Crystal data

$C_{12}H_{12}N_2$
M_r = 184.24
Monoclinic
$P2_1/c$
a = 6.775 (5) Å
b = 11.146 (3) Å
c = 7.055 (4) Å
β = 111.72 (6)°
V = 494.9 (4) Å^3
Z = 2
D_x = 1.241 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 50 reflections
θ = 3.24–24.89°
μ = 0.075 mm^{-1}
T = 150 (2) K
Prism
0.35 × 0.32 × 0.11 mm
Colourless

Data collection

Delft Instruments FAST-TV area-detector diffractometer
Scan method: Darr *et al.* (1993)
Absorption correction: none
1612 measured reflections
742 independent reflections

613 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.100
$\theta_{\rm max}$ = 24.89°
$h = -7 \rightarrow 8$
$k = -12 \rightarrow 6$
$l = -8 \rightarrow 7$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.135
S = 1.065
742 reflections
65 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0766P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max}$ = 0.010
$\Delta\rho_{\rm max}$ = 0.213 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.266 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C1	1.338 (2)	C2—C3	1.383 (3)
N1—C5	1.353 (2)	C3—C4	1.377 (2)
C1—C2	1.390 (3)	C4—C5	1.386 (2)
C1—C6	1.503 (3)	C5—C5$^{\rm i}$	1.485 (3)
C1—N1—C5	118.37 (15)	C4—C3—C2	118.94 (18)
N1—C1—C2	122.28 (16)	C3—C4—C5	119.26 (16)
N1—C1—C6	116.12 (18)	N1—C5—C4	122.08 (15)
C2—C1—C6	121.60 (17)	N1—C5—C5$^{\rm i}$	116.50 (18)
C3—C2—C1	119.06 (17)	C4—C5—C5$^{\rm i}$	121.41 (17)

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

The absence of any intensity decay was confirmed by comparing intensities of equivalent reflections at the beginning and end of data collection. The methyl groups were allowed torsional freedom during the course of the refinement. H atoms were included in calculated positions (riding model), with $U_{\rm iso}$ set at 1.2 (CH) and 1.5 (CH_3) times the $U_{\rm eq}$ of the parent atoms.

Data collection: *MADNES* (Pflugrath & Messerschmidt, 1989). Cell refinement: *REFINE* in *MADNES*. Data reduction: *ABSMAD* (Karaulov, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SNOOPI* (Davies, 1983). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1167). Services for accessing these data are described at the back of the journal.

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5,15-Bis(3,5-di-*tert*-butylphenyl)-10,20-bis(trimethylsilylethynyl)porphyrin

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Abstract

In the title compound, $C_{58}H_{70}N_4Si_2$, the acetylene groups lie in the plane of the porphyrin π system. The angle between the plane of each phenyl ring and the plane of the porphyrin is 62.39 (4)°. There are no π–π

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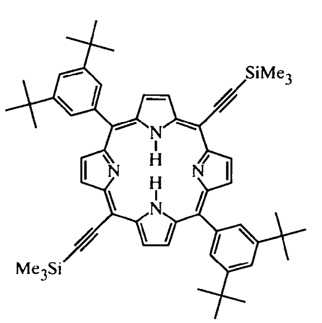
interactions between neighbouring porphyrin rings in the crystal structure.

Comment

meso-Ethynyl porphyrins have attracted attention because of their use in the synthesis of conjugated electronic materials (Piet *et al.*, 1997; Milgrom *et al.*, 1997; Lecours *et al.*, 1996). We recently reported (Wilson & Anderson, 1996) an efficient synthesis of 5,15-bis-(3,5-di-*tert*-butylphenyl)-10,20-bis(trimethylsilylethynyl)-porphyrin, (I), in two steps from pyrrole. This is a useful monomer from which to build conjugated porphyrin oligomers because the 3,5-di-*tert*-butylphenyl substituents make these compounds very soluble in organic solvents, presumably by blocking the π–π interactions which normally lead to porphyrin aggregation. The crystal structure reported here shows that porphyrin π–π stacking is prevented in the solid state.



(I)

Each molecule lies across a crystallographic inversion centre and has imposed C_i symmetry (Fig. 1). The 24 atoms of the porphyrin macrocycle all lie within 0.08 Å of their least-squares plane. The axes of the acetylene group (C11···Si1) and the aryl ring (C16···C19) form angles of 16.81 (6) and 18.34 (4)°, respectively, with this mean plane. The plane of each aryl ring is twisted by 62.39 (4)° with respect to the plane of the porphyrin. A search of the Cambridge Structural Database (Allen & Kennard, 1993) showed that this is typical for porphyrins with neither β-pyrollic nor *ortho*-aryl substituents; 462 fragments of this type were identified, giving a mean aryl–porphyrin torsion angle of 71 (11)°.

The triple-bond length is 1.2067 (19) Å, which is normal for an arylethynyltrimethylsilane (mean 1.19 Å) (Nieger *et al.*, 1996; Fujita *et al.*, 1995); conjugation to the porphyrin does not significantly affect the C≡C bond length. A similar observation has been made for the crystal structures of two other 5,15-diaryl-10,20-diethynylporphyrins (Lecours *et al.*, 1996).

The shortest intermolecular contacts are between methyls of the *tert*-butyl and trimethylsilane groups (H···H distances vary from 2.35 to 2.80 Å). The π–π stacking interactions which are often found in porphyrin crystal-packing arrangements (Hunter & Sanders, 1990) seem to be blocked by the presence of the bulky aryl substituents.

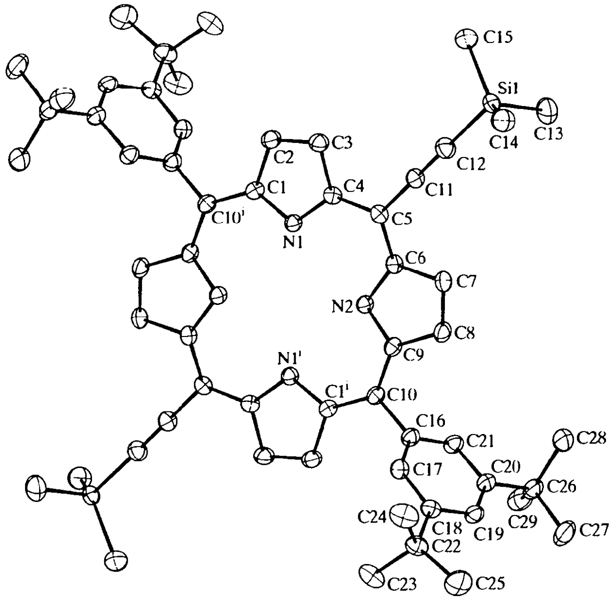


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

The title compound was synthesized as described earlier (Wilson & Anderson, 1996). Crystals suitable for X-ray studies were obtained by slow evaporation of a solution in CHCl$_3$–MeOH–CH$_3$CN (3:1:1).

Crystal data

$C_{58}H_{70}N_4Si_2$
$M_r = 879.36$
Monoclinic
$P2_1/n$
$a = 13.436\ (2)$ Å
$b = 14.584\ (4)$ Å
$c = 14.327\ (3)$ Å
$\beta = 104.891\ (15)°$
$V = 2713.0\ (10)$ Å^3
$Z = 2$
$D_x = 1.076$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 22.31$–$42.35°$
$\mu = 0.877$ mm^{-1}
$T = 213\ (2)$ K
Plate
0.45 × 0.30 × 0.15 mm
Dark blue

Data collection

Enraf–Nonius MACH-3 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.742$, $T_{max} = 0.877$

4731 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 74.27°$
$h = -16 \rightarrow 16$
$k = -18 \rightarrow 18$
$l = 0 \rightarrow 17$

11 202 measured reflections
5500 independent reflections

3 standard reflections
frequency: 120 min
intensity decay: 4.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.120$
$S = 1.055$
5500 reflections
290 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0727P)^2 + 0.5393P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.377$ e Å^{-3}
$\Delta\rho_{\min} = -0.332$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0023 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected torsion angles (°)*

N1—C4—C5—C11	178.99 (11)	C11—C5—C6—C7	2.64 (17)
C3—C4—C5—C11	−1.86 (18)	C1^{i}—C10—C16—C17	60.51 (16)

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

The title structure was solved by direct methods followed by Fourier synthesis and refined by anisotropic full-matrix least-squares methods for all non-H atoms; the H atoms were placed at calculated positions and refined as riding using *SHELXL*97 (Sheldrick, 1997) defaults [N—H 0.87, C—H 0.94 and C—H(methyl) 0.97 Å]. The two central H atoms (N—H) were located from a ΔF map and found to be disordered over the four N atoms; they were placed in four calculated positions, each with 50% occupancy.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1995). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *XCAD*-4 (Harms & Wolcaldo, 1996). Program(s) used to solve structure: *SHELXS*90 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97. Molecular graphics: *CAMERON* (Watkin *et al.*, 1993). Software used to prepare material for publication: *SHELXL*97 and *PARST*95 (Nardelli, 1995).

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Δ^4-7,7-Ethylenedioxy-10-methyloctal-1-one[†]

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Abstract

The structure of an important decaline intermediate, $C_{13}H_{18}O_3$, in the total synthesis of corymbolone has been determined. The structure is stabilized by van der Waals interactions only.

Comment

Corymbolone is a natural sesquiterpene extracted from an Amazon forest plant called Piri-piri. The unrefined extract from this plant is used by Brazilian Indians to induce abortion. During recent work (Souza *et al.*, 1993; Muzzi & Ferraz, unpublished results) which culminated in the total synthesis of corymbolone, (I) (Garbarino *et al.*, 1985), and corymbolol (Nyasse *et al.*, 1988), the title compound, (II), was obtained as an advanced intermediate in five steps starting from the Wieland–Miescher ketone. The title compound was also observed as an intermediate in other syntheses (Guile *et al.*, 1992).

[†] Alternative name: 4a′-methyl-1′,2′,3′,4′,6′,7′-hexahydrospiro[1,3-dioxolane-2,2′-naphthalen]-5′(4a′*H*)-one.