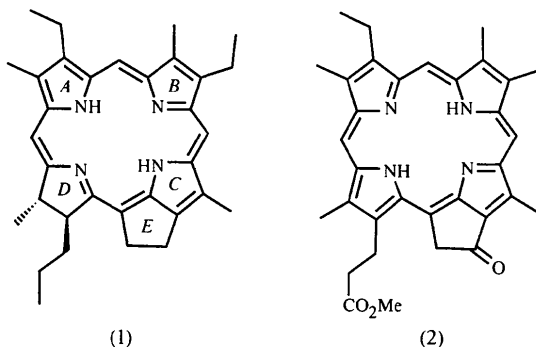## References

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Structure and Conformation of Photosynthetic Pigments and Related Compounds. 10. Comparison of a Phytochlorin and Phytoporphyrin Derived from Chlorophyll a

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Abstract

The crystal and molecular structures of 17-decarboxy-ethyl-13¹-deoxo-17-propylphytochlorin, $C_{33}H_{40}N_4$, (1), and phytoporphyrin methyl ester, $C_{34}H_{36}N_4O_3$, (2), are compared. Compound (1) shows structural parameters similar to those of other naturally occurring phytochlorins. Owing to the absence of any heteroatom functionalities at the periphery, no close contacts are observed in the packing of (1), in contrast to those normally found in other chlorophyll derivatives. Compound (2) presents the first structure of a free-base pheoporphyrin and forms chains stabilized by C—H···O=C and π–π interactions.

interactions. In contrast to the structure of (1) and other chlorins, the two pyrrole H atoms in (2) are located at rings *B* and *D*.

Comment

The structure of the phytochlorin (1) derived from chlorophyll *a* was determined in order to obtain information on the crystal packing of a pheophorbide *a* derivative containing no O functionalities. This was achieved in (1) by removal of the 13¹ oxo group and substitution of the 17-propionic acid group present in chlorophyll *a* with a propionyl group.

(1)   (2)

Compound (1) crystallized with two crystallographically independent molecules in the asymmetric unit, mainly distinguished by the conformation of the C17 propionyl groups (Fig. 1). The structural parameters of the macrocycles agree well with those of other pheophorbides related to chlorophyll *a* (Hoppe, Will, Gassmann & Weichselgartner, 1969; Gassmann, Strell, Brandl, Sturm & Hoppe, 1971; Fischer, Templeton, Zalkin & Calvin, 1972; Kratky, Isenring & Dunitz, 1977; Smith, Goff, Fajer & Barkigia, 1982, 1983; Senge & Smith, 1992). The hydroporphyrin character is clearly evidenced by the elongated C17—C18 and C37—C38 bond lengths [1.552 (5) and 1.551 (5) Å, respectively]. With the exception of the reduced ring *D*, both macrocycles are almost planar. The average deviation of the 26 atoms comprising the phytochlorin macrocycle system is 0.031 Å in (1) and 0.065 Å in (2). The largest deviations from the respective N_4 planes are observed for C18 [0.28 (5) Å] and C38 [0.42 (5) Å].

The chlorins form molecular stacks in the crystal, repeating the (1)–(1)–(2)–(2)–(1) motif. Whereas the interplanar separations of the N_4 planes are of the order of 3.5 Å, there is almost no π overlap of the ring systems as indicated by center-to-center separations of the order of 7.9 (1) Å and lateral shifts of the macrocycle centers against each other by about 7.03 (3) Å [geometrical parameters as defined by Scheidt & Lee (1987)]. Thus, in contrast to other phytochlorins, in the absence of any heteroatom functionalities at the phytochlorin periphery, no close contacts and only very weak π–π interactions are observed.
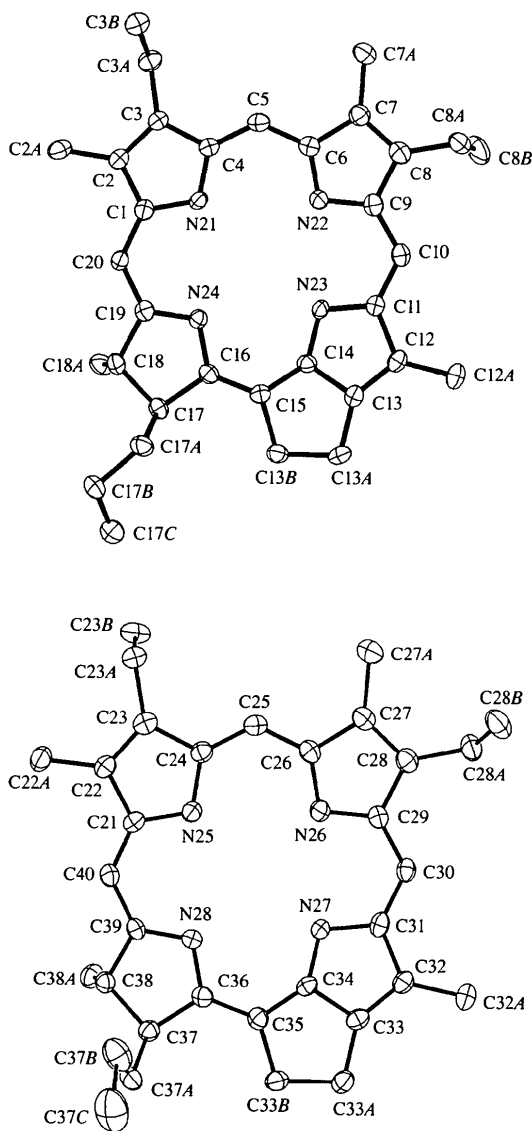
Fig. 1. Molecular structure and numbering scheme for the two crystallographically independent molecules of (1). H atoms have been omitted for clarity and ellipsoids are drawn for 50% occupancy.

Compound (2) presents the first example of a structure of a free-base pheophorphyrin. Compounds of this type, often called geo- or petroporphyrins, are found in geological deposits and derive from plant chlorophylls (Treibs, 1934; Callot, 1991). So far, only structures of some metallo-geoporphyrins have been published (Pettersen, 1969, 1971; Ekstrom *et al.*, 1983; Miller, Hambley & Taylor, 1984; Senge, Smith & Smith, 1993). These compounds are directly related to phytochlorins such as (1), the difference being the oxidation level of ring *D*. The molecular structure of (2) shows overall structural parameters that are similar to other porphyrins

(Scheidt & Lee, 1987) (Fig. 2). The oxidized character of ring *D* is shown by the shortened C17—C18 bond length [1.378 (3) Å] and the porphyrin character of the ring systems leads to an essentially planar macrocyclic system. The average deviation from planarity for the 26 atoms comprising the phytoporphyrin system is 0.041 Å. A significant difference from (1) or other chlorins is found in the location of the pyrrole H atoms. Whereas in phytochlorins they are located in rings *A* and *C*, (2) bears N—H groups in rings *B* and *D*. This is evidenced by differences in the C_α—N—C_α angles which are widened in rings *A* and *C* [average value 104.4 (2)°] compared with rings *B* and *D* [average angle 110.4 (2)°]. The respective values found in the corresponding phytochlorin methyl ester (Senge & Smith, 1992) are 110.5 (7) (rings *A* and *C*) and 107.1 (7)° (rings *B* and *D*).

The crystal packing of (2) is characterized by the formation of polymeric chains of dimeric porphyrin aggregates, which are held together by a combination of weak π and C—H···O interactions (Fig. 3). A dimer unit is stabilized by formation of a weak π–π aggregate [interplanar separation: 3.52 (5) Å; lateral shift of the porphyrin centers: 5.67 (5) Å] and by interactions between the C81 methylene group and the ester carbonyl O atom of the C17 substitutent [H81*B*···O2 2.48 (1) Å]. The propionic acid methyl ester groups are folded towards the neighboring macrocycle in a clamp-like conformation. Neighboring units are stabilized *via* interaction of the C13¹ carbonyl O atom and the methyl
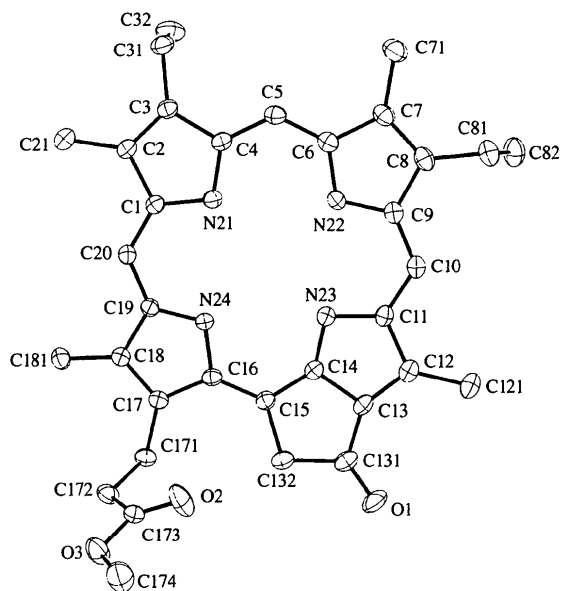

Fig. 2. Molecular structure and numbering scheme for (2). H atoms have been omitted for clarity and ellipsoids are drawn for 50% occupancy.

H atoms of the ester group [H17G··O1 2.42(1) Å]. Owing to the folding back of the propionic acid ester groups towards each other, the outer faces of each polymer can form weak π–π aggregates with the next chain above and below. These interchain aggregates are slightly stronger (interplanar separation: 3.48 Å; lateral shift of the centers: 5.03 Å) than the intrachain aggregates mentioned above. Nevertheless, all aggregates described here are weak, especially when compared with the strong aggregates observed for metalloporphyrins (Scheidt & Lee, 1987).
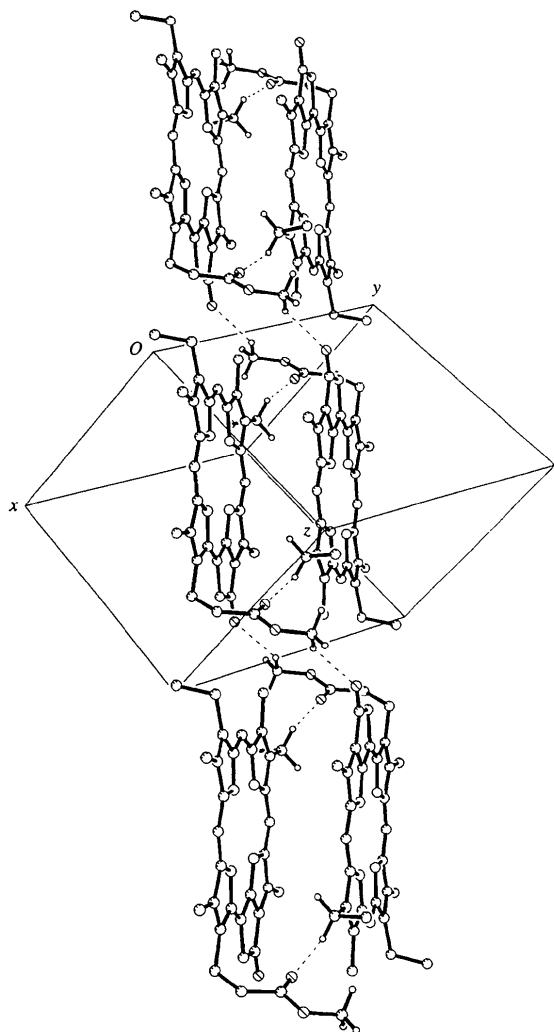

Fig. 3. View of the chains formed by (2) in the crystal. Only H atoms involved in weak C—H···O interactions (dashed lines) are shown.

Experimental

Compound (1) was prepared synthetically as described by Abraham, Rowan, Smith & Smith (1993). Compound (2) was prepared synthetically as described by Fischer & Orth (1940) and Kenner, McCombie & Smith (1973). For both (1) and

(2), crystals were grown from CH_2Cl_2/n-hexane and mounted according to Hope (1994).

Compound (1)

Crystal data

$C_{33}H_{40}N_4$	Mo $K\alpha$ radiation
$M_r = 492.69$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 35
$P2_1$	reflections
$a = 7.875\,(3)$ Å	$\theta = 12$–$15°$
$b = 24.756\,(10)$ Å	$\mu = 0.070$ mm^{-1}
$c = 14.582\,(6)$ Å	$T = 126\,(2)$ K
$\beta = 104.26\,(3)°$	Parallelepiped
$V = 2755.2\,(19)$ Å^3	$0.60 \times 0.43 \times 0.28$ mm
$Z = 4$	Green
$D_x = 1.188$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens $R3m/V$ diffractometer	4933 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.051$
Absorption correction:	$\theta_{max} = 27.5°$
ΔF ($XABS2$; Parkin,	$h = -10 \rightarrow 9$
Moezzi & Hope, 1995)	$k = 0 \rightarrow 32$
$T_{min} = 0.96$, $T_{max} = 0.98$	$l = 0 \rightarrow 18$
6946 measured reflections	2 standard reflections
6474 independent reflections	every 198 reflections
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0596P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.058$	$+ 0.8366P]$
$wR(F^2) = 0.140$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.022$	$(\Delta/\sigma)_{max} = 0.003$
6474 reflections	$\Delta\rho_{max} = 0.34$ e Å^{-3}
667 parameters	$\Delta\rho_{min} = -0.28$ e Å^{-3}
H-atom parameters	Extinction correction: none
constrained	Scattering factors from
	International Tables for
	Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °) for (1)

N21—C1	1.375 (5)	C13—C13A	1.496 (5)
N21—C4	1.377 (5)	C13A—C13B	1.566 (6)
N22—C6	1.365 (5)	C13B—C15	1.531 (5)
N22—C9	1.373 (5)	C14—C15	1.388 (6)
N23—C14	1.358 (5)	C15—C16	1.384 (5)
N23—C11	1.385 (5)	C16—C17	1.518 (5)
N24—C16	1.356 (5)	C17—C18	1.552 (5)
N24—C19	1.361 (5)	C18—C19	1.522 (5)
C12—C13	1.376 (6)	C37—C38	1.551 (5)
C13—C14	1.418 (5)		
C1—N21—C4	110.6 (3)	N23—C14—C13	109.0 (3)
C6—N22—C9	105.6 (3)	C15—C14—C13	114.2 (3)
C14—N23—C11	108.5 (3)	C16—C15—C14	127.1 (4)
C16—N24—C19	109.0 (3)	C16—C15—C13B	126.8 (4)
C10—C11—C12	130.9 (4)	C14—C15—C13B	106.0 (3)
N23—C11—C12	108.0 (3)	N24—C16—C15	121.6 (3)
C13—C12—C11	106.1 (3)	N24—C16—C17	113.0 (3)
C12—C13—C14	108.4 (3)	C15—C16—C17	125.4 (3)
C12—C13—C13A	142.1 (4)	C16—C17—C18	101.7 (3)
C14—C13—C13A	109.5 (3)	C19—C18—C17	102.4 (3)
C13—C13A—C13B	103.1 (3)	N24—C19—C20	124.1 (3)
C15—C13B—C13A	107.1 (3)	N24—C19—C18	112.1 (3)
N23—C14—C15	136.8 (4)		

Compound (2)

Crystal data

$C_{34}H_{36}N_4O_3$
$M_r = 548.67$
Triclinic
$P\bar{1}$
$a = 9.703\ (3)$ Å
$b = 11.906\ (2)$ Å
$c = 13.685\ (3)$ Å
$\alpha = 99.11\ (2)°$
$\beta = 107.84\ (2)°$
$\gamma = 106.67\ (2)°$
$V = 1388.1\ (6)$ Å^3
$Z = 2$
$D_x = 1.313$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 31
  reflections
$\theta = 11-14°$
$\mu = 0.085$ mm^{-1}
$T = 126\ (2)$ K
Plate
$0.6 \times 0.4 \times 0.2$ mm
Red

Data collection

Siemens $R3m/V$ diffractom-
  eter
ω scans
Absorption correction:
  ΔF (XABS2; Parkin,
  Moezzi & Hope, 1995)
  $T_{min} = 0.95,\ T_{max} = 0.98$
6753 measured reflections
6376 independent reflections

4627 reflections with
  $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 27.5°$
$h = -12 \rightarrow 11$
$k = -15 \rightarrow 15$
$l = 0 \rightarrow 17$
2 standard reflections
  every 198 reflections
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.199$
$S = 1.037$
6376 reflections
370 parameters
H-atom parameters
  constrained

$w = 1/[\sigma^2(F_o^2) + (0.091P)^2 + 1.4171P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.59$ e Å^{-3}
$\Delta\rho_{min} = -0.62$ e Å^{-3}
Extinction correction: none
Scattering factors from
  International Tables for
  Crystallography (Vol. C)

Table 2. Selected geometric parameters (Å, °) for (2)

N21—C4	1.368 (3)	C13—C14	1.434 (3)
N21—C1	1.374 (3)	C13—C131	1.458 (4)
N22—C6	1.362 (3)	C131—C132	1.538 (4)
N22—C9	1.374 (3)	C132—C15	1.517 (3)
N23—C14	1.351 (3)	C14—C15	1.403 (3)
N23—C11	1.383 (3)	C15—C16	1.391 (3)
N24—C19	1.356 (3)	C16—C17	1.437 (3)
N24—C16	1.380 (3)	C17—C18	1.378 (3)
C11—C12	1.455 (3)	C18—C19	1.440 (3)
C12—C13	1.368 (3)		
C4—N21—C1	105.0 (2)	N23—C14—C13	112.4 (2)
C6—N22—C9	110.2 (2)	C15—C14—C13	112.3 (2)
C14—N23—C11	103.8 (2)	C16—C15—C14	123.9 (2)
C19—N24—C16	110.6 (2)	C16—C15—C132	128.7 (2)
C10—C11—C12	124.5 (2)	C14—C15—C132	107.4 (2)
C13—C12—C11	104.1 (2)	N24—C16—C15	119.7 (2)
C12—C13—C14	107.3 (2)	N24—C16—C17	107.0 (2)
C12—C13—C131	144.3 (2)	C15—C16—C17	133.3 (2)
C14—C13—C131	108.4 (2)	C18—C17—C16	107.4 (2)
O1—C131—C132	124.0 (2)	C17—C18—C19	107.9 (2)
C13—C131—C132	106.7 (2)	N24—C19—C20	125.9 (2)
C15—C132—C131	105.2 (2)	N24—C19—C18	107.1 (2)
N23—C14—C15	135.3 (2)	C20—C19—C18	126.9 (2)

The pyrrole and *meso*-carbon H atoms were located in difference maps. For refinement, all H atoms were placed in calculated positions and refined using a riding model assuming planar geometry at the N atom. All calculations were performed using the *SHELXTL-Plus* program system (Sheldrick, 1994). The absolute structure of (1) could not be determined from the Flack (1983) parameter but was chosen with reference to the absolute structure of chlorophyll *a* from which this compound was derived chemically.

For both compounds, data collection: *P3* (Siemens, 1990); cell refinement: *P3*; data reduction: *XDISK* (Siemens, 1989) and *SHELXTL-Plus* (Sheldrick, 1994); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *XP* (Siemens, 1994) and *SHELXTL-Plus*; software used to prepare material for publication: *XCIF* and *SHELXTL-Plus*.

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Diisopropyl Hydrazocarboxylate–Triphenylphosphine Oxide Adduct†

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Abstract

Crystals of the title complex, $C_8H_{16}N_2O_4.C_{18}H_{15}OP$, belong to the $P2_1/c$ space group. The triphenylphosphine oxide and diisopropyl hydrazocarboxylate molecules form a stable centrosymmetric 2:2 complex through a series of hydrogen bonds.

Comment

Etter has undertaken a systematic study of complexes incorporating the triphenylphosphine oxide molecule (see, for example, Etter, Rasmussen, Gleason, Kress, Duerst & Gillard, 1986; Etter & Panunto, 1988; Etter & Reutzel, 1991, 1992; Etter, Urbanczyk-Lipkowska, Zia-Ebrahimi & Panunto, 1990). Since triphenylphosphine oxide is a very strong proton acceptor it often forms highly stable crystalline complexes with other molecules. These crystals are often reasonably large and well developed (Etter & Baures, 1988). Etter has also shown that triphenylphosphine oxide may be used to displace and modify the hydrogen-bonding pattern occurring in some of the organic molecules with which it forms complexes.

The bonds distances and angles in the triphenylphosphine oxide molecule, *A*, are normal; the P=O bond is 1.492 (1) Å, while the P—C bonds average

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† Alternative name: isopropyl 3-(isopropoxycarbonyl)carbazate-triphenylphosphine oxide (1/1).

1.797 Å. In the diisopropyl hydrazocarboxylate molecule, *B*, the central N41—N51 bond is 1.381 (2) Å and there is a *gauche* torsion angle, $\tau = 72°$, around this bond. All the C—H distances in molecule *A* are in the range 0.88 (3)–1.04 (3) Å, with U_{iso} values between 0.056 (5) and 0.150 (11) Å^2. The two N—H distances in molecule *B* are 0.82 (2) and 0.90 (2) Å.
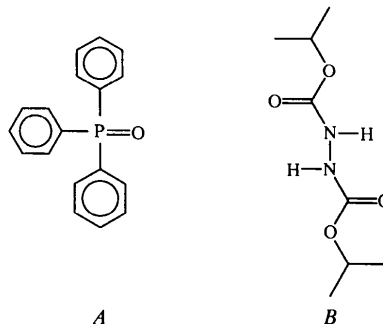
Four molecules (two *A* + two *B*) are connected to each other through hydrogen bonds of the N—H(*B*)···O(*A*) type and form a centrosymmetric ten-membered ring. There is a three-center hydrogen bond involving the phosphoryl O atom, H(*B*)···O(*A*)···H(*B*). This system is not symmetrical since the two N···O bonds are 2.896 (2) and 2.880 (2) Å, while the two N—H···O bond angles are 159 (2) and 172 (2)°. Each phosphoryl O atom is connected to NH groups of two centrosymmetrically related diisopropyl hydrazocarboxylate molecules. Although there is no report of such an arrangement with phosphines, a comparable eight-membered ring system has been observed in a diacetamide–benzamide host–guest assembly (Etter & Reutzel, 1991). The carbonyl O atoms of molecule *B* do not participate in hydrogen bonding. The C=O bond lengths are 1.202 (2) and 1.206 (2) Å.
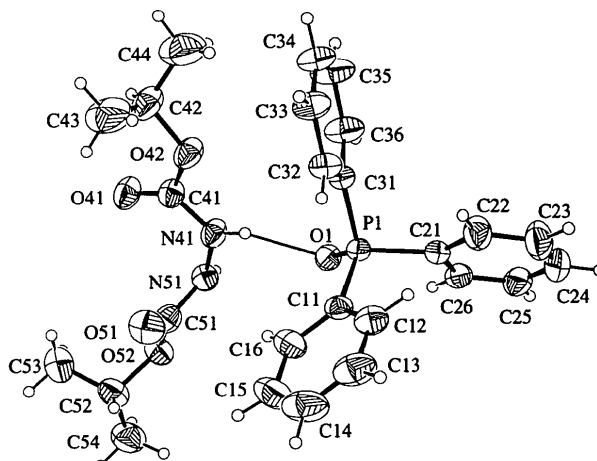

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the two structural units, $C_{18}H_{15}PO$ and $C_8H_{16}N_2O_4$, and the atomic numbering schemes. The ellipsoids are drawn at the 40% probability level, while the H atoms are represented as spheres of arbitrary size.