fractometer by using monochromatized Mo Kα (λ = 0.71069 Å) radiation and a yellow crystal measuring 0.25 × 0.25 × 0.11 mm. Cell parameters were determined by least-squares refinement, the setting angles of 25 accurately centered reflections ($2\theta > 20°$) being used. Throughout data collection the intensities of three standard reflections (005, 030, 400) were monitored at regular intervals and this indicated no significant crystal decomposition. The intensities were corrected for Lorentz and polarization effects but no correction for absorption was deemed necessary. Reflections with $I > 3\sigma(I)$ were used for structure solution and refinement.

The structure was solved by direct methods and refined by blocked-cascade least-squares procedures. All non-hydrogen atoms were refined with anisotropic thermal parameters. The benzene ring hydrogen atoms were included in calculated positions with isotropic thermal parameters equal to the isotropic equivalent of their carrier atoms. The position of the N1 hydrogen was determined from a difference map and successfully refined. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with $w = [\sigma^2(F_o) + 0.00144F_o^2]^{-1}$. A final difference map showed no features >0.27 e Å^{-3}. All calculations (including diagrams) were performed on a Nova 4X computer using SHELXTL.[5] Final bond lengths and angles are given in Table I. Equations of mean planes are available from P.J.S.

Crystal data at −125 °C: $C_{14}H_9N_9$, M_r = 303.3, triclinic, space group $P\bar{1}$, a = 8.482 (2), b = 9.109 (4), and c = 10.268 (4) Å, α = 72.89 (3)°, β = 74.13 (3)°, γ = 60.27 (2)°, U = 650.6 (4) Å^3, F(000) = 312, Z = 2, D_c = 1.55 g cm^{-3}, μ(Mo Kα) = 0.98 cm^{-1}, ω scans, $2\theta_{max}$ = 52°, N = 2286, N_0 = 1591211 parameters, S = 1.00, R = 0.039, R_w = 0.041.

Supplementary Material Available: Atom coordinates and thermal parameters are listed in Tables 2-4 as supplementary material which includes tabulations of structure factors. Atom coordinates (Table 2) and thermal parameters (Table 3) for compound 6 (2 pages); observed and calculated structure factors for 6 (Table 4) (10 pages). Ordering information is given on any current masthead page.

(5) Sheldrick, G. M. SHELXTL User Manual, Revision 4, Nicolet XRD Corporation, Madison, WI, 1984.

Identification of a Pair of Atropisomeric Porphyrins by ^{1}H NMR Investigations on Their Zinc Derivatives

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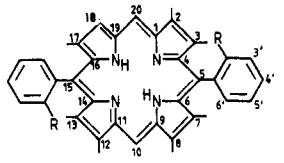
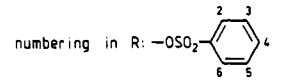
The phenomenon of atropisomerism in porphyrins with meso aryl substituents was described in 1969 for the first time by Gottwald and Ullman, who obtained four isomers in the synthesis of 5,10,15,20-tetrakis(2-hydroxyphenyl)-porphyrin.[1] Since then atropisomerism has been reported for tetra-meso[2] as well as di-meso[3] substituted aryl-porphyrins. The identification of the various atropisomers of the tetraarylporphyrins was based on a combination of arguments. In the first place the quantities of each isomer, present in the equilibrium mixture ($\alpha\alpha\alpha\alpha$:$\alpha\alpha\alpha\beta$:$\alpha\alpha\beta\beta$:$\alpha\beta\alpha\beta$ = 1:4:2:1) allow the $\alpha\alpha\alpha\beta$ and $\alpha\alpha\beta\beta$ isomers to be distinguished from the two others. Secondly, the $\alpha\alpha\alpha\alpha$ atropisomer is usually assumed to be the most polar isomer, with the lowest R_f value in adsorption chromatography. Finally, the ^{1}H NMR spectrum of the pure $\alpha\alpha\alpha\beta$ isomer shows three different sets of resonances for the meso arylprotons, unlike the other three isomers.[4] For the di-meso arylporphyrins, where only two atropisomers are to be expected in a statistical ratio of 1:1, identification was mainly based on the polarity (R_f value) and in a few cases verified by attaching a bridging alkyl chain which encompasses one face of the $\alpha\alpha$ isomer.[3]

During our synthetic work[5] we prepared a number of 5,15-diaryloctamethylporphyrins **1**. For the compounds **1a-f** the purified product contained two isomers, as was evident from the ^{1}H NMR spectrum which showed two sets of signals.



1

1a R = −OSO$_2$−C$_6$H$_4$−4F
1b R = −OSO$_2$−C$_6$H$_5$
1c R = −OSO$_2$−C$_6$H$_4$−4tBu
1d R = −OSO$_2$−C$_6$H$_4$−4OCH$_3$
1e R = −OSO$_2$−C$_6$H$_2$−2,4,6-triMe
1f R = −O(CH$_2$)$_2$−OSO$_2$−C$_6$H$_4$−4F



For **1a** the two isomers were separated. By refluxing for 30 h a xylene solution of the compound which was eluted as the first fraction from the silica gel column, a mixture of the isomers was reformed. On account of its higher R_f value we assigned the $\alpha\beta$ structure to this isomer. In the ^{1}H NMR spectrum in $CDCl_3$ solution the $\alpha\beta$ form showed a higher upfield shift Δδ for the sulfonylaryl protons than the $\alpha\alpha$ isomer.[6] This seemed reasonable as in the folded conformation, preferred by these porphyrins,[5] the phenyl groups of the $\alpha\beta$ form can occupy a position nearer to the centre of the porphyrin ring current than those of the $\alpha\alpha$ form. For the compounds **1b-f** we did not isolate the atropisomers but simply assumed the $\alpha\beta$ structure for the isomer with the higher upfield shifts Δδ (Table I; for

Table I. ^{1}H NMR Data for the Atropisomers of 1a-f

	chemical shift δ (upfield shift Δδ[a]) for the phenyl protons in R (ppm)			
	αα isomer		αβ isomer	
	H2,H6	H3,H5	H2,H6	H3,H5
1a	6.09 (1.81)	4.92 (2.31)	5.73 (2.17)	4.41 (2.82)
1b[b]	6.00 (1.83)	5.06 (2.30)	5.71 (2.12)	4.57 (2.79)
1c	5.95 (1.83)	5.42 (2.13)	5.81 (1.97)	5.16 (2.39)
1d	5.80 (1.99)	4.42 (2.58)	5.69 (2.10)	4.16 (2.84)
1e	-	4.94 (2.06)	-	4.06 (2.94)
1f	6.24 (1.68)	4.88 (2.38)	5.99 (1.93)	4.56 (2.70)

[a] Δδ for a proton is defined as (δ value in the aldehyde 2-R-C$_6$H$_4$CHO) − (δ value in the porphyrin). [b] For H4 δ (Δδ) αα isomer, 5.53 (2.01); δ (Δδ) αβ isomer, 4.92 (2.62).

(1) Gottwald, L. K.; Ullman, E. F. *Tetrahedron Lett.* **1969**, 3071.
(2) See for a review: Freitag, R. A.; Barber, D. C.; Inoue, H.; Whitten, D. G. Mechanistic Studies of Thermal and Photoinduced Atropisomerisation of Substituted Tetraphenyl Porphyrins in Solution and Organized Assemblies. In *Porphyrins, Excited States and Dynamics*; Gouterman, M., Rentzepis, P. M., Straub, K. D. Eds.; American Chemical Society: Washington DC, 1986; Chapter 19 and references cited in this chapter.
(3) Gunter, M. J.; Mander, L. N. *J. Org. Chem.* **1981**, *46*, 4792. Young, R.; Chang, C. K. *J. Am. Chem. Soc.* **1985**, *107*, 898. Ogoshi, H.; Saita, K.; Sakurai, K.; Watanabe, T.; Toi, H.; Aoyama, Y. *Tetrahedron Lett.* **1986**, *27*, 6365. Aoyama, Y.; Kamohara, T.; Yamagishi, A.; Toi, H.; Ogoshi, H. *Tetrahedron Lett.* **1987**, *28*, 2143.
(4) Crossley, M. J.; Field, L. D.; Forster, A. J.; Harding, M. M.; Sternhell, S. *J. Am. Chem. Soc.* **1987**, *109*, 341.
(5) In the folded conformation of **1a-f** both aryl groups of the side chains are folded over the porphyrin ring, one above and one below (αβ isomer), or both at the same face (αα isomer). See: Sanders, G. M.; van Dijk, M.; van Veldhuizen, A.; van der Plas, H. C.; Hofstra, U.; Schaafsma, T. J. *J. Org. Chem.* **1988**, *53*, 5272.
(6) In ref 5 we defined the upfield shifts Δδ as the difference in δ for a sulfonylaryl proton in the porphyrin and the same proton in a reference compound, viz. the aldehyde used in the synthesis.

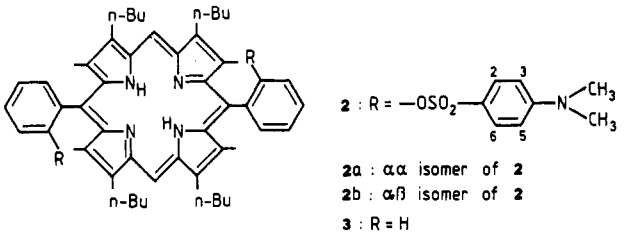
0022-3263/91/1956-1301$02.50/0

Table II. Properties of the Atropisomers 2a and 2b

	R_f (silica gel, chloroform)	δ (Δδ) (ppm) H2,H6	H3,H5	$N(CH_3)_2$
2a	0.38	5.32 (2.22)	3.66 (2.92)	1.23 (1.84)
2a–Zn		5.49 (2.05)	3.71 (2.87)	1.23 (1.84)
2a–Zn + pyridine-d_5		5.42 (2.12)	3.84 (2.74)	1.43 (1.64)
2b	0.28	5.52 (2.02)	3.51 (3.07)	0.81 (2.26)
2b–Zn		5.22 (2.32)	2.87 (3.71)	0.27 (2.80)
2b–Zn + pyridine-d_5		5.85 (1.69)	4.21 (2.37)	1.49 (1.58)

complete NMR spectra see ref 5).

The assignment of structure to the atropisomers was thus based on the R_f value (for **1a**) and on the Δδ values (**1b–f**). We now report a case in which these assignment rules do not hold, e.g. with 5,15-bis[2-[[[4-(dimethylamino)phenyl]sulfonyl]oxy]phenyl]-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphyrin **2**.



Results and Discussion

Properties of the Atropisomers of 2. Compound **2** was synthesized from the corresponding dipyrrolylmethane in the usual way;[5] chromatography of the reaction product gave two compounds **2a** and **2b** which were atropisomers according to their elemental analyses and mass and ^1H NMR spectra.

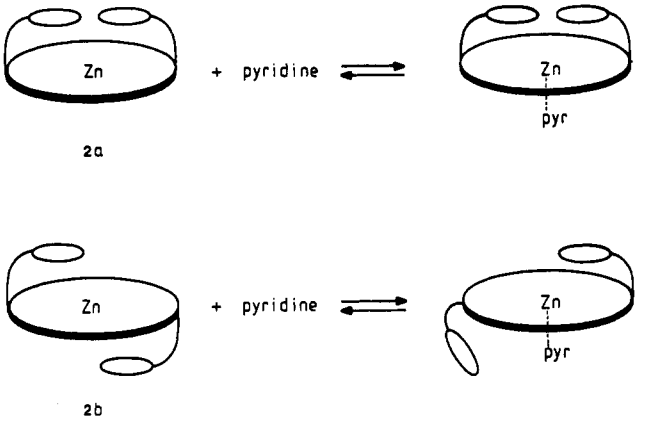
The properties of the two isomers are given in Table II. The compound with the highest R_f value gave the lowest Δδ values for the dimethylanilino protons except for H_2,H_6; thus assignment of the structure was not possible by our simple rules. We solved this problem by preparing zinc derivatives of **2a** and **2b** and measuring their ^1H NMR spectra in $CDCl_3$ solution before and after addition of an excess of deuterated pyridine (Table II; complete data are given in the Experimental Section).

The Δδ values of **2a** do not change much upon introduction of zinc and addition of excess of pyridine. Evidently, pyridine, which is known to act as a fifth ligand for zinc in the tetraaryl Zn–porphyrins,[7] hardly disturbs the conformation of the porphyrin upon formation of the bond to zinc. This is to be expected for the αα isomer, which has an unoccupied porphyrin face (Scheme I). The other isomer, **2b**, behaves differently. Introduction of zinc causes an increase in the upfield shifts for the dimethylanilino protons; addition of pyridine then lowers the Δδ values a great deal. It is clear that, in this case, the formation of the fifth ligand involves a reorientation of the dimethylanilino groups and an increase in the percentage of nonfolded conformations in the conformational equilibrium. These facts are consistent with the αβ structure, in which both sides of the porphyrin ring are occupied.

We concluded from these results that **2a** is the αα atropisomer in spite of its higher R_f value, and **2b** the αβ isomer. To prove this simple reasoning we carried out more detailed investigations on the complexation of the zinc derivatives of **2a** and **2b** with pyridine by ^1H NMR techniques.

(7) Miller, J. R.; Dorough, G. D. *J. Am. Chem. Soc.* **1952**, *74*, 3977.

Scheme I



Low-Temperature ^1H NMR Study on Ligation of the Zinc Derivatives of 3, 2a, and 2b by Pyridine. It may seem surprising that the two dimethylanilino side chains are equivalent in the ^1H NMR spectrum of the pyridine complex of the αβ form, **2b**–Zn. Two explanations can be offered. The first is that the zinc porphyrin forms a dipyridinate, although for tetraphenylporphyrins only monopyridinates have been observed.[7-10] The second explanation is that an exchange takes place between free and ligated pyridine molecules, which is rapid on the NMR time scale and which leads not only to averaged δ values for the pyridine protons, but also to averaged shifts for the protons of the two side chains. The lower upfield shift for the latter protons would then be due to an increased percentage of nonfolded conformations (in which ligation of zinc by pyridine is possible) in the conformational equilibrium. Rapid exchange of pyridine ligand molecules has been reported in the literature for zinc tetraphenylporphyrins[8,9,11] and for magnesium tetraphenyl- and etioporphyrins.[12] The literature data thus suggest that the second explanation, i.e. rapid exchange in a monopyridinate, is the most likely one. To prove this we carried out ^1H NMR experiments on the zinc derivatives of **2a** and **2b**. As the spectra proved to be rather complex, we first investigated the behavior of a more simple porphyrin, the zinc derivative of 5,15-diphenyl-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphyrin **3**.

Upon addition of about 1 equiv of pyridine to a solution of **3**–Zn in $CDCl_3$, only one set of signals was observed for the α, β, and γ protons of pyridine, indicating a rapid exchange between free and ligated pyridine molecules and weighted average δ values (see Table III).

Lowering the temperature of the 1:1 mixture induced a shift to high field for the pyridine protons, due to increased complex formation; moreover, the signals broadened considerably. At 203 K the pyridine signals became sharp again and a small peak developed at δ = 8.76, which was ascribed to Hα of free pyridine. Evidently, at this temperature the rate of exchange is sufficiently low to give separate signals for the free and ligated pyridine molecules. From the integration ratio at 203 K we concluded that a monopyridinate is present. After addition of a second equivalent of pyridine the temperature was raised again

(8) Kirksey, C. H.; Hambright, P.; Storm, C. B. *Inorg. Chem.* **1969**, *8*, 2141.
(9) Abraham, R. J.; Bedford, G. R.; Mc Neillie, D.; Wright, B. *Org. Magn. Reson.* **1980**, *14*, 418. Abraham, R. J.; Bedford, G. R.; Wright, B. *Org. Magn. Reson.* **1982**, *18*, 45.
(10) Nardo, J. V.; Dawson, J. H. *Inorg. Chim. Acta* **1986**, *123*, 9.
(11) Storm, C. B.; Turner, A. H.; Swann, M. B. *Inorg. Chem.* **1984**, *23*, 2743.
(12) Storm, C. B.; Corwin, A. H. *J. Org. Chem.* **1964**, *29*, 3700.

Table III. Chemical Shifts of the Pyridine Protons upon Addition of Pyridine to a Solution of 2.6 μmol of 3-Zn in 0.5 mL of $CDCl_3$

temp (K)	μmol of pyridine added		δ pyridine protons Hα	Hβ	Hγ	calcd K (L mol^{-1})	calcd ΔG (kJ mol^{-1})
297	2.5		5.28	6.28	6.95	415	-14.7
203	2.5	ligated	*a*	5.30	6.19	*b*	
		free	8.76	*a*	*a*		
240	5.0		5.4	6.33	6.96	10400	-18.5
273	5.0		5.62	6.40	7.00	1780	-17.0
303	5.0		6.56	6.69	7.22	258	-14.0
313	5.0		6.97	6.78	7.27	163	-13.3

[a] Not determined due to overlap with other peaks. [b] K could not be calculated as the area of the free pyridine peak was too small for accurate measurement.

Table IV. δ Values of the Complexes of 3-Zn, 2a-Zn, and 2b-Zn with Pyridine at Low Temperature

complex	temp (K)	δ pyridine protons Hα	Hβ	Hγ	δ dimethylanilino protons H2,H6	H3,H5	$N(CH_3)_2$
3-Zn	203	2.4[a]	5.30	6.19			
2a-Zn (ααβ)	213	*b*	5.45	6.28	4.90	3.08	*b*
2a-Zn (ααα)	213	*b*	5.17	5.90	6.45	5.33	*b*
2b-Zn	203	2.4[a]	5.30	6.10	5.16	2.85	0.40
					6.40	5.38	2.69

[a] Calculated value. [b] Not determined due to overlap with other peaks.

Table V. Chemical Shifts of the Pyridine and Dimethylanilino Protons upon Addition of 2.25 μmol of Pyridine to Solutions of 2.65 μmol of 2a-Zn and 2b-Zn in 0.5 mL of $CDCl_3$

	temp (K)		δ pyridine protons Hα	Hβ	Hγ	δ dimethylanilino protons H2,H6	H3,H5	$N(CH_3)_2$	calcd K (L mol^{-1})	calcd ΔG (kJ mol^{-1})
2a-Zn	298		4.88	6.12	6.78	5.43	3.76	1.34		
	270		*a*	5.80	6.48	5.37	3.70	1.30		
	258		*a*	5.66	6.40	5.22	3.35	*a*		
	213	ααβ:	*a*	5.45	6.28	4.90	3.08	~1.0		
		ααα:	*a*	5.17	5.90	6.45	5.33	~2.3-2.5		
2b-Zn	315		7.45	6.95	7.45	5.29	3.07	0.45	50	-10.3
	303		7.20	6.88	7.38	5.39	3.26	0.62	67	-10.6
	273		~6.5	6.68	7.20	5.51	3.50	0.86	125	-11.0
	245		~5.6	6.42	7.01	5.62	3.84	1.08	258	-11.3
	203	ligated:	*a*	5.30	6.10	5.16, 6.40	2.85, 5.38	0.40, 2.69	*b*	
		free:	8.70	7.50	*a*	-	-	-		

[a] Assignment not possible due to overlap or broadened signals. [b] K was not calculated as the area of the free pyridine peaks could not be measured accurately.

and NMR spectra were measured at various temperatures.

The chemical shifts of Hβ and Hγ in the pyridinate of 3-Zn at 203 K are given in Table IV. The signal of Hα was hidden under the porphyrin signals. By using the mole fractions, calculated from the chemical shifts of Hβ and Hγ in the way described below, we calculated a δ value of 2.4 ppm for Hα in the pyridinate of 3-Zn.

As the chemical shifts of Hα, Hβ, and Hγ of free pyridine in $CDCl_3$ solution at 203 K are 8.65, 7.32, 7.75, respectively, the ring current shifts Δδ in the pyridinate of 3-Zn are as follows: Δδ (Hα) = 6.23; Δδ (Hβ) = 2.02; Δδ (Hγ) = 1.56. These shifts agree reasonably well with those reported for zinc tetraphenylporphyrin[11] (6.13, 1.80, 1.35 for Hα, Hβ, Hγ, respectively).

From the δ values of the pyridinate of 3-Zn and those of free pyridine in $CDCl_3$ at 203 K, the mole fractions of ligated and free pyridine were calculated at various temperatures using the relationship

$$\delta = x_f\delta_f + (1 - x_f)\delta_l$$

where δ is the measured chemical shift of a pyridine proton (Hα, β, or γ), δ_f is the chemical shift of a free pyridine proton (Hα, β, or γ), δ_l is the chemical shift of a ligated pyridine proton (Hα, β, or γ), and x_f is the mole fraction of free pyridine. From the mole fractions, values of K and ΔG were obtained for the equilibrium

pyridine + 3-Zn ⇌ 3-Zn pyridinate

The results are given in Table III. The K value found for the complexation of 3-Zn at 297 K is much lower than the equilibrium constants reported for zinc tetraphenylporphyrin in the literature: 6025 at 25 °C in benzene,[8] 6220 at 20.3 °C in benzene.[7] The temperature dependency of ΔG allowed us to calculate the following ΔH and ΔS values: ΔH = -39.7 kJ mol^{-1}; ΔS = -85 J K^{-1} mol^{-1} (Table VI). The ΔH value agrees very well with the value reported in the literature for zinc tetraphenylporphyrin by Miller and Dorough[7] (ΔH = -9.2 kcal mol^{-1} or -38.4 kJ mol^{-1}). The ΔS value, however, is significantly more negative than the value obtained by these investigators (-14 cal K^{-1} mol^{-1} or -59 J K^{-1} mol^{-1}).[7] We explain this difference by the presence of methyl and *n*-butyl substituents on the porphyrin ring, the free rotation of which will be restricted by an attached molecule of pyridine. Other investigators report different ΔH and ΔS values for complex formation between pyridine and zinc tetraphenylporphyrin, e.g. ΔH = -4.0 kcal mol^{-1} or -16.7 kJ mol^{-1} and ΔS = 0 cal K^{-1} mol^{-1}.[13]

After establishing the rapid exchange of pyridine at room temperature in the pyridinate of 3-Zn, we carried out the same experiments with the zinc derivatives of **2a** and **2b** (Table V). Addition of 0.85 equiv of pyridine to

(13) Cole, S. J.; Curthoys, G. C.; Magnusson, E. A.; Phillips, J. N. *Inorg. Chem.* **1972**, *11*, 1024.

Table VI. ΔH and ΔS Values for Ligation of 3-Zn and 2b-Zn with Pyridine in $CDCl_3$

	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
3-Zn	-39.7	-85
2b-Zn	-15.7	-17.5

$CDCl_3$ solutions of the zinc derivatives of **2a** and **2b** again gave weighted average δ values for the pyridine protons. The large difference between these values for **2a** and **2b** suggests that ligation of the $\alpha\alpha$ isomer proceeds much easier than that of the $\alpha\beta$ isomer.

Cooling of the solution of **2a**-Zn resulted in an upfield shift of the pyridine protons due to increased complex formation (Table V). Moreover, the peaks broadened. At 213 K, however, the signals became sharper and the spectrum showed two sets of ligated pyridine signals and two sets of dimethylanilino signals, roughly in a ratio 2:1.

The spectral data can be explained by assuming that two different monopyridinates are formed; the main product is a complex in which pyridine is bound on the free face of the porphyrin ring ($\alpha\alpha$ isomer, β-pyridyl), and the minor product is a complex with pyridine and the two dimethylanilino groups at the same face of the porphyrin ($\alpha\alpha$ isomer, α-pyridyl). The δ values for these complexes are given in Table IV. Formation of a dipyridinate or a 1:1 mixture of a di- and a monopyridinate is excluded due to the 2:1 ratio between the two sets of pyridyl and side-chain resonances. Calculation of the mole fractions of the two complexes and free pyridine at various temperatures was rather complicated and led to unreliable results. Thus, we were not able to determine ΔG, ΔH, and ΔS values for the two ligation equilibria.

Similarly, an upfield shift and broadening of the pyridyl resonances were noted upon cooling of the solution of **2b**-Zn in $CDCl_3$ with pyridine. At 203 K a great number of broad peaks was observed, of which only the free and ligated pyridyl resonances could be assigned (Table V). When the solution was prepared with pyridine-d_5 a less complicated spectrum resulted at 203 K and two sets of signals were observed for the dimethylanilino protons in a 1:1 ratio, indicating that the two side chains are no longer equivalent in the pyridinate. A set of high-field signals was assigned to the dimethylanilino substituent at the porphyrin face opposite to the attached pyridine. The δ values of these protons are almost equal to those of the starting substance **2b**-Zn without pyridine. A second set of signals at lower field was assigned to the dimethylanilino group lying on the same face of the porphyrin ring as the pyridyl ligand. The increased distance from the center of the ring current will explain the lower δ values, which agree nicely with those of the α-pyridyl complex of the $\alpha\alpha$ isomer **2a**-Zn. Since the δ values for Hβ and Hγ in the monopyridinate are known, it is possible to calculate the mole fractions of free and ligated pyridine in the solution at various temperatures and from these the ΔG, ΔH, and ΔS values. For Hα in the monopyridinate the same δ value was assumed as in the complex of 3-Zn; the mole fractions obtained, assuming an identical chemical shift for Hα in the 3-Zn and **2b**-Zn complexes, agreed very well with those calculated from the chemical shifts of Hβ and Hγ. The results of these calculations are given in Table VI.

The smaller negative value of ΔH for **2b**-Zn compared with 3-Zn can be explained by the fact that **2b**-Zn prefers a folded conformation, as shown before,[5] which is stabilized by Van der Waals interactions and probably also by intramolecular ligation between zinc and the dimethylamino group. This interaction is lost in the pyridine complex. The high degree of order in the folded conformation of the starting substance **2b**-Zn probably also explains the smaller negative value of ΔS for the ligation equilibrium with pyridine. In conclusion, the results described above support the assignment of the $\alpha\alpha$ structure to **2a** and the $\alpha\beta$ structure to **2b** since two different monopyridinates can be envisaged for the $\alpha\alpha$ atropisomer, while only the $\alpha\beta$ atropisomer should exhibit nonequivalent dimethylanilino groups upon ligation.

Table VII. Visible Absorption Maxima of 2a, 2b, 3 and Their Zinc Derivatives and Pyridinates in $CHCl_3$ Solution

	λ_{max} (nm)			
	Soret	β-band	α-band	other
2a	412	-	-	508, 542, 575, 626
2a-Zn	413	539	576	-
2a-Zn with pyridine	423	547	577	-
2b	414	-	-	510, 543, 578, 629
2b-Zn	418	542	578	-
2b-Zn with pyridine	422	545	578	-
3	410	-	-	508, 542, 575, 626
3-Zn	411	539	575	-
3-Zn with pyridine	423	551	582	-

Intramolecular Ligation in 2b-Zn. Our investigations support the previously described[5] idea that in the $\alpha\beta$ isomer **2b**-Zn a weak intramolecular coordination occurs between zinc and the dimethylamino group. We base this on the fact that introduction of zinc in **2b** leads to a significant increase in upfield shift due to the shorter distance required for ligand formation (see Table II). On the other hand, the $\alpha\alpha$ isomer **2a** shows a slight decrease in upfield shift upon introduction of zinc since coordination is probably inhibited by steric effects. The positions of the Soret absorption band in the UV absorption spectrum support our hypothesis (Table VII).

Upon introduction of zinc a red shift of 1 nm was noted for the Soret band of **2a** and **3**, whereas for the $\alpha\beta$ isomer **2b** a red shift of 4 nm was observed. Since it is known from the literature[13-15] that ligand formation leads to a red shift in the absorption maximum of the zinc derivative of tetraphenylporphyrin, we consider the larger red shift of **2b** an indication for a weak internal ligation of zinc. Formation of the pyridinate produced a red shift of 10 nm for **2a**-Zn, of 12 nm for 3-Zn, and of only 4 nm for **2b**-Zn. In the literature[16] a similar diminished red shift and even a blue shift of the Soret band have been reported following addition of pyridine to 4,4'-bipyridyl capped zinc porphyrins which exhibit internal ligation.

Conclusions

The identity of the two atropisomers of **2** was established by a ^{1}H NMR study on ligation of their zinc derivatives by pyridine. At room temperature free and ligated pyridine molecules are in rapid exchange. At 203 K exchange became slow on the NMR time scale; at this temperature two different monopyridinates were observed for the $\alpha\alpha$ atropisomer, while the $\alpha\beta$ isomer gave only one monopyridinate with nonequivalent (dimethylamino)phenyl groups.

The K value for complexation of 3-Zn with pyridine is much lower than the value reported in the literature for zinc tetraphenylporphyrin. This is probably caused by entropy factors. For ligation of the $\alpha\beta$ atropisomer, **2b**-Zn, smaller negative ΔS values were observed than for 3-Zn. This difference can be explained by the high degree of order in the starting substance, **2b**-Zn, due to folding and

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Table VIII. ^{1}H NMR Chemical Shifts of 2a, 2b, 3 and Their Zinc Derivatives in $CDCl_3$

	chemical shift δ^a							
	2a	2a-Zn	2a-Zn with pyridine-d_5[b]	2b	2b-Zn	2b-Zn with pyridine-d_5[b]	3	3-Zn
H10,20	10.16	10.06	9.98	10.12	10.10	9.96	10.20	10.18
H6′	8.32	8.26	8.30	8.02	8.11	8.10	8.01	8.03
H5′	7.72	7.72	7.64	7.68	7.73	7.64	7.67	7.76
H4′	7.87	7.89	7.81	7.88	7.88	7.82	7.67	7.76
H3′	7.92	7.89	7.93	7.94	7.88	7.96	7.67	7.76
H2′	-	-	-	-	-	-	8.01	8.03
H2,H6	5.32	5.49	5.42	5.52	5.22	5.85	-	-
H3,H5	3.66	3.71	3.84	3.51	2.87	4.21	-	-
$N(CH_3)_2$	1.23	1.23	1.43	0.81	0.27	1.49	-	-
CH_3 (pyrrole)	2.55	2.50	2.48	2.51	2.53	2.43	2.46	2.42
CH_2 (α-butyl)	3.94	3.89	3.91	3.94	3.97	3.87	3.93	3.92
CH_2 (β-butyl)	2.17	2.16	2.09	2.21	2.21	2.11	2.17	2.13
CH_2 (γ-butyl)	1.77	1.78	1.70	1.83	1.85	1.72	1.71	1.73
CH_3 (δ-butyl)	1.12	1.13	1.06	1.16	1.19	1.09	1.10	1.08
NH	-2.49	-	-	-2.89	-	-	-2.33	-

[a] See structure for numbering of the protons. [b] The δ values given in this column are slightly different from those given in Table V, because of the large excess of added pyridine-d_5, resulting in increased complex formation, especially for **2b**-Zn.

intramolecular ligation. The assumption of intramolecular ligation in **2b**-Zn is supported by ^{1}H NMR and UV data.

Experimental Section

The ^{1}H NMR spectra were recorded on a 200-MHz Bruker AC-200E spectrometer. All spectra were measured in $CDCl_3$ solution. The UV spectra were measured on a Beckman DU-7 and a Varian DMS 100 spectrophotometer in $CHCl_3$ solution. The porphyrins **2a**, **2b**, and **3** and their zinc derivatives gave satisfactory CHN analyses, when we assumed the presence of 0-0.25 mol of CH_2Cl_2 per mole of porphyrin. The tendency of ortho-substituted 5,15-diphenylporphyrins to occlude solvent molecules has been described before.[5] The FD mass spectra, measured on a MS 902 equipped with a VG ZAB console, showed parent peaks at m/z 1140 (**2a** and **2b**), m/z 1202-1208 (**2a**-Zn and **2b**-Zn), m/z 742 (**3**), and m/z 802-808 (**3**-Zn). These values are in accordance with the structures proposed. Chromatography was performed on silica gel (Merck, 0.040-0.063 mm).

Preparations. 5,15-Bis[2-[[[4-(dimethylamino)phenyl]sulfonyl]oxy]phenyl]-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphyrin (2). A mixture of 2.0 g (6.6 mmol) of 2-[[[4-(dimethylamino)phenyl]sulfonyl]oxy]benzaldehyde,[5] 1.88 g (6.6 mmol) of 3,3′-di-*n*-butyl-4,4′-dimethyl-2,2′-dipyrrolylmethane,[5] and 0.33 g of *p*-toluenesulfonic acid in 80 mL of methanol was stirred for 6 h at room temperature and left overnight in the refrigerator. The precipitate of hexahydroporphyrin (2.64 g, 70%) was sucked off, washed with cold methanol, dried, and dissolved in 250 mL of THF. A solution of 1.91 g (8.4 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in 50 mL of THF was added gradually over a period of 5 min, and the mixture was stirred for 1 h at room temperature. The precipitate of crude **2b** was filtered off, washed with THF, and purified by column chromatography over silica gel (gradient elution with CH_2Cl_2 containing 1-5% of methanol). The yield of pure $\alpha\beta$ atropisomer **2b** was 0.41 g (11% overall from aldehyde). ^{1}H NMR: see Table VIII. From the filtrate, resulting from the DDQ oxidation step, the solvent was removed in vacuo. The residue (crude **2a**) was purified by column chromatography over silica gel (elution with CH_2Cl_2). Yield: 0.72 g of pure $\alpha\alpha$ atropisomer, **2a** (19% overall from aldehyde). ^{1}H NMR: see Table VIII.

5,15-Diphenyl-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphyrin (3). To a solution of 2.12 g (20 mmol) of benzaldehyde and 5.72 g (20 mmol) of 3,3′-di-*n*-butyl-4,4′-dimethyl-2,2′-dipyrrolylmethane in 250 mL of methanol, 1.00 g of *p*-toluenesulfonic acid was added. The mixture was stirred for 2 h at room temperature and left overnight in the refrigerator. The precipitated hexahydroporphyrin was filtered off and washed with cold methanol, yield 6.4 g (86%). To a solution of 6.4 g of the hexahydroporphyrin (8.6 mmol) in 350 mL of THF, a solution of 7.49 g (33 mmol) of DDQ in 100 mL of THF was added. The mixture was stirred for 2 h at room temperature. The THF was evaporated in vacuo, and the residue was dissolved as far as possible in 150 mL of CH_2Cl_2. After filtration 400 mL of a mixture of methanol and triethylamine, 3:1, was added to the filtrate with stirring. After stirring for another half hour the precipitate was sucked off and washed with cold methanol, yield 5.1 g (80%). To obtain an analytically pure sample the product was chromatographed over silica gel, eluent CH_2Cl_2. ^{1}H NMR: see Table VIII.

Zinc Derivatives of 2a, 2b, and 3. The zinc derivatives of **2a**, **2b**, and **3** were obtained by adding a solution of 0.5 g (2.3 mmol) of zinc acetate dihydrate in 10 mL of methanol to a solution of 100 mg of **2a**, **2b** (0.09 mmol), or **3** (0.13 mmol) in 100 mL of CH_2Cl_2. The mixture was kept in an ultrasonic bath for $^1/_2$ h. After washing the solution with water and filtraftion of the organic layer the solvent was removed in vacuo; the zinc derivatives were obtained in practically quantitative yield. ^{1}H NMR: see Table VIII.

Formation of Pyridinates. All experiments were carried out in the NMR tube. The ^{1}H NMR spectra obtained by adding a 25-fold excess of pyridine-d_5 to $CDCl_3$ solutions of **2a**-Zn and **2b**-Zn are given in Table VIII. The results of the low-temperature ^{1}H NMR measurements on **3**-Zn, **2a**-Zn, and **2b**-Zn in the presence of pyridine are given in Tables III and V.

Improved Synthesis of Cubane-1,2,4,7-tetracarboxylic Acid

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We report here a simplification in the synthesis of cubane-1,2,4,7-tetracarboxylic acid (**3**), a key intermediate from which other cubane derivatives are synthesized. Limitations in the synthetic routes to this compound have prevented the preparation of other, interesting cubane compounds.

The original breakthrough in the synthesis of functionalized cubanes was made by Eaton and co-workers[1] with the discovery that *N,N*-diisopropylamide groups could be

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