Synthesis and Crystal Structure of bis[24]dithahexaphyrin(1.0.0.1.0.0)

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The [24]dithahexaphyrin(1.0.0.1.0.0) dimer (bis[24]dithahexaphyrin(1.0.0.1.0.0)), molecular formula $C_{100}H_{94}N_8S_4$, was isolated. The crystal structure of the compound was determined by single-crystal X-ray diffraction at 200(2)K, and was assigned to the monoclinic space group $P2_1/c$ with $a = 14.8374(15)\text{\AA}$, $b = 25.661(3)\text{\AA}$, $c = 24.038(2)\text{\AA}$, $\beta = 93.736(1)^\circ$, $V = 9133.1(16)\text{\AA}^3$, $D_x = 1.117\text{ g/cm}^3$, and $Z = 4$. From 18,645 independent reflections, $R1 [I > 2\sigma(I)]$ was determined to be 0.0734, and $wR2$ was found to be 0.1683. This value was calculated for all of the reflection data. The dimer contains an antiaromatic molecule.

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Porphyrins and porphyrinoid compounds are widespread in nature,¹ and are commonly produced in chemical laboratories² because they provide a basis for designing new materials having unique properties.³ The versatile applicability of these compounds results from their unique optical properties combined with the natural state of their synthetic forms.⁴ The optical features, redox characteristics, and HOMO-LUMO energy gap of these compounds can be significantly modified by extending their porphyrin ring structures. Various π -extended porphyrins have been synthesized *via* oxidative aromatic coupling,⁵ with many analogs possessing tetrapyrrolic macrocycle, naphthalene, higher hydrocarbon, and heterocyclic compounds as an additional unit. Oligo and polyporphyrins have also been actively exploited in molecular architectures.⁶ Osuka *et al.* reported on an Ag^+ -promoted *meso-meso* coupling reaction of Zn-5,15-diarylporphyrin.⁷ They synthesized a series of *meso-meso*-linked porphyrin arrays up to 128-mer, which at that time was the longest discrete molecule ever made. Further extension of this synthetic strategy remains a serious challenge. In fact, extensive efforts have been made to synthesize porphyrin arrays that can be realized in various functional units

and molecular devices.

Elsewhere, the synthesis of expanded porphyrins based on bipyroles and terpyroles has received considerable attention. The first reported expanded porphyrin, sapphyrin⁸ ([22]pentaphyrin(1.1.1.1.0)), contains the bipyrole subunit within a pentapyrrolic aromatic framework. Other examples of bipyrole-derived expanded porphyrins are smaragdypyrin, rosarin, and rubyrin.⁹ In the present study, cross coupling of [24]dithahexaphyrin(1.0.0.1.0.0) occurred due to the presence of

Fig. 1 Structure of bis[24]dithahexaphyrin(1.0.0.1.0.0).

Table 1 Crystal data and experimental data

Empirical formula: $C_{100}H_{94}N_8S_4$	
Formula weight = 1534.07	
Temperature = 200(2)K	
Crystal system: Monoclinic	Space group: $P2_1/c$
$a = 14.8374(15)\text{\AA}$	
$b = 25.661(3)\text{\AA}$	$\beta = 93.736(1)^\circ$
$c = 24.038(2)\text{\AA}$	
$V = 9133.1(16)\text{\AA}^3$	$Z = 4$
$D_x = 1.117\text{ g/cm}^3$	$D_m(\text{floatation}) = \text{not measured}$
Radiation: Mo K_α ($\lambda = 0.71073\text{ \AA}$)	
$\mu(\text{Mo } K_\alpha) = 0.153\text{ mm}^{-1}$	$F(0\ 0\ 0) = 3256$
Crystal size = $0.10 \times 0.09 \times 0.08\text{ mm}^3$	
No. of reflections collected = 97030	
No. of independent reflections = 18645	
θ range for data collection: 1.16 to 26.37°	
Data/restraints parameters: 18645/0/1017	
Goodness-of-fit on $F^2 = 1.192$	
Final R indices [$I > 2\sigma(I)$]: $R1 = 0.0734$, $wR2 = 0.1683$	
R indices (all data): $R1 = 0.1624$, $wR2 = 0.1787$	
$(\Delta\sigma)_{\text{max}} = 0.000$	
$(\Delta\rho)_{\text{max}} = 0.340\text{ e}\text{\AA}^{-3}$	$(\Delta\rho)_{\text{min}} = -0.307\text{ e}\text{\AA}^{-3}$
Measurement: Bruker APEX II ULTRA CCD SYSTEM	
Programs system: APEX2	
Structure Solution: SHELXS-97	
Structure determination: SHELXS-97	
CCDC deposition number: 986962	

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Fig. 2 ORTEP view of title compound; hydrogen atoms are omitted for clarity.

Fig. 3 Intermolecular π - π stacking in the title compound. Hydrogen atoms are omitted for clarity.

p-chloranil. The products were purified by silica-gel chromatography. The orange fraction was collected, and crystals were grown by slow diffusion in dichloromethane and *n*-hexane.

X-ray intensity data of 97,030 reflections (of which 18,645 are unique) were collected at 200(2)K on a Bruker CCD X-ray diffractometer (Apex II Ultra CCD System). The radiation source was graphite-monochromated Mo K_{α} ($\lambda = 0.71073$ Å). The crystallographic data and details of the data collection are given in Table 1. The structure was solved by direct methods using SHELXS97.¹⁰ All non-hydrogen atoms of the molecule were located in the best E-map. A full-matrix least-squares refinement was conducted using SHELXL97.¹⁰ All H atoms

were geometrically positioned with $N-H = 0.88$ Å, $C-H = 0.95 - 1.00$ Å, and refined by a riding model with $U_{iso}(H) = 1.2 U_{eq}(C/N)$, except for the methyl group where $U_{iso}(H) = 1.5 U_{eq}(C)$. The final refinement cycles for 97,030 observed reflections converged to $R = 0.0734$ and $wR(F2) = 0.1787$. The residual electron densities ranged from -0.307 to 0.340 eÅ⁻³. The atomic scattering factors were taken from International Tables for X-ray Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4). The selected bond lengths and bond angles are given in Table 2S, while Table 3S provides selected torsion angles. An atom-labeled ORTEP view of the title compound is shown in Fig. 2.

The bond lengths along the first and second 24π -conjugation loops of the title compound fall between 1.467(6) and 1.336(4) Å and 1.469(6) and 1.346(6), respectively, consistent with the ranges of aromatic bond lengths. The title compound comprises a pair of [24]dithahexaphyrin(1.0.0.1.0.0) groups linked at the β -pyrrole positions. The bond length and torsion angle of adjacent [24]dithahexaphyrin(1.0.0.1.0.0) macrocycles in the compound are 1.432(5) and $-83.6(5)^{\circ}$, respectively. In addition, the π - π interactions of the pyrrol rings in the unit cell was observed. For example, the calculated distance between C79 and N14 was 3.478 Å. A packing diagram is given in Fig. 3.

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