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7,8,17,18-Tetrabromo-5,10,15,20-tetraphenylporphyrin, C₄₄H₂₆Br₄N₄

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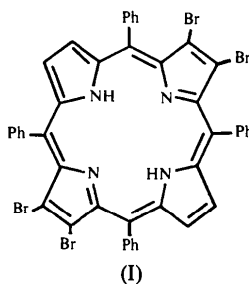
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Abstract

The molecular structure determination of the title compound shows that four Br atoms are located on antipodal pyrrole rings. The macrocyclic skeleton, including the four Br atoms, is almost planar, in spite of the presence of the bulky Br atoms on the porphyrin periphery.

Comment

There is increasing interest in reactions of the pyrrole rings on the periphery of porphyrins. With regard to the electrophilic bromination on 5,10,15,20-tetraphenylporphyrin (TTP), the reported results have been contradictory (Crossley, Burn, Chew, Cuttance & Newsom, 1991; Callot, 1974). Callot (1974) suggested that there existed one Br atom per pyrrole ring, but the results reported by Crossley *et al.* (1991) indicated four Br atoms on the antipodal pyrrole rings. In order to resolve this discrepancy, we prepared the title compound, (I), following the literature method (Crossley *et al.*, 1991) and obtained suitable specimens for crystal structure analysis by layering a solution of the title compound in CHCl₃ with petroleum/piperidine (333–363 K).



Our results show that four Br atoms are located on the antipodal (transannular) pyrrole rings, as shown in Fig. 1; this is in agreement with the conclusion drawn by Crossley *et al.* (1991). Thus, electrophilic bromination

occurs regiospecifically at the antipodal pyrrole ring of free-base porphyrin.

The C12—C13 and C42—C43 bond lengths are 1.33 (2) and 1.36 (2) Å, respectively, and the distances between N1 and N1ⁱ, and N2 and N2ⁱ, are 4.21 (2) and 4.10 (2) Å, respectively. The corresponding C—C bond lengths and N···N distances in TPP are 1.345 and 4.2 Å, respectively (Silvers & Tulinsky, 1964). The observed deviations are attributable to the electron-withdrawing properties of the Br atoms on the pyrrole rings. Adjacent pyrrole rings in the title compound are tilted by 4.8 (5)° with respect to each other, indicating that the macrocycle skeleton is almost planar despite the large-volume Br atoms on the porphyrin periphery.

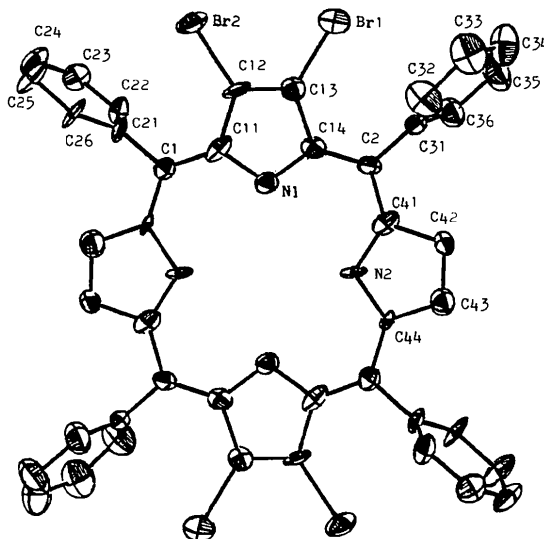


Fig. 1. A view of the molecular structure with 50% probability displacement ellipsoids. H atoms are omitted for clarity.

Experimental

Crystal data

C₄₄H₂₆Br₄N₄
M_r = 930
Monoclinic
P2₁/n
a = 13.945 (8) Å
b = 6.751 (8) Å
c = 19.326 (3) Å
β = 101.4 (9)°
V = 1783.3 Å³
Z = 2
D_x = 1.73 Mg m⁻³
D_m = 1.774 Mg m⁻³

Data collection

Enraf–Nonius CAD-4
diffractometer
ω/2θ scans [width (0.99 +
0.35tanθ)° in ω; speed
4° min⁻¹]

Mo Kα radiation
λ = 0.71073 Å
Cell parameters from 25
reflections
θ = 10–14°
μ = 4.5 mm⁻¹
T = 293 K
Prism
0.4 × 0.3 × 0.2 mm
Purple

1931 observed reflections
[F_o > 3σ(F_o)]
R_{int} = 0.022
θ_{max} = 25°
h = 0 → 16

Absorption correction: $k = 0 \rightarrow 8$
 refined from ΔF $l = -23 \rightarrow 23$
 3532 measured reflections 3 standard reflections
 2204 independent reflections intensity decay: 15%

Refinement

Refinement on F $(\Delta/\sigma)_{\max} = 0.08$
 $R = 0.074$ $\Delta\rho_{\max} = 0.64 \text{ e } \text{\AA}^{-3}$
 $wR = 0.081$ $\Delta\rho_{\min} = 0.0 \text{ e } \text{\AA}^{-3}$
 $S = 3.89$ Extinction correction: none
 1517 reflections Atomic scattering factors
 283 parameters from *International Tables*
 H-atom parameters not for *X-ray Crystallography*
 refined (1974, Vol. IV)
 $w = 1/\sigma^2(F)$

C14—C2—C31 122 (1) N2—C44—C43 106 (1)
 C14—C2—C41 123 (1) C1'—C44—C43 126 (1)
 C31—C2—C41 114 (1) C12—C11—N1 109 (1)
 Symmetry code: (i) $-x, -y, -z$.

Data collection was performed using *CAD-4 Software* (Enraf-Nonius, 1989). All calculations were performed on a PDP11/44 computer with *SDP* (Enraf-Nonius, 1985) programs. The structure was solved by direct methods and difference Fourier syntheses; refinement was by the full-matrix least-squares method. The coordinates of the H atoms were calculated according to theoretical methods.

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Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Br1	0.3823 (1)	0.4604 (3)	0.0159 (1)	5.07 (4)
Br2	0.2451 (1)	0.7266 (2)	0.10589 (8)	3.72 (3)
C12	0.2054 (9)	0.479 (2)	0.0658 (7)	2.6 (3)
C13	0.2557 (9)	0.385 (2)	0.0241 (7)	2.4 (3)
C11	0.117 (1)	0.368 (2)	0.0668 (7)	2.6 (3)
C14	0.1984 (9)	0.211 (2)	-0.0047 (7)	2.02 (2)
N1	0.1145 (7)	0.207 (2)	0.0230 (5)	2.3 (2)
N2	0.0778 (7)	-0.153 (1)	-0.0622 (6)	2.0 (2)
C1	0.0491 (9)	0.405 (2)	0.1083 (7)	2.5 (3)
C2	0.2222 (9)	0.078 (2)	-0.0532 (7)	2.4 (3)
C21	0.0691 (9)	0.555 (2)	0.1648 (7)	2.5 (3)
C22	0.136 (1)	0.514 (2)	0.2272 (7)	3.4 (3)
C23	0.152 (1)	0.651 (2)	0.2808 (7)	3.3 (3)
C24	0.104 (1)	0.827 (2)	0.2732 (9)	4.6 (4)
C25	0.040 (1)	0.873 (2)	0.2133 (9)	4.3 (4)
C26	0.020 (1)	0.737 (2)	0.1597 (7)	3.3 (3)
C31	0.3055 (9)	0.110 (2)	-0.0875 (7)	2.7 (3)
C32	0.295 (1)	0.259 (3)	-0.1409 (9)	4.9 (4)
C33	0.460 (1)	0.185 (3)	-0.1560 (9)	5.7 (5)
C34	0.381 (1)	0.299 (3)	-0.170 (1)	5.7 (5)
C35	0.469 (1)	0.034 (4)	-0.106 (1)	6.0 (5)
C36	0.388 (1)	0.001 (2)	-0.0732 (8)	4.0 (3)
C41	0.165 (1)	-0.089 (2)	-0.0778 (7)	2.6 (3)
C42	0.1831 (9)	-0.219 (2)	-0.1345 (6)	2.6 (3)
C43	0.105 (1)	-0.344 (2)	-0.1504 (7)	3.2 (3)
C44	0.0397 (9)	-0.310 (2)	-0.1052 (7)	2.2 (2)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Br1—C13	1.86 (1)	C1—C11	1.38 (2)
Br2—C12	1.88 (1)	C1—C21	1.47 (2)
C12—C13	1.33 (2)	C1—C44'	1.39 (2)
C12—C11	1.45 (2)	C2—C14	1.38 (2)
C13—C14	1.47 (2)	C2—C31	1.46 (2)
N1—C11	1.38 (2)	C2—C41	1.41 (2)
N1—C14	1.38 (2)	C41—C42	1.47 (2)
N2—C41	1.38 (2)	C42—C43	1.36 (2)
N2—C44	1.38 (2)	C43—C44	1.40 (2)
Br2—C12—C13	122 (1)	C12—C11—C1	127 (1)
Br2—C12—C11	130 (1)	N1—C11—C1	124 (1)
C13—C12—C11	108 (1)	C13—C14—N1	108 (1)
Br1—C13—C12	123 (1)	C13—C14—C2	126 (1)
Br1—C13—C14	129 (1)	N1—C14—C2	126 (1)
C12—C13—C14	108 (1)	N2—C41—C2	130 (1)
C11—N1—C14	108 (1)	N2—C41—C42	105 (1)
C41—N2—C44	111 (1)	C2—C41—C42	124 (1)
C11—C1—C21	120 (1)	C41—C42—C43	107 (1)
C11—C1—C44'	127 (1)	C42—C43—C44	110 (1)
C21—C1—C44'	113 (1)	N2—C44—C1'	128 (1)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1026). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Homogentisic Acid

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Abstract

The plane of the acetic acid side chain of the title compound (2,5-dihydroxybenzeneacetic acid, $\text{C}_8\text{H}_8\text{O}_4$) is nearly perpendicular to that of the benzene ring. Molecules are linked through hydrogen bonds of the $\text{O—H} \cdots \text{O}$ type.

Comment

Homogentisic acid, (I), is a famous intermediate of phenylalanine and tyrosine metabolism (Martin, Mayes & Rodwell, 1983). It is found in the urine of patients with alkaptonurea. It is produced by oxidation of *p*-