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Structure and Conformation of Photosynthetic Pigments and Related Compounds. XI.† 5,10,15,20-Tetrabutylbacteriochlorin

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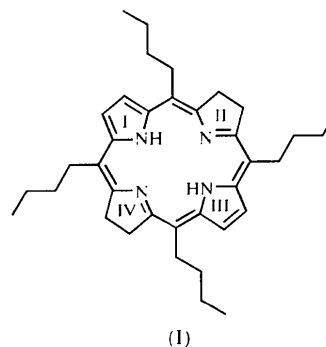
Abstract

The structure of the title compound, $C_{36}H_{50}N_4$, is the first example of a tetra-*meso*-substituted free-base bacteriochlorin (2,3,12,13-tetrahydroporphyrin). While general structural characteristics are similar to other hydrophorphyrins, the present structure presents one of the few examples of a hydrophorphyrin with a planar macrocycle conformation.

Comment

Bacteriochlorins are the main photoactive chromophores of photosynthetic bacteria (Scheer, 1989). They are distinguished from their parent porphyrins by a higher degree of saturation, *i.e.* they constitute 2,3,12,13-tetra-

hydrophorphyrins. Despite their importance, few crystal structures of bacteriochlorins have been published, notably those of methyl bacteriopheophorbide a (Barkigia *et al.*, 1981, 1989; Barkigia & Gottfried, 1994) and three synthetic bacteriochlorins (Barkigia *et al.*, 1984, 1991; Waditschatka *et al.*, 1985). Renewed interest in this class of compounds arose from current studies on the conformation flexibility of tetrapyrroles (Barkigia *et al.*, 1988), which is believed to allow a modulation of the physicochemical chromophore properties *in vivo*; see Senge (1992) for a general review. No structure of tetra-*meso*-substituted free-base bacteriochlorin was known and so we performed a structure determination of the title compound, (I), as a basis for further theoretical studies.



The general structural characteristics are typical for a tetrahydroporphyrin. This includes the $C\beta-C\beta$ single bond in the reduced pyrrole ring [$C7-C8 = 1.512(2) \text{ \AA}$ versus $C2-C3 = 1.374(2) \text{ \AA}$], a slightly smaller $C\alpha-N-C\alpha$ angle in ring II [$109.0(1)^\circ$], localization of the pyrrole H atoms at the pyrrole rings, and core expansion compared with the respective porphyrins; see Barkigia & Gottfried (1994) for a detailed description of bacteriochlorin characteristics. For example, the core size (defined as the vector length from the geometric centre of the four N atoms to the N atoms) is $2.149(5) \text{ \AA}$ in the title compound compared with $2.059(6) \text{ \AA}$ in the parent porphyrin. The structural differences between the pyrrole and pyrroline quadrants are smaller in the title compound than, for example, in bacteriopheophorbide a. The macrocycle exhibits a planar conformation. The average deviation of the 24 macrocycle atoms from their least-squares plane is $0.018(2) \text{ \AA}$. The largest deviations are observed for the $C\beta$ atoms C2 and C3, which are displaced from the least-squares plane of the four N atoms by $0.06(1)$ and $0.07(1) \text{ \AA}$, respectively. The tilt of the pyrrole rings is minimal; ring I is tilted by $2.0(1)^\circ$ and the reduced ring II by $0.40(5)^\circ$ against the N_4 plane. In contrast to other bacteriochlorin structures, the title compounds packs in the crystal without formation of π stacks. Instead, the molecules pack in a ‘—|—|’-type arrangement. The packing, unit-cell parameters and coordinate positions for the non-H atoms are very similar to those of the parent 5,10,15,20-

† Part X: Senge & Smith (1997). *Acta Cryst.* **C53**, 1314–1318.

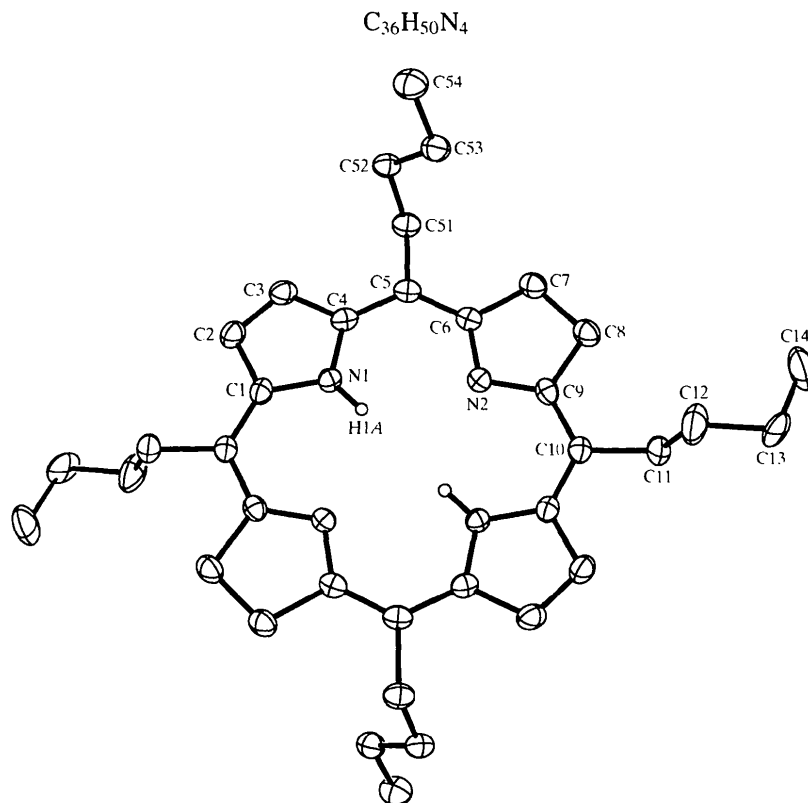


Fig. 1. The molecular structure of (1) showing 50% probability displacement ellipsoids. Side-chain H atoms have been omitted for clarity and only one orientation is shown for the butyl chain at C5.

tetrabutylporphyrin (Senge, Kalisch & Runge, 1998; Senge *et al.*, 1998).

Experimental

The title compound was prepared as described recently by Senge, Kalisch & Runge (1998). Crystals were grown by slow diffusion of methanol into a solution of the bacteriochlorin in dichloromethane. Handling of the crystals was performed as described by Hope (1994).

Crystal data

$C_{36}H_{50}N_4$
 $M_r = 538.80$
 Monoclinic
 $P2_1/c$
 $a = 13.137(5) \text{ \AA}$
 $b = 9.405(5) \text{ \AA}$
 $c = 12.416(8) \text{ \AA}$
 $\beta = 96.72(4)^\circ$
 $V = 1523.5(14) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.175 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

Siemens R3m/V diffractometer

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 42 reflections
 $\theta = 22\text{--}27^\circ$
 $\mu = 0.069 \text{ mm}^{-1}$
 $T = 126(2) \text{ K}$
 Parallelepiped
 $0.45 \times 0.22 \times 0.16 \text{ mm}$
 Intense metallic green

3065 reflections with
 $I > 2\sigma(I)$

ω scans

Absorption correction:

XABS2 (Parkin *et al.*, 1995)

$T_{\min} = 0.970$, $T_{\max} = 0.989$

4896 measured reflections

4443 independent reflections

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.056$

$wR(F^2) = 0.141$

$S = 1.042$

4443 reflections

204 parameters

H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0564P)^2 + 0.4758P]$

where $P = (F_o^2 + 2F_c^2)/3$

$R_{\text{int}} = 0.029$

$\theta_{\text{max}} = 30.01^\circ$

$h = -18 \rightarrow 18$

$k = 0 \rightarrow 13$

$l = 0 \rightarrow 17$

2 standard reflections

every 198 reflections

intensity decay: <1%

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.225 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.265 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

N1—C1	1.378 (2)	C4—C5	1.411 (2)
N1—C4	1.3830 (19)	C5—C6	1.393 (2)
N2—C9	1.3578 (19)	C6—C7	1.518 (2)
N2—C6	1.3672 (19)	C7—C8	1.512 (2)
C1—C10'	1.409 (2)	C8—C9	1.519 (2)
C1—C2	1.425 (2)	C9—C10	1.397 (2)
C2—C3	1.374 (2)	C10—C11	1.409 (2)
C3—C4	1.416 (2)	C10—C11	1.521 (2)

C1—N1—C4	110.91 (13)	C6—C5—C51	118.64 (14)
C9—N2—C6	109.00 (12)	C4—C5—C51	115.41 (14)
N1—C1—C10'	127.69 (13)	N2—C6—C5	126.21 (13)
N1—C1—C2	105.98 (14)	N2—C6—C7	111.76 (13)
C10'—C1—C2	126.33 (14)	C5—C6—C7	122.02 (13)
C3—C2—C1	108.39 (15)	C8—C7—C6	103.71 (13)
C2—C3—C4	108.53 (14)	C7—C8—C9	103.20 (13)
N1—C4—C5	127.38 (14)	N2—C9—C10	126.31 (14)
N1—C4—C3	106.17 (13)	N2—C9—C8	112.33 (13)
C5—C4—C3	126.44 (14)	C10—C9—C8	121.36 (14)
C6—C5—C4	125.95 (13)	C9—C10—C1'	126.30 (14)

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

The pyrrole H atom was located in a difference map and refined using isotropic displacement parameters. Other H atoms were placed in calculated positions and refined using a riding model. The *meso*-butyl chain located at C5 was disordered. The two outer C atoms (C13 and C14) were each refined as disordered over two positions with equal occupancies. H atoms were modelled accordingly.

Data collection: *P3* (Siemens, 1990). Cell refinement: *P3*. Data reduction: *XDISK* in *SHELXTL-Plus* (Siemens, 1994). Program(s) used to solve structure: *SHELX97* (Sheldrick, 1997). Program(s) used to refine structure: *SHELX97*. Molecular graphics: *XP* in *SHELXTL-Plus*. Software used to prepare material for publication: *SHELX97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1301). Services for accessing these data are described at the back of the journal.

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o-Nitrobenzaldehyde Isonicotinoylhydrazone

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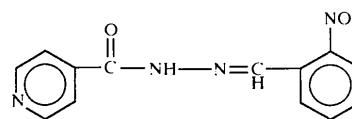
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Abstract

The title compound, C₁₃H₁₀N₄O₃, is planar and exists in the keto tautomeric form. The crystal packing is stabilized by weak intermolecular hydrogen bonds involving the N3···N4 and C2···O1 atoms of neighbouring molecules.

Comment

Photochromism based on tautomerism by hydrogen transfer in anils, *aci*-nitro and related compounds has been the subject of extensive study (Chichibabin *et al.*, 1925; Ellam *et al.*, 1974; Dürr & Bouas-Laurent, 1990; Kimura *et al.*, 1993; Hadjoudis, 1994; Lambi *et al.*, 1995). Although the title compound has been prepared and its photochromic properties described (Ellam *et al.*, 1974), its crystal structure has not been reported. Hence, we report herein the crystal structure of *o*-nitrobenzaldehyde isonicotinoylhydrazone, (I).



(I)

The N2—C7 [1.264 (3) Å] and N2—N3 [1.373 (3) Å] distances correspond to N=C double and N—N single bonds, respectively. These are comparable to those in 2,2'-azinodimethyldiphenol [1.285 (7) and 1.386 (9) Å; Xu *et al.*, 1994] and *p*-nitrobenzaldehyde nicotinoylhydrazone monohydrate [1.274 (2) and 1.376 (2) Å; Lu *et al.*, 1996]. The C8=O3 double bond distance [1.212 (3) Å] falls within the normal range for C=O double bonds (Lu *et al.*, 1996) suggesting that the molecule is in the keto form. The molecule is planar except for the nitro group [torsion angle O1—N1—C1—C2 = 38.9 (4)°]. An intramolecular hydrogen bond exists between C7 and O2 [C7···O2 2.850 (3) Å], while weak intermolecular N3—H3A···N4(1 - x, -1/2 + y, 3/2 - z) [3.101 (3) Å] and C2—H2···O1(2 - x, -1 - y, 1 - z)