A Kinetic Study of Thermal Rotational Isomerization of 5,10,15,20-Tetrakis(*o*-aminophenyl)porphyrin and 5,10,15,20-Tetrakis(*o*-pivaloylaminophenyl)porphyrin

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Synopsis. Rates of thermal interconversion of atropisomers of 5,10,15,20-tetrakis(*o*-aminophenyl)porphyrin and 5,10,15,20-tetrakis(*o*-pivaloylaminophenyl)porphyrin have been determined.

It is well known that four atropisomers of *ortho*-substituted tetraarylporphyrins can be thermally or photochemically interconverted by rotation about a porphyrin-aryl bond.[1-4,6] In a previous paper,[4] we reported the isomerization reactions of tetrakis(*o*-cyanophenyl)porphyrin (ToCNPP) atropisomers. Herein we report the isomerization rates of 5,10,15,20-tetrakis(*o*-aminophenyl)porphyrin ($ToNH_2PP$) and 5,10,15,20-tetrakis(*o*-pivaloylaminophenyl)porphyrin (ToPivPP) studied at various temperatures in order to compare the effects of the *ortho* substituents on the atropisomerization.

Experimental

$ToNH_2PP$ was synthesized by methods described in the literature.[1] Calcd for $C_{44}H_{34}N_8 \cdot H_2O$; C, 76.21; H, 5.20; N, 16.16. Found: C, 76.38; H, 4.68; N, 16.01%. The separation of $ToNH_2PP$ into the four atropisomers was carried out by column chromatography on silica gel eluted with 98:2 chloroform–methanol. The preparation and purification of the four atropisomers of ToPivPP was described previously.[5]

The isomerization reactions of $ToNH_2PP$ were conducted in toluene or 1,1,2-trichloroethane solutions heated at a temperature range of 65 to 95 °C. The quantity of each isomer at appropriate reaction times was evaluated spectrometrically on the chloroform extracts of the TLC spots, or measured directly by the integrated peak area recorded on a TLC scanner.

The isomerization reactions of ToPivPP were monitored by the NMR spectral changes recorded on a JEOL FX-100 spectrometer operating in FT mode. The NMR signals due to the methyl protons of the pivaloylamino substituent allow an unambiguous assignment to each of the four conformations as described.[5] The isomerization of ToPivPP was carried out by dipping an NMR tube containing a toluene-d_8 solution of the isomers into the heated oil bath.

Results and Discussion

Thermal rotation of one substituted phenyl ring about the phenyl–porphyrin bond lead to the stereochemical isomerization reactions among the atropisomers of $ToNH_2PP$ or ToPivPP as shown schematically in Fig. 1. The R_f values on TLC eluted with 95:5 chloroform–methanol are 0.26, 0.18, 0.07, and 0.03 for $\alpha\beta\alpha\beta$-, $\alpha\alpha\beta\beta$-, $\alpha\alpha\alpha\beta$-, and $\alpha\alpha\alpha\alpha$-isomer of $ToNH_2PP$, respectively.

On permitting a toluene solution of $ToNH_2PP$ isomers to stand for 2 d at 80 °C, the four isomers were present in 0.15, 0.27, 0.49, and 0.09 ratio for the $\alpha\beta\alpha\beta$-, $\alpha\alpha\beta\beta$-, $\alpha\alpha\alpha\beta$-, and $\alpha\alpha\alpha\alpha$-isomers, respectively. The ratio was close to the statistical 1:2:4:1 ratio expected in equilibrium for the case where there is no mutual interaction between the *ortho* substituents.[4] The free energy difference corresponding to the small deviation from the ideal ratio was evaluated to be at most 0.4 kJ mol^{-1}. This value is small enough to be ignored in the rate constant determination. Therefore the rate data could be processed by assuming the idealized statistical ratio at equilibrium. Under these conditions, each isomer is considered to possess four equivalent rotational bonds. Thus, a relationship in the rate constants is deduced as follows: $k_r=k_2=k_6=k_4/2=k_1/4=k_3/4=k_5/4$, where k_r is the rate constant for the rotation about one phenyl–porphyrin bond of any isomer. The observed rate constants entered in Fig. 1 are consistent with this relationship within the experimental errors. The values of k_r were determined from several independent experiments at 65, 75, 85, 93, and 95 °C.

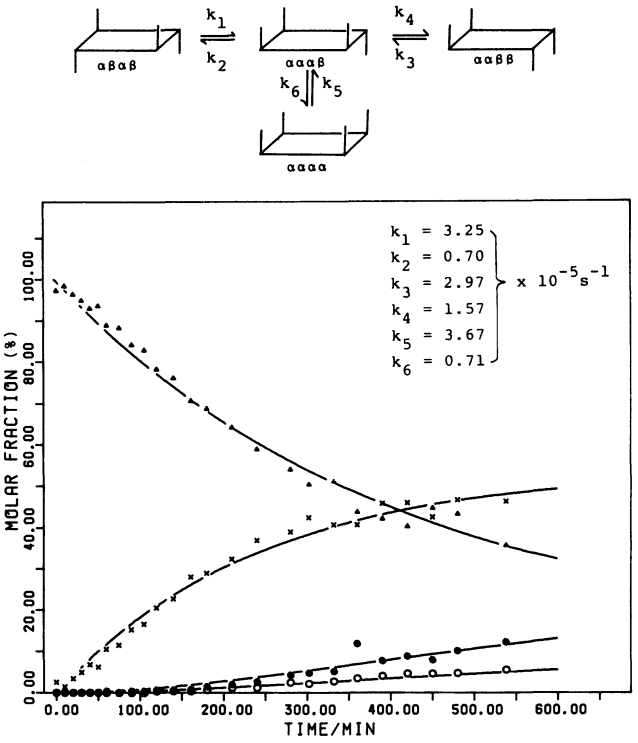

Fig. 1. Time course of isomerization starting from $\alpha\alpha\alpha\alpha$- isomer of $ToNH_2PP$ at 65 °C.
(○) $\alpha\beta\alpha\beta$; (●) $\alpha\alpha\beta\beta$; (×) $\alpha\alpha\alpha\beta$; (▲) $\alpha\alpha\alpha\alpha$. The solid lines are the best fit curves computed from the rate constants in the frame.

The equilibrium mixture of ToPivPP atropisomers produced by heating a solution of $\alpha\alpha\alpha\alpha$-

Table 1. Activation parameters for the rotation of the *ortho*-substituted phenyl ring about the porphyrin-phenyl bond in free base tetraaryl porphyrins

Substituent group	ΔG^*/kJ mol^{-1}					ΔH^*/kJ mol^{-1}	ΔS^*/J deg	Ref
	296 K	333 K	338 K	354 K	433 K	(333 K)		
Piv[a]		125.6				66.6	−177	This work
HA[b]				118.5[c]		54.4	−168[c,d]	(6)
NH_2	113.2[e]	115.6[e]	115.9	117.0[e]	122.3[e]	91.6	−72	This work
CN		103.0[c]				87.0	−60	(4)
OH	100							(2)
CH_3O					108			(3)

a) Pivaloylamino. b) Hexadecyloylamino. c) Derived from the rate constant for the isomerization of $\alpha\alpha\alpha\alpha$- to $\alpha\alpha\alpha\beta$-isomer. d) 354 K. e) Extrapolated value.

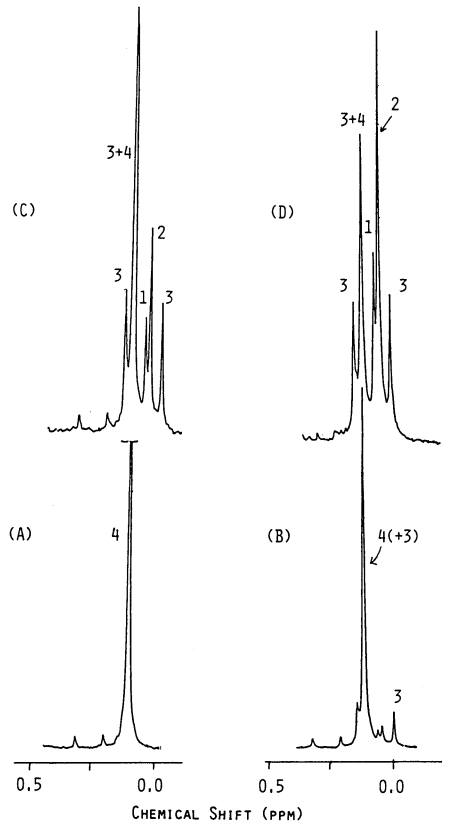

Fig. 2. NMR spectral changes during atropisomerization of ToPivPP at 90°C. Reaction time (A) 0 h (B) 30 h (C) 76 h (D) more than 720 h and the signal assignment 1.$\alpha\beta\alpha\beta$; 2.$\alpha\alpha\beta\beta$; 3.$\alpha\alpha\alpha\beta$; 4.$\alpha\alpha\alpha\alpha$ are shown.

isomer at 90°C for more than 30 d contained four isomers in a ratio of 0.14:0.28:0.47:0.11 for the respective $\alpha\beta\alpha\beta$, $\alpha\alpha\beta\beta$, $\alpha\alpha\alpha\beta$, and $\alpha\alpha\alpha\alpha$-isomers. This ratio is surprisingly close to the statistical ratio.[6] Hence, the rate determination was carried out with the $\alpha\alpha\alpha\alpha$-isomer by assuming the same relationship as in the $ToNH_2PP$ case. The outline of the NMR spectral changes during the atropisomerization reaction of ToPivPP and the signal assignment to each isomer are shown in Fig. 2. The rate constants for rotation about one axis were determined graphically. The k_r values for ToPivPP were obtained at 60, 90, and 103°C. The derived kinetic parameters are listed in Table 1.

The rotational barrier is brought about mainly by the steric hindrance of the *ortho* substituent on the phenyl ring. The bulk of the substituents is the most important factor to affect the height of the barrier. The evaluation of the barrier depending on the *ortho* substituents requires comparison of data at the same temperature. For this purpose, the extrapolation using the Arrhenius activation energy measured in a wide range of temperatures will be effective. The thermochemical activation parameters reported for some *ortho* substituents of tetraarylporphyrin free bases are summarized in Table 1 using the data of the NH_2 group as a common standard. The order of Piv>HA~NH_2>CN>CH_3O~OH with decreasing ΔG^* values was observed as the effect of substituents. The order is reasonable in view of the bulk of the *ortho* substituents, although the high barrier for the NH_2 group is remarkable. The actual friction for rotational isomerization generated by the two protons of NH_2 may be much more resistive than that expected by the simple comparison of the ionic radii.

Another remarkable feature of the kinetic parameters is the difference in the entropy of activation dependent on the substituents. All ΔS^* took negative values.[6] The order was Piv~THA>NH_2~CN with decreasing of the absolute values of ΔS^*. The order is also compatible with the bulk of the *ortho* substituents. This suggests that a bulky substituent at the *ortho* position makes a large contribution to the entropy term in the energy of activation for the rotational isomerization reaction.

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6) R. A. Freitag, J. A. Mercer-Smith, and D. G. Whitten, *J. Am. Chem. Soc.*, **103**, 1226 (1981), communicated a nonstatistical distribution of ToPivPP atropisomers detected by spectrophotometric methods although the ratio was unreported. It seems that there is some disagreement in the spectral observations for ToPivPP between these authors and us.[5] Their rate data obtained at two temperatures for ToPivPP were not entered in Table 1.