

29H,31H-Tetrabenzo[*b,g,l,q*]porphinShinji Aramaki^a and
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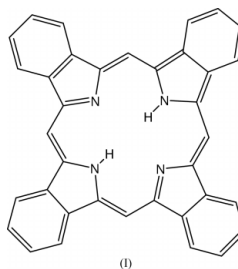
Key indicators

Single-crystal X-ray study
T = 93 K
Mean $\sigma(\text{C}-\text{C})$ = 0.005 Å
R factor = 0.033
wR factor = 0.066
Data-to-parameter ratio = 10.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, C₃₆H₂₂N₄, has recently been found to exhibit an excellent field effect transistor characteristic. The molecule is not entirely flat in its crystal structure (*i.e.* not *D*_{2h}) but is slightly deformed, as characterized by crystallographic *C*_i symmetry. The molecules are stacked along the *b* axis in a herring-bone fashion.

Comment

Both metal-containing and metal-free porphyrins are widely known as materials useful for applications in biological systems and electronic devices (Milgrom, 1997). As early as 1940, Woodward (1940) published the space group and lattice parameters of the title compound (H₂P), (I), *viz.* *P*2₁/*a*, *a* = 17.2 Å, *b* = 6.61 Å, *c* = 12.2 Å and β = 122.5°. Quite recently, H₂P has attracted attention as a material for organic FET (field effect transistor) applications (Aramaki & Ono, 2003). For this reason, the present structure analysis has been undertaken in order to improve the FET characteristics on the basis of the structural information. The unit-cell transformation of the present structure from *P*2₁/*n* to *P*2₁/*a* gives lattice parameters [*a* = 17.413 (1) Å, *b* = 6.5910 (7) Å, *c* = 12.405 (1) Å and β = 122.841 (7)°] that are in fairly good agreement with those of Woodward (1940).



An ORTEPIII (Burnett & Johnson, 1996) plot of H₂P is shown in Fig. 1. The molecular symmetry is not *D*_{2h} but *C*_i, because the molecule, located about an inversion center, is not entirely flat. The angles between the plane of the four N atoms [N1/N1ⁱ/N2/N2ⁱ; symmetry code: (i) 1 - *x*, -*y*, 2 - *z*] and the planes of the benzene rings are 6.96 (1)° for the C2-C7 plane and its symmetry-related plane, and 6.42 (1)° for the C11-C16 plane and its symmetry-related plane. These values indicate that the molecule, which is entirely flat (*D*_{2h}) in solution (as shown by geometry optimization of molecular-orbital calculations, as well as the solution spectrum), becomes slightly deformed on going from the solution to the solid state, as found in various phthalocyanine compounds (Mizuguchi *et al.*, 1995). The phthalocyanine analogue of H₂P is metal-free β -

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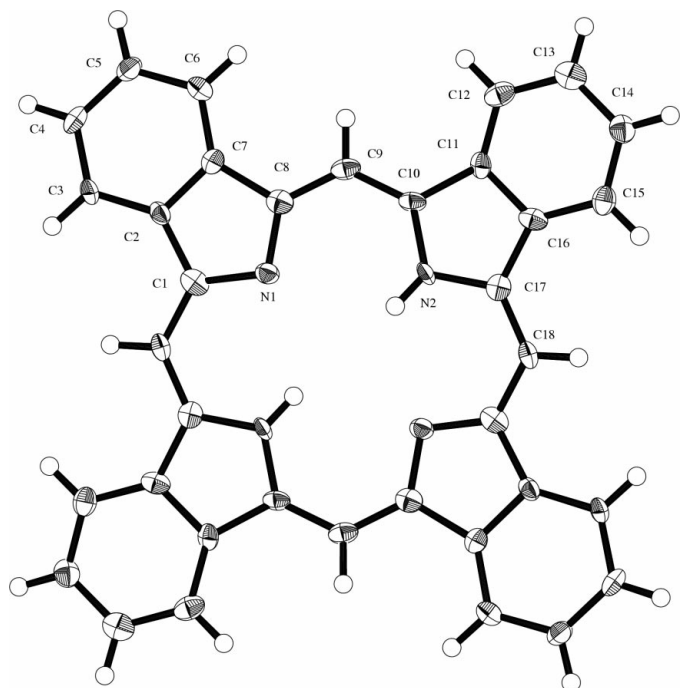


Figure 1
A view of the molecular structure of (I), showing 50% displacement ellipsoids for non-H atoms.

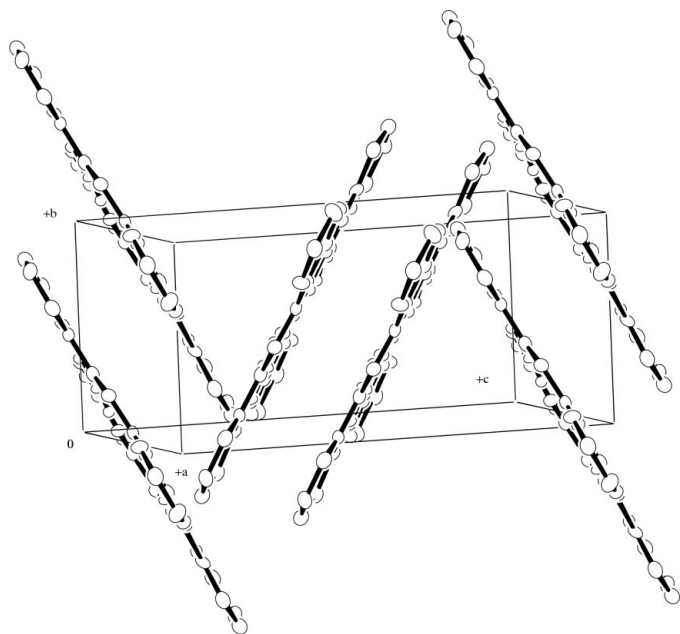


Figure 2
The packing arrangement in (I).

phthalocyanine (H_2Pc ; Mizuguchi & Matsumoto, 1999). Although the bond parameters of H_2P are quite similar to those of H_2Pc , the lattice parameters are appreciably different [H_2Pc : $P2_1/a$, $a = 19.870$ (7) Å, $b = 4.731$ (7) Å, $c = 14.813$ (7) Å and $\beta = 121.98$ (4)°; Matsumoto *et al.*, 1999]. Nevertheless, both molecules are stacked in the same way along the b axis, *i.e.* in a herring-bone fashion, as shown in Fig. 2.

Experimental

1,4:8,11:15,18:22,25-Tetraethano-29*H*,31*H*-tetrabenzo[*b,g,l,q*]porphine is a precursor of the title compound (H_2P) that gives H_2P by thermal decomposition. The precursor was prepared according to the method of Ito *et al.* (2000). Single crystals of H_2P were grown directly by thermal decomposition of the precursor at about 610 K in a closed system under high vacuum. A number of needle-like crystals were obtained over a period of 72 h. H_2P is usually prepared *via* a route involving metal salts such as those of Zn and Cd. As a result, a small amount of the metal inevitably remains as an impurity in the final product. In contrast, the above synthesis, through a non-metallic precursor, is a good method for avoiding metal inclusion. This is especially important for the electronic application of H_2P , *e.g.* as an FET, where the purity plays a decisive role.

Crystal data

$C_{36}H_{22}N_4$	$D_x = 1.417 \text{ Mg m}^{-3}$
$M_r = 510.60$	Cu $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 4837 reflections
$a = 12.405$ (1) Å	$\theta = 3.6\text{--}68.2^\circ$
$b = 6.5910$ (7) Å	$\mu = 0.66 \text{ mm}^{-1}$
$c = 14.927$ (1) Å	$T = 93.2 \text{ K}$
$\beta = 101.445$ (8)°	Needle, blue
$V = 1196.2$ (2) Å ³	$0.30 \times 0.05 \times 0.05 \text{ mm}$
$Z = 2$	

Data collection

Rigaku R-Axis RAPID imaging-plate diffractometer	2013 independent reflections
ω scans	419 reflections with $F^2 > 2\sigma(F^2)$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$R_{\text{int}} = 0.111$
$T_{\text{min}} = 0.817$, $T_{\text{max}} = 0.968$	$\theta_{\text{max}} = 68.2^\circ$
10 724 measured reflections	$h = -14 \rightarrow 14$
	$k = -6 \rightarrow 6$
	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.033$	$w = 1/[\sigma^2(F_o^2)]$
$wR(F^2) = 0.066$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 0.33$	$\Delta\rho_{\text{max}} = 0.07 \text{ e \AA}^{-3}$
2013 reflections	$\Delta\rho_{\text{min}} = -0.11 \text{ e \AA}^{-3}$
184 parameters	

Table 1

Selected geometric parameters (Å, °).

N1—C1	1.384 (4)	C1—C18 ⁱ	1.382 (5)
N1—C8	1.362 (4)	C8—C9	1.384 (5)
N2—C10	1.369 (4)	C9—C10	1.400 (4)
N2—C17	1.394 (4)	C17—C18	1.386 (4)
C1—N1—C8	106.6 (3)	C8—C9—C10	127.5 (4)
C10—N2—C17	111.7 (3)	N2—C10—C9	126.9 (4)
N1—C1—C18 ⁱ	124.8 (4)	N2—C17—C18	124.6 (4)
N1—C8—C9	126.4 (3)	C1 ⁱ —C18—C17	128.3 (3)

Symmetry code: (i) $1 - x, -y, 2 - z$.

The H atom of the NH group was found in a difference-density map and the coordinates were refined. The N—H distance is 0.84 (3) Å. All other H atoms were positioned geometrically (C—H = 0.948–0.952 Å) and not refined [fixed, with $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$]. The fact that the ratio of observed to unique reflections is about 21% can presumably be attributed to the use of an extremely small single crystal. The size of the crystal may also account for the poor goodness-of-fit.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SHELX86* (Sheldrick, 1985); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *TEXSAN*.

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