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Synthesis and inversion barriers of undeca- and dodeca-substituted saddle shaped porphyrin complexes☆

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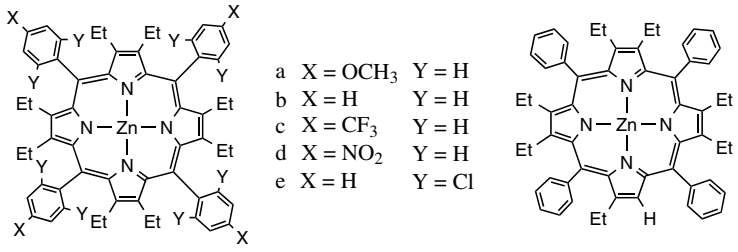
Abstract—Synthesis and barriers to inversion of a series of highly saddle shaped complexes are reported. The $\Delta G^{\neq}$ has decreased by 8 kJ mol^{-1} at 243 K when the *meso* phenyl groups are replaced by bulkier 2,6-dichlorophenyl groups, and by 17 kJ mol^{-1} when one of the peripheral ethyl groups is removed.

Highly deformed porphyrin complexes have attracted much attention because they serve not only the unique ligand field of the central metal ions but also the unique platform to recognize the ligand molecules.[1] One of the important factors to accomplish the above mentioned properties is the rigidity of porphyrin core. In the course of our research to reveal the effects of porphyrin deformation on the electronic structure of metal porphyrinates,[2] we have found that the rigidity of the saddled porphyrin ring is greatly influenced by the peripheral modification. Here, we report the synthesis of saddle shaped Zn(II)(OETArP)(**1a**–**e**) and Zn(II)(HpETPP)(**2**) together with their activation parameters for ring inversion determined by the dynamic ^{1}H NMR spectroscopy (Scheme 1).[3,4]

The free base porphyrins (OETArP)H_2 were prepared from 3,4-diethylpyrrole and the corresponding substituted benzaldehydes in CH_2Cl_2 solution according to the literature method.[5] Treatment of these porphyrins with zinc acetate in refluxing CH_2Cl_2–THF solution in the presence of anhydrous sodium sulfate gave the corresponding zinc complexes **1a**–**e**. (HpETPP)H_2 was similarly prepared from benzaldehyde-d_5 and a 3:1 mixture of 3,4-diethylpyrrole and 3-ethylpyrrole in the presence of $BF_3{\cdot}OEt_2$ in refluxing CH_2Cl_2 solution; deuterated benzaldehyde was used to simplify the ^{1}H NMR spectrum. The porphyrinogen thus formed was oxidized by DDQ. In addition to (HpETPP)H_2, several porphyrin compounds represented as (Et_x–TPP)H_2 (x = 4–8) were formed. In principle, there are 4, 4, and 5 geometrical



Zn(OETArP) (**1a**-**1e**) Zn(HpETPP) (**2**)

Scheme 1. Complexes examined in this study.

Keywords: Nonplanar porphyrins; Inversion barriers; Dynamic NMR.
☆The Eyring's plots are given as Supplementary data.
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isomers for the compounds with $x = 4$, 5, and 6, respectively; $(OETPP)H_2$ and $(HpETPP)H_2$ where $x = 8$ and 7, respectively, have no geometrical isomers. Separation and purification of $(HpETPP)H_2$ from 15 possible porphyrin compounds were carried out by the repeated column chromatography on basic alumina (activity I). Elution with CH_2Cl_2 yielded a mixture of compounds with $x = 4$, 5, and 6 as easily eluted components. Pure $(HpETPP)H_2$ was obtained in 13% yield when CH_2Cl_2/MeOH (0.5%) was used as an eluent. Treatment of this porphyrin with zinc acetate gave **2**, which was further purified by recrystallization from CH_2Cl_2–methanol. ^1H NMR (CD_2Cl_2, δ ppm, 298 K): 0.41 (CH_3), 0.43 (CH_3), 0.49 (CH_3), 0.52 ($2CH_3$), 0.69 (CH_3), 0.97

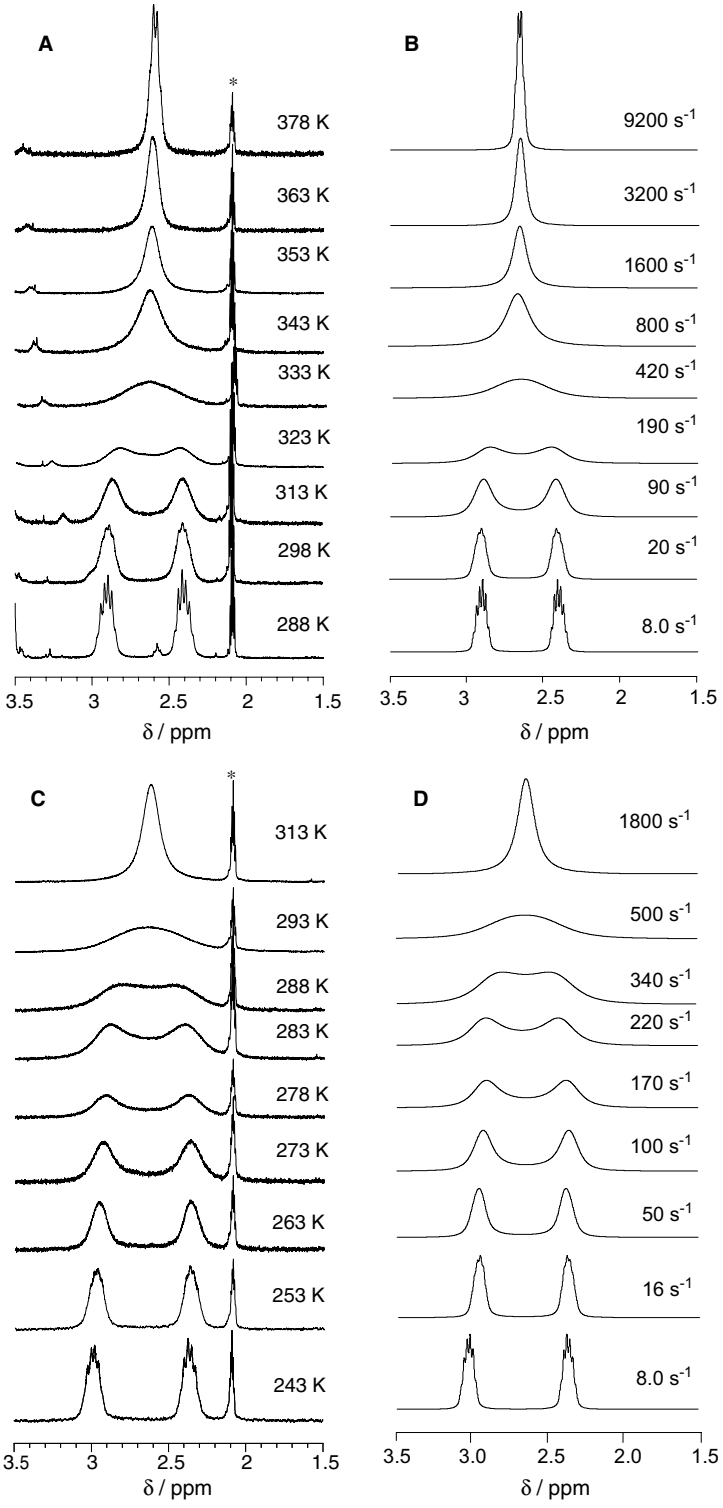

Figure 1. (A) Temperature dependent ^1H NMR spectra of the methylene signals of **1a**. (B) Simulated spectra of **1a**. (C) Temperature dependent ^1H NMR spectra of the methylene signals of **1e**. (D) Simulated spectra of **1e**. The asterisks * in (A) and (C) are due to the solvent.

Table 1. Activation parameter and rate constants in toluene-d_8 solutions

Complexes	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J mol^{-1} K^{-1}	$\Delta G^{\neq}$ (243 K)/kJ mol^{-1}	k (243 K)/s^{-1}
1a	68.4	8.6	66.3	0.028
1b	67.5	13.2	64.3	0.075
1c	62.5	9.1	60.3	0.55
1d	69.7	17.3	65.5	0.042
1e	52.3	−15.2	56.0	4.6
2	—	—	46.9	430

(CH_3), 2.3–2.4 ($5CH_2$), 2.45 (CH_2), 2.52 (CH_2), 8.07 (pyrrole-H). FAB-MS: $m/z = 895$ $(MH)^+$. The ^{1}H NMR spectra of **1a**–**e** and **2** were taken in CD_2Cl_2 solution at 298 K. While the methylene protons of each ethyl group in **1a**–**d** were nonequivalent and gave two broad multiplets at δ = ca. 2.0 and 2.6 ppm, those of **1e** gave a broad singlet at $\delta = 2.45$ ppm, suggesting that the inversion rates are very much different between **1a**–**d** and **1e**.

The activation parameters for ring inversion were determined on the basis of the computer simulation of the observed spectra taken in toluene-d_8 solution.[5,6] Figure 1 shows the observed and calculated NMR spectra of the methylene parts of **1a** and **1e** as typical examples. Table 1 lists the activation parameters of **1** determined by the Eyring's plots; they are given as Supplementary data. Figure 2 shows the temperature dependent NMR spectra of the methylene parts of **2**. In contrast to the case of **1**, the activation parameters of **2** were much more difficult to determine. This is because all the 14 protons of methylene groups in **2** become nonequivalent when the ring inversion is frozen on the NMR timescale.

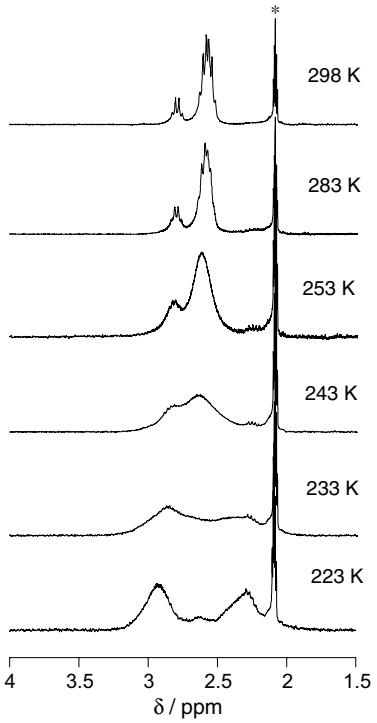

Figure 2. Temperature dependent ^{1}H NMR spectra of the methylene signals of **2**. The solvent peaks are signified by *.

The ^{1}H NMR spectrum at 298 K indicates that seven methylene groups are separated into two groups in a 1:6 ratio at 2.76–2.83 and 2.52–2.63 ppm, respectively. The inversion of the porphyrin ring is fast on the NMR timescale because one methylene group at 2.76–2.83 ppm exhibited clear quartet due to the coupling with the methyl group. As the temperature was lowered, each of the two groups of signals broadened and split into two broad signals below 243 K. Thus, the activation free energy was roughly estimated to be 46.9 kJ mol^{-1} at 243 K,[7] which is also listed in Table 1 together with the rate constants for inversion. The data in Table 1 indicate that the $\Delta G^{\neq}$ values in **1a**–**d** have little correlation with the electronic properties of *para* substituents; both **1a** and **1d** carrying electron donating *p*-OCH_3 and electron withdrawing *p*-NO_2 groups, respectively, have shown slightly larger $\Delta G^{\neq}$ than unsubstituted **1b**. Clear substituent effect was observed, however, when bulky chloro groups were introduced at the *ortho* positions; **1e** has a fairly small $\Delta H^{\neq}$ and a negative $\Delta S^{\neq}$ as compared with those of **1b**. The results strongly indicate the existence of the steric repulsion between the chloro groups and porphyrin core. The repulsion could destabilize the most stable conformation of the complex and increase the dynamic flexibility at the ground state for inversion, resulting in the decrease in both $\Delta H^{\neq}$ and $\Delta S^{\neq}$. Much larger decrease in inversion barrier ($\Delta G^{\neq}$) was observed in **2** where one of the pyrrole-Et groups was removed. The barrier of **2** decreased by 17 kJ mol^{-1} at 243 K as compared with that of **1b**, which corresponds to the increase in the rate constant by 5700 times. Since the major reason for the inversion barrier in saddled porphyrin ring is the steric repulsion between the *meso* and β-pyrrole substituents at the transition state for inversion,[5] the large decrease observed in **2** should be ascribed to the loss of one of the pyrrole-Et groups.

In summary, we have revealed on the basis of the dynamic NMR method that the inversion barriers of highly saddled porphyrin rings are greatly influenced by the peripheral modification. We are currently doing research to determine the inversion barriers in five geometrical isomers of Zn(Et_6–TPP), which will reveal the relationship between the peripheral substitution patterns and the barriers to ring inversion.

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Supplementary data

Erying's plots of **1a**–**e**. Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.tetlet.2005.05.100.

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6. Computer simulation was performed with gNMR software purchased from Adept Scientific, Amor Way, Letchworth Herts SG6 1ZA, UK.
7. Difference in chemical shifts of diastereotopic CH_2 protons at the coalescence temperature (T_c = 243 K) was estimated to be 0.64 ppm (192 Hz) on the basis of the ^{1}H NMR spectra at lower temperatures. The inversion rate constant at this temperature was calculated to be 430 s^{-1}, which corresponds to $\Delta G^{\neq}$ = 46.9 kJ mol^{-1}.