The azuliporphyrin-carbaporphyrin connection†

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Under base catalyzed conditions, reaction of azuliporphyrin 3 with *tert*-butyl hydroperoxide affords the benzocarbaporphyrins 2a and 2b; a mechanism for the formation of 2b is proposed.

Recently, diverse monocyclic dialdehydes have been shown to condense with tripyrranes [2,5-bis(pyrrol-2-ylmethyl)pyrroles] under the so-called '3 + 1' conditions[1] to give structural analogs of the porphyrins including oxybenziporphyrin **1**[2] and carbaporphyrins **2**.[3–6] Lash and Chaney reported[4] that azulene-1,3-dicarbaldehyde condensed with a tripyrrane in the presence of 5% TFA in CH_2Cl_2 to give the unique borderline aromatic macrocycle 'azuliporphyrin' **3** (Scheme 1) in good yield. In complete contrast, Breitmaier[5] found that under somewhat different conditions these reactants afforded low yields of benzocarbaporphyrins **2a–c** where the seven-membered ring of the azulene precursor has undergone a ring contraction to give the fused benzo moiety of **2**. No explanation for the origins of these materials was offered, but it should be noted that **2a** can be more directly obtained in excellent yields and isomerically pure form from 1,3-diformylindene.[3] Azuliporphyrin **3** is a cross-conjugated system for which dipolar resonance contributors (*e.g.* **4**) can be written that impart a degree of porphyrinoid aromaticity onto the macrocycle and this view is supported by the observation of a weak diatropic ring current in the proton NMR spectrum of **3**.[4] This feature is greatly enhanced in the presence of acid due to the increased ability of the aromatic species to allow charge delocalization.[4]

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2a X = Y = H
b X = CHO, Y = H
c X = H, Y = CHO

Scheme 1

During the course of our studies, we noted that addition of small amounts of pyrrolidine to an NMR solution of the sparingly soluble azuliporphyrin caused the green solution to turn brown. The resulting NMR spectrum (Fig. 1) displayed a carbaporphyrin-like ring current[3] where the internal CH was shifted upfield from δ 1.5 in **3** to δ −7 and the external *meso*-protons were similarly deshielded to resonate near δ 10. The seven-membered ring protons nearest to the macrocycle produced a broadened 2H doublet at δ 7.85 and a 2H dd was noted near δ 6. These data implied that **3** had undergone a nucleophilic substitution on the seven-membered ring to give the pyrrolidine–carbaporphyrin adduct **5** (Scheme 1). The process must be regioselective as a single symmetrical isomer dominates the NMR spectrum, but the reaction is reversible and removal of pyrrolidine simply afforded starting material. Further evidence for the formation of a carbaporphyrin structure comes from UV–VIS spectroscopy; addition of pyrrolidine causes a Soret-like band to emerge near 400 nm (Fig. 2).

The observed reactivity of the seven-membered ring suggested that the azuliporphyrin system could be functionalized

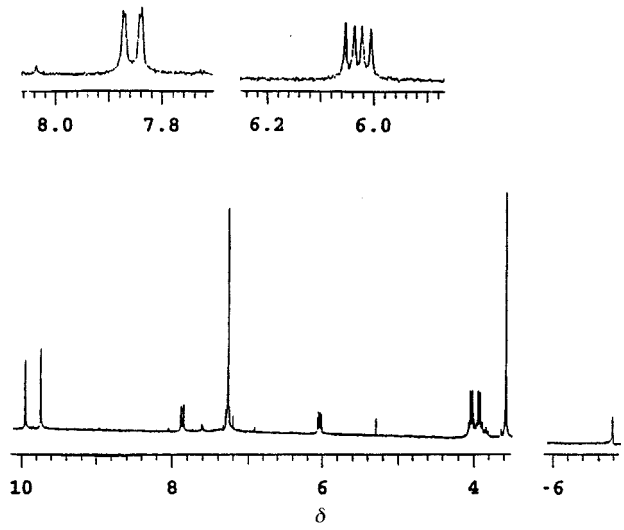


Fig. 1 Partial 300 MHz ^{1}H NMR spectrum of azuliporphyrin **3** in the presence of trace pyrrolidine in $CDCl_3$. The region between δ 1 and 4 is obscured by the pyrrolidine absorptions.

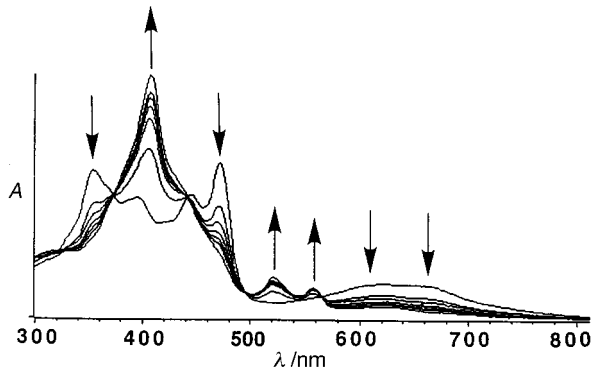
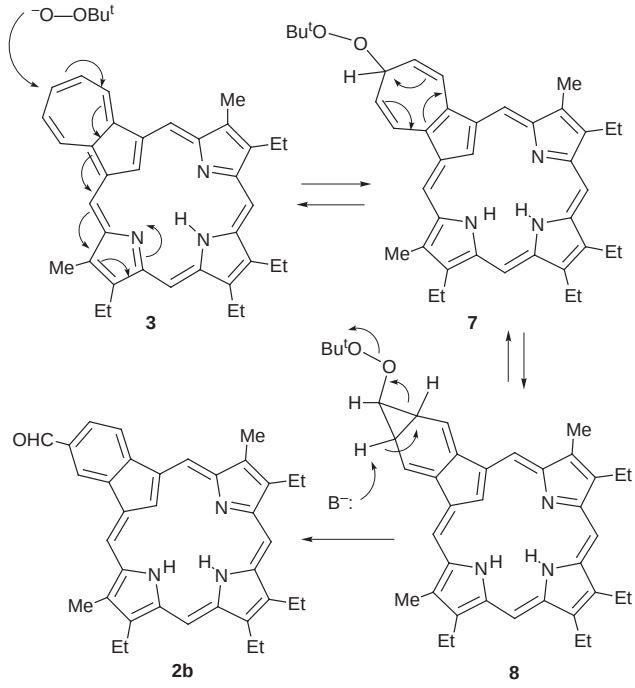


Fig. 2 Electronic absorption spectra of azuliporphyrin **3** in $CHCl_3$ with 0, 1000, 2000, 3000, 4000, 5000 or 9000 equiv. of pyrrolidine. The development of a Soret band near 400 nm is clearly evident.

under suitable reaction conditions. We were particularly interested in the possibility of generating the fused tropone structure **6**, which might be formed by an addition-elimination process. However, attempts to form **6** by reacting **3** with NaOCl were unsuccessful. Alkaline solutions of H_2O_2 reacted with **3** to give complex mixtures of products that appeared to be carbaporphyrins, and this prompted us to investigate the reaction of **3** with *tert*-butyl hydroperoxide. Interestingly, when the reaction was carried out with Bu^{t}OOH (5 equiv.) in KOH–MeOH and CH_2Cl_2 at room temperature, benzoporphyrin **2a** was the main isolatable product (30%) together with a small amount of **2b**. On the other hand, the formyl derivative **2b** was the predominant product (40%) when the reaction was carried out with Bu^{t}OOH and Bu^{t}OK in CH_2Cl_2, although some **2a** (15%) was also isolated in this case. Carbaporphyrin **2a** was identical to our previously synthesized material[3] and structure **2b** was fully characterized by NMR and mass analysis.§

The formation of **2b** can be rationalized by the mechanism shown in Scheme 2. Following nucleophilic attack by the *tert*-butyl peroxide anion, the adduct **7** may undergo a Cope rearrangement to give the cyclopropane **8** and subsequent elimination of *tert*-butyl alcohol would give the aldehyde **2b**. A third carbaporphyrin appears to be present by TLC (very minor) and may correspond to **2c**; this would result from the initial nucleophilic attack occurring at a different position on the azulene ring. The formation of **2a** may also arise from intermediate **8**, in this case by elimination of *tert*-butyl alcohol and carbon monoxide. Aldehyde **2b** cannot be an intermediate in the formation of **2a** as it does not decarbonylate or oxidize under these reaction conditions, although it is possible that **2a** arises from the elusive tropone **6** instead. It is noteworthy that tropylium salts also ring contract, in this case to form benzene, upon oxidation with hydrogen peroxide or MCPBA and a similar mechanism has been proposed for this chemistry.[7] Clearly our observations help to explain the results obtained by the Bonn group, although the complex mixtures of reagents used in their studies makes mechanistic investigations impractical. The new results also demonstrate that isomerically pure functionalized carbaporphyrins are easily obtainable from azuliporphyrin and this will allow further aspects of the chemistry of this remarkable new carbaporphyrin family to be explored.



Scheme 2

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Notes and References

† Part 11 of the series 'Conjugated Macrocycles Relalted to the Porphyrins'. Part 10: M. J. Hayes and T. D. Lash, *Chem. Eur. J.*, 1998, **4**, 508.

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§ *Selected data* for **2b**: δ_H(300 MHz, $CDCl_3$) −7.12 (1H, s), −4.45 (2H, br s), 1.79–1.89 (12H, 4 overlapping triplets), 3.51 (3H, s), 3.52 (3H, s), 3.90–4.05 (8H, 4 overlapping quartets), 8.10 (1H, d, *J* 7.5), 8.67 (1H, d, *J* 7.5), 9.06 (1H, s), 9.70 (1H, s), 9.71 (1H, s), 9.78 (1H, s), 9.80 (1H, s), 10.36 (1H, s); HRMS: Calc. for $C_{36}H_{37}N_3O$: 527.2937. Found: 527.2933. The proton NMR spectrum shows no indication of tautomeric species at room temperature, adding further support to our previous suggestion (ref. 3) that the German group had isolated isomeric mixtures of carbaporphyrins in their studies (ref. 5).

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