NN'-Dimethylporphyrins

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Summary The formation and some spectroscopic properties of *NN'*-dimethylaetioporphyrin-I and *NN'*-dimethyloctaethylporphyrin are described.

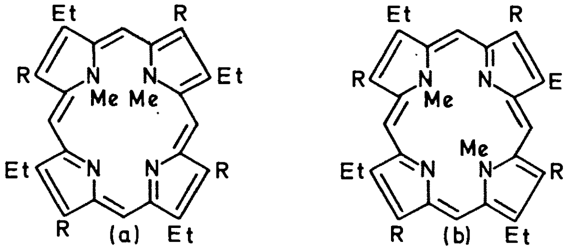
OVER thirty years have elapsed since the first report of the preparation of an *N*-methylporphyrin,[1] and several other *N*-alkylporphyrins have subsequently been described.[2–4] However, we now report that *NN'*-dimethylporphyrins are also formed by the direct methylation of the parent porphyrins, albeit in lower yield than the *N*-monomethyl derivatives.

N.m.r. spectra ($CDCl_3$) (τ-values).

	NN'-Dimethyl- aetioporphyrin-I monohydrochloride	*NN'*-Dimethyl- octaethylporphin monohydrochloride
N-C*H*$_3$	15·92 (3H) 15·88 (3H)	15·70 (6H)
N-*H*	13·76 (1H)	13·70 (1H)
β-CH$_2$·C*H*$_3$	7·9—8·9 *m*	7·8—8·6 *m*
β-C*H*$_2$·CH$_3$	5·8—6·3 *m*	6·2—6·5 *m*
β-C*H*$_3$	6·60, 6·58, 6·33, 6·27	
meso-*H*	−0·21 (1H), −0·33 (3H)	−0·10 (1H), −0·43 (3H)

During the chromatographic purification of *N*-methylaetioporphyrin-I, required for spectroscopic studies, it was observed that the top portion of the alumina column remained pale green. This coloured material could only be removed by fairly polar solvent mixtures (*e.g.* chloroform containing 10—20% methanol), and the greenish-red eluent after evaporation to dryness gave a low yield of a deep violet crystalline product, m.p. 219—222° (uncorr.)(λ_{max} in $CHCl_3$: 401, 540, 574, and 620 nm). The n.m.r. spectrum ($CDCl_3$) clearly showed two high-field *N*-methyl proton resonances in addition to the expected signals for the peripheral methyl, ethyl, and meso-proton resonances (Table). The high-field NH resonance and the similarity in shape of the visible spectrum to that of the monocationic salts of *N*-monomethylporphyrins (*cf.* ref. 3) (λ_{max} in $CHCl_3$: 391, 530, 561, and 600 nm), although shifted to a longer wavelength, indicated that the new product was the monohydrochloride‡ of *NN'*-dimethylaetioporphyrin-I (Ia). The two *N*-methyl groups are probably situated on adjacent nitrogen atoms as in (Ia), one above and one below the plane of the ring, rather than on opposite nitrogens, as in (Ib), because the meso-proton resonances are split in a 3 : 1 ratio and the four peripheral methyl groups give rise to four distinct signals.

These findings have now been amply confirmed by the isolation of *NN'*-dimethyloctaethylporphin (IIa), as its monohydrochloride, § m.p. 189—190° (in 25% yield), and *N*-methyloctaethylporphin,§ m.p. 218—219° (40%), by direct methylation of octaethylporphin.¶ The visible spectra of the *NN'*-dimethyloctaethylporphin and its salts were closely similar to those of the aetioporphyrin-I analogue and the n.m.r. spectrum of the hydrochloride (Table) also showed similar characteristics, although the two *N*-methyl resonances gave rise to a singlet, presumably owing to the higher degree of symmetry in this case.



(I)R = Me
(II)R = Et

The relatively high basicity of these *NN'*-dimethylporphyrins is quite striking for not only were they isolated as their salts from alumina columns, but the free bases (λ_{max} in $CHCl_3$: 402, 438 infl. 541, 573, 627, and 652 nm) were quite unstable and rapidly reverted to the monocationic salts, either on exposure to the laboratory atmosphere, or by proton abstraction from solvent. They are thus more basic than *N*-monomethylporphyrins[3] (pK_a 11·3 and 0·7), and much more basic than *N*-unsubstituted porphyrins[3] (pK_a 7·2 and 4·2). This is presumably a consequence of the increasing distortion caused by the insertion of first one, and then two, methyl groups into the limited space available in the centre of the porphyrin ring system. It does seem quite remarkable that the normally planar macrocycle is sufficiently flexible to accommodate two such groups and without appreciable loss of aromatic character.[5] On the other hand *N*-monomethylporphyrins have long been known to form stable metal complexes.[2] It is hoped that *X*-ray crystallographic studies will provide detailed information on these points, and positively locate the relative positions of the two *N*-methyl groups.

Another unusual feature of the behaviour of these two *NN'*-dimethylporphyrins is that the mass spectra of the mono-hydrochlorides show parent ions at 508 (for Ia) (Found: 508·357 ± 0·0025; Calc. for $C_{34}H_{44}N_4$: 508·356),

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‡ This hydrochloride did not analyse well but a satisfactory elemental analysis was obtained on the corresponding perchlorate, m.p. 224—226°.

§ A good elemental analysis was obtained.

¶ The octaethylporphin used in these experiments was generously provided by Professors Inhoffen and Pommer.

and 564** (for IIa) (Found: 564·419 ± 0·0025; Calc. for $C_{38}H_{52}N_4$: 564·419) *i.e.* 2 mass units *higher* than the molecular weights of the free bases. The parent ion in each case is also the base peak, and almost the only other significant peak in each spectrum corresponds to fragmentation of one methyl group, *i.e.* at 493 (for Ia) and 549 (for Ib).

The formation of $M + 1$ ions from a variety of organic compounds is well known (*e.g.* nitriles, amines, esters, ethers, *etc.*) but $M + 2$ ions are relatively rare. Most porphyrins behave normally giving intense molecular ions,[6] and in only one previous instance[7] has an $M + 2$ ion been reported; on the other hand the formation of $M + 2$ ions appears to be a fairly general phenomenon with 1,2-naphthaquinones.[8] In both these examples[7,8] the phenomenon has been ascribed to a reductive process, but whether this is the case in the present instance remains to be determined.

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** Injection of a small amount of deuterium oxide into the spectrometer gave rise to a slight but significant increase in the intensity of the $M + 3$ and $M + 4$ peaks.

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