Crystal and Molecular Structure of a Non-metallo, N-Substituted Porphyrin, 21-Ethoxycarbonylmethyl-2,3,7,8,12,13,17,18-octaethylporphyrin

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The title compound crystallises in the triclinic system, space group $P\bar{1}$, with $a = 14\cdot485(2)$, $b = 14\cdot957(2)$, $c = 10\cdot360(1)$ Å, $\alpha = 92\cdot81(6)$, $\beta = 101\cdot36(6)$, $\gamma = 103\cdot68(5)°$, $Z = 2$. Least-squares refinement of atomic and thermal parameters, based on 2145 independent reflections measured on a diffractometer, converged to R $0\cdot071$. Three geometrically different pyrrole rings are observed and the stereochemical consequences of substitution at nitrogen are discussed.

MANY structural analyses [1-5] of porphyrins and metalloporphyrins have been undertaken in recent years, but there is limited structural information about N-substituted porphyrins, and the stereochemical effects of substitution at nitrogen. The present analysis was undertaken to elucidate the consequences of such substitution.

EXPERIMENTAL

Crystal Data.—$C_{43}H_{59}IN_4O_2$, $M = 860\cdot9$. Triclinic, $a = 14\cdot485(2)$, $b = 14\cdot957(2)$, $c = 10\cdot360(1)$ Å, $\alpha = 92\cdot81(6)$, $\beta = 101\cdot36(6)$, $\gamma = 103\cdot68(5)°$ (Delauney reduced cell), $U = 2127\cdot3$ Å^3, $D_m = 1\cdot25$, $Z = 2$, $D_c = 1\cdot259$, $F(000) = 422$. Space group $P\bar{1}(C_i^1)$. Mo-$K_{\bar{\alpha}}$ radiation, $\lambda = 0\cdot70926$ Å; $\mu(\text{Mo-}K_{\alpha}) = 8\cdot06$ cm^{-1}.

Preliminary cell dimensions were obtained from precession photographs and were subsequently adjusted by least-squares refinement of the setting angles of twelve reflections measured on a Hilger and Watts Y290 four-circle diffractometer by use of Mo-K_{α} radiation with a graphite crystal monochromator. The crystal used was a small black needle of dimensions $0\cdot3 \times 0\cdot15 \times 0\cdot10$ mm. Intensity data were collected by the θ—2θ step-scan procedure, each reflection being scanned in 50 one-second steps of $0\cdot01°$ from $0\cdot25°$ below to $0\cdot25°$ above $2\theta_{\text{calc}}$. Stationary-background counts were measured for 25 s at each end of the scan range. The intensities of three standard reflections were monitored periodically to check crystal and electronic stability. Intensities were collected for reflections with $\theta(\text{Mo-}K_{\alpha}) \leqslant 22°$, and 2145 reflections for which $I \geqslant 3\sigma(I)$ were accepted as being significantly above background, and only these were used in the subsequent analysis. These were corrected for Lorentz and polarisation effects, but not for absorption.

Structure Analysis.—Approximate co-ordinates of the iodide ion were derived from a three-dimensional Patterson synthesis. A structure-factor calculation based on this gave R $0\cdot38$. The co-ordinates of the atoms of the substituted octaethylporphyrin molecule were obtained from two subsequent electron-density distributions. Least-squares refinement of positional and isotropic thermal parameters, with the program CRYLSQ [6] in the blocked mode, gave R $0\cdot145$. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F^2)$. Scattering factors

† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[1] L. E. Webb and E. B. Fleischer, *J. Chem. Phys.*, 1965, **43**, 3100.

[2] T. A. Hamor, W. S. Caughey, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1965, **87**, 2305.

[3] A. Stone and E. B. Fleischer, *J. Amer. Chem. Soc.*, 1968, **90**, 2735.

[4] D. M. Collins, W. R. Scheidt, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1972, **94**, 6689.

were taken from ref. 7 except those for hydrogen.[8] Anomalous dispersion was accounted for by taking values of f' and f'' for iodine from ref. 9. A difference synthesis calculated at this point clearly showed a molecule of solvent acetone and anisotropic thermal motion of the iodide ion. Accounting for these effects reduced R to $0\cdot086$. A further difference map was then calculated which showed the two inner hydrogens attached to nitrogens on opposite pyrrole rings, the four methine hydrogens, the sixteen methylene hydrogens of the ethyl groups, and anisotropic motion associated with the $-CO_2Et$ group. After refinement with these hydrogen atoms included at calculated positions as fixed atom contributors (B $4\cdot0$ Å^2) and allowing for anisotropic thermal vibration of the $-CO_2Et$ group R converged at $0\cdot071$ for the 2145 independent reflections. The $-CH_3$ hydrogens of the ethyl groups were not well resolved in the difference map and were therefore excluded from the calculations. During the final cycle of refinement all variable parameter shifts were $<0\cdot2\sigma$ and the adequacy of the weighting scheme was indicated by a subsequent analysis of $w(|F_o - F_c|)^2$ vs. F_o and $\sin\theta/\lambda$ which showed no systematic trends. There were no peaks in the final difference map $>0\cdot4$ eÅ^{-3}. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20875 (4 pp., 1 microfiche).†

DISCUSSION

Figure 1 shows the molecule, with the atom numbering system used. Final co-ordinates and thermal parameters are listed in Tables 1 and 2, and torsion angles in Table 3.

The space group ($P\bar{1}$, C_i^1) of the title compound (I), imposes no crystallographic restrictions on the symmetry of the molecule and three different types of pyrrole ring can thus be distinguished: the N-substituted ring, and the two rings with, and one without hydrogen bonded to nitrogen. The accuracy of the determinations is such as to allow some comparison between them. The molecule has effectively (though not crystallographically) a mirror plane perpendicular to the mean molecular plane through $N(1)$ and $N(3)$. This permits averaging equivalent bond lengths and angles to obtain the values in Figure 2.

[5] D. M. Collins and J. L. Hoard, *J. Amer. Chem. Soc.*, 1970, **92**, 3761.

[6] ' *X*-Ray System,' version July 1970, eds. J. M. Stewart, F. A. Kundell, and J. C. Baldwin, as implemented on the I.C.L. 1906 A at the S.R.C. Atlas Computer Laboratory, Chilton, Berks.

[7] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[8] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[9] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

In metalloporphyrins the pyrrole rings are generally equivalent whereas in free base porphyrins two rings have hydrogen bonded to nitrogen and two do not. In porphin [1] and the tetragonal form of tetraphenyl-porphin [10] static disorder prevents the observation of differences between the two kinds of ring, each appearing to have a ' half-hydrogen ' attached to the nitrogen. In the triclinic form of tetraphenylporphin,[11] tetra-n-

TABLE 1

(a) Fractional co-ordinates ($\times 10^4$) and isotropic temperature factors ($\text{Å}^2 \times 10^3$) of non-hydrogen atoms

	x	y	z	U
I	1852(1)	7603(1)	1210(1)	*
O(1)	665(6)	3547(9)	5252(10)	*
O(2)	1438(7)	3267(9)	7160(10)	*
C(39)	501(12)	2729(19)	7440(21)	*
C(40)	534(18)	1766(17)	7462(31)	*
O(3)	2901(11)	1174(10)	1127(15)	147(5)
N(1)	2476(6)	4234(6)	4503(9)	28(3)
N(2)	4133(7)	3333(7)	5537(10)	31(3)
N(3)	5201(7)	5054(7)	6962(10)	37(3)
N(4)	3750(7)	6040(7)	5830(9)	30(3)
C(1)	2206(9)	3402(8)	3677(12)	30(3)
C(2)	2581(9)	2652(9)	3892(12)	40(4)
C(3)	3451(9)	2614(9)	4794(13)	35(4)
C(4)	3777(9)	1781(9)	5047(13)	40(4)
C(5)	4653(9)	2052(9)	5904(12)	35(4)
C(6)	4858(9)	3011(8)	6238(12)	29(3)
C(7)	5627(9)	3564(9)	7155(13)	37(4)
C(8)	5777(9)	4506(9)	7544(12)	34(4)
C(9)	6510(9)	5037(9)	8679(12)	34(3)
C(10)	6391(9)	5878(9)	8787(12)	33(3)
C(11)	5576(9)	5897(9)	7691(12)	35(4)
C(12)	5243(9)	6693(8)	7491(12)	33(3)
C(13)	4392(9)	6755(9)	6652(13)	38(4)
C(14)	3984(9)	7542(8)	6509(12)	31(3)
C(15)	3135(9)	7286(9)	5621(13)	38(4)
C(16)	2951(9)	6325(9)	5156(12)	35(4)
C(17)	2157(9)	5765(9)	4233(12)	38(4)
C(18)	1982(9)	4847(9)	3857(12)	31(3)
C(19)	1349(9)	4368(9)	2700(13)	37(4)
C(20)	1492(9)	3491(9)	2569(12)	36(4)
C(21)	3188(10)	828(10)	4448(14)	57(4)
C(22)	2344(13)	450(12)	5057(17)	89(6)
C(23)	5306(10)	1422(9)	6456(14)	50(4)
C(24)	5088(12)	1102(11)	7770(17)	79(5)
C(25)	7210(9)	4631(9)	9613(13)	42(4)
C(26)	6740(11)	4119(10)	10,692(15)	67(5)
C(27)	6858(9)	6642(9)	9834(13)	43(4)
C(28)	6279(11)	6768(10)	10,874(15)	61(4)
C(29)	4493(9)	8480(9)	7234(13)	43(4)
C(30)	4326(11)	8537(11)	8693(16)	72(5)
C(31)	2413(10)	7863(9)	5213(14)	49(4)
C(32)	1674(12)	7775(12)	6053(17)	84(6)
C(33)	632(9)	4742(9)	1743(13)	45(4)
C(34)	−327(11)	4659(11)	2232(17)	70(5)
C(35)	954(9)	2691(9)	1518(13)	48(4)
C(36)	129(11)	1990(11)	1992(16)	74(5)
C(37)	2392(8)	4147(8)	5929(11)	33(3)
C(38)	1410(9)	3611(9)	6022(13)	43(4)
C(41)	2331(15)	526(14)	435(20)	105(6)
C(42)	1379(16)	131(15)	698(21)	129(8)
C(43)	2643(18)	27(18)	−627(26)	159(9)

* These atoms were refined anisotropically.

(b) Thermal parameters ($\text{A}^2 \times 10^3$) of atoms refined aniso-tropically expressed in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}h^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I	90(1)	108(1)	94(1)	41(1)	20(1)	34(1)
O(1)	40(7)	175(12)	55(8)	2(7)	−1(5)	40(8)
O(2)	67(8)	154(11)	69(8)	8(8)	0(6)	68(8)
C(39)	38(12)	183(25)	128(18)	−32(15)	29(12)	94(19)
C(40)	124(21)	97(20)	265(34)	−6(17)	96(21)	46(22)

(c) Fractional co-ordinates ($\times 10^4$) of the calculated hydrogen atom positions. Atoms are labelled with the number of the atom to which they are attached. U is 0·051 for all

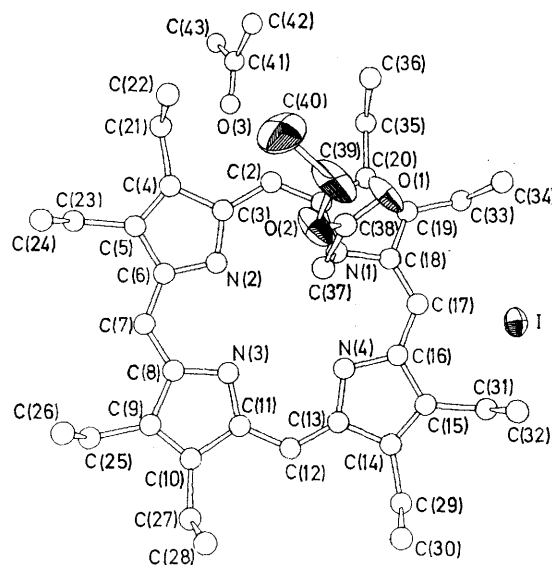|	x	y	z
H(21a)	3643	376	4570
H(21b)	2918	860	3449
H(23a)	6032	1791	6609
H(23b)	5173	841	5770
H(25a)	7800	5173	10,097
H(25b)	7450	4162	9072
H(27a)	7002	7260	9377
H(27b)	7527	6527	10,319
H(29a)	4226	8983	6736
H(29b)	5236	8585	7284
H(31a)	2062	7655	4218
H(31b)	2800	8564	5299
H(33a)	473	4357	798
H(33b)	948	5434	1644
H(35a)	1459	2352	1289
H(35b)	642	2973	685
H(37a)	2519	4814	6405
H(37b)	2916	3822	6384
H(2N)	4113	3970	5544
H(4N)	3824	5419	5740
H(2)	2177	2017	3312
H(7)	6171	3235	7601
H(12)	5700	7327	8020
H(17)	1616	6115	3810

FIGURE 1 The molecule viewed perpendicular to the plane defined by N(2), N(3), and N(4) showing the numbering system used and thermal motion of the atoms refined anisotropically (ellipsoids are scaled to include 30% probability)

propylporphin,[12] porphin (redetermined),[13] and octa-ethylporphin,[14] however, two distinct hydrogens attached to opposite nitrogens were observed together with small, but significant, geometrical differences between the two types of ring.

In (I) two clearly distinct inner hydrogens are again

[10] M. J. Hamor, T. A. Hamor, and J. L. Hoard, J. Amer. Chem. Soc., 1964, 86, 1938.
[11] S. J. Silvers and A. Tulinski, J. Amer. Chem. Soc., 1967, 89, 3331.
[12] P. W. Codding and A. Tulinsky, J. Amer. Chem. Soc., 1972, 94, 4151.
[13] E. M. L. Chen and A. Tulinsky, J. Amer. Chem. Soc., 1972, 94, 4144.
[14] J. W. Laugher and J. A. Ibers, J. Amer. Chem. Soc., 1973, 95, 5148.

attached to opposite nitrogens, N(2) and N(4). In these rings the C_α–C_β bonds are shorter, the C_β–C_β bonds longer, the C_α–N–C_α angles larger, and the N–C_α–C_β angles smaller than in the ring without hydrogen on N. These differences are the same as those found for the ordered free base porphyrins [11-14] and probably would be observed for all free base porphins which were not disordered.

TABLE 2

(a) Interatomic distances (Å)

O(1)–C(38)	1·19(2)	C(9)–C(25)	1·52(2)
O(2)–C(39)	1·49(2)	C(10)–C(11)	1·47(2)
O(2)–C(38)	1·31(2)	C(10)–C(27)	1·47(2)
C(39)–C(40)	1·45(4)	C(11)–C(12)	1·40(2)
O(3)–C(41)	1·21(2)	C(12)–C(13)	1·39(2)
N(1)–C(1)	1·40(2)	C(13)–C(14)	1·44(2)
N(1)–C(18)	1·41(2)	C(14)–C(15)	1·34(2)
N(1)–C(37)	1·51(2)	C(14)–C(29)	1·51(2)
N(2)–C(3)	1·36(1)	C(15)–C(16)	1·44(2)
N(2)–C(6)	1·36(2)	C(15)–C(31)	1·52(2)
N(3)–C(8)	1·38(2)	C(16)–C(17)	1·40(2)
N(3)–C(11)	1·37(2)	C(17)–C(18)	1·36(2)
N(4)–C(13)	1·37(1)	C(18)–C(19)	1·40(2)
N(4)–C(16)	1·40(2)	C(19)–C(20)	1·38(2)
C(1)–C(2)	1·37(2)	C(19)–C(33)	1·52(2)
C(1)–C(20)	1·42(2)	C(20)–C(35)	1·52(2)
C(2)–C(3)	1·43(2)	C(21)–C(22)	1·49(2)
C(3)–C(4)	1·45(2)	C(23)–C(24)	1·53(2)
C(4)–C(5)	1·36(2)	C(25)–C(26)	1·56(2)
C(4)–C(21)	1·51(2)	C(27)–C(28)	1·52(2)
C(5)–C(6)	1·41(2)	C(29)–C(30)	1·58(2)
C(5)–C(23)	1·54(2)	C(31)–C(32)	1·49(3)
C(6)–C(7)	1·38(2)	C(33)–C(34)	1·55(3)
C(7)–C(8)	1·40(2)	C(35)–C(36)	1·57(2)
C(8)–C(9)	1·47(2)	C(37)–C(38)	1·49(2)
C(9)–C(10)	1·31(2)	C(41)–C(42)	1·45(3)
C(41)–C(43)	1·50(4)		

(b) Valency angles (°)

C(39)–O(2)–C(38)	117·8(12)	N(4)–C(13)–C(12)	125·1(13)
O(2)–C(39)–C(40)	108·0(19)	N(4)–C(13)–C(14)	106·6(10)
C(1)–N(1)–C(18)	107·4(9)	C(12)–C(13)–C(14)	128·3(11)
C(1)–N(1)–C(37)	115·7(9)	C(13)–C(14)–C(15)	108·4(11)
C(18)–N(1)–C(37)	114·8(10)	C(13)–C(14)–C(29)	122·7(11)
C(3)–N(2)–C(6)	109·1(11)	C(15)–C(14)–C(29)	128·9(13)
C(8)–N(3)–C(11)	104·2(9)	C(14)–C(15)–C(16)	109·4(12)
C(13)–N(4)–C(16)	110·7(11)	C(14)–C(15)–C(31)	127·4(12)
N(1)–C(1)–C(2)	125·9(10)	C(16)–C(15)–C(31)	123·0(10)
N(1)–C(1)–C(20)	107·6(11)	N(4)–C(16)–C(15)	104·9(9)
C(2)–C(1)–C(20)	126·5(11)	N(4)–C(16)–C(17)	125·6(12)
C(1)–C(2)–C(3)	127·8(11)	C(15)–C(16)–C(17)	129·4(13)
N(2)–C(3)–C(2)	127·3(13)	C(16)–C(17)–C(18)	128·0(13)
N(2)–C(3)–C(4)	107·5(11)	N(1)–C(18)–C(17)	125·5(10)
C(2)–C(3)–C(4)	125·2(11)	N(1)–C(18)–C(19)	108·3(11)
C(3)–C(4)–C(5)	106·4(11)	C(17)–C(18)–C(19)	125·9(12)
C(3)–C(4)–C(21)	123·2(11)	C(18)–C(19)–C(20)	108·2(11)
C(5)–C(4)–C(21)	130·4(14)	C(18)–C(19)–C(33)	126·4(12)
C(4)–C(5)–C(6)	108·3(12)	C(20)–C(19)–C(33)	125·4(10)
C(4)–C(5)–C(23)	126·4(11)	C(1)–C(20)–C(19)	108·3(10)
C(6)–C(5)–C(23)	125·3(10)	C(1)–C(20)–C(35)	122·8(12)
N(2)–C(6)–C(5)	108·6(9)	C(19)–C(20)–C(35)	128·8(11)
N(2)–C(6)–C(7)	123·1(12)	C(4)–C(21)–C(22)	114·0(13)
C(5)–C(6)–C(7)	128·2(12)	C(5)–C(23)–C(24)	110·5(13)
C(6)–C(7)–C(8)	127·2(13)	C(9)–C(25)–C(26)	112·8(12)
N(3)–C(8)–C(7)	124·1(10)	C(10)–C(27)–C(28)	115·9(11)
N(3)–C(8)–C(9)	110·2(11)	C(14)–C(29)–C(30)	111·0(11)
C(7)–C(8)–C(9)	125·5(12)	C(15)–C(31)–C(32)	112·7(13)
C(8)–C(9)–C(10)	108·2(11)	C(19)–C(33)–C(34)	110·8(12)
C(8)–C(9)–C(25)	124·3(11)	C(20)–C(35)–C(36)	112·5(12)
C(10)–C(9)–C(25)	127·3(10)	N(1)–C(37)–C(38)	112·0(9)
C(9)–C(10)–C(11)	105·7(10)	O(1)–C(38)–O(2)	122·0(13)
C(9)–C(10)–C(27)	129·8(12)	O(1)–C(38)–C(37)	126·8(13)
C(11)–C(10)–C(27)	124·2(12)	O(2)–C(38)–C(37)	111·0(10)
N(3)–C(11)–C(10)	111·8(12)	O(3)–C(41)–C(42)	122·0(21)
N(3)–C(11)–C(12)	126·5(11)	O(3)–C(41)–C(43)	119·9(20)
C(10)–C(11)–C(12)	121·8(10)	C(42)–C(41)–C(43	117·6(17)
C(11)–C(12)–C(13)	126·9(10)		

TABLE 2 (Continued)

(c) Intermolecular contacts (Å) within the sum of the contact radii 1·8 Å for C, N, and O, 2·4 Å for I

C(31) ⋯ I	4·047(14)	N(4) ⋯ N(2^V)	3·574(15)
C(21) ⋯ O(3)	3·463(21)	C(12) ⋯ N(2^V)	3·432(17)
C(42) ⋯ I^I	4·041(24)	C(13) ⋯ N(2^V)	3·427(18)
C(43) ⋯ I^I	4·200(27)	C(6) ⋯ N(4^V)	3·365(17)
C(27) ⋯ ·O(2^{II})	3·547(16)	C(7) ⋯ N(4^V)	3·428(17)
C(28) ⋯ O(2^{II})	3·540(18)	C(12) ⋯ C(3^V)	3·367(19)
C(30) ⋯ C(24^{II})	3·579(23)	C(13) ⋯ C(5^V)	3·584(19)
C(39) ⋯ I^{III}	3·869(10)	C(14) ⋯ C(5^V)	3·469(19)
C(32) ⋯ O(1^{III})	3·462(17)	C(13) ⋯ C(6^V)	3·388(19)
C(36) ⋯ I^{IV}	4·109(16)	C(16) ⋯ C(7^V)	3·438(20)
C(25) ⋯ I^V	4·007(15)	C(20) ⋯ C(10^V)	3·567(19)
C(27) ⋯ O(3^V)	3·420(21)		

Roman numeral superscripts refer to the following co-ordinate transformations:

I	$x, y - 1, z$	IV	$-x, 1 - y, -z$
II	$1 - x, 1 - y, 2 - z$	V	$1 - x, 1 - y, 1 - z$
III	$-x, 1 - y, 1 - z$		

The most striking difference is between the geometry of the N-substituted rings and the others. Grigg et al.[15] suggested that as the alkyl-substituted nitrogen in
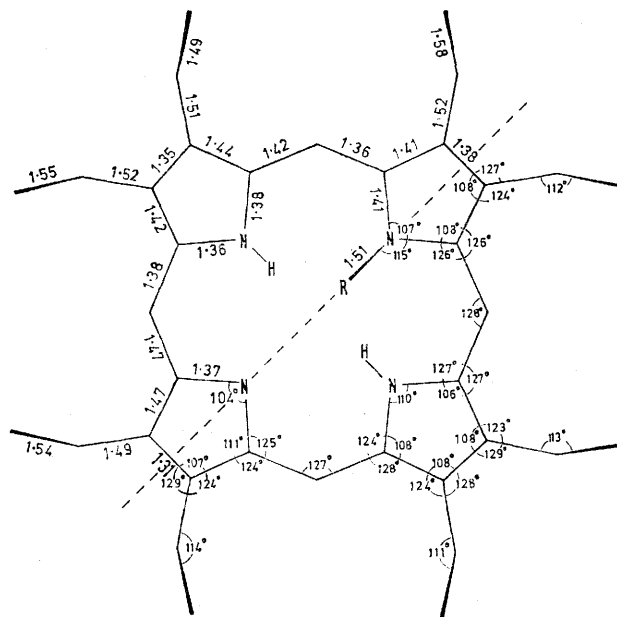

FIGURE 2 Bond lengths and angles obtained by averaging equivalent halves of the molecule. σ Values for the bond lengths are ca. 0·01 Å and for angles ca. 1°

copper(II) 8,12-diethyl-2,3,7,13,17,18,21-heptamethyl-corrole [16] (II) is essentially sp^3 hybridised then this should also be the case for N-substituted porphyrins. Indeed the geometry around the alkyl substituted nitrogen in (I) is consistent with sp^3 hybridisation. Other similarities with the same ring in (II) are the longer C_β–C_β and N–C_α bonds and the shorter C_α–C_β bond (Figure 2) compared with other pyrrole rings in porphyrins, and the fact that the ring has an envelope conformation, being folded about C(1), C(18) [Table 4, plane (b)], and is distorted from the plane defined by N(2), N(3), and N(14) by 19·1°, all of which supports

[15] R. Grigg, G. Shelton, A. Sweeney, and A. W. Johnson, J.C.S. Perkin I, 1972, 1789.

[16] R. Grigg, T. J. King, and G. Shelton. Chem. Comm., 1970, 56.

the hypothesis [12] that to some extent at least the conjugated chromophore bypasses the alkylated nitrogen.

The N(2), N(3), and N(4) pyrrole rings are individually approximately planar (Table 4) and are inclined down

TABLE 3

Torsion angles (°). The angle A–B–C–D is defined as positive if, when viewed along the B–C bond, atom A must be rotated clockwise to eclipse atom D. The standard deviations of the angles are ca. 1°

C(38)–O(2)–C(39)–C(40)	111	N(3)–C(8)–C(9)–C(25)	174
C(39)–O(2)–C(38)–O(1)	3	C(7)–C(8)–C(9)–C(10)	−175
C(39)–O(2)–C(38)–C(37)	178	C(7)–C(8)–C(9)–C(25)	−0
C(18)–N(1)–C(1)–O(2)	174	C(8)–C(9)–C(10)–C(11)	−0
C(18)–N(1)–C(1)–C(20)	−4	C(8)–C(9)–C(10)–C(27)	172
C(37)–N(1)–C(1)–C(2)	−55	C(25)–C(9)–C(10)–C(11)	−175
C(37)–N(1)–C(1)–C(20)	125	C(25)–C(9)–C(10)–C(27)	−2
C(1)–N(1)–C(18)–C(17)	−169	C(8)–C(9)–C(25)–C(26)	−81
C(1)–N(1)–C(18)–C(19)	5	C(10)–C(9)–C(25)–C(26)	93
C(37)–N(1)–C(18)–C(17)	60	C(9)–C(10)–C(11)–N(3)	1
C(37)–N(1)–C(18)–C(19)	−125	C(9)–C(10)–C(11)–C(12)	−179
C(1)–N(1)–C(37)–C(38)	−52	C(27)–C(10)–C(11)–N(3)	−172
C(18)–N(1)–C(37)–C(38)	73	C(27)–C(10)–C(11)–C(12)	6
C(6)–N(2)–C(3)–C(2)	−178	C(9)–C(10)–C(27)–C(28)	−97
C(6)–N(2)–C(3)–C(4)	−0	C(11)–C(10)–C(27)–C(28)	74
C(3)–N(2)–C(6)–C(5)	2	N(3)–C(11)–C(12)–C(13)	10
C(3)–N(2)–C(6)–C(7)	−175	C(10)–C(11)–C(12)–C(13)	−168
C(11)–N(3)–C(8)–C(7)	176	C(11)–C(12)–C(13)–N(4)	−2
C(11)–N(3)–C(8)–C(9)	1	C(11)–C(12)–C(13)–C(14)	173
C(8)–N(3)–C(11)–C(10)	−1	N(4)–C(13)–C(14)–C(15)	−0
C(8)–N(3)–C(11)–C(12)	179	N(4)–C(13)–C(14)–C(29)	−178
C(16)–N(4)–C(13)–C(12)	177	C(12)–C(13)–C(14)–C(15)	−177
C(16)–N(4)–C(13)–C(14)	0	C(12)–C(13)–C(14)–C(29)	4
C(13)–N(4)–C(16)–C(15)	−0	C(13)–C(14)–C(15)–C(16)	0
C(13)–N(4)–C(16)–C(17)	179	C(13)–C(14)–C(15)–C(31)	175
N(1)–C(1)–C(2)–C(3)	−15	C(29)–C(14)–C(15)–C(16)	178
C(20)–C(1)–C(2)–C(3)	162	C(29)–C(14)–C(15)–C(31)	−6
N(1)–C(1)–C(20)–C(19)	1	C(13)–C(14)–C(29)–C(30)	−81
N(1)–C(1)–C(20)–C(35)	−174	C(15)–C(14)–C(29)–C(30)	100
C(2)–C(1)–C(20)–C(19)	−177	C(14)–C(15)–C(16)–N(4)	−0
C(2)–C(1)–C(20)–C(35)	7	C(14)–C(15)–C(16)–C(17)	179
C(1)–C(2)–C(3)–N(2)	−6	C(31)–C(15)–C(16)–N(4)	−175
C(1)–C(2)–C(3)–C(4)	175	C(31)–C(15)–C(16)–C(17)	4
N(2)–C(3)–C(4)–C(5)	−1	C(14)–C(15)–C(31)–C(32)	−89
N(2)–C(3)–C(4)–C(21)	177	C(16)–C(15)–C(31)–C(32)	85
C(2)–C(3)–C(4)–C(5)	176	N(4)–C(16)–C(17)–C(18)	3
C(2)–C(3)–C(4)–C(21)	−4	C(15)–C(16)–C(17)–C(18)	−176
C(3)–C(4)–C(5)–C(6)	2	C(16)–C(17)–C(18)–N(1)	12
C(3)–C(4)–C(5)–C(23)	−178	C(16)–C(17)–C(18)–C(19)	−160
C(21)–C(4)–C(5)–C(6)	−175	N(1)–C(18)–C(19)–C(20)	−4
C(21)–C(4)–C(5)–C(23)	2	N(1)–C(18)–C(19)–C(33)	176
C(3)–C(4)–C(21)–C(22)	−74	C(17)–C(18)–C(19)–C(20)	170
C(5)–C(4)–C(21)–C(22)	103	C(17)–C(18)–C(19)–C(33)	−9
C(4)–C(5)–C(6)–N(2)	−3	C(18)–C(19)–C(20)–C(1)	1
C(4)–C(5)–C(6)–C(7)	174	C(18)–C(19)–C(20)–C(35)	176
C(23)–C(5)–C(6)–N(2)	178	C(33)–C(19)–C(20)–C(1)	−178
C(23)–C(5)–C(6)–C(7)	−4	C(33)–C(19)–C(20)–C(35)	−3
C(4)–C(5)–C(23)–C(24)	−92	C(18)–C(19)–C(33)–C(34)	−83
C(6)–C(5)–C(23)–C(24)	85	C(20)–C(19)–C(33)–C(34)	97
N(2)–C(6)–C(7)–C(8)	2	C(1)–C(20)–C(35)–C(36)	77
C(5)–C(6)–C(7)–C(8)	−174	C(19)–C(20)–C(35)–C(36)	−97
C(6)–C(7)–C(8)–N(3)	−6	N(1)–C(37)–C(38)–O(1)	−28
C(6)–C(7)–C(8)–C(9)	168	N(1)–C(37)–C(38)–O(2)	157
N(3)–C(8)–C(9)–C(10)	−0		

towards the centre by 4·8, 11·7, and 2·2° with respect to the plane defined by N(2), and N(4) [plane (a), Table 4), whereas the N(1) ring is inclined up towards the centre (by 19·1°) from this plane. The inclinations of the N(2) and N(4) rings to some extent relieves the steric interaction between H(2N) and H(4N) by increasing the distance between them to 2·38 Å which is ca. 0·2 Å longer than if the rings were coplanar. The inclination of the N(1) ring prevents steric interaction between the acetic residue and the rest of the molecule.

TABLE 4

Least-square planes expressed in the form $Px + Qy + Rz = S$, with displacements (Å) of atoms from these planes

(a) Planes and deviations

Plane (a): N(2), N(3), N(4)

N(1) 0·284, C(1) −0·053, C(2) −0·014, C(3) 0·068, C(4) 0·201, C(5) 0·168, C(6) 0·086, C(7) 0·138, C(8) 0·156, C(9) 0·442, C(10) 0·457, C(11) 0·156, C(12) 0·085, C(13) 0·039, C(14) 0·086, C(15) 0·064, C(16) 0·010, C(17) −0·024, C(18) −0·014, C(19) −0·417, C(20) −0·467, C(21) 0·371, C(23) 0·249, C(25) 0·779, C(27) 0·840, C(29) 0·103, C(31) 0·186, C(33) −0·754, C(35) −0·784, H(2N) −0·117, H(4N) −0·009

Plane (b): N(1), C(1), C(18), C(19), C(20)

N(1) −0·027, C(1) 0·017, C(18) 0·027, C(19) −0·017, C(20) 0, C(2) 0·090, C(17) 0·212, C(33) −0·065, C(35) −0·097, C(37) 1·131

Plane (c): N(2), C(3)—(6)

N(2) −0·006, C(3) −0·004, C(4) 0·013, C(5) −0·017, C(6) 0·014, C(2) −0·051, C(7) 0·108, C(21) 0·084, C(23) −0·039, H(2N) −0·043

Plane (d): N(3), C(8)—(11)

N(3) −0·008, C(8) 0·004, C(9) 0·002, C(10) −0·007, C(11) 0·009, C(7) −0·071, C(12) 0·009, C(25) −0·099, C(27) −0·162

Plane (e): N(4), C(13)—(16)

N(4) 0·002, C(13) −0·002, C(14) 0·002, C(15) −0·001, C(16) 0, C(12) 0·042, C(17) 0·001, C(29) −0·037, C(31) 0·091, H(4N) 0·027
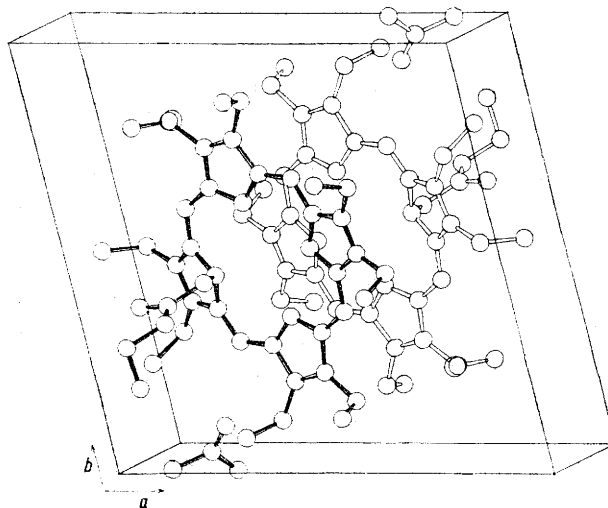
(b) Equations

	P	Q	R	S	σ *
(a)	−8·577	−2·197	9·086	0·754	0
(b)	11·366	2·701	−6·959	0·851	0·023
(c)	−8·960	−0·946	9·117	1·036	0·013
(d)	10·474	2·388	−7·897	1·166	0·008
(e)	−8·535	−2·729	8·987	0·389	0·002

(c) Angles (°) between the planes

(b)–(a)	19·1	(c)–(a)	4·8	(c)–(b)	20·2
(d)–(a)	11·7	(d)–(b)	7·5	(d)–(c)	12·9
(e)–(a)	2·2	(e)–(b)	18·2	(e)–(c)	6·9
(e)–(d)	11·0				

* σ is the r.m.s. deviation of the atoms (those defining the plane) from the plane.

FIGURE 3   Unit-cell contents viewed down c*

The packing environment is in many ways similar to that of porphin,[1] *i.e.* the molecules pack in overlapping pairs (related by a centre of symmetry) at about the graphite layer separation (3·4 Å) [Figure 3, Table 2(c)], the main difference being that porphin is approximately planar overall whereas (I) is very nonplanar. The inclinations of the N(1) and N(3) pyrrole rings are such that the angle between them is only 7·5° and as these rings overlap in adjacent molecules it is possible that the unexpectedly large deviation of the N(3) pyrrole ring [plane (d)] from plane (a) of 11·7° is caused by

forces which allow closer packing of the pairs. This form of packing also necessitates all the ethyl groups pointing approximately perpendicularly away from the molecular plane on the same side as the acetic residue. The geometries of the acetic residue and of the solvent acetone are as expected within experimental error.