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Synthesis and Nonplanar Macrocyclic Characters of Hexa-, Octa-, and Decaphenylporphyrins

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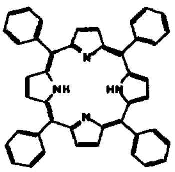
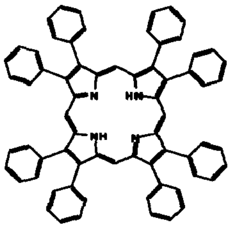
Abstract: Porphyrins bearing six, eight, and ten phenyl groups are synthesized using mixed condensation of benzaldehyde with pyrrole and diphenylpyrrole and their nonplanar macrocyclic characters are demonstrated by UV-visible and NMR spectroscopy.

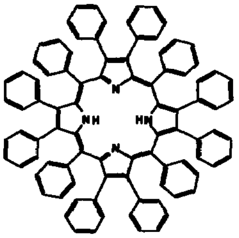
As part of study concerning the conformation-reactivity relationship of porphyrins, we have recently developed the chemistry of highly substituted 2,3,5,7,8,10,12,13,15,17,18,20-dodecaphenylporphyrin (DPP).[1,2] When phenyl groups are introduced to the eight β-pyrrole carbon positions of planar 5,10,15,20-tetraphenylporphyrin (TPP) or to the four *meso*-carbon positions of planar 2,3,7,8,12,13,17,18-octaphenylporphyrin (OPP),[3] the resulting porphyrin macrocycle of DPP adopts so-called "saddle type" conformation with the four pyrrole rings tilted up and down the mean porphyrin plane.[1,2]



TPP

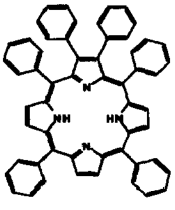


OPP

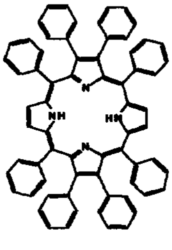


DPP

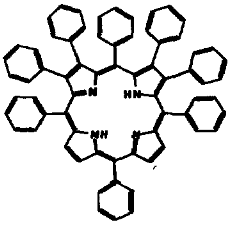
Clearly, such nonplanar distortion of DPP macrocycle is caused by the steric overcrowding of peripheral phenyl groups. The partial introduction of phenyl groups to the β-positions of TPP would give porphyrin macrocycles with varying conformations and degrees of nonplanarity.[4] Herein we report the synthesis of such types of four new porphyrins, 2,3,5,10,15,20-hexaphenylporphyrin (HPP), 2,3,5,7,8,10,15,20-octaphenylporphyrin (*cis*-OPP), 2,3,5,10,12,13,15,20-octaphenylporphyrin (*trans*-OPP), and 2,3,5,7,8,10,12,13,15,20-decaphenylporphyrin (DecPP). With a series of seven, in total, phenyl-substituted porphyrins,



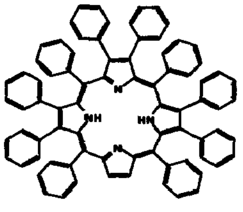
HPP



***trans*- OPP**



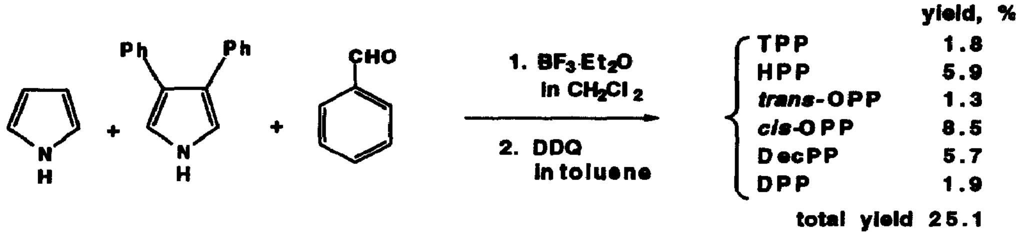
***cis*- OPP**



DecPP

UV-visible and NMR spectroscopic properties are found to vary systematically with the number of phenyl substituents and to show correlation with degrees of macrocyclic nonplanarity.

Scheme I



The four new porphyrins were directly synthesized by the method of mixed condensation. Typically, benzaldehyde (1 equiv), pyrrole (0.5 equiv), and 3,4-diphenylpyrrole (0.5 equiv) were dissolved in dichloromethane followed by addition of a catalytic amount of $BF_3 \cdot Et_2O$, and the solution was stirred under Ar for 3 h. The porphyrinogens resulted were oxidized to porphyrin macrocycles with 2,3-dichloro-5,6-dicyanobenzoquinone in refluxing toluene for 1 h.[5] This procedure would give a statistically produced mixture of TPP, HPP, *trans*-OPP, *cis*-OPP, DecPP, and DPP in the ratio of 1:4:2:4:4:1, respectively, if the condensation reactivity of pyrrole would be the same as that of 3,4-dipenylpyrrole. The TLC of the crude mixture on silica gel/$CHCl_3$ showed the six expected porphyrins roughly in the theoretical ratio with R_F values decreasing with the number of phenyl substituents. For preparative purpose, each porphyrin was separated by using the usual column chromatography.[6] The isolated yields after recrystallization are given in Scheme I. The structures of the new porphyrins were determined by FAB MS and ^1H NMR spectroscopy: HPP and DecPP were readily identified by FAB MS and two isomers of *trans*-OPP and *cis*-OPP were distinguished by ^1H NMR.[7]

UV-visible spectral properties of the new porphyrins are compared with those of TPP, OPP and DPP in Table I. The phenyl substituents have large effect on the UV-visible spectra, gradually red-shifting the Soret and Q bands in the order of TPP < OPP < HPP < *trans*-OPP < *cis*-OPP < DecPP < DPP. It is very tempting to suppose that the red-shift is a direct result of nonplanar macrocyclic distortion that is caused by steric repulsion of the adjacent *meso*- and β-phenyl groups.[1,3a] This suggestion is supported by comparing the absorption maxima of three isomers of octaphenylporphyrins (OPP << *trans*-OPP < *cis*-OPP). In OPP, there is no phenyl

Table I UV-visible and ^1H NMR spectral data for phenyl substituted porphyrins.

	UV-visible,[a] λ_{max}/nm					^1H NMR[b]
Porphyrin	Soret	$Q_y(1,0)$	$Q_y(0,0)$	$Q_x(1,0)$	$Q_x(0,0)$	δ_{NH}/ppm
TPP	417	514	548	590	645	-2.78
HPP	423	519	554	595	652	-2.47
trans-OPP	433	528	567	597	676	-2.05
cis-OPP	437	534	577	616	676	-1.85
DecPP	456	547	587	644	702	-1.30
DPP	468	564	617		722	-1.0
OPP	423	515	551	583	635	-3.03[c]

[a] UV-visible spectra were recorded in dichloromethane. [b] ^1H NMR spectra were recorded in $CDCl_3$ at 27 °C. [c] Chemical shift of p-isopropylphenyl derivatives.[3]

groups at the *meso*-position, thus no steric repulsion with the planar macrocyclic structure retained, hence no red-shift in the absorption maxima. By contrast, *trans*-OPP and *cis*-OPP have four sets of the adjacent *meso*- and β-phenyl groups which sterically induce macrocyclic distortion with considerable red-shifts in the absorption maxima. In *cis*-OPP, the steric interaction continues over seven phenyl groups (buttresing effect), causing stronger distortion and lager red-shift in comparison with *trans*-OPP.

The ^{1}H NMR spectra also demonstrate the nonplanar distortion of the macrocycles. It has been well known that the internal pyrrole NH protons are strongly deshielded by the ring current effect of porphyrin macrocycle. The NH protons of planar TPP and OPP were observed at -2.78 and -3.03 ppm, respectively. On the other hand, the NH protons of nonplnar DPP were less deshielded and obseved at -1.0 ppm. This is due to the reduction of the porphyrin ring current caused by distortion of the macrocycle. The NH resonances of the four new porphyrins are observed in the intermediate region and the chemical shifts are well correlated with UV-visible data (Figure 1). Evidently, the degree of macrocyclic nonplanarity is increased with the number of phenyl substituents.

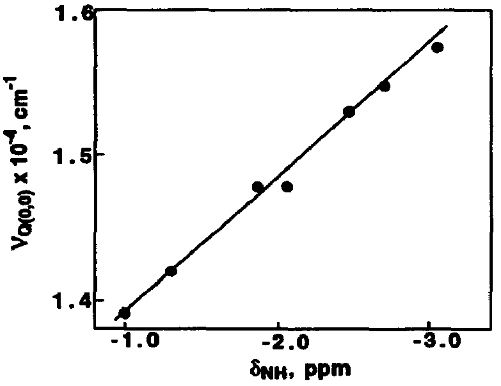
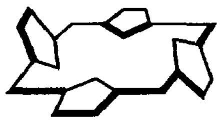
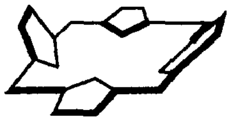
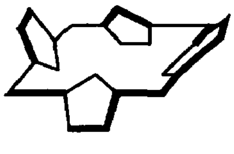


Figure 1
Correlation of the Q$_x$(0,0) band frequency ($\nu_{Qx(0,0)}$) with the chemical shift of the internal pyrrole NH protons (δ_{NH}) for a series of phenyl substituted porphyrins.

X-ray diffraction studies have shown that the macrocycle of DPP is highly distorted to saddle-shaped conformation.[3b,8] Although X-ray structures are not known, the four new porphyrins may adopt conformations different from that of DPP because of different number and distribution of phenyl substituents. For example, "chair-shaped" or "boat-shaped" conformation is expected for *trans*-OPP. In sum, the conformations of macrocycles and degrees of nonplanar distortion in phenyl substituted porphyrins vary over a wide range depending upon the number and positions of the phenyl groups introduced. Needless to say, the final proof must await study by X-ray diffraction.


chair-shaped


boat-shaped


saddle-shaped

Further studies on the electrochemical redox properties, acid-base properties, and metal incorporation rates of the four new porphyrins are now underway, details of which will be reported elsewhere.

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6. The six porphyrins were separated by column chromatography on silica gel with dichloromethane, dichloromethane-chloroform, and chloroform as eluents. Each of the fractions was rechromatographed on silica gel or neutral alumina. Detailed procedures will be described in the full manuscript.

7. ^{1}H NMR ($CDCl_3$, 27 °C) and FAB MS ($CHCl_3$/*m*-nitrobenzylalchol) data of the porphyrins are as follows:
HPP: ^{1}H NMR δ -2.47 (2H, br s, NH), 6.82-6.92 (10H, m, β-PhH), 7.17 (4H, t, *J* = 7 Hz, *meso*-PhH_m), 7.26 (2H, tt, *meso*-PhH_p), 7.70-7.75 (6H, m, *meso*-$\text{PhH}_{m,p}$), 7.79 (4H, d, *J* = 7 Hz, *meso*-PhH_o), 8.22 (4H, dd, *J* = 7 Hz, *meso*-PhH_o), 8.54 (2H, d, *J* = 4.52 Hz, β-H), 8.70 (2H, d, *J* = 4.52 Hz, β-H), 8.80 (2H, s, β-H); FAB-MS, *m/z* 767 $(M + H)^+$.
***trans*-OPP:** ^{1}H NMR δ -2.05 (2H, br s, NH), 6.82-6.88 (12H, m, β-$\text{PhH}_{m,p}$), 6.92 (8H, d, *J* = 7.69 Hz, β-PhH_o), 7.20 (8H, m, *meso*-PhH_m), 7.26 (4H, tt, *J* = 1.35, 7.23 Hz, *meso*-PhH_p), 7.83 (8H, d, *J* = 7 Hz, *meso*-PhH_o), 8.36 (4H, s, β-H); FAB-MS, *m/z* 919 $(M + H)^+$.
***cis*-OPP:** ^{1}H NMR δ -1.85 (2H, br s, NH), 6.62-6.82 (20H, m, β-PhH), 6.74 (1H, tt, *J* = 1.36, 7.23 Hz, *meso*-PhH_p), 6.84 (2H, m, *meso*-PhH_m), 7.24 (4H, m, *meso*-PhH_m), 7.31 (2H, tt, *J* = 1.35, 7.24 Hz, *meso*-PhH_p), 7.58 (2H, dd, *J* = 7 Hz, *meso*-PhH_o), 7.73 (3H, t, *J* = 7 Hz, *meso*-$\text{PhH}_{m,p}$), 7.80 (4H, dd, *J* = 7 Hz, *meso*-PhH_o), 8.21 (2H, dd, *J* = 7 Hz, *meso*-PhH_o), 8.46 (2H, br d, *J* = 4.52 Hz, β-H), 8.57 (2H, d, *J* = 4.52 Hz, β-H); FAB-MS, *m/z* 919 $(M + H)^+$.
DecPP: ^{1}H NMR δ -1.30 (2H, br s, NH), 6.59-6.88 (36H, m, β-PhH and *meso*-$\text{PhH}_{m,p}$), 7.17 (4H, t, *J* = 7 Hz, *meso*-PhH_m), 7.27 (2H, tt, *J* = 7 Hz, *meso*-PhH_p), 7.62 (4H, m, *meso*-PhH_o), 7.79 (4H, d, *J* = 7 Hz, *meso*-PhH_o), 8.21 (2H, br s, β-H); FAB-MS, *m/z* 1071 $(M + H)^+$.

8. Takeda, J.; Sato, M.; Satow, M. Manuscript in preparation.

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