# Porphyrin Dimers Linked by Conjugated Butadiynes

Dennis P. Arnold\* and Lisa J. Nitschinsk

Centre for Instrumental and Developmental Chemistry, Queensland University of Technology, G.P.O. Box 2434, Brisbane, Oueensland 4001, Australia.

(Received in UK 27 July 1992)

Abstract: 1,3-Butadiynes R-C=C-C=C-R, where R = 5'-substituted nickel(II) octaethylporphyrin (NiOEP) (1e), 2'-substituted nickel(II) 5',10',15',20'-tetraphenylporphyrin (NiTPP) (4e), and 2'-substituted nickel(II) heptaethylporphyrin (NiHEP) (5d), have been prepared from the respective bromovinyl species by dehydrobromination and oxidative coupling. The published synthesis of (1e) has been improved to achieve a 40% yield for four steps from NiOEP. The metal-free bis(OEP) diyne was prepared by acid treatment of (1e), while more strenuous conditions led to a novel furan substituted at the 2- and 5-positions with OEP units. The visible absorption spectra of the 5'- and 2'-substituted diynes differ markedly, the former compounds exhibiting split absorption bands and red shifts indicative of extensive chromophore interaction.

The synthesis of porphyrin dimers and oligomers covalently linked by rigid spacer groups is a fertile area of research at present. There are two major reasons to pursue such work. The first is the need to understand electron transfer between porphyrin rings, as a means of probing photosynthetic mechanisms. To this end, many elegant studies have resulted in dimers and oligomers linked by bridges such as *o*-, *m*-, and *p*-phenylene groups<sup>1-6</sup>, biphenyls<sup>6-8</sup>, naphthalenes<sup>9</sup>, anthracenes<sup>6,10</sup>, and phenanthrolines<sup>11</sup>. The optical spectra of these aggregates have been studied in some detail<sup>6, 9</sup>. In most cases, the  $\pi$ -systems of the porphyrins and aromatic bridges are essentially orthogonal, because of steric interference between *ortho*-hydrogens on the bridges and neighbouring porphyrin substituents. The second thrust of this work is in the area of molecular electronics, where porphyrins may be part of conducting polymers ("molecular wires"<sup>12</sup>), or photovoltaic devices<sup>13</sup>. In such applications, enforced coplanarity of the porphyrin sub-units may be more desirable. The work of Crossley *et al.*<sup>12</sup> and others<sup>14</sup> has led to promising oligomers of porphyrins linked by fused pyrazinoquinoxaline rings, and a bis-porphyrin joined by a common benzene ring has also been reported<sup>15</sup>. Red-shifted absorption bands in these compounds indicate a narrowing of the HOMO-LUMO band gap, in the former case into the region expected for semi-conductors<sup>12</sup>.

In 1978, Arnold *et al.*<sup>16</sup> reported the first synthesis of a *meso*-ethynyl porphyrin, nickel(II) *meso*ethynyloctaethylporphyrin, and described its facile conversion to the green 1,3-butadiyne dimer. The butadiyne bridge offers some interesting properties, in that it is rigid, linear, conjugated, and sterically nondemanding. Bis-porphyrins linked by such a group may have the porphyrin chromophores either coplanar or orthogonal and still retain overlap between  $\pi$ -orbitals of the porphyrin and the alkyne. Conjugated diacetylenes have been extensively studied for their application to molecular electronics, especially regarding non-linear optical properties<sup>17</sup>. While the intense light absorption of the porphyrins would not be useful in the latter field, the potential for solid state conduction and contributions to understanding of porphyrin-porphyrin interactions, makes such molecules important candidates for study. These ideas are being pursued independently by others, and there have been two recent reports of the synthesis of *meso*tetraalkynylporphyrins<sup>18,19</sup>. Acetylene coupling has been used by Maruyama<sup>20</sup> in an extension of the phenylene bridging systems to the synthesis of systems comprising porphyrin-phenylene-polyynephenylene-porphyrin. Despite the monumental work involved in their synthesis, these oligomers did not show extensive electronic interaction between the porphyrin units, because of the orthogonal phenylene rings. Anderson and Sanders<sup>21</sup> have used acetylene coupling to build dimers and trimers of porphyrins with large cavities occupied by donor ligands, but again these structures involved phenylene units as well, to obtain the necessary geometries. Porteau *et al.*<sup>22</sup> prepared thin films by oxidative coupling of alkyne groups in tetrakis(propargyl)pyridinium porphyrins, but there would be expected to be little electronic communication between neighbouring  $\pi$ -systems in such polymers. We now report the preparation of some novel bis(porphyrinyl)-1,3-butadiynes, including a much improved synthesis of the original example.

### **RESULTS AND DISCUSSION**

The previously reported synthesis of the bis[octaethylporphyrinatonickel(II)] (NiOEP) dimer (1e), used the *meso*-vinyl compound (1c), which underwent substitutive bromination to *meso*-bromovinyl (1b), dehydrobromination to *meso*-ethynyl (1d), and oxidative coupling<sup>16</sup>. Vinyl compound (1c) was prepared by Wittig methylenation of aldehyde (1a) or Grignard addition followed by acid-catalysed dehydration. The overall yield of these steps was 14% from unsubstituted NiOEP. Our modified synthesis uses the bromomethylene ylide, to afford *trans*- (1b) in one step from (1a), in 55% yield. Only trace amounts of the *cis*-isomer were observed. Column chromatography separated (1b) readily from unreacted (1a), which can be recovered. Attempts to raise this yield have not succeeded. The dehydrobromination to the purple, oxidatively unstable (1d) was carried out, as reported<sup>16</sup>, using sodium hydride in 1,2-dimethoxyethane containing a little DMSO. We have found that this reaction requires careful monitoring by TLC, since overreaction generates several by-products from solvent involvement, and extreme difficulty is then experienced in purification. If the reaction is quenched as soon as (1b) has been consumed (usually less than two hours), a high yield of (1d) is obtained. This crude product is then readily oxidatively coupled to the green dimer (1e), using copper (II) acetate in pyridine<sup>16</sup>.

The more polar by-products from a dehydrobromination which was allowed to proceed too long, were separated by preparative TLC and identified by their <sup>1</sup>H NMR spectra. These products include (1c), the *cis*- and *trans*- $\beta$ -methoxyvinyl (1f), *cis*- and *trans*- $\beta$ -(2'-methoxyethoxy)vinyl (1g), and a trace of the *trans*-enol (1h), or the bis(porphyrinyl) enol ether. For confirmation, the methyl enol ethers (1f) were prepared by reaction of aldehyde (1a) with methoxymethylenetriphenylphosphorane. Work-up as for (1b) gave a 1.6:1 mixture of *trans*- and *cis*- (1f), separable by preparative TLC, in 55% total yield. The stabilities of these enol derivatives have not been studied, but the porphyrinyl acetaldehyde was not detected even after repeated TLC using silica gel and eluants containing chloroform. The formation of these numerous products from attack on the solvent 1,2-dimethoxyethane may be another example of the ability of NiOEP and CuOEP systems to undergo electron transfer processes<sup>23</sup>.



We can now prepare the NiOEP diyne dimer (1e) in *ca*. 40% overall yield from NiOEP. Naturally we were interested in extensions to other metal derivatives. There are two approaches to this, viz. to use various metallo derivatives of the earlier starting materials, or to follow the sequence through with nickel, then demetallate the dimer and insert other metals. The first alternative was quickly abandoned, since the Wittig reactions did not proceed for either the zinc or copper(II) OEP aldehydes. Demetallation of (1e) was attempted by treatment with 98% sulfuric acid for 2 hours. Neutralization and isolation did not give the free base (2), but rather a compound to which we have assigned the novel structure (3), i.e. a furan substituted at the 2- and 5-positions with the OEP unit. This proposal is in accord with all the spectroscopic data, as follows. The mass spectrum indicates a formula with only one oxygen [so it is not a bis(enol) or its diketo form], there is no fragmentation into symmetrical halves, and very weak doubly charged ions are observed at m/z ca. 567. The <sup>1</sup>H NMR spectrum indicates a symmetrical diporphyrin, and especially informative are the peaks due to the ethyl groups at the 3' and 7' positions. In both the alkyne (1d), and the butadiyne (1e), these protons appear downfield of the rest of the ethyl groups, because of the anisotropy of the C $\equiv$ C group. In (3), these peaks shift *upfield*, as expected for the electronic effect of an aromatic ring which is orthogonal to the

porphyrin plane. Such shifts are typical of the phenylene-bridged dimers reported by Maruyama *et al.*<sup>1b, 1f, 14</sup> and Sessler *et al.*<sup>1d</sup>. The 3- and 4-protons of the furan ring appear as a singlet at 7.48 ppm, and the attached carbons at 119.2 ppm. Furyl-substituted porphyrins are very rare in the literature. *meso*-Tetrakis(2-furyl)porphyrin was prepared in very low yield by Treibs and Häberle<sup>24</sup>, and *meso*-tetrakis[2-(3'-ethoxycarbonyl)furyl]porphyrin was reported by Momenteau *et al.*<sup>25</sup>. The latter compound exhibited <sup>1</sup>H NMR signals at 7.4 and 8.0 ppm for the furan ring protons, in a similar region to those of (3). The visible spectrum of (3) is similar to those of dimers linked by phenylene bridges, the Soret band being broadened with a shoulder on the long wavelength side. The Q-bands are somewhat broadened, but not split (see below).

It was apparent therefore, that prolonged treatment of (1e) in concentrated acid resulted not only in demetallation, but also in protonation of the diyne bridge and subsequent hydration/cyclo-dehydration. Use of the milder medium 10% concentrated sulfuric acid in trifluoroacetic acid, led after 30 minutes to a good yield of the required free base (2), which exhibited all the expected spectroscopic data. The visible spectra of the three dimers (1e), (2), and (3) are compared in Figure 1. The multiple splitting of the Soret bands for both (1e) and (2) is presumably indicative of much stronger chromophore interaction than observed in phenylene linked dimers, in line with the postulate outlined above. The split Q bands in (2), and the increased absorption in the red for (1e), are consistent with observations for the "planar-fused" dimers of Crossley and Burn<sup>12</sup>, and Kobayashi *et al.*<sup>15</sup>, in which the porphyrin  $\pi$ -system has been expanded.



Fig. 1. Absorption spectra of (1e) (---), (2) (----) and (3) (----), at 6.5 x 10<sup>-6</sup> M in CHCl<sub>3</sub>.

The coupling of ethynyl porphyrins has now been extended to the formation of a butadiyne bridge attached to  $\beta$ -pyrrole positions. The readily available *meso*-tetraphenylporphyrin (TPP) was explored first. The same series of steps was carried out, starting with the nickel complex of the aldehyde (4a). Bromomethylenation gave a *ca*. 2:1 mixture of *trans*- and *cis*- $\beta$ -bromovinyl NiTPP (4b) in 70% yield. Dehydrobromination as before led to the alkyne (4c), together with a little of the vinyl compound (4d). Both

(4b) and (4c) are unusually soluble for NiTPP species, and are red/orange in solution. In contrast with the OEP compound, this alkyne is much more stable to oxidative coupling, and (4c) was isolated and purified. It can be subjected to repeated preparative TLC in air, with only slight dimerization occurring. Copper(II) oxidation readily gave the dimer (4e) in 55% yield. The NMR spectra of all these compounds show features typical of 2-substituted TPP derivatives, especially the AB quartet (J ca. 5 Hz) for the non-equivalent 7, 8 protons of the porphyrin ring(s). In addition, the protons of the phenyl groups on the *meso*-position(s) next to the triple bond in (4c) and (4e) experience upfield shifts due to anisotropy effects. The assignments of these protons were assisted by examination of 500 MHz <sup>1</sup>H spectra. Moreover in (4c), the shielding effect of the phenyl group on the alkyne proton is apparent. This proton resonates at 3.21 ppm, while it appears at 4.42 ppm in the OEP compound (1d).



The recent work of Vicente and Smith<sup>26</sup> on functionalisation of the ethyl groups of OEP has enabled us to prepare the  $\beta$ -linked heptaethylporphyrin (HEP) diyne (5d). Using their method, OEP free base was converted to 2-(2'-bromovinyl)-HEP (5a), although in our hands a reaction time greater than one hour led to formation of isomers of bis(bromovinyl)hexaethylporphyrin. Insertion of nickel gave (5b), which was dehydrobrominated to alkyne (5c), which in turn was oxidatively coupled to dimer (5d). Like the TPP alkyne (4e), (5c) was rather stable to aerial oxidation, but (5d) was readily formed in the presence of copper(II). In contrast to (1e) and (4e), the HEP diyne undergoes an irreversible reaction on silica gel and during slow crystallization, with the production of an extremely insoluble material. For this reason, a sample of analytical purity was not obtained. The NMR spectra of freshly prepared solutions display all the expected features to support the proposed structure.



The availability of these model butadiyne dimers enables study of the interaction via a conjugated butadiyne, of porphyrin chromophores containing substituents of different types. Despite strenuous efforts,

we have not succeeded in growing single crystals of any of the diyne complexes for structural studies. The materials all form feathery aggregates of very small crystals from a variety of solvents. We therefore have no concrete evidence for the planarity or otherwise of these molecules. The visible absorption spectra of the two types of dimer, i.e. *meso*-linked or  $\beta$ -linked, differ considerably. Figure 2 shows the spectra of the NiTPP and NiHEP dimers, which can be contrasted with the spectrum of (1e) in Figure 1. Whether these differences reflect a geometrical difference e.g., coplanarity in the OEP compound and not in the TPP and HEP dimers, may not be answered until an X-ray structure determination is possible. The marked red-shift induced by *meso*-alkynyl substituents has been noted also by Anderson, and taken as evidence of good communication between the  $\pi$ -electrons of the triple bond and the porphyrin<sup>19</sup>. The preparations of butadiyne dimers containing two different porphyrin rings, and of a variety of other metal derivatives of (2) are currently being pursued.



Fig. 2. Absorption spectra of (4e) (---, 5.8 x 10<sup>-6</sup> M) and (5d) (----, 3.7 x 10<sup>-6</sup> M) in CHCl<sub>3</sub>.

# **EXPERIMENTAL**

#### General

Silica gel 60 (35-70 mesh, Merck) was used for column chromatography and Kieselgel 60 (Merck) was used for preparative thin layer chromatography on 20 x 20 cm glass plates, with adsorbent thickness 1 or 1.5 mm. Analytical TLC was carried out on pre-coated Merck silica gel 60  $F_{254}$  aluminium plates (0.2 mm thick). Solvents for chromatography were Nanograde, A.R. or pre-distilled. THF was distilled from LiAlH<sub>4</sub>, and pyridine from KOH. Other anhydrous solvents were purchased from Aldrich. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Unity 300 MHz instrument, in CDCl<sub>3</sub> solution, using the solvent signal as internal reference (<sup>1</sup>H 7.25 ppm, <sup>13</sup>C 77.0 ppm). Visible absorption spectra were recorded on a Varian DMS-100 spectrophotometer, in CHCl<sub>3</sub> solution. FAB mass spectra were obtained at the Mass Spectrometry Service, University of Adelaide. The strongest peak in the molecular ion cluster is quoted

below. Infrared spectra were recorded on a Perkin Elmer 1600 F.T. instrument as KBr pellets. Microanalyses were obtained at the Microanalytical Service, University of Queensland, Brisbane. Organic solutions were dried over anhydrous sodium sulfate before evaporation.

Bromomethyltriphenylphosphonium bromide was prepared by refluxing triphenylphosphine and dibromomethane (1:1 molar ratio), in dry toluene under N<sub>2</sub> for 8 h. The slightly sticky precipitate was collected by filtration and recrystallized by dissolving in minimum ethanol and adding ethyl acetate, with scratching and cooling, to yield white crystals (37%). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  5.75 (d, 2H, <sup>2</sup>J<sub>PH</sub> 6.8 Hz, CH<sub>2</sub>), *ca.* 7.8 (m, 18H, phenyl groups). <sup>13</sup>C NMR:  $\delta$  16.2 (d, <sup>1</sup>J<sub>PC</sub> 53.9 Hz, CH<sub>2</sub>), 117.3 (d, <sup>1</sup>J<sub>PC</sub> 88.6 Hz, 4° C), 130.7 (d, <sup>3</sup>J<sub>PC</sub> 13.1 Hz, *m*-C), 134.3 (d, <sup>2</sup>J<sub>PC</sub> 10.6 Hz, *o*-C), 135.9 (d, <sup>4</sup>J<sub>PC</sub> 2.5 Hz, *p*-C).

# Porphyrin Starting Materials

OEP was prepared by the method of Sessler *et al.*<sup>27</sup> Nickel(II) was inserted using Ni(OAc)<sub>2</sub>.4H<sub>2</sub>O in glacial acetic acid, and aldehyde (1a) was prepared as described<sup>23a</sup>. NiTPP and its aldehyde (3a) were prepared by literature methods<sup>28,29</sup>. 2-(2'-Bromoethenyl)-3, 7, 8, 12, 13, 17, 18-heptaethylporphyrin (5a) was prepared by the method of Vicente and Smith<sup>26</sup>, except that the reaction was stopped after 1 h, and preparative TLC was conducted using CH<sub>2</sub>Cl<sub>2</sub>/petroleum spirit 30/70. Several bands other than (5a) and unreacted OEP were also investigated, and appeared from <sup>1</sup>H NMR spectra to be isomers of di- and poly(bromovinyl) compounds.

#### Octaethylporphyrin Derivatives

5-trans-(2'-Bromoethenyl)-2,3,7,8,12,13,17,18-octaethylporphyrinatonickel(II) (1b). Butyllithium (1.6 M in hexane, 6.8 mL, 10.9 mmol) was added dropwise to a stirred suspension of bromomethyltriphenylphosphonium bromide (4.75 g, 10.9 mmol) in anhydrous THF (120 mL) under N<sub>2</sub>. The resulting bright yellow solution was stirred for 10 min, then solid aldehyde (1a) (1.35 g, 2.18 mmol) was added, and the resulting solution was stirred at room temperature for 1.5 h, during which the colour changed form green to red. Water (100 mL) was added, and the porphyrins were extracted into benzene (2 x 100 mL). The combined organic layers were dried and evaporated to yield a red/brown solid. Column chromatography using 25% CHCl3/hexane gave a major red band which was collected and the residue recrystallized from CHCl3/methanol to yield deep purple needles of *trans*-(1b) (0.83 g, 55%). The more polar green band of unreacted aldehyde was also recovered. The spectra were in agreement with those in the literature<sup>16</sup>.

5-Ethynyl-2,3,7,8,12,13,17,18-octaethylporphyrinatonickel(II) (1d). The above bromovinyl compound (0.83 g, 1.19 mmol) was dissolved in dry 1,2-dimethoxyethane (250 mL) and treated with NaH (60% dispersion in oil, 0.55 g, prewashed with ether), and DMSO (0.7 mL). The mixture was heated under reflux, and the progress of the reaction was monitored by TLC to observe the disappearance of (1b) and the appearance of the purple (1d). When conversion was judged to be complete (ca. 1.5 h), the solvent was evaporated, and the residue was extracted with CHCl<sub>3</sub> (2 x 100 mL). The CHCl<sub>3</sub> solution was washed with water, dried, and evaporated to give crude (1d). The spectral data were in agreement with those in the literature<sup>16</sup>. Further purification was not attempted as oxidation to the green dimer proceeds spontaneously.

Over-reaction in the dehydrobromination resulted in the formation of several more polar compounds, which in one case were separated by preparative TLC using 25% CHCl<sub>3</sub>/hexane. In order of elution, these bands were shown by <sup>1</sup>H NMR to contain the following compounds: (i) (1c), by comparison with the literature<sup>30</sup>; (ii) (1d); (iii) a mixture of *trans*-(1f) (see below) and another *trans*-vinyl compound, presumably the enol (1h), <sup>1</sup>H NMR :  $\delta$  5.31 (d, J 15 Hz, -CH=CH-X), 8.63 (d, J 15 Hz, -CH=CH-X), 9.41 (s, meso H), 9.43 (s, 2 x meso H); (iv) pure *trans*-(1f); (v) *cis*-(1f) (see below); (vi) a little *cis*-(1f), but mostly *trans*-2'methoxyethoxy enol ether (1g), <sup>1</sup>H NMR :  $\delta$  *ca*. 1.8 (overlapping t, CH<sub>3</sub>), 3.47 (s, OCH<sub>3</sub>), 3.68 (half of A<sub>2</sub>B<sub>2</sub>, -OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), *ca*. 3.9 (overlapping q, CH<sub>2</sub>), 4.13 (half of A<sub>2</sub>B<sub>2</sub>, -OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 5.40 (d, J 12.5 Hz, -CH=CHOR), 8.22 (d, J 12.5 Hz, -CH=CHOR), 9.48 (s, meso H), 9.50 (s, 2 x meso H).

5-(2'-Methoxyethenyl)-2,3,7,8,12,13,17,18-octaethylporphyrinatonickel(II) (1f). (cis/trans mixture) These were prepared as for (1b), using butyllithium (1.6 M in hexane, 0.23 mL, 0.37 mmol), methoxymethyltriphenylphosphonium chloride (Aldrich, 125 mg, 0.37 mmol), THF (15 mL), and aldehyde (1a) (45 mg, 0.073 mmol). The red residue after work up as above was purified by preparative TLC, eluting with 25% CHCl<sub>3</sub>/hexane. The major red band was collected and recrystallized from CHCl<sub>3</sub>/methanol to yield red needles of *trans*-(1f) (16 mg, 34%) <sup>1</sup>H NMR: δ *ca.* 1.7 (overlapping t, 24H, CH<sub>3</sub>), *ca.* 3.8 (overlapping q, 16H, CH<sub>2</sub>), 3.85 (s, 3H, OCH<sub>3</sub>), 5.34 (d, 1H, J 12.3 Hz, -CH=CHOCH<sub>3</sub>), 8.08 (d, 1H, J 12.3 Hz, -CH=CHOCH<sub>3</sub>), 9.39 (s, 1H, meso H), 9.42 (s, 2H, meso H). Mass spectrum m/z 646 (M<sup>+</sup>). Anal. calcd. for C<sub>39</sub>H<sub>48</sub>N<sub>4</sub>NiO: C, 72.3; H, 7.5; N 8.7. Found C, 72.4; H, 7.6; N, 8.5%. UV-Vis λ<sub>max</sub> (ε) 406 (139400), 532 (9800), 565 (14400) nm. The second prominent red band was shown to be the *cis*-isomer (10 mg, 21%). <sup>1</sup>H NMR: δ *ca.* 1.7 (overlapping t, 24H, CH<sub>3</sub>), *ca.* 3.8 (overlapping q, 16H, CH<sub>2</sub>), 6.33 (d, 1H, J 6.9 Hz, -CH=CHOCH<sub>3</sub>), 7.65 (d, 1H, J 6.9 Hz, -CH=CHOCH<sub>3</sub>), 9.43 (s, 3H, meso H).

1,4-Bis[2',3',7',8',12',13',17',18'-octaethylporphyrinatonickel(II)-5'-yl]-1,3-butadiyne (1e). The foregoing crude ethynyl compound (1d) was dissolved in dry pyridine (150 mL), copper(II) acetate monohydrate (0.26 g) was added, and the mixture was stirred at 60° for 2 h, during which the solution became dark green. After cooling, the mixture was poured into 2 M HCl (1.2 L), extracted with CHCl<sub>3</sub> (2 x 200 mL) and washed with water. The dried CHCl<sub>3</sub> solution was evaporated, and the residue was recrystallized from CHCl<sub>3</sub>/methanol to yield very dark green microcrystals (585 mg, 80% from bromovinyl compounds). Spectral data were in accord with the literature<sup>16</sup>, and the <sup>13</sup>C NMR spectrum was recorded:  $\delta$  17.4, 18.1, 19.4, 21.7 (ethyl groups), 88.6, 91.7 (C=C), 93.5 (4° meso C), 97.6 (2 x meso CH), 97.8 (4 x meso CH), 137.6, 140.1, 141.8, 142.9, 143.6, 145.1, 145.6 (ring carbons).

1,4-Bis[2',3',7',8',12',13',17',18'-octaethylporphyrin-5'-yl]-1,3-butadiyne (2). Dimer (1e) (170 mg, 0.14 mmol) was dissolved in trifluoroacetic acid (15 mL), and concentrated H<sub>2</sub>SO<sub>4</sub> (1.5 mL) was added. The mixture was stirred at room temperature for 30 min, after which the green/brown solution was poured into ice-cold saturated NaHCO<sub>3</sub> solution, and extracted with CHCl<sub>3</sub> (3 x 50 mL). The combined CHCl<sub>3</sub> layers were dried and evaporated to yield a residue which was recrystallized from CHCl<sub>3</sub>/methanol, giving fine very dark green microcrystals of (2) (118 mg, 76%). <sup>1</sup>H NMR:  $\delta$  -2.5 (br, 4H, NH), *ca.* 1.9 (overlapping t, 36H, CH<sub>3</sub>), 2.13 (t, 12H, CH<sub>3</sub> of 3', 7' ethyl groups), *ca.* 4.1 (overlapping q, 16H, CH<sub>2</sub>), 4.17 (q, 8H, CH<sub>2</sub> of 2', 8' ethyl groups), 4.60 (q, 8H, CH<sub>2</sub> of 3', 7' ethyl groups), 9.94 (s, 2H, meso H), 10.15 (s,

4H, meso H). <sup>13</sup>C NMR:  $\delta$  17.5, 18.4, 19.6, 22.1 (ethyl groups), 88.1, 89.0 (C=C), 95.0 (4° meso C), 97.6 (2 x meso CH), 98.1 (4 x meso CH), 141.1, 141.5, 142.1, 143.3, 144.4, 145.0, 147.5 (ring carbons). Mass spectrum m/z 1114.7 (M<sup>+</sup>). Anal. calc. for C<sub>76</sub>H<sub>90</sub>N<sub>8</sub>: C, 81.8; H, 8.1; N, 10.0. Found C, 81.8; H, 8.4; N, 9.8%. IR v<sub>max</sub> (cm<sup>-1</sup>) 3228 w (NH), 2119 w (C=C). UV-Vis  $\lambda_{max}$  ( $\epsilon$ ) 416 sh (132400), 432 (169600), 445 (183300), 475 (122700), 514 (31000), 579 (35400), 598 (36000), 659 (22400), 675 (21500) nm.

2,5-Bis[2',3',7',8',12',13',17',18'-octaethylporphyrinatonickel(II)-5'-yl]furan. (3). The bis(nickel) dimer (1e) (50 mg, 0.041 mmol) was dissolved in concentrated H<sub>2</sub>SO<sub>4</sub> (5 mL), and stirred at room temperature for 2 h. Work up as for (2) above gave a residue which was recrystallized from CHCl<sub>3</sub>/methanol to give dark green/brown microcrystals (24 mg, 52%). <sup>1</sup>H NMR:  $\delta$  -2.64 (br, 4H, NH), 1.44 (t, 12H, CH<sub>3</sub> of 3', 7' ethyl groups), *ca*. 1.9 (overlapping t, 36H, CH<sub>3</sub>), 3.76 (q, 8H, CH<sub>2</sub> of 3',7' ethyl groups), *ca*. 4.0 (overlapping q, 24H, CH<sub>2</sub>), 7.48 (s, 2H, furan β-H), 9.86 (s, 2H, meso H), 10.05 (s, 4H, meso H). <sup>13</sup>C NMR:  $\delta$  17.9, 18.2, 18.4, 18.5, 19.7, 21.4, (ethyl groups), 97.1 (2 x meso CH), 97.6 (4 x meso CH), 102.2 (4' meso C), 119.2 (furan β-C), 141.1-145.2 (ring carbons), 152.7 (furan α-C). Mass spectrum m/z 1133.6 (M+1). Anal. calc. for C<sub>76</sub>H<sub>92</sub>N<sub>8</sub>O: C, 80.5; H, 8.2; N, 9.9. Found C, 79.3; H, 8.2; N, 9.5%. UV-Vis λ<sub>max</sub> (ε) 405 (182500), 446 sh (85000), 507 (26300), 541 (15400), 580 (14400), 626 (12800) nm.

#### Tetraphenylporphyrin Derivatives

2-(2'-Bromoethenyl)-5,10,15,20-tetraphenylporphyrinatonickel(II) (4b). Purple crystals of a ca. 1:2 mixture of cis- and trans-isomers (452 mg, 71%, from CHCl<sub>3</sub>/methanol), were obtained as for the OEP compound (1b), using butyllithium (1.6 M in hexane, 2.6 mL), bromomethyltriphenyl-phosphonium bromide (2.39 g, 4.1 mmol), aldehyde (4a) (573 mg, 0.82 mmol) in THF (100 mL). The product (4b) is bright orange/red in solution, and was separated from a small amount of unreacted (4a) by column chromatography, eluting with 50% CHCl<sub>3</sub>/hexane. <sup>1</sup>H NMR:  $\delta$  6.13 (d, J<sub>cis</sub> 7.8 Hz, CH=CHBr), 6.72 (d, J<sub>trans</sub> 13.7 Hz, -CH=CHBr), 7.7 (m, m-, p-H of phenyl groups), 7.9 (m, o-H of phenyl group next to vinyl group), 8.0 (m, o-H of other phenyl groups), 8.68 (s, 1H,  $\beta$ -H on C-3), 8.7 (m, 7H,  $\beta$ -H). Mass spectrum m/z 776 (M<sup>+</sup>, <sup>58</sup>Ni, <sup>81</sup>Br). UV/Vis  $\lambda_{max}$  (rel. int.) 422 (34.4), 535 (2.6), 566 sh (1.0) nm.

2-Ethynyl-5,10,15,20-tetraphenylporphyrinatonickel(II) (4c). Mixed bromovinyl compounds (4b) (397 mg, 0.51 mmol) and sodium hydride (263 mg, 60% dispersion in oil) in dry 1,2-dimethoxyethane (100 mL) containing DMSO (0.3 mL) were refluxed and stirred under N<sub>2</sub> for 4 h. The orange/red solution was reduced to dryness, extracted with chloroform (2 x 100 mL), and the combined chloroform layers were washed with water. After drying, the solvent was removed to leave a residue which was subjected to preparative TLC, eluting with 25% CHCl<sub>3</sub>/hexane. The second orange/red band was collected and the product crystallized from CHCl<sub>3</sub>/methanol, to give purple microcrystals of (4c) (280 mg, 79%). The faster moving band was shown by <sup>1</sup>H NMR spectroscopy, to be the vinyl compound (4d)<sup>29</sup>. <sup>1</sup>H NMR:  $\delta$  3.21 (s, 1H, -C=CH), 7.58 (t, 2H, *m*-H of 20-phenyl group), 7.7 (m, 10H, other *m*-, and *p*-H), 7.89 (d, 2H, *o*-H of 20-phenyl group), 8.0 (m, 6H, other *o*-H), 8.65 (d, 1H, J 4.8 Hz,  $\beta$ -H on C-17 or C-18), 8.7 (m, 5H,  $\beta$ -H), 8.82 (d, 1H, J 4.8 Hz,  $\beta$ -H on C-18 or C-17), 8.99 (s, 1H,  $\beta$ -H on C-3). <sup>13</sup>C NMR:  $\delta$  78.1 (-C=CH), 85.1 (-

C=CH), 118.7, 118.8, 118.9, 119.1 (meso C), 124.7 ( $\beta$ -C-C=CH), 126.5-143.2 (phenyl and porphyrin ring carbons). Mass spectrum m/z 694 (M<sup>+</sup>, <sup>58</sup>Ni). IR v<sub>max</sub> (cm<sup>-1</sup>) 3294 w (=CH), 2095 vvw (C=C). Anal. calcd. for C<sub>46</sub>H<sub>28</sub>N<sub>4</sub>Ni: C, 79.4; H, 4.1; N, 7.9. Found C, 79.5; H, 4.1; N, 8.1%. UV-Vis  $\lambda_{max}$  ( $\epsilon$ ) 423 (229900), 536 (15900), 566 (6400) nm.

1,4-Bis[(5,10,15,20-tetraphenylporphyrinatonickel(II)-2'-yl]-1,3-butadiyne (4e). The above alkyne (4c) (26 mg, 0.038 mmol) was treated with copper(II) acetate monohydrate (8 mg) in dry pyridine (5 mL) at 60° for 8 h. Isolation as for (1e) gave a residue which was subjected to preparative TLC, eluting with 25% CHCl3/hexane. The dark purple/green component was isolated, and recrystallized from CHCl3/methanol to give (4e) as very dark green microcrystals (14 mg, 55%). <sup>1</sup>H NMR:  $\delta$  7.56 (distorted t, 2H, p-H of 20'phenyl groups), ca. 7.7 (m, 20H, m-, and other p-H), 7.87 (d, 4H, o-H of 20'-phenyl group), ca. 8.0 (m, 12H, other o-H), 8.69 (d, 2H, J 5 Hz,  $\beta$ -H on C-17' or C-18'), 8.73 (m, 8H,  $\beta$ -H), 8.78 (d, 2H, J 5 Hz,  $\beta$ -H on C-18' or C-17'), 9.02 (s, 2H,  $\beta$ -H on C-3'). <sup>13</sup>C NMR:  $\delta$  80.4, 83.2 (C=C), 118.7, 118.9, 119.0, 119.1 (meso C), 125.0 ( $\beta$ -C-C=C-), 127.0-143.3 (phenyl and porphyrin ring carbons). Mass spectrum m/z 1388 (M+2, <sup>58</sup>Ni, <sup>58</sup>Ni). Anal. calcd. for C<sub>92</sub>H<sub>54</sub>N<sub>8</sub>Ni<sub>2</sub>: C, 79.6; H, 3.9; N, 8.1. Found C, 79.6; H, 3.9; N, 8.0%. UV-Vis  $\lambda_{max}$  ( $\epsilon$ ) 432 (195100), 542 (28600), 593 (32400) nm.

# Heptaethylporphyrin Derivatives

2-(2'-Bromoethenyl)-3,7,8,12,13,17,18-heptaethylporphyrinatonickel(II) (5b). Free base (5a) (127 mg, 0.2 mmol) was dissolved in glacial acetic acid (15 mL). Nickel(II) acetate tetrahydrate (130 mg) was added, and the reaction mixture was refluxed for 2 h with stirring. After cooling, methanol was added to precipitate the product, which was collected and recrystallized from CHCl3/methanol, to give (5b) as red needles (127 mg, 91%). <sup>1</sup>H NMR:  $\delta$  1.82 (overlapping t, 21H, CH3), 3.93 (overlapping q, 14H, CH2), 7.15 (d, 1H, J 14.0 Hz, -CH=CHBr), 8.47 (d, 1H, J 14.0 Hz, -CH=CHBr), 9.68 (s, 1H, meso H), 9.70 (s, 2H, 2 x meso H), 9.72 (s, 1H, meso H). <sup>13</sup>C NMR:  $\delta$  17.7, 18.2, 19.6, 20.2 (ethyl groups), 97.0, 97.9 (meso C), 109.1 (-CH=CHBr), 130.5 (-CH=CHBr), 138.8-143.1 (ring carbons). Anal. calcd. for C<sub>36</sub>H<sub>41</sub>BrN<sub>4</sub>Ni: C, 64.7; H, 6.2; N, 8.4. Found C, 63.6; H, 6.1; N, 8.2%. UV-Vis  $\lambda_{max}$  ( $\epsilon$ ) 399 (177800), 522 (10150), 564 (23500) nm.

2-Ethynyl-3,7,8,12,13,17,18-heptaethylporphyrinatonickel(II) (5c). The above bromovinyl compound (5b) (100 mg, 0.15 mmol) was dehydrobrominated as for (1b) and (4b), using sodium hydride (67 mg), 1, 2-dimethoxyethane (30 mL) and DMSO (0.1 mL). After 2 h refluxing, the usual work-up, with recrystallization from CHCl3/methanol, gave (5c) as purple crystals (63 mg, 71%). <sup>1</sup>H NMR:  $\delta$  1.82 (overlapping t, 18H, CH3), 1.90 (t, 3H, CH3 of 3-ethyl group), 3.9 (overlapping q, 12H, CH2), 4.10 (q, 2H, CH2 of 3-ethyl group), 4.14 (s, 1H, -C=CH), 9.70, 9.72, 9.77, 10.01 (all s, 4H, meso H). <sup>13</sup>C NMR:  $\delta$  17.2, 18.0, 18.1, 18.15, 18.2, 19.6, 21.1 (ethyl groups), 78.7 (-C=CH), 86.2 (-C=CH), 96.5, 96.8, 98.1, 98.2 (meso C), 120.6 ( $\beta$ -C-C=CH), 138.5-150.0 (ring carbons). UV-Vis  $\lambda_{max}$  ( $\epsilon$ ) 398 (163800), 521 (9400), 555 sh (15100), 564 (23400) nm.

1,4-Bis[3',7',8',12',13',17',18'-heptaethylporphyrinatonickel(II)-2'-yl]-1,3-butadiyne (5d). This compound was prepared as for (1e) and (4e), using (5c) (52 mg, 0.089 mmol), pyridine (10 mL) and copper(II) acetate monohydrate (20 mg), heating at 60° for 2 h. Isolation as above and recrystallization from CHCl<sub>3</sub>/methanol gave (5d) as dark green/purple crystals (33 mg, 62%). A sample of analytical purity was not obtained (see above). <sup>1</sup>H NMR:  $\delta$  1.85 (overlapping t, 30H, CH<sub>3</sub>), 1.94 (t, 6H, CH<sub>3</sub> of 18'-ethyl group), 2.06 (t, 6H, CH<sub>3</sub> of 3'-ethyl group), 3.93 (overlapping q, 20H, CH<sub>2</sub>), 4.06 (q, 4H, CH<sub>2</sub> of 18'-ethyl group), 4.28 (q, 4H, CH<sub>2</sub> of 3'-ethyl group), 9.73, 9.83, 10.20 (all s, 2:1:1, 8H, meso H). <sup>13</sup>C NMR:  $\delta$  17.6, 18.1, 19.6, 21.4 (ethyl groups), 79.2, 84.0 (-C=C-), 96.6, 96.9, 98.4, 98.5 (meso C), 120.5 ( $\beta$ -C-C=CH), 138.5-151.1 (ring carbons). Mass spectrum m/z weak cluster 1170-1174 (M<sup>+</sup>, <sup>58</sup>Ni <sup>58</sup>Ni requires 1172.5). IR v<sub>max</sub> (cm<sup>-1</sup>) 2130 w (C=C). UV-Vis  $\lambda_{max}$  (rel. int.) 407 (10.1), 522 (1.0), 556 sh (1.1), 586 (3.0) nm.

# ACKNOWLEDGEMENTS

This research was supported by a grant from the Australian Research Council. We thank Dr J.P. Bartley for assistance with the NMR spectrometers, and Dr J. Blok for assistance with the preparation of the camera-ready typescript.

# REFERENCES

- 1. Meier, H.; Kobuke, Y.; Kugimiya, S. J. Chem. Soc., Chem. Commun. 1989, 923.
- Osuka, A.; Nakajima, S.; Nagata, T.; Maruyama, K.; Toriumi, K. Angew. Chem. Int. Ed. Engl. 1991, 30, 582-584.
- 3. Tabushi, I.; Sasaki, T. Tetrahedron Lett. 1982, 1913-1916.
- 4. Sessler, J. L.; Hugdall, J.; Johnson, M. R. J. Org. Chem. 1986, 51, 2838-2840.
- 5. Sessler, J. L.; Johnson, M. R.; Lin, T.-Y.; Creager, S. E. J. Am. Chem. Soc. 1988, 110, 3659-3661.
- 6. Nagata, T.; Osuka, A.; Maruyama, K. J. Am. Chem. Soc. 1990, 112, 3054-3059.
- 7. Helms, A.; Heiler, D.; McLendon, G. J. Am. Chem. Soc. 1991, 113, 4325-4327.
- 8. Heiler, D.; McLendon, G.; Rogalskyj, P. J. Am. Chem. Soc. 1987, 109, 604-606.
- 9. Osuka, A.; Maruyama, K. J. Am. Chem. Soc. 1988, 110, 4454-4456.
- 10. Chang, C. K.; Abdalmuhdi, I. J. Org. Chem. 1983, 48, 5388-5390.
- 11. Chardon-Noblat, S.; Sauvage, J.-P. Tetrahedron 1991, 47, 5123-5132.
- 12. Crossley, M. J.; Burn, P. L. J. Chem. Soc., Chem. Commun. 1991, 1569-1571.
- 13. Lamrabte, A.; Momenteau, M.; Maillard, P.; Seta, P. J. Mol. Elec. 1990, 6, 145-153.
- 14. Narang, S. C.; Ventura, S. U. S. Pat. 4, 908, 442, 1990, appl. no.: 247, 590, Sep. 23, 1988.
- 15. Kobayashi, N.; Numao, M.; Kondo, R.; Nakajima, S.; Osa, T. Inorg. Chem. 1991, 30, 2241-2244.
- 16. Arnold, D. P.; Johnson, A. W.; Mahendran, M. J. Chem. Soc., Perkin Trans 1 1978, 366-370.
- 17. Stiegman, A. E.; Graham, E.; Perry, K. J.; Khundhar, L. R.; Cheng, L.-T.; Perry, J. W. J. Am. Chem. Soc. 1991, 113, 7658-7666.
- 18. Proess, G.; Pankert, D.; Hevesi, L. Tetrahedron Lett. 1992, 33, 269-272.
- 19. Anderson, H. L. Tetrahedron Lett. 1992, 33, 1101-1104.
- 20. Maruyama, K.; Kawabata, S. Bull. Chem. Soc. Japan 1990, 63, 170-175.

- (a) Anderson, H. L.; Sanders, J. K. M. Angew. Chem. Int. Ed. Engl. 1990, 29, 1400-1403. (b) Anderson, H. L.; Sanders, J. K. M.J. Chem. Soc., Chem. Commun. 1989, 1714-1715.
- 22. Porteau, F.; Palacin, S.; Ruaudel-Teixier, A.; Barraud, A. Makromol. Chem., Macromol. Symp. 1991, 46, 37-45.
- (a) Arnold, D. P.; Johnson, A. W.; Winter, M. J. Chem. Soc., Perkin Trans. 1 1977, 1643-1647. (b) Arnold, D. P.; Gaete-Holmes, R.; Johnson, A. W.; Smith, A. R. P.; Williams, G. J. Chem. Soc., Perkin Trans. 1 1978, 1660-1670. (c) Vicente, M. G. H.; Smith, K. M. J. Org. Chem. 1991, 56, 4407-4418.
- 24. Treibs, A; Häberle, N. Liebigs Ann. Chem. 1968, 718, 183-207.
- 25. Momenteau, M.; Loock, B.; Bisagni, E. J. Heterocyclic Chem. 1979, 16, 191-192.
- 26. Vicente, M. G. H.; Smith, K. M. Tetrahedron 1991, 34, 6887-6894.
- 27. Sessler, J. L.; Mozaffari, A.; Johnson, M. R. personal communication.
- 28. Johnson, E. C.; Dolphin, D. Inorganic Syntheses 1980, XX, 143-144.
- 29. Callot, H. J. Tetrahedron Lett. 1973, 29, 899-901.
- 30. Callot, H. J. Bull. Soc. Chim. Fr. 1973, 3413-3416.