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Dinaphthoporphycenes

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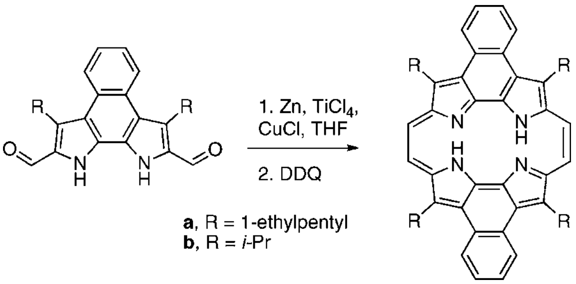
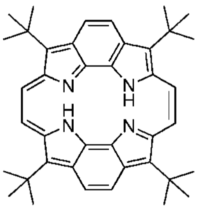
ABSTRACT



Naphthobipyrrole is a potentially useful building block for porphyrin and porphyrin analogue synthesis. Reported here is a simple, generalizable synthetic route to α-formylated, *β*-substituted naphthobipyrroles and their use in the preparation of binaphthoporphycenes. The resulting binaphthoporphycenes possess a planar geometry as determined via a single-crystal X-ray diffraction analysis; they also display absorption maxima that are bathochromically shifted compared to simple porphycenes.

Systems with extended conjugation pathways have attracted considerable attention in recent years due to their useful optical properties. This is particularly true in the case of porphyrin derivatives, where systems with larger π-electron peripheries have been explicitly targeted for synthesis due to their red-shifted light-absorbing properties. Such motivations have provided an incentive to develop so-called expanded porphyrins (i.e., systems with larger cores than their tetrapyrrolic "parents").[1] However, they have also led to the study of a number of other analogues. Among these latter are "fused" systems, wherein multiple direct links exist between the aromatic subunits present in various porphyrin and porphyrin analogues (e.g., pyrroles). Such systems generally display lower energy electronic transitions in the UV−vis spectral region, as well as enhanced nonlinear optical behavior. For instance, the lowest energy $\lambda_{\max}$ for a linearly fused octaporphyrin was found to be 2800 nm.[2] However, the preparation of fused porphyrin derivatives generally requires a near-herculean synthetic effort and often produces the target compounds in limited quantities.



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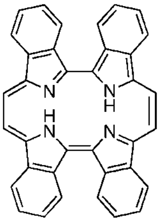

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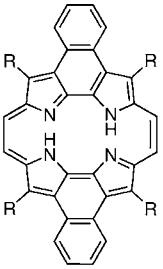

3a, R = 1-ethyl-pentyl
3b, R = *i*-Pr

An alternative approach to producing π-extended porphyrin-type frameworks involves annulation of additional aromatic rings onto the periphery of the macrocyclic core. To date, linearly annulated tetrabenzo-, tetranaphtho-, and tetraanthroporphyrins in the form of their respective zinc complexes have been studied in detail; these systems exhibit bathochromic shifts with the $\lambda_{\max}$ for the lowest-energy

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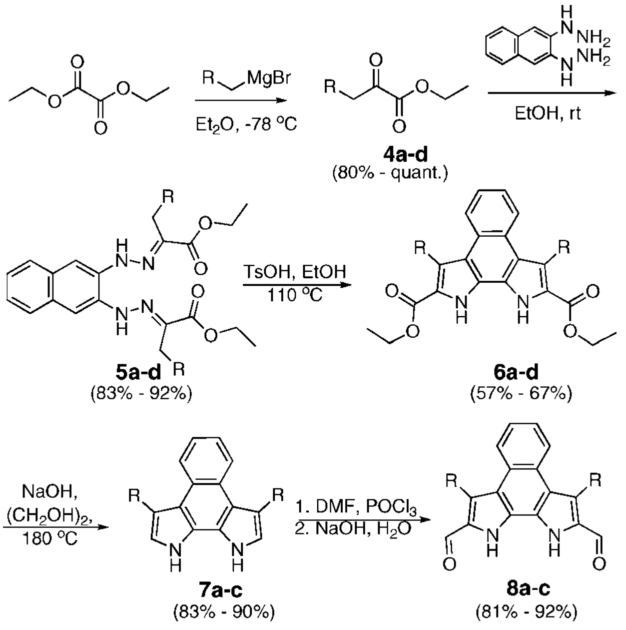
transition being moved to ca. 810 nm (Q-band) from the 602 nm seen for the lowest-energy Q-band of zinc tetraphenylporphyrin.[3] The palladium complexes of these annulated systems were also found to behave as efficient sensitizers for optical up-conversion via triplet−triplet annihilation when mixed with appropriate dyes.[4] Crossley and co-workers recently reported even greater efficiency in triplet−triplet annihilation up-conversion by using a palladium tetraquinoxaline porphyrin.[5]

Other annulated porphyrin analogues are known. These include but are not limited to azuliporphyrin,[6] phenanthroline porphyrins,[7] and benzosapphyrin.[8] However, much less is known about annulated porphycenes. In fact, to the best of our knowledge, only the fused *meso*-benzoporphycenes, dibenzoporphycene **1**,[9] and tetrabenzoporphycenes **2**[10] have been reported in the literature. On the other hand, the interesting optical and coordination features of porphycenes[11] provide an incentive to extend this limited class of compounds to include other annulated porphycene derivatives. With this goal in mind, we report here a simple and efficient route to dinaphthoporphycenes **3a** and **b**. We show that these flat systems display optical features that are bathochromically shifted compared to the parent porphycene.

The synthesis of the dinaphthoporphycenes **3a** and **b** is summarized in Scheme 1. It relies on the intermolecular McMurry coupling of dialdehyde precursors pioneered by Vogel,[12] as do most other syntheses of porphycenes.[13] The problem is thus one of preparing the appropriate annulated diformylated naphthobipyrroles. One potential precursor is the unsubstituted **7d**; this is a known compound.[14] However, this particular bipyrrole has been shown to react with various electrophiles (diazonium salts, Vilsmeier−Haack formylation, aminomethylation reaction) predominantly at the so-called β positions (i.e., at carbons 3 and 8);[15] this makes it less than ideal for our purposes. We therefore sought an alternative approach that would give diformylated naphthobipyrroles, such as **8a**−**c**, wherein the reactive β positions are blocked with alkyl groups. Here, an ancillary consideration was that the judicious choice of β-substituents would provide a means of modulating the solubility of these intermediates, as well as that of the final porphycene targets.

Scheme 1. General Route to Disubstituted Naphthobipyrroles



a R = 1-(ethyl)pentyl, **b** *i*-Pr, **c** *n*-C$_5$H$_{11}$, **d** R = H

To create systems with high solubility in organic media, branched alkyl chains are attractive as β-substituents. Such branched species have been used as solubilizing groups in, for example, polymer chemistry;[16] further, one particular branched system, 2-ethylhexane, functionalized at carbon 1 as both the halide and corresponding Grignard reagent, is commercially available. Therefore, our initial efforts focused on creating a bipyrrole containing this particular β-substituent. As a complement to this work, we also targeted the synthesis of analogues bearing the smaller *n*-pentyl and *i*-propyl substituents.

With the above considerations in mind, diethyl oxalate was reacted with the requisite Grignard reagents at −78 °C in accord with literature procedures.[17] This gave the corresponding ethyl α-oxocarboxylates **4a**−**c** in good yields. Ethyl pyruvate **4d** is commercially available.

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Subsequent reaction with 2,3-naphthalene bishydrazine[18] in ethanolic media at rt led to the nearly quantitative conversion to the corresponding bishydrazones **5a−d**. Compounds **5a−c** are new compounds. However, the bishydrazone **5d** was reported as an intermediate leading to the synthesis of **7d** (vide supra). However, full characterization data were lacking, with only melting point and elemental analysis results being provided.[14]

Interestingly, compounds **5a−d** exist in two different geometric isomeric forms. The individual species in question can be isolated via column chromatography over silica gel if desired. However, these compounds behave identically in the following step, namely, the Fischer indole synthesis. Thus, they were generally used without further purification.[19]

Subjecting **5a−c** to a 10-fold excess of *p*-toluenesulfonic acid hydrate in ethanol under reflux gave the diethyl 3,8-dialkyl-1,10-dihydro-benzo[e]pyrrolo[3,2-g]indole-2,9-dicarboxylate derivatives **6a−c** in good to excellent yields after purification via recrystallization or filteration through a short silica gel column. We found these conditions[20] to be superior to the use of polyphosphoric ester in unspecified concentration as originally used for the preparation **6d**.[14]

It is worth noting that diesters **6a−c** are also formed as a mixture of isomers, presumably different conformers arising from the restricted rotation of the alkyl substituents. The interconversion rate between the various isomers was such that in some cases the ^{1}H NMR signals were broadened, and in others more than one species could be observed at rt. In the case of the test system **6a**, heating the sample to 100 °C served to simplify the spectrum, producing one corresponding to a time-averaged symmetric species.

Diesters **6a−c**, which contain blocking β-substituents, were saponified and decarboxylated to produce the α-free species **7a−c**. This was done using a standard one-pot procedure that involves heating at reflux in ethylene glycol under an inert atmosphere.[21] This gave **7a−c** in 83−90% yield.

Vilsmeier−Haack formylation served to convert **7a−c** to **8a−c** in almost quantitative yield. As expected, **8a** had the highest solubility and proved soluble in most common organic solvents. The isopropyl-substituted dialdehyde **8b** showed moderate solubility, which allowed for crystallization from halogenated solvents, such as dichloroethane. On the other hand, compound **8c**, bearing linear *n*-pentyl substituents, proved minimally soluble in THF. In our estimation, this made this particular derivative less attractive for use in porphycene synthesis.[22]

Given the solubility characteristics of **8c**, only diformylbipyrroles **8a** and **8b** were subject to McMurry coupling.[21] Here, THF solutions of each aldehyde were added dropwise to the preformed titanium reagent in THF at reflux. This was done under an inert atmosphere over the course of 6 h by means of a syringe pump. The reaction mixtures were then maintained at reflux overnight. A basic workup then yielded a yellow-green fluorescent solution that was assumed to be dihydroporphycene (porphycenogen). This assignment was made on the basis of what was seen in the case of **1**; here, it was found that the corresponding porphycenogen is rather stable and can be isolated.[22]

Oxidation of the presumed porphycenogens was expected to give the desired porphycenes. To facilitate this process, 1 equiv of DDQ was added. This caused the solution to turn dark blue, as would be expected were the oxidation successful. After chromatographic purification over silica gel, porphycenes **3a** and **3b** were isolated in 52% and 15% yield, respectively.

As proved true for the intermediate bipyrrole derivatives **6a** and **8a**, porphycene **3a** bearing branched alkyl substituents showed poorly resolved ^{1}H NMR spectral features at rt. While not established unequivocally, this broadening is ascribed to hindered rotation of the branched alkyl groups and the existence of two or more tautomeric species at room temperature. In the event, an increase in spectral resolution could be achieved by heating the sample to 100 °C in toluene-d_8 (Figure 1).

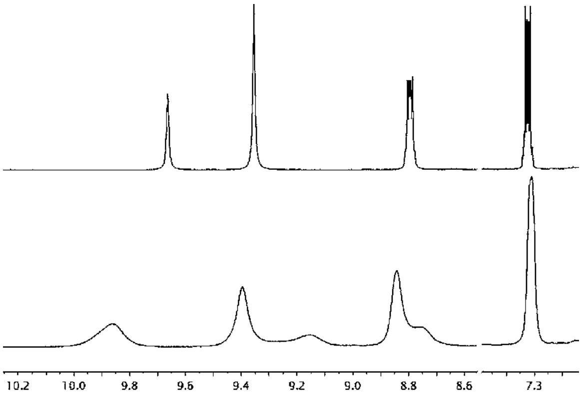

Figure 1. ^{1}H NMR spectra (low field portion) of porphycene **3a** in toluene-d_8 at 27 °C (bottom) and 100 °C (top).

Both porphycenes **3a** and **3b** display NH proton resonances at ca. 9.3 ppm ($CDCl_3$, rt, 400 MHz). This is in marked contrast to the original unsubstituted porphycene (NH resonance at 3.2 ppm, $CDCl_3$, 300 MHz).[12] However, it is in agreement with what is seen for the dibenzoporphycene **1** (NH signal at 10.6 ppm; $CDCl_3$).[23]

Both **3a**,**b** showed identical features in their respective UV−vis spectra (dichloromethane). In particular, Q bands

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(19) For more details see Figure S1 in Supporting Information.

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(22) Recently, we became aware that the group of Panda made **8c** and apparently carried it on to the corresponding porphycene. However, no structural data were presented. (Panda, P. K.; Sarma, T. *Abstracts of the Sixth International Conference on Porphyrins and Phthalocyanines (ICPP6)*; New Mexico, USA, 2010, p 191.)

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were seen at 725, 671, and 556 nm, and a Soret band was observed at 404 nm with shoulder at 389 nm (Figure 2). Qualitatively, these spectral features are typical for porphycenes and are thought to reflect a lower symmetry than typically found in porphyrins. In accord with design expectations, however, the visible portion of the spectrum is somewhat red-shifted as compared to nonannulated porphycenes (e.g., 2,7,12,17-tetrapropylporphycene for which Q bands at 634, 602, and 562 nm are seen).[24] These differences are attributed to the bipyrrole-fused naphthalene groups and to the resulting extension of the π-electron framework. Although further analyses are required, these structural changes relative to nonannulated porphycenes may also give rise to a possible intruder state,[9b] reflected in a weak transition at ca. 505 nm. Compound **3b** proved weakly fluorescent in dichloromethane.

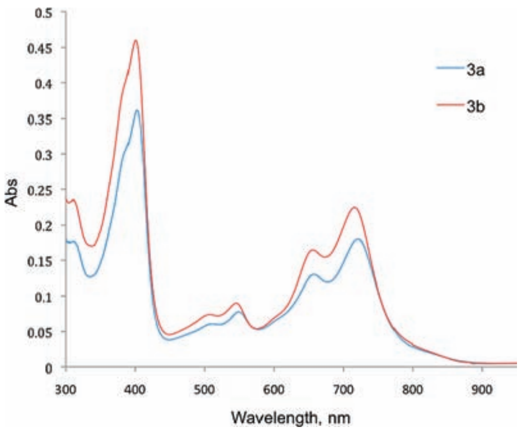

Figure 2. UV−vis spectra for **3a** and **3b** recorded in dichloromethane (0.11 mM).

Due to its higher crystallinity (and corresponding ease in handling) relative to **3a**, porphycene **3b** was subject to more detailed analysis using cyclic voltammetry. This particular annulated porphycene displays a reversible two-step oxidation process, which is characterized by peak potentials at 0.89 and 1.24 V (cyclic voltammetry, 1.5 mM/0.1 M TBAPF$_6$/DCM vs SCE; 100 mV/s). The fact that oxidation is more facile with respect to the tetrapropyl porphycene parent is considered consistent with a larger π-electron framework being present in **3**.[25] The observation of a reversible, anodically shifted reduction wave at −0.78 V (vs −1.04 V for the tetrapropyl system) provides further support for this conclusion. However, in contrast to what is seen in the case of the parent tetrapropyl porphycene, a second cathodic wave could not be observed in the case of **3b**.

This same, less soluble, isopropyl-substituted porphycene (i.e., **3b**) also yielded X-ray diffraction grade single crystals upon recrystallization from chloroform/hexane. The resulting structure revealed that this particular naphthoporphycene is nearly planar (Figure 3). The average deviation for the nitrogen atoms from the mean plane (excluding isopropyl groups) is ±0.15 Å. On the basis of this structural parameter, **3b** is slightly more distorted than tetrapropylporphycene for which the corresponding deviation is ±0.04 Å.[12] The shortest N−N distance in **3b** is 2.49 Å, whereas the corresponding separation in the parent, nonannulated porphycenes is typically 2.63 Å.[12] These structural differences, together with the NMR spectroscopic data discussed above, provide support for the notion that the N−H−N hydrogen bonds in the π-extended porphycenes reported here are stronger than those present in the original, nonannulated porphycenes.

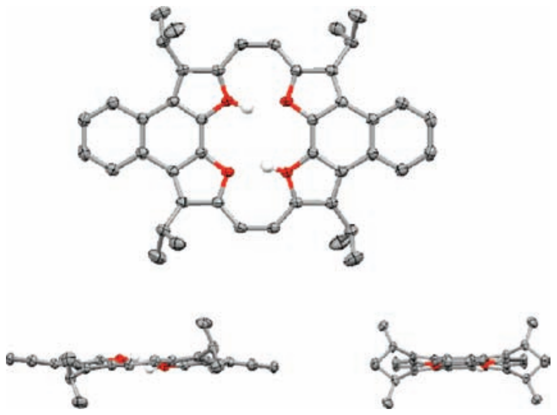

Figure 3. Three orthogonal views of the X-ray structure of **3b**. All hydrogen atoms bound to carbon atoms are omitted for clarity. Thermal elipsoids were scaled to the 50% probability level.

In conclusion, we have demonstrated a facile route to disubstituted naphthobipyrroles **6**−**8a**,**c**, chemistry that we think provides new precursors for use in porphyrin analogue synthesis. We have demonstrated the utility of these building blocks via the rational preparation of annulated porphycenes with extended π-frameworks. To the best of our knowledge, one of these products, porphycene **3b**, is the first annulated porphycene to be subject to X-ray diffraction-based structural analysis. Detailed physicochemical studies of it and other new porphycene analogues are currently in progress.

Acknowledgment. This work was supported by the National Institutes of Health (grant no. CA68682 to J.L.S) and the National Science Foundation (grant no. 0741973 for the X-ray diffractometer). Support under the WCU (World Class University) program (*R*32-2008-000-10217-0) is also acknowledged.

Supporting Information Available: Experimental procedures and characterization data of new compounds. X-ray crystallographic data of compound **3b** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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