Pergamon

Tetrahedron Letters, Vol. 37, No. 28, pp. 4873-4876, 1996
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0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)00998-7

Versatile "3 + 1" Syntheses of Acenaphthoporphyrins, a New Family of Highly Conjugated Tetrapyrroles

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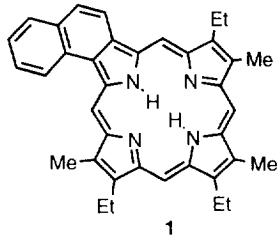
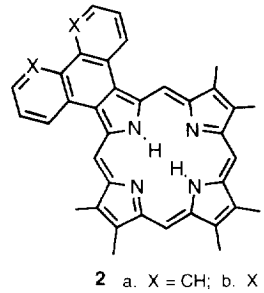
Abstract: *Acenaphthoporphyrins, a new group of porphyrins with strongly red shifted electronic absorption spectra, have been prepared by the acid catalysed condensation of a pyrrole-2,5-dicarboxaldehyde with acenaphthotripyrranes; similarly, c-annelated pyrroledialdehydes afforded the related opp-diacenaphthoporphyrins and a mixed porphyrin system with fused phenanthrene and acenaphthylene rings.* Copyright © 1996 Elsevier Science Ltd

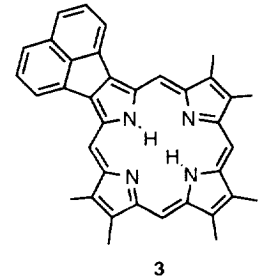
The porphyrins and phthalocyanines are among the most widely studied classes of organic compounds,[1,2] and have many applications in the areas of material science, catalysis, nanotechnology and medicine. In some of these applications, systems with strong absorptions in the red/near infrared region are required.[3] Porphyrins show a strong absorption in the near ultraviolet near 400 nm (the Soret band) and four smaller bands in the visible region, although the longest wavelength absorption is generally < 630 nm. Several strategies have been explored to produce red shifted porphyrinoid chromophores, including syntheses of expanded porphyrins[4] and suitably modified hydroporphyrins.[5] An alternative possibility is to extend the porphyrin chromophore by adding fused aromatic subunits. Benzo-,[6,7] naphtho- (e.g. **1**),[7,8] phenanthro- (**2a**)[9] and phenanthrolinoporphyrins (**2b**)[10] have been synthesized, but these systems, somewhat surprisingly, showed rather limited bathochromic shifts. In this paper, we report the synthesis of a new group of extended porphyrins, the acenaphthoporphyrins (**3**), that show remarkably red shifted uv-vis spectra in stark contrast to previously reported annelated porphyrins.



1



2 a. X = CH; b. X = N

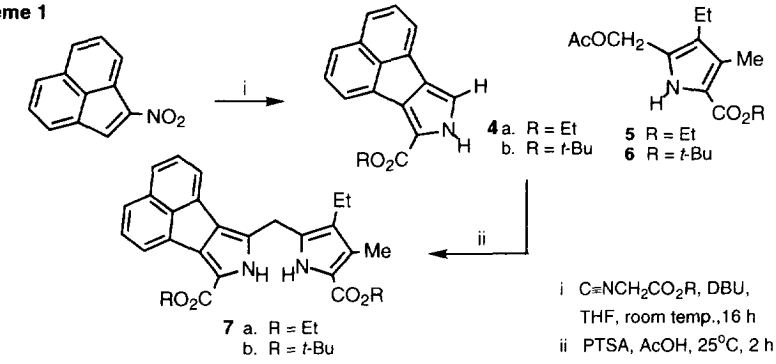


3

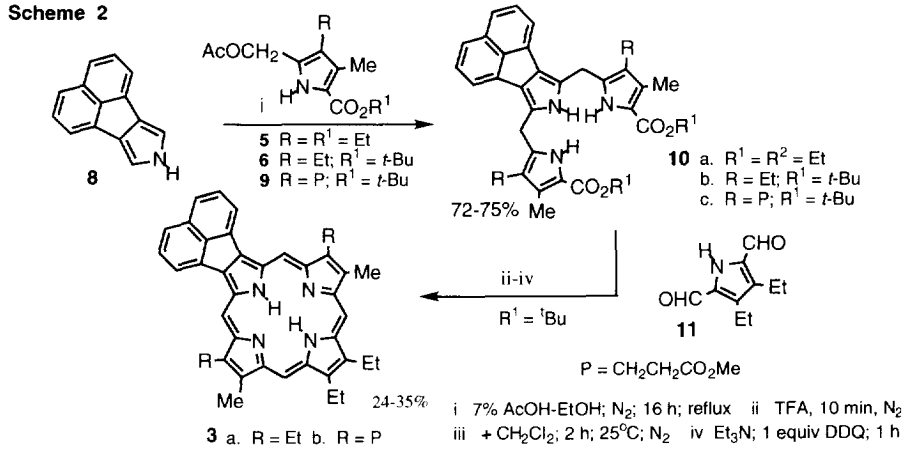
Previously, our group[11] and others[12] demonstrated that certain nitroarenes condense with isocyanoacetates in the presence of the non-nucleophilic base DBU to give *c*-annelated pyrroles. This approach allowed the preparation of suitable pyrrolic precursors for the synthesis of porphyrins **2a** and **2b**.[9,10] Condensation of 1-nitroacenaphthylene[13] with ethyl or *tert*-butyl isocyanoacetate similarly gave the corresponding acenaphthopyrroles **4** in 44-45% yield (Scheme 1). Pyrrole **4a** underwent an acid catalyzed condensation with

acetoxymethylpyrrole **5** to afford the dipyrrylmethane **7a**; similarly, **4b** condensed with pyrrole **6** to yield the related di-*tert*-butyl ester **7b**. Dipyrrylmethanes are commonly converted into porphyrins by first removing the ester protective groups and carrying out a condensation with a dipyrrylmethanedialdehyde in the presence of a suitable acid catalyst.[14] This "2 + 2" approach (the MacDonald condensation) works well for the synthesis of naphthoporphyrins **1** and phenanthroporphyrins **2a**. However, poor yields of impure porphyrin products resulted from our attempts to condense acenaphthodipyrrylmethanes **7** with dipyrrylmethanedialdehydes under these conditions.

Scheme 1



Scheme 2

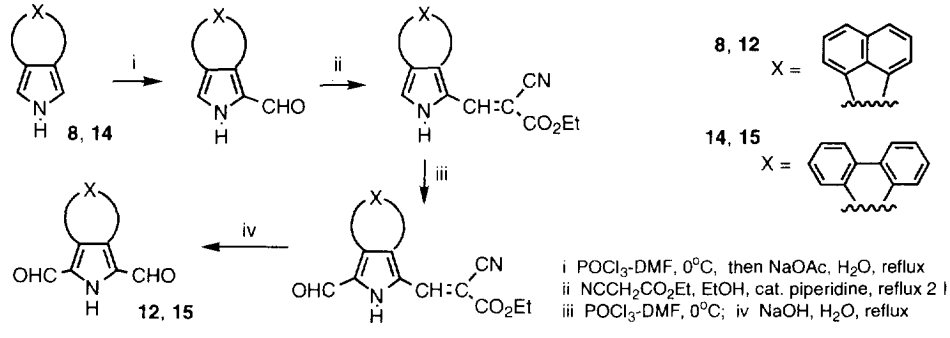


At this stage, we turned to the little used "3 + 1" variant on the MacDonald condensation.[10,15,16] Treatment of ethyl ester **4a** with potassium hydroxide in refluxing ethylene glycol afforded the unsubstituted tetracycle **8** in 70-83% yield (Scheme 2). Condensation of **8** with two equivalents of an acetoxymethylpyrrole (**5**, **6** or **9**) in refluxing acetic acid-ethanol gave the required tripyrranes **10**.[17] The use of such mild conditions allowed the introduction of *tert*-butyl ester protective groups. This was a convenience, as the ester groups of **10b** or **10c** could be cleaved with TFA at room temperature. Dilution of the mixture with dichloromethane, followed by condensation with the known pyrroledialdehyde **11**,[18] neutralisation with triethylamine and oxidation with one

equivalent of DDQ allowed the generation of acenaphthoporphyrins **3** in a one flask sequence. Following chromatography on neutral alumina and recrystallization from chloroform-methanol, porphyrins **3a**[19] and **3b** were isolated in 24-35% yield. Unlike porphyrins **1**, **2a** and **2b**, the uv-vis spectra of these new tetrapyrroles showed large bathochromic shifts relative to octaalkylporphyrins, in addition to a Soret band that was split into three components.

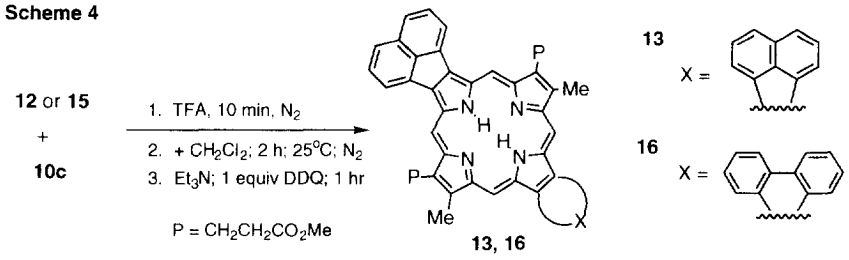
The unusual and potentially valuable spectroscopic characteristics of these monoacenaphthoporphyrins led us to investigate the synthesis of related chromophores. An acenaphthopyrroledialdehyde **12** was prepared in an overall 88% yield from **8** using a formylation, protection, reformylation, deprotection strategy based upon an earlier synthesis[20] of 2,5-pyrroledicarboxaldehyde (Scheme 3). Condensation of **12** with tripyrrane **10c** afforded the *opp*-diacenaphthoporphyrin **13**[19] in 21% yield (Scheme 4). The presence of the second acenaphthylene unit induced impressive additional bathochromic shifts and produced a strong band near 700 nm.

Scheme 3



The versatility of the "3 + 1" approach was further demonstrated by preparing a mixed porphyrin system with fused acenaphthylene and phenanthrene subunits. Phenanthro[9,10-*c*]pyrrole **14** was converted into the corresponding dialdehyde **15** (Scheme 3); subsequent condensation of **15** with acenaphthotripyrrane **10c** afforded the mixed porphyrin system **16**[19] in good yield. Interestingly, **16** showed only a small red shift in its uv-vis absorption bands compared to acenaphthoporphyrins **3**, confirming our earlier conclusion[9] that phenanthrene units behave more like auxochromes than part of a truly extended chromophore.

Scheme 4



Acenaphthoporphyrins show remarkably red shifted spectra and are easily prepared by the "3 + 1" approach. The previously underused "3 + 1" methodology also provides access to many related highly conjugated systems, including diacenaphthoporphyrins and porphyrins with mixed ring fusions.

Acknowledgements.

This material is based upon work supported by the National Science Foundation under Grant No. CHE-9500630 and the University Research Fund of Illinois State University. We also thank the National Science Foundation (Grant Nos. CHE-9001175 and DUE-9452437) for providing funds to purchase two Varian 300 MHz NMR spectrometers. Mass spectral data were obtained from the Mass Spectral Laboratory, School of Chemical Sciences, University of Illinois at Urbana-Champaign, supported in part by a grant from the National Institute of General Medical Sciences (GM 27029).

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17. General procedure for the preparation of tripyrranes **10**: A mixture of **8** (0.500 g) and **5** (1.387 g) in acetic acid (2 mL) and ethanol (30 mL) was stirred and refluxed under a nitrogen atmosphere for 16 h. The solution was cooled, poured into 100 mL of ice-water and allowed to stand for 3 h. The precipitate was filtered, dried *in vacuo* and recrystallized from chloroform to give **10a** (1.17 g; 77%) as a pale yellow powder, mp 258-260°C. ^{1}H NMR ($CDCl_3$): δ 0.93 (6H, t, 2 x pyrrole-CH_2CH_3), 1.03 (6H, t, 2 x OCH_2CH_3), 2.22 (6H, s, 2 x pyrrole-CH_3), 2.47 (4H, q, 2 x pyrrole-CH_2), 3.43 (4H, br, 2 x pyrrole-CH_2CH_3), 4.13 (4H, s, 2 x bridge-CH_2), 7.47-7.57 (6H, m, 6 x acenaphthylene-H), 9.12 (1H, br), 11.15 (2H, br) (3 x NH). Tripyrranes **10b** and **10c** could not be recrystallized and these vacuum dried powders were used without further purification.
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19. Selected spectroscopic data: **3a**: Uv-vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 390 (4.82), 432 (5.04), 454 (4.87), 528 (4.19), 571 (4.21), 598 (4.11), 660 nm (4.16); Uv-vis (0.5% TFA-$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 445 (5.31), 557 (4.05), 575 (4.21), 624 nm (4.57); ^{1}H NMR ($CDCl_3$): δ - 3.23 (2 x NH), 1.89-97 (12H, m, 4 x CH_2CH_3), 3.61 (6H, s, 2 x porphyrin-CH_3), 4.07-4.13 (8H, m, 4 x CH_2CH_3), 7.95 (2H, t), 8.04 (2H, d, J = 7.5 Hz), 8.90 (2H, d, J = 6.3 Hz) (6 x acenaphthylene-H), 9.99 (2H, s), 10.43 (2H, s) (4 x *meso*-H); HRMS (EI): Calcd for $C_{40}H_{38}N_4$: 574.30965. Found: 574.30973. **13**: Uv-vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 440 (5.06), 476 (5.24), 548 (4.33), 624 (4.24), 692 nm (4.80); Uv-vis (0.5% TFA-$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 471 (5.37), 595 (4.12), 600 (4.12), 660 nm (4.89); ^{1}H NMR (TFA-$CDCl_3$): δ - 3.16 (2H, br), - 3.01 (2H, br) (4 x NH), 3.31 (4H, t, J = 7.5 Hz, CH_2CH_2CO), 3.74 (6H, s), 3.81 (6H, s) (2 x porphyrin-CH_3 and 2 x OCH_3), 4.61 (4H, t, J = 7.5 Hz, CH_2CH_2CO), 8.14 (4H, t), 8.35 (4H, d, J = 8.4 Hz), 9.16 (2H, d, J = 6.9 Hz), 9.27 (2H, d, J = 6.9 Hz), 11.04 (2H, s), 11.26 (2H, s) (4 x *meso*-H); HRMS (FAB): Calcd for $C_{50}H_{38}N_4O_4$ + H: 759.2971. Found: 759.2968. **16**: Uv-vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 435 (5.21), 539 (4.05), 584 (4.56), 611 (4.53), 674 nm (4.14); Uv-vis (0.5% TFA-$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 467 (5.40), 593 (4.18), 649 nm (4.78); ^{1}H NMR (TFA-$CDCl_3$): δ - 3.15 (1H, br), - 2.67 (1H, br), - 2.00 (2H, br) (4 x NH), 3.26 (4H, t, J = 7 Hz, CH_2CH_2CO), 3.72 (12H, s, 2 x porphyrin-CH_3 and 2 x OCH_3), 4.51 (4H, t, J = 7 Hz, CH_2CH_2CO), 8.11-8.21 (4H, m), 8.30-8.34 (4H, m), 9.26 (4H, t), 9.93 (2H, d, J = 8.4 Hz), 11.19 (2H, s), 11.44 (2H, s) (4 x *meso*-H); HRMS (FAB): Calcd for $C_{52}H_{40}N_4O_4$ + H: 785.3128. Found: 785.3132.
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(*Received in USA* 8 *April* 1996; *revised* 14 *May* 1996; *accepted* 15 *May* 1996)