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5,15-Bis(3,5-di-*tert*-butylphenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetrapropylporphyrin

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Key indicators

Single-crystal X-ray study
T = 200 K
Mean σ(C–C) = 0.006 Å
R factor = 0.087
wR factor = 0.182
Data-to-parameter ratio = 15.1

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

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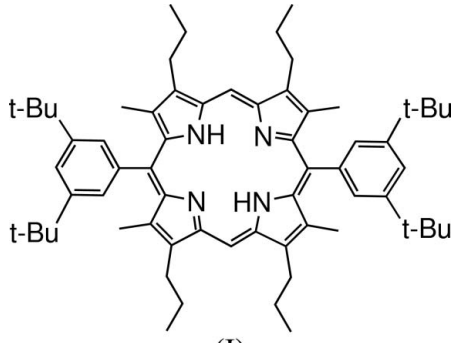
The title molecule, $C_{64}H_{86}N_4$, possesses a crystallographically imposed centre of symmetry with a rectangular distortion of the porphyrin core. In the crystal structure, molecules form laddered assemblies *via* partial π stacking of porphyrins. The assemblies are further formed into layers separated by *tert*-butyl groups.

Comment

Crystal structures of 5,15-diaryl-2,8,12,18-tetra-alkyl-3,7,13,17-tetramethylporphyrins commonly form layers *via ortho* and *meta* C—H phenyl edge to porphyrin face interactions (Bond *et al.*, 2002, 2003; Boyd & Hosseini, 2006). The 2,8,12,18-alkyl groups on the surface of these two-dimensional assemblies separate the layers by interdigitation. Introduction of substituents on the 5,15-diaryl groups can disrupt this arrangement. The title compound, (I), formed by an acid-catalysed reaction of 2,8-dimethyl-3,7-dipropyl-5,10-dihydrodipyrromethane with 3,5-di(*tert*-butyl)benzaldehyde followed by oxidation of the porphyrinogen ring, has *tert*-butyl groups that inhibit phenyl edge to porphyrin face contacts.



(I)

The molecular structure of (I) is shown in Fig. 1. The molecule possesses a crystallographic centre of symmetry. All bond lengths and angles of the porphyrin core are comparable to those determined in similar porphyrin derivatives (Senge *et al.*, 1997; Bond *et al.*, 2002; Boyd & Hosseini, 2006). The porphyrin core is nearly planar, with an r.m.s. deviation from the 24-atom porphyrin mean plane of 0.031 (3) Å. Within the plane, there is an elongation of the porphyrin core along the 5,15 direction, with N···N distances of 3.164 (4) and 2.723 (4) Å parallel and perpendicular to this direction, respectively. The *ipso* C atoms of the 3,5-*tert*-butylphenyl groups attached to the porphyrin ring in the *meso* positions are in an *anti* arrangement with displacements above and below the porphyrin mean plane of 0.118 (5) Å. The *n*-propyl

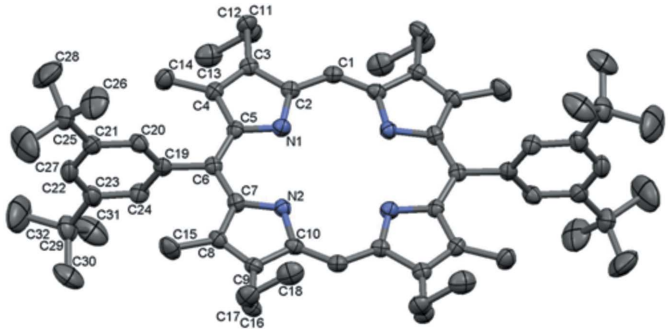


Figure 1
The structure of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted. Unlabelled atoms are related to labelled atoms by the symmetry code ($-x$, $-y$, $1-z$).

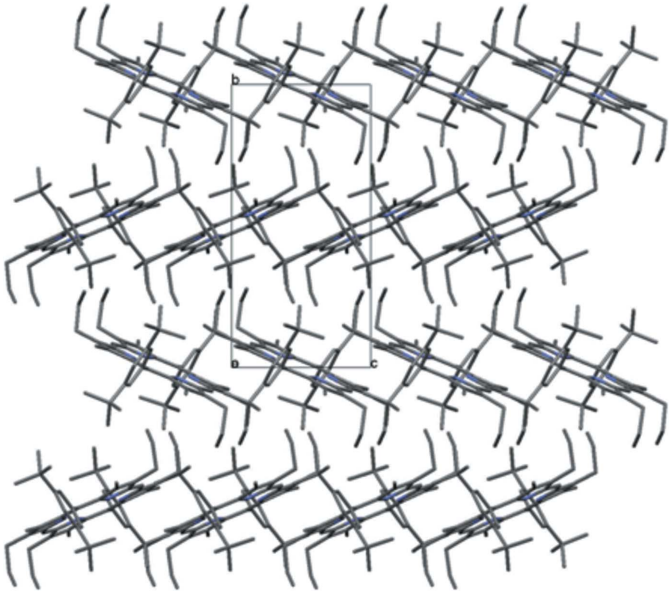


Figure 2
Porphyrin ladders aligned in a two-dimensional assembly, viewed along the *a* axis, showing partial π stacking. H atoms have been omitted.

groups are oriented with the 2 and 8 groups and the 12 and 18 groups pointing in opposite directions with respect to the porphyrin plane.

Molecules related by translation along the *c* axis form ladders with the shortest C1$\cdots$C1^{i} distance of 3.572 (5) Å [symmetry code: (i) $-x$, $-y$, $2-z$], indicating a possible π–π interaction. The porphyrin rings make an angle of 25.46 (2)° with respect to the *c* axis. There are two kinds of ladders in the crystal structure with differently oriented porphyrin planes (Fig. 2). These arrangements are similar to those observed in an analogous 3,5-di(trimethylsilylethynyl)phenyl porphyrin (Darling *et al.*, 1999). The ladders stack with the *n*-propyl groups covering the offset portion of a porphyrin from a neighbouring ladder to form a two-dimensional assembly. Alternating ladders in this assembly are stacked in opposite directions (Fig. 2). The two-dimensional layers thus formed are separated by interleaving of the *tert*-butyl groups on their surfaces.

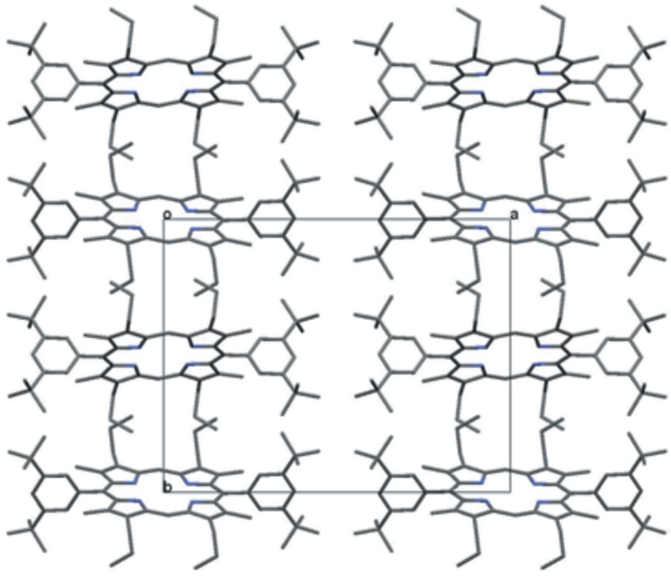


Figure 3
Two-dimensional assemblies separated by *tert*-butyl groups, viewed along the *c* axis, showing the layer structure. H atoms have been omitted.

Experimental

The title compound was prepared by the reaction of 2,8-dimethyl-3,7-dipropyl-5,10-dihydrodipyrromethane (Sessler *et al.*, 1986) with 3,5-di(*tert*-butyl)benzaldehyde (1:1) using a method similar to that previously reported by Young *et al.* (1985). 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone was used instead of *o*-chloroanil for the oxidation of the porphyrinogen. The product was purified using column chromatography (silica) and characterized by ^{1}H NMR spectroscopy. Crystals were grown by evaporation of a dichloromethane solution.

Crystal data

$C_{64}H_{86}N_4$
M_r = 911.37
Monoclinic, $P2_1/c$
a = 20.9467 (6) Å
b = 16.3352 (5) Å
c = 8.0916 (1) Å
β = 97.486 (1)°
V = 2745.09 (12) Å^3
Z = 2
D_x = 1.103 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.06 mm^{-1}
T = 200 (2) K
Needle, red
0.44 × 0.07 × 0.04 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.854, T_{max} = 0.999
12519 measured reflections
4786 independent reflections
2464 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 25.1°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.088
$wR(F^2)$ = 0.182
S = 1.06
4786 reflections
316 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0276P)^2 + 3.8177P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0049 (7)

All H atoms were placed in calculated positions (C—H = 0.95–0.99 Å, N—H = 0.88 Å) and refined using a riding model, with U_{iso}(H) values of 1.2 or 1.5 times U_{eq} of the parent atom. The large amplitude of the anisotropic displacement factors for the methyl group C atoms C26–C28 and C30–C32 may be correlated with an unresolved disorder in the *tert*-butyl groups.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *MERCURY* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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