

## 5,10,15,20-Tetrakis[(4-ethylcarbonyl)oxy]-phenylporphyrin

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## Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$

$R$  factor = 0.065

$wR$  factor = 0.161

Data-to-parameter ratio = 18.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The crystal structure of the title compound,  $\text{C}_{56}\text{H}_{46}\text{N}_4\text{O}_8$ , shows the porphyrin core to be composed of four pyrrole rings linked through methene carbon bridges. Each molecule lies across a crystallographic inversion center. The porphyrin core is planar, which facilitates  $\pi$ -electron delocalization. The inner nitrogen H atoms are found localized on opposite pyrrole rings and these rings differ structurally from the other two pyrrole rings.

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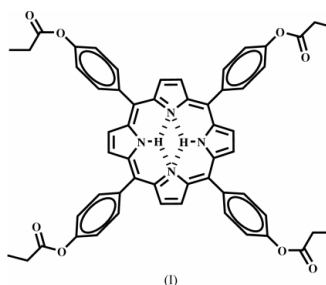
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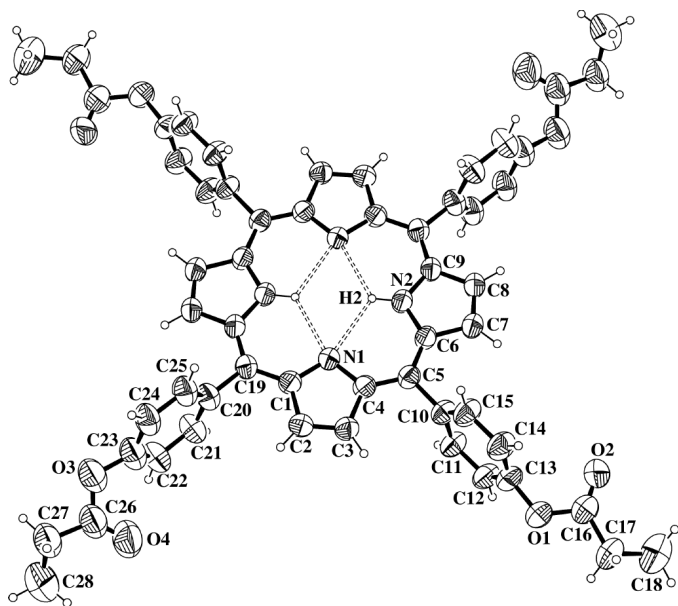
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## Comment

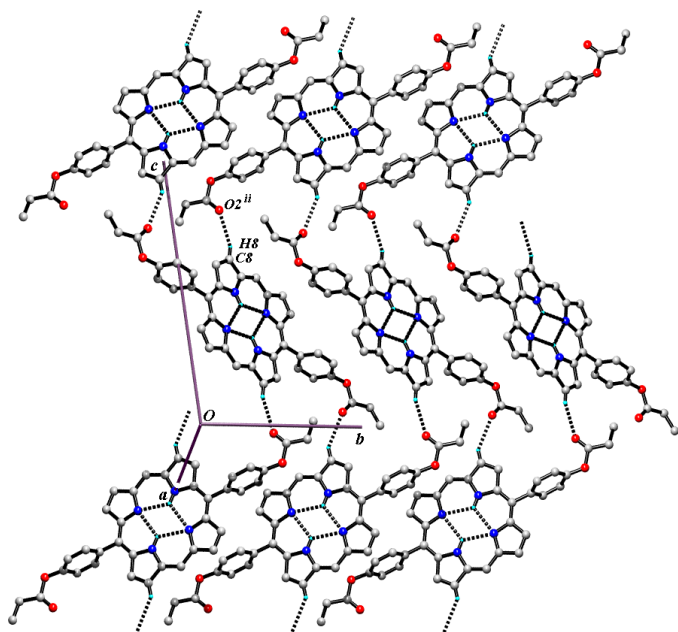
Porphyrins are receiving attention as photosensitizers in prospective photochemical electron-transfer systems for solar energy conversion (Morstyn & Kaye, 1990; Zanelli & Kaelin, 1990; Mehta *et al.*, 1993). In addition, porphyrins are important prosthetic groups for a number of metalloproteins and enzymes, and their function depends on the metal ion and the nature of the axial ligand, as well as on the specific environment provided by the polypeptide chain (Dolphin, 1978; Conn *et al.*, 1996). In the present study, the synthesis and X-ray crystal structure of the title compound, (I), is reported.



The porphyrin macrocycle is composed of four pyrrole rings linked through methene carbon bridges. Each molecule possesses a crystallographic inversion center. The porphyrin core is planar, which facilitates  $\pi$ -electron delocalization. The redetermination of the structure of porphine was reported by Chen & Tulinsky (1972), and it suggests that there are two structurally different pairs of pyrrole rings. Similarly, the title compound has two localized imino hydrogen atoms on opposite pyrrole rings and these rings differ structurally from the other two pyrrole rings. The imino H atoms cannot occupy adjacent pyrrole rings due to steric and electronic interactions which would increase the potential energy of this configuration. Hence they should be present on diametrically opposed rings. Two dominant resonance structures of tetraphenylporphyrin (TPP), each with 18  $\pi$  electrons, have been reported by Silvers & Tulinsky (1967). The title porphyrin structure corresponds approximately to a structure expected of a hybrid



**Figure 1**  
The structure of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme of the asymmetric unit.



**Figure 2**  
A part of the crystal structure, showing the formation of a sheet through C—H...O interactions and the  $R_4^4(54)$  motif. The ester group (C20–C28) and H atoms not taking part in the interactions are omitted. Dotted lines represent hydrogen bonds.

of the two predominant classic resonance forms of the macrocyclic ring system. The pyrrolyl protons are equivalent in the NMR spectra, appearing as a singlet at lower field. The pyrrole N—H protons apparently undergo fast exchange in deuteriochloroform solution, since their resonances are not visible in the NMR spectra.

The structure of the porphyrin core is very similar to other free base porphyrins (Silvers & Tulinsky, 1967, Chen & Tulinsky, 1972, Codding & Tulinsky, 1972, Little & Ibers,

1975). The chemically equivalent bonds around the 24-atom core have similar bond lengths. The 24-atom core is planar with an r.m.s. deviation from the the plane of 0.021 (3) Å, and the two independent pyrrole ring planes are tilted slightly at an angle of 2.1 (3)°. The imino H atoms are displaced on opposite sides with respect to the porphyrin macrocycle. The distance between the two imino H atoms is 2.33 (4) Å, which is slightly shorter than those values found in porphine (2.41 Å), and comparable with those in TPP (2.36 Å) and octaethylporphyrin (OEP) [2.36 (4) Å] (Codding & Tulinsky, 1972, Silvers & Tulinsky, 1967, Lauher & Ibers, 1973). The imino H atoms form bifurcated intramolecular hydrogen bonds with the adjacent unprotonated N atoms (Table 2). Owing to the steric effect of the bulky phenyl group, the four planes of the phenyl groups are almost perpendicular to the porphyrin macrocycle. Therefore, the angles between the planes of the first pyrrole ring containing N1 and its neighboring two phenyl rings containing C10 and C20 are 86.1 (2)° and 84.0 (1)°, respectively, while those between the planes of the second pyrrole ring containing N2 and its neighboring two phenyl rings containing C10 and C20<sup>i</sup> are 84.0 (2)° and 84.1 (2)°, respectively (for symmetry code see Table 2).

Each individual porphyrin molecule is linked to four molecules by four C8—H8...O2 weak hydrogen bonds, in two of them acting as donor and two as acceptor. This interaction generates a  $R_4^4(54)$  graph-set ring (Etter *et al.*, 1990) as shown in Fig. 2. These rings are joined in a sheet, extended along all the crystal, by C(12) chains.

## Experimental

A 250 ml three-necked round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser was charged with 4-hydroxybenzaldehyde (2.46 g, 20.2 mmol), acetic anhydride (12 ml), and propionic acid (100 ml) and stirred for 15 min at 383 K. Pyrrole (1.36 g, 20.6 mmol) was added slowly, and the mixture was refluxed for 1.0 h. The resulting solution was then cooled to room temperature and kept overnight. The purple crystals were filtered, washed with hot water and ethanol to remove traces of propionic acid, and dried in a vacuum oven to give a 12% yield (547 mg, 0.606 mmol): TLC  $R_f$  0.95 (dichloromethane);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  -2.77 (s, 2H, NH), 1.45 (t,  $J$  = 8.0 Hz, 12H,  $\text{CH}_3$ ), 2.80 (q,  $J$  = 7.2 Hz, 8H,  $\text{CH}_2$ ), 7.54 (d,  $J$  = 8.4 Hz, 8H, ArH), 8.26 (d,  $J$  = 8.8 Hz, 8H, ArH), 8.92 (s, 8H,  $\beta$ -pyrrole-H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 75 Hz)  $\delta$  9.18, 27.97, 119.27, 119.86, 131.17, 135.27, 139.44, 150.76, 173.05; FT-IR (KBr) 3318 (br, NH), 3037 (w), 2979 (w), 1760 (s, C=O), 1594 (s, C=C), 1503 (m), 1198 (s), 1139 (s), 968 (s), 799 (s)  $\text{cm}^{-1}$ ; UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  nm ( $\epsilon$ ,  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ): 418 ( $4.72 \times 10^5$ ), 446 ( $1.95 \times 10^4$ ), 514 ( $1.85 \times 10^5$ ), 548 ( $8.42 \times 10^3$ ), 590 ( $5.75 \times 10^2$ ), 646 ( $5.21 \times 10^2$ ); MS (FAB)  $m/z$  (relative intensity) 903 ( $M^+$ ).

## Crystal data

$\text{C}_{56}\text{H}_{46}\text{N}_4\text{O}_8$	$D_x = 1.283 \text{ Mg m}^{-3}$
$M_r = 902.97$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from all reflections
$a = 9.4045$ (10) Å	$\theta = 1.8\text{--}28.3^\circ$
$b = 10.9423$ (11) Å	$\mu = 0.09 \text{ mm}^{-1}$
$c = 23.4260$ (19) Å	$T = 293$ (2) K
$\beta = 104.187$ (4)°	Pillar, violet
$V = 2337.2$ (4) Å <sup>3</sup>	0.25 × 0.20 × 0.15 mm
$Z = 2$	

## Data collection

Bruker CCD area detector diffractometer	5626 independent reflections
$\varphi$ and $\omega$ scans	928 reflections with $I > 2\sigma(I)$
Absorption correction: $\psi$ scan (North <i>et al.</i> , 1968)	$R_{\text{int}} = 0.057$
$T_{\text{min}} = 0.969$ , $T_{\text{max}} = 0.990$	$\theta_{\text{max}} = 28.3^\circ$
14 839 measured reflections	$h = -12 \rightarrow 12$
	$k = -11 \rightarrow 14$
	$l = -28 \rightarrow 30$

## Refinement

Refinement on $F^2$	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.065$	$w = 1/[\sigma^2(F_o^2) + (0.049P)^2]$
$wR(F^2) = 0.161$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.80$	$(\Delta/\sigma)_{\text{max}} < 0.001$
5626 reflections	$\Delta\rho_{\text{max}} = 0.26 \text{ e } \text{\AA}^{-3}$
311 parameters	$\Delta\rho_{\text{min}} = -0.31 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

N1—C4	1.381 (5)	N2—C6	1.398 (5)
N1—C1	1.399 (5)	N2—H2	0.92 (2)
N2—C9	1.393 (5)		
C4—N1—C1	105.5 (4)	C9—N2—H2	127 (3)
C9—N2—C6	111.0 (4)	C6—N2—H2	122 (3)

Table 2

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N2—H2 $\cdots$ N1	0.92 (3)	2.34 (3)	2.918 (6)	121 (3)
N2—H2 $\cdots$ N1 <sup>i</sup>	0.92 (3)	2.33 (3)	2.879 (6)	118 (3)
C8—H8 $\cdots$ O2 <sup>ii</sup>	0.93	2.56	3.312 (6)	139

Symmetry codes: (i)  $1-x, -y, -z$ ; (ii)  $-x, y - \frac{1}{2}, -\frac{1}{2} - z$ .

The H atoms bonded to C atoms were placed in geometrically calculated positions and refined as riding, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  [ $1.5U_{\text{eq}}(\text{C})$  for the methyl H atoms]. The imino H atom (H2) was located in a difference Fourier synthesis and refined by restraining the distance H2—N2 to 0.96 (2)  $\text{\AA}$ . The C26—C27, C27—C28 bond lengths were restrained to 1.500 (3)  $\text{\AA}$  in the refinement. Similar-distance restraints were used for the bonds involving atoms O1 and O3. During anisotropic refinement, the atomic displacement para-

eters of the end-chain atoms were poorly defined and the temperature factors of atoms C18 and C28 were higher than those of atoms C17 and C27 because of the easily vibrating ends of the chains far away from the porphyrin ring. Attempts to refine a disordered model for these groups were unsuccessful, and displacement parameter restraints (SHELXL97; Sheldrick, 1997) were used to get the final structure. As a result, the geometric parameters involving the end chain atoms are only a rough approximation to reality. The poor data-to-parameter ratio is due to the contribution of the floppy ester group in the low angle data only.

Data collection: SMART (Bruker, 1998); cell refinement: SMART; data reduction: SAINT (Bruker, 2000); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: NRCVAX (Gabe *et al.*, 1989); software used to prepare material for publication: SHELXL97.

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