

Reversible caterpillar-motion like isomerization in a *N,N'*-dimethyl hexaphyrin(1.1.1.1.1.1) induced by two-electron oxidation or reduction†

Masaaki Suzuki and Atsuhiko Osuka*

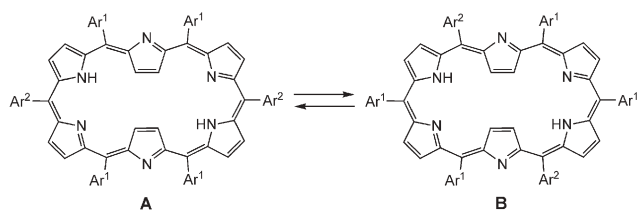
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Caterpillar-motion like rotational isomerization of *meso*-aryl substituted [26]- and [28]hexaphyrins has been revealed for the first time. Two-electron oxidation and reduction induce reversible interconversion between *N,N'*-dimethyl [26]- and [28]hexaphyrins with a rotational isomerization, in which the *N*-methylated pyrroles move from the corner in the former to the centre in the latter.

Expanded porphyrins with conjugated pyrrolic macrocycles larger than porphyrin are an interesting class of molecules that exhibit unique physical and chemical properties that are difficult to find in porphyrins.^{1,2} Among these, *meso*-hexakis(pentafluorophenyl) substituted hexaphyrin (**1**) with a 26 π -electronic circuit can be regarded as a real homolog of porphyrin with an 18 π -electronic circuit in respect of strong aromaticity.³ In fact, the ¹H NMR spectrum of **1** exhibits doublets at 9.42 and 9.09 ppm due to the outer β -protons and a singlet at -2.43 ppm due to the inner β -protons. A notable difference in the chemical reactivity of **1** from those of porphyrins is its easy and quantitative reduction to stable [28]hexaphyrin **2**. Another key structural difference is its rectangular shape consisting of two different pyrroles, four corner pyrroles and two inverted pyrroles at the centre, which contrasts with the square shape of porphyrin consisting of four identical pyrroles except the presence or absence of NH proton. This inequality may lead to a structural isomerization shown in Scheme 1, where a caterpillar-motion like macrocyclic ring rotation changes the position of *meso*-aryl substituents. Such a structural isomerization, which can be detected for hexaphyrins that have a *meso*-substituent pattern like **A** and **B** has, to the best of our knowledge, never been reported before.



Scheme 1 A possible rotational isomerization between hexaphyrins **A** and **B**.

Department of Chemistry, Graduate School of Science, Kyoto University, and Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency, Sakyo-ku, Kyoto, 606-8502, Japan. E-mail: osuka@kuchem.kyoto-u.ac.jp; Fax: +81 75 753 3970; Tel: +81 75 753 4008

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Initially, we examined the possibility of such a structural isomerization using [26]hexaphyrin **3** and **4** that were prepared from the reaction of 5,10-bis(pentafluorophenyl)tripyrane with 2,4,6-trifluorobenzaldehyde in 1:1 ratio.^{3e,4} These hexaphyrins do not isomerize at 0 °C but gradually isomerize at 40 °C toward the equilibrated mixture consisting of **3** and **4** in a 2.5:1 ratio. Thus the isomer **3** is more stable than **4** in spite of the same steric hindrance at the *ortho*-positions of the *meso*-substituted aryl groups. The isomer **3** is less polar and was separated from **4** by silica gel column chromatography while separation of **4** was more difficult due to the tailing nature of **3**. Variable temperature ¹H NMR spectroscopy on pure **3** has determined the activation energy of the rotational isomerization to be only 1.4 kJ mol⁻¹. The rotational isomerization has been also examined for [28]hexaphyrins **5** and **6** that were prepared by NaBH₄ reduction of **3** or **4**. Reduction of the pure **3** with NaBH₄ readily gave a mixture of **5** and **6** in a ratio of 1:6.7. Extensive heating of this mixture did not cause any changes, hence indicating this to be an equilibrated mixture. Interestingly, the similar reduction of a mixture that contained mainly **4** at room temperature provided essentially the same mixture of **5** and **6**, suggesting an even smaller activation barrier for the interconversion between **5** and **6**.

In the course of our studies on *meso*-aryl substituted expanded porphyrins, we examined *N*-methylation of **1**.⁵ Initially, the deprotonation of **1** was attempted with tetrabutylammonium fluoride (TBAF). Addition of TBAF to a CH₂Cl₂ solution of **1** caused changes in absorption pattern as shown in Fig. 2, in which the Soret-like band at 568 nm of **1** was shifted to 601 nm and sharpened with a shoulder at 617 nm. These spectral changes have been assigned due to formation of a doubly deprotonated hexaphyrin. Such a species was also detected in the ¹H NMR spectrum, which exhibited a singlet at -4.33 ppm due to the inner pyrrolic β -protons and doublets at 9.21 and 9.51 ppm due to the outer pyrrolic β -protons. These data indicate an enhanced diatropic ring current for the dianion compared with **1**. Crystals of the dianion suitable for X-ray diffraction analysis were grown by vapor diffusion of hexane to its chloroform solution. In the solid state, the dianion shows a more planar macrocycle with the mean plane deviation of 0.155 Å compared with the parent [26]hexaphyrin **1** that shows the mean plane deviation of 0.410 Å.^{3a} In addition, the dianion displays almost no bond length alternation for the two C–C bonds at the methene bridges in line with the enhanced diatropic ring current (Supporting Information†). Two tetrabutylammonium cations are found just above and below the negatively charged nitrogen atoms of the dianion of **1** with *ca.* 4.14 Å separations, plausibly for the charge compensation. Collectively, these data support the enhanced aromaticity for the

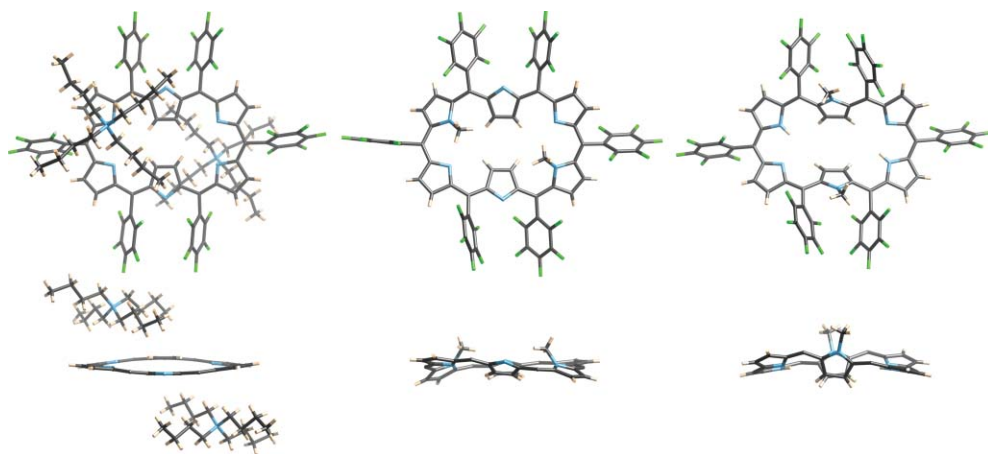


Fig. 1 Crystal structures of dianion of **1** (left), **8** (centre), and **9** (right). Upper: top views; lower: side views. In side views, *meso*-aryl groups are omitted for clarity.†

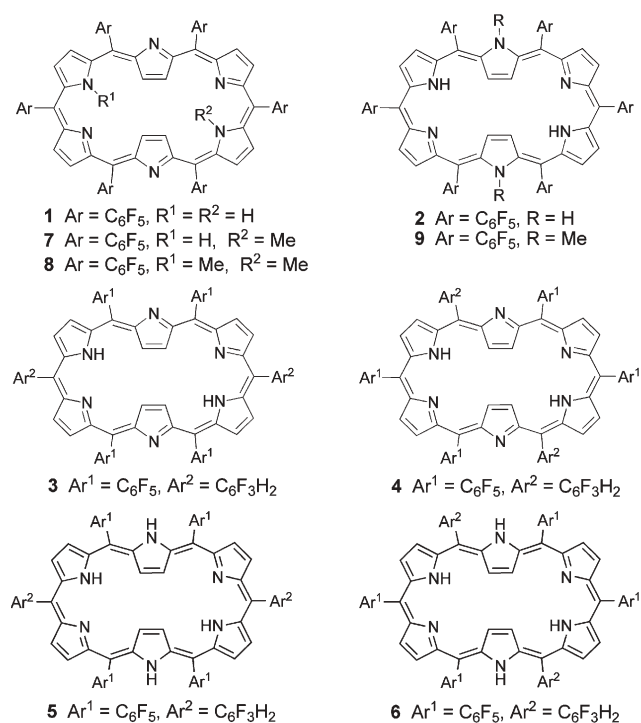


Chart 1 Molecular structures of hexaphyrins.

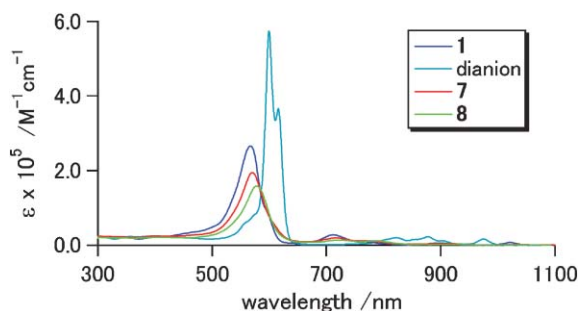
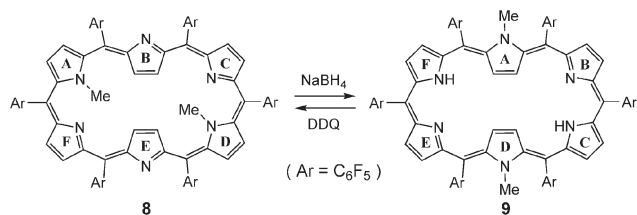


Fig. 2 UV-visible absorption spectra of **1**, dianion of **1**, **7**, and **8** in CH₂Cl₂.

dianion of **1**, probably because of favourable π -electronic delocalization.

Addition of excess amounts of methyl iodide to a solution of the dianion and subsequent refluxing led to formation of mono *N*-methyl [26]hexaphyrin **7** and *N,N'*-dimethyl [26]hexaphyrin **8** both as green solids in varying amounts that depended on the amount of methyl iodide and reaction time. The *N*-methyl protons of **7** appear at -3.31 ppm and those of **8** appear at -2.94 ppm, indicating the preservation of strong diatropic ring current for these [26]hexaphyrins. The structure of **8** has been determined by X-ray diffraction analysis, which shows a ruffled structure with the mean plane deviation of 0.326 Å and *N*-methylations at the diagonal corner pyrroles with a *syn*-arrangement of the *N*-methyl groups (Fig. 1). The N–C bond lengths in the pyrroles A and D are $1.46(1)$ and $1.49(1)$ Å, respectively, being similar to those of *N*-methylated porphyrins.⁶ The absorption spectra of **7** and **8** are similar to that of **1** in respect of the presence of a Soret-like band and Q-band-like bands, but the Soret-like bands are red-shifted and broadened in the order of **1** (568 nm) < **7** (570 nm) < **8** (578 nm). Other alkylating agents such as ethyl iodide or benzyl bromide did not give the corresponding *N*-alkylated compounds, probably due to steric reasons.

In a next step, [26]hexaphyrin **8** was reduced with NaBH₄ to give *N,N'*-dimethyl [28]hexaphyrin **9** quantitatively. The ¹H NMR spectrum of **9** showed a singlet at 2.42 ppm due to the *N*-methyl groups that was not observed in the ¹H NMR spectrum of *N,N'*-di-CD₃ labelled compound prepared from the reaction of the dianion of **1** and methyl iodide-*d*₃. The inner and outer pyrrolic β -protons appeared at 4.37 and 7.19 ppm, respectively, indicating that the diatropic ring current was largely lost but somewhat retained as in the case of [28]hexaphyrin **2**. The structure of **9** was solved by single crystal X-ray diffraction analysis (Fig. 2). Curiously, the *N*-methylated pyrrole rings, which are located at the corner in **8**, are moved to the centre of long side with inversion in **9**, indicating the occurrence of a caterpillar-motion like macrocyclic ring rotation during the reduction. The [28]hexaphyrin **9** shows a distorted ruffled conformation with the mean plane deviation of 0.444 Å. Comparison of the skeletal deviations of the macrocycle atoms from the 36 atoms mean plane reveals more distortion in **9** than **8** (Supporting Information†). In **9**, the



Scheme 2 A reversible interconversion between **8** and **9** mediated by two-electron oxidation or reduction.

N-methyl groups on the pyrroles A and D are orienting in the same direction with the N–C bond length of 1.470(4) Å and such pyrroles are nearly perpendicular to the mean plane of the macrocycle with tilting angles of 43.7°. The absorption spectrum of **9** is similar to that of **2** (Supporting Information†).

Importantly, the oxidation of **9** with DDQ regenerated **8** quantitatively, thus permitting the reversible interconversion between **8** and **9** with concurrent caterpillar-motion like isomerization.⁷ In contrast to **3–6**, the conformations of **8** and **9** were found to be rather rigid and related rotational isomerization was severely prohibited, as revealed by variable temperature ¹H NMR measurements that did not detect any spectral changes even at 140 °C. The explanation for the observed conformational preferences for **8** and **9** are not clear at the present stage. One possible reason may be as follows. The *N*-methyl groups at the pyrroles A and D as found for **9** may suffer from more steric hindrance through the interactions with the flanking *meso*-substituted pentafluorophenyl groups nearby. Thus, the preferred conformation of **9** may be accounted for in terms of stabilization due to the hydrogen bonding interaction between the pyrroles B and C and E and F that exceeds the steric hindrance of the *N*-methyl groups. In the [26]hexaphyrin **8**, such hydrogen bonding interaction is absent, which guides the *N*-methyl pyrroles to take a corner position with less steric interaction.

In summary, we have revealed the caterpillar-motion like rotational isomerization of *meso*-aryl substituted hexaphyrins for the first time. Such an isomerization is prohibited both in *N,N'*-dimethylated [26]hexaphyrin **8** and its [28]hexaphyrin **9**. However these two hexaphyrins **8** and **9** are quantitatively interconvertible *via* two-electron reduction and oxidation processes, which are accompanied by the rotational isomerization that moves the *N*-methylated pyrroles at the corner in **8** to the centre of the long side in **9**. Application of this interesting isomerization is an attractive next project worthy of further investigation.

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Notes and references

† Crystal data of dianion of **1**: C₆₆H₁₂F₃₀N₆·2(C₁₆H₃₆N)₂·(C₆H₁₄) = 2030, monoclinic, space group *C2/c* (No.15), *a* = 28.13 (3), *b* = 19.70 (3), *c* = 18.13 (3) Å, β = 103.83 (6)°, *V* = 9757 (23) Å³, *Z* = 4, *D*_{calcd.} = 1.742 g cm⁻³, *T* = -150 °C, *R*_f = 0.065 (*I* > 2σ(*I*)), *R*_w = 0.188 (all data), GOF = 0.864. Single crystal of dianion was obtained by slow evaporation of **1** with tetrabutylammonium triphenyldifluorosilicate (TBAT) in CH₂Cl₂-hexane mixed solvent. CCDC: 270832. Crystal data of **8**: C₆₈H₁₈F₃₀N₆·2(CHCl₃) = 1728, monoclinic, space group *P2₁/c* (No. 14), *a* = 13.73 (8), *b* = 20.42 (1), *c* = 22.93 (1) Å, β = 90.13 (5)°, *V* = 6429 (6) Å³, *Z* = 4, *D*_{calcd.} = 1.785 g cm⁻³, *T* = -150 °C, *R*_f = 0.098 (*I* > 3σ(*I*)), *R*_w = 0.132 (*I* > 3σ(*I*)), GOF = 1.096. CCDC: 270833. Crystal data of **9**: C₆₈H₁₈F₃₀N₆·2(CH₂Cl₂) = 1661, monoclinic, space group *C2* (No. 5), *a* = 34.11 (5), *b* = 6.491 (9), *c* = 14.94 (3) Å, β = 106.88.13 (6)°, *V* = 3165 (8) Å³, *Z* = 2, *D*_{calcd.} = 1.742 g cm⁻³, *T* = -150 °C, *R*_f = 0.035 (*I* > 3σ(*I*)), *R*_w = 0.033 (*I* > 3σ(*I*)), GOF = 0.943. CCDC: 270834. See <http://dx.doi.org/10.1039/b506586k> for crystallographic data in CIF or other electronic format.

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