p-Nitrophenyl[36]trithianonaphyrin(1.0.0.1.0.0.1.0.0) with a Weak Antiaromatic Character

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p-Nitrophenyl[36]trithianonaphyrin(1.0.0.1.0.0.1.0.0), C₇₅H₆₉N₉O₆S₃, was isolated. The crystal structure was determined by single-crystal X-ray diffraction at 200(2)K and belonged to the monoclinic space group *Cc*. The lattice parameters are *a* = 24.986(4) Å, *b* = 23.548(4) Å, *c* = 13.762(7) Å, β = 101.358(2)°, *V* = 7939(2) Å³, *D_x* = 1.078 g/cm³, and *Z* = 4; *R*₁ [*I* > 2σ(*I*)] and *wR*₂ are 0.0656 and 0.1368, respectively, for 17971 independent reflections. The results of a ¹H NMR study suggested that the title compound has a weak antiaromatic character because of a slight distortion of its large macrocyclic ring, as determined by single-crystal X-ray analysis. Single-crystal X-ray analysis also revealed that the 2,5-substituted thiophene rings are inverted in the title compound.

(Received January 20, 2015; Accepted February 11, 2015; Published on web March 10, 2015)

Since the discovery of expanded porphyrins,^{1,2} more investigations have been conducted from many viewpoints. In the early stages of studies on expanded porphyrins, most investigations involved the preparation of synthetic expanded porphyrins, or improvements in their syntheses.³ A recent study on expanded porphyrins, however, was conducted from the viewpoints of aromaticity, chemical modification, and conformation.⁴ In the intervening years, the investigation of expanded porphyrin chemistry has included the construction of a new π system.⁵

In 1992, Ibers and co-workers⁶ inserted a thiophene moiety into a bipyrrrole unit to construct a new 26 π -aromatic macrocyclic compound *via* McMurry coupling. The

incorporation of a thiophene moiety into the bipyrrrole unit was expected to produce a large macrocyclic compound, 2,5-bis(4-propyl-2-pyrrolyl)thiophene, because of the distances between these outer α -pyrroles. As herein described, we investigated new antiaromatic macrocyclic ligands to react a 2,5-bis(4-propyl-2-pyrrolyl)thiophene unit with *p*-nitrobenzaldehyde.

The compound 2,5-bis(4-propyl-2-pyrrolyl)thiophene (**1**) was synthesized by a method reported by Ibers and co-workers. Compound **1** was reacted with *p*-nitrobenzaldehyde using

Fig. 1 Structure of *p*-nitrophenyl[36]trithianonaphyrin(1.0.0.1.0.0.1.0.0).

Table 1 Crystal data and experimental data

Empirical formula: C ₇₅ H ₆₉ N ₉ O ₆ S ₃	
Formula weight = 1288.57	
<i>T</i> = 200(2)K	
Crystal system: Monoclinic	Space group: <i>Cc</i>
<i>a</i> = 24.986(4) Å	
<i>b</i> = 23.548(4) Å	β = 101.358(2)°
<i>c</i> = 13.762(2) Å	
<i>V</i> = 7939(2) Å ³	<i>Z</i> = 4
<i>D_x</i> = 1.078 g/cm ³	<i>D_m</i> (Floatation) = not measured
Radiation: Mo <i>K</i> _α (λ = 0.71073 Å)	
μ (Mo <i>K</i> _α) = 0.145 mm ⁻¹	<i>F</i> (0 0 0) = 2712
Crystal size = 0.20 × 0.03 × 0.02 mm ³	
No. of reflections collected = 44912	
No. of independent reflections = 17971	
θ range for data collection: 1.20 to 27.48°	
Data/Restraints/Parameters = 17971/2/845	
Goodness-of-fit on <i>F</i> ² = 0.775	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] : <i>R</i> ₁ = 0.0656, <i>wR</i> ₂ = 0.1368	
(Δ/σ) _{max} = 0.000	
(Δρ) _{max} = 0.400 eÅ ⁻³	(Δρ) _{min} = -0.331 eÅ ⁻³
Measurement: Bruker APEX II ULTRA CCD SYSTEM	
Programs system: APEX2	
Structure Solution: SHELXS-97	
Structure determination: SHELXS-97	
CCDC deposition number: 1043012	

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

trifluoroacetic acid in dichloromethane under an argon atmosphere at room temperature for 3 h. After the reaction mixture was neutralized, the crude product was passed through an alumina column. The products were again purified by chromatography on a silica-gel column. The third blue main fraction gave *p*-nitrophenyl[36]trithionaphyrin(1.0.0.1.0.0.1.0.0) (**2**) (Fig. 1).⁷

The ¹H NMR spectrum of **2** is shown in Figs. 1S and 2S. The ¹H NMR spectrum of **2** gave evidence of weak antiaromaticity. In the case of compound **2**, the inner pyrrole NH proton was observed at 17.3 ppm. The pyrrole β-proton was 6.0 ppm as an upfield shift; however, thiophene β-proton is 9.7 ppm, as shown by the downfield shift. These results indicated that the proton NMR spectrum of **2** gave evidence in support of weak antiaromaticity. X-ray intensity data for 44912 reflections (of which 17971 were unique) were collected at 200(2)K on a Bruker CCD X-ray diffractometer (Apex II Ultra CCD system) using a graphite-monochromated Mo K_α (λ = 0.71073 Å) radiation source. The structure was solved by direct methods using the SHELXS97 software program.⁸ All nonhydrogen atoms of the molecule were located in the best E-map. A full-matrix least-squares refinement was conducted using SHELXL97.⁸ All H atoms were geometrically positioned with N-H = 0.88 Å and C-H = 0.95 – 1.00 Å, and refined using 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 converged to R = 0.0656 and wR(F²) = 0.1368 for the observed 17971 reflections. The residual electron densities ranged from –0.331 to 0.400 eÅ^{–3}. The atomic scattering factors were taken from the International Tables for X-ray Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4). The crystallographic data are summarized in Table 1. Selected bond lengths are given in

Fig. 3 Side view of the title compound **2**.

Table 1S. The harmonic oscillator model of the aromaticity (HOMA) value was calculated using the X-ray crystallographic data (Table 1S) for compounds **2** by using Cyranski's equation.⁹ The calculated HOMA value was 0.742. This value suggested that the title compound **2** possessed a conjugated π orbital as a general aromatic compound. An ORTEP view of the title compound with atomic labeling is shown in Fig. 2.

p-Nitrophenyl[36]dithianonaphyrin(1.0.0.1.0.0.1.0.0) has a slightly twisted conformation, with the exception of the *meso*-phenyl rings, because of its large 4*n* π-electronic networks; this twisting is obvious from the side view in Fig. 3. The *meso*-phenyl rings are nearly perpendicular to the mean plane of the *meso* carbon atoms (dihedral angles: 82.75°, 97.57°, and 79.95°). Three intramolecular hydrogen bonding interactions involving NH...N (1.998 Å, 144.96°; 2.017 Å, 146.37°; and 2.005 Å, 143.56°) occur on the bipyrrylmethene moiety.

The bond lengths are comparable to typical aromatic bond lengths, as shown in Table 2, suggesting a 36π-electron delocalization pathway. The 36π circuit average bond length of compound **2** was calculated to be 1.401 Å, which is within the normal range of aromatic bond lengths (Table 2). The bond angles around the 2,5-substituted thiophene, which were inverted thiophene rings in **2**, were 148.01°, 150.5°, and 148.1°. These values were calculated by the angle between C5–C4 and C75–C1, C24–C26 and C29–C30, and C50–C51 and C55–C54, respectively.

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