of the pyrroles and the bridges between them ($C\alpha$–C_{meso}) is evident and is most consistent with resonance forms of the tautomer in which the protons are localized on nitrogens N2 and N4 (protons at those positions are required for satisfactory refinements of both the $P2_1/n$ and $P\bar{1}$ structures).

The reduced rings II and IV bearing the exocyclic methylene group serve as synthetic analogues of rings II of BChl and BPheo *b*. The inductive effect of the double bond is reflected in the asymmetry of the ring: the C3–C4 bond is shorter than C1–C2 by 0.05 Å and 0.03 Å from the average of $C\alpha$–$C\beta$ bonds in several hydroporphyrins;[11] C1–N1 and C4–N1 also differ unlike the corresponding distances in pyrrole rings I and III. The C2–C3–C4 angle is stretched 5.6° relative to C1–C2–C3.

The enlarged cores observed in hydroporphyrins,[8-10] in which Ct–N distances to the reduced rings are longer than those to the pyrroles, are also evident in the present bacteriochlorin as well: Ct–N1 = 2.105 vs. Ct–N2 = 2.084 Å.

The macrocycle itself is effectively planar, with the largest deviations from the 24-atom core of −0.068 (2) and 0.066 Å at C2 and C3 and an out of plane displacement of 0.194 Å for C25. Individually, ring II is planar but slightly twisted as evidenced by a C1–C2–C3–C4 torsion angle of 5.3 (2)°. In comparison, ring III is flat, with atomic deviations of 0.00 Å and a value of 0.2 (2)° for the C6–C7–C8–C9 torsion angle. The planarity of the molecule is in sharp contrast to the distortions found in several hydroporphyrins where the torsional angles are as large as 48°.[9] The planarity of this synthetic model lends support to the suggestion advanced by Davis et al.[5] that BChl *b* is planar in *Rhodopseudomonas viridis* RC's.

The molecules of **3** pack in chains in which ring I of one molecule overlaps ring III of its neighbor with a vertical separation of 3.59 Å, indicative of π–π interactions. Significantly, the *same* overlap is observed in the $P\bar{1}$ and $P2_1/n$ crystal habits even though the latter includes molecules of solvation. The present results and those previously reported for a metal-free isobacteriochlorin,[8a] and for methyl-bacteriopheophorbide[3b] and -pheophorbide *a*,[12] suggest that π–π interactions alone can promote aggregation of these derivatives and thereby provide a mechanism for exciton migration in the crystal similar to those observed in vivo.[13] Indeed, although the synthetic bacteriochlorin (**3**) lacks the fifth ring, acetyl group, and magnesium atom of BChls *a* (**1**) or *b* (**2**), the packing of any two molecules of the model (Figure 2) mimics surprisingly well the overlapping structure **4** proposed[6] for the primary donors in bacterial reaction centers.[15]

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Note Added in Proof. The structure of *R. viridis* RC's at 3-Å resolution shows that rings I of the two BChls *b* of the special pair overlap with a vertical separation of ~3 Å and a Mg to Mg distance of ~7 Å to be compared with a separation of 3.6 Å and a center to center distance of 8.1 Å between overlapping molecules of **3**. (Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *J. Mol. Biol.*, in press. We thank these authors for communicating their results prior to publication.)

Supplementary Material Available: Experimental details, atom coordinates and anisotropic vibrational parameters for the non-hydrogen atoms, some least-squares planes, some intermolecular contacts, idealized positions for the hydrogen atoms, and a listing of the observed and calculated structure amplitudes for both crystal habits of **3** and a comparison of bond distances in several hydroporphyrins (41 pages). Ordering information is given on any current masthead page.

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(11) See supplementary material for a comparison of bond distances and angles in several hydroporphyrins.

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(13) That such interactions in the crystal duplicate spectral features observed in vivo is evidenced by single crystals of methylbacteriopheophorbide *a*[14] and methyl- or ethylchlorophyllide *a*:[12] the first absorption bands are red shifted by 90 and 77 nm, respectively, relative to the spectra in solution.

(14) Hanson, L. K. *Proc. DOE Sol. Photochem. Conf., 7th, 1983* **1983**, LBL-16794, 135.

(15) One role of the magnesium and oxygen functional groups in vivo may well be to anchor the macrocycles in the protein so as to enhance the inherent tendency of the bacteriochlorin framework to form π–π aggregates.

Additions and Corrections

Nonvertical Triplet Excitation Transfer to *cis*- and *trans*-Stilbene

[*J. Am. Chem. Soc.* **1984**, *106*, 3144]. Jack Saltiel,* Gary R. Marchand, Ewa Kirkor-Kaminska, William K. Smothers, Warren B. Mueller, and James L. Charlton

Page 3146, right column, 21st and 22nd lines: The sentence should read as follows—If $k_{-en} \ll k_{-dif}$ (case b′) then $k_{obsd} = K_{dif}k_{en}$, and if $k_{-en} \gg k_{-dif}$ (case b″) then $k_{obsd} = k_{dif}K_{en}$.