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Synthesis and Structural Characterization of Meso-tetrakis(3,4-dimethoxyphenyl)Porphyrin

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ABSTRACT

Sterically hindered and electron releasing group attached on meso phenyl containing porphyrin are of great interest in the scientific community. This report emphasize on the synthetic as well as structural characterization of meso-tetrakis(3,4-dimethoxyphenyl)porphyrin.

Keywords: porphyrin, crystal, methoxy, synthesis

INTRODUCTION

Porphyrins and their analogues materials serve different applications. Metalloporphyrins assemblies has been used as building block for tailored materials properties during the past decades the [1]. These fascinating molecules have broad applications as field responsive materials, particularly for optoelectronic applications [2-4]. The facile substitution of the periphery of various porphyrins has generated a series of unusual liquid crystalline materials [5-8]. The porphyrins ligand serves as a platform on which one can erect desirable molecular and materials properties, including very large dipole moments [9], polarizabilities [10], and hyperpolarizabilities [11-13]. The nonlinear optical properties of these materials can be explored in optical communications, data storage, and electro-optical signal processing [14-18]. The porphyrin π -radical makes these systems especially interesting for photoionization processes [19-25], closely related to the so-called ion pair reaction centre of photosynthesis and the photo-generation of electron transfer [26]. Porphyrins can interact with chemical species (chemo-responsive) also in contrast to their interaction with applied electric [27], magnetic or electromagnetic fields. The materials based on chemo-responsive are less advanced e.g. porphyrins solids, being highly porous, are involved in the current development of molecular based molecular sieves or shape- selective solid catalysts and in sensor applications [28-31]. In this paper, we have reported the single crystal structure of sterically hindered porphyrin for future applications.

EXPERIMENTAL

Materials and methods

The synthesis of 3, 4-dimethoxytetraphenylporphyrin was carried using reported method [22] and details are as 1.0 g (6.0 mmol) of 3, 4-dimethoxybenzaldehyde was dissolved in 50 ml of argon-purged dimethylformamide. 0.5 mL conc. HCl was added into it followed by drop wise addition of 0.42 mL (6.0 mmol) of freshly distilled pyrrole. The mixture was stirred under argon for a 1 hour. The final reaction mixture was refluxed for 8 hour in air. The solvent was evaporated on water bath and washed with hot water. The crude product was extracted by flash chromatography over silica gel using 10% ethyl acetate-chloroform mixture. The desired porphyrin was finally purified by column chromatography over silica gel using 7% ethyl acetate-chloroform mixture. The yield of the purple crystal compound was calculated to 25%.

Analytical data

^1H (CDCl_3 , 400MHz); δ -2.81 (br s, -NH, pyrrole), 3.93 (s, 12H, m-OCH₃), 4.11 (s, 12H, p-OCH₃), 7.17 (d, 4H, phenyl), 7.67 (d, 4H, phenyl), 7.70 (s, 4H, phenyl), 8.83 (s, 8H, pyrrole); ^{13}C (CDCl_3 , 400MHz); 56.2 (m-OCH₃),

56.3 (p-OCH₃), 127.46 (meso-carbon), 134.85 (β-C, pyrrole), 147.1 (α-C, pyrrole), 109.51, 118.3, 119.9, 148.95; λ_{max} (CHCl₃; logε); 425 (5.63), 464 (4.17), 519 (4.28), 559 (4.04), 593 (3.78), 649 (3.14); FAB mass (m/z): 856.

RESULTS AND DISCUSSION

The diffraction quality single crystals of meso-tetrakis(3,4-dimethoxyphenyl)porphyrin were grown by direct solvent diffusion of n-hexane in a saturated solution of porphyrin in chloroform in a long cylindrical tube standing on several days at room temperature. A dark purple rectangular block shaped single crystal of meso-tetrakis(3,4-dimethoxyphenyl)porphyrin having approximate dimensions of crystal size 0.20 × 0.10 × 0.07 mm was mounted for data collection. A total no. of 17352 reflections (2.20 < Q < 28.33°) were collected of which 6395 no. of unique reflections (R (int) 0.0612) were used. This crystal was solved under the space group of I-4 in tetragonal system. Final R=0.0634 for 6395 no of unique reflections with I > 2σ Max/min residual density 0.470 and -0.268 e Å⁻³. The asymmetric unit (Z=4) contains two one fourth of two structurally different porphyrin molecules which are separated by each other and one disordered chloroform solvent molecule. The two Cl atoms of chloroform are disordered over four positions (Cl1A, Cl1B, Cl2A and Cl2B) and were refined using free part variable, due the disorderness of the solvent we are unable to put the hydrogen atom in chloroform. The ORTEP and DIAMOND views of free base porphyrin are shown in **Figures 1 and 2** respectively where hydrogen atoms are omitted due to clarity. The anisotropic parameters for all non-hydrogen atoms are listed below in **Table 1**. The selected bond lengths and bond angles are summarized in **Table 2**. A crystallographic data is tabulated in the **Table 3**.

In the crystal structure of meso-tetrakis(3,4-dimethoxyphenyl)porphyrin, asymmetric unit contains ¼ of the two porphyrin molecule that is why we are unable to fix the hydrogen atom on the nitrogen of pyrrole ring. Out of the two molecule, one porphyrin molecule is almost planar and other is saddle in shape as compared with the structure of H₂TPP [23]. The porphyrin core of the planar molecule consisting of 24 atoms which is non planar and the deviation from the mean plane does not exceed 0.1 Å but in the case of saddle molecule the deviation from the mean plane does not exceed 0.4 Å. The meso phenyl ring in the saddle porphyrin attached to the carbon atoms C17 are not perpendicular to the mean plane of the porphyrin ring and make a dihedral angle of 47.80 with the core as compared to the angles 61.1 and 63.10 in H₂TPP. The torsion angles of C18-C17-C19-C24=126.2, C16-C17-C19-C24=52.9° were observed in the saddle molecule. The meso phenyl groups in the saddle porphyrin are more tilted in the case of meso-tetrakis(3, 4-dimethoxyphenyl)porphyrin as compared to the H₂TPP. But in the case of planar porphyrin the phenyl rings are almost planar and are oriented almost perpendicular to the porphyrin ring at an angle of 75.4-91.1° as compared to that for meso-tetrakis(3,5-dihydroxyphenyl)porphyrin and meso-tetrakis(3,5-dinitrophenyl)porphyrin 56.0°-68-5° [24]. The observed bond lengths and bond angles of porphyrin macrocycles are not significantly different from those of H₂TPP [23] as observed in the present case of meso-tetrakis(3,4-dimethoxyphenyl)porphyrin. The

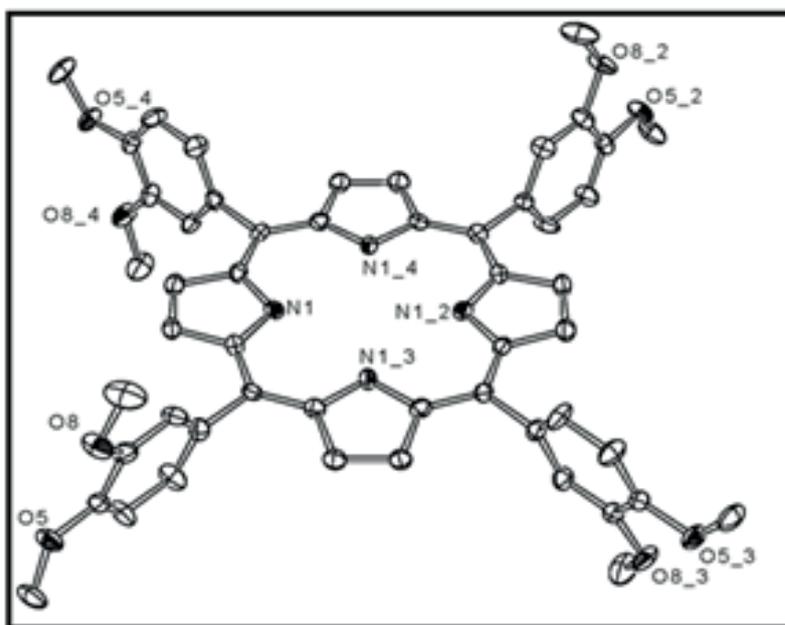


Figure 1: ORTEP view of meso-tetrakis(3, 4-dimethoxyphenyl)porphyrin.

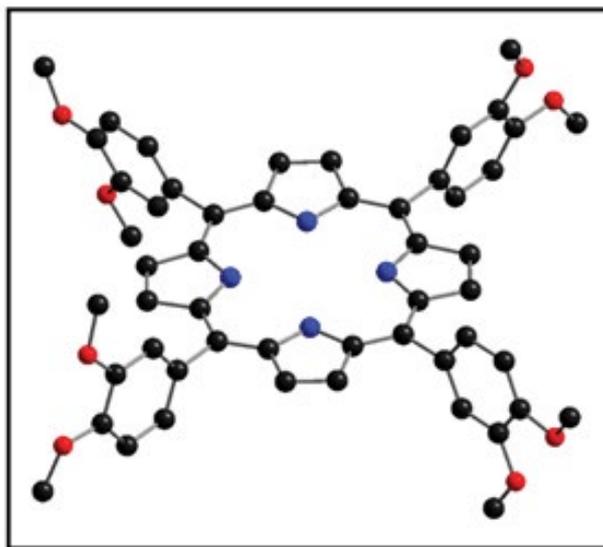


Figure 2: A DIAMOND view of meso-tetrakis(3, 4-dimethoxyphenyl)porphyrin.

Table 1: Atomic coordinates (X 104) and equivalent isotropic displacements parameters ($\text{\AA}^2 \times 10^3$) for meso-tetrakis(3, 4-dimethoxyphenyl)porphyrin. U(eq) is defined as one third of the trace of the orthogonolized U_{ij} tensor.

	X	Y	Z	U(eq)
O(2)	892 (1)	2589 (1)	6794 (1)	23 (1)
O(3)	-85 (1)	1962 (1)	7696 (1)	25 (1)
N(1)	5655 (2)	3966 (2)	4998 (2)	18 (1)
O(5)	3712 (2)	-286 (1)	4971 (1)	27 (1)
O(8)	3735 (2)	493 (2)	3763 (1)	30 (1)
C(5)	4546 (2)	2991 (2)	5002 (2)	17 (1)
C(17)	3076 (2)	757 (2)	7551 (2)	15 (1)
C(21)	1208 (2)	1986 (2)	7204 (2)	18 (1)
N(10)	3872 (2)	-491 (2)	7504 (1)	16 (1)
C(4)	5353 (2)	3206 (2)	4978 (2)	19 (1)
C(11)	4170 (2)	1719 (2)	4360 (2)	23 (1)
C(19)	2240 (2)	1079 (2)	7613 (2)	17 (1)
C(22)	671 (2)	1648 (2)	7703 (2)	19 (1)
C(3)	6004 (2)	2648 (2)	4935 (2)	21 (1)
C(23)	932 (2)	1051 (2)	8160 (2)	20 (1)
C(6)	4348 (2)	2116 (2)	5005 (2)	20 (1)
C(24)	1714 (2)	770 (2)	8109 (2)	21 (1)
C(10)	3966 (2)	925 (2)	4363 (2)	23 (1)
C(14)	2854 (2)	-1356 (2)	7261 (2)	20 (1)
C(20)	1980 (2)	1693 (2)	7152 (2)	17 (1)
C(1)	6473 (2)	3909 (2)	4976 (2)	17 (1)
C(16)	3164 (2)	-71 (2)	7460 (2)	15 (1)
C(25)	1421 (2)	2965 (2)	6290 (2)	31 (1)
C(15)	2533 (2)	-617 (2)	7297 (2)	17 (1)
C(12)	3554 (3)	-680 (2)	5635 (2)	33 (1)
C(18)	3719 (2)	1304 (2)	7599 (2)	14 (1)
C(9)	3953 (2)	498 (2)	5018 (2)	21 (1)
C(8)	4148 (2)	879 (2)	5648 (2)	27 (1)
C(2)	6694 (2)	3074 (2)	4941 (2)	23 (1)
C(7)	4343 (2)	1691 (2)	5646 (2)	27 (1)

C(26)	-692 (2)	1513 (3)	8061 (2)	29 (1)
C(13)	3705 (3)	902 (3)	3095 (2)	43 (1)
Cl(3A)	8520 (7)	1834 (6)	5964 (10)	91 (3)
Cl(3B)	8429 (4)	1895 (3)	5811 (6)	37 (3)
Cl(2A)	9254 (2)	1960 (2)	4593 (1)	57 (1)
Cl(2B)	9849 (3)	1748 (2)	4959 (3)	98 (2)
Cl(1A)	9640 (2)	824 (2)	6241 (2)	68 (1)
Cl(1B)	10095 (2)	1127 (2)	5709 (2)	69 (2)
C(27A)	9445 (3)	1829 (3)	5668 (4)	85 (2)

Table 2: Selected bond distance (Å) and bond angles (deg) for meso-tetrakis(3, 4-dimethoxyphenyl)porphyrin.

Bond distance			
O(2)-C(21)	1.367 (4)	N(10)-C(18)#2	1.366 (4)
O(2)-C(25)	1.432 (4)	N(10)-C(16)	1.378 (4)
O(3)-C(22)	1.369 (4)	N(1)-C(4)	1.367 (4)
O(3)-C(26)	1.432 (4)	N(1)-C(1)	1.371 (4)
O(5)-C(9)	1.372 (4)	O(8)-C(10)	1.380 (4)
O(5)-C(12)	1.419 (4)	O(8)-C(13)	1.415 (5)
C(17)-C(18)	1.413 (5)	C(17)-C(16)	1.402 (4)
C(18)-N(10)#4	1.366 (4)	Cl(3A)-C(27A)	1.640 (9)
Cl(3B)-C(27A)	1.722 (8)	Cl(2A)-C(27A)	2.026 (8)
Cl(2B)-C(27A)	1.482 (7)	Cl(2B)-Cl(1B)	1.781 (7)
Cl(1A)-C(27A)	2.014 (7)	Cl(1B)-C(27A)	1.599 (6)
C(27A)-H(27A)	0.98	C(18)-C(14)#4	1.438 (4)
Bond angles			
C(21)-O(2)-C(25)	116.5 (3)	C(22)-O(3)-C(26)	116.7 (3)
C(4)-N(1)-C(1)	107.6 (3)	C(9)-O(5)-C(12)	116.2 (3)
C(10)-O(8)-C(13)	117.4 (3)	C(18)#2-N(10)-C(16)	107.4 (2)
N(1)-C(4)-C(5)	126.5 (3)	N(1)-C(4)-C(3)	109.0 (3)
N(1)-C(1)-C(5)#3	126.0 (3)	N(1)-C(1)-C(2)	108.8 (3)
N(10)#4-C(18)-C(17)	126.0 (3)	N(10)#4-C(18)-C(14)#4	108.7 (3)
C(8)-C(9)-O(5)	124.6 (3)	O(5)-C(9)-C(10)	115.8 (3)

Table 3: Summary of X-ray crystallographic data for complexes meso-tetrakis(3, 4-dimethoxyphenyl)porphyrin.

Parameters	Compound
Empirical formula	C ₅₄ H ₄₆ C ₁₆ N ₄ O ₈
Formula weight	1091.65
Temperature	100(2) K
Wavelength	0.71069 Å
Crystal system	Tetragonal
Space group	I-4
a	16.713(5) Å
b	16.713(5) Å
c	18.507(5) Å
α	90.000(5)°
β	90.000(5)°
γ	90.000(5)°
Volume	5169(3) Å ³
Z	4
Density (calculated)	1.403 Mg/m ³
Absorption coefficient	0.391 mm ⁻¹
F (000)	2256
Refinement method	Full-matrix least-squares on F ²
Goodness-of-fit on F ²	1.042
Final R indices [I>2σ(I)]	R1 = 0.0634, wR2 = 0.1240
R indices (all data)	R1 = 0.0932, wR2 = 0.1365

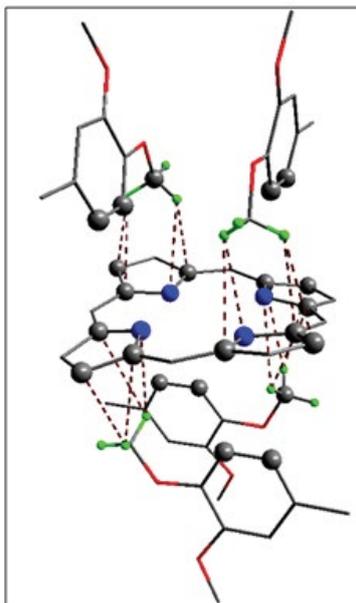


Figure 3: H-bonding between the methoxy groups of planar porphyrin molecule with the pyrrole ring of non-planar porphyrin, meso phenyl rings and hydrogen atoms are omitted for clarity.

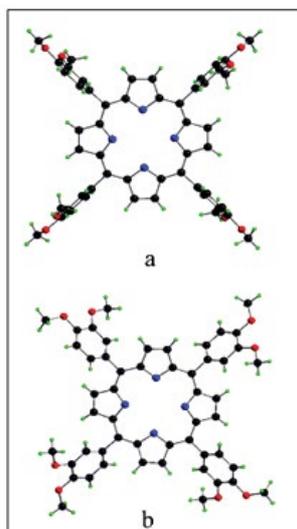


Figure 4a: A DIAMOND view of the planar (a) and saddle (b) conformation.

torsion angles of $C1-C5-C6-C11=85.05$ and $C4-C5-C6-C7=84.84^\circ$ were observed. The meso phenyl group attached to the $C5$ carbon atom of the planar ring makes a dihedral angle of 82.7° to the porphyrin core, a slight deviation occurs from the perpendicular position. Interesting feature observed in this porphyrin is the mixture of ruffled and planar molecule in the unit cell packed one after one. This may be explained on the basis of the fact observed in the structure that main cause for this type of behavior of this porphyrin is hydrogen bonding between the hydrogen of the methoxy group of planar molecule to the nitrogen as well as carbon of the pyrrole ring of another molecule which turns into the saddle shape which has been shown in the **Figure 3**. 1,3 pyrrole of the ring are making hydrogen bond from top side from the mean plane while 2,4 pyrrole make hydrogen bond with bottom side from the mean plane. This type of hydrogen bonding is $C-H \cdots \pi$ type interaction. The distance between the $C-H$ of methoxy group making hydrogen bond with π -orbital of the pyrrole is 2.96 \AA . A DIAMOND view of planar and saddle conformation of free base porphyrin has been presented in the **Figure 4a** (insight **Figure 4a**, a= planar, b= saddle). The angle between the two opposite pyrrole formed by the plane passing through the pyrrole was found to be 23.72° and the views through

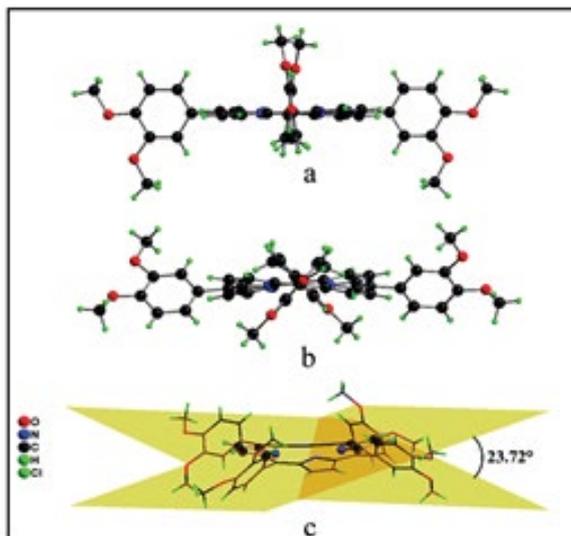


Figure 4b: Views through different positions (insight Figure 4b a= view through 1, 2 nitrogen atoms of saddle porphyrin, b= view through 1, 2 nitrogen atoms of planar porphyrin and c= showing two plane through 1, 3 pyrroles rings and angle between the two opposite pyrrole).

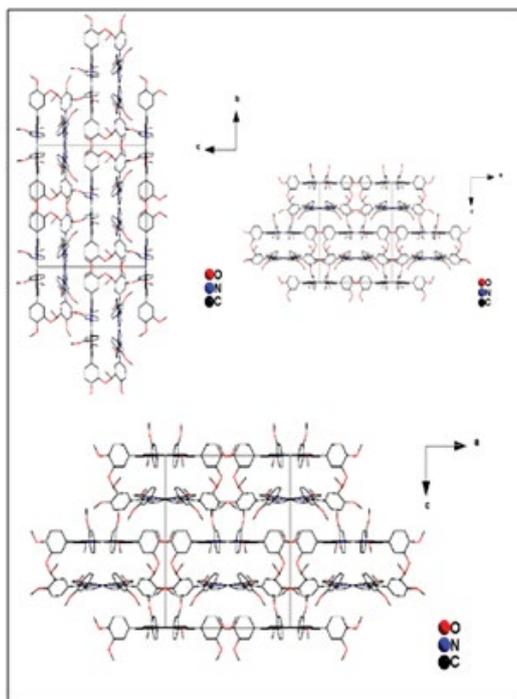


Figure 5: Unit cell packing diagram in compound and hydrogen atoms are omitted for clarity.

the different positions have been presented in the **Figure 4b**. The unit cell packing diagram is shown in the **Figure 5** where hydrogen atoms are omitted for clarity. The porphyrins rings are arranged in one dimension only with CH – π interaction and π - π staking interaction among the porphyrin rings. The distance between the oxygen atoms of para methoxy group of planar molecule to that of two neighboring methoxy group of ruffled porphyrin in one dimensional array is 5.204 Å while that of oxygen atoms of meta position is 4.893 Å with the methoxy group of para positions. The intermolecular closest distance between the aryl group carbon and methoxy group oxygen is 2.38 Å. The distance between the nuclear least square plane of planar molecule and ruffled molecule is 4.627 Å.

CONCLUSION

In this paper, we have shown that crystal structure of 3,4-dimethoxyphenylporphyrin show unique hydrogen bonding interaction and have potential to be used in several porphyrin based materials in different applications.

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