] to be part of the reaction center that initiates the electron-transport chain that fixes carbon dioxide (photosystem I).

Acknowledgment. This research was supported by grants from the National Science Foundation (CHE-81-20891, at UCD) and the U.S. Department of Energy, Division of Chemical Sciences, under Contract DE-AC02-76CH00016 (at BNL). We are grateful to Prof. N. Pfennig for a gift of the *C. Vibrioforme* strain.

Supplementary Material Available: Positional and anisotropic thermal parameters for the non-hydrogen atoms of methyl 4-neopentyl-5-ethylbacteriopheophorbide *d* (2 pages). Ordering information is given on any current masthead page.

---

(14) Rebeiz, C. A. *ChemTech.* **1982**, *12*, 52–63 and references therein.

(15) Dörnemann, D.; Senger, H. *Photochem. Photobiol.* **1982**, *35*, 821–826.

Synthesis, Structure, and Photochemistry of Tetracarbonyl(fulvalene)diruthenium. Thermally Reversible Photoisomerization Involving Carbon–Carbon Bond Activation at a Dimetal Center

K. Peter C. Vollhardt* and Timothy W. Weidman

Department of Chemistry, University of California, Berkeley and the Materials and Molecular Research Division Lawrence Berkeley Laboratory, Berkeley, California 94720

Received November 19, 1982

The η^5:η^5-fulvalene ligand constitutes an attractive matrix on which to firmly affix two metal atoms in close enough proximity to enable metal–metal bonding while allowing complexes to retain dinuclear character after potential metal–metal bond fission. We report here a new synthetic approach to dimetallafulvalenes,[1] some preliminary chemistry of a diruthenium derivative, and its unexpected photoreactions.

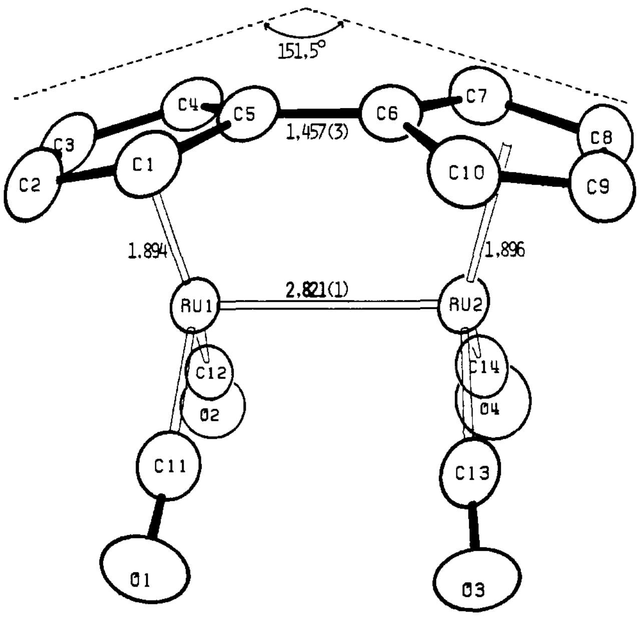


Figure 1. ORTEP drawing showing the geometry, labeling, and important bond lengths (Å) for all non-hydrogen atoms in tetracarbonyl(η^5:η^5-fulvalene)diruthenium (**2**). Ellipsoids are scaled to represent the 50% probability surface.

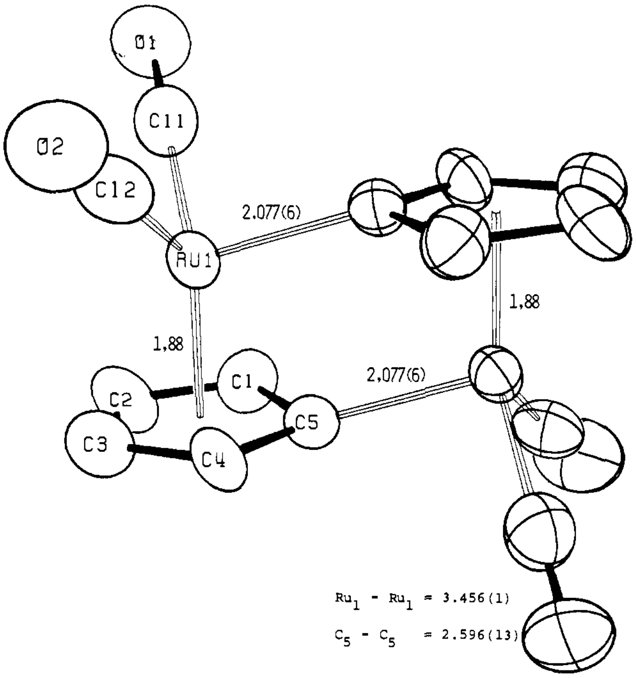
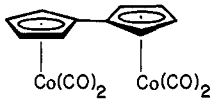
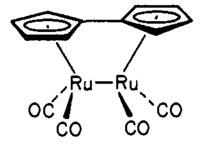


Figure 2. ORTEP drawing of **6**.

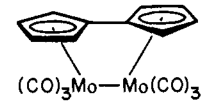
We have found that dihydrofulvalene, prepared in THF,[1a] becomes suitable for direct reaction with metal carbonyls after extraction into water-washed heptane.[2] Addition of the latter to boiling solutions of $Co_2(CO)_8$ (CH_2Cl_2) or $Ru_3(CO)_{12}$ (glyme) and/or $Mo(CO)_6$ (glyme) results in good yields of complexes **1**–**4**.[3]



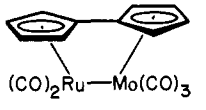
1



2



3



4

---

(1) For alternative approaches from fulvalene dianion, see: (a) Smart, J. C.; Curtis, C. J. *Inorg. Chem.* **1977**, *16*, 1788. (b) Davison, A.; Smart, J. C. *J. Organomet. Chem.* **1973**, *49*, C43. (c) Smart, J. C.; Curtis, C. J. *J. Am. Chem. Soc.* **1977**, *99*, 3518. (d) Smart, J. C.; Pinsky, B. L.; Fredrich, M. F.; Day, V. W. *Ibid.* **1979**, *101*, 4369. (e) McKinney, R. J. *J. Chem. Soc., Chem. Commun.* **1980**, 603. (f) Köhler, F. H.; Doll, K. H.; Prössdorf, W.; Müller, J. *Angew. Chem.* **1982**, *94*, 154; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 151; *Angew. Chem. Suppl.* **1982**, 283. From η^5-halocyclopentadienyl complexes by Ullmann-type coupling, see: (g) Hedberg, F. L.; Rosenburg, H. *J. Am. Chem. Soc.* **1969**, *91*, 1258. (h) Rausch, M. D.; Kovar, R. F.; Kraihanzel, C. S. *Ibid.* **1969**, *91*, 1259. (i) Rausch, M. D.; Genetti, R. A. *J. Org. Chem.* **1970**, *35*, 3888. (j) Neuse, E. W.; Loonat, M. S. *Transition Met. Chem.* **1981**, *6*, 260. (k) Bednarik, L.; Neuse, E. W. *J. Org. Chem.* **1980**, *45*, 2032. (l) Nesmeyanov, A. N.; Sedova, N. N.; Moiseev, S. K.; Sazonova, V. A. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1980**, 1171. From η^5-cyclopentadienyl complexes by reductive coupling, see: (m) Antropiusovā, H.; Dosedlovā, A.; Hanuš, V.; Mach, K. *Transition Met. Chem.* **1981**, *6*, 90. (n) Gell, K. I.; Harris, T. V.; Schwartz, J. *Inorg. Chem.* **1981**, *20*, 481. (o) Berry, M.; Cooper, J.; Green, M. L. H.; Simpson, S. J. *J. Chem. Soc., Dalton Trans.* **1980**, 29. (p) Barral, M. C.; Green, M. L. H.; Jimenez, R. *Ibid.* **1982**, 2495. (q) Pez, G. P. *Adv. Organomet. Chem.* **1981**, *19*, 1. (r) Pez, G. P.; Apgar, P.; Crissey, R. K. *J. Am. Chem. Soc.* **1982**, *104*, 482. (s) Pez, G. P. *Ibid.* **1981**, *103*, 8072. (t) Lemenovskii, D. A.; Konde, S. A.; Perevalova, E. G. *J. Organomet. Chem.* **1982**, *226*, 223 and the references therein.

(2) Details will be the subject of a full paper.

0002-7863/83/1505-1676$01.50/0