A Conformationally Constrained Conjugated Porphyrin Dimer

Jeffrey J. Gosper* and Mukhtar Ali

Molecular Probes Unit, Department of Chemistry, Brunel University, Uxbridge, Middlesex, UK UB8 3PH

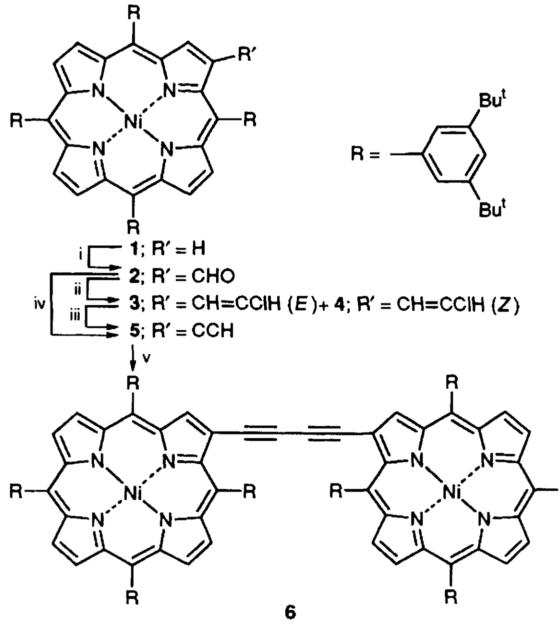
The synthesis, conformational analysis, and electronic absorption spectrum of a soluble, conformationally constrained porphyrin dimer linked *via* a buta-1,3-diyne unit attached to the β-pyrrolic positions is reported.

In recent years there has been considerable research directed towards the synthesis and study of systems involving multiple porphyrin macrocycles. Most of this effort has concentrated on porphyrin arrays where either no or limited conjugation exists between the porphyrin units. Such systems are finding applications in areas such as photodynamic therapy in cancer treatment[1] and as models for electron transfer reactions that take place during photosynthesis.[2] There are far fewer examples of investigations involving multiporphyrin arrays in which extensive conjugation exists between the porphyrin macrocycles.[3–11] Such systems could allow direct electronic communication between the porphyrins and thereby be of interest in the field of molecular electronics.

In most functionalized porphyrins, 'biphenyl like' steric interactions between the porphyrin macrocycle and appended functionality restricts such systems from attaining coplanarity. As such, highly conjugated multiporphyrin systems are difficult to design and synthesize. Acetylene groups attached directly to the porphyrins provide a means of minimizing these steric interactions, yet facilitate conjugation between connected porphyrins. Initially, we have concentrated on the synthesis and study of a dimeric porphyrin system in which the conjugating linker is a buta-1,3-diyne (diacetylene). In this paper we report the synthesis and some physical properties of a system which connects two porphyrins *via* their β-pyrrolic positions. However, this type of linkage is not limited to the β-positions and the described work is part of a larger programme to prepare and study a wide range of highly conjugated porphyrin oligomers.

At the outset of this work there were very few reported examples of porphyrins bearing acetylene functionality,[4–6] and only one example of a dimeric system.[6] More recently, Arnold and Nitschinsk,[7,8] and Anderson,[9] have extended this area of chemistry to a range of dimeric systems based on tetraphenyl- and octaalkyl-porphyrins. We chose the readily soluble 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin to be the basis of our dimeric system. The *tert*-butyl groups assist in solubility and also in constricting the conformational freedom of the target dimer.

Porphyrin **2**[†][‡] can be converted into chloroalkenes **3** and **4** in virtually quantitative yield by treatment with chloromethyltriphenylphosphonium iodide and a single equivalent of potassium *tert*-butoxide in THF at −78 °C (Scheme 1). The ratio of **3** to **4** obtained in this reaction is 4 : 1. This mixture of chloroalkenes can be subsequently converted to acetylenic porphyrin **5** in 86% yield by treatment with further *tert*-butoxide. The dehydrochlorination can be achieved *in situ* during the Wittig reacton, if excess *tert*-butoxide is used. In this case **5** is obtained in 78% yield directly from **2**. Unlike the acetylenic porphyrin of Arnold *et al.*[6] porphyrin **5** is completely stable to column chromatography over silica. More remarkably, this compound is also stable to standard Glazer oxidative coupling, as well as the Hay variation,[12] which successfully couples closely related systems.[7,9] Oxidative coupling of **5** can be achieved using a mixture of tetrakis(triphenylphosphonium)palladium(0), chloroacetone, copper(I) iodide, and triethylamine in benzene under nitrogen at room temperature,[13] although the reaction rate is still rather slow. After a reaction period of a few days, dimer **6** can be isolated in fair yield (50%) along with a significant amount of unreacted starting porphyrin (38%).[§] Raising the reaction temperature and/or increasing the equivalents of reactants, failed to enhance the reaction rate or yield of dimer **6**. (2-Ethynyl-5,10,15,20-tetraphenylporphyrinato)nickel(II),[7] which lacks the *tert*-butyl groups, was shown to be efficiently coupled under the above conditions to give the corresponding dimer in 86% yield. In this case, dimerization was complete within 45 min at room temperature, whereas oxidative



Scheme 1 *Reagents and conditions* i, DMF–$POCl_3$; ii, $ClCH_2Ph_3PI$, Bu^{t}OK (1 equiv.) in THF; iii, Bu^{t}OK; iv, $ClCH_2Ph_3PI$, excess Bu^{t}OK in THF; v, CuI, Et_3N, $ClCH_2COMe$, $Pd(PPh_3)_4$ in C_6H_6

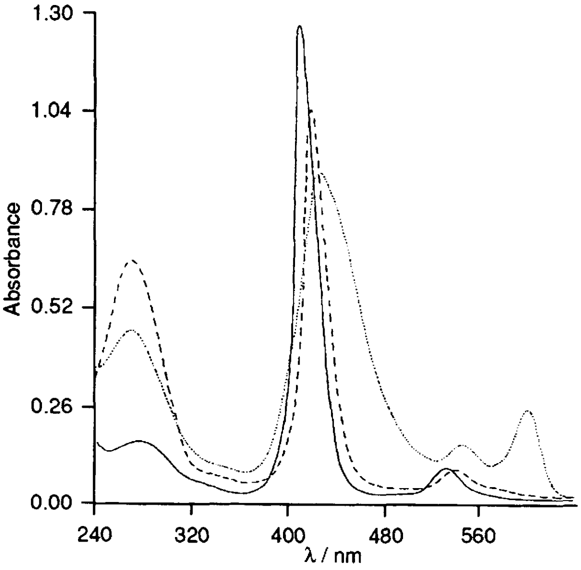


Fig. 1 Electronic absorption spectra of **1** (solid line), **5** (dashed line), and **6** (dotted line) in chloroform, at concentrations of 8.9, 8.8 and 2.9 µmol dm^{-3} respectively

coupling using standard Glazer conditions gave a yield of only 55% after 8 h at 60 °C.[7] The mechanism of this palladium–copper catalysed reaction is not known. However, Kundu *et al.*[14] have recently shown that the palladium is the active catalytic species in the dimerization process.

Dimer **6** is readily soluble in a range of organic solvents, having much greater solubility then the corresponding tetraphenylporphyrinatonickel(II) dimer which lacks the solubilising *tert*-butyl groups. Scheme 1 summarizes the sequences of reactions leading to the target dimer.

Molecular mechanics conformational analysis indicates that dimer **6** has considerable conformational restriction about the buta-1,3-diyne linker. This analysis shows that only those conformations which have porphyrin–porphyrin angles [as defined by the angle (C(3)–C(2)–C(2′)–C(3′)] of 145–215° are within 10 kcal mol^{-1} of the global minimum, which occurs at an angle of 165°. The major steric interactions enforcing this conformational restriction occur between the *tert*-butyl groups on the C-20 and C-20′ aryl substituents. These groups must adopt a position on opposite sides of the butadiyne linker in order to minimize these interactions. A similar conformational analysis on a system lacking any *tert*-butyl groups predicts that this system has much greater conformational freedom, with conformations in the region of 80–280° having energies within 10 kcal mol^{-1} of the minimum.

The electronic absorption spectra of the parent porphyrin **1**, acetylenic porphyrin **5**, and dimer **6** are shown in Fig. 1. The acetylene group on the β-position has a small but observable effect upon the electronic structure of the porphyrin system, with a 6 nm bathochromic shift being observed between the bands of porphyrin **5** compared with those of **1**. The Soret band of dimer **6** shows a further 7 nm bathochromic shift with significant broadening compared to that of monomer **5**. Soret broadening has been observed in other butadiyne linked bisporphyrins,[7,9] with Anderson attributing this broadening to exciton coupling. Additionally, the Q bands have been significantly red-shifted, with the α-band at 597 nm being clearly visible in the dimer. These changes indicate that electronic perturbation has occurred upon dimerization. However, the observed changes in the electronic absorption spectrum are far less than that observed for a related buta-1,3-diyne *meso*-,*meso*-linked system,[7] which indicates that *meso*-connection leads to a much greater perturbation of the electronic structure of the porphyrin than does β-connection.

We gratefully acknowledge the financial support of M. A. by the Ministry of Education, Government of Pakistan.

Received, 29th March 1994; Com. 4/01886I

Footnotes

† Porphyrin **2** was prepared in excellent yield by the Vilsmeier formylation of the parent porphyrin **1**.

‡ All new porphyrins have been characterized by analytical and/or spectroscopic means.

§ Dimer **6** is readily separated from unreacted **5** by column chromatography over flash silica eluting with dichloromethane–light petroleum (bp 60–80 °C, 10:90).

References

1 R. K. Pandey, F.-Y. Shiau, C. J. Medford, T. J. Dougherty and K. M. Smith, *Tetrahedron Lett.*, 1990, **31**, 789.
2 A. Osuka, K. Maruyama, I. Yamazaki and N. Tamai, *J. Chem. Soc., Chem. Commun.*, 1988, 1243.
3 M. J. Crossley and P. L. Burn, *J. Chem. Soc., Chem. Commun.*, 1987, 39.
4 H. J. Callot, *Bull. Soc. Chim. Fr.*, 1974, 1492; *Tetrahedron Lett.*, 1973, 4987.
5 V. D. Rumyantseva, A. F. Mironov, R. P. Evstigneeva, A. N. Stepanov, A. A. Perov and S. E. Kupriyanov, *Zh. Obshch. Khim.*, 1979, **49**, 883.
6 D. P. Arnold, A. W. Johnson and M. Mahendran, *J. Chem. Soc., Perkin Trans. 1*, 1978, 366.
7 D. P. Arnold and L. J. Nitschinsk, *Tetrahedron*, 1992, **48**, 8781.
8 D. P. Arnold and L. J. Nitschinsk, *Tetrahedron Lett.*, 1993, **34**, 693.
9 H. L. Anderson, *Inorg. Chem.*, 1994, **33**, 972.
10 N. Kobayashi, M. Numao, R. Kondo, S. Nakajima and T. Osa, *Inorg. Chem.*, 1991, **30**, 2241.
11 M. G. H. Vincente and K. M. Smith, *J. Org. Chem.*, 1991, **56**, 4407.
12 A. S. Hay, *J. Org. Chem.*, 1962, **27**, 3320.
13 R. Rossi, A. Carpita and C. Bigelli, *Tetrahedron Lett.*, 1985, **26**, 523.
14 N. G. Kundu, M. Pal and C. Chowdhury, *J. Chem. Res.*, 1993, (*S*) 432.