Reduction of Dicationic Porphyrin with N^{21},N^{22}- and N^{23},N^{24}- Double Bridge

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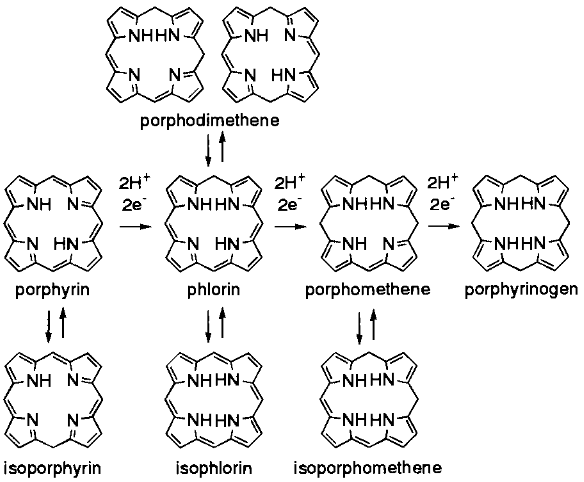
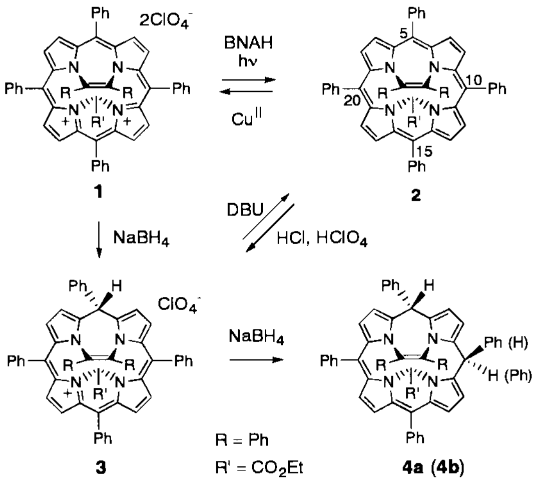
(Received March 16, 2001; CL-010230)

Novel 5*H*,10*H*-isoporphomethenes were obtained by the NaBH$_4$ reduction of dicationic porphyrin with N^{21},N^{22}-(1,2-diphenyletheno) and N^{23},N^{24}-(ethoxycarbonylmethano) double bridge.

A variety of reduced forms of porphyrin with different oxidation states are known and they include isomeric forms arising from imine–enamine tautomerism, for instance, between porphyrin and isoporphyrin.[1] Phlorin, isophlorin, and porphodimethenes are two-electron reduced porphyrins. Porphomethene and isoporphomethene are four-electron reduced forms and porphyrinogen is a six-electron reduced form.[2] Since these compounds are readily isomerized to chlorins or oxidized to porphyrin, their isolation and characterization are not easy.[3] We have been studying on redox chemistry of *N*,*N'*-bridged porphyrins and succeeded to obtain 5*H*-phlorins,[4] 15*H*-phlorins,[5] and isophlorins[6] with remarkable stability. We describe here that dicationic doubly *N*,*N'*-bridged porphyrin **1** undergoes hydride attack at the 5-*meso* position and then at the 10-*meso* position to give monocationic 5*H*-phlorin **3** and neutral isoporphomethenes **4a** and **4b**.



We have recently isolated both of 18π-aromatic porphyrin **1** and 20π-antiaromatic isophlorin **2** when N^{21},N^{22}-(1,2-diphenyletheno) and N^{23},N^{24}-(ethoxycarbonylmethano) double bridges were introduced.[6] While photoirradiation of **1** by a xenon lamp for 1 min in the presence of *N*-benzylnicotinamide (3 equiv) caused two-electron reduction to give **2** in 66% yield, **1** was reduced with 1 molar equiv of NaBH$_4$ in THF at room temperature for 5 min to give 5*H*-phlorin perchlorate **3**[7] in 91% yield. The same compound was formed in 91% yield when the isophlorin **2** in THF was protonated with aqueous 1% HCl soln followed by anion exchange with 1% aqueous HClO$_4$ soln. Spectroscopic properties of **3** are consistent with the stereochemistry where hydride attacks on the *exo* side of the 5-*meso* position of **1**. The observed NOE correlation between the singlet at 4.22 ppm due to the *meso*-proton and the doublet at 5.34 ppm due to the *ortho*-phenyl protons at the N^{21},N^{22}-bridge is consistent with the presence of 5-*exo*-proton on the basis of the 5*H*-phlorin model structure **3'** as depicted in Figure 1. This stereochemistry is similar to the case of NaBH$_4$ reduction of monocationic N^{21},N^{22}-(1,2-diphenyletheno)-bridged porphyrin.[4] The preferential reduction of **1** at the 5-*meso* position over the 15-*meso* position is explained in terms of a greater strain imposed by the N^{21},N^{22}-(1,2-diphenyletheno)-bridge on the porphyrin ring than N^{23},N^{24}-(carboethoxymethano)-bridge.



Scheme 1.

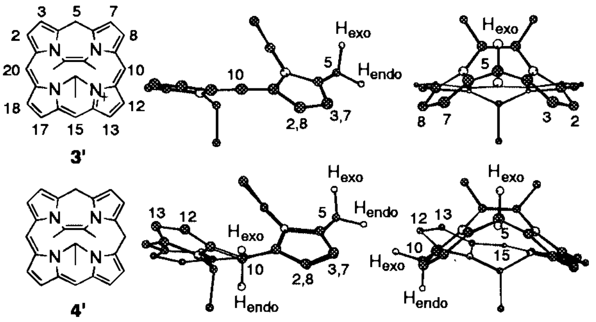


Figure 1. Optimized geometries on the AM1 level (side-on views of the porphyrin plane) of a model 5*H*-phlorin **3'** (top) and a model 5*H*,10*H*-isoporphomethene **4'** (bottom) having N^{21},N^{22}-(MeC=CMe) and N^{23},N^{24}-(CHMe) double bridge.

The further reduction of **3** with 5 molar equiv of $NaBH_4$ proceeded cleanly in THF at room temperature for 10 min to give 5*H*,10*H*-isoporphomethenes **4a**[8] and **4b**[8] in 31% and 36% yields, respectively, after chromatographic separation on silica gel (R_f values on a TLC plate with benzene: 0.80 and 0.57). UV–vis spectra of **4a** (539 nm) and **4b** (531 nm) indicate that multiple *meso*-positions are saturated. Nucleophilic addition of hydride to **3** is expected to occur at the 10-*meso* position rather than at the 15-*meso* position because the latter must lead to the structure with charge separation. The ^1H NMR spectral pattern of **4a** and **4b** is consistent with 5*H*,10*H*-isoporphomethene. As far as we know, these compounds are the first example of isoporphomethene, whereas some *meso*-alkylated porphomethenes have recently been isolated.[9] ROESY correlation between the 10-*meso*-proton at 5.69 ppm and the N^{23},N^{24}-methine proton at 6.84 ppm provides evidence in support for *trans* relationship of the 5-*meso*-proton and the 10-*meso*-proton for **4a**. A remarkable up-field shift observed for the 12-pyrrole-β-proton (4.98 ppm) of **4a** can be ascribed to the ring current effect of the 10-*meso*-phenyl group that is on the *exo* side as depicted in the model structure **4'** of Figure 1. On the other hand, the ring current effect of the 10-*meso*-phenyl group on the *endo* side of **4b** causes upfield shifts of the ethyl ester protons of the N^{23},N^{24}-methano bridge as seen in Table 1.

Table 1. ^1H NMR Chemical shifs (δ) of porphyrin dication (**1**), phlorin monocation (**3**), and isoporphomethenes (**4a**) and (**4b**)

	1	**3**	**4a**	**4b**
pyrrole-β-H	9.68, 8.96	7.72, 7.32	5.53, 5.81	6.10, 6.00
	9.42, 8.58	7.47, 7.09	5.80, 5.58	5.92, 5.69
			4.98, 5.90	6.15, 5.89
			6.44, 5.70	6.31, 5.64
5-*meso*-H	–	4.22	5.34	5.38
10-*meso*-H	–	–	5.69	5.63
bridge-phenyl *o*-H	3.03	5.34	6.65, n.d	6.53, 6.55
m-H	6.25	6.76	6.97, n.d	7.02, 6.94
p-H	6.53	6.95	7.07, n.d	7.06, 7.05
$CO_2CH_2CH_3$ (CH_2)	2.18	3.34	4.22	3.46
$CO_2CH_2CH_3$ (CH_3)	0.05	0.71	1.25	0.94
N,*N'*-CH	–5.79	0.86	6.84	6.38

Measured in $CDCl_3$.

Since the ^1H chemical shifts of the *meso*-protons and pyrrole-β-protons of **4a** and **4b** are very similar to those of *meso*-tetraphenylporphyrinogen (5.38 ppm for *meso*-H; 5.68 and 5.78 ppm for pyrrole-β-H),[10] there is no residual ring current in **4a** and **4b**. The π-conjugation should be completely interrupted at the 10-*meso* position where two adjacent pyrroles are tilted in the opposite directions as seen in the model structure of **4'**. On the other hand, two pyrroles next to the saturated 5-*meso* position are tilted in the same direction (see **3'** and **4'** in Figure 1). This fixed conformation allows π-orbitals at the 4 and 6-positions to come close and effects conjugation across the 5-*meso* position. Although the chemical shifts of pyrrole-β-protons are diagnostic of the ring current effect, they may be influenced by other factors such as charge.[11] The great upfield shift of the N^{23},N^{24}-methine proton of **3** at 0.86 ppm in comparison with that of **4a** at 6.84 ppm well illustrates homoaromatic character of **3**. Taking into consideration the chemical shifts (–5.79 ppm) of the corresponding proton of **1**, diamagnetic ring current of **3** is estimated to be half as much as that of **1**.

In conclusion, unusual two- and four-electron reduced states of porphyrin chromophore were obtained with the aid of N^{21},N^{22}- and N^{23},N^{24}- double bridge.

This work was supported by a Grant-in-Aid for Scientific Research (No.12440186) from the Ministry of Education, Science, Sports, and Culture, Japan, and by Photonics Material Laboratory of the Graduate School of Science and Technology of Kobe University.

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7 **3**: Yield 91%; MS (ESI in MeOH): *m/z* 877.27 (calcd for $C_{62}H_{45}N_4O_2$ (M – ClO_4), 877.35); UV–vis (CH_2Cl_2): λ_{max}(log ε) 376 (4.57), 451 (4.93), 526 (3.79), 778 (4.47) nm; Anal. Calcd for $C_{62}H_{45}N_4O_6Cl\cdot1.5(H_2O)$: C, 74.13; H, 4.82; N, 5.58%; Found: C, 74.40; H, 4.55; N, 5.51%; ^1H NMR (δ, $CDCl_3$): see Table 1.

8 **4a**: Yield 31%; MS (ESI in MeOH): *m/z* 878.29 (calcd for $C_{62}H_{46}N_4O_2$ (M), 878.36); UV–vis (CH_2Cl_2): λ_{max}(log ε) 511 (4.33), 539 (4.35) nm; Anal. Calcd for $C_{62}H_{46}N_4O_2$: C, 84.71; H, 5.27; N, 6.38%; Found: C, 84.76; H, 5.78; N, 6.02%; ^1H NMR (δ, $CDCl_3$): see Table 1. **4b**: Yield 36%; MS (ESI in MeOH): *m/z* 878.30 (calcd for $C_{62}H_{46}N_4O_2$ (M), 878.36); UV–vis (CH_2Cl_2): λ_{max}(log ε) 506 (4.33), 531 (4.36) nm; Anal. Calcd for $C_{62}H_{46}N_4O_2\cdot0.5(H_2O)$: C, 83.85; H, 5.33; N, 6.31%; Found: C, 83.96; H, 5.54; N, 6.10%; ^1H NMR (δ, $CDCl_3$): see Table 1.

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