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3,6,13,16-Tetrabromo-2,7,12,17-tetrapropylporphycene

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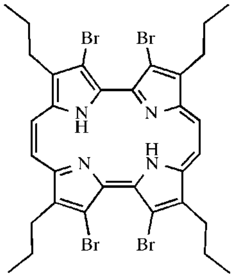
The title compound [systematic name: 3,10,13,20-tetrabromo-4,9,14,19-tetrapropyl-21,22,23,24-tetraazapentacyclo[16.2.1.-$1^{2,5}.1^{8,11}.1^{12,15}$]tetracosa-2(22),3,5,7,9,11,13,15(24),16,18,20-undecaene], $C_{32}H_{34}Br_4N_4$, crystallizes in two distinct crystalline forms, *viz*. monoclinic prisms and triclinic plates, and the first of these is described here. The molecule of the prismatic form has a centre of symmetry and a more warped structure than that of the triclinic plate-like form. The shape of the central N_4 cavity is rectanglar, enlarged in the direction of the methine-bridge C atoms, and the N···N distances are 2.713 (3) and 2.818 (3) Å.

Comment

Porphycene is one of the unique isomers of porphyrin first synthesized in 1986 (Vogel *et al.*, 1986). This isomer exhibits geometries of the N_4 coordination site which deviate noticeably from the ideal square shape of the porphyrin core, and its unique structural properties result in interesting catalysis of the complexes it forms with metals (Hayashi *et al.*, 2001). We have found that the title porphycene exists in the solid state in two crystalline forms, *viz*. prisms and plates, with distinctly different structures. The triclinic plate form has a rectangular N_4 coordination site, enlarged in the bromo-substituted direction (Will *et al.*, 1990). The monoclinic prismatic form, (I), is discussed in detail here.



(I)

The molecular structure of (I) and the atom-numbering scheme are shown in Fig. 1. The monoclinic form, (I), has a more warped structure than the triclinic form, which has an almost planar structure caused by π–π stacking between the aromatic rings, with the closest distance between rings being about 3.2 Å (Will *et al.*, 1990).

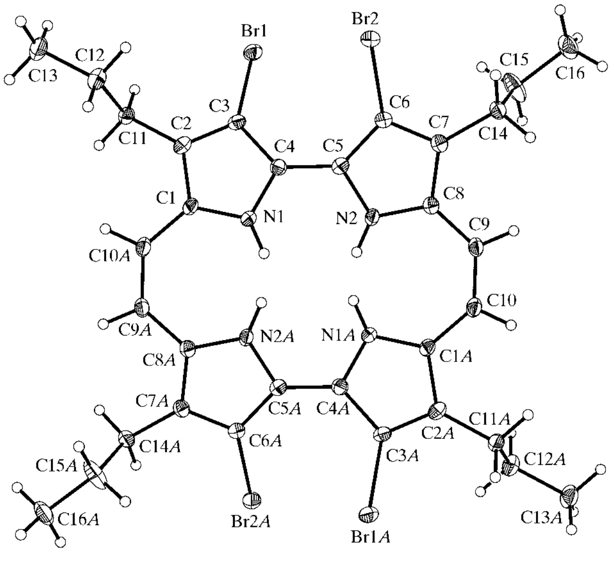


Figure 1
A view of the molecular structure of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The four inner H atoms are disordered. Atoms labelled with the suffix *A* are at the symmetry position ($-x$, $-y$, $2 - z$).

The angle between adjacent pyrrole planes is 21.8 (1)° for (I), but only 6.6 (5)° for the triclinic structure. The maximum shift of the 24 peripheral atoms from the least-squares plane of the $C_{20}N_4$ porphycene core is 0.309 (2) Å for C3. The shape of the central N_4 cavity is rectangular, enlarged in the direction of the methine-bridge C atoms, with N1···N2($-x$, $-y$, $2 - z$) and N1···N2 distances of 2.709 (3) and 2.818 (3) Å, respectively. This shape is different from that of the triclinic form, in which the core is lengthened vertically (Will *et al.*, 1990).

The macrocycle of (I) chelates with various transition metal ions, such as Co^{2+}, Cu^{2+} and Ni^{2+}, to form divalent metal complexes in moderate yield. Metalloporphyrins containing halogenated substituents at the pyrrole ring exhibit a high efficiency for catalysis in the oxidation of organic substrates, due to saddling of the macrocyclic structure and a large positive shift in the central metal redox couple (Grinstaff *et al.*, 1994). Similarly, the Co^{III}/Co^{II} redox couple for the cobalt complex of (I) is observed at −0.14 V *versus* Ag/AgCl in pyridine, with a considerable positive shift due to the tetra-

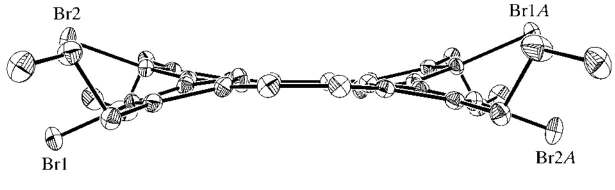


Figure 2
A side view of the molecule of (I). H atoms have been omitted for clarity.

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bromo substituents; the value is −0.35 V *versus* Ag/AgCl for the unsubstituted analogue. Studies of the catalytic properties of various metal complexes with bromo-substituted porphycene are currently in progress in our laboratory.

Experimental

The title compound was synthesized according to the method published by Will *et al.* (1990). Crystals suitable for X-ray diffraction were obtained by slow evaporation from a saturated dichloromethane–*n*-hexane solution. Distinct crystals, both prisms and plates, grew within 3 d. The prismatic crystal form, (I), was used in this study.

Crystal data

$C_{32}H_{34}Br_4N_4$
$M_r = 794.27$
Monoclinic, $P2_1/c$
$a = 13.6720\ (8)$ Å
$b = 8.0201\ (5)$ Å
$c = 14.4687\ (9)$ Å
$\beta = 106.101\ (1)^\circ$
$V = 1524.27\ (16)$ Å^3
$Z = 2$
$D_x = 1.731$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5386 reflections
$\theta = 2.9$–30.4°
$\mu = 5.31$ mm^{-1}
$T = 90\ (2)$ K
Prism, purple
0.24 × 0.19 × 0.15 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.325$, $T_{\max} = 0.451$
9484 measured reflections
3111 independent reflections
2751 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.028$
$\theta_{\max} = 26.4^\circ$
$h = -17 \rightarrow 16$
$k = -7 \rightarrow 10$
$l = -17 \rightarrow 18$
191 standard reflections
frequency: 290 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.082$
$S = 1.07$
3111 reflections
183 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 0.7118P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 1.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.61$ e Å^{-3}

H atoms were located in calculated positions and allowed to ride on the corresponding parent atoms, with C—H distances in the range 0.95–0.99 Å and N—H distances of 0.88 Å. The two imino H atoms are distributed with half occupancy over each of the four possible positions because of intramolecular tautomerization.

Table 1
Selected geometric parameters (Å, °).

Br1—C3	1.882 (2)	C8—C9	1.404 (4)
Br2—C6	1.878 (3)	C9—C10	1.382 (4)
C4—C5	1.413 (4)		
C4—C3—Br1	127.95 (19)	C5—C6—Br2	126.86 (19)
N1—C4—C5	119.9 (2)	C6—C7—C8	106.1 (2)
C5—C4—C3	131.3 (2)	N2—C8—C9	126.0 (2)
N2—C5—C4	120.3 (2)	C9—C8—C7	125.9 (2)
C4—C5—C6	134.4 (2)	C10—C9—C8	130.8 (2)

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1071). Services for accessing these data are described at the back of the journal.

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