Dimeric Porphyrins linked by Conjugated Groups containing Triple Bonds: the Crystal Structure of the Nickel Octaethylporphyrin Dimer Bridged by 2,5-Diethynylthiophene

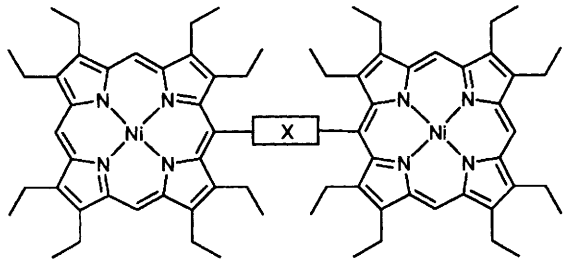
Dennis P. Arnold,[a] David A. James,[a] Colin H. L. Kennard[b] and Graham Smith[a]

[a] *Centre for Instrumental and Developmental Chemistry, Queensland University of Technology, GPO Box 2434, Brisbane, Australia 4001*

[b] *Department of Chemistry, The University of Queensland, St. Lucia, Australia 4072*

The conjugated bridge and the attached *meso*-carbons in the title dimer are almost coplanar; the porphyrin rings are ruffled and distorted in this vicinity, indicating strong interporphyrin interaction *via* the π-orbitals of the diethynylthiophene unit.

There now exists a voluminous literature on porphyrin dimers and oligomers linked by unsaturated bridges, in which inter-porphyrin conjugation is prevented by steric interactions of the bridging unit with peripheral substituents.[1] The first example of a truly conjugated porphyrin dimer was reported by Johnson and coworkers in 1978.[2] The then unique type of optical spectrum exhibited by the bis(NiOEP)butadiyne **1**† was noted in that paper. Recently we[3] and others[1,4] have reported synthetic, spectroscopic and electrochemical studies of a number of bis- and oligo-porphyrins linked in a linear fashion *via* bridges containing the carbon–carbon triple bond as a conjugating 'molecular wire'. Anderson has developed novel routes to 'porphyrin ladders' consisting of octaalkylporphyrin units linked by butadiyne bridges in the *meso*, *meso* positions.[1] Therien and coworkers have further revealed the potential of the *meso*-ethynylporphyrin motif for the generation of multichromophore arrays, using palladium-catalysed coupling chemistry.[4] Whilst this area is burgeoning from the synthetic and empirical spectroscopic viewpoints, structural data have been lacking so far. We independently initiated the use of palladium chemistry to form dimeric ethynylporphyrins,[5] and have now prepared a range of NiOEP dimers linked by octatetrayne, butenyne, octadienediyne, diethynylarene, and diethynylheteroarene bridges, whose spectra and electrochemistry are presently being studied.[6] During this work, we prepared the thiophene-bridged dimer **2**.‡ This communication reports the X-ray crystal structure determination of **2**,§ which is both the first porphyrin dimer linked by a conjugated bridge, and the first alkynylporphyrin to be thus characterised.



1 X = C≡C–C≡C

2 X = C≡C–(S)–C≡C

3 X = C≡C–(C6H4)–C≡C

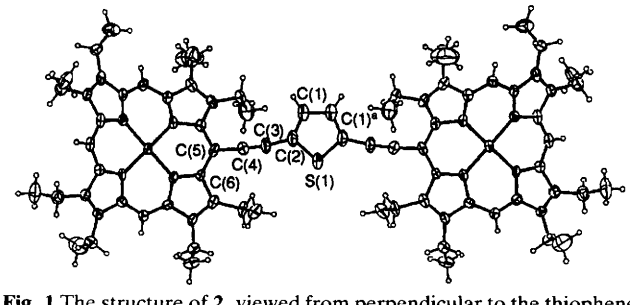


Fig. 1 The structure of **2**, viewed from perpendicular to the thiophene plane. Selected bond lengths (Å) and angles (°): S(1)–C(2) 1.68(2), C(2)–C(1) 1.37(3), C(2)–C(3) 1.41(2), C(3)–C(4) 1.18(2), C(4)–C(5) 1.45(2), C(1)–C(1)ᵃ (a: $-x+1, y, -z+\frac{1}{2}$) 1.40(4); C(2)–S(1)–C(2)ᵃ 96(1), S(1)–C(2)–C(1) 108(1), S(1)–C(2)–C(3) 124(2), C(2)–C(3)–C(4) 172(2), C(3)–C(4)–C(5) 175(2), C(4)–C(5)–C(6) 120(1).

The molecule has crystallographically imposed two-fold symmetry, and exhibits several notable features. The 'face-on' view (Fig. 1) shows distortion of the bond angles in the diethynylthiophene unit, such that the porphyrins bend away from the sulfur side of the ring. This bending has the effect of making the two triple bonds almost co-linear, and would cause steric interference between the thiophene hydrogens and the nearby ethyl groups, were it not for the fact that the adjacent pyrrole rings tilt out of the mean plane of the porphyrin units. This is obvious in the side-on view (Fig. 2), in which a general 'ruffling' of the porphyrin cores is also seen.[7] The Ni–N distances [1.91(1) Å (mean)] are typical for distorted nickel(II) porphyrin structures.[7] There is clearly strong π-orbital overlap across the bridge, since the unit C_{meso}–C≡C–thiophene–C≡C–C_{meso} is almost planar in this direction. The Ni···Ni distance within one molecule is 17.0 Å, and the shortest intermolecular Ni···Ni distance (6.09 Å) is between molecules related by the *c* glide operation ($-x, y, \frac{1}{2}-z$).

It is interesting to compare the visible spectra of **2**, the butadiyne **1**,[2] and the analogous dimer **3** linked by the 1,4-diethynylbenzene unit.[5] The major B-band splittings in the spectra of **1** and **2** are similar ($\Delta\nu$ = 2905 and 2785 cm^{-1}, respectively), indicating little interruption of the conjugation pathway by the insertion of the thiophene ring, whereas the splitting for **3** is only *ca.* 1100 cm^{-1},[5] and that for the 1,3-phenylene analogue is less than 400 cm^{-1}.[6] This is presumably a manifestation of the lesser aromaticity of thiophene, and hence its greater ability to act as an electron conduit, when compared with benzene. The 1,3-phenylene dimer may suffer steric constraints which prevent the near-planarity required for conjugation. Therien has argued that the large B-band splittings seen in the spectra of his monoyne-linked diphenylporphyrin dimer and trimer require coplanarity of the chromophores,[4] whereas Anderson has proposed that the degree of interaction in his butadiyne dimers is rather insensitive to torsional angle.[1] An intriguing point is the difficulty we, and presumably others, have had in obtaining single crystals of a variety of these alkyne-linked species. Could this be due to a lack of strongly-preferred rigid geometries, or is it merely coincidental? Attempts to rationalise the spectra of these strongly-interacting porphyrin dimers

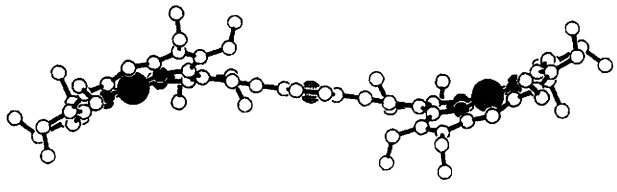


Fig. 2 The structure of **2**, viewed down the two-fold axis, with hydrogens omitted

by exciton coupling theory are bound to fail, since the interchromophore interactions do not fall off rapidly with separation (*e.g.* **1** *vs.* **2**).[1,4,8] The understanding of the novel spectra of these conjugated oligoporphyrins is a fertile field for spectroscopic and theoretical studies, which we are presently undertaking.

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Footnotes

† OEP = dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin.

‡ Compound **2** was prepared by reacting *meso*-ethynylNiOEP with 2,5-diiodothiophene in a 2 : 1 molar ratio in NEt_3, using $PdCl_2/PPh_3$ as catalyst. Separation by column chromatography (silicagel 60, 230–400 mesh, 25% $CHCl_3$–hexane as eluant) led to the isolation of **2** in 30% yield, as well as butadiyne **1** and the monomers *meso*-2′-thienylethynyl- and 5′-iodo-2′-thienylethynylNiOEP. Repetition with a 5 : 1 excess of diiodide yielded mainly the latter monomer as the major product.

§ *Crystal data* for **2**: $C_{80}H_{88}N_8Ni_2S$, M_r = 1311.1, monoclinic, space group *C*2/*c*, a = 20.463(1), b = 21.107(2), c = 16.174(2) Å, β = 100.765(7)°, V = 6863(1) Å^3, $F(000)$ = 2784, Z = 4, D_c = 1.269 g cm^{-3}, Mo-Kα radiation (λ 0.71073 Å); μ(Mo-Kα) = 6.3 cm^{-1}, T = 298(2) K. Intensity data were collected on an Enraf-Nonius CAD-4 four-circle diffractometer from a lozenge shaped specimen measuring 0.20 × 0.20 × 0.08 mm. Of 6331 reflections collected up to $2\theta_{max}$ = 50°, 6026 were unique (collection range: h, −24 to 23; k, −1 to 25; l, −9 to 19; R_{int} = 0.06). The data were corrected for absorption using semi-empirical methods.[9] The structure was solved using SHELXS-86[10] and refined to residuals R_1, wR_2 and S of 0.071, 0.22 and 0.83 respectively [based on 1752 reflections with $F_o > 4\sigma(F_o)$ for 414 refined parameters] (SHELXL-93[11]) using anisotropic thermal parameters for all non-hydrogens. Hydrogens were inserted in calculated positons with positional and thermal parameters riding. Atomic coordinates, bond lengths and angles, and thermal parameters, have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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