CHARACTERIZATION OF DECAMETHYL AND ETHOXYCARBONYL PENTAPHYRINS

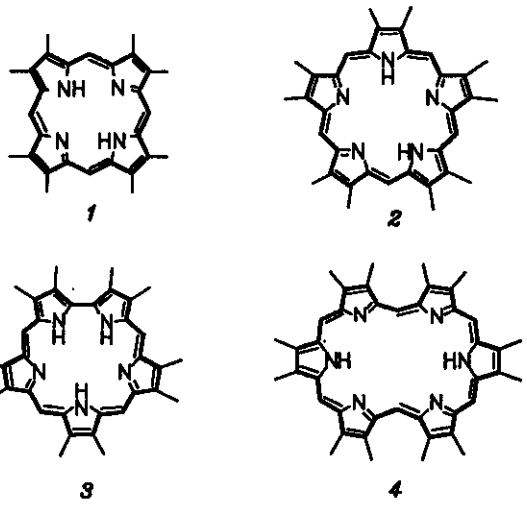
Richmond E. Danso-Danquah, Lily Y. Xie, and David Dolphin*

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C., Canada, V6T 1Z1

Abstract – The syntheses of decamethyl- and ethoxycarbonyl-pentaphyrins are described. Their spectroscopic characterizations are presented in comparison with the permethyl derivatives of porphyrin, sapphyrin and hexaphyrin. The ethoxycarbonyl containing pentaphyrins are the only examples, amongst the expanded polypyrrolic macrocycles, that have an electron withdrawing group directly attached to the macrocyclic ring system. Elimination of a pyrrole and methine carbon unit in the mass spectrometer has been observed as a common feature for the pentaphyrin free bases as well as their metal derivatives.

A recent synthetic paper on hexaphyrin[1] in this journal has prompted us to report our results on the characterization of decamethylpentaphyrin and related derivatives. Although the first example of a pyrrolic macrocycle with more than four rings was reported by Woodward[2] in 1966, the full characterization and experimental details on the synthesis of decamethylsapphyrin was not published until 1983.[3] Gossauer succeeded in the synthesis of the pentaphyrin chromophore in the same year.[4] The challenge of making the permethyl derivative of pentaphyrin appealed to us in that it would make a nice comparison of the chemistry and spectroscopic properties with the existing octamethylporphyrin and decamethylsapphyrin. Despite the current interest in the properties of expanded polypyrrolic macrocycles[5] for their application in photodynamic therapy,[6,7] anion binding,[8-10] and complexation with lanthanides for MRI paramagnetic contrast agents,[11] pentaphyrins have received much less attention compared to sapphyrins which are also pentapyrrolic aromatic macrocycles. The first metal complex of a pentaphyrin, uranyl pentaphyrin was recently reported by Sessler and co-workers[12] and

the pentapyrrolic framework was confirmed by X-ray diffraction analysis. With the synthesis of dodecamethylhexaphyrin, the permethyl derivatives of four different pyrrole-containing macrocycles, i.e. octamethylporphyrin (**1**),[13] decamethylsapphyrin (**2**),[3] decamethylentaphyrin (**3**), and dodecamethylhexaphyrin (**4**),[14] are now available for spectroscopic comparison.

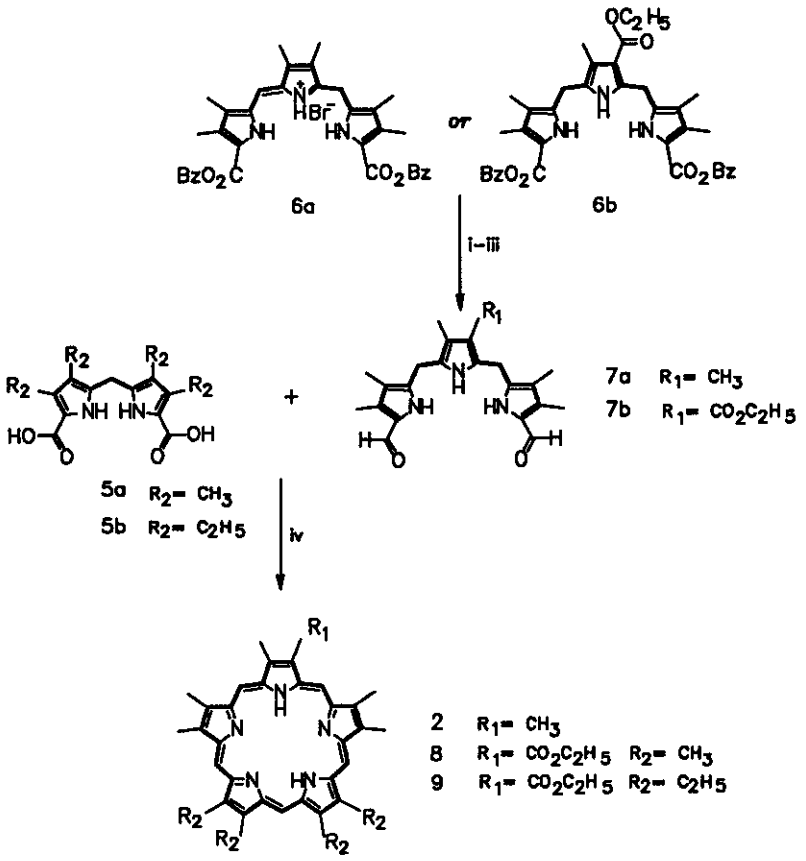


Our efforts in the synthesis of pentaphyrins was stimulated by the rational synthesis of sapphyrin.[3] Substitution of the bipyrrole dialdehyde in the sapphyrin synthesis by a dipyrromethane dialdehyde and condensing it with tripyrrane seemed to be the most obvious approach to pentaphyrin at the time. Tripyrrane diacids and dialdehydes were coupled with dipyrromethane dialdehyde and diacid respectively in the presence of catalytic amounts of *p*-toluenesulfonic acid in oxygenated ethanol or methanol. The coupling reactions were monitored by uv-vis spectrum for several days and in some cases for weeks, yielding only porphyrins instead of the pentapyrrole macrocycles.[15] Another attempt was made to use a tripyrrane and dipyrromethane dialdehyde in methylene chloride with anhydrous hydrogen chloride, but once again this invariably give only porphyrin.[16] In fact, when a dipyrromethane dialdehyde was allowed to cyclize with linear oligopyrroles (tri-, tetra- and pentapyrrolic analogs of dipyrromethanes) under mild conditions (25% HI in acetic acid at room temperature), only one cyclic tetrapyrrole was formed in each case which was subsequently oxidized to porphyrin.[17] Today the preparation of pentaphyrin is still limited basically to one route, i.e., coupling of an α,α'-unsubstituted dipyrro-

methanes, with a bisformyltripyrrane in acetic acid in the presence of HBr. It is noteworthy that formation of pentaphyrin was observed as a by-product in the coupling of tripyrrane and tripyrrane dialdehyde in the synthesis of hexaphyrin as a result of eliminating one pyrrolic unit.[1]

In general α,α'-unsubstituted tripyrranes and dipyrromethanes without electron withdrawing groups are unstable. α,α'-Dicarboxydipyrromethanes are known to readily undergo decarboxylation under acidic conditions. It was thus decided in this study to use dicarboxylic acid derivatives instead of the α,α'-unsubstituted analogs, a minor variation from the literature procedure.[4,12] The effect of an electron-withdrawing group on the macrocycle was also considered. Tripyrranes, vulnerable to acid-catalyzed fragmentation in the absence of electron-withdrawing groups, became the obvious candidates for introduction of a stabilizing electron withdrawing group, thus an ethoxycarbonyl group was introduced to the central pyrrolic unit of tripyrranes (**6b** and **7b**). We also changed the β-substituents of the diacids from the tetramethyl (**5a**) to tetraethyl (**5b**), in order to examine how the solubility of the dipyrromethane diacid would affect macrocyclic formation (Scheme I). The yield for decamethylpentaphyrin (**2**), which is less soluble than **8** and **9**, was found to be lower than that for the other two derivatives, but changing from the methyl group (**5a**) to ethyl (**5b**) did not noticeably affect the yield.

The pentaphyrins described here and elsewhere[4,5] all exhibit intense Soret-like absorption bands in the 450-470 nm region for the free base and the tricationic forms. For example, the trication of decamethylpentaphyrin has a Soret band at 455 nm (ε 3.0×10^{5} $M^{-1}cm^{-1}$). This is at a longer wavelength than that of the corresponding dicationic octamethylporphyrin (414 nm, ε 2.67×10^{5}),[3] but close to that of the dicationic decamethylsapphyrin (456.6 nm, ε 5.94×10^{5}). The Soret band of the tetracation of dodecamethylhexaphyrin is, however, even more bathochromatically shifted (553 nm, ε 7.4×10^{4}). With additional absorption bands at longer wavelengths for octamethylporphyrin (four bands between 500-630 nm),[3] sapphyrin (four bands between 600-700 nm),[3] the optical spectra of pentaphyrins display only one broad band between 600-700 nm. The absorption data originally reported for the free base pentaphyrin chromophore by Rexhausen and Gossauer in CH_2Cl_2 [λ nm (log ε) 367 (3.74), 458 (3.58), 642 (3.78), 695 (3.55)][5] is in disagreement with our data for free base decamethyl-



Reagents and conditions: i) H_2, 10% Pd/C in THF, room temperature; ii) DMF, Ar, reflux; iii) PhCOCl, DMF, 0°C; $NaHCO_3$; iv) 30% HBr in HOAc; Chloranil.

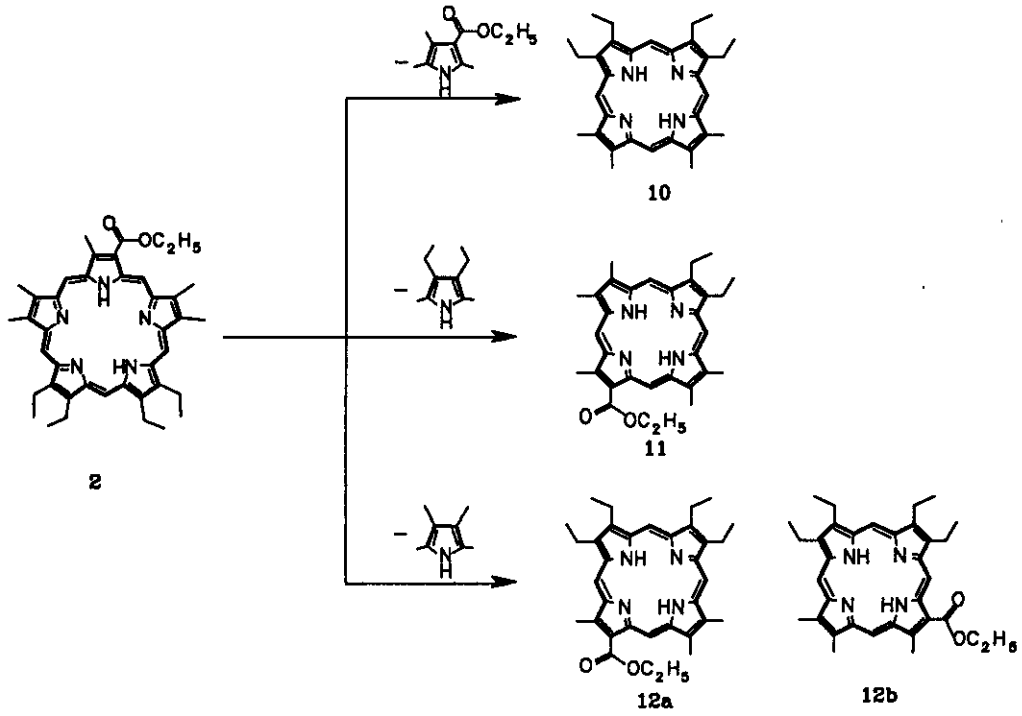
Scheme 1

pentaphyrin (474, 670 nm). It is however, similar to the data for tricationic decamethylpentaphyrin (380, 455, 595, 645, 705 nm, log ε 3.77, 5.47, 2.95, 3.89, 3.55). Protonation by acidic impurities in the solvent must have occurred in their case, manifesting the strongly basic nature of the pentaphyrin chromophore similar to that of the sapphyrins. The spectrum of the free base was obtained in the presence of triethylamine. The direct attachment of an ethoxycarbonyl group onto the pentaphyrin macro ring extends the conjugation. As a result, the Soret and the longest absorption band were shifted a further 3~8 and 10~16 nm to the red respectively. Nmr spectra of the pentaphyrin derivatives are consistent with the presence of a diamagnetic ring current larger than that of the porphyrin system. Decamethylpentaphyrin tris(hydrotrifluoroacetate) exhibits a single resonance at δ 12.49

corresponding to a set of five methine protons. The ten peripheryl methyl groups were observed as a singlet at δ 4.41 while the inner NH protons appeared at -5.52 ppm. The corresponding resonances for octamethylporphyrin bis(hydrotrifluoroacetate) are seen at 10.98, 3.78, -4.82 respectively.[18] These resonances of decamethylpentaphyrin are close to those of decamethylsapphyrin (11.51 and 11.70 for meso, 4.04, 4.08, 4.19 and 4.22 for methyl, -4.84, -5.0 and -5.46 for NH).[3] The anisotropic shift is, however, comparable to that of dodecamethylhexaphyrin whose resonances appear at 12.30 and -7.52 ppm for the *exo* and *endo* methine protons and 4.38 and 4.19 for the peripheral methyl groups. The simplicity of the nmr spectra of octamethylporphyrin and decamethylpentaphyrin that both exhibit only three resonances for three types of protons confirms that decamethylpentaphyrin is a true homologue of octamethylporphyrin. Sapphyrin displays splitting in all three types of resonances due to the omission of one methine bridge and hexaphyrin due to the inversion of two methine bridges.

In the porphyrin system, the *meso*-methine protons and the inner NH protons are usually the most nmr sensitive to variation of β substituents. Among the pentaphyrins described in this paper, the effect of an ester side chain on the nearest methine and NH protons is apparent. Replacement of an ethoxycarbonyl for a methyl group caused the splitting of methine and NH resonances into multiple singlets, the ethoxycarbonyl group also exerts deshielding effects on these protons. The methine protons of 2-ethoxycarbonylnonamethylpentaphyrin (**8**) appeared at 11.91, 12.00, 12.12 and 13.29; while the nearest methine proton shifted downfield, the others moved upfield compared to the decamethylpentaphyrin methine resonance. The same trend is seen with 2-ethoxycarbonyl-3,7,8,22,23-pentamethyl-12,13,17,18-tetraethylpentaphyrin (**9**) whose methine protons appeared at 12.16, 12.23, 12.40 and 13.43. A downfield shift of about 0.9 ppm is comparable to the shift caused by the CO_2CH_3 group on the nearest methine group of a 2- or 4- substituted deuteroporphyrin (0.7 ppm).[19] Deshielding for the inner NH protons were also observed with the largest change of ~1.2 ppm compared to the decamethyl derivative (-4.33 for **8** and -4.23 for **9**). An ethoxycarbonyl group isolated from the macrocyclic ring by two CH_2 units does not affect the methine resonances as much (12.47, 12.48 and 12.55).[4]

All the pentaphyrins in this study exhibit interesting patterns in their electron impact mass spectroscopy. For decamethylpentaphyrin, an intense peaks at *m/z* 476 corresponding to the iron complex of octamethylporphyrin was observed, the metal was picked up in the ion source which is commonly observed with metal-free porphyrin mass spectroscopy.[20] The same fragmentation feature was seen for the zinc complex of decamethylpentaphyrin (**13**), the base peak was at *m/z* 484, the mass of zinc octamethylporphyrin. Thus the complex, like the metal free pentaphyrin nucleus, rearranged to give a zinc complex of the porphyrin with loss of pyrrole and methine carbon fragments. The zinc complex of decamethylsapphyrin was reported to behave in a similar way[3] although the sapphyrin free base was stable toward electron bombardment. For sapphyrin, loss of a pyrrole adjacent to the direct pyrrole linkage seemed to be prefered, clearly favoring the formation of porphyrin. However in the case of pentaphyrin, random extrusion of a monopyrrolic unit to give a porphyrin is expected. Indeed the substituted pentaphyrin, 2-ethoxycarbonyl-3,7,8,22,23-pentamethyl-12,13,17,18-tetraethylpentaphyrin (**9**), rearranged to three porphyrins corresponding to the loss of three separate pyrrolic units (Scheme 2, **10, 11, 12a** and **12b**).



Scheme 2

Macrocyclic ring contraction from five to four rings also occured when the uranyl complex of superphthalocyanine, containing five iminoisoindoline subunits, was treated with acid or other metal ions.[21]

EXPERIMENTAL

5,5'-Biscarboxy-3,3',4,4'-tetramethyl-2,2'-dipyrromethane (**5a**) and 5,5'-biscarboxy-3,3',4,4'-tetraethyl-2,2'-dipyrromethane (**5b**) were prepared according to literature procedures.[4] Silica gel GF (Analtech, 2 mm on 20x20 cm) was used for preparative thin layer chromatography. Melting points were determined with a Thomas Model 40 micro hot stage melting point apparatus. Electronic absorption spectra were recorded using a Cary 17 spectrometer. Nuclear magnetic resonance spectra were recorded on a Bruker WH-400 spectrometer for ^{1}H and a Varian XL-300 spectrometer for $^{13}C\{^{1}H\}$. Mass spectra were recorded on a Varian MAT CH4-B or a Kratos/AEI MS-902 spectrometer.

5-(5-Benzyloxycarbonyl-3,4-dimethylpyrrol-2-ylmethyl)-5'-benzyloxycarbonyl-3,3',4,4'-tetramethyl-2,2'-dipyrromethene hydrobromide (6a). 5-Benzyloxycarbonyl-5'-t-butoxycarbonyl-3,3',4,4'-tetramethyl-2,2'-dipyrromethane[3] (1.3 g, 3 mmol) in a round bottom flask was treated with trifluoroacetic acid (5 ml) under a nitrogen atmosphere at room temperature for 5 min. 5-Benzyloxycarbonyl-5-formyl-3,4-dimethylpyrrole[22] (0.77 g, 3 mmol) previously dissolved in methanol (60 ml) was added in one portion. The red solution was stirred for an additional 90 min followed by the addition of 30% HBr in acetic acid (1 ml), and ether (25 ml). Stirring was continued for another 15 min until reddish-orange crystals had formed. The crystals were filtered, washed with ether, then air dried, to yield 1.59 g (76%). mp 197-199°C. ^{1}H Nmr ($CDCl_3$) δ 2.03 (s, 3H), 2.06 (s, 3H), 2.25 (s, 6H), 2.86 (s, 6H), 4.50 (s, 2H), 5.29 (s, 2H), 5.50 (s, 2H), 7.30 (m, 10H), 7.50 (s, 1H), 10.67 (s, 1H), 12.45 (s, 1H), 14.86 (s, 1H); ms (EI) *m/z* 577 (M^{+}- Br, 8), 336 (24), 242 (26), 108 (43), 91 (100).

2,5-Bis(5-formyl-3,4-dimethylpyrrol-2-methyl)-3,4-dimethylpyrrole (7a). A mixture of tripyrrin hydro-

bromide **6a** (1.4 g, 2.2 mmol), triethylamine (5 drops) and anhydrous sodium acetate (3 g) were dissolved in THF (600 ml). 10% Palladium on charcoal (0.2 g) was added and the mixture was hydrogenated at room temperature under atmospheric pressure. Hydrogen uptake was complete in 1 h. The catalyst was removed by filtration and the filtrate was evaporated to dryness in vacuo. The crude product was used in the next reaction.

In an apparatus consisting of a 150 ml Erlenmeyer flask fitted with a Claisen adapter and a gas inlet, DMF (5 ml) was heated to reflux. To the boiling DMF, under argon, were successively added 4x5 ml DMF portions of the α, α'-biscarboxypyrrole prepared in the above reaction. Decarboxylation was monitored by the optical absorption spectrum and was completed in 30 min. The solution was chilled on ice and used in the next reaction without purification.

Benzoyl chloride (2.0 g, 14.2 mmol) was added in a rapid dropwise fashion to the above reaction mixture which was stirred for 30 min to ensure complete reaction and left to stand at room temperature for 2 h. Water (60 ml) and sodium bicarbonate (2.0 g, excess) were added, the reaction mixture was heated on a steam bath for 1 h, during which time the product coagulated into crystalline lumps. The mixture was cooled, the solid collected by filtration, washed with water and recrystallized from methylene chloride-methanol to yield 0.61 g (76%). mp > 240°C. ^{1}H Nmr ($CDCl_3$) δ 1.98 (s, 6H), 2.28 (s, 6H), 2.48 (s, 6H), 3.93 (s, 4H), 8.02 (s, 1H), 9.29 (s, 1H), 9.43 (s, 1H). 10.05 (s, 1H), 10.18 (s, 1H); ms (EI) *m/z* 565 (M^+, 2), 258 (77), 229 (24), 201 (36), 136 (100), 123 (30), 108 (40), 94 (36).

2,5-Bis-(5-benzyloxycarbonyl-3,4-dimethylpyrrol-2-ylmethyl)-3-ethoxycarbonyl-4-methylpyrrole (6b). 2-Benzyloxycarbonyl-5-chloromethyl-3,4-dimethylpyrrole[15] (12.0 g, 43 mmol) and 3-ethoxycarbonyl-4-methyl-pyrrole[23] (3.3 g, 22 mmol) were dissolved in methylene chloride (60 ml) and stirred for 15 min at room temperature. The solvent was boiled down to a small volume on the steam bath. Methanol (50 ml) was added to displace methylene chloride. The methanol solution was cooled, the precipitate was collected by filtration and washed with methanol. The product was found to be a mixture containing the desired product and 5,5'-benzyloxycarbonyl-3,3',4,4'-tetramethyl-2,2'-dipyrromethane. The mixture was separated by fractional

recrystallization from methylene chloride and petroleum ether (1:2). The desired product which was more soluble in methylene chloride was recrystallized from THF/methanol to yield 5.5 g (39%). mp 181-182°C. ^{1}H Nmr ($CDCl_3$) δ 1.38 (t, 3H, J=7.0 Hz), 1.75 (s, 3H), 1.83 (s, 3H), 2.40 (s, 3H), 2.46 (s, 6H), 3.38 (q, 2H, J=7.0 Hz), 4.1-4.5 (m, 8H), 7.25 (m, 10H), 9.58 (s, 1H). 10.93 (s, 1H), 11.52 (s, 1H); ms (EI) *m/z* 635 (M^+, 3), 594 (60), 436 (100), 315 (41), 91 (90).

2,5-Bis-(5-formyl-3,4-dimethylpyrrol-2-ylmethyl)-3-ethoxycarbonyl-4-methylpyrrole. (7b) 2,5-Bis-(5-benzyloxycarbonyl)-3,4-dimethylpyrrole (**6b**) (1.3 g, 2 mmol) was hydrogenated and decarboxylated in a similar fashion as described in the synthesis of **7a**. Formylation of the tripyrrane was carried out using phosphorous oxychloride and DMF at 0°C in 30 min. The solution was poured onto crushed ice. Solid sodium bicarbonate was added until the solution became slightly basic and then heated on a steam bath. The hot solution was filtered to remove brown tar and heated until the solution became turbid, and a grey solid formed. Heating was continued for a further half hour, the mixture was cooled, and the solid was filtered and washed with water. The product was recrystallized in methylene chloride-methanol to yield 0.78 g (92%). mp 220-221°C. ^{1}H Nmr ($CDCl_3$) δ 1.36 (t, 3H, J=7.0 Hz), 1.95 (s, 3H), 1.97 (s, 3H), 2.20 (s, 3H), 2.21 (s, 3H), 2.29 (s, 3H), 3.79 (s, 2H), 4.30 (q, 2H, J=7.0 Hz), 4.31 (s, 2H), 8.97 (s, 1H), 9.01 (s, 1H), 10.06 (s, 1H), 10.97 (s, 1H), 11.03 (s, 1H). Ms (EI) *m/z* 423 (M^+, 100), 300 (59), 287 (45), 254 (53), 213 (38), 136 (57).

2,3,7,8,12,13,17,18,22,23-Decamethylpentaphyrin (2). Dipyrromethane diacid (**5a**) (40 mg, 0.13 mmol) was dissolved in methylene chloride (300 ml) under argon. After stirring the solution for 30 min, the tripyrrane dialdehyde (**7a**) (50 mg, 0.13 mmol) was added. The solution was stirred for 10 min and acidified with 30% HBr in acetic acid (0.9 ml). The color of the reaction mixture changed from yellow to pinkish-red and then to red which did not change after 2 more hours. Chloranil (0.3 g, excess) was added to effect oxidation and the reaction mixture was stirred for a further 36 h. Development of the reaction was followed by uv-visible spectroscopy. The solvent was removed on a rotary evaporator and the residual product chromatographed using

silica gel GF plates (Analtech) with fluorescent indicator and ethyl acetate as eluent. Yield 12.0 mg solid (21%). ^{1}H Nmr ($CDCl_3$/1% TFA) δ 4.41 (s, 30H), 12.49 (s, 5H), -5.52 (s, 5H). ^{13}C Nmr (TFA) δ 14.5, 102.0, 142.7, 147.3; ms (EI) *m/z* 476 (3); ms (FAB) *m/z* 528 (M^++H), 529 (M^++2H); uv-vis (CH_2Cl_2/TFA) λ_{max} (log ε) 380 (3.77), 455 (5.77), 595 (2.95), 645 (3.89), 705 (3.55). (CH_2Cl_2/Et_3N) 474 (4.05) 670 (3.31).

2-Ethoxycarbonyl-3,7,8,12,13,17,18,22,23-nonamethylpentaphyrin (8) was prepared via the same procedure as described for **2** but using tripyrrane dialdehyde (**7b**). Yield 32%. ^{1}H Nmr ($CDCl_3$/1% TFA) δ -4.33 (s, 1H), -4.63 (s, 1H), -4.70 (s, 1H), -4.76 (s, 1H), -4.80 (s, 1H), 1.95 (t, 3H, J=7.5 Hz), 4.13 (s, 6H), 4.15 (s, 12H), 4.19 (s, 6H), 4.51 (s, 3H), 5.18 (q, 2H, J=7.5 Hz), 11.91 (s, 2H), 12.00 (s, 1H), 12.12 (s, 1H), 13.29 (s, 1H). ^{13}C Nmr (30% TFA/$CDCl_3$) δ 12.8, 12.9, 29.8, 64.6, 97.6, 97.7, 99.5, 101.2, 101.6, 131.5, 136.5, 138.0, 138.4, 140.3, 140.3, 140.6, 141.7, 141.7, 141.9, 142.1, 142.4, 143.8, 165.5; ms (EI) *m/z* 587 (M^++2H, 4.7), 588 (M^++3H, 2.6), 480 (41), 452 (11), 422 (23); ms (FAB) *m/z* 586, 587; uv-vis (CH_2Cl_2/TFA) λ_{max} (log ε) 365 (3.99), 458 (5.68), 595 (3.66), 645 (4.27), 715 (4.01); (CH_2Cl_2/Et_3N) 345 (4.53), 450 (4.73), 642 (4.01).

2-Ethoxycarbonyl-3,7,8,22,23-pentamethyl-12,13,17,18-tetraethylpentaphyrin (9) was prepared *via* the same procedure as described for **2** but using dipyrromethane diacid (**5b**) and tripyrrane dialdehyde (**7b**). Yield 30%. ^{1}H Nmr ($CDCl_3$/TFA) δ -4.23 (s, 1H), -4.48 (s, 1H), -4.55 (s, 1H), -4.58 (s, 1H), -4.61 (s, 1H), 2.05 (t, 3H, J=7.0 Hz), 2.17 (m, 12H), 4.26 (s, 3H), 4.27(s, 3H), 4.33 (s, 6H), 4.65 (s, 3H), 4.75 (m, 8H), 5.30 (q, 2H, J=7.0 Hz), 12.16 (s, 2H), 12.23 (s, 1H), 12.40 (s, 1H), 13.43 (s, 1H). ^{13}C Nmr (30% TFA/$CDCl_3$) δ 13.0, 14.5, 17.6, 17.7, 17.9, 20.7, 20.8, 27.3, 29.7, 63.8, 96.2, 96.5, 98.5, 101.2, 101.7, 131.5, 136.2, 137.7, 138.2, 139.7, 140.1, 140.5, 141.1, 141.4, 141.6, 142.3, 142.5, 143.1, 144.1, 147.8, 148.1, 148.6, 164.8; ms (EI) *m/z* 642 (M^++2H, 12.7), 536 (100), 508(52), 478 (63); ms (FAB) *m/z* 642, 643; uv-vis (CH_2Cl_2/TFA) λ_{max} (log ε) 370 (5.10), 63 (6.18), 603 (4.67), 652 (4.96), 721 (4.79); (CH_2Cl_2/Et_3N) 350 (5.21), 450 (5.44), 645 (4.74).

Zinc (2,3,7,8,12,13,17,18,22,23-Decamethylpentaphyrin) (13) Decamethylpentaphyrin (**2**) (20 mg) was

dissolved in methanol (20 ml) and stirred in the dark for 5 min. A saturated methanol solution of zinc acetate (1 ml) and anhydrous sodium acetate (0.1 g) were added and the resulting reaction mixture was stirred at room temperature for 5 h and allowed to stand at room temperature for 3 days. Methylene chloride (50 ml) was added, the solution was washed twice with water (15 ml) dried over magnesium sulphate and evaporated at room temperature in vacuo to give 15 mg solid (67%). Ms (EI) *m/z* 591 (3), 484 (100); ms (FAB) *m/z* 591, 592; uv-vis (CH_2Cl_2) λ_{max} (nm) 388, 395, 468, 495, 600, 628, 655.

ACKNOWLEDGEMENT

We thank the Natural Sciences and Engineering Research Council of Canada for the financial support.

REFERENCES

1. R. Charrière, T. A. Jenny, H. Rexhausen, and A. Gossauer, *Heterocycles*, 1993, **36**, 1561.
2. R. B. Woodward, Aromaticity Conference, Sheffield, 1966.
3. V. J. Bauer, D. L. Clive, D. Dolphin, J. B. Paine, III, F. L. Harris, M. M. King, J. Loder, S-W. C. Wang, and R. B. Woodward, *J. Am. Chem. Soc.*, 1983, **105**, 6429.
4. H. Rexausen and A. Gossauer, *J. Chem. Soc., Chem. Commun.*, 1983, 275.
5. J. L. Sessler and A. K. Burrell, *Top. Cur. Chem.*, 1991, **161**, 177.
6. M. L. Judy, J. L. Matthews, and J. L. Sessler, *Photochem. Photobiol.*, 1991, **53**, 101.
7. G. Schermann, R. Schmidt, A. Volcker, H. D. Brauer, H. Mertes, and B. Franck, *Photochem. Photobiol.*, 1990, **52**, 741.
8. M. Tabata, K. Kaneko, Y. Murakami, Y. Hisaeda, and H. Mimura, *Microchem. J.*,1994, **49**, 136.
9. J. L. Sessler, H. Furuta, and V. Kral, *Supramol. Chem.*, 1993, **1**, 209.
10. J. L. Sessler, D. A. Debra, M. J. Cyr, and H. Furuta, *J. Chem. Soc., Chem. Commun.*, 1991, 1733.
11. J. L. Sessler, T. Murai, and G. Hemmi, *Inorg. Chem.*, 1989, **28**, 3390.
12. A. K. Burrell, G. Hemmi, V. Lynch, and J. L. Sessler, *J. Am. Chem. Soc.*, 1991, **113**, 4690.

13. R. J. Abraham, A. H. Jackman, and G. W. Kenner, *J. Chem. Soc.*, 1961, 3468.

14. A. Gossauer, *Bull. Soc. Chim. Belg.*, 1983, **92**, 793.

15. J. B. Paine III, Ph. D. Thesis, Harvard University, Cambridge, Massachusetts, U.S.A., 1973.

16. R. A. Sawka, M.Sc. Thesis, Univeristy of British Columbia, Vancouver, B.C. Canada, 1976.

17. B. Franck, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 343.

18. A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, 1965, 1620.

19. H. Scheer and J. J. Katz, 'Porphyrins and Metalloporphyrins', ed. by K. M. Smith, Elsevier, Amsterdam, 1975, p. 399.

20. H. Budzikiewicz, 'The Porphyrins', Vol. 3, ed. by D. Dolphin, Academic Press, New York, 1978, p. 399.

21. T. J. Marks and D. R. Stojakovic, *J. Chem. Soc., Chem. Commun.*, 1975, 29.

22. G. M. Badger and A. D. Ward, *Aust. J. Chem.*, 1964, **17**, 649.

23. H. Fischer and H. Orth, "Die Chem. Des Pyrroles", Vol. 1, p. 246.

Received, 20th June, 1995