2,8,12,18-Tetrabutyl-3,7,13,17-tetramethyl-5,15-bis(3-nitrophenyl)porphyrinogen methanol disolvate

Peter D. W. Boyd,* Ali Hosseini and Clifton E. F. Rickard

Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand

Correspondence e-mail:
pdw.boyd@auckland.ac.nz

The title compound, $C_{52}H_{66}N_6O_4 \cdot 2CH_3OH$, is a 5,15-diaryl-octaalkylporphyrinogen. The molecule is centrosymmetric, with the pyrrole rings adopting a 1,2-alternate arrangement. The methanol molecules are included in the tetrapyrrole cavity through hydrogen bonding and $O-H\cdots\pi$ interactions. The molecules form chains in the crystal structure *via* phenyl $C-H\cdots\pi$-pyrrole stacking.

Comment

The synthesis of 5,15-diaryloctaalkylporphyrins from the corresponding dipyrromethane is a two-step procedure involving an acid-catalysed reaction with an arylaldehyde to form a porphyrinogen, followed by oxidation of the tetra-pyrrolic macrocycle to the porphyrin (Young *et al.*, 1985). During the synthesis of 5,15-bis(3-nitrophenyl)-2,8,12,18-tetrabutyl-3,7,13,17-tetramethylporphyrin from 2,8-dimethyl-3,7-dibutyl-5,10-dihydrodipyrromethane and 3-nitrobenz-aldehyde, yellow crystals of the title intermediate porphyrin-ogen, (I), were formed. The structure of (I) is the first reported for this type of porphyrinogen intermediate bridged by methylene –CH_2– groups.

(I)
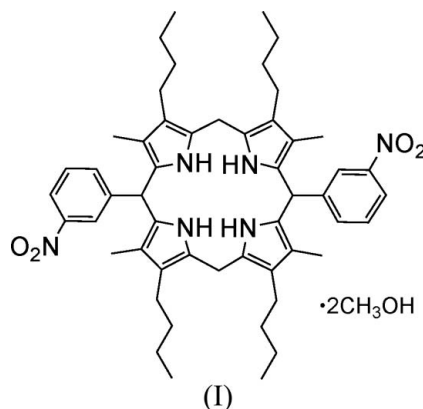
The molecular structure of (I) is shown in Fig. 1. The molecule possesses a crystallographic inversion centre. Bond lengths and angles in the porphyrinogen ring core are comparable with those found in similar calix[4]pyrrole derivatives (Gale *et al.*, 1998; Turner *et al.*, 1998). The porphyrin-ogen ring adopts a 1,2-alternate conformation, similar to that found in calix[4]arenes (Arduini *et al.*, 1997) and some calix[4]pyrroles (Turner *et al.*, 1998). The centrosymmetrically related methanol molecules lie above and below the porphyrinogen ring. These are connected to the macrocycle *via* two hydrogen bonds between methanol atom O3 and the pyrrole H atoms on atoms N1 and N2 (Table 1). Each methanol H atom is centred over the N1-pyrrole ring *via* an
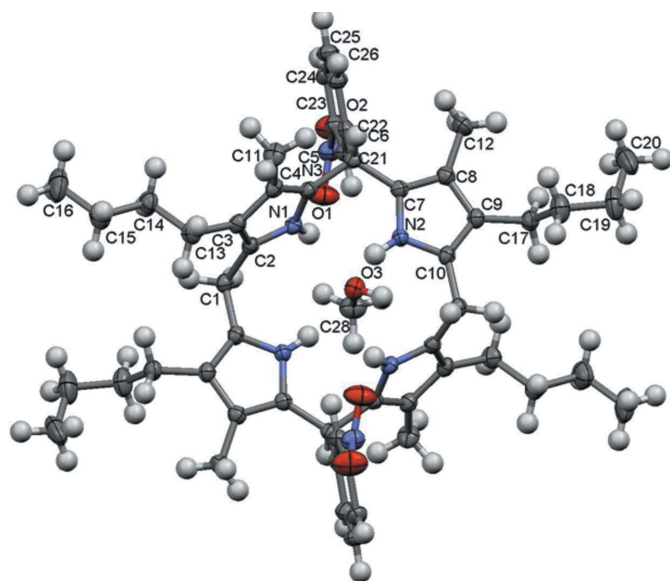
Figure 1
The molecular structure of (I), with 50% probability displacement ellipsoids (arbitrary spheres for H atoms). Unlabelled atoms are related to labelled atoms by the symmetry operator $(-x, -y, -z)$.
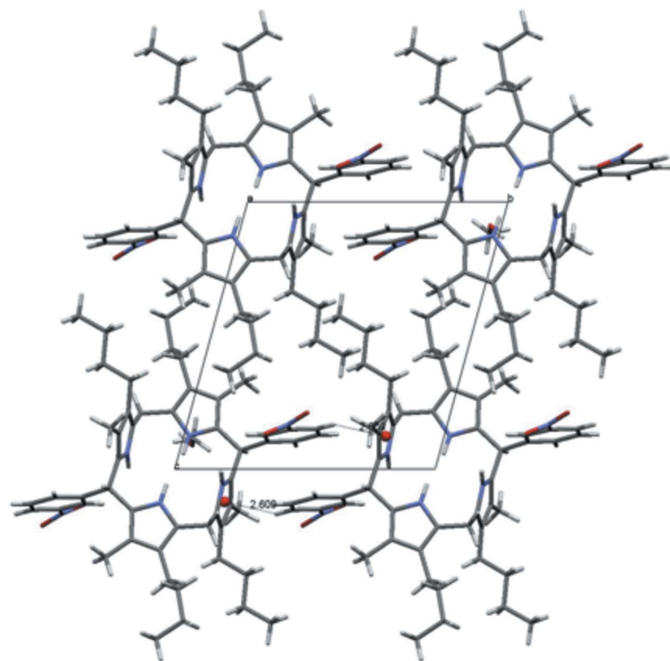

Figure 2
The porphyrin chains of (I), aligned in a two-dimensional assembly, viewed along the a axis. Phenyl $C—H\cdots\pi$ interactions are shown as thin lines and red spheres denote ring centroids.

O—H$\cdots\pi$ interaction, with an H3$\cdots Cg$ separation of 2.62 Å and an O3—H3$\cdots Cg$ angle of 131° (Cg is the centroid of the N1-pyrrole ring).

A C—H$\cdots\pi$ interaction between the nitrophenyl group and the pyrrole ring occurs in the crystal structure, with a C24—H24$\cdots Cg^a$ angle of 150° and an H24$\cdots Cg^a$ [symmetry code: (a) $-x, -y, -z$] separation of 2.61 Å. Weak intermolecular C11—H11$C\cdots$O2 hydrogen bonding is also observed in the crystal structure (Table 1).

Experimental

A mixture of 4,4′-di-butyl-3,3′-dimethyl-2,2′-dipyrrylmethane (1.04 g, 3.63 mmol) and 3-nitrobenzaldehyde (0.552, 3.65 mmol) in methanol (100 ml) was flushed with nitrogen in the absence of light and cooled in an ice bath for 30 min. To this mixture, trifluoroacetic acid (140 µl) was added and the solution was stirred for 2 h, during which time yellow crystals of (I) were formed (0.986 g, 32%).

Crystal data

$C_{52}H_{66}N_6O_4\cdot 2CH_4O$	$V = 1263.42\ (3)$ Å^3
$M_r = 903.19$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 1.187$ Mg m^{-3}
$a = 8.2665\ (1)$ Å	Mo $K\alpha$ radiation
$b = 12.2138\ (1)$ Å	$\mu = 0.08$ mm^{-1}
$c = 13.0914\ (2)$ Å	$T = 150\ (2)$ K
$\alpha = 104.754\ (1)°$	Thick plate, yellow
$\beta = 97.430\ (1)°$	$0.34 \times 0.32 \times 0.18$ mm
$\gamma = 92.499\ (1)°$	

Data collection

Siemens SMART CCD area-detector diffractometer	4571 independent reflections
ω scans	4193 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{int} = 0.026$
9845 measured reflections	$\theta_{max} = 25.3°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1122P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.044$	$+ 0.8341P]$
$wR(F^2) = 0.145$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.81$	$(\Delta/\sigma)_{max} = 0.003$
4571 reflections	$\Delta\rho_{max} = 0.25$ e Å^{-3}
302 parameters	$\Delta\rho_{min} = -0.29$ e Å^{-3}
H-atom parameters constrained	

Table 1
Hydrogen-bond geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N1—H1$A\cdots$O3	0.88	2.22	2.9930 (16)	147
N2—H2$A\cdots$O3^i	0.88	2.25	3.0881 (17)	160
C11—H11$C\cdots$O2^{ii}	0.98	2.48	3.312 (2)	143

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, -y + 1, -z$.

Methyl H atoms were placed in calculated positions, with C—H = 0.98 Å, and torsion angles were refined to fit the electron density; $U_{iso}(H) = 1.5U_{eq}(C)$. Other H atoms were placed in calculated positions, with N—H = 0.88 Å and C—H = 0.95–1.00 Å, and were refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(N,C)$.

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: *MERCURY* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

Arduini, A., Domiano, L., Pochini, A., Secchi, A., Ungaro, R., Ugozzoli, F., Struck, O., Verboom, W. & Reinhoudt, D. N. (1997). *Tetrahedron*, **53**, 3767–3776.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Gale, P. A., Sessler, J. L. & Kral, V. (1998). *Chem. Commun.* pp. 1–8.

Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Siemens (1995). *SHELXTL* (Version 5), *SMART* (Version 4.050) and *SAINT* (Version 4.050). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Turner, B., Botoshansky, M. & Eichen, Y. (1998). *Angew. Chem. Int. Ed.* **37**, 2475–2478.

Young, R., Chris, K. & Chang, C. K. (1985). *J. Am. Chem. Soc.* **107**, 898–909.