Synthesis and Crystal Structure of 5,15-Bis(3,5-di-*tert*-butylphenyl)-10-(phenylethynyl)-20-(trimethylsilyl)ethynylporphyrin

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The crystal structure of the title compound, C₆₁H₆₆N₄Si(I) displays a highly unsymmetric molecular entity involving three different substituents on the *meso*-positions. The molecular units in the crystal are intermolecularly bonded to each other via π - π , and CH- π interactions, resulting in the genesis of a 2D structural motif. This compound crystallizes in the triclinic system of the $P\bar{1}$ space group with the following cell parameters: $a = 8.9729(10)$, $b = 19.167(2)$, $c = 20.763(2)$ Å; $\alpha = 65.932(2)^\circ$, $\beta = 81.356(2)^\circ$, $\gamma = 86.051(2)^\circ$, $Z = 2$.

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It has been of research interest for a long time to study the effect of substituents on the degree and type of non-planar deformations of the porphyrin ring induced by those substituents.^{1,2} A slight change on the periphery of the porphyrin macrocycles leads to two common types of non-planar deformations, ruffling or saddling, and changes in the chemical properties of the porphyrin macrocycles, such as redox behavior and photophysical properties.³⁻⁵

In order to study the effect of the substituents on the planarity of the porphyrin macrocycles, herein, we report on the synthesis and crystal structure of C₆₁H₆₆N₄Si(I). This compound was synthesized by the reaction of *meso*-(3,5-di-*tert*-butylphenyl)-dipyrromethane, trimethylsilylpropynal and phenylpropargyl aldehyde. A single crystal was grown by a CH₂Cl₂/CH₃OH solution. Detailed synthetic and X-ray crystal structure determination procedures were described in supporting information. The molecular structure reveals the presence of three different groups on the four *meso*-positions (Fig. 1). The

two *meso*-positions, 5 and 15, are occupied by 3,5-bis(*tert*-butyl)phenyl groups, while another two *meso*-positions, 10 and 20, are placed with phenylethynyl and trimethylsilyl ethynyl groups, respectively. A structural examination of molecular entity revealed the presence of a highly distorted structure (Fig. 2). The deviations of all atoms associated with the central porphyrin core and the planes associated with aryl rings were examined with respect to the least-squares plane of a 24-membered macrocyclic porphyrin core. All of the atoms related to the porphyrin core deviate from the mean plane by 0.13 Å, while the distances in between the nitrogen atoms, N1...N2 = 2.891(7), N2...N3 = 2.960(9), N3...N4 = 2.881(8), N4...N1 =

Fig. 1 Chemical diagram of I.

Table 1 Crystal and experimental data

Chemical formula = C ₆₁ H ₆₆ N ₄ Si	
Formula weight = 883.27	
$T = 213$ K	
Crystal system: triclinic	Space group: $P\bar{1}$
$a = 8.9729(10)$ Å	$\alpha = 65.932(2)^\circ$
$b = 19.167(2)$ Å	$\beta = 81.356(2)^\circ$
$c = 20.763(2)$ Å	$\gamma = 86.051(2)^\circ$
$V(\text{Å}^3) = 3223.3(6)$	$Z = 2$
$D_x = 0.910$ g/cm ³	
Radiation: Mo K_α ($\lambda = 0.71073$ Å)	
$\mu(\text{Mo } K_\alpha) = 0.070$ mm ⁻¹	$F(0\ 0\ 0) = 948$
Crystal size = $0.30 \times 0.10 \times 0.05$ mm ³	
No. of reflections collected = 10778	
No. of independent reflections = 6644	
θ range for data collections = 1.88 to 20.81°	
Data/Restrains/Parameters = 6644/66/623	
Goodness-of-fit on $F^2 = 0.916$	
R indices [$I > 2\sigma(I)$]: $R1 = 0.0980$, $wR2 = 0.2531$	
R indices (all data): $R1 = 0.1474$, $wR2 = 0.2801$	
$(\Delta\rho)_{\max} = 0.00$	
$(\Delta\rho)_{\max} = 0.393$ e Å ⁻³	$(\Delta\rho)_{\min} = 0.308$ e Å ⁻³
Measurement: SIEMENS SMART CCD	
Program system: SADABS	
Structured determination: SHELXS-97	
CCDC deposition number: 755628	

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Fig. 2 ORTEP structure of 1. Thermal ellipsoids are drawn at the 30% probability level and hydrogen atoms are omitted (except the N-H atoms) for clarity.

2.967(10) Å show a discrepancy. It has been reported that such distortion diminishes the steric strain.² The planes derived from two 3,5-bis(*tert*-butyl) groups present on the *meso*-positions and *trans* to each other, deviate from the mean porphyrin plane by 73.12° and 60.97° in opposite rotation, while the aryl plane associated with phenylethynyl group deviates (27.55°) into a less extent. The variation in the deviations of the aryl groups with the mean plane reveals the steric effect of the groups where such twisting reduces the steric repulsion between phenyl and the hydrogen atoms at the β -positions of neighboring pyrrole rings.⁶ A comparison of these results with our recent report⁷ on a centrosymmetric compound, 5,15-bis(3,5-di-*tert*-butylphenyl)-10,20-bis(phenylethynyl)porphyrin, bearing varied plane deviations associated with di(*tert*-butyl)phenyl (59.19°) and phenylethynyl groups (17.17°), reveals that the presence of a sterically bulky trimethylsilylethynyl group leaves more distortion in the plane of the porphyrin macrocycle. Herein, it is interesting to examine the bond lengths associated with ethynyl carbons, C(α)-C(β) and the angles C(*meso*)-C(α)-C(β) due to presence of two different groups in the conjugation with this group. The bond lengths associated with ethynyl C-C bonds lie in the range of 1.19 – 1.22 Å, while the angles C10(*meso*)-C35(α)-C36(β) = 176.7(7)° and C20(*meso*)-C60(α)-C61(β) = 178.1(7)° are also much closer. The bond lengths and bond angles associated with these groups well corroborate with our recent report on 5,15-bis(3,5-di-*tert*-butylphenyl)-10,20-bis(phenylethynyl)porphyrin⁷ and related reports.^{8,9} These studies reveal the absence of any obvious electronic genesis due to these

groups about the ethyne units. The molecular structure further extends into the 2D structural assembly via π - π and CH- π intermolecular interactions. As shown in Figs. S1 and S2 (see supporting information), the three CH- π (H44(*tert*-butylphenyl)- π (phenylethynyl) = 3.073, H41(phenylethynyl)- π (porphyrin core) = 3.107, H63A(trimethylsilyl)- π (*tert*-butylphenyl) = 3.189 Å), and one π - π (π (phenylethynyl)- π (porphyrin core) = 4.939 Å) are involved in the development of a 1D structural motif where porphyrin molecules are bonded to one another in an ABAB pattern.¹⁰ The π - π interactions involved in the organization of the 1D structure are face to the edge interaction rather than the typical offset face-to-face interactions with a porphyrin core and a phenylethynyl group of the adjacent porphyrin molecule. These 1D structures are further bonded to each other via one additional π - π (π (porphyrin core) $\cdots$ π (phenylethynyl) = 4.101 Å) bonding, and afford the 2D structural motif (Fig. S3; see supporting information).

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