

5,15-Bis(*p*-methylphenyl)-2,8,12,18-tetra-butyl-3,7,13,17-tetramethylporphyrin

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The centrosymmetric title compound, $C_{54}H_{66}N_4$, is a 5,15 diaryloctaalkyl free base porphyrin. The planar 24-atom porphyrin core has a significant in-plane distortion commonly observed in these types of molecules along the 5,15 direction. The porphyrin molecules are arranged in the crystal structure in two-dimensional assemblies *via* phenyl-edge-to-porphyrin-face interactions.

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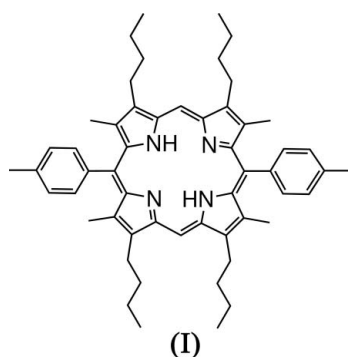
Key indicators

Single-crystal X-ray study
 $T = 83\text{ K}$
 Mean $\sigma(C-C) = 0.004\text{ \AA}$
 Disorder in main residue
 R factor = 0.067
 wR factor = 0.154
 Data-to-parameter ratio = 15.7

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

Comment

The title compound, (I), was formed and isolated during the synthesis of a mixed 5,15-diarylporphyrin. Reaction of 2,8-dimethyl-3,7-dibutyl-5,10-dihydrodipyrromethane with 4-methylbenzaldehyde and 4-nitrobenzaldehyde (2:1:1) in dichloromethane gave a mixture of the 5,15-bis(4-methylphenyl)-, (I), bis(4-nitro)- and 5-(4-methylphenyl)-15-(4-nitrophenyl)porphyrins.



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 observed in similar porphyrin derivatives (Senge *et al.*, 1997; Bond *et al.*, 2002). The porphyrin is essentially planar, with an r.m.s. deviation from the 24-atom porphyrin mean plane of 0.043 Å. Within the plane there is a significant elongation of the porphyrin core along the 5,15 direction, with N...N distances of 3.160 (3) and 2.716 (3) Å parallel and perpendicular, respectively, to this direction. The *ipso*-C atoms of the 4-methylphenyl groups attached to the porphyrin ring in the *meso* positions are in an *anti* arrangement with displacements above and below the porphyrin plane of 0.331 (3) Å. The *n*-butyl 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.

The porphyrin molecules in the crystal structure form chains connected by edge-to-face interactions between a 4-

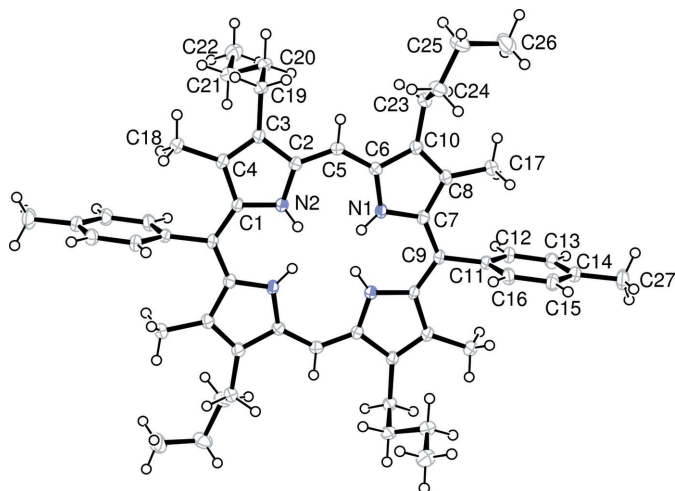


Figure 1

A plot of (1), showing 50% probability displacement ellipsoids for non-H atoms and H atoms as arbitrary spheres. The occupancy factor for each amino H atom is 0.5. Unlabelled atoms are related to labelled atoms by the symmetry code $(-x, -y, -z)$.

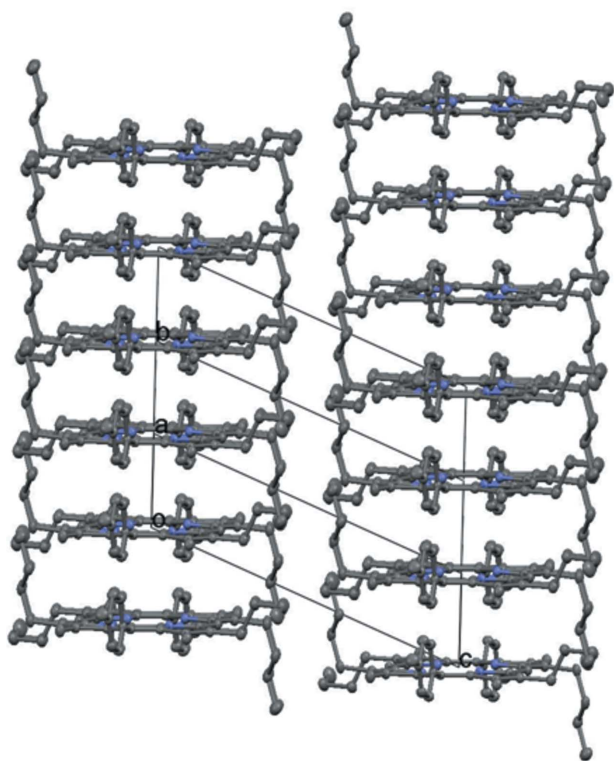


Figure 2

Two-dimensional porphyrin assemblies separated by peripheral *n*-butyl groups. H atoms have been omitted.

methylphenyl and the porphyrin ring, as previously found in related porphyrins (Bond *et al.*, 2002). Two phenyl H atoms are in close approach to the N2/C1–C4 pyrrole rings ($H \cdots \text{centroid} = 2.84 \text{ \AA}$), on either side of the porphyrin ring, at distances expected for $C-H \cdots \pi$ interactions (Medaković *et al.*, 2004). The porphyrin interplanar separation is $3.673(2) \text{ \AA}$ with the planes parallel. There are further close approaches of phenyl H atoms to the C8 atoms of porphyrins

in adjacent chains. This leads to two-dimensional porphyrin assemblies separated by *n*-butyl groups in a similar manner to the *n*-hexyl porphyrins (Bond *et al.*, 2002) (Fig. 2).

Experimental

Compound (1) was prepared using a similar method to that reported previously (McCallien *et al.*, 1997). A solution of 2,8-dimethyl-3,7-dibutyl-5,10-dihydropyromethane (0.499 g, 2.2 mmol), 4-nitrobenzaldehyde (0.134 g, 0.89 mmol) and, 4-methylbenzaldehyde (0.1 ml, 0.85 mmol) in dichloromethane (60 ml) was saturated with nitrogen for 15 min. Trifluoroacetic acid (0.24 μl) was then added and the resulting mixture was stirred at room temperature for 2 h under nitrogen. 2,3-Dichloro-4,5-dicyano-1,4-benzoquinone (0.6 g, 2.6 mmol) was added and the mixture was stirred for 15 min. Saturated sodium bicarbonate (50 ml) was added and the organic layer was washed with water ($3 \times 50 \text{ ml}$), dried and purified using column chromatography [silica, hexane–dichloromethane (60:40) eluant]. The product was characterized by ^1H NMR spectroscopy. Crystals of (1) were grown by slow evaporation of a hexane–diethyl ether solution (1:1).

Crystal data

$\text{C}_{54}\text{H}_{66}\text{N}_4$
 $M_r = 771.11$
 Triclinic, $P\bar{1}$
 $a = 7.0708(1) \text{ \AA}$
 $b = 10.8464(2) \text{ \AA}$
 $c = 15.4009(1) \text{ \AA}$
 $\alpha = 108.474(1)^\circ$
 $\beta = 102.774(1)^\circ$
 $\gamma = 91.093(1)^\circ$

$V = 1087.46(3) \text{ \AA}^3$
 $Z = 1$
 $D_x = 1.177 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 0.07 \text{ mm}^{-1}$
 $T = 83(2) \text{ K}$
 Lath, purple
 $0.52 \times 0.16 \times 0.04 \text{ mm}$

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: none
 9807 measured reflections

4112 independent reflections
 2863 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$
 $\theta_{\text{max}} = 25.8^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.067$
 $wR(F^2) = 0.154$
 $S = 1.19$
 4112 reflections
 262 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0219P)^2 + 1.3557P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$

H atoms were placed in calculated positions ($N-H = 0.86 \text{ \AA}$ and $C-H = 0.93-0.97 \text{ \AA}$) and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2$ or 1.5 times $U_{\text{eq}}(\text{C})$.

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: *ORTEP III* (Burnett & Johnson, 1996) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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