Towards hydrocarbon analogues of the porphyrins: synthesis and spectroscopic characterization of the first dicarbaporphyrin†

Timothy D. Lash,* Jennifer L. Romanic, Michael J. Hayes and John D. Spence

Department of Chemistry, Illinois State University, Normal, Illinois 61790-4160, U.S.A. E-mail: tdlash@ilstu.edu

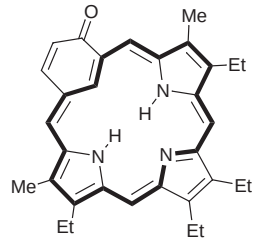
Received (in Corvallis, OR, USA) 8th December 1999, Accepted 5th March 1999

Condensation of 3,4-diethylpyrrole with 1,3-diformylindane in the presence of catalytic HBr afforded, following oxidation with $FeCl_3$, the first example of a dicarbaporphyrin in moderate yield; this novel bridged annulene system retains a strong diamagnetic ring current in ^{1}H NMR spectroscopy as well as a porphyrin-like UV–VIS spectrum.

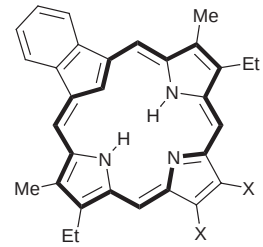
The nature of aromaticity in porphyrins and related structures has been the subject of much debate,[1] although these systems are commonly described as bridged diaza[18]annulenes.[2] This description also helps to explain the properties of synthetic porphyrinoids such as porphyrin isomers[3] and expanded porphyrins.[4] Nonetheless, the nitrogen atoms clearly play an important role in the spectroscopic and chemical properties of Nature's [18]annulenes. In earlier studies, the replacement of pyrrole subunits with furan and/or thiophene rings was explored.[3,5] While the resulting porphyrin analogues had substantially modified properties they retained the aromatic characteristics that are associated with the tetrapyrrolic structures. However, it has only been very recently that porphyrin analogues with carbocyclic rings replacing one of the pyrrolic moieties have been reported.[6–9] These include oxybenziporphyrin (**1**),[6] tropiporphyrin,[7] carbaporphyrins (*e.g.* **2**)[8] and carbachlorins.[9] It is noteworthy that all of these structures show powerful diamagnetic ring currents by ^{1}H NMR where the internal CHs resonate near $\delta -7$ and the external *meso*-protons mostly appear downfield between δ 9 and 10.[6–9] Although the substitution of one nitrogen by a carbon atom does not significantly disrupt the aromaticity of these macrocycles, it remains less than clear whether hydrocarbon porphyrinoids such as **3** would similarly retain porphyrin-like aromatic properties. While at the present time the characteristics of the tetracarbaporphyrin system **3** remain open to speculation, we now report the next step towards this hypothetical system.

During our earlier work on the synthesis of carbaporphyrins **2**,[8] we reacted the diformylindene intermediate **4** with diethylpyrrole **5** in the presence of TFA in CH_2Cl_2 (Scheme 1). Following neutralization, a nonpolar orange–brown band was collected from column chromatography on alumina that appeared to correspond to the dicarbaporphyrin **6**. The yield for this chemistry was very low (< 0.1%), but this is perhaps not surprising as the relatively high oxidation level of **4** must require that some type of reduction takes place in order to generate the aromatic porphyrinoid **6**. While these observations demonstrated that syntheses of dicarbaporphyrins are achievable, the methodology was not suitable for synthesizing more than trace amounts of material.

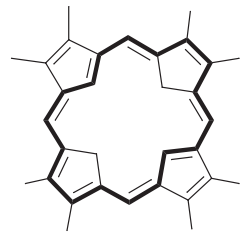
Given our recent successes in utilizing aliphatic dialdehydes in the synthesis of carbachlorins,[9] diformylindane **7** was considered to be a better choice for these investigations. This previously unknown compound was synthesized in two steps from norbornadiene derivative **8**[10] (Scheme 2). Oxidation of **8** with $KMnO_4$ afforded the diol **9** in 45% yield, and subsequent



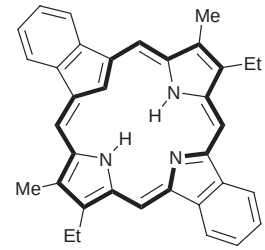
1



2a X = Et
b X–X = $(CH_2)_4$

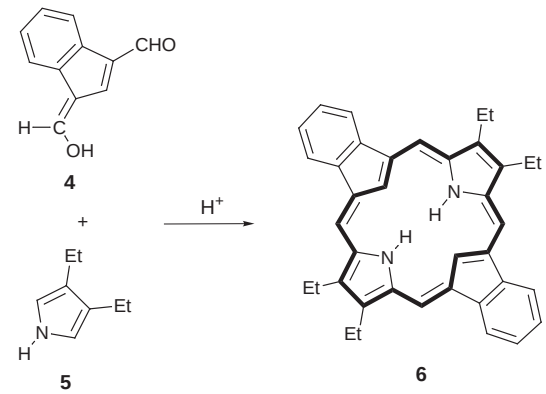


3



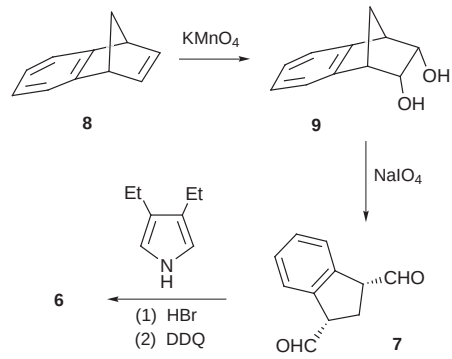
10

reaction with $NaIO_4$ afforded the required dialdehyde **7** as a pale yellow oil (quantitative). Condensation of **7** with diethylpyrrole **5** in the presence of TFA in CH_2Cl_2, followed by oxidation with 0.52 equiv. of DDQ, afforded the dicarbaporphyrin in low yields. Some improvement was observed when HBr was used as the acid catalyst, although the yields were still generally only approximately 1–2%. However, superior results (4.0–7.8%) were obtained when the DDQ oxidation was replaced by a brief treatment with aqueous $FeCl_3$. In this procedure, the acidic CH_2Cl_2 solution was washed successively with water, 0.1% $FeCl_3$ solution, water and saturated $NaHCO_3$. The crude material was chromatographed on Grade III neutral alumina eluting with CH_2Cl_2, and the colored fractions combined and further chromatographed on Grade I alumina. The first orange–brown band was evaporated and recrystallized from $CHCl_3$–MeOH to give the new porphyrinoid as dull purple crystals.‡



Scheme 1

† Part 15 of the series 'Conjugated Macrocycles Related to the Porphyrins'. Part 14: M. J. Hayes, J. D. Spence and T. D. Lash, *Chem. Commun.*, 1998, 2409.



Scheme 2

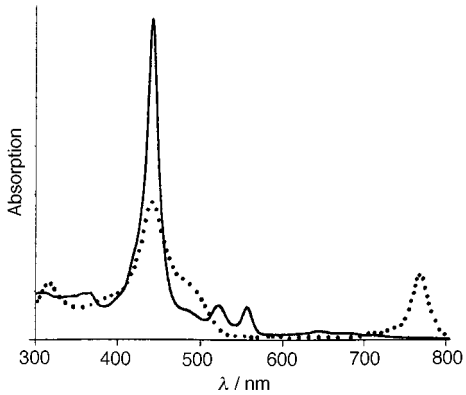
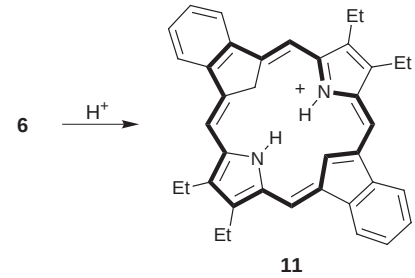


Fig. 1 UV–VIS spectra of dicarbaporphyrin **6**: free base in $CHCl_3$ (bold line); monocation **11** in 0.1% TFA–$CHCl_3$ (dotted line).

Solutions of the dicarbaporphyrin proved to be unstable, even in the absence of light, producing unidentified green materials. As a precaution, all manipulations were carried out with low ambient lighting and the columns, flasks and separatory funnels were covered with aluminium foil to limit photodegradation. In crystalline form, dicarbaporphyrin **6** appears to be reasonably stable and can be stored indefinitely.

Dicarbaporphyrin **6** was only sparingly soluble in $CDCl_3$, and this led to some problems in obtaining quality proton NMR spectra for this species. Trace impurities, together with the instability problems, led to the presence of small impurity peaks but otherwise the data were in full agreement with the proposed structure. Owing to the high level of symmetry in **6**, all four *meso*-protons are equivalent and resonate at δ 9.8. In addition, the internal CH protons appeared upfield at δ −5.7, while the NHs were noted at δ −4.8. It is evident that this species possesses a strong diamagnetic ring current and this supports the formulation of **6** as a bridged annulene structure with porphyrinoid aromaticity. A dibenzomonocarbaporphyrin **10** has also been prepared by dehydrogenation of **2b** with DDQ in refluxing toluene, and this structurally similar compound provides some useful comparisons. For the ^{1}H NMR spectra of carbaporphyrin **10** in $CDCl_3$, the external *meso*-protons appeared at δ 10.04 and 10.06, while the internal CH resonated at δ −6.6 and the NHs were observed near δ −4. These data indicate that the macrocyclic ring current is slightly greater in **10** compared to **6**, possibly due to the more crowded cavity in the latter which contains four hydrogens, compared to three in the former, and this factor may perturb that planarity of the structure. Further evidence for the porphyrin-like nature of **6** comes from the UV–VIS spectrum in $CHCl_3$ (Fig. 1) which shows a strong Soret band at 442 nm, together with a series of Q absorptions between 500 and 700 nm. EI mass spectrometry shows a strong molecular ion at *m/z* 520 and a small amount of benzylic fragmentation together with doubly charged ions of 25–30% the intensity of the base peak.

When small amounts of TFA were added, the brown solution turned green due to C-protonation to give the related cation **11**



Scheme 3

(Scheme 3). Although 0.1% TFA–$CHCl_3$ was sufficient to fully protonate the dicarbaporphyrin, further protonation to a dication was not observed even in 50% TFA–$CHCl_3$. The UV–VIS spectrum for **11** was radically altered (Fig. 1), showing a broadened Soret band of much lower intensity together with a strong absorption in the far red near 760 nm (Fig. 1). The proton NMR spectrum for **6** in TFA-$CDCl_3$ confirmed the presence of a strong aromatic ring current, although the lower symmetry of structure **11** resulted in a larger number of resonances; two 2H singlets were noted for the *meso*-protons near δ 10, while the upfield region showed the internal CH_2 at δ −4.3, the remaining CH at δ −3.3 and the two NHs near δ −1. The two benzo units also displayed surprisingly different chemical shifts and one of the 2H multiplets was shifted downfield to δ 9.7. These data are consistent with a benzo[18]annulene formulation for **11** where the C-protonated indene unit directs 18π-electron delocalization through one of the fused benzene rings.

The synthesis of the first dicarbaporphyrin represents an important step forward and allows us to set our sights on still further modified porphyrin analogs such as the tetracarbaporphyrin system **3**, a structure that must now be considered to be the Holy Grail in this research area. However, the marked decrease in stability of the dicarbaporphyrin system may not bode well for these investigations.

This work was supported by the National Science Foundation under Grant No. CHE-9732054, the Camille and Henry Dreyfus Scholar/Fellow Program and the Donors of the Petroleum Research Fund, administered by the American Chemical Society.

Notes and references

‡ *Selected data* for **6**: mp > 300 °C; λ_{max}($CHCl_3$)/nm ($\log_{10}\varepsilon$) 442 (5.29), 522 (4.28), 556 (4.29), 643 (3.66); λ_{max}(0.1% TFA–$CHCl_3$)/nm ($\log_{10}\varepsilon$) 439 (4.96), 581 (3.71), 629 (3.62), 697 (3.88), 766 (4.67); δ_H(400 MHz, $CDCl_3$) −5.68 (2H, br s), −4.82 (2H, br s), 1.83 (12H, t, *J* 7.5), 3.97 (8H, q, *J* 7.5), 7.74 (4H, m), 8.76 (4H, m), 9.79 (4H, s); δ_H(400 MHz, TFA–$CDCl_3$) −4.34 (2H, br s), −3.30 (1H, br s), −0.95 (2H, br s), 1.66–1.71 (12H, m), 3.79–3.86 (8H, m), 7.72–7.75 (2H, m), 8.55–8.59 (4H, m), 9.72–9.75 (2H, m), 10.02 (2H, s), 10.35 (2H, s); δ_C(TFA–$CDCl_3$) 17.30, 17.80, 19.13, 19.52, 33.01, 105.68, 113.14, 120.86, 123.15, 123.55, 127.97, 131.30, 135.53, 136.44, 137.87, 140.13, 141.73, 142.24, 143.06, 143.73; HRMS: Calc. for $C_{38}H_{36}N_2$: 520.28785. Found: 520.28783. Calc. for $C_{38}H_{36}N_2.^1/_2H_2O$: C, 86.16; H, 7.04; N, 5.29. Found: C, 86.12; H, 6.68; N, 4.50%).

1 *E.g.* M. K. Cyranski, T. M. Krygowski, M. Wisiorowski, N. J. R. van E. Hommes and P. von R. Schleyer, *Angew. Chem., Int. Ed.*, 1998, **37**, 177.
2 E. Vogel, W. Haas, B. Knipp, J. Lex and H. Schmickler, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 406; T. D. Lash and S. T. Chaney, *Chem. Eur. J.*, 1996, **2**, 944.
3 E. Vogel, *J. Heterocycl. Chem.*, 1996, **33**, 1461.
4 J. Ayub and D. Dolphin, *Chem. Rev.*, 1997, **97**, 2267.
5 M. J. Broadhurst, R. Grigg and A. W. Johnson, *J. Chem. Soc. (C)*, 1971, 3681.
6 T. D. Lash, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2533.
7 T. D. Lash and S. T. Chaney, *Tetrahedron Lett.*, 1996, **37**, 8825.
8 T. D. Lash and M. J. Hayes, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 840; T. D. Lash, *Chem. Commun.*, 1998, 1683.
9 M. J. Hayes and T. D. Lash, *Chem. Eur. J.*, 1998, **4**, 508.
10 T. F. Mich, E. J. Nienhouse, T. E. Farina and J. J. Tufariello, *J. Chem. Educ.*, 1968, **45**, 272.

Communication 8/09639B