

Structure of a Non-Mesogen Porphyrin, 5,10,15,20-Tetrakis[4-(1-hexyloxy)phenyl]porphyrin

BY MRINALINI G. WALAWALKAR, M. NETHAJI AND V. KRISHNAN*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560 012, India

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Abstract. 2,7,12,17-Tetrakis[4-(1-hexyloxy)phenyl]-21,22,23,24-tetraazapentacyclo[16.2.1.1^{3,6}.1^{8,11}.1^{13,16}]-tetracos-1,3,5,7,9,11(23),12,14,16,18(21),19-undecene, $C_{68}H_{78}N_4O_4$, $M_r = 1015.4$, orthorhombic, $Pcan$, $a = 10.931$ (6), $b = 18.907$ (3), $c = 28.959$ (6) Å, $V = 5985$ (4) Å³, $Z = 4$, $D_x = 1.127$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.65$ cm⁻¹, $F(000) = 2184$, $T = 291$ K, final $R = 0.0853$, $wR = 0.0907$ for 1353 significant reflections [$|F_o| \geq 4.0\sigma|F_o|$]. The porphyrin ring is planar and bears four long alkyl chains; two of the alkyl chains are above the macrocyclic porphyrin plane while the other two are below the plane. The phenyl rings are perpendicular to this plane. The porphyrin nuclei are packed loosely in tilted columns along the y axis.

Introduction. Porphyrins bearing long alkyl chains are important from a molecular electronic point of view since they exhibit thermotropic mesomorphism (Goodby, Robinson, Teo & Clad, 1980; Gregg, Fox & Bard, 1987, 1989*a,b*; Giroud-Godquin & Maitlis, 1991; Shimizu, Miya, Nagata, Ohta, Matsumura, Yamamoto & Kusabayashi, 1991). In the course of our study on tetraalkylporphyrins, it was found that 5,10,15,20-tetrakis[4-(1-hexadecyloxy)phenyl]porphyrin exhibits a discotic lamellar phase, though the lower homologue, the title compound, does not exhibit mesomorphic transitions (Walawalkar & Krishnan, 1992). The structure of the title compound becomes important in understanding the mesomorphic behaviour of the higher homologue. The structures of alkyl porphyrins thus far determined are those of 5,10,15,20-tetrakis(1-propyl)porphyrin (Coddling & Tulinsky, 1972) and a Zn^{II} derivative of 5,10,15,20-tetrakis[4-(1-octyl)phenyl]porphyrin (Chiaroni, Riche, Bied-Charreton & Dubois, 1988).

Experimental. Air-stable single crystals of X-ray quality were obtained as pink parallelepiped plates by cooling a chloroform solution to 273 K. A crystal

of dimensions $0.70 \times 0.50 \times 0.02$ mm was chosen for diffraction studies. 25 well centered reflections in the range $16 \leq 2\theta \leq 32^\circ$ were chosen to refine the unit-cell parameters. Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation in the range $2 \leq 2\theta \leq 36^\circ$ ($0 \leq h \leq 9$, $0 \leq k \leq 16$, $0 \leq l \leq 25$) using ω - 2θ scans. Intensities of three reflections checked after every 1 h showed no significant decay in the intensity measurements. In all, 2455 reflections were measured, of which 2055 were unique and 1353 had [$|F_o| \geq 4.0\sigma|F_o|$]. The data were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1986). Full-matrix least-squares refinement was carried out on $|F_o|$ for non-H atoms with anisotropic thermal parameters using *SHELX76* (Sheldrick, 1976). One of the two alkyl chains showed large thermal vibrations. The H atoms were located in difference Fourier maps and refined isotropically with individual weighting schemes based on counting statistics, where $w = [\sigma^2(|F_o|) + 0.00001F_o^2]^{-1}$. The final discrepancy factors were $R = 0.0853$, $wR = 0.0907$, $S = 2.89$ for 427 refined parameters; $(\Delta/\sigma)_{\max} = 0.18$, $(\Delta/\sigma)_{\min} = -0.17$. The residual electron density in the final difference map was less than 0.33 e Å⁻³, with a minimum of -0.17 e Å⁻³. The scattering factors were used as in *SHELX76*. The low accuracy of the structure may result from the poor quality of the crystal, caused by the large thermal vibrations in the alkyl chains.

Discussion. A perspective view of the molecule with atomic labelling is shown in Fig. 1. The fractional atomic coordinates and bond distances and angles are given in Tables 1† and 2, respectively.

† Lists of H-atom coordinates, anisotropic thermal parameters, bond lengths and bond angles involving H atoms, torsion angles for non-H atoms, least-squares planes and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55503 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Address for correspondence: Jawaharlal Neharu Centre for Advanced Studies, Indian Institute of Science Campus, Bangalore-560 012, India.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for non-H atoms

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
N1	0.0797 (7)	0.0618 (5)	0.4505 (3)	56 (4)
C1	0.1413 (10)	0.0367 (7)	0.4129 (4)	62 (5)
C2	0.1848 (9)	0.0954 (8)	0.3859 (3)	66 (4)
C3	0.1542 (10)	0.1552 (5)	0.4077 (4)	62 (5)
C4	0.0866 (10)	0.1348 (7)	0.4490 (5)	62 (5)
C5	0.0378 (10)	0.1782 (6)	0.4832 (5)	53 (5)
C6	-0.0216 (9)	0.1580 (6)	0.5226 (4)	52 (5)
C7	-0.0690 (10)	0.2045 (5)	0.5567 (5)	64 (5)
C8	-0.1217 (9)	0.1643 (7)	0.5885 (4)	70 (6)
C9	-0.1088 (9)	0.0914 (6)	0.5762 (4)	55 (6)
C10	-0.1550 (9)	0.0351 (7)	0.6010 (4)	60 (5)
N2	-0.0440 (7)	0.0884 (5)	0.5350 (3)	57 (4)
C11	0.0534 (12)	0.2565 (6)	0.4744 (3)	60 (5)
C12	-0.0269 (9)	0.2950 (7)	0.4475 (4)	71 (5)
C13	-0.0144 (11)	0.3659 (7)	0.4391 (4)	76 (5)
C14	0.0820 (11)	0.4021 (7)	0.4598 (4)	62 (5)
C15	0.1616 (11)	0.3662 (7)	0.4880 (4)	81 (5)
C16	0.1437 (11)	0.2953 (8)	0.4943 (4)	93 (6)
O1	0.0911 (7)	0.4726 (4)	0.4491 (2)	78 (3)
C21	0.1861 (11)	0.5121 (5)	0.4741 (3)	91 (5)
C22	0.1863 (10)	0.5839 (5)	0.4511 (4)	80 (4)
C23	0.2410 (10)	0.5827 (5)	0.4028 (4)	79 (5)
C24	0.2560 (11)	0.6549 (6)	0.3814 (4)	107 (6)
C25	0.3149 (14)	0.6537 (8)	0.3334 (5)	142 (7)
C26	0.3426 (17)	0.7281 (8)	0.3137 (6)	204 (10)
C31	-0.2399 (15)	0.0503 (5)	0.6418 (5)	70 (6)
C32	-0.3624 (16)	0.0519 (7)	0.6348 (5)	113 (7)
C33	-0.4442 (18)	0.0714 (9)	0.6689 (8)	156 (10)
C34	-0.3892 (19)	0.0862 (8)	0.7110 (9)	140 (10)
C35	-0.2701 (20)	0.0864 (6)	0.7218 (4)	103 (7)
C36	-0.1887 (11)	0.0668 (7)	0.6847 (7)	108 (7)
O2	-0.4832 (11)	0.1084 (5)	0.7480 (4)	177 (6)
C41	-0.4209 (18)	0.1261 (9)	0.7844 (5)	169 (9)
C42	-0.5600 (25)	0.1656 (12)	0.8135 (7)	196 (12)
C43	-0.6517 (27)	0.1169 (13)	0.8200 (7)	207 (13)
C44	-0.7537 (24)	0.1596 (16)	0.8428 (9)	250 (17)
C45	-0.8502 (25)	0.1118 (16)	0.8468 (10)	260 (17)
C46	-0.9221 (24)	0.0919 (12)	0.8070 (9)	238 (14)

Table 2. Bond distances (\AA) and bond angles ($^\circ$) involving non-H atoms

N1—C1	1.37 (1)	C15—C16	1.37 (2)
N1—C4	1.38 (2)	O1—C21	1.47 (1)
C1—C2	1.44 (2)	C21—C22	1.51 (1)
C2—C3	1.34 (2)	C22—C23	1.52 (2)
C3—C4	1.46 (2)	C23—C24	1.51 (2)
C4—C5	1.39 (2)	C23—C25	1.53 (2)
C5—C6	1.37 (2)	C25—C26	1.55 (2)
C5—C11	1.51 (2)	C31—C32	1.35 (2)
C6—C7	1.42 (2)	C31—C36	1.40 (2)
C6—N2	1.39 (1)	C32—C33	1.38 (3)
C7—C8	1.33 (2)	C33—C34	1.39 (3)
C8—C9	1.43 (2)	C34—C35	1.34 (3)
C9—C10	1.38 (2)	C34—O2	1.54 (3)
C9—N2	1.39 (1)	C35—C36	1.44 (2)
C10—C31	1.53 (2)	O2—C41	1.30 (2)
C11—C12	1.38 (2)	C41—C42	1.89 (3)
C11—C16	1.36 (2)	C42—C43	1.37 (4)
C12—C13	1.37 (2)	C43—C44	1.53 (4)
C13—C14	1.39 (2)	C44—C45	1.39 (4)
C14—C15	1.37 (2)	C45—C46	1.44 (4)
C14—O1	1.37 (2)		
C1—N1—C4	107 (1)	C13—C14—C15	120 (1)
N1—C1—C2	109 (1)	C15—C14—O1	125 (1)
C1—C2—C3	108 (1)	C14—C15—C16	118 (1)
C2—C3—C4	107 (1)	C11—C16—C15	125 (1)
N1—C4—C3	108 (1)	C14—O1—C21	116 (1)
C3—C4—C5	128 (1)	O1—C21—C22	104 (1)
N1—C4—C5	123 (1)	C21—C22—C23	113 (1)
C4—C5—C11	114 (1)	C22—C23—C24	114 (1)
C4—C5—C6	128 (1)	C23—C24—C25	114 (1)
C6—C5—C11	118 (1)	C24—C25—C26	114 (1)
C5—C6—N2	124 (1)	C10—C31—C36	119 (1)
C5—C6—C7	126 (1)	C10—C31—C32	119 (1)
C7—C6—N2	110 (1)	C32—C31—C36	122 (1)
C6—C7—C8	107 (1)	C31—C32—C33	123 (2)
C7—C8—C9	110 (1)	C32—C33—C34	114 (2)
C8—C9—N2	108 (1)	C33—C34—O2	112 (2)
C8—C9—C10	125 (1)	C33—C34—C35	128 (2)
C10—C9—N2	127 (1)	C35—C34—O2	119 (2)
C9—C10—C31	119 (1)	C34—C35—C36	115 (2)
C6—N2—C9	106 (1)	C31—C36—C35	118 (1)
C5—C11—C16	123 (1)	C34—O2—C41	107 (1)
C5—C11—C12	123 (1)	O2—C41—C42	92 (1)
C12—C11—C16	115 (1)	C41—C42—C43	113 (2)
C11—C12—C13	124 (1)	C42—C43—C44	104 (2)
C12—C13—C14	119 (1)	C43—C44—C45	104 (2)
C13—C14—O1	116 (1)	C44—C45—C46	121 (3)

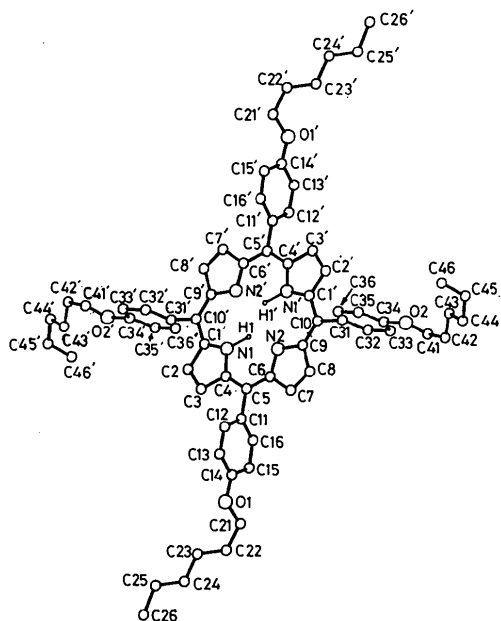


Fig. 1. PLUTO (Motherwell & Clegg, 1978) diagram of the molecule with atom labelling.

The molecule has D_{2d} symmetry. The asymmetric part contains two pyrrole rings (N1—C1—C2—C3—C4 and N2—C6—C7—C8—C9) which make an angle of $1.3 (4)^\circ$. The porphyrin core consisting of 24 atoms is almost planar and the *meso* phenyl rings attached to the C atoms C5 and C10 make dihedral angles of $83.7 (2)$ and $83.4 (3)^\circ$, respectively, with the core, whereas in the case of *meso*-tetraphenylporphyrin (Silvers & Tulinsky, 1967) the dihedral angle is about 60° . The alkyl chains on the phenyl rings (C11—C16 and C31—C36) are above the molecular plane of 24 atoms. The imino H atoms H1 and H1' are present on the opposite pyrrole rings (N1—C1—C2—C3—C4 and N1'—C1'—C2'—C3'—C4') similar to the situation observed for the *meso*-tetraphenylporphyrin (Silvers & Tulinsky, 1967). Substitution of alkyl chains at the 4-position of the phenyl rings does not have any influence on the structure of the porphyrin core.

The distance between terminal C atoms (C26 and C46) of the adjacent chains in the molecule is 18.9\AA . The porphyrin rings are arranged in tilted stacks as

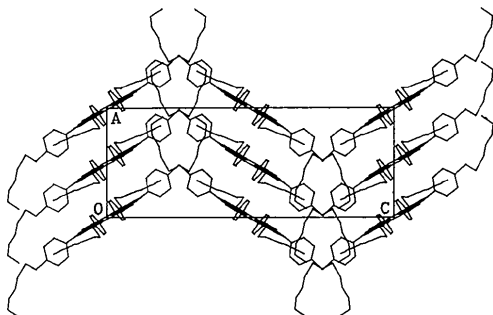


Fig. 2. Packing diagram of the molecules in the unit cell viewed down the *b* axis.

in Fig. 2. The phenyl ring attached to C5 is stacked along the *a* axis with a distance of 6.25 (2) Å. The molecule forms zigzag chains running along the *c* axis. The packing of the molecules in the unit cell is governed by van der Waals interactions.

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Structure of Methyl 4-*O*-Benzoyl-6-bromo-3-tosyl-2,6-dideoxy- β -D-arabino-hexopyranoside

BY MAREK J. JEDRZEJAS, RONALD J. BAKER,* ROGER W. BINKLEY, ROBERT L. R. TOWNS,* NANCY ADAIR, MARIA ANDRAS, FRIEDUN ANWARI, ZHENHUA CHEN, ROBERT HUFF, XIAOGAO LIU, ROBERT MARTUCH AND MICHAEL SKLADANY

Department of Chemistry, Cleveland State University, Cleveland, OH 44115, USA

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Abstract. $C_{21}H_{23}BrO_7S$, $M_r = 499.37$, monoclinic, $P2_1$, $a = 8.897$ (3), $b = 8.213$ (2), $c = 15.334$ (4) Å, $\beta = 102.69$ (3)°, $V = 1093$ (1) Å³, $Z = 2$, $D_m = 1.51$, $D_x = 1.517$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 19.89$ cm⁻¹, $F(000) = 512$, $T = 295$ K, final $R = 0.044$, $wR = 0.048$ for 1473 independent reflections with $I > 2.0\sigma(I)$ and 271 variables. The compound contains a substituted pyranose ring in the normal chair conformation. The bromomethylene, benzoyl and tosyl substituents are equatorial and the methoxy is axial.

Introduction. As part of a synthesis of several naturally occurring oligosaccharides found in the anti-

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 WALAWALKAR, M. G. & KRISHNAN, V. (1992). In preparation.

cancer agent mithramycin, a variety of partially protected monosaccharides have been prepared (Binkley, 1985). The title compound is a previously unisolated intermediate in the preparation of 2,6-dideoxy sugars to be used as oligosaccharide building blocks (Binkley & Sivik, 1986) and represents the first reported structural characterization of this class of compound by single-crystal X-ray diffraction.

Experimental. The title compound was formed in 30% yield by stirring an ethyl acetate solution of methyl 4-*O*-benzoyl-2,6-dibromo-2,6-dideoxy- β -D-arabino-hexopyranoside in the presence of Raney nickel powder for 24 h under an atmosphere of hydrogen. The Raney nickel was removed by filtration.

* Authors to whom correspondence should be addressed.