Nitration of *N*-Confused Porphyrin

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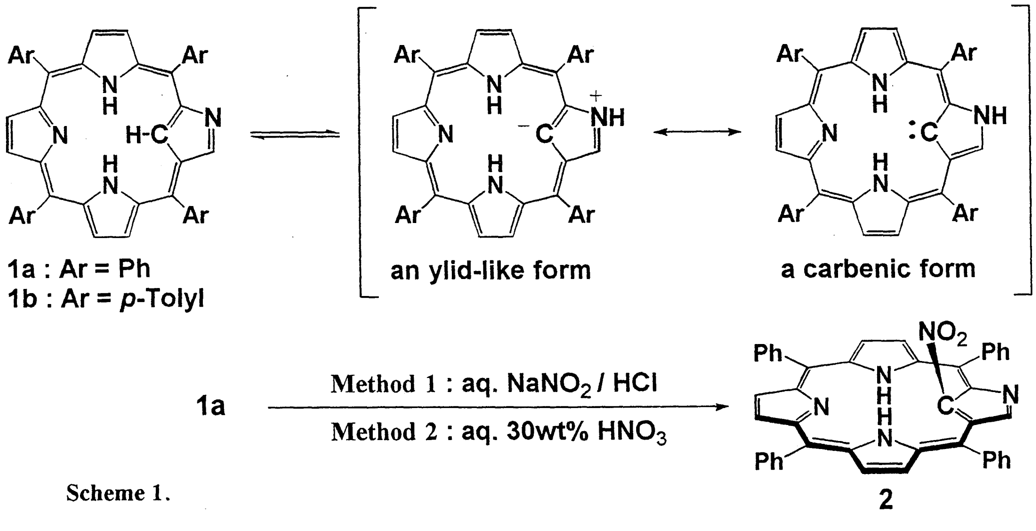
The internal carbon of the inverted pyrrole in *N*-confused tetraphenylporphyrin **1** (5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrin) was nitrated by using the following aqueous solutions at room temperature for several minutes; (1) $NaNO_2$ / HCl (yield 71%) and (2) 30 wt% nitric acid (yield 27%).

A new type of porphyrin isomer, *N*-confused porphyrin **1**, is isolated and characterized independently by us (Furuta)[1] and by Polish researchers (Latos-Grazynsky)[2]. The key skeleton of the *N*-confused porphyrin is the α - β' linked, inverted pyrrole ring which has an internal carbon-proton bond and a nitrogen on external of the ring. Stepwise syntheses of this inverted type of porphynoid become increasingly reported.[3] Displacing the internal proton onto the peripheral nitrogen allows us to depict the porphyrin ring as a carbenic tautomer as shown in Scheme 1. In Ni(II)-*N*-confused porphyrin, the contribution of the carbene lone pair to a highly favorable covalent interaction between the Ni(II) and the internal carbon is supposed (Ghosh)[4] from the *ab initio* calculation. It has been shown that methylation onto the internal carbon of the *N*-confused porphyrins.[2c] In addition to interests on its organometallic property, the seemingly reactive structures, an ylid-like and a carbenic forms, caused us to wonder how the internal carbon responds to electrophilic reagents. Here through nitration we test the reactivity of the internal carbon of **1** to see if the reactivity is high enough to induce aromatic substitution. We report on the nitration of the internal carbon. This aromatic substitution on the internal carbon is the first instance of the free-base form of *N*-confused porphyrin.

Nitration onto the free-base form of **1a** has been performed with aqueous $NaNO_2$/HCl at room temperature (Method 1). Aqueous hydrochloric acid solution (3.3 wt%, 100 ml) of sodium nitrite (1.0 g) was mixed with 60 ml of dichloromethane solution of **1a** (100 mg). The two layers, oily and aqueous, were vigorously stirred at room temperature for one min. TLC analysis of this reaction mixture showed a single product which could be seen as dark green spot at R_f 0.7 (Merck Kieselgel $60F_{254}$, CH_2Cl_2). After neutralizing the reaction mixture, the oily layer was removed, and the residue was column-chromatographed on silica gel with dichloromethane. Collection of the first greenish band followed by recrystallization with hexane yielded 76 mg (71%) greenish powder.[5] The yield of the compound varied with the acid concentration. No reaction proceeded without the acid. Use of the acid in a concentration higher than 3.3 wt% reduced the yields because of a reddish byproduct formation (TLC, R_f 0.5, CH_2Cl_2). IR spectrum of the greenish powder shows two typical peaks for nitro group at 1470 cm^{-1} (ν_{as}) and 1290 cm^{-1}(ν_s). FAB-mass spectrum shows the parent peak at m/z = 661.00 (M + H) possessing a fragment at m/z = 615.00 (M - NO_2 + H). Even after the nitration, the so-called Soret (470 nm) and Q bands (648 nm and 697 nm) are observable in its electronic absorption spectrum as shown in Figure 1. These facts, including elemental analysis,[6] indicate that one nitro, not a nitroso, group is introduced into **1a**.

The position of the nitro group in the product **2** was investigated by NMR spectroscopy. The internal C-H proton of **1** provides a sharp singlet signal at a remarkably high field, -5.02 ppm in CD_2Cl_2, due to the ring current.[1a] This distinguishable signal disappears as nitration takes place. In ^{13}C-NMR spectrum given in Figure 2, the internal carbon of **2** appears at a lower field by 15.4 ppm than that of the C-H in **1** (99.2 ppm). The 99.2 ppm peak of the internal carbon of **1** shows a cross contour to the ^{1}H signal being at -5.02 ppm in CH-COSY spectrum.[1a] On the other hand, the 114.6 ppm signal of the internal carbon of the nitrated porphyrin is not relevant to any proton at all in its CH-COSY spectrum.[5] On the basis of these results, it can be



Scheme 1.

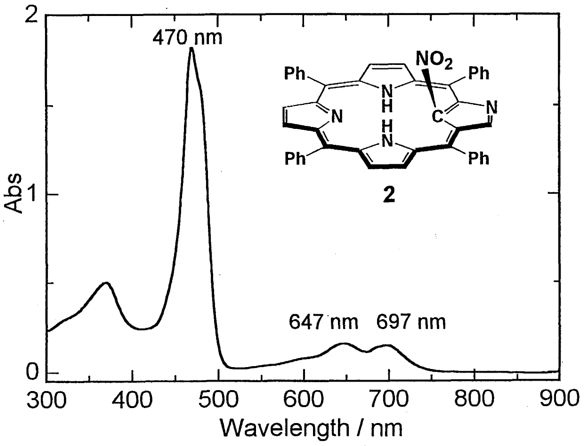


Figure 1. UV-vis absorption spectrum of **2** (CH_2Cl_2, 2.0×10^{-5} M, room temperture, cell length 1cm)

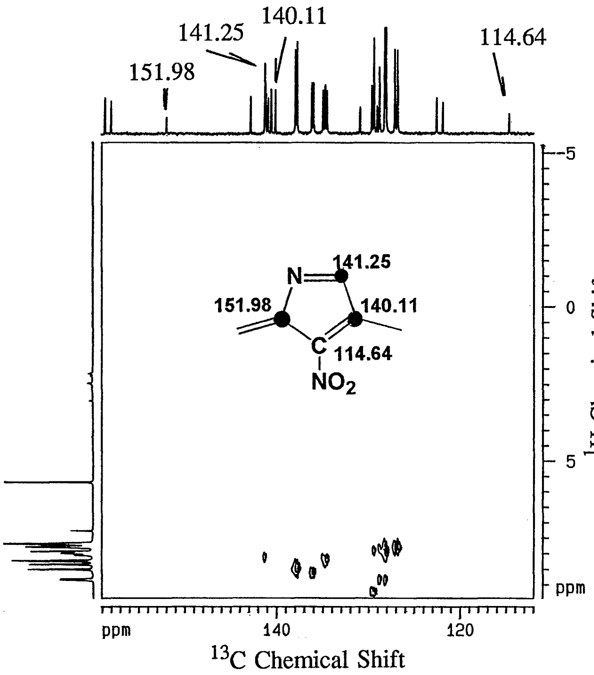


Figure 2. CH-COSY spectrum of **2** ($CDCl_3$, TMS, 25 ℃). Inset indicates a set of ^{13}C chemical shifts for the inverted pyrrole of **2**.

reasonably deduced that the internal carbenic C-H is substituted by an electron-withdrawing nitro group which causes the downfield shift in the NMR spectra.

The nitrated *N*-confused porphyrin can also be isolated in a 27% yield by using aqueous 30 wt% nitric acid without sulfuric acid at room temperature for several min (Method 2). For the two nitration procedure, we interpret that both nitronium and nitrosonium[7] ions are plausible electrophiles for the internal carobn of **1**. Attempt to clarify its precise nitration process is an ongoing subject.

The high reactivity[8] of the internal C-H is likely to be an untapped resource for designing a new supramolecular assembly. X ray structual analysis and transformation of the nitro group to other functional form for instrumental optical materials are underway.

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References and Note

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5 **^{1}H-NMR**(300 MHz, $CDCl_3$); δ 9.23 (1H, d, pyrrole), 9.19 (1H, d, pyrrole), 8.81(2H, d, pyrrole), 8.60(1H, d, pyrrole), 8.60(1H, d, pyrrole), 8.45(4H, d, o-phenyl), 8.24-8.13(4H, m, o-phenyl), 8.09 (1H, s, pyrrole), 7.92-7.78(12H, m, p-phenyl), -3.0(2H, br, NH). **^{13}C-NMR**(75 MHz, $CDCl_3$) for the inverted pyrrole, see Figure 2; δ 151.98(methine), 141.25(CH), 140.11(methine), 114.64(C-NO_2). **CH-COSY**($CDCl_3$); (^{13}C, ^{1}H) = (129.37, 9.23), (129,61, 9.19), (128.76, 8.81), (128.16, 8.81), (136.18, 8.60), (135.98, 8.60), (141.25, 8.09). **UV-Vis**(CH_2Cl_2)λ_{max}; 369 nm (logε 4.56), 470 nm (logε 5.10), 647 nm (logε 4.06), 697 nm (logε 4.05). **IR** (KBr); 1290 cm^{-1} (NO_2, ν_s), 1470 cm^{-1} (NO_2, ν_{as}), 722 cm^{-1} ($\nu_{C\text{-}N}$). **FAB-MS**; 661 (M+H) and 615 (M-NO_2+H).

6 Anal. (the presence of dicloromethane detected in the ^{1}H-NMR); Found: C, 69.28, H, 4.00, N, 8.97%. Calcd for $C_{44}H_{29}N_4NO_2 \cdot (CH_2Cl_2)_{1.5}$: C, 69.42, H, 4.09, N, 8.89%.

7 Electrophilic attack by nitrosonium ion followed by oxidation with O_2 in air is a candidate for the nitration process.

8 As opposed to the relatively mild reaction conditions of the Method 1 and 2, nitration of the phenyl groups of ordinary tetraphenylporphrin generally requires more concentrated HNO_3 such as fuming nitric acid.[9]

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