Electronic Supplementary Material (ESI) to:

Syntheses, Structures, Modification, and Optical Properties of \textit{meso}-Tetraphenyl-2,3-dimethoxychlorin and Two Isomeric \textit{meso}-Tetraaryl-2,3,12,13-tetrahydroxybacteriochlorins

Lalith P. Samankumara, Matthias Zeller, Jeanette A. Krause, and Christian Brückner*

*Corresponding Author: Department of Chemistry, University of Connecticut, Unit 3060, Storrs, CT 06269-3060, U.S.A.
Fax: +860-486-2981; Tel: +860-486-2743; E-mail: c.bruckner@uconn.edu

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**Figure ESI-78.** $^1$H NMR Spectrum (400 MHz, CDCl$_3$) of **15d**
Comparison of the UV-Vis spectra of $E$ and $Z$ isomers of selected tetraol and tetramethoxy bacteriochlorin derivatives:

![Graph showing UV-Vis spectra of 4b-Z (solid red trace) vs 4b-E (broken black trace) in CH$_2$Cl$_2$.](image1)

**Figure ESI-79.** UV-vis spectra of 4b-$Z$ (solid red trace) vs 4b-$E$ (broken black trace) in CH$_2$Cl$_2$

![Graph showing UV-Vis spectra of 7d-Z (solid red trace) vs 7d-E (broken black trace) in CH$_2$Cl$_2$.](image2)

**Figure ESI-80.** UV-vis spectra of 7d-$Z$ (solid red trace) vs 7d-$E$ (broken black trace) in CH$_2$Cl$_2$
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Figure ESI-82. Collision-induced tandem mass spectrum (ESI+, 100%CH$_3$CN) of 7b-E
X-ray Crystal Structure Determination – General

Diffraction data were collected on a Bruker AXS SMART6000 CCD at 150(2) K (compound 5a) or a Bruker AXS SMART APEX CCD diffractometer at 100(2) K (all others) using monochromatic Mo Kα radiation with omega scan technique. The unit cells were determined, the data were collected, integrated corrected for absorption using SMART v5.628, SAINT v6.28A and SADABS v2.03 (compound 5a) or the Apex2 suite of programs (all others). The structures were solved by direct methods and refined by full matrix least squares against F2 against all reflections using SHELXTL. All hydrogen atoms were placed in calculated positions and were isotropically refined with a displacement parameter of 1.5 (methyl, hydroxyl) or 1.2 times (all others) that of the adjacent carbon, oxygen or nitrogen atom.

X-ray Crystal Structure Determination – Compound 4b-E · 4 MeOH

See also Table 3 (crystal Data) and the cif file of this structure. The crystal used was found to be consisting of two independent crystallites. The orientation matrices for the two components were identified using the program Cell Now, and the two components were integrated using Saint. The data were corrected for absorption using twinabs, and the structure was solved and refined using direct methods with only the non-overlapping reflections of component below a d-spacing threshold of 0.75. The Rint value given is for all reflections before the cutoff at d = 0.75 and is based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twin fractions (TWINABS (Sheldrick, 2007)).

Figure ESI-83. ORTEP Representation of 4b-E, top view, and numbering used. Ellipsoids at 50% probability level. The molecule is located on a crystallographic inversion center.
X-ray Crystal Structure Determinations – 4d-Z·4.62 CHCl₃
See also Table 3 (crystal Data) and the cif file of this structure

Figure ESI-84. ORTEP Representation of 4d-Z, top view, and numbering used. Ellipsoids at 50% probability level.

Figure ESI-85. ORTEP Representation of 4d-Z, side view, with CHCl₃ solvates. Ellipsoids at 50% probability level.

One chloroform molecule is inversion disordered over two sites with an occupancy ratio of 0.59(1) to 0.41(1). The carbon atoms in both moieties were constrained to have identical ADPs. Two other chloroform molecules refined to be only partially occupied with occupancies of 0.820(6) and 0.801(6), respectively.
X-ray Crystal Structure Determinations – 5a
See also Table 3 (crystal Data) and the cif file of this structure

**Figure ESI-86.** ORTEP Representation of 5a, and numbering used. Ellipsoids chosen at 50% probability.
X-ray Crystal Structure Determinations – 7d-\(E\) · 4 CH\(_2\)Cl\(_2\)
See also Table 3 (crystal Data) and the cif file of this structure

**Figure ESI-87.** ORTEP Representation of 7d-\(E\), top view, and numbering system used. Molecule located on a crystallographic inversion center. Ellipsoids at 50% probability level.

**Figure ESI-88.** ORTEP Representation of 7d-\(E\), top view, with CHCl\(_3\) solvates. The molecule is located on a crystallographic inversion center. Ellipsoids at 50% probability level.
X-ray Crystal Structure Determinations – 11a
See also Table 3 (crystal Data) and the cif file of this structure

![Figure ESI-89](image)

**Figure ESI-89.** ORTEP Representation of 11a, top view, and numbering used. The molecule is located on and disordered around a crystallographic 4-fold axis (see Figure ESI-91), and only one set of disordered atoms representing one individual molecule is shown. Ellipsoids at 50% probability level. Symmetry operators: (i) y, -x-1, -z+2; (ii) -x, -y, z; (iii) -y+1, x, -z+2. Labels for the phenyl rings are only shown for the crystallographically independent unit.

![Figure ESI-90](image)

**Figure ESI-90.** ORTEP Representation of 11a, side view. The molecule is located on and disordered around a crystallographic 4-fold axis and only one set of disordered atoms representing one individual molecule is shown. Ellipsoids at 50% probability level.
Figure ESI-91. ORTEP Representation of 11a, also showing the disorder. The molecule is located on a crystallographic 4-fold axis. Ellipsoids at 50% probability level.

**Note:**
Friedel pairs were merged prior to refinement.
The molecule, while itself asymmetric, is located on a four fold axis and thus disordered. Three pyrrol and two differently oriented dihydropyrrol-ol are disordered with each other in a ratio of 6 to 0.55(1) to 0.45(1).
Bond distances within the minor dihydropyrrol-ol sections were restrained to be chemically meaningful. As reference were used the known values found in the related di-hydroxyl compound. sp³-C-O distances were restrained to 1.41(2), sp³-C-sp³-C distances to 1.54(2) and sp²-C-sp³-C distances to 1.52(2) Å. Overlapping carbon atoms and the two oxygen atoms were constrained to have identical ADPs, and the overlapping C atoms were restrained to be approximately isotropic (within a standard deviation of 0.01 Å²).
Table ESI-1. Comparison of the optical properties of a porphyrin and its corresponding benzylic alcohol derivative.

<table>
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<tr>
<th>Porphyrin -CH₃/CH₂R</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;/nm (g/M&lt;sup&gt;1&lt;/sup&gt;cm&lt;sup&gt;-1&lt;/sup&gt;), reference</th>
<th>Porphyrin – CH₂OH/CHOHR</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;/nm (g/M&lt;sup&gt;1&lt;/sup&gt;cm&lt;sup&gt;-1&lt;/sup&gt;), reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Porphyrin -CH₃/CH₂R" /></td>
<td><img src="image2" alt="Solvent: CHCl₃" /> 399(177827), 498 (13489), 536 (9332), 567 (2344), 618 (4265)</td>
<td><img src="image3" alt="Higuchi, H.; Shinbo, M.; Usuki, Masanobu; Takeuchi, M.; Hasegawa, Y.; Tani, K.; Ojima, J. Bull. Chem. Soc. Jpn. 1999, 72, 1887-1898." /></td>
<td><img src="image4" alt="Solvent: CH₃Cl₂" /> 400 (15910), 498 (15400), 534 (12700), 566 (9600), 620 (7200)</td>
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<td><img src="image5" alt="Porphyrin – CH₂OH/CHOHR" /></td>
<td><img src="image6" alt="Solvent: CH₃Cl₂" /> 408.2, 507.6, 540.5, 578.0, 628.9</td>
<td><img src="image7" alt="Wu, G.-Z.; Gan, W.-X.; Leung, H.-K. J. Chem. Soc. Faraday Trans. 1991, 87(18), 2933-2937." /></td>
<td><img src="image8" alt="Solvent: CH₃Cl₂" /> 401.6, 505.0, 540.5, 574.7, 628.9</td>
</tr>
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<td><img src="image9" alt="Porphyrin – CH₂OH/CHOHR" /></td>
<td><img src="image10" alt="Solvent: CHCl₃" /> 403(239000), 503 (14600), 538 (5200), 566 (6500)</td>
<td><img src="image11" alt="Ponomarev, G. V.; Shul'ga, A. M. Chem. Heterocycl.Compd.(Engl. Transl.), 1984, 20(4), 383-388." /></td>
<td><img src="image12" alt="Solvent: CH₃Cl₂" /> 402, 502 (14600), 537 (6000), 565 (6100), 618 (815)</td>
</tr>
<tr>
<td><img src="image17" alt="Porphyrin – CH₂OH/CHOHR" /></td>
<td><img src="image18" alt="Freeman, B. A.; Smith, K. M.; Synth. Commun. 1999, 29(11), 1843-1856." /></td>
<td><img src="image19" alt="Torpey, J. W.; de Montellano, P. R. O. J. Org. Chem. 1995, 60(7), 2195-2199." /></td>
<td><img src="image20" alt="Solvent: CH₃Cl₂" /> 402 (186208), 499 (14454), 533 (8318), 568 (6761), 621.5 (4266).</td>
</tr>
</tbody>
</table>

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| Lee, D. A.; Smith, K. M. | Solvent: CHCl<sub>3</sub>  
400, 499, 533, 567, 594, 621  
Kojo, S.; Sano, S.  
Burns, D. H.; Caldwell, T. M.; Burden, M. W.  
The UV–vis spectrum of chlorin 3a shows a small (10 nm) hypsochromatic shift of the Q band relative to the corresponding chlorin.  
Burns, D. H.; Li, Y. H.; Shi, D. C.; Delaney, M. O.  
|---|---|
| Chau, D. D.; Clezy, P. S.; Henderson, R. W.; Pham, H.-Ph.; Ravi, B. N.  
Mironov, A. F.; Nizhnik, A. N.; Deruzhenko, I. V.; Bonnett, R.  
Ponomarev, G. V.; Maravin, G. B.  
| Kojo, S.; Sano, S.  
Crossley, M. J.; Harding, M. M.; Tansey, C. W.  
Terazono, Yuichi; Dolphin, David  
Solvent: CH<sub>2</sub>Cl<sub>2</sub>  
417, 514, 546, 588, 644  
417 (407378), 519 (165958), 552 (47863), 591 (37153), 648 (29512) |
| Solvent: CH<sub>2</sub>Cl<sub>2</sub>  
λ<sub>max</sub> (log ε): 388 (5.20), 496 (4.03), 522 (3.54), 544 (3.21), 594 (3.57), 618 (3.62), 648 (4.61)  
Ph |  
Burns, D. H.; Caldewl, T. M.; Burden, M. W.  
The UV–vis spectrum of chlorin 3a shows a small (10 nm) hypsochromatic shift of the Q band relative to the corresponding chlorin.  
Burns, D. H.; Li, Y. H.; Shi, D. C.; Delaney, M. O.  