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Wittig Reaction on Chlorin: Formation of an Unexpected Chlorin−Spirochlorin Dimer with Significant Overlap between the π Electron System

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The charge separation in photosynthetic organisms occurs in membrane proteins called reaction centers (RC). To date, two RCs, those from *Rd. viridis*[1] and *Rd. sphaeroids*,[2] have been characterized structurally at 2.3−3.1 Å by X-ray diffraction. In such RCs, the primary electron donor is dimeric bacteriochlorophylls (Bchl), the so-called "special pair" (SP).[3] A desire to understand the intricacies of natural photosynthesis has motivated many chemists and molecular biologists to synthesize and to study a wide variety of arrays of covalently linked porphyrins.[4] However, only a few attempts have been made to create synthetic models of the special pair.[7] Thus, our goal has been to develop a methodology for the preparation of cofacial chlorin dimers with partial overlap as models for the special pair.

Officer and colleagues[8] have recently shown that a variety of porphyrin dimers can be constructed by using porphyrin-derived Wittig reagents. This chemistry offers a versatile approach for the preparation of a variety of porphyrin-based free base and heterometalated dimers.

In our attempts to synthesize such dimers, we thought it worthwhile to prepare the Wittig reagents of the desired linkers first and then react them with chlorin and bacteriochlorin monomers individually. Initially, the bis-phosphonium salt **2** (derived from 2,2′-(bromomethyl)bisphenyl) was used as a starting material. The Wittig reagent **2** in the presence of DBU was reacted with chlorin **1**[9] dissolved in dichloromethane to afford a 2,2-bis-chlorin **3** in 60% yield. The formation of **3** was confirmed by ^{1}H NMR and high-resolution mass spectrometry (HRMS). The presence of eight meso protons in the range of 8.8−9.8 ppm clearly indicated a dimer possessing an asymmetric structure. Various NMR experiments and model studies[10] confirmed the asymmetry in dimer **3** is due to the biphenyl-type anisotropic effect. To our surprise, the bis-chlorin **3** was found to be unstable if the reaction was left for a longer period of time ($\sim$24 h) and slowly converted to an unexpected chlorin−spirochlorin dimer **4** linked via a tetrahydrobenzophenanthrene bridge. The rate of this transformation was found to be dependent on the reaction conditions used. The structure of dimer **4** was confirmed by HRMS and NMR studies, including two-dimensional ^{1}HROESY and COSY experiments and preliminary single-crystal X-ray studies (not shown). To the best of our knowledge, dimer **4** is the first structurally characterized chlorin−spirochlorin dimer exhibiting a remarkable π electron overlap. As shown in Scheme 1, the mechanism of the formation of this novel dimer is possibly due to the intramolecular [4 + 2] Diels−Alder cycloaddition of the unsaturated alkyl side chain in **3**.

To compare the resonances of various protons of dimer **4** with a related chlorin, the 8-formylvinyl chlorin **1** was reacted with (*p*-methylbenzyl)phosphonium bromide to afford the chlorin **1a** (Scheme 1). Compared to the model chlorin **1a**, the ^{1}H NMR spectrum of dimer **4** showed unique characteristics due to the π electron interactions between the two chlorin macrocycles. For example; the resonances for the meso protons in the model chlorin **1a** were observed in the region of 8.5−10 ppm; however, in dimer **4**, the meso proton labeled as "v" of the chlorin part shifted drastically to 4.89 ppm, exhibiting an upfield shift of 3.86 ppm relative to the chlorin **1a**. On the other hand, the meso proton from the spirocholorin labeled as "k" and "n" show 0.80 and 2.08 ppm upfield shifts. Unlike vinyl protons "g", "s", and "t" of the chlorin moiety, which appeared at 8.35, 6.48, and 6.15 ppm, respectively, the vinyl proton "w", "G", and "M" from the spirochlorin showed significantly upfielded resonances at 4.66, 3.66, and 3.25 ppm, respectively. Furthermore, the 12-methyl resonance "T" of the chlorin part of the dimer was observed at −0.13 ppm, exhibiting an upfield shift of about 3.50 ppm, whereas the 2-methyl signal "S" of the spirochlorin was shifted 3.41 ppm upfield relative to chlorin **1a**. Surprisingly, the two protons adjacent to ring C of the chlorin labeled as "z" and "M′" have very different shifts with M′ being 0.84 ppm upfield of z. In dimer **4**, compared to the resonances for the −NH protons of ring A of the chlorin and ring C of the spirochlorin, the −NH protons of ring C (chlorin) and ring A (spirochlorin) produced upfield shifts of $\sim$2.00 ppm. This is due to the large ring current produced by the system, which naturally affect the adjacent ring due to partial chlorin−spirochlorin overlap, thus causing a strong shielding effect (see Scheme 1). The nature of the overlap between the pyrrole ring C of the chlorin and ring A of the spirochlorin in dimer **4** was further resolved by performing a 2D-ROESY experiment (600 MHz) at 30 °C (**4** was dissolved in 0.5% pyridine-d_5/CDCl$_3$). A few through-space cross-peaks, due to interchlorin subunit proton−proton interactions ($<\sim$3.5 Å) were also observed. For example, proton z of the chlorin shows a cross-interaction with the 18-methyl "K" of the spirochlorin. Our observations are consistent with a structure where the chlorin units are present in such a way that the pyrrole ring A of the spirochlorin overlaps the pyrrole ring C of the opposite chlorin. This intermolecular interaction was further confirmed by the energy-optimized structure of chlorin−spirochlorin **4**, obtained by molecular modeling (Figure 1) starting from the partially refined X-ray coordinates.

The presence of a hydroxy functionality in the chlorin system (ring B) of the dimer **4** was also supported by its

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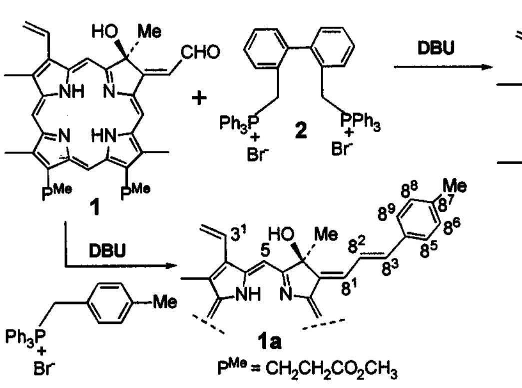
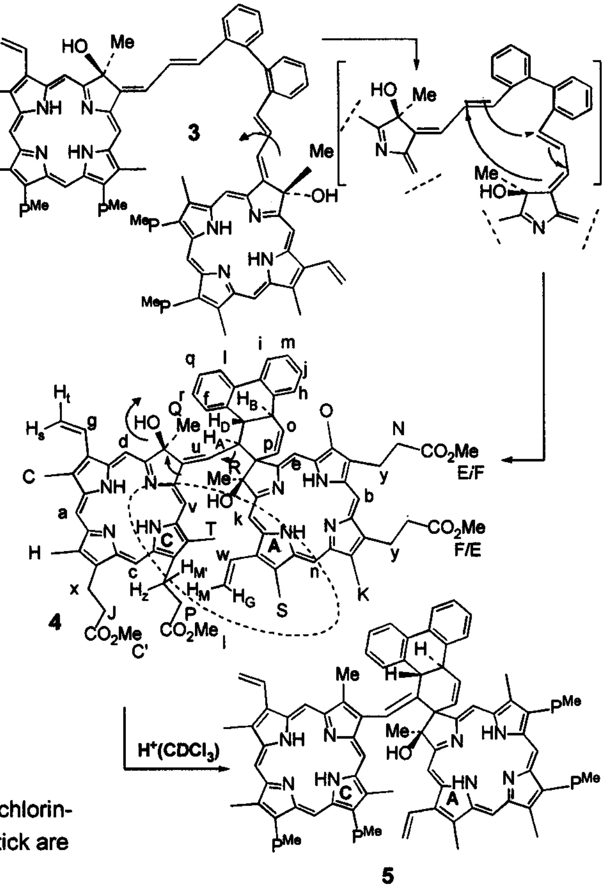
Scheme 1. Formation of the Chlorin-Spirochlorin Dimer 4

(in the NMR spectrum, the protons circled with dotted lines show the significant upfield shifts [see the text])





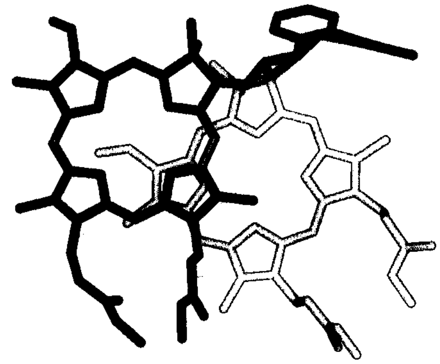


Figure 1. The structure of the energy optimized chlorin-spirochlorin dimer **4** where white stick and dark stick are used for chlorin and spirochlorin respectively.

transformation to a porphyrin−spirochlorin dimer **5**, which was formed upon leaving the NMR sample in $CDCl_3$ (without pyridine) at room temperature for an extended period of time. The dehydration product so obtained was isolated by preparative TLC, and the structure was assigned on the basis of UV−vis, HRMS, and NMR data.

Logically, the formation of dimer **5** can be explained by the dehydration of dimer **4** caused by a trace amount of acid present in $CDCl_3$ used as a NMR solvent.[11] In the electronic absorption spectrum of dimer **5**, the appearance of a new band at 578 nm with an additional 18 nm red shift for the Soret band in the dimer also indicated the presence of a porphyrin system. Furthermore, compared to **4**, the NMR spectrum of **5** showed entirely different structural features. For example, the vinyl protons attached to the porphyrin macrocycle and those of the spirochlorin system appeared in the range of 7.5−8.5 ppm, generally reported for chlorin and porphyrin systems. In the NMR spectrum of **4**, the upfield resonances at −0.13 and 0.18 ppm were assigned to the 12-methyl T of the chlorin and 2-methyl S of the spirochlorin; however, in dimer **5**, they appeared in the usual range of 2−3 ppm. These results indicate that porphyrin−spirochlorin dimer **5** possesses linear geometry and, thus, lacks cofacial $\pi-\pi$ interactions observed for dimer **4**.

The absorption and fluorescence emission spectra were measured in dichloromethane. The ground-state absorption spectra of dimer **4** reveal a Soret band at 390 nm and distinct Q-bands at 504, 540, and 663 nm. Excitation of dimer **4** at 388, 505, 540, or 664 nm gave a fluorescence emission band at 674 nm. In both dimers, the long-wavelength absorption was observed at 664 nm. However, dimer **5** exhibited a remarkable red shift in the Soret band appearing at 409 nm. The Q-band at 574 nm belongs to one of the bands (etio type) of the newly formed porphyrin system. Excitation of all the bands at 409, 505, 538, 574, or 664 nm afforded an emission at 672 nm. Interestingly, the two emission bands generally observed at 635−645 nm (strong) and 690−700 nm (weak) for a typical porphyrin macrocycle were found to be absent in the fluorescence spectrum of **5**, indicating that in this dimer porphyrin and chlorin moieties are not behaving as an individual molecule, but as a single macrocycle.

In conclusion, the new class of dimeric systems discussed here is the first example of chlorin−spirochlorin and porphyrin−spirochlorin dimers. The preparation of similar and related heterodimers consisting of chlorin and bacteriochlorin macrocycles as free bases or heterometalated analogues with variable linkages and their detailed photophysical studies are currently in progress.

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Supporting Information Available: Experimental details and spectroscopic and characterization data for compounds **1a** and **3**−**5**; molecular modeling procedure (17 pages).

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