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N-METHYLATION OF ETIOPORPHYRIN I AND OCTAALKYL-5-AZAPORPHYRINS

X-RAY STRUCTURE OF TRANS-N_a, N_b-DIMETHYLETIOPORPHYRIN I TRIIODIDE

AJITA M. ABEYSEKERA, RONALD GRIGG* and JADWIGA TROCHA-GRIMSHAW
Department of Chemistry, Queen's University, Belfast BT9 5AG, Northern Ireland

and

KIM HENRICK
Chemistry Department, Polytechnic of North London, Holloway, London N7 8DB, England

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Abstract—Improved procedures are reported for the preparation of mono-, di- and tri-N-methyl-etioporphyrin I. Demethylation of N_a, N_b, N_c-trimethyletioporphyrin I under acidic, basic or thermal conditions gives N_a, N_b-dimethyl etioporphyrin I. N-Methylation of octaalkyl-5-azaporphyrins leads, in general, to mixtures of the isomeric mono-, di- and tri-N-alkylated 5-azaporphyrins. An X-ray crystal structure of N_a,N_b-dimethyl etioporphyrin I triiodide confirms the *trans* arrangement of the N-Me groups. The two N-methylated pyrrole rings are twisted 27° to each other.

N-Methylation of octaalkylporphyrins (**1a**)[1,2] and meso-tetraphenylporphyrin[3] has been shown to produce mixtures of mono-, di- and tri-N-methylporphyrins with the product distribution varying with conditions and nature of the alkylating agent. The usual methylating agents are methyl iodide and methyl fluorosulphonate.[1-4] Samples of mono- and di-N-methyletioporphyrin were required for studies with di-μ-chloro-bisdicarbonylrhodium[5] and the present work was initiated to provide improved methylation procedures. The original McEwen procedure for N-methylporphyrins[4] involved heating the porphyrin with methyl iodide in a sealed tube at 100° and produces both mono- and di-N-methylporphyrins.[1,2] The product distribution from this procedure is sensitive to the purity of the methyl iodide and substantial amounts of unreacted porphyrin are often obtained. It appeared likely that a major factor affecting the product distribution was the high basicity of the mono- and di-N-methylporphyrins[1,2,6] resulting in protonation, and consequent deactivation to further methylation, of these species. This led us to study the effect of buffering the reaction mixture and has resulted in simple, high yield, procedures for mono-(1b), di-(2) and tri-(3)-N-methyletioporphyrins (Table 1). Of particular note is the effectiveness of dimethylsulphate as a methylating agent for the synthesis of the *trans*-N_a,N_b-dimethylporphyrin (2; X = Cl; 70%).† Several groups of workers[2,4] have reported dimethyl sulphate to be ineffective as a methylating agent. This erroneous conclusion has arisen due to failure of the previous workers to buffer the solution effectively with consequent protonation and deactivation of the porphyrin. The effect of buffering is illustrated by a methylation experiment using etioporphyrin I-methyl iodide-sodium acetate. After heating in boiling chloroform for 2 days a 1:1 mixture of **1b** and **2** had been formed. On cooling the mixture, adding excess anhydrous potassium carbonate and keeping at room temperature for 24 hr the di-N-methylporphyrin (**2**) was obtained in quantitative yield. In contrast when **3** was heated in boiling chloroform containing a trace of hydriodic acid for 3 hr it was converted into a 1:1 mixture of **2** and **3**. In an NMR tube experiment **3**(X = I) was dissolved in deuteropyridine and heated at 110° for 8 hr when it was converted into a 1:1 mixture of **2** and **3**. Heating **3**(X = I) in o-dichlorobenzene at 150–160° for 4 hr also gave (2; 68%). These latter experiments are of interest with regard to the source of the two isomeric N_a,N_c-dimethylporphyrins (**4** and **5**) reported previously.[1,2] Thus demethylation of **3** under the above conditions occurs selectively at the ring A (or C) nitrogen and not at the ring (B) nitrogen. No trace of the isomeric N_a,N_c-dimethylporphyrins (**4** and **5**) was detected in these experiments. Furthermore the N_a,N_b-dimethylporphyrin iodide (**2**; X = I) did not rearrange to the N_a, N_c-isomer on heating at 180° for 2 hr. Heating **2**(X = I) in trifluoroacetic acid at 100° for 15 hr also failed to effect rearrangement to the N_a,N_c-isomer.

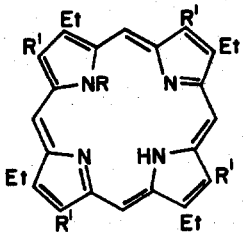
We have previously studied N-alkylation of unsymmetrical polypyrrolic macrocycles in both meso-unsymmetrical macrocycles (corroles,[7] thiaphlorins[8]) and unsymmetrically β-substituted macrocycles (chlorins).[1] However no studies on the meso-unsymmetrical 5-monoazaporphyrins (**6**) have yet been reported. This is an interesting case because it offers a fifth potential site of alkylation, the meso-N atom. We find that **6a** reacts with methyl iodide in boiling chloroform to give a 1:1 mixture of the two N-methylazaporphyrins (**7a** and **7b**), together with a small amount of dimethylated product (NMR). An analogous result was obtained from the alkylation of **6b** under the same conditions when a 1:1 mixture of **7c** and **7d** was produced. The production of 1:1 mixtures of the two possible isomers was clearly demonstrated by the NMR spectra of the products particularly in the meso-proton (*ca* τ 0.5–1.0) and N-Me (*ca*

†Anion exchange during work up.

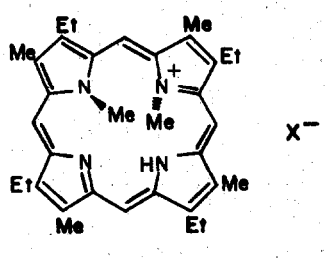
Table 1. N-Methylation of etioporphyrin I in boiling chloroform

Alkylating Agent	Buffering Agent	Reaction Time (h)	Product (%)			
			1b	2	3	EPI [a]
MeI	-	48	65	-	-	-
MeI[b,c]	-	288	-	71	-	-
MeI[c,d]	HI	288	38	5	-	26
MeI	HCO_2Na	24	62	8	-	-
MeI	CH_2ClCO_2Na	8	100[e]	-	-	-
MeI	$CHCl_2CO_2Na$	16	92[e]	8[e]	-	-
MeI	K_2CO_3	42	-	-	92	-
MeI	Na_2CO_3	48[f]	-	37	-	45
Me_2SO_4	K_2CO_3	48[g]	-	70	-	7.5

a. Recovered etioporphyrin I
b. Rigorously purified methyl iodide
c. Sealed tube at 100°
d. EPI (500mg), MeI (20ml) and concentrated HI (0.1ml)
e. Yield estimated from nmr spectrum of reaction mixture
f. Reaction carried out in boiling acetone
g. Reaction carried out at room temperature.



1 **a**: R = H, R' = alkyl
b: R = R' = Me



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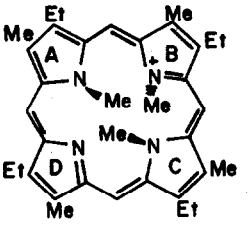

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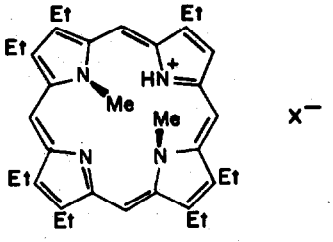

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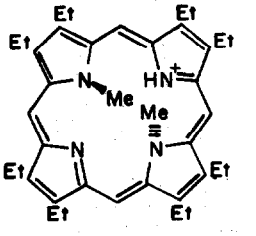

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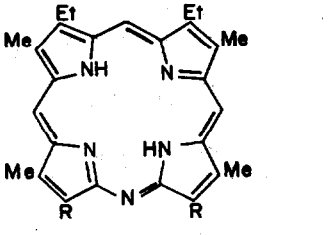


6 **a**: R = Et
b: R = Me

τ 14) regions, e.g. (**7a,b**) exhibited meso-proton signals at τ 0.59 (1H), 0.62 (1H), 0.75 (2H) and 0.89 (1H) and N-Me signals at τ 13.82 (3H) and 14.24 (3H). Meso-N-methylation could be excluded since NMR signals for a meso-N-Me group would not appear above 10τ. Moreover the meso-N atom appears to have no effect on the relative rates of alkylation at the various pyrrolic N atoms (assuming kinetic control) unlike the strong directing effect observed in the, albeit non-aromatic, meso-thiaphlorins.[8] A zinc complex of **7c,d** could be prepared under standard conditions as a 1:1 mixture of the complexes of **7c** and **7d**. The only notable feature of the NMR spectrum of the mixed zinc complexes was the marked broadening of one (τ 13.87) of the two N-Me signals (τ 13.87 and 13.99).

Di-N-methylation of **6b** occurred when **6b** was heated in boiling chloroform with dimethyl sulphate and anhydrous potassium carbonate. The product was a mixture of N,N'-dimethylated isomers. Assuming the N-Me groups on adjacent pyrrole rings to be *trans* orientated, there are five possible isomers of the N,N'-dimethylated product of **6b**, i.e. (*cis*- and *trans*-**7**, R=R^1=R^2=Me) and **8-10**. However, only **8** and **10** possess a two-fold axis of symmetry passing through the meso-N atom and C(15)‡ and thus the NMR spectra of **8** and **10** are expected to exhibit two signals (1H: 2H) for the meso-protons and a single peak for the N,N'-dimethyl protons. The remaining structures (*cis*- and *trans*-**7**, R=R^1=R^2=Me), and **9** should show three separate meso-proton signals and two peaks for the two N-Me groups. The NMR of the major product of the reaction conforms to that expected for **8** or **10**, exhibiting signals at τ −0.46 (1H), 0.03 (2H) and 14.87 (6H). Moreover the methylene quartet of the two Et groups is not a simple quartet, favouring **8** as the major product. The tilting of the N-methylated pyrrole rings must be such as to restrict the rotation of the ethyl-β carbon bond giving rise to the observed AA^{1}X$_3$ pattern. Crystallisation of the crude product gave the major isomer **8** leaving a minor unsymmetrical isomer (~6:1, NMR) whose NMR spectrum ($CDCl_3$) had meso-proton signals at τ −0.29, −0.1, 0.34 and N-Me signals at τ 14.51 and 14.73.

The symmetry properties of the various N-alkylated polypyrrolic macrocycles are reflected in their NMR spectra (Table 2). However, it is not possible to distinguish between isomers such as *cis*- and *trans*-N$_a$,N$_b$-octaethylporphyrin by NMR spectroscopy alone. The *trans* nature of the two N-Me groups was demonstrated in this case by the partial resolution of the compound as its D-camphor10-sulphonate.[1] The meso-proton pattern of N$_a$,N$_b$-dimethylethioporphyrin iodide and triiodide differed, showing that anions may influence the spectrum (Table 2). When both *cis*- and *trans*-isomers are obtained as in the case of N$_a$, N$_c$-dimethyl octaethylporphyrin, non-symmetry arguments can be used to distinguish between the two isomers. Thus, in this case, the compound having the higher field meso-proton signals and lower field N-Me signal is assigned the *cis*-structure due to the greater distortion of the macrocycle and consequent greater reduction in ring current compared to the *trans*-isomer.[1,2]

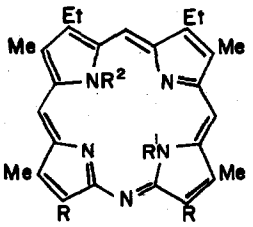
Slow (8 day) tri-N-methylation of **6b** occurs in boiling chloroform containing methyl iodide and anhydrous potassium carbonate. The slow reaction is accompanied by formation of tarry by-products from which a single tri-N-methylporphyrin was isolated. The product is tentatively formulated as **11a** assuming that it arises from further methylation of **8**. Like N,N',N''-trimethyl octaethylporphyrin[2] (**11a**) showed unusual behaviour in its mass spectrum in that the base peak corresponded to P+1. Further evidence for intermolecular reactions in the mass spectrometer came from the mass spectrum of **11a** which exhibits strong peaks (~50% of the base peak) at mass units 16 and 31 higher than the nominal molecular ion. The isolation of only **11a** from the tri-N-methylation of **6b** may be fortuitous or may reflect the influence

‡Assuming the N–H proton in (**8**) is shared with the adjacent pyrrole ring nitrogen atom and can pass through the plane of the porphyrin ring.

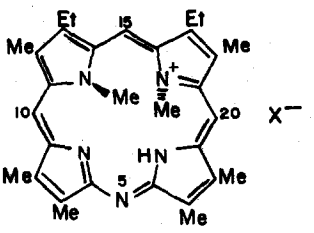
Table 2. Chemical shifts ($CDCl_3$) of meso-protons and N-methyl protons of various N-methylated polypyrrolic macrocycles

Compound	Meso-H (τ)	N-Methyl (τ)
7a and 7b	0.59(1), 0.62(1), 0.75(2) 0.78(1), 0.89(1)	13.82(3), 14.24 (3)
8	-0.46(1), 0.03(2)	14.87(6)
11	0.29(1), 0.52(1), 0.7(1)	12.78(3) 12.94(3), 15.39(3)
1, R=Me, R^1= Et	0.62(2), 0.11(2)	14.76 (3)
2 (X=I)*	-0.31(3H), -0.14(1H)	15.86 (3), 15.90 (3)
4	0.32(4)	13.52(6)
5	0.20(4)	15.30(6)
3	0.10(3), 0.15(1)	13.89(3), 13.95(3), 17.06(3)

* when X=I_3^- the pattern of the meso-proton signals was τ -0.32 (2H), -0.22 (1H) and -0.13 (1H)



7 **a**: R = Et, R^1 = Me, R^2 = H
b: R = Et, R^1 = H, R^2 = Me
c: R = R^1 = Me, R^2 = H
d: R = R^2 = Me, R^1 = H



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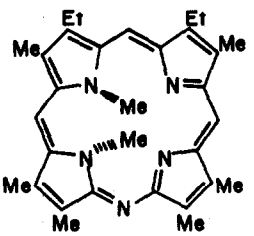

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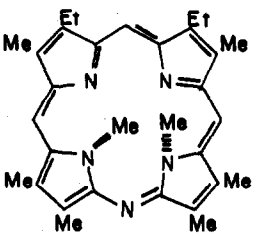

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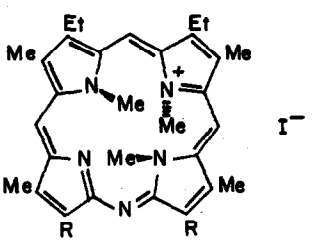
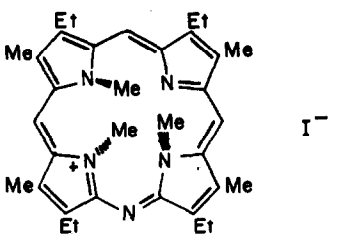


11 **a**: R = Me
b: R = Et



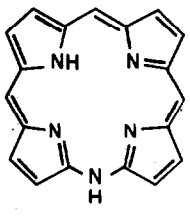
12

of β-alkyl groups since **6a** gave a 50:50 mixture of two tri-N-methylated products (**11b** and **12**) under the same conditions. Although no attempt was made to isolate **11b** and **12**, the NMR spectrum of the crude product showed six meso-proton signals between 0 – 1τ and six N-Me signals (Fig. 1).

The mixture of N-Me azaporphyrins (**7a** and **7b**) is very basic and the product obtained from the reaction is the green hydriodide from which the free base can be obtained by chromatography on basic alumina. Brown solutions of the free base in chloroform revert to the protonated (green) form on keeping. A similar marked increase in basicity is shown by N-methylated porphyrins.[1,2] The electronic spectrum of the free base of **7a,b** shows a bathochromic shift in the Soret and Q bands relative to **7**(R=Et, R^1=R^2=H). The conversion of **7a,b** to the monocations could be accomplished by the addition of acetic acid. Two clear isobestic points were observed at 623 and 558 nm.

The N,N'-dimethylated compound **8** was extremely basic and could only be isolated as its green sulphate salt. It is not deprotonated by pyridine, aqueous sodium

Fig. 1.



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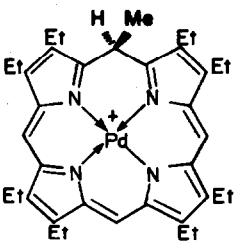

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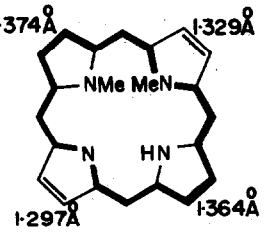

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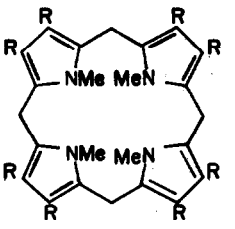

16 R = CH_2CO_2H

bicarbonate, or basic alumina. This enhanced basicity of N,N'-dialkylated macrocycles is common to the porphyrins, corroles and dioxocorroles.[1] The progressive decrease in the planarity of the macrocycle in going from mono- to di- to tri-N-Me azaporphyrin is reflected in a progressive shift of the Soret band to longer wavelengths (386→393→407 nm).

The results of the N-methylation studies with 5-azaporphyrins clearly demonstrate the inner N atoms are far more reactive in S_N2 reactions than the meso-N atom. This may be rationalised on steric grounds. The lone pair of electrons on the meso-N atom lie in the plane of the macrocycle and the approach of the methylating agent is subject to considerable steric hindrance by the β-alkyl groups flanking the meso-N atom. Reaction at a pyrrolic N atom, however, requires an out-of-plane approach of the methylating agent which is unhindered by the β-alkyl substituents. Reaction at a pyrrolenine N atom, where the lone pair points towards the centre of the macrocycle is not favoured but tilting of the "pyrrolenine" ring would facilitate the reaction. Tilting of the individual 5-membered rings within the macrocycle is apparently not difficult as demonstrated by the comparative ease of tri-N-methylation of porphyrins and by X-ray studies on porphyrins[9] and metalloporphyrins.[10] It is worth noting that if azaporphyrins existed as the tautomer (13) then the trajectory of approach of a reagent to the bridging NH group in an S_N2 reaction would be comparatively unhindered. We have previously observed an example of a related reaction in studies of the meso-methylation of palladium octaethylporphyrin by methyl fluorosulphonate when the NMR spectrum of the reaction mixture showed the clean formation of the intermediate (14).[1]

Mono-N-substituted porphyrins and corroles have been the subject of a number of X-ray structure determinations but to our knowledge no report of a di-N-substituted porphyrin has yet appeared. Thus the X-ray crystal structure of 2(X = I_3^-) was undertaken (Fig. 2). The essential features of the structure are the expected *trans*-relationship of the two N-Me groups (Fig. 3) and the consequent distortions of the macrocycle (Tables 3–6). The two N-methylated rings are twisted 27° to each other while the remaining two pyrrole rings are nearly co-planar, lying at an angle of only 4° to each other. The four N atoms are almost co-planar (Table 6a) with a maximum deviation from planarity of 0.08 Å. The two N-methylated pyrrole rings lie at an angle of 37° and 32° respectively to the N_4 plane, while the other rings lie at angles of 4° and 1° respectively to the N_4 plane (Table 6c). The C_α–N–C_α bond angles indicate the presence of a localised amino H atom even though the position of this atom could not be located from the final difference map. Thus previous X-ray structures of porphyrins demonstrate a relationship between C_α–N–C_α bond angle and location of amino H atom(s). N atoms without H atoms have C_α–N–C_α bond angles of *ca* 105.6–106.3° whilst C_α–NH–C_α bond angles are *ca* 107.8–109.9°.[11–14] The C_α–N–C_α angles for 2(X = I_3^-) are 109°, 110°, 108° and 105° (Table 5c) for the pyrrole rings 1–4 respectively where rings 1 and 2 are N-methylated. Thus ring 3 is assumed to carry a localised H atom.

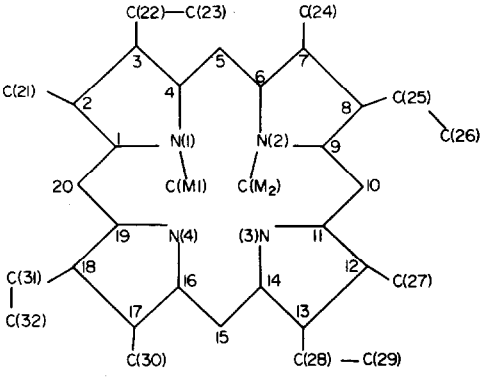

Fig. 2. Crystallographic numbering.

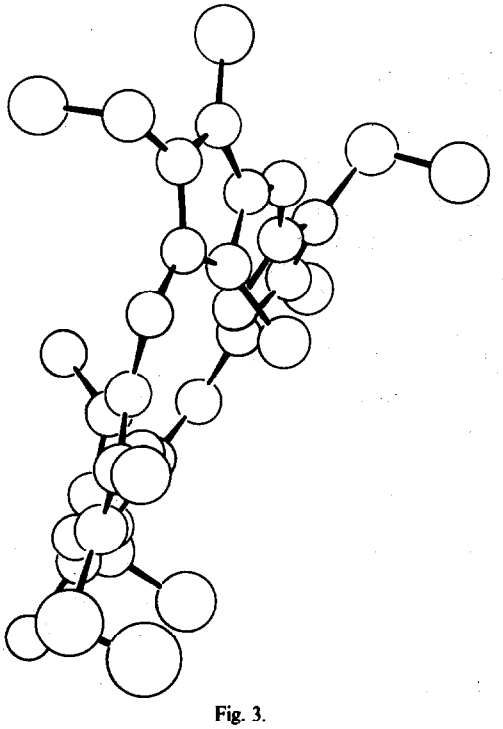

Fig. 3.

Table 3. Atomic fractional cell coordinates ($I \times 10^5$, others $\times 10^4$) for the compound, $H(CH_3)_2(Etio\text{-}I)^+I_3^-$

Atom	x/a	y/b	z/c
I(1)	7082 (7)	7130 (8)	37701 (11)
I(2)	22870 (7)	14987 (7)	22316 (10)
I(3)	40000 (9)	22490 (11)	8268 (14)
N(1)	6521 (6)	5130 (7)	2609 (9)
N(2)	7715 (6)	7233 (7)	3008 (9)
N(3)	8802 (6)	6354 (7)	287 (9)
N(4)	7856 (6)	4363 (6)	133 (9)
C(1)	6476 (7)	4061 (8)	2507 (12)
C(2)	6263 (7)	3866 (8)	3858 (11)
C(3)	6198 (7)	4813 (8)	4769 (12)
C(4)	6371 (7)	5725 (8)	4008 (11)
C(5)	6441 (7)	6721 (8)	4464 (12)
C(6)	6946 (8)	7444 (8)	3863 (11)
C(7)	6823 (8)	8528 (9)	3977 (12)
C(8)	7474 (8)	8911 (9)	3177 (12)
C(9)	8073 (7)	8112 (8)	2547 (11)
C(10)	8765 (8)	8201 (9)	1620 (12)
C(11)	9153 (8)	7413 (9)	601 (12)
C(12)	9906 (7)	7556 (8)	-343 (11)
C(13)	10005 (7)	6609 (8)	-1209 (11)
C(14)	9304 (7)	5854 (8)	-817 (11)
C(15)	9115 (7)	4777 (8)	-1409 (12)
C(16)	8435 (7)	4087 (8)	-1015 (11)
C(17)	8190 (7)	2971 (8)	-1674 (11)
C(18)	7494 (7)	2616 (8)	-971 (11)
C(19)	7278 (7)	3458 (8)	192 (11)
C(20)	6694 (7)	3327 (9)	1294 (12)
C(21)	6181 (9)	2813 (9)	4194 (14)
C(22)	6087 (8)	5003 (9)	6321 (12)
C(23)	7048 (9)	5144 (11)	7007 (15)
C(24)	5998 (9)	9017 (10)	4788 (15)
C(25)	7693 (12)	10147 (13)	3117 (19)
C(26)	7136 (14)	10184 (15)	2041 (19)
C(27)	10489 (8)	8595 (9)	-342 (13)
C(28)	10690 (9)	6374 (10)	-2386 (13)
C(29)	10254 (11)	6390 (12)	-3796 (15)
C(30)	8677 (9)	2425 (10)	-2979 (13)
C(31)	6969 (8)	1512 (9)	-1267 (13)
C(32)	6078 (10)	1435 (12)	-2092 (16)
C(M1)	6251 (8)	5575 (9)	1423 (12)
C(M2)	8373 (8)	6516 (9)	3305 (13)

The pattern of bond lengths (Table 5) at the periphery of the macrocycle indicates the major conjugated pathway is as shown in **15**. The N atoms bearing the N-Me substituents have N-Me bond lengths of 1.496 and 1.481 Å. These may be compared to values of 1.54 and 1.568 Å observed for N-Me copper[15] and N-Et nickel complexes of corroles,[16] in which the N atoms are believed to be sp^3 hybridised.[15] N-Alkylated porphyrins have N–C bond lengths between 1.456–1.51 Å,[17] whilst the non-delocalised porphyrinogen (16) has N-Me bond lengths of 1.462 Å.[18] Summation of the C–N–C bond angles about the methylated N atoms gives values of 353° and 349° for (2; $X = I_3^-$). This compares with values of 324° for the N-Me copper corrole[15] and 326° for the N-Et

Table 4. Thermal parameters ($\times 10^3$ Å^2) for the compound, $H(CH_3)_2(Etio\text{-}I)^+I_3^-$

Atom type	U	Atom type	U
N(1)	52 (2)	C (16)	48 (3)
N(2)	57 (2)	C (17)	53 (3)
N(3)	55 (2)	C (18)	53 (3)
N(4)	50 (2)	C (19)	50 (3)
C(1)	55 (3)	C (20)	58 (3)
C(2)	55 (3)	C (21)	77 (4)
C(3)	57 (3)	C (22)	63 (3)
C(4)	52 (3)	C (23)	92 (4)
C(5)	58 (3)	C (24)	86 (4)
C(6)	56 (3)	C (25)	124 (6)
C(7)	64 (3)	C (26)	145 (7)
C(8)	65 (3)	C (27)	68 (3)
C(9)	54 (3)	C (28)	74 (4)
C(10)	62 (3)	C (29)	106 (5)
C(11)	59 (3)	C (30)	76 (4)
C(12)	55 (3)	C (31)	72 (3)
C(13)	51 (3)	C (32)	105 (5)
C(14)	53 (3)	C (M1)	63 (3)
C(15)	56(3)	C (M2)	63 (3)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	117 (1)	81 (1)	87 (1)	-1 (1)	-21 (1)	19 (1)
I(2)	100 (1)	71 (1)	74 (1)	12 (5)	-22 (1)	-1 (1)
I(3)	114 (1)	153 (1)	114 (1)	-6 (1)	12 (1)	- 7 (1)

Table 5. Molecular dimensions for the compound, $H(CH_3)_2(Etio\text{-}I)^+I_3^-$

(a) I_3^- Group

I(1) - I(2)	2.901 (1)	I(1) - I(2) - I(3)	175.2 (1)
I(2) - I(3)	2.955 (2)		
I(1) ... I(1)	3.789 (2)		

(b) Distances, Å

N(1) - C(M1)	1.496 (13)	N(2) - C(M2)	1.481 (12)
N(1) - C(1)	1.381 (12)	N(1) - C(4)	1.408 (12)
N(2) - C(6)	1.378 (12)	N(2) - C(9)	1.378 (12)
N(3) - C(11)	1.395 (12)	N(3) - C(14)	1.368 (12)
N(4) - C(16)	1.387 (12)	N(4) - C(19)	1.381 (11)
C(1) - C(2)	1.429 (14)	C(3) - C(4)	1.432 (14)
C(6) - C(7)	1.436 (14)	C(8) - C(9)	1.449 (14)
C(11) - C(12)	1.425 (14)	C(13) - C(14)	1.435 (14)
C(16) - C(17)	1.473 (13)	C(18) - C(19)	1.458 (13)
C(2) - C(3)	1.374 (13)	C(7) - C(8)	1.329 (14)
C(12) - C(13)	1.364 (13)	C(17) - C(18)	1.297 (13)

Table 5. (*Contd.*)

C(1) - C(20)	1.410 (14)	C(4) - C(5)	1.404 (13)
C(5) - C(6)	1.358 (13)	C(9) - C(10)	1.338 (14)
C(10) - C(11)	1.422 (14)	C(14) - C(15)	1.405 (13)
C(15) - C(16)	1.361 (13)	C(19) - C(20)	1.379 (14)
C(2) - C(21)	1.485 (12)	C(7) - C(24)	1.525 (15)
C(12) - C(27)	1.517 (14)	C(17) - C(30)	1.517 (14)
C(3) - C(22)	1.499 (15)	C(8) - C(25)	1.634 (17)
C(13) - C(28)	1.496 (14)	C(18) - C(31)	1.527 (14)
C(22) - C(23)	1.519 (15)	C(25) - C(26)	1.455 (20)
C(28) - C(29)	1.543 (17)	C(31) - C(32)	1.509 (16)

(c) Angles, deg

C(1) - N(1) - C(M1)	121.8 (9)	C(4) - N(3) - C(M3)	122.2 (8)
C(6) - N(2) - C(M2)	119.9 (9)	C(9) - N(2) - C(M2)	119.1 (9)
C(1) - N(1) - C(4)	108.8 (9)	C(6) - N(2) - C(9)	110.3 (9)
C(11) - N(3) - C(14)	108.2 (9)	C(16) - N(4) - C(19)	105.3 (8)
N(1) - C(1) - C(2)	107.9 (9)	N(1) - C(4) - C(3)	106.9 (9)
N(2) - C(6) - C(7)	107.1 (9)	N(2) - C(9) - C(8)	104.9 (9)
N(3) - C(11) - C(12)	107.7 (9)	N(3) - C(14) - C(13)	108.5 (9)
N(4) - C(16) - C(17)	109.3 (8)	N(4) - C(19) - C(18)	109.6 (9)
C(1) - C(2) - C(3)	108.2 (10)	C(2) - C(3) - C(4)	108.2 (10)
C(6) - C(7) - C(8)	107.5 (10)	C(7) - C(8) - C(9)	110.2 (10)
C(11) - C(12) - C(13)	108.1 (10)	C(12) - C(13) - C(14)	107.4 (9)
C(16) - C(17) - C(18)	107.4 (9)	C(17) - C(18) - C(19)	109.5 (9)
C(4) - C(5) - C(6)	127.1 (11)	C(9) - C(10) - C(11)	130.0 (11)
C(14) - C(15) - C(16)	127.2 (10)	C(19) - C(20) - C(1)	129.9 (10)
C(20) - C(1) - N(1)	124.6 (10)	N(1) - C(4) - C(5)	122.3 (10)
C(5) - C(6) - N(2)	123.6 (10)	N(2) - C(9) - C(10)	128.2 (10)
C(10) - C(11) - N(3)	124.8 (10)	N(3) - C(14) - C(15)	122.6 (9)
C(15) - C(16) - N(4)	122.8 (9)	N(4) - C(19) - C(20)	124.9 (10)
C(20) - C(1) - C(2)	127.3 (10)	C(3) - C(4) - C(5)	130.7 (10)
C(5) - C(6) - C(7)	129.3 (11)	C(8) - C(9) - C(10)	126.6 (10)
C(10) - C(11) - C(12)	127.3 (10)	C(13) - C(14) - C(15)	128.9 (10)
C(15) - C(16) - C(17)	127.9 (10)	C(18) - C(19) - C(20)	124.8 (10)
C(1) - C(2) - C(21)	124.5 (10)	C(3) - C(2) - C(21)	127.2 (11)
C(6) - C(7) - C(24)	121.3 (10)	C(8) - C(7) - C(24)	130.9 (11)
C(11) - C(12) - C(27)	124.6 (10)	C(13) - C(12) - C(27)	127.2 (11)
C(16) - C(17) - C(30)	122.7 (9)	C(18) - C(17) - C(30)	129.8 (10)
C(2) - C(3) - C(22)	127.1 (11)	C(4) - C(3) - C(22)	124.4 (10)
C(7) - C(8) - C(25)	125.2 (11)	C(9) - C(8) - C(25)	123.8 (11)
C(12) - C(13) - C(28)	127.6 (10)	C(14) - C(13) - C(28)	125.0 (10)
C(17) - C(18) - C(31)	127.5 (10)	C(19) - C(18) - C(31)	124.1 (9)
C(3) - C(22) - C(23)	110.1 (10)	C(8) - C(25) - C(26)	100.8 (14)
C(13) - C(28) - C(29)	111.9 (10)	C(18) - C(31) - C(32)	112.4 (10)

nickel corrole.[16] Thus although (2; $X = I_3^-$) shows some shift towards sp^3 hydridisation it is still nearer to the sp^2 state. We recently suggested that the methylated N atoms of two rhodium (I) complexes of N-methylated corroles were sp^3 hybridised.[5] However, since the summation of the C–N–C bond angles of the N-methylated rings gives values of 344° and 347° it is clear these are also nearer to sp^2 hybridisation. Finally, there appears to be no interaction of the I_3^- ion with the porphyrin ring. The I–I–I chain is not linear but slightly bent with an angle of 175.2°.

EXPERIMENTAL

General details were as described previously.[5]

N-*Methyletioporphyrin* I. Etioporphyrin I (1 g) was dissolved in $CHCl_3$ (100 ml) and MeI (20 ml) and excess sodium formate

Table 6(a). Least-squares planes for $H(CH_3)_2(Etio\text{-}I)^+I_3^-$

Atoms forming the plane	Deviations from the Plane, Å					
	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5	Plane 6
N(1)	0.08	0.012				
N(2)	-0.08		-0.003			
N(3)	0.09			-0.007		
N(4)	-0.09				0.004	
C(1)		-0.007				
C(2)		0.001				
C(3)		0.006				
C(4)		-0.011				
C(5)						-0.05
C(6)			0.008			
C(7)			-0.009			
C(8)			0.008			
C(9)			-0.003			
C(10)						0.05
C(11)				0.004		
C(12)				-0.001		
C(13)				-0.004		
C(14)				0.006		
C(15)						-0.05
C(16)					0.002	
C(17)					-0.008	
C(18)					0.011	
C(19)					-0.009	
C(20)						0.05

Table 6(b). Least-squares planes for $H(CH_3)_2(Etio\text{-}I)^+I_3^-$

Equations of Least-Squares Planes $mX + nY + pZ = 1$ in Orthogonal Coordinates

Plane	m	n	p	l
N_4	-0.70971	0.25597	-0.65635	-5.23909
Pyrrole 1	-0.98136	-0.07802	-0.17564	-9.16498
Pyrrole 2	-0.69134	0.19170	-0.69664	-5.38854
Pyrrole 3	-0.71706	0.25451	-0.64888	-5.42636
Pyrrole 4	-0.60822	-0.27591	-0.74427	-9.28154
meso-C	-0.75367	0.15759	-0.63808	-6.44404

Table 6(c). Least-squares planes for $H(CH_3)_2(Etio\text{-}I)^+I_3^-$ angles between the planes, deg.

Plane	2	3	4	5	6
1	37.6	31.8	4.5	0.6	6.3
2		41.5	38.2	37.1	32.9
3			27.6	31.9	27.1
4				4.8	5.3
5					5.9

added. The mixture was boiled under reflux for 24 hr, cooled and the inorganic salts removed by filtration. The filtrate was concentrated and chromatographed on neutral alumina. Chloroform–benzene (1:1) eluted a red-brown fraction which on work up and crystallisation from $CHCl_3$–MeOH afforded N-*methyletioporphyrin* (810 mg; 62%) as purple plates, m.p. 245°.[4] A second fraction was eluted with $CHCl_3$–5% MeOH and afforded N_a,N_b-dimethyl etioporphyrin I (130 mg; 8%).

N_a,N_b-*Dimethyletioporphyrin I* (2)

(a) Etioporphyrin I (500 mg) was dissolved in $CHCl_3$ (50 ml) and MeI (10 ml) and NaOAc (2 g) added. The mixture was boiled under reflux for 2 days when the NMR spectrum of an aliquot showed it to consist of a 50:50 mixture of N-Me- and N_a,N_b-dimethyl-etioporphyrin I. A further portion of MeI (10 ml) and excess anhyd K_2CO_3 were then added and the mixture kept at room temp for 24 hr. The inorganic salts were removed by filtration and the filtrate evaporated to dryness. The residue was recrystallised from MeOH–NaIaq to give N_a,N_b-*dimethyletioporphyrin hydriodide* (653 mg; 98%) as purple needles, m.p. dec. 272–290°. (Found: C, 64.05; H, 7.10; N, 8.50; I, 20.00. $C_{34}H_{43}IN_4$ requires: C, 64.35; H, 6.80; N, 8.85; I, 20.05%). τ −0.31(s, 3H, 3x meso-H), −0.14 (s, 1H, meso-H), 5.90–6.22 (m, 8H, 4×$\underline{CH_2}$Me), 6.33, 6.40, 6.61, 6.65 (all s, all 3H, Me), 8.09, 8.11, 8.34, 8.56 (all t, all 3H, $CH_2\underline{Me}$), 13.88 (s, 1H, N$\underline{H}$), 15.86 and 15.90 (both s, both 3H, N$\underline{Me}$). The triiodide salt was prepared by addition of iodine solution to a solution of iodide in $CHCl_3$–MeOH. The triiodide salt, m.p. 195°, separated as purple plates from $CHCl_3$–MeOH (Found: C, 45.75; H, 4.95; I, 42.90; N, 6.10. $C_{34}H_{43}I_3N_4$ requires C, 45.95; H, 4.85; I, 42.85; N, 6.30%). The triiodide exhibited a slightly different NMR spectrum to the iodide. τ −0.32 (s, 2H, meso-H), −0.22 (s, 1H, meso-H), −0.13 (s, 1H, meso-H), 5.85–6.30 (m, 8H, 4×$\underline{CH_2}$Me), 6.33, 6.40, (both s, both 3H, 2×Me), 6.63 (s, 6H, 2×$\overline{Me}$), 8.08, 8.11, 8.33, 8.55 (all t, all 3H, 4×$CH_2\underline{Me}$), 13.85 (s, 1H, N$\underline{H}$), 15.80 and 15.86 (both s, both 3H, NMe).

(b) Etioporphyrin I (200 mg) was dissolved in $CHCl_3$ (50 ml) and $MeSO_4$ (5 ml) and excess anhyd K_2CO_3 added. On keeping at room temp for 2 days the colour had changed from red to greenish-red and the mixture was worked up in the usual way but shaking the $CHCl_3$ soln with sat NaClaq to effect anion exchange. Chromatography on alumina gave a small amount of unchanged etioporphyrin I and N_a,N_b-dimethyletioporphyrin I hydrogen chloride (160 mg; 70%), m.p. 300° (Found: Cl, 6.55. $C_{34}H_{43}N_4Cl$ requires: Cl, 6.53%).

N_a,N_b,N_c-*Trimethyletioporphyrin I* (3)

(a) Etioporphyrin I (500 mg) was dissolved in $CHCl_3$ (50 ml) and MeI (10 ml) and excess anhyd K_2CO_3 added. The mixture was boiled under reflux for 24 hr, MeI (10 ml) added and heating continued for a further 18 hr. The inorganic salts were removed by filtration, the solvent evaporated and the residue crystallised from $CHCl_3$–MeOH to which a few drops of NaIaq had been added. N_a,N_b,N_c-trimethyletioporphyrin iodide (620 mg; 92%), m.p. > 300°, separated as purple prisms.

(b) N_a,N_b-Dimethyletioporphyrin I iodide (200 mg) was dissolved in $CHCl_3$ (20 ml) and MeI (15 ml) and excess anhyd K_2CO_3 added. The mixture was boiled under reflux for 1 hr, cooled, the inorganic salts removed by filtration and the filtrate evaporated to dryness. The residue was crystallised from MeOH containing a few drops of NaIaq to afford N_a,N_b,N_c-trimethyletioporphyrin I iodide (140 mg, 51%). (Found: C, 64.60; H, 6.75; I, 19.25; N, 8.35. $C_{35}H_{45}IN_4$ requires: C, 64.80; H, 7.00; I, 19.55; N, 8.65%). τ 0.07 (s, 2H, meso-H), 0.11 (s, 1H, meso-H), 0.14 (s, 1H, meso-H), 6.12–6.55 (m, 8H, 4×CH_2Me), 6.60, 6.64, 6.94, 6.99 (all s, all 3H, 4×Me), 8.36, 8.59, 8.80, 8.88 (all t, all 3H, CH_2Me), 13.90, 13.95 and 17.08 (all s, all 3H, NMe).

The triiodide salt was prepared by dissolving the iodide (140 mg) in $CHCl_3$ (3 ml), adding I_2 (67 mg) and warming the soln with addition of MeOH to promote crystallisation. The product (185 mg) was then recrystallised from $CHCl_3$–MeOH to afford the triiodide (135 mg, 69%), m.p. 216–218°, as purple needles. (Found: C, 45.55; H, 4.70; I, 42.85; N, 5.80. $C_{35}H_{45}I_3N_4$ requires: C, 46.55; H, 5.0; I, 42.20; N, 6.20%).

Conversion of N_a,N_b-N_c-*trimethyletioporphyrin* I *into* N_a,N_b-*dimethyletioporphyrin I*

(a) N_a,N_b,N_c-Trimethyletioporphyrin iodide (25 mg) was heated at 150–160° for 1 hr in *o*-dichlorobenzene. The solvent was removed and the NMR spectrum of the residue showed it to contain N_a,N_b-dimethyletioporphyrin I (*ca* 68%).

(b) N_a,N_b,N_c-Trimethyletioporphyrin I iodide (10 mg) was heated at 110° in deuteropyridine (0.5 ml) in a sealed NMR tube. The NMR spectrum after 8 hr showed it to be a 50:50 mixture of N_a,N_b,N_c-trimethyl- and N_a,N_b-dimethyl-etioporphyrin I.

(c) N_a,N_b,N_c-Trimethyletioporphyrin I iodide (20 mg) was boiled under reflux in $CHCl_3$ (2 ml) containing 1 drop of conc HI for 3 hr. The soln was then cooled, washed with K_2CO_3aq and water, dried (Na_2SO_4) and the solvent evaporated. The NMR spectrum of the residue showed it to be a 50:50 mixture of N_a,N_b,N_c-trimethyl- and N_a,N_b-dimethyletioporphyrin I.

3,7,13,17 - *Tetraethyl* - 2,8,12,18,21 - *pentamethyl* - 5 - *monoazaporphyrin* (7a) *and* 3,7,13,17 - *tetraethyl* - 2,8,12,18,23 - *pentamethyl* - 5 - *monoazaporphyrin* (7b)

3,7,13,17-Tetraethyl-2,8,12,18-tetramethyl-5-monoazaporphyrin (100 mg) was gently boiled under reflux in a 1:1 (v/v) mixture (100 ml) of $CHCl_3$ and MeI for 4 days. The green solid obtained after evaporation of the solvent was chromatographed on an alumina column using $CHCl_3$ as eluant. A fast moving brown band was eluted which on crystallisation from methylene chloride-pentane deposited the less soluble starting material. The brown-purple solid obtained from the mother liquor was the product (88 mg, 85%) which was shown by NMR (below) to be a 1:1 mixture of the N-21- and N-23-Me isomers. Crystallisation from methylene chloride–ether gave the product as purple plates, m.p. 219–220° (Found: C, 76.66; H, 7.80; N, 14.08. $C_{32}H_{39}N_5{\cdot}\frac{1}{2}H_2O$ requires: C, 76.42; H, 8.04; N, 13.93%). m/e 493 (P^+), 479, 478 (P–Me), 464 (P–Et) λ_{max} 631, 575, 540, 506, 386 nm; τ 0.59 (1H), 0.62(1H), 0.75(2H), 0.78(1H), 0.89(1H) (all s, *meso*-H), 6.00–7.25 (m, 40H, Me and CH_2), 8.32–9.00 (m, 24H, CH_2Me), 13.82 (s, 3H, NMe) and 14.24 (s, 3H, NMe).

2,3,7,8,12,18,23,24-*Octamethyl*-13,17-*diethyl*-5-*monoazaporphyrin sulphate* (8)

2,3,7,8,12,18-Hexamethyl-13,17-diethyl-5-monoazaporphyrin (120 mg) was boiled under reflux in $CHCl_3$ (200 ml) containing Me_2SO_4 (25 ml) and anhyd K_2CO_3 (7 g) for 2 days. The mixture was then filtered, and the green filtrate washed with $NaHCO_3$aq, water and dried ($MgSO_4$). The solvent was removed under reduced pressure and a small amount of unhydrolysed Me_2SO_4 was removed using an oil pump. The green solid was chromatographed on alumina. $CHCl_3$ eluted a small amount of starting material and the product (83 mg, 59%) was eluted as a green band by $CHCl_3$–EtOH (1:1). Crystallisation from methylene chloride–ether gave the product (20 mg, 14%), as purple plates, m.p. > 300°. (Found: C, 70.50; H, 7.26; N, 13.12. $C_{31}H_{38}N_5{\cdot}\frac{1}{2}(SO_4)$ requires: C, 70.41; H, 7.26; N, 13.25%), *m/e* 481 (free base + 2, 72), 480(55), 479(free base, 100), 467(17), 466(13), 465(free base -Me, 31) λ_{max} 615, 588, 393 nm τ −0.46 (s, 1H, *meso*-H), 0.03 (s, 2H, *meso*-H), 6.16 (two overlapping q, 4H, CH_2), 6.50 (s, 6H, Me), 6.57 (s, 6H, Me), 6.78 (s, 6H, Me), 8.62 (t, 6H, $CH_2\underline{Me}$), 14.87 (s, 6H, NMe).

2,3,7,8,12,18,21,23,24-*Nonamethyl* - 13,17 - *diethyl* - 5 - *monoazaporphyrin iodide* (11a)

2,3,7,8,12,18-Hexamethyl-13,17-diethyl-5-monoazaporphyrin (220 mg) was gently boiled under reflux for 8 days in a mixture (200 ml) of $CHCl_3$ and MeI (1:1, v/v) containing anhyd K_2CO_3 (5 g). The solvent was evaporated and the brown residue chromatographed on a short (2") alumina column eluting with $CHCl_3$. Longer columns caused decomposition of the product. Some unreacted starting material and a light brown band which eluted first were discarded. This was followed by the product as a brown band. The sticky solid obtained on evaporation of the solvent was triturated with ether to give the product as a blackish solid (135 mg, 44.5%). Crystallisation from methylene chloride–ether gave the product as dark purple plates, m.p. > 300°. (Found: C, 62.06; H, 6.80; N, 10.92. $C_{32}H_{40}N_5I$ requires: C, 61.82; H, 6.50;

N, 11.27%) *m/e* 495 (P+1), 480; λ_{max} 407 nm. τ 0.29 (s, 1H, *meso*-H), 0.52 (s, 1H, *meso*-H), 0.71 (s, 1H, *meso*-H), 5.5–9.3 (m, β-alkyl), 12.78 (s, 3H, NMe), 12.94 (s, 3H, NMe), 15.39 (s, 3H, NMe).

2,3,7,8,12,18,21 - *Heptamethyl* - 13,17 - *diethyl* - 5 - *monoazaporphyrin* (7c) *and* 2,3,7,8,12,18,23 - *heptamethyl* - 13,17 - *diethyl* - 5 - *monoazaporphyrin* (7d)

2,3,7,8,12,18-Hexamethyl-13,17-diethyl-5-monoazaporphyrin (100 mg) was boiled under reflux in a mixture (100 ml) of $CHCl_3$ and MeI (1:1, v/v) for 4½ days. The solvent was removed under reduced pressure and the green residue dissolved in $CHCl_3$ and filtered through a short silica column. $CHCl_3$ eluted a small amount of starting material. Elution with $CHCl_3$–EtOH (1:1, v/v) gave a green soln. Evaporation of the solvent gave a green solid which was dissolved in $CHCl_3$ and filtered through a short alumina column, eluting with $CHCl_3$. The brown soln obtained gave the product (100 mg) as a purple solid on evaporation of the solvent. The NMR spectrum of the solid indicated that it was an approximately 1:1 mixture of the N-21 and N-23 Me compounds and contained, *inter alia*, signals at τ 0.23 (s, 1H, *meso*-H), 0.28 (s, 1H, *meso*-H), 0.40 (s, 2H, *meso*-H), 0.43 (s, 1H, *meso*-H), 0.52 (s, 1H, *meso*-H), 13.80 (s, 3H, NMe) and 14.19 (s, 3H, NMe).

Zinc complex

The above 1:1 mixture of **7c** and **7d** (60 mg) was dissolved in 2:1 v/v $CHCl_3$–MeOH (45 ml) and boiled under reflux for 5 min with zinc acetate (100 mg). The solvent was then evaporated and the residue chromatographed on alumina eluting with $CHCl_3$. A small purple band eluted first which contained a small amount of zinc 2,3,7,8,12,18-hexamethyl-13,17-diethyl-5-monoazaporphyrin. $CHCl_3$–EtOH (3:1) eluted a purple–green band. This eluate was washed with NaIaq, water, dried (Na_2SO_4) and the solvent evaporated. The residue was crystallised from $CHCl_3$ to give a 1:1 mixture of the Zn complexes of **7c** and **7d** (50 mg, 58.8%), m.p. dec from 175° (Found: C, 54.80; H, 5.10, N, 10.40. $C_{30}H_{34}IN_5Zn$ requires: C, 54.85; H, 5.25; N, 10.65%). *m/e* 528 (M–I), 513, 498; τ −0.06 (s, 3H, *meso*-H), 0.07 (s, 1H, *meso*-H), 0.11 (s, 1H, *meso*-H), 0.25 (s, 1H, *meso*-H), 6.13 (m, 8H, 4× CH_2Me), 6.54–6.72 (overlapping s, 36H, 12× Me), 8.19 (overlapping t, 9H, CH_2ME), 8.60 (t, 3H, CH_2Me), 13.87 (s, 3H, NMe) and 13.99 (s, 3H, NMe).

Crystallography

Data were recorded in the $3 \leq \theta \leq 25°$ range [MoK_α radiation, graphite monochromator, λ(MoK_α) = 0.71069 Å] on a Philips PW 1100 automatic four-circle diffractometer with a $\theta-2\theta$ scan mode. Weak reflections which gave $I_t - 2(I_t)^{1/2} < I_b$ on the first scan were not further examined (I_t is the intensity at the top of the reflection peak and I_b is the mean of two preliminary 5s background measurements on either side). Of the remaining reflections, those for which the total intensity recorded in the first scan (I_t) was <500 counts were scanned twice to increase their accuracy. A constant scan speed of 0.05° s^{-1} and a variable scan width of $(0.80 + 0.05 \tan\theta)°$ were used, with a background measuring time proportional to I_b/I_t. Three standard reflections were measured every 5 hr during data collection and showed no significant variations in intensity.

The intensities were calculated from the peak and background measurements with a programme written for the PW 1100 diffractometer. The variance of intensity, $\sigma(I)$, was calculated as the sum of the variance due to counting statistics and $(0.04\,I)^2$, where the term in I^2 was introduced to allow for other sources of error. I and $\sigma(I)$ were corrected for Lorentz and polarization factors. No absorption corrections were applied. The final data set consisted of 2679 independent reflections of which 95 for which $I < 3\sigma(I)$ were rejected. The structure was solved by standard Patterson and Fourier methods and refined by full matrix least-squares calculations.[19] The C–H hydrogen atoms coordinates were estimated geometrically (with C–H = 1.08 Å assumed) and for refinement allowed to ride on their respective C atom coordinates. The N–H hydrogen atom position could not be obtained from a (F_o–F_c) synthesis. Neutral-atom scattering factors were used, those for I being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).

For the final stages of refinement the iodine atoms were allowed to assume anisotropic thermal parameters. In the final cycle the mean shift/σ was 0.02 and the maximum 0.97. The final $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o| = 0.052$, and $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2} = 0.057$, where $w = 2.408$ $(\sigma^2|F_o|)^{-1}$. The final difference map showed no significant features. The final atomic parameters are listed in Tables 3 and 4.

Crystal data. $H(CH_3)_2$(Etio-I)$^+$ I_3^-, $C_{34}H_{43}N_4I_3$, M = 888. Mo-K_α radiation (graphite monochromator), λ = 0.71069 Å. Space group $P\bar{1}$. **a**, Å 14.262 (2), **b**, Å 13.151 (3), **c**, Å 9.847 (5), α, deg. 102.8 (1), β, deg. 88.4 (2), γ, deg. 96.5 (1), **V**, Å^3 1789.1, F(000) 868, **Z** 2. Crystal dimensions, mm 0.15 × 0.10 × 0.20, μ, cm^{-1} 24.6. Final no. of variables 211. Unique data used $I \geq 3\sigma$ (I) 2584.

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Supplementary Material

Atomic Fractional Cell Coordinates (× 10^4) at Calculated Positions for $H(CH_3)_2$ (Etio − I)$^+$ I_3^- for the Hydrogen Atoms.

Atom	x/a	y/b	z/c
H(5)	6033 (7)	7020 (8)	5377 (12)
H(10)	9085 (6)	8989 (9)	1645 (12)
H(15)	9538 (7)	4471 (8)	−2302 (12)
H(20)	9361 (7)	2537 (9)	1212 (12)
H(21a)	6088 (9)	2142 (9)	3330 (14)
H(21b)	5592 (9)	2788 (9)	4903 (14)
H(21c)	6827 (9)	2799 (9)	4732 (14)
H(22a)	5639 (8)	4364 (9)	6606 (12)
H(22b)	5778 (8)	5727 (9)	6696 (12)
H(23a)	6962 (9)	5334 (11)	8125 (15)
H(23b)	7616 (9)	5668 (11)	6711 (15)
H(23c)	7211 (9)	4344 (11)	6673 (15)
H(24a)	5540 (9)	8513 (10)	5310 (15)
H(24b)	5605 (9)	9237 (10)	3996 (15)
H(24c)	6268 (9)	9714 (10)	5536 (15)
H(25a)	8412 (12)	10317 (13)	2769 (19)
H(25b)	7551 (12)	10707 (13)	4061 (19)
H(26a)	7401 (14)	11000 (15)	2151 (19)

Supplementary Material

Atomic Fractional Cell Coordinates ($\times 10^4$) at Calculated Positions for $H(CH_3)_2$ (Etio − I)$^+I_3^-$ for the Hydrogen Atoms.

Atom	x/a	y/b	z/c
H(26b)	6375 (14)	10099 (15)	1997 (19)
H(26c)	7412 (14)	9728 (15)	1094 (19)
H(27a)	10414 (8)	9079 (9)	687 (13)
H(27b)	10199 (8)	8952 (9)	-1101 (13)
H(27c)	11227 (8)	8521 (9)	-565 (13)
H(28a)	11304 (9)	6948 (10)	-2213 (13)
H(28b)	10901 (9)	5604 (10)	-2430 (13)
H(29a)	10829 (11)	6164 (12)	-4494 (15)
H(29b)	10152 (11)	7197 (12)	-3766 (15)
H(29c)	9616 (11)	5891 (12)	-4160 (15)
H(30a)	9385 (9)	2813 (10)	-2993 (13)
H(30b)	8272 (9)	2578 (10)	-3808 (13)
H(30c)	8703 (9)	1590 (10)	-3127 (13)
H(31a)	6769 (8)	1302 (9)	-291 (13)
H(31b)	7430 (8)	967 (9)	-1836 (13)
H(32a)	5649 (10)	698 (12	-2136 (16)
H(32b)	6399 (10)	1438 (12)	-3099 (16)
H(32c)	5642 (10)	2071 (12)	-1815 (16)
H(M1a)	6011 (8)	4924 (9)	585 (12)
H(M1b)	6681 (8)	6162 (9)	1002 (12)
H(M1c)	5649 (8)	5912 (9)	1956 (12)
H(M2a)	8332 (8)	6221 (9)	4248 (13)
H(M2b)	9082 (8)	6868 (9)	3177 (13)
H(M2c)	8193 (8)	5877 (9)	2423 (13)

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