Nitrosation and Nitrosylation of Haemoproteins and Related Compounds. Part 3.[1] Attack at the Vinyl Groups of Protoporphyrin Dimethyl Ester. *X*-Ray Analysis of 8¹(*E*)-8²-Nitroprotoporphyrin Dimethyl Ester

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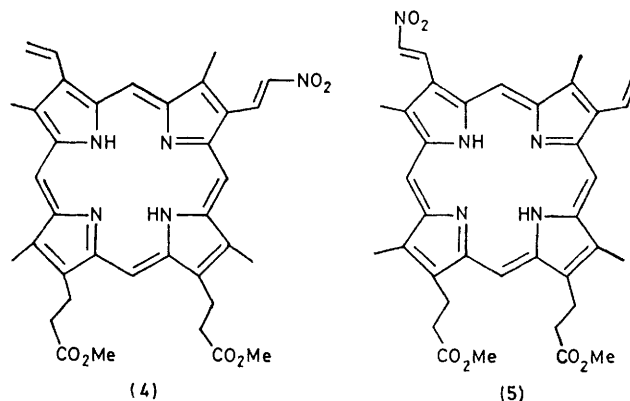
Treatment of heptaethyl(vinyl)porphyrin (1) with acidified nitrite solution gives a greenish porphyrin which is shown to be 2¹(*E*)-3,7,8,12,13,17,18-heptaethyl-2-(2-nitrovinyl)porphyrin, (2). Protoporphyrin dimethyl ester (3) similarly treated gives a mixture of compounds, including two greenish porphyrins which are formulated as the analogous 3(8)-(2-nitrovinyl)-8(3)-vinyldeuteroporphyrin derivatives. The less-polar isomer was crystalline and shown to be 8¹(*E*)-8²-nitroprotoporphyrin dimethyl ester (4) by *X*-ray analysis. Crystals are triclinic, space group *P*Ī, *a* = 10.591(4), *b* = 12.967(1), *c* =14.203(2) Å, α = 105.79(1), β = 94.91(3), γ = 94.99(2)°. The structure was solved by direct methods and refined to *R* 0.082.

THE reactions between nitrous acid and a haemoprotein might reasonably be expected to occur at one (or more) of three sites: the metal atom, the porphyrin ligand, and the protein. Reactions at the first two sites were considered in Part 1 of this series,[2] where it was shown that octaethylporphyrin underwent *meso*-nitration on treatment with acidified nitrite mixtures. Mesoporphyrin dimethyl ester behaved similarly. Protoporphyrin dimethyl ester and protohaemin dimethyl ester, on the other hand, gave complex mixtures, including green pigments, which arose, it was thought, because reaction could occur at the vinyl groups as well as the *meso*-positions. It was speculated [2] that this reaction might explain the 'nitrite greening' or 'nitrite burn' reported occasionally in incorrectly cured meat.[3]

To simplify the problem, a study was made initially using heptaethylvinylporphyrin (1) as a model. Treatment with excess of sodium nitrite in aqueous acetic acid–tetrahydrofuran gave a novel greenish substance which was isolated by preparative t.l.c. The electronic spectrum of this substance was unusual in that it had a split Soret peak ($\lambda_{max.}$ 378, 431 nm) and a four-banded absorption at lower energy which resembled that observed with porphyrins with electron-withdrawing substituents (rhodo, oxorhodo type spectra).[4] Combustion

(1) R = —CH=CH₂

(2) R = —CH≐CH-NO₂

(3)

and mass spectroscopic data indicated the molecular formula $C_{36}H_{43}N_5O_2$, while the i.r. spectrum suggested the presence of a conjugated nitro-group (ν 1 505, 1 315 cm⁻¹). The n.m.r. spectrum supported structure (2). The *meso*-positions were unsubstituted (δ 10.0, 9.94, 9.90, and 9.78) and the olefinic protons appeared
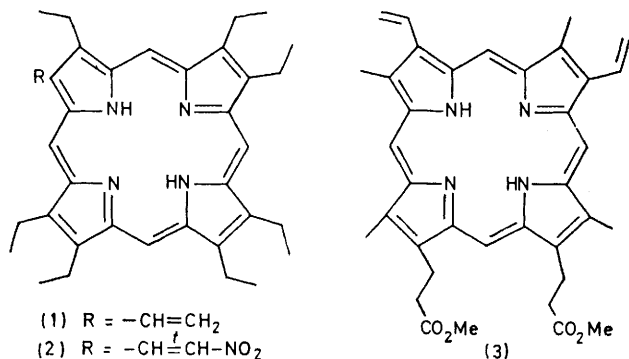
as an AB quartet (δ 9.43, 8.12) with *J* 14 Hz indicating the *trans*-configuration at the double bond.

Treatment of protoporphyrin dimethyl ester (3) with an acidified nitrite solution under similar conditions gave

(4)   (5)

a complex mixture of components which proved difficult to purify. Preparative t.l.c. gave a greenish fraction (together with numerous minor red products) which was separated further by h.p.l.c. into two main components. The less mobile material was not obtained pure, but the more mobile one behaved as a single substance, and was the subject of detailed study. It was obtained as dark green prisms from methanol–1,2-dichloroethane, and had an electronic spectrum (Figure 1) rather similar to that of the model nitrovinyl compound (2), but clearly of the oxorhodo-type.[4] This type of visible spectrum has also been described by Nichol [5] for 3²-(8²)-formylprotoporphyrin dimethyl ester. When adsorbed on silica the substance appeared green, but in solution was dichroic, being green by reflected but red by transmitted light. The n.m.r. spectrum again supported the β-nitrovinyl formulation, but the exact location of the substituent as shown in (4) was determined by *X*-ray crystallography.

The molecular structure of (4) is illustrated in Figure 2 and the molecular geometry is given in Table 1. The imino-hydrogen atoms are seen to be located at N(21) and N(23). Codding and Tulinsky [6] have calculated average geometries for the pyrrole and pyrrolenine rings in porphyrins using the structural data for porphyrin, *meso*-tetraphenylporphyrin, and *meso*-tetra-n-propylpor-

phyrin. The mean bond lengths and angles of the two types of ring in the present structure do not differ significantly from these averaged values, and differ by $<1\sigma$ from the corresponding values for mesoporphyrin dimethyl ester.[7] Thus, although as judged from the changes in electronic spectra the π energy levels are significantly altered, the substitution of the strongly electron withdrawing β-nitrovinyl group in the macrocycle has not led to a noticeable distortion of the aromatic framework.
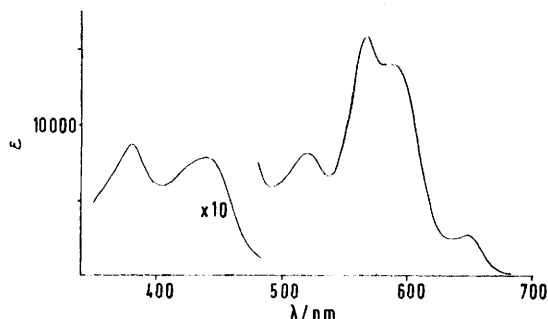

FIGURE 1　Electronic absorption spectrum of $8^1(E)$-8^2-nitroprotoporphyrin dimethyl ester (4) in chloroform
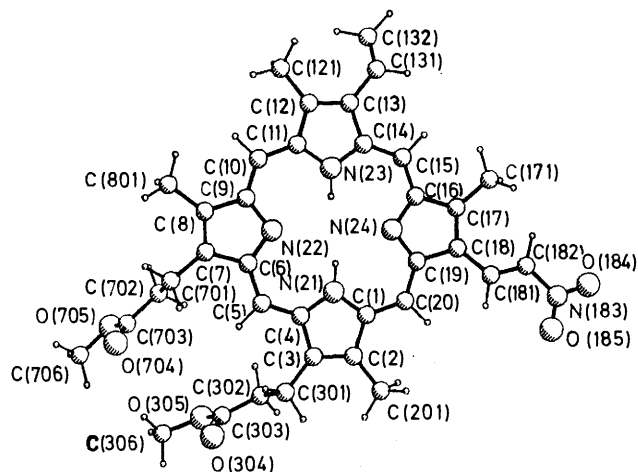

FIGURE 2　Molecular structure and atom numbering scheme for (4). Hydrogen atoms are numbered according to the carbon or nitrogen atom to which they are bonded; the atom numbering scheme shown here is used only in the crystallographic part of the paper

The 24-atom porphyrin core is essentially planar, all but one of the out-of-plane displacements being $\leqslant 0.06$ Å (Table 2). The five-membered rings are planar but each is slightly inclined ($\leqslant 3°$) to the least-squares plane of the porphyrin macrocycle. The rings are canted with respect to each other by angles of 1—5°, the largest tilts involving ring C(1)—(4), N(21). In mesoporphyrin dimethyl ester[7] one ring with methyl and methyl propionate substituents is inclined at 2.5° to the plane of the porphyrin macrocycle, whereas the inclinations of the other rings are ca. 1.5°. This additional twisting was attributed[7] to the packing requirements of the methyl propionate chain in the crystal structure and several short O · · · H contacts (2.65—2.85 Å) were observed between the methoxycarbonyl-groups of adjacent mole-

TABLE 1

Bond lengths (Å) and angles (°) of compound (4), with estimates of standard deviations in parentheses

(a) Bond lengths (Å)

C(2)—C(1)	1.445(6)	C(301)—C(3)	1.501(8)
C(20)—C(1)	1.395(7)	C(302)—C(301)	1.541(9)
N(21)—C(1)	1.366(6)	C(302)—C(303)	1.481(9)
C(3)—C(2)	1.362(7)	C(303)—O(304a)	1.234(11)
C(4)—C(3)	1.441(6)	C(303)—O(304b)	1.295(19)
C(5)—C(4)	1.380(7)	O(305)—C(303)	1.287(9)
N(21)—C(4)	1.362(6)	O(305)—C(306)	1.448(8)
C(6)—C(5)	1.400(6)	C(701)—C(7)	1.499(7)
C(7)—C(6)	1.469(7)	C(702)—C(701)	1.514(8)
N(22)—C(6)	1.356(6)	C(703)—C(702)	1.484(8)
C(8)—C(7)	1.353(6)	O(704)—C(703)	1.182(9)
C(9)—C(8)	1.455(7)	O(705)—C(703)	1.296(8)
N(22)—C(9)	1.373(6)	C(706)—O(705)	1.444(7)
C(10)—C(9)	1.377(6)	C(801)—C(8)	1.507(8)
C(11)—C(10)	1.383(7)	C(121)—C(12)	1.498(6)
C(12)—C(11)	1.438(6)	C(131)—C(13)	1.474(7)
N(23)—C(11)	1.371(6)	C(132)—C(131)	1.256(9)
C(13)—C(12)	1.379(7)	C(171)—C(17)	1.488(7)
C(14)—C(13)	1.455(6)	C(181)—C(18)	1.452(7)
C(15)—C(14)	1.388(7)	C(182)—C(181)	1.300(8)
N(23)—C(14)	1.367(6)	N(183)—C(182)	1.465(8)
C(16)—C(15)	1.380(6)	O(184)—N(183)	1.214(8)
C(17)—C(16)	1.454(7)	O(185)—N(183)	1.206(8)
N(24)—C(16)	1.380(6)	C(30)—Cl(1a)	1.639(13)
C(18)—C(17)	1.371(6)	C(30)—Cl(1b)	1.490(16)
C(19)—C(18)	1.455(7)	C(31)—Cl(2a)	1.744(12)
C(20)—C(19)	1.393(6)	C(31)—Cl(2b)	1.848(19)
N(24)—C(19)	1.363(6)	C(31)—C(30)	1.220(19)
C(201)—C(2)	1.508(8)		

(b) Bond angles (°)

C(20)—C(1)—C(2)	126.8(5)	C(171)—C(17)—C(16)	124.6(4)
N(21)—C(1)—C(2)	107.7(5)	C(171)—C(17)—C(18)	128.9(5)
N(21)—C(1)—C(20)	125.4(4)	C(19)—C(18)—C(17)	106.4(5)
C(3)—C(2)—C(1)	107.4(4)	C(181)—C(18)—C(17)	130.0(5)
C(201)—C(2)—C(1)	124.2(5)	C(181)—C(18)—C(19)	123.6(4)
C(201)—C(2)—C(3)	128.4(5)	C(20)—C(19)—C(18)	124.5(5)
C(4)—C(3)—C(2)	107.5(4)	N(24)—C(19)—C(18)	110.8(4)
C(301)—C(3)—C(2)	128.8(4)	N(24)—C(19)—C(20)	124.6(5)
C(301)—C(3)—C(4)	123.8(5)	C(19)—C(20)—C(1)	126.6(5)
C(5)—C(4)—C(3)	126.0(5)	C(4)—N(21)—C(1)	109.3(4)
N(21)—C(4)—C(3)	108.1(5)	H(21)—N(21)—C(1)	122.5(23)
N(21)—C(4)—C(5)	126.0(4)	H(21)—N(21)—C(4)	126.1(23)
C(6)—C(5)—C(4)	126.6(5)	C(9)—N(22)—C(6)	105.9(4)
C(7)—C(6)—C(5)	123.4(5)	C(14)—N(23)—C(11)	109.5(4)
N(22)—C(6)—C(5)	125.8(5)	H(23)—N(23)—C(11)	124.6(24)
N(22)—C(6)—C(7)	110.8(4)	H(23)—N(23)—C(14)	125.8(24)
C(8)—C(7)—C(6)	106.0(4)	C(19)—N(24)—C(16)	106.1(4)
C(701)—C(7)—C(6)	125.2(4)	C(302)—C(301)—C(3)	112.6(5)
C(701)—C(7)—C(8)	128.7(5)	C(301)—C(302)—C(303)	113.7(5)
C(9)—C(8)—C(7)	106.7(5)	O(305)—C(303)—C(302)	113.9(6)
C(801)—C(8)—C(7)	127.6(5)	C(302)—C(303)—O(304a)	124.5(8)
C(801)—C(8)—C(9)	125.7(4)	C(302)—C(303)—O(304b)	111.8(10)
N(22)—C(9)—C(10)	124.5(5)	O(305)—C(303)—O(304a)	120.0(7)
N(22)—C(9)—C(8)	110.5(4)	O(305)—C(303)—O(304b)	113.1(12)
C(10)—C(9)—C(8)	125.0(5)	C(306)—O(305)—C(303)	119.6(5)
C(11)—C(10)—C(9)	127.5(5)	C(702)—C(701)—C(7)	111.3(4)
C(12)—C(11)—C(10)	126.4(5)	C(703)—C(702)—C(701)	113.4(5)
N(23)—C(11)—C(10)	125.2(4)	O(704)—C(703)—C(702)	125.1(6)
N(23)—C(11)—C(12)	108.5(5)	O(705)—C(703)—C(702)	114.8(6)
C(13)—C(12)—C(11)	107.1(4)	O(705)—C(703)—O(704)	120.0(6)
C(121)—C(12)—C(11)	124.9(5)	C(706)—O(705)—C(703)	119.0(5)
C(121)—C(12)—C(13)	128.1(5)	C(132)—C(131)—C(13)	129.0(7)
C(14)—C(13)—C(12)	107.4(4)	C(182)—C(181)—C(18)	126.4(5)
C(131)—C(13)—C(12)	129.3(5)	N(183)—C(182)—C(181)	120.2(5)
C(131)—C(13)—C(14)	123.2(5)	O(184)—N(183)—C(182)	115.6(5)
C(15)—C(14)—C(13)	127.1(5)	O(185)—N(183)—C(182)	121.1(6)
N(23)—C(14)—C(13)	107.5(4)	O(185)—N(183)—O(184)	123.3(6)
N(23)—C(14)—C(15)	125.4(4)	C(31)—C(30)—Cl(1a)	135.9(10)
C(16)—C(15)—C(14)	127.9(5)	C(31)—C(30)—Cl(1b)	129.2(14)
C(17)—C(16)—C(15)	124.5(5)	C(30)—C(31)—Cl(2a)	117.2(10)
N(24)—C(16)—C(15)	125.2(5)	C(30)—C(31)—Cl(2b)	110.9(11)
N(24)—C(16)—C(17)	110.3(4)	Cl(1b)—C(30)—Cl(1a)	49.7(5)
C(18)—C(17)—C(16)	106.4(5)	Cl(2b)—C(31)—Cl(2a)	61.3(6)

TABLE 2

Least-squares planes and atom deviations (Å). The equations of planes are expressed in direct space as $Px + Qy + Rz = S$. Atoms marked * are not included in the calculation of the plane nor in the root-mean square deviation, Δ

Plane (1): C(1)—(20), N(21)—(24)

$$6.697x - 6.070y + 9.769z = 6.893$$

[C(1) 0.039, C(2) 0.105, C(3) 0.063, C(4) −0.014, C(5) −0.060, C(6) −0.059, C(7) −0.019, C(8) 0.019, C(9) −0.011, C(10) 0.008, C(11) 0.012, C(12) 0.047, C(13) 0.060, C(14) 0.013, C(15) 0.008, C(16) −0.014, C(17) −0.041, C(18) −0.063, C(19) −0.033, C(20) 0.010, N(21) −0.007, * H(21) −0.248, N(22) −0.055, N(23) −0.014, * H(23) −0.012, N(24) 0.003]

Δ 0.042 Å

Plane (2): C(1)—(4), N(21)

$$6.563x - 6.656y + 9.707z = 6.368$$

[C(1) −0.009, C(2) 0.006, C(3) −0.001, C(4) −0.005, N(21) 0.009, * H(21) −0.189]

Δ 0.007 Å

Plane (3): C(6)—(9), N(22)

$$6.852x - 5.692y + 9.689z = 7.034$$

[C(6) 0.002, C(7) −0.003, C(8) 0.003, C(9) −0.002, N(22) 0.000]

Δ 0.002 Å

Plane (4): C(11)—(14), N(23)

$$6.618x - 5.779y + 9.967z = 7.021$$

[C(11) 0.004, C(12) −0.005, C(13) 0.004, C(14) −0.002, N(23) −0.001, * H(23) 0.030]

Δ 0.003 Å

Plane (5): C(16)—(19), N(24)

$$6.867x - 5.826y + 9.626z = 7.095$$

[C(16) −0.005, C(17) 0.005, C(18) −0.003, C(19) −0.001, N(24) 0.004]

Δ 0.004 Å

Plane (6): C(13), C(131), C(132)

$$8.032x - 0.258y + 7.721z = 8.419$$

Plane (7): C(18), C(181), C(182), N(183), O(184), O(185)

$$5.500x - 4.086y + 11.453z = 7.805$$

[C(18) −0.008, C(181) 0.027, C(182) −0.019, N(183) −0.002, O(184) 0.010, O(185) −0.008]

Δ 0.015 Å

Interplanar angles (°)

(i) Between porphyrin core and pyrrole rings:
   (1)–(2) 3.0, (1)–(3) 2.0, (1)–(4) 1.8, (1)–(5) 1.5

(ii) Between pyrrole rings:
   (2)–(3) 4.9, (2)–(4) 4.5, (2)–(5) 4.3, (3)–(4) 1.6, (3)–(5) 0.7, (4)–(5) 1.9

(iii) Involving vinyl and nitrovyinyl groups:
   (1)–(6) 27.7, (4)–(6) 26.6, (1)–(7) 13.8, (5)–(7) 13.7

cules. No such inter- or intra-molecular contacts occur in the present structure. There are a number of intermolecular contacts ≤3.5 Å between porphyrin molecules (Table 3) although there is no indication that the tilting of pyrrole ring C(1)—(4), N(21) is caused by such contacts.

The vinyl and nitrovinyl groups lie out of the plane of the porphyrin macrocycle and are inclined at angles of 27 and 14° respectively to the five-membered rings to which they are attached. Values of 26 and 32° have been reported for the interplanar angles between the vinyl groups and the macrocycle in protoporphyrin dimethyl ester.[8]

The crystal structure consists of discrete molecules of porphyrin and dichloroethane solvent: a view of the

TABLE 3

Intermolecular distances <3.5 Å between porphyrin molecules

C(10) · · · C(1I)	3.497	C(16) · · · C(16II)	3.436
C(11) · · · C(4I)	3.454	C(17) · · · C(16II)	3.424
C(14) · · · C(5I)	3.372	C(181) · · · C(14II)	3.491
C(16) · · · C(7I)	3.376	C(182) · · · C(11II)	3.466
C(19) · · · C(8I)	3.426	C(171) · · · C(706III)	3.285
C((18) · · · C(15II)	3.370		

Roman numeral superscripts refer to the following equivalent positions relative to the asymmetric unit at x, y, z:

   I $1 - x$, $1 - y$, $1 - z$ III $1 + x$, y, $-1 + z$
   II $2 - x$, $1 - y$, $1 - z$

structure down the a^* axis is shown in Figure 3. The only abnormally short intermolecular distance in the structure involves one of the fractional chlorine atoms of the disordered dichloroethane molecule.

Since the product isolated as a pure substance from the nitrosation of protoporphyrin dimethyl ester is the 8^2-nitro-derivative (4), it is reasonable to conclude that the second component, which has very similar spectroscopic and chromatographic behaviour, has the isomeric 3^2-nitro-structure (5). These compounds together make up an important part (ca. 30% isolated) of a complex and difficult mixture which contains several minor red components. The latter have not been investigated but presumably arise by meso-nitration and by addition
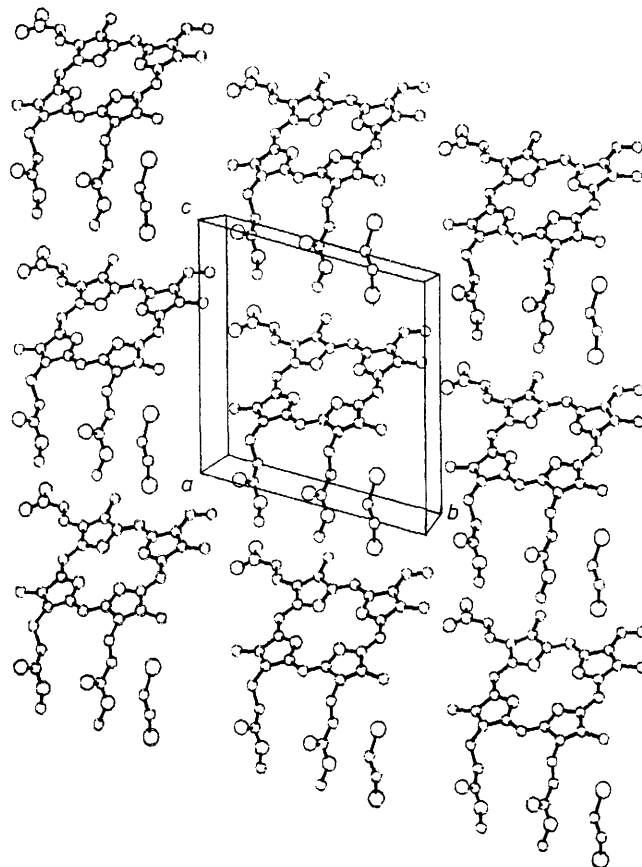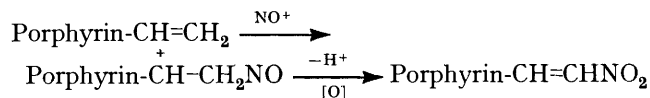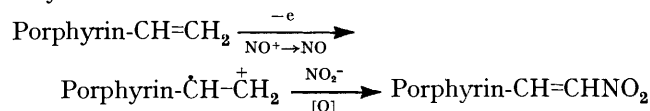

FIGURE 3   View of structure of (4) down the a^* axis. Only one set of fractional chlorine atoms of the disordered dichloroethane solvent has been included; Cl(1b) and Cl(2b) have been omitted for clarity

and oxidation reactions occurring at the vinyl groups. The formation of the β-nitrovinyl function can be rationalised as proceeding *via* a pseudobenzylic carbonium ion, thus:

$$\text{Porphyrin-CH=CH}_2 \xrightarrow{\text{NO}^+}$$

$$\overset{+}{\text{Porphyrin-CH-CH}_2\text{NO}} \xrightarrow[\text{[O]}]{-\text{H}^+} \text{Porphyrin-CH=CHNO}_2$$

a reaction which finds some analogy in the formylation of protohaemin dimethyl ester using the Vilsmeier reagent.[5] Alternatively or additionally, a radical-cation pathway may be involved:

$$\text{Porphyrin-CH=CH}_2 \xrightarrow[\text{NO}^+\rightarrow\text{NO}]{-e}$$

$$\overset{+}{\text{Porphyrin-}}\overset{\cdot}{\text{C}}\text{H-CH}_2 \xrightarrow[\text{[O]}]{\text{NO}_2^-} \text{Porphyrin-CH=CHNO}_2$$

EXPERIMENTAL

General experimental and spectroscopic procedures have been described.[9] Light petroleum had b.p. 40—60 °C.

Reaction of Nitrous Acid with 3,7,8,12,13,17,18-*Heptaethyl-2-vinylporphyrin* (1).—Heptaethyl(vinyl)porphyrin [10] (1) (15 mg) in tetrahydrofuran (105 ml) and dichloromethane (1 ml) was treated (ice-bath, N_2 flush) with 67% aqueous acetic acid (45 ml). After 5 min aqueous sodium nitrite (0.75 g in 10 ml, nitrogen flushed) was added dropwise over 5 min to the stirred solution. The mixture was stirred (ice-bath) for a further 30 min, and then poured into water (700 ml) and extracted with dichloromethane (2 × 90 ml). The organic layer was washed (saturated sodium hydrogencarbonate, and water) and taken to dryness under reduced pressure. Preparative layer chromatography [silica gel H, 400 × 400 × 1 mm, used immediately after activation at 130° and irrigated with light petroleum–acetone (9 : 1)] gave two major bands, the most mobile being unchanged starting material. The second major component present (green on the plate) was extracted with chloroform. The solution was filtered and evaporated to give 3,7,8,12,13,17,18,-*heptaethyl-2,-(2-nitrovinyl)porphyrin*, compound (2), (5.1 mg, 31%) which could be crystallised with much loss from dichloromethane–methanol as a purple solid, m.p. *ca.* 235—240 °C (decomp.) (Found: C, 75.1; H, 7.9; N, 12.1. M^+, 577.343. $C_{36}H_{43}N_5O_2$ requires C, 74.85; H, 7.5; N, 12.1%. M, 577.342); λ (CHCl₃) 378 (80 200), 431 (69 000), 518 (5 100), 568 (15 400), 586 (15 700), and 646infl. (1 600); λ (CHCl₃–CF₃CO₂H) 424, 528infl., 562, and 612; ν (KBr) 3 310, 1 610, 1 525infl., 1 505, 1 460, 1 450, 1 315vs, 1 288, 1 218, 962, 830, 740, and 692. δ (CDCl₃) 10.0, 9.94, 9.90, and 9.78 (all s, *meso*-protons); 9.43 and 8.12, (AB quartet, *J* 14 Hz, *trans*-olefinic protons); 4.2—3.6 (m, C*H*₂); and 2.05—1.70 (m, C*H*₃); *m/e* (169 °C) 577 (100%), 532 (M − NO₂ + 2H, 29%).

Reaction of Nitrous Acid With Protoporphyrin Dimethyl Ester.—Protoporphyrin dimethyl ester (3) (50 mg) in tetrahydrofuran (300 ml) was treated (ice-bath, N_2, with stirring) with sodium nitrite (3.15 g) in water (80 ml) and then with 67% aqueous acetic acid (200 ml). The solution was stirred (ice-bath, N_2) for 30 min and then poured into water (1.5 l). Extraction with chloroform, washing the organic extract in turn with water, saturated sodium hydrogencarbonate and water, followed by evaporation of the solvent, gave a residue which was chromatographed on silica gel H [400 × 400 × 2 mm irrigated with chloroform–light petroleum–methanol (35 : 25 : 1.8)].

Four main bands were observed. In order of decreasing polarity these were: (i) a red band, showing six components when examined on h.p.l.c. [1 ft × ¼ in i.d. μ-Porasil, ethyl acetate—light petroleum–chloroform (5 : 12 : 1), 2 ml min⁻¹]; (ii) a minor red component, etio-type spectrum, which gave one peak on h.p.l.c.; (iii) a green component (16.5 mg, 30%), which gave two main peaks on h.p.l.c., and (iv) a red band, identified (t.l.c., e.s.) as starting material. In a similar reaction but carried out for 80 min, protoporphyrin dimethyl ester (20 mg) gave 5.8 mg of the most polar component(s) (i), 0.7 mg of component (ii), 5.6 mg of the green component (iii), and only a trace of unchanged starting material.

The green porphyrin (iii) could be crystallised from chloroform–methanol, but h.p.l.c. (for conditions see later) showed that fractional crystallisation did not effect an appreciable separation of the two components. A partial separation could be obtained by preparative t.l.c. [chloroform–light petroleum–diethyl ether–methanol–acetonitrile-acetic acid (6 : 11 : 3 : 0.4 : 0.2 : 0.2)] but was difficult to reproduce because of the complexity of the solvent system.

The green porphyrin mixture showed the following properties. Crystallisation from chloroform-methanol gave a microcrystalline solid which lost crystallinity at *ca.* 180 °C and bubbled at 190—195 °C (Found: N, 11.55%. $C_{36}H_{37}$-N_5O_6 requires N, 11.0%), *m/e* (241°) no M^+ seen, 590 (100%, M − NO₂ + H); ν (CsI) 3 300, 1 727, 1 608, 1 497, 1 430, 1 312s, 1 288, 1 225, 1 162, 1 030, 950, 826, 722, and 700; λ (CHCl₃) 380, 438, 520, 567, 588, and 648; λ (CHCl₃–CF₃CO₂H) 424, 562, and 612. On basification with aqueous NaHCO₃ the original absorption was restored.

A portion of the mixture of green porphyrin esters was separated by repeated h.p.l.c. [2 ft × ⅜ in i.d., Si60 Lichrosorb 5μ silica, ethyl acetate–light petroleum (2 : 3), 1.2 ml min⁻¹] into two main fractions. The second fraction was not obtained pure but the first fraction (retention volume 78 ml) appeared to behave as a single substance. It was crystallised from chloroform–methanol to give dark green prisms, m.p. 218—220 °C, of 8²-*nitroprotoporphyrin dimethyl ester* (4), λ (CHCl₃) 380 (80 400), 438 (75 000), 521 (8 000), 567 (15 700), 586 (14 000), and 648 (2 900). λ (CHCl₃–CF₃CO₂H) 426, 526infl., 561, and 611. δ (CDCl₃, 200 MHz) 9.89, 9.86, 9.39, and 9.09 (all s, *meso*-protons); 8.85 and 7.63, (AB quartet, *J* 13 Hz, nitrovinyl); 8.04 [(m, H at C(3¹)]; 6.29 [(m, 2 H at C(3²)]; 4.32 (bq, 2 × Ar*CH*₂); 3.70 (s), 3.67 (not resolved), 3.53 (s), and 3.39 (s) (Ar–Me); 3.66 (s, 2 × CO₂Me) and 3.25 (bq, 2 × CH₂CO). For *X*-ray analysis a crystal of (4) was grown from 1,2-dichloroethane-methanol by the isothermal distillation method.

Crystal Data.—$C_{36}H_{37}N_5O_6$·$C_2H_4Cl_2$, $M = 734.7$, Triclinic, $a = 10.591(4)$, $b = 12.967(1)$, $c = 14.203(2)$ Å, $\alpha = 105.79(a)$, $\beta = 94.91(3)$, $\gamma = 94.99(2)°$, $U = 1\,857.7$ Å³, $Z = 2$, $D_c = 1.32$ g cm⁻³, $F(000) = 776$. λ (Cu-K_α) = 1.541 78 Å; μ (Cu-K_α) = 19.0 cm⁻¹. Space group $P\bar{1}$.

Preliminary unit-cell dimensions and the crystal system were determined from oscillation and Weissenberg photographs. Intensities of 5 502 unique reflexions (3.0 ≤ θ ≤ 60.0°) were measured from a crystal *ca.* 0.63 × 0.10 × 0.08 mm on a Nonius CAD 4 diffractometer by use of Ni-filtered Cu-K_α radiation and an ω–2θ scan. Accurate cell parameters were obtained by least-squares analysis from the setting angles of 25 reflexions. Two intensity-control reflexions measured at 1 h intervals showed an approximately linear decrease in intensity of 12% during data collection. A fade correction and Lorentz polarization

TABLE 4

Fractional co-ordinates ($\times 10^4$) for the non-hydrogen atoms in compound (4), with estimated standard deviations in parentheses

	x	y	z
C(1)	7 401(4)	7 412(3)	6 628(3)
C(2)	7 098(4)	8 269(3)	7 437(3)
C(3)	6 101(4)	7 862(3)	7 824(3)
C(4)	5 782(4)	6 746(3)	7 271(3)
C(5)	4 832(4)	6 037(3)	7 433(3)
C(6)	4 559(4)	4 937(3)	6 939(3)
C(7)	3 585(4)	4 217(3)	7 200(3)
C(8)	3 633(4)	3 222(3)	6 588(3)
C(9)	4 614(4)	3 332(3)	5 953(3)
C(10)	4 956(4)	2 501(3)	5 221(3)
C(11)	5 898(4)	2 553(3)	4 612(3)
C(12)	6 245(4)	1 668(3)	3 860(3)
C(13)	7 236(4)	2 074(3)	3 446(3)
C(14)	7 492(4)	3 225(3)	3 938(3)
C(15)	8 411(4)	3 954(3)	3 755(3)
C(16)	8 681(4)	5 042(3)	4 224(3)
C(17)	9 651(4)	5 757(3)	3 975(3)
C(18)	9 616(4)	6 763(3)	4 602(3)
C(19)	8 634(4)	6 648(3)	5 235(3)
C(20)	8 332(4)	7 482(3)	6 004(3)
N(21)	6 597(3)	6 508(3)	6 571(2)
N(22)	5 159(3)	4 383(3)	6 187(2)
N(23)	6 662(3)	3 469(3)	4 631(2)
N(24)	8 087(3)	5 607(3)	4 999(2)
C(201)	7 792(5)	9 395(4)	7 757(4)
C(301)	5 413(4)	8 412(3)	8 665(3)
C(302)	5 803(4)	8 124(4)	9 620(3)
C(303)	4 789(6)	8 195(5)	10 283(4)
O(304a)	3 842(8)	8 674(5)	10 223(5)
O(304b)	3 704(18)	7 704(17)	9 818(12)
O(305)	5 101(3)	7 924(3)	11 072(3)
C(306)	4 169(5)	7 893(4)	11 756(4)
C(701)	2 774(4)	4 549(3)	8 021(3)
C(702)	3 458(4)	4 528(4)	8 995(3)
C(703)	2 729(5)	4 922(4)	9 843(4)
O(704)	1 819(5)	5 386(4)	9 826(3)
O(705)	3 122(3)	4 671(3)	10 633(2)
C(706)	2 473(5)	5 015(5)	11 499(3)
C(801)	2 848(4)	2 186(3)	6 562(3)
C(121)	5 616(4)	531(3)	3 597(3)
C(131)	7 968(4)	1 507(4)	2 666(3)
C(132)	8 169(8)	534(5)	2 424(5)
C(171)	10 482(4)	5 415(4)	3 180(3)
C(181)	10 335(4)	7 786(4)	4 652(3)
C(182)	11 316(5)	7 923(4)	4 190(4)
N(183)	11 932(5)	9 012(4)	4 298(4)
O(184)	12 873(4)	9 059(3)	3 873(3)
O(185)	11 510(6)	9 798(3)	4 775(4)
Cl(1a)	−207(4)	2 145(3)	8 187(2)
Cl(1b)	844(6)	2 134(5)	8 757(6)
Cl(2a)	399(3)	2 341(2)	11 095(2)
Cl(2b)	101(10)	1 028(8)	10 162(7)
C(30)	−148(13)	2 571(11)	9 389(8)
C(31)	−606(9)	2 241(10)	10 027(7)

corrections were applied to the data but no allowance was made for absorption effects.

The structure was solved by direct methods (SHELX-76).[11] The centrosymmetric space group was suggested by the E statistics $(\langle |E^2 - 1| \rangle = 1.06)$ and confirmed by the satisfactory refinement. Despite renormalisation of E values for reflexions with $h = 2n$ there was a tendency for such reflexions to dominate the starting set selected by the automatic direct-methods routine. Therefore six hand-selected reflexions with $h = 2n + 1$ were included in the starting set, the origin-defining and 12 remaining multi-solution reflexions being selected by the program. An E map calculated using 418 reflexions with $E \geqslant 1.7$ showed 42

out of the 51 non-hydrogen atom positions in the asymmetric unit. Isotropic full-matrix least-squares refinement followed by a difference synthesis revealed the positions of the remaining atoms including the disordered chlorine atoms of the dichloroethane solvent molecule.

The solvent molecule was refined using a disordered model. Each chlorine atom was refined as two fractional atoms with a common isotropic temperature factor and the sum of the site-occupation factors constrained to unity. The site-occupation factors were then fixed at their refined values and anisotropic thermal parameters were refined for the fractional atoms. A similar procedure was used to refine O(304) which was also found to be disordered. Blocked full-matrix least-squares refinement [3 719 data, $F \geqslant 3\sigma(F)$] with anisotropic temperature factors for all heavy atoms gave R 0.11.

Out of the 39 hydrogen atoms of the porphyrin molecule, 37, including H(21) and H(23), were located from a difference synthesis. Owing to the shortage of data, hydrogen atoms bonded to carbon were inserted in calculated positions [C–H 1.08 Å] and refined using a riding model, except those of the vinyl group and the C(201) methyl group; the latter did not refine satisfactorily with a riding model. These hydrogen atoms were included in positions obtained from the difference map and refined with C–H bond lengths constrained to 1.080(5) Å: the imino-hydrogen atoms were treated similarly with N–H bond lengths constrained to 1.00(5) Å. Two isotropic hydrogen thermal parameters were refined, one for the hydrogen atoms of the porphyrin ring [0.069(4) Å^2] and one for the hydrogen atoms of the side groups [0.145(4) Å^2]. Owing to the high thermal parameters and disorder no attempt was made to include the hydrogen atoms of dichloroethane. A final difference map revealed no peaks of electron density >0.3 e Å^{-3}.

The refinement converged at R 0.082, R' 0.063 $\{R' = \Sigma w^{\frac{1}{2}} \Delta / \Sigma w^{\frac{1}{2}} |F_0|\}$ for 528 parameters; reflexions were weighted as $w = 1/\sigma^2(F_0)$. Ten strong low-angle reflexions suffering from extinction were omitted from the final refinement. Fractional atom co-ordinates are given in Table 4. Hydrogen-atom co-ordinates, anisotropic thermal parameters, and structure factor tables are given in Supplementary Publication No. SUP 22639 (20 pp.).*

REFERENCES

[1] Part 2, R. Bonnett and P. Nicolaidou, J.C.S. Perkin I, 1979, 1969.

[2] R. Bonnett, A. A. Charalambides, and R. A. Martin, J.C.S. Perkin I, 1978, 974.

[3] J. B. Fox and J. S. Thomson, Biochemistry, 1964, 3, 1323.

[4] J. E. Falk, 'Porphyrins and Metalloporphyrins,' Elsevier, Amsterdam, 1964, p. 74.

[5] A. W. Nichol, J. Chem. Soc. (C), 1970, 903.

[6] P. W. Codding and A. Tulinsky, J. Amer. Chem. Soc., 1972, 94, 4151.

[7] R. G. Little and J. A. Ibers, J. Amer. Chem. Soc., 1975, 97, 5363.

[8] W. S. Caughey and J. A. Ibers, J. Amer. Chem. Soc., 1977, 99, 6639.

[9] R. Bonnett and A. F. McDonagh, J.C.S. Perkin I, 1973, 881.

[10] R. Bonnett, P. Cornell, and A. F. McDonagh, J.C.S. Perkin I, 1976, 794.

[11] SHELX-76, Program for Crystal Structure Determination, G. M. Sheldrick, University of Cambridge, 1976.

* For details see Notice to Authors No. 7, J.C.S. Perkin I, 1978, Index issue.