N-Methylated Tetraphenylporphins

By **Hassan M. G. Al-Hazimi** and **Anthony H. Jackson,*** Department of Chemistry, University College, Cardiff CF1 1XL
Alan W. Johnson * and **Manfred Winter,** School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

Methylation of *meso*-tetraphenylporphin affords *N*-methyl, *trans*-N_aN_b-dimethyl, and *trans.trans*-$N_aN_bN_c$-trimethyl derivatives. The structures of the products were assigned from n.m.r. data, and that of the N_aN_b-dimethylporphin was confirmed by ethylation to form the unsymmetrical N_aN_b-dimethyl-N_c-ethyl derivative. The $N_aN_bN_c$-trimethylporphin decomposed on heating to give N_aN_b-dimethyl- and *N*-methyl-tetraphenylporphins. In none of our experiments was either of the isomeric *cis*- and *trans*-N_aN_c-dimethylporphins found, in contrast to earlier findings in the octa-alkylporphin series. The results are discussed in relation to the effects of the *meso*-phenyl and *N*-methyl groups on distortion of the aromatic nucleus.

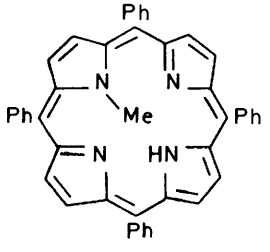
meso-TETRAPHENYLPORPHIN (TPP) has been widely used in recent years to study the properties of the porphin macrocycle, largely perhaps because it is the most readily accessible porphin. A wide variety of *meso*-tetraphenylporphins bearing acidic, neutral, or basic phenyl substituents have also been prepared, and their physicochemical properties and *X*-ray crystal structures have been investigated.[1] The relatively bulky phenyl groups in TPP have an important steric effect on the shape of the macrocycle (as shown by *X*-ray studies), but the electronic effects are less important because the *meso*-phenyl substituents cannot become coplanar with the macrocycle. In the light of our earlier interests [2-4] in the effects of *N*-methylation of octa-alkylporphins on both the geometry and the aromatic character of the porphin ring system, we decided to investigate the *N*-methylation of TPP; this paper describes the results of studies undertaken independently in Cardiff and in Sussex.

TPP was prepared essentially by Adler's method,[5] small amounts of tetraphenylchlorin formed as a by-product being removed by oxidation [6] with DDQ. Methylations of TPP were carried out with both methyl iodide and methyl fluorosulphate and gave mixtures of mono-, di-, and tri-*N*-methylated derivatives. For example, in the absence of solvent, heating with methyl iodide afforded the dimethylated derivative as the major product, although a substantial amount of TPP was also recovered, even after prolonged heating at 100 °C in a sealed tube. In refluxing chloroform solution, however, the major product was the tri-*N*-methyl-TPP although again a substantial amount of TPP was recovered. It seems likely that the initial methylation is slow, but that subsequent formation of the di-*N*-methyl derivative is fairly rapid owing to the relatively high basicity of the mono-*N*-methyl-TPP as compared with TPP; if no solvent is present the di-*N*-methyl-TPP crystallises out as its hydriodide and hence is protected from the further methylation which occurs in chloroform solution (Table). Lavallee and Gebala [7] have described similar preparations

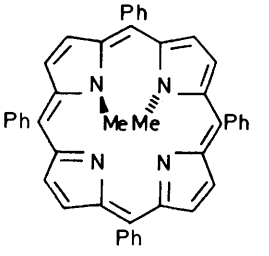
[1] E. B. Fleischer, *Accounts Chem. Res.*, 1970, **3**, 105.
[2] G. R. Dearden and A. H. Jackson, *Chem. Comm.*, 1970, 205; M. J. Broadhurst, R. Grigg, G. Shelton, and A. W. Johnson, *ibid.*, p. 231; R. Grigg, A. Sweeney, and A. W. Johnson, *ibid.*, p. 1237; R. Grigg, A. Sweeney, G. R. Dearden, A. H. Jackson, and A. W. Johnson, *ibid.*, p. 1273.
[3] R. Grigg, G. Shelton, A. Sweeney, and A. W. Johnson, *J.C.S. Perkin I*, 1972, 1789.
[4] A. H. Jackson and G. R. Dearden, *Annals New York Acad. Sci.*, 1973, **206**, 151.
[5] A. D. Adler, L. Sklar, F. R. Longo, J. Finarelli, and M. Finarelli, *J. Org. Chem.*, 1967, **32**, 476.
[6] K. M. Smith and M. J. Sutton, *Tetrahedron Letters*, 1973, 2887.
[7] D. K. Lavellee and A. E. Gebala, *Inorg. Chem.*, **1974**, **13**, 2004.

of *N*-methyltetraphenylporphin by treatment with methyl iodide or methyl fluorosulphate in connection with their studies of the dissociation of its copper complex; they also observed the formation of further methylated products but these were not characterised.

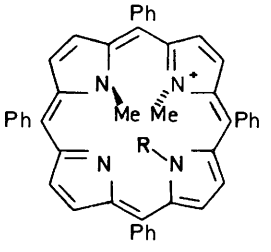
The *N*-methyl derivatives of TPP obtained in this way were separated by chromatography on alumina with increasingly polar solvents ranging from toluene (or light petroleum) to ethyl acetate and then chloroform –methanol. TPP was eluted first, followed by a green band which gave a deeply coloured eluate on concentration; crystallisation afforded the mono-*N*-methyl-TPP (1) as the violet free base. Two other green bands were subsequently eluted, the first of which proved to be the N_aN_b-dimethyl derivative (2) and the second the *trans,trans*-$N_aN_bN_c$-trimethyl-TPP (3a) as shown by



(1)



(2)



Cl⁻

(3)
a; R = Me
b; R = Et

n.m.r. spectroscopy (see below). The structure of the former was also confirmed by heating with ethyl iodide: the N_aN_b-dimethyl-N_c-ethyl-TPP (3b) was formed and its unsymmetrical character was clearly demonstrated by its n.m.r. spectrum. In our initial experiments the N_aN_b-dimethyl compound was obtained in the monocationic form, but subsequently, however, in the course of careful chromatographic searches for the isomeric compounds, it was obtained as the free base. This was unexpected in view of our experience with the analogous N_aN_b-dimethylocta-alkylporphins, for these could only be obtained in free base form in solution [3,4] and rapidly reverted to monocation. However, the lower basicity of N_aN_b-dimethyl-TPP may be due to the 'ruffled' character of the TPP nucleus.[1] In spite of numerous experiments, and careful chromatographic and spectroscopic examination of the products, no evidence was obtained for the formation of more than one *NN'*-dimethyl derivative, in contrast to the situation with octa-alkylporphins where *trans*-N_aN_b- and *trans*- and *cis*-N_aN_c-dimethyl derivatives were obtained.[4] The absence of the N_aN_c-dimethyl derivatives in the TPP series is probably due to steric effects. Even in the case of the octaethylporphin (OEP) only small amounts of the *trans*-N_aN_c-dimethyl derivative were obtained, so that the additional deviation from planarity caused by the *meso*-phenyl substituents of TPP readily accounts for the absence of the *trans*-N_aN_c-dimethyl-TPP. In the octa-alkylporphin series the *cis*-N_aN_c-dimethyl derivatives were formed as a result of thermal decomposition of the trimethyl compound during the reaction, or during isolation. It seems that the $N_aN_bN_c$-trimethyl-TPP is much more stable, again because of the more 'ruffled' nature of the macrocycle in the TPP series. The $N_aN_bN_c$-trimethyl-TPP was unchanged after heating for 1 h at 100 °C but in refluxing *o*-dichlorobenzene it decomposed and gave a mixture of the N_aN_b-dimethyl- and *N*-methyl-TPP as well as TPP; the isolation of the N_aN_b-dimethyl derivative rather than the N_aN_c-dimethyl derivative confirms the above conclusions.

Attempts to prepare the nickel complex of *N*-methyl-TPP by heating with nickel acetate in acetic acid led to loss of the *N*-methyl group and formation of nickel TPP. However, treatment under similar conditions with zinc acetate gave an unstable green zinc complex. The related copper complex prepared by Lavallee and Gebala [7] is also unstable and dissociates in dimethylformamide solution, whereas the copper complex of TPP is more stable: the copper can only be removed under strongly acidic conditions. Very recently Lavallee [8] has also reported the ready demethylation of the copper complex by amines; a similar *N*-demethylation of zinc *N*-methyl-OEP was described earlier by Hambright.[9]

The *N*-methyl-TPP metal complexes are also appreciably less stable than those of *N*-methyl-OEP. The differences between the two series may be attributed to the greater steric strain in the *N*-methyl-TPP derivatives in achieving coplanarity of the four nitrogen atoms in the metal complexes, and this is shown by comparisons of the electronic spectra with those of *N*-methyl-OEP metal complexes and of *N*-methylated TPP monocations (see below).

Electronic Spectra.—The spectra of *N*-methyloctaethylporphin (free base, monocation, and dication) differ little from those of the parent porphyrin, except for small bathochromic shifts and minor changes in intensities of the various bands. However *N*-methyl-TPP free base has a 'rhodo' type visible spectrum (band III > IV > II ⩾ I) in contrast to TPP which has a typical 'aetio' type spectrum (band IV > III > II > I).

Spectroscopic titrations of *N*-methyl-TPP with glacial acetic acid, or trifluoroacetic acid, in chloroform solution gave results very similar to those obtained by Lavallee and Gebala; [7] both the green mono- and di-cations were obtained and well defined isosbestic points were observed

[8] D. K. Lavallee, *Inorg. Chem.*, 1976, **15**, 691.
[9] B. Shears and P. Hambright, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 679.

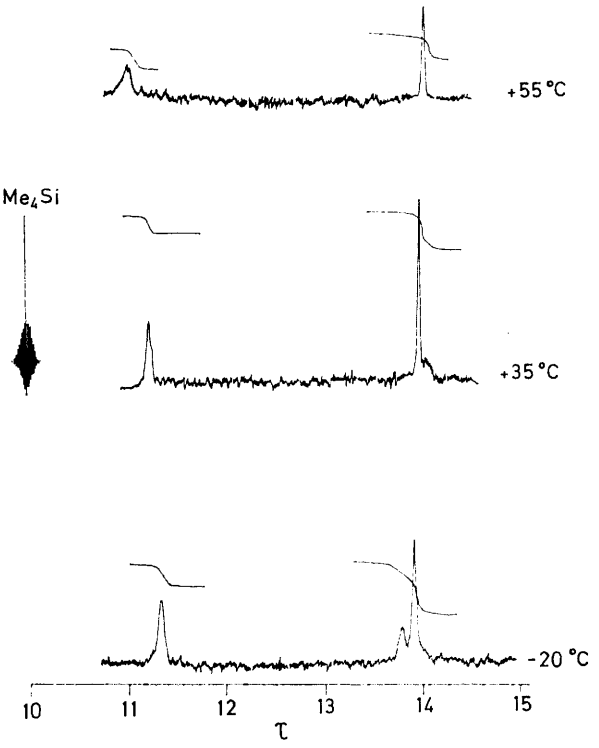
for the separate processes. It was clear from these titrations and from our earlier results [4] that *N*-methyl-TPP was much less basic than *N*-methyl-octa-alkylporphins and that the two pK_a values were closer together; indeed Lavallee and Gebala [7] estimate that the two values for *N*-methyl-TPP are 5.64 and 3.85 (for titrations with perchloric acid in nitrobenzene solution) whereas Neuberger and Scott [10] estimated that for *N*-methyl-coproporphyrin-I in aqueous solution the pK_a values were 11.3 and 0.7, respectively.

On titrating the N_aN_b-dimethyl-TPP with acid, the Soret band undergoes a hypsochromic shift and increases slightly in intensity on formation of the monocation; on further protonation it increases in intensity again and undergoes a bathochromic shift. The visible region of the monocation is very similar to that of *N*-methyl-TPP and changes to a single more intense band in the dication. The $N_aN_bN_c$-trimethyl-TPP also shows two bands in the visible spectrum of its monocation, and a single band in that of the dication. There is in fact a close similarity in the general shapes of the spectra of the monocations of the mono-, di-, and tri-*N*-methyl-TPP. The dicationic spectra of the three derivatives are also similar in general appearance but successive methylation causes both the Soret and the visible bands to shift to longer wavelengths. (Similar effects were observed in the *N*-alkyl-octa-alkylporphin series.[4])

The visible spectra of the zinc, cobalt, and copper complexes of *N*-methyl-TPP are unlike those of any of the mono- or di-cationic forms of the mono-, di-, and tri-*N*-methyl derivatives of TPP, whereas they are similar to those of the metal complexes of *N*-methylocta-alkylporphins, and of the monocations of *N*-methyl-, N_aN_b-dimethyl-, and $N_aN_bN_c$-trimethyl-octa-alkylporphins,[3,4] but shifted to longer wavelength. This suggests that the geometry of the metal complexes of *N*-methyl-TPP is much closer to that of the metal complexes of *N*-methylocta-alkylporphins, whereas the macrocycles in the *N*-methylated TPP free bases and mono- and di-cations are considerably distorted from planarity owing to the presence of the *meso*-phenyl groups (*cf.* ref. 1).

N.m.r. Spectra.—The n.m.r. spectrum of *N*-methyl-TPP in deuteriochloroform shows the *N*-methyl resonance at high field, and the signal for the two peripheral protons on pyrrole ring A bearing the *N*-methyl group is also shifted upfield to τ 2.54. The singlet assigned to the peripheral protons on the opposite pyrrole ring C has a similar chemical shift to that in TPP (τ 1.14), suggesting that this ring stays approximately in the plane of the macrocycle, whereas ring A is appreciably twisted from the plane. The resonances of the peripheral protons on the other two rings (B and D) form an AF quartet, presumably because the rings are slightly twisted (about an axis through N_b and N_d) out of plane; the upfield doublet may thus be assigned to the pair of protons nearest the *N*-methylated ring.

In the n.m.r. spectrum of the dication of *N*-methyl-TPP in TFA the *N*-methyl resonance is at lower field than that in the free base. The resonances of the peripheral protons of the *N*-methylated ring (A) are also at highest field, but in contrast to the free base, the resonance of the ring C peripheral protons is at higher field than those of the protons on rings B and D. More interestingly there are two NH resonances, at τ 11.24 (2 H) (rings B and D) and 14.08 (1 H) (ring C) whereas the dication of *N*-methyl-OEP in TFA or sulphuric acid shows only one resonance [4] for two protons at high field (τ 13.90). It was assumed in the latter case that the second proton added was undergoing a rapid exchange with acid,[4] and this was not slowed sufficiently even by lowering the temperature to −35 °C. Variable temperature experiments with *N*-methyl-TPP in trifluoracetic acid (TFA) showed that at about 55 °C the high-field signal disappeared (Figure). We concluded that the additional distortion caused by the *meso*-phenyl groups in *N*-methyl-TPP, as compared with *N*-methyl-OEP, probably increases the basicity of the monocation (whereas the free base of *N*-methyl-TPP is less basic than that of *N*-methyl-OEP); these conclusions are confirmed by Lavallee and Gebala's pK_a determinations referred to above. Evidence for the greater degree of distortion in *N*-methyl-TPP dication is shown by the NH resonance at τ 11.24 which is 2.66 p.p.m. to lower field than that in the spectrum of *N*-methyl-OEP dication, presumably because the NH groups of rings B and D are substantially twisted out of coplanarity with the main plane of the macrocycle. However, evaporation of the *N*-methyl-TPP



High-field region of the ^1H n.m.r. spectrum of *N*-methyl-TPP in TFA

[10] A. Neuberger and J. J. Scott, *Proc. Roy. Soc.*, *A*, 1952, **213**, 307.

solution to dryness *in vacuo* afforded the monocationic species (as shown by the visible spectrum), thus showing behaviour similar to that of *N*-methyl-octa-alkylporphins.[4]

N.m.r. spectroscopic titrations were also carried out with *N*-methyl-TPP by addition of TFA to a solution of the free base in deuteriochloroform. During the titration the chemical shifts of the *N*-methyl protons increased as the monocation was formed, and then slowly decreased as further acid was added and the dication was formed. Furthermore, the *N*-methyl signals observed in the earlier part of the titration (up to the monocation stage) were rather broad, and this was attributed to slow proton exchange between free base and monocation. This was confirmed by variable temperature studies of the spectra of *N*-methyl-TPP in the presence of 0.5 equiv. of TFA; two broad *N*-methyl resonances were observed at lower temperatures but these broadened, and then collapsed into a single signal at τ 14.6 above 40 °C. These results are similar to those observed with the *N*-methylocta-alkylporphrins studied earlier (*cf.* ref. 4), except that the temperature needed to cause rapid equilibration (on the n.m.r. time scale) is much higher in the case of *N*-methyl-TPP. Presumably in the monocation the two central protons are on opposite nitrogens flanking the *N*-methylated ring as this would cause least steric hindrance; thus steric repulsions between the NH groups would allow more space for the *N*-methyl group to lie in the overall plane of the macrocycle, and this would account for its high-field shift relative to that in the free base and the dication. Further protonation (of the monocation) on the nitrogen opposite the *N*-methyl group would increase the steric interactions in the centre of the macrocycle and force the *N*-methyl groups out of the plane again, and this would account for the decrease in its chemical shift.

As described above, N_aN_b-dimethyl-TPP was obtained as the free base in crystalline form after careful chromatography, in contrast to other di-*N*-alkylated porphins, which could only be obtained as the free bases in solution. The n.m.r. spectrum of N_aN_b-dimethyl-TPP free base showed a singlet at τ 14.9 corresponding to the two *N*-methyl groups and a singlet at τ 1.82 attributed to the peripheral hydrogen atoms on the non-alkylated rings (C and D). In the spectra of the mono- and di-cations, however, the latter protons gave rise to an AB quartet, perhaps owing to the greater rigidity of the cationic forms. This confirmed that the *N*-methyl groups were on neighbouring rings; moreover the n.m.r. spectrum of the derived *N*-ethyl-*NN'*-dimethyl-TPP showed two separate *N*-methyl resonances, whereas if the *N*-methyl groups had been on opposite rings only one *N*-methyl resonance would have been observed.

The spectra of the *NN'N''*-trimethyl-TPP monocation and dication clearly show one *N*-methyl resonance at higher field than the other two and this behaviour confirms the *trans,trans*-relationship of the *N*-methyl groups. These *N*-methyl resonances are, however, at lower field than those of the corresponding *NN'N''*-trimethyl-OEP; thus it may again be concluded that the *meso*-phenyl groups sterically inhibit attainment of the same degree of planarity in the TPP series as in the OEP series.

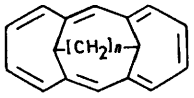
Mass Spectra.—The mass spectra of the mono-, di-, and tri-*N*-methyl derivatives of TPP all showed abundant ions at *m/e* values up to three mass units higher than their nominal molecular weights. Some typical spectra are reported in the Experimental section, although the data obtained showed some variation in the relative intensities of the various ions, *e.g.* the degree of fragmentation of the *N*-methyl groups increased as the source temperature was increased (in the electron impact spectra) or as the wire-current was increased (in the field desorption spectra). This type of behaviour is very similar to that observed with *N*-substituted octa-alkylporphins.[4] The zinc complex of *N*-methyl-TPP (chloride salt) showed abundant ions in its field desorption spectrum corresponding to the chloride complex, and similar, but weaker, ions were observed in the electron impact spectrum; the base peaks in the electron impact spectrum corresponded to zinc tetraphenylporphin (*i.e.* to loss of both the *N*-methyl groups and the chlorine ligand), and these were also the only fragment ions observed in the field desorption spectrum.

Conclusions.—The results in the *N*-methyl-TPP series as well as the *N*-methyl-OEP series emphasise the considerable degree of distortion from planarity which the porphin ring system can undergo without loss of aromatic character. The variations in the *N*-methyl chemical shifts and those of the peripheral protons can all be accounted for essentially by distortions of the individual rings from coplanarity with the overall plane of the macrocycle, so that they are affected to a greater or lesser extent by the aromatic ring current. As we have suggested previously, however, for the *N*-methyl-OEP derivatives [4] and for *N*-unsubstituted porphins,[11] *N*-substitution and protonation may in themselves also have a small effect on the overall ring current in respect of the distortion caused to the macrocycle. The latter effect may, however, be relatively small, and Fleischer [12] has commented on the relative rigidity of the dicationic species and the distortion from planarity which occurs. The close similarity of the spectra of the dications of the mono-, di-, and tri-methyl derivatives of TPP to that of the dication of TPP itself indicates that their geometry is similar with pairs of opposite rings tilted up or down from the overall plane of the macrocycle.

Our results may be compared with those obtained by Vogel [13] for a series of methylene-bridged annulenes (4); even when the length of the bridge is increased to four methylene groups the conjugated system still retains its

[11] R. J. Abraham, *Mol. Phys.*, 1961, **4**, 145.
[12] A. Stone and E. B. Fleischer, *J. Amer. Chem. Soc.*, 1968, **90**, 2735.
[13] E. Vogel, plenary lecture, South West Regional Symposium of the Perkin Division of the Chemical Society, Cardiff, 25th March, 1975; E. Vogel, J. Sanbroek, and W. Wagemann, *Angew. Chem. Internat. Edn.*, 1975, **14**, 564; E. Vogel, W. Sturm, and H.-D. Cremer, *ibid.*, 1970, **9**, 516.

aromatic character (as judged by the n.m.r. spectra), even though it is considerably bowed from planarity.



(4)

It also seems likely that a certain degree of bond fixation may occur in the *N*-methylated TPP derivatives (just as in the OEP series) and that one or more of the nitrogens may have a substantial degree of sp^3 character in the various compounds and their mono- and dicationic salts; the nitrogen bearing the methyl group in the zinc *N*-methyl-TPP must, of course, be sp^3 hybridised. It is interesting that the structure of N_aN_b-dimethyl-TPP (2) is effectively fixed in one of the two types of Kekulé form which can be written for porphins, in which the peripheral carbons on rings C and D are ' outside ' the main 18π-conjugated system. The other type of Kekulé form is shown in structure (1); in this case it is the peripheral carbon atoms on the opposite rings A and C which are ' outside ' the main 18π-system.

EXPERIMENTAL

Electronic and n.m.r. spectra were recorded on Perkin-Elmer SP 800, and Perkin-Elmer R14 (100 MHz) and R32 (90 MHz) instruments, respectively. Electron impact (e.i.) mass spectra were determined at 70 eV and 50 μA and field desorption (f.d.) mass spectra at wire currents up to 20 mA, with a Varian CH5D instrument; the intensities of the peaks were variable, and we record only the positions of the major ions (>10%) and which ion is the base peak in each spectrum.

Methylation of meso-*Tetraphenylporphin.*—The results of a typical reaction are given below; results of some other experiments are recorded in the Table.

Some representative preparations of *N*-methylated *meso*-tetraphenylporphins

Conditions of reaction with methyl iodide	*N*-Methyl-TPP (%)	N_aN_b-Dimethyl-TPP (%)	Tri-*N*-methyl-TPP (%)	Recovered TPP (%)
Reflux, 3 days	10	47	2	23
16 h, 100 °C, sealed tube	3	45	1	20
3 h, 100 °C, sealed tube	1	38	0	34
Reflux in chloroform, 4 days	0	1	21	41

A mixture of *meso*-tetraphenylporphin (500 mg), methyl iodide (20 ml), and anhydrous K_2CO_3 (1.0 g) was sealed, under nitrogen, in a thick-walled glass tube and heated (100—110 °C) overnight with exclusion of light. The cooled mixture was dissolved in chloroform; the solution was filtered, and the solvent removed *in vacuo*. The residue was then chromatographed on alumina (toluene as eluant) to obtain *meso*-tetraphenylporphin (120 mg, 24%).

Elution with toluene–ethyl acetate (9 : 1 v/v) yielded *N*-methyl-*meso*-tetraphenylporphin (32 mg, 6%) as fine purple prisms [from benzene–light petroleum (b.p. 60—80°)], m.p. ≮300° (Found: C, 85.9; H, 4.6; N, 8.6. Calc. for $C_{45}H_{32}N$; C, 85.95; H, 5.1; N, 8.9%), $\lambda_{max.}$ ($CHCl_3$) 433 (log ε 5.49), 533(3.94), 578(4.11), 620(3.49), and 682(3.46), $\lambda_{max.}$ [monocation (TFA) in $CHCl_3$] 442(5.44), 626(4.32), and 677(4.36), $\lambda_{max.}$ [dication (TFA) in $CHCl_3$] 445 (5.54) and 678 nm (4.68); *m/e* (e.i.) 630, 629, and 628(100%) (M^+), 627, 551 [(M — Ph)$^+$], and 314 (M^{2+}), *m/e* (f.d.) 631, 630, 629, and 628 (M^+); τ (free base in $CDCl_3$) 14.10 (NCH_3), 2.54 (s, 1- and 2-H), 1.54 (d, 3- and 8-H), 1.36 (d, 4- and 7-H), 1.18 (s, 5- and 6-H), 1.6—1.85 (m, *o*-phenyl H), and *ca.* 2.2 (m, *m*- and *p*-phenyl H), τ (monocation in $CDCl_3$) 14.80 (NCH_3), 2.33 (s, 1- and 2-H), *ca.* 1.39 (s, 3- and 8-H), *ca.* 1.27 (d, 4- and 7-H), 1.58 (d, 5- and 6-H), 1.3—1.7 (m, *o*-phenyl H), and *ca.* 2.0 (m, *m*- and *p*-phenyl H), τ (dication in TFA) 11.24 (2 × NH), 14.08 (NH), 13.97 (NCH_3), 2.17 (s, 1- and 2-H), 1.04 (d, 3- and 8-H), 0.85 (d, 4- and 7-H), 1.09 (s, 5- and 6-H), 1.1—1.5 (m, *o*-phenyl H), and *ca.* 1.8 (m, *m*- and *p*-phenyl H).

A deep green band was then eluted by ethyl acetate to give trans-N_aN_b-*dimethyl*-meso-*tetraphenylporphin* (215 mg, 41%). On recrystallisation from methylene chloride–hexane it formed an amorphous green solid, m.p. 246—248° (Found: C, 85.9; H, 5.3; N, 8.4. $C_{46}H_{35}N_4$ requires C, 85.8; H, 5.5; N, 8.7%), $\lambda_{max.}$ ($CHCl_3$) 460 (log ε 5.26), 642sh (4.19), and 710(4.02), $\lambda_{max.}$ [monocation (TFA) in $CHCl_3$] 442(5.38), 624(4.33), and 669(4.33), $\lambda_{max.}$ [dication (TFA) in $CHCl_3$] 453(5.44) and 693 nm (4.68); *m/e* (e.i.) 645, 644, and 643 (100%) [(M + 1)$^+$], 642, 630, 629, 628, 627, 614, 321.5, 321(30) (M^{2+}), and 413, *m/e* (f.d.) 644, 643, and 642 (100) (M^+), 641, and 640; τ (free base in $CDCl_3$), 14.90 (s 2 NMe), *ca.* 2.3 (d, 2- and 3-H), *ca.* 2.0 (d, 1- and 4-H), 1.82 (s, 5-, 8-, 6-, and 7-H), 1.3—1.7 (m, *o*-phenyl H), and *ca.* 2.2 (m, *m*- and *p*-phenyl H), τ (monocation in $CDCl_3$) 14.77 (s, 2 NMe), 2.31 (d, 2- and 3-H), 2.01 (d, 1- and 4-H), 1.2—1.5 (m, 5-, 8-, 6-, and 7-H), 1.2—1.8 (m, *o*-phenyl H) and *ca.* 2.1 (m, *m*- and *p*-phenyl H), τ (dication in TFA) 14.42 (s, 2 NMe), 2.01 (d, 2- and 3-H), *ca.* 1.73 (d, 1- and 4-H), 1.12 (d, 5- and 8-H), 0.95 (d, 6- and 7-H), 1.1—1.5 (m, *o*-phenyl H), and *ca* 1.8 (m, *m*- and *p*-phenyl H).

Elution of the column with chloroform–methanol (9 : 1 v/v) gave another green porphyrin, crystallised from methylene chloride–light petroleum (b.p. 60—80°) to give $N_aN_bN_c$-*trimethyl*-meso-*tetraphenylporphin iodide* (30 mg, 6%) as steel-blue needles, m.p. 205—208° (Found: C, 69.95, 70.6; H, 5.0; N, 7.1, 6.9. $C_{47}H_{37}IN_4$ requires C, 71.9; H, 4.75; N, 7.1. $C_{47}H_{37}IN_4,H_2O$ requires C, 70.3; H, 4.9; N, 6.9%); $\lambda_{max.}$ [$CHCl_3$ (monocation)] 464.5 (log ε 5.04), 684(4.30), and 714(4.32), $\lambda_{max.}$ ($CHCl_3$–TFA) 467(5.39) and 724 nm (4.72); *m/e* (e.i.) 659 and 658 [(M + 1)$^+$], 644, 643, 630, 629, 628, 627, 615, 614, 552, 328, 314, and 307, *m/e* (f.d.) 660, 658(100%), 644, 643, 642, 630, 629, and 628; τ ($N_aN_bN_c$-trimethyl-TPP chloride) (monocation in $CDCl_3$) 15.57 (N-Me), 13.12 (N_aMe, N_cMe), 2.73 (d, 2- and 5-H), 2.55 (d, 1- and 6-H), 1.81 (s, 3- and 4-H), 1.60 (s, 7- and 8-H), *ca.* 1.35 (m, *o*-phenyl H), *ca.* 1.55 (m, *o*-phenyl H), *ca.* 2.07 (m, *m*- and *p*-phenyl H), τ (dication in TFA) 13.6 (NH), 14.72 (N_bMe), 13.18 (N_aMe, N_cMe), 2.22 (d, 2- and 5-H), *ca.* 1.8 (m, 1- and 6-H), 1.70 (s, 3- and 4-H), 0.91 (s, 7- and 8-H), 1.1—1.4 (m, *o*-phenyl H), and *ca.* 1.8 (m, *m*- and *p*-phenyl H).

N_c-*Ethyl*-N_aN_b-*dimethyl*-meso-*tetraphenylporphin.*— A mixture of N_aN_b-dimethyl-TPP (20 mg) in chloroform (10 ml), ethyl iodide (1.00 ml), and potassium carbonate (100 mg) was heated under reflux with exclusion of light for 2 h. The potassium carbonate was then filtered off and washed

with chloroform. The combined filtrates were evaporated to dryness and the residue was chromatographed on alumina; elution of the column with ethyl acetate yielded traces of N_aN_b-dimethyl-TPP. Chloroform–methanol (9 : 1 v/v) then eluted a bright green band; the product was crystallised from methanol by addition of aqueous sodium iodide at the b.p. Recrystallisation from methylene chloride–light petroleum (b.p. 40—60°) gave N_c-*ethyl*-N_aN_b-*dimethyl*-meso-*tetraphenylporphin iodide* (21 mg, 73%) as purple needles, m.p. 195—198° (decomp.) (Found: C, 73.5; H, 5.1; N, 7.2. $C_{48}H_{39}IN_4$ requires C, 72.3; H, 4.9; N, 7.0%); $\lambda_{max.}$ ($CHCl_3$) 466 (log ε 5.14), 686(4.29), and 715 (4.34), $\lambda_{max.}$ (TFA–$CHCl_3$) 468(5.43) and 728 nm (4.69); *m/e* (f.d.) 674, 673, and 672(100%), 671, 670, 658, 657, 656, 655, 654, 643, 642, 629, and 628; N_c-ethyl-N_aN_b-dimethyl-TPP chloride (monocation in $CDCl_3$) 15.60 (N_bMe), 13.38 (N_aMe,N_cMe), 10.62 (t, N·CH_2·CH_3), 13.50 (m, N·C*H*H·CH_3), 14.18 (m, N·C*H*H·CH_3), 2.75 (d, 2- and 5-H), 2.52 (d, 1- and 6-H), 1.73 (s, 3- and 4-H), 1.55 (s, 7- and 8-H), *ca.* 1.4 (m, *o*-phenyl H), *ca* 1.6 (m, *o* -phenyl H), and *ca.* 2.03 (m, *m*- and *p*-phenyl H), τ (dication in TFA) 13.65 (NH), 14.73 (N_bMe), 13.38 (N_aMe, N_cMe), 10.42 (t, N·CH_2·CH_3), *ca.* 13.5 (m, N·C*H*H·CH_3), 14.15 (m, N·C*H*H·CH_3), 2.20 (q, 2- and 5-H), *ca.* 1.8 (m, 1- and 6-H), 1.68 (s, 3- and 4-H), 0.89 (s, 7- and 8-H), 1.1—1.5 (m, *o*-phenyl H), and *ca.* 1.80 (m, *m*- and *p*-phenyl H).

Zinc N-*Methyl*-meso-*tetraphenylporphin Chloride.*—*N*-Methyl-TPP (5 mg) in chloroform (5 ml) was heated with zinc acetate in methanol (0.2 ml; saturated solution). The mixture was evaporated to dryness and the residue was chromatographed on alumina (grade III) in ethyl acetate. A small amount of *N*-methyl-TPP was eluted first, followed by the bluish-green zinc complex (3 mg), $\lambda_{max.}$ ($CHCl_3$) 438 (log ε 5.66), 450(5.46), 564(4.24), 616(4.43), and 663(4.11), τ ($CHCl_3$) 13.85 (NMe) and 1.3—3.2(m); *m/e* (e.i.) 730, 729, 728, 727, 726, 694, 693, 692, 691, 690, 681, 680, 679, 678, 677, 676(100%), 601, 600, 599, 598, 339, 338.5, 338, 337.5, 300, 299.5, 299, 298.5, and 298, *m/e* (f.d.) 732, 731, 730, 729, 728, 727(100%), 726, 725, 679, 678, 677, 676, and 675.

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