described for **9**: ^{31}P NMR (acetone-d_6) δ -45.7; ^{1}H NMR (acetone-d_6) δ 8.0 (1 H, br s, NH), 7.80 (1 H, d, H_6), 6.18 (1 H, dd, $H_{1'}$), 5.83 (1 H, d, H_5), 5.32 (1 H, m, $H_{3'}$), 4.23 (1 H, m, $H_{4'}$), 4.35-4.30 (2 H, m, $H_{5'/5''}$), 3.80 (6 H, d, OCH_3, J = 13.0 Hz), 2.41-2.28 (2 H, m, $H_{2'/2''}$), 1.90 (6 H, s, CH_3 dioxaphosphole).

3'-*O*-Acetylthymidine 5'-(Dimethyl phosphate) (14). An ozone/oxygen stream was passed through a cooled (0 °C) solution of 500 mg of 3'-*O*-acetylthymidine 5'-(dimethyl phosphite) in 10 mL of anhydrous dichloromethane. After 20 min, TLC using butanone as eluent indicated complete conversion of the phosphite into **14** (R_f 0.30): ^{31}P NMR (acetone-d_6) δ 6.9; ^{1}H NMR (acetone-d_6) δ 8.8 (1 H, br s, NH), 8.15 (1 H, s, H_6), 6.23 (1 H, dd, $H_{1'}$), 5.32 (1 H, m, $H_{3'}$), 4.32 (1 H, m, $H_{4'}$), 4.18-4.06 (2 H, m, $H_{5'/5''}$), 3.85 (6 H, d, OCH_3, J = 11.3 Hz), 2.41-2.30 (2 H, m, $H_{2'/2''}$), 2.05 (3 H, s, acetyl), 1.87 (3 H, s, 5-CH_3).

2'-Deoxy-3'-*O*-acetyladenosine 5'-(Dimethyl phosphate) (15). This compound was prepared from 2'-deoxy-3'-*O*-acetyladenosine 5'-(dimethyl phosphite) according to the procedure that was given for **14**. The product was obtained as a colorless glass (R_f 0.14, eluent butanone/triethylamine, 95:5 v/v): ^{31}P NMR (acetone-d_6) δ 6.7; ^{1}H NMR (acetone-d_6) δ 8.3 and 8.25 (2 × 1 H, s, H_2/H_8), 7.04 (2 H, br s, NH), 6.12 (1 H, dd, $H_{1'}$), 5.55 (1 H, m, $H_{3'}$), 4.37 (1 H, m, $H_{4'}$), 4.20-4.07 (2 H, m, $H_{5'/5''}$), 3.78 (6 H, d, OCH_3, J = 11.2 Hz), 2.38-2.27 (2 H, m, $H_{2'/2''}$), 2.18 (3 H, s, acetyl).

2'-Deoxy-3'-*O*,*N*^{4}-diacetylcytidine 5'-(Dimethyl phosphite). This compound was synthesized from dimethoxy(*N*,*N*-dimethylamino)phosphine (0.51 g, 3.8 mmol) and 2'-deoxy-3'-*O*,*N*^{4}-diacetylcytidine (0.6 g, 1.9 mmol) by following the procedure that was described for 3'-*O*-acetylthymidine 5'-(dimethyl phosphite). Chromatography on a Woelm silica gel column using dry butanones as eluent yielded the product as a colorless glass (R_f 0.46): yield, 420 mg (55%).

2'-Deoxy-3'-*O*,*N*^{4}-diacetylcytidine 5'-(Dimethyl phosphate) (16). This compound was prepared from 2'-deoxy-3'-*O*,*N*^{4}-diacetylcytidine 5'-(dimethyl phosphite), according to the procedure that was given for **14**. This product was isolated as a slightly colored glass (R_f 0.12; eluent butanone): ^{31}P NMR (acetone-d_6) δ 5.9; ^{1}H NMR (acetone-d_6) δ 8.3 (1 H, br s, NH), 7.75 (1 H, d, H_6), 6.20 (1 H, dd, $H_{1'}$), 5.90 (1 H, d, H_5), 5.42 (1 H, m, $H_{3'}$), 4.38 (1 H, m, $H_{4'}$), 4.19-4.06 (2 H, m, $H_{5'/5''}$), 3.81 (6 H, d, OCH_3, J = 11.3 Hz), 2.41-2.17 (2 H, m, $H_{2'/2''}$).

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Studies on the Conformation of 5,15-Diarylporphyrins with (Arylsulfonyl)oxy Substituents[1]

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Dimeso-substituted octaalkylporphyrins, carrying an (arylsulfonyl)oxy group at the ortho position of the two (meso) phenyl groups, were synthesized from dipyrrolylmethanes and aldehydes. On account of a ^{1}H NMR upfield shift in $CDCl_3$ solution of 2-5 ppm for the aryl protons, a folded conformation is assumed in which the substituted aryl groups lie right above and below the porphyrin plane. In $CDCl_3/CF_3COOH$ solution the upfield shifts are absent. The results of low-temperature ^{1}H NMR measurements and ring-current calculations agreed with our assumptions. The sulfonyloxy group promotes folding of the molecule more than the ester, sulfonyl, sulfinyl, thio, or methylene group. In zinc porphyrins carrying anthraquinone substituents, intramolecular coordination was observed. ΔG, ΔH, and ΔS values for the various conformational equilibria were calculated from the NMR data. We suggest van der Waals interactions with a contribution of charge transfer as the driving force for the folding of the molecule.

The mechanism of the charge separation step in photosynthesis is the subject of continuing investigations, mostly on porphyrins, preferably with well-defined geometries.[2] In the course of our synthetic work in this field we prepared a 5,15-diaryl-2,3,7,8,12,13,17,18-octamethylporphyrin, carrying a tosylate group in the β-position of an ethoxy side chain, attached at the ortho (meso) aryl position, i.e. **6b** (Figure 1). The ^{1}H NMR spectrum of this compound in $CDCl_3$ solution showed an unexpectedly large upfield shift for the aromatic tosylate protons: 2.03 and 3.06 ppm for H2',H6' and H3',H5', respectively, compared to the δ values of a reference compound, the corresponding aldehyde RCHO (**7b**) used in the synthesis (Scheme I). In the following we use $\Delta\delta$ values, defined as δ for a proton in the aldehyde **7**, $-\delta$ for the corresponding proton in the porphyrin **6** (see for numbering of the protons Figure 1).[3] Since upon 10-fold dilution of a solution of **6b** we did not observe a significant change of δ values, we exclude intermolecular association and explain the observed shifts

(1) Part of this work has been described in a preliminary communication: Sanders, G. M.; van Dijk, M.; Koning, G. P.; van Veldhuizen, A.; van der Plas, H. C. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 243, and in Sanders, G. M.; van Dijk, M.; van Veldhuizen, A.; van der Plas, H. C. *J. Chem. Soc., Chem. Commun.* **1986**, 1311.

(2) See for some recent references: Hunter, C. A.; Nafees Meah, M.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1988**, 692. Schmidt, J. A.; McIntosh, A. R.; Weedon, A. C.; Bolton, J. R.; Connolly, J. S.; Hurley, J. K.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1988**, *110*, 1733. Sanders, G. M.; van Dijk, M.; van Veldhuizen, A.; van der Plas, H. C. *J. Chem. Soc., Chem. Commun.* **1986**, 1311 and the references cited in these articles.

(3) The use of, e.g., the *p*-(mesoaryl)-substituted isomer of **6a** as reference compound instead of the aldehyde RCHO **7a** did not make a significant difference.

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Table I. Upfield Shifts $\Delta\delta$ of the Phenyl Protons of 6a–r in $CDCl_3$ Solution

compd	R	$\Delta\delta$[a] H2′,H6′	H3′,H5′	other
6a	$OSO_2C_6H_4$(4′-Me)	2.07	2.96	
6b	$O(CH_2)_2OSO_2C_6H_4$(4′-Me)	2.03	3.06	
6c	$O(CH_2)_3OSO_2C_6H_4$(4′-Me)	1.00	1.16	
6d	$O(CH_2)_4OSO_2C_6H_4$(4′-Me)	0.76	0.78	
6e	$O(CH_2)_6OSO_2C_6H_4$(4′-Me)	0.20	0.10	
6f	$OSO_2C_6H_4$(4′-F)	2.17	2.82	
6g	$OSO_2C_6H_5$	2.13	2.79	H4′, 2.62
6h	$OSO_2C_6H_4$(4′-*t*-Bu)	1.97	2.39	
6i	$OSO_2C_6H_4$(4′-cyclohexyl)	2.13	2.87	
6j	$OSO_2C_6H_4$(4′-OCH_3)	2.10	2.84	
6k	$OSO_2C_6H_4$(4′-$N(CH_3)_2$)	2.04	2.68	
6l	$OSO_2C_6H_4$(4′-NO_2)	2.58	3.67	
6m	$OSO_2C_6H_2$(2′,4′,6′-triMe)		2.94	
6n	$OSO_2C_6H_2$(2′,4′,6′-triiPro)		0.98	

compd	R	H2′	H3′	H4′	H5′	H6′
6o	$O(CH_2)_2OSO_2C_6H_4$(4′-F)	1.99	2.70		2.70	1.99
6p	$O(CH_2)_2OSO_2C_6H_4$(3′-NO_2)	4.43		3.52	3.75	3.64

compd	R	H2′,H6′	H3′,H5′	H8′,H12′	H9′,H11′
6q	$OSO_2C_6H_4C_6H_4$(10′-F)	2.28	3.10	2.40	0.88
6r	$OSO_2C_6H_4C_6H_4$(10′-NO_2)	2.47	3.55	3.05	1.14

[a] For a given proton $\Delta\delta = \delta$(aldehyde) − δ(porphyrin); numbering of the positions according to Figure 1; the bond between the phenyl rings in biphenyl is between positions 4′ and 7′.

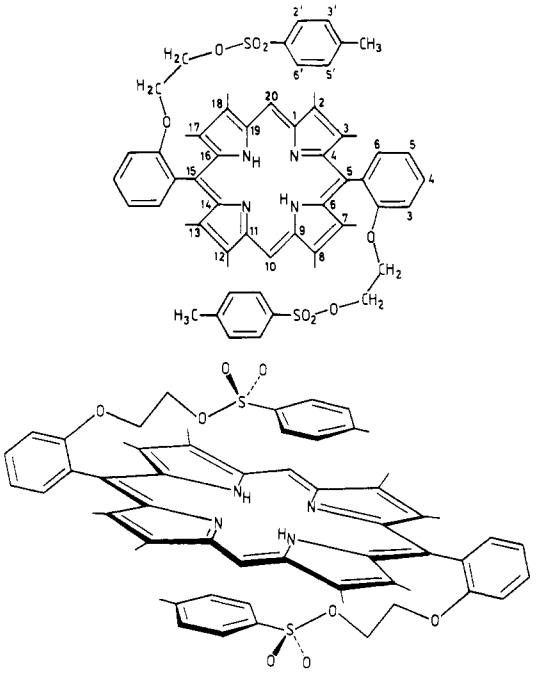
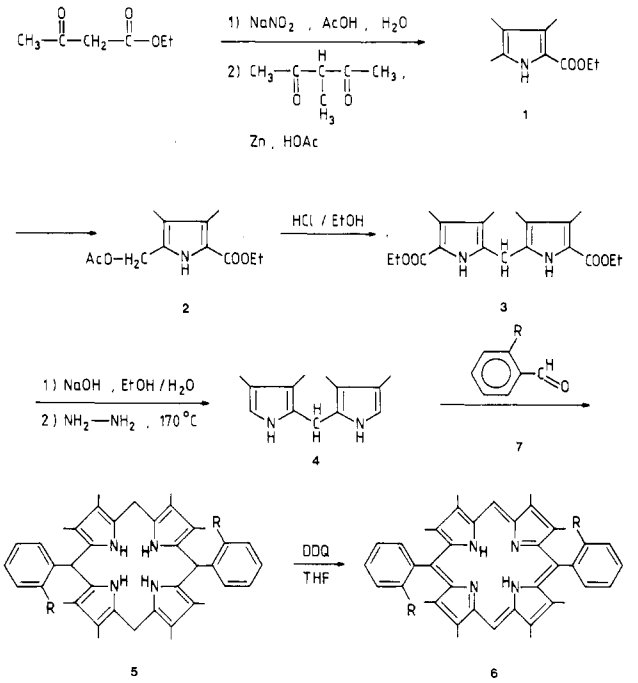


Figure 1. Structure and folded conformation of **6b**.

by an appreciable contribution of a conformation in which both aryl groups are folded over the porphyrin, one above and one below (α,β-atropisomer). The protons of these aryl groups undergo an upfield shift as a result of the porphyrin ring current. As this folding may lead to geometrically well defined model compounds, we investigated the scope of the phenomenon by preparing a number of similarly substituted porphyrins (**6a–r**) in which the length of the connecting alkylene chain and the nature of the sulfonylaryl group were varied (see Table I).

All octamethyldiarylporphyrins were obtained from the same precursor, i.e. (3,4,3′,4′-tetramethyl-2,2′-dipyrrolyl)-methane (**4**), by the method reported by Gunter and Mander.[4] Compound **4** was prepared by a series of reactions described in the literature[5-7] (Scheme I). The

Scheme I. Synthesis of Porphyrins (See for R Tables I and VII)



syntheses of the aldehydes **7** are given in the Experimental Section.

The $\Delta\delta$ values for the sulfonylaryl protons in the compounds **6a–r** are given in Table I.

It is not well possible to distinguish the signals of H2′,H6′ from those of H3′,H5′ in the ^{1}H NMR spectra of **6a–e** and **6h–l** because the magnitude of the ring-current shift is unknown and will differ for the different positions. Substituent effects are therefore of no help in the assignment. To cope with this problem we synthesized the

(4) Gunter, M. J.; Mander, L. N. *J. Org. Chem.* **1981**, *46*, 4792.

(5) Johnson, A. W.; Markham, E.; Price, R.; Shaw, K. B. *J. Chem. Soc.* **1958**, 4254.

(6) Johnson, A. W.; Kay, I. T.; Markham, E.; Price, R.; Shaw, K. B. *J. Chem. Soc.* **1959**, 3416.

(7) Clezy, P. S.; Nichol, A. W. *Aust. J. Chem.* **1965**, *18*, 1835.

Table II. δ (ppm) and Δδ Values of the Porphyrins 8a–g in $CDCl_3$ Solution

compd		H1′	H3′	H4′	H5′	H6′	H7′	H8′	H2″,H6″	H3″,H5″	$N(CH_3)_2$
8a	δ	6.51	5.35	3.90	6.92	7.41	7.41	7.24	5.29	3.28	0.66
	Δδ[a]	2.29	2.90	4.60	1.41	0.48	0.48	1.09	2.25	3.30	2.41
8b	δ	5.39	6.58	5.92	7.51	7.48	7.21	5.46	5.20	2.89	0.30
	Δδ	3.41	1.67	2.58	0.82	0.41	0.68	2.87	2.34	3.69	2.77
8c	δ	6.32	5.06	3.60	6.89	7.41	7.41	7.26			
	Δδ	2.48	3.19	4.90	1.44	0.48	0.48	1.07			
8d	δ	5.50	6.25	5.50	7.43	7.43	7.14	5.64			
	Δδ	3.30	2.00	3.00	0.90	0.46	0.75	2.69			
8e	δ								5.53	3.52	0.80
	Δδ								2.01	3.06	2.27
8f	δ								5.23	2.88	0.29
	Δδ								2.31	3.70	2.78
8g	δ	6.53	5.32	3.85	6.94	7.43	7.43	7.28	5.25	3.25	0.63
	Δδ	2.27	2.93	4.65	1.39	0.46	0.46	1.05	2.29	3.33	2.44

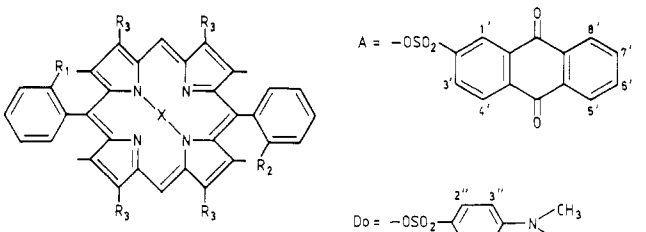
[a] Δδ:δ(proton in 2-(R_1 or R_2)-benzaldehyde) − δ(proton in porphyrin).

fluorine-containing compounds **6f** and **6o** as well as **6g** in which hydrogen–fluorine and hydrogen–hydrogen coupling enable us to make an unambiguous assignment. In analogy we assigned the signals in the other compounds. In the symmetrically trisubstituted compounds **6m** and **6n** and in the asymmetrically substituted nitro compound **6p** the assignment gave no problems. In the bis[(phenylsulfonyl)oxy] derivatives **6q** and **6r**, the maximal upfield shift Δδ was observed for H3′,H5′; evidently, these protons are nearest to the center of the porphyrin ring current.

For some of the compounds **6** (**6f–h,j,m,o,r,v**) we observed in the NMR spectrum a second set of signals for the sulfonylphenyl protons. We assume that besides the α,β-atropisomer some α,α-atropisomer is being formed in the reaction.[8] The fact that we did not find both atropisomers for all compounds **6** may be due to the isolation procedures applied. For **6f**, we were able to separate the mixture of the atropisomers by chromatography over silica gel. The isomer with the higher R_f value was assumed to be the α,β-form, in analogy with data given in the literature.[9] By refluxing a xylene solution of this α,β-isomer, a mixture of the α,α- and α,β-forms was obtained. In the other compounds showing atropisomerism, we likewise assigned the lower field signals to the α,α-isomers. Usually, the α,α-form was the minor component (10–35%); in **6f** and **6g**, however, it was present for about 60%. The Δδ values given in Table I are referring to the α,β-isomers.

The results of Table I indicate a preference for a folded conformation for all porphyrins **6** with a (sulfonyloxy)aryl group connected by a short chain (0–2 C atoms). We assume that these folded forms are stabilized by van der Waals interactions with a considerable contribution of charge transfer interaction, i.e. a HOMO–LUMO interaction of the donor–acceptor type between the electron-rich porphyrin and the electron-poor sulfonylphenyl system. The extra high upfield shifts for the protons of the nitro-containing compounds **6l**, **6p**, and to a less extent **6r** seem to corroborate this picture. The significantly lower Δδ values for compounds **6h** and **6n** are probably caused by steric factors. In the longer chain compounds (3 or more C atoms) the negative influence of the restricted motion of the sulfonylaryl group in the folded form will surpass the attractive interaction, resulting in less folding.

In the literature a folding tendency has been described for benzyl phenyl sulfones and *N*-[(arylsulfonyl)-methyl]-*N*-methylcarbamates,[10] and *p*-toluenesulfonic esters of aromatic hydrocarbons.[11] Several explanations have been offered for the phenomenon, viz. a repulsive interaction between the lone pairs on the sulfur oxygens and the π electron cloud (benzyl phenyl sulfones[10,12]), the formation of π molecular complexes,[11] a general attractive interaction between aromatic groups like the London dispersion forces.[13]



8a: R_1 = A; R_2 = Do; R_3 = Et; X = H_2
8b: R_1 = A; R_2 = Do; R_3 = Et; X = Zn
8c: R_1 = R_2 = A; R_3 = Et; X = H_2
8d: R_1 = R_2 = A; R_3 = Et; X = Zn
8e: R_1 = R_2 = Do; R_3 = Et; X = H_2
8f: R_1 = R_2 = Do; R_3 = Et; X = Zn
8g: R_1 = A; R_2 = Do; R_3 = *n*-Bu; X = H_2

Figure 2. Porphyrin model compounds synthesized.

On account of the results obtained we designed an acceptor–porphyrin–donor triad molecule with the acceptor (anthraquinone) and donor (dimethylaniline) groups situated at short distance from the central porphyrin by means of connecting sulfonyloxy groups, e.g. **8a** and its zinc derivative **8b** (Figure 2).

Because of their better solubility we prepared tetramethyltetraethylporphyrins instead of the octamethyl compounds **6**. For comparison we also synthesized the porphyrins with two anthraquinone groups (**8c**) and two dimethylaniline groups (**8e**) and their zinc derivatives (**8d** and **8f**). The results of investigations on the photophysical properties of **8a** will be published elsewhere;[14] we mention here only that **8a** undergoes very fast electron transfer upon irradiation from the porphyrin to the anthraquinone group. Again, the ^1H NMR spectra of **8a–f** in $CDCl_3$ so-

(8) In the α,α-atropisomer the substituents, attached to the mesoaryl groups lie on the same side of the porphyrin plane, in the α,β-atropisomer on opposite sides (see also ref 9).

(9) (a) Gottwald, L. K.; Ullman, E. F. *Tetrahedron Lett.* **1969**, 3071. (b) Collman, J. P.; Gagne, R. R.; Reed, C. A.; Halbert, T. R.; Lang, G.; Robinson, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 1427.

(10) Van Est-Stammer, R. Dissertation, Groningen, 1973.

(11) (a) Bentley, M. D.; Dewar, M. J. S. *Tetrahedron Lett.* **1967**, 5043. (b) Dewar, M. J. S.; Thompson, C. C. *Tetrahedron Suppl.* **1966**, *7*, 97.

(12) Van Est-Stammer, R.; Engberts, J. B. F. N. *Can. J. Chem.* **1973**, *51*, 1187.

(13) (a) Kobayashi, K.; Kodama, Y.; Nishio, M.; Sugawara, T.; Iwamura, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3560. (b) Kunieda, N.; Endo, H.; Hirota, M.; Kodama, Y.; Nishio, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3110.

(14) Hofstra, U.; Schaafsma, T. J.; Sanders, G. M.; van Dijk, M.; van der Plas, H. C.; Johnson, D. G.; Wasielewski, M. R., submitted for publication in *Chem. Phys. Lett.*

lution showed signals for the protons of the anthraquinone and dimethylaniline groups at very high field. The upfield shifts are given in Table II.

The introduction of zinc in the DPA porphyrin **8a** affects the upfield shifts of the dimethylanilino protons slightly and those of the anthraquinone protons considerably: in the free base **8a** H4′ shows the highest upfield shift in the left-hand ring and H5′ does so in the right-hand ring, whereas in the zinc derivative **8b** $\Delta\delta$ is largest for H1′ and H8′. We explained this difference by a change in conformation, due to coordination of the five-coordinate zinc atom with the C=O group between H1′ and H8′. Ring-current calculations were carried out to confirm this hypothesis.

Ring-Current Calculations. The conformations of **8a** and **8b** in $CDCl_3$ were calculated from the ^1H NMR ring-current shifts. The sign and the magnitude of the ring current induced chemical shifts are determined by the position and the orientation of the anthraquinone or dimethylaniline group with respect to the porphyrin molecule. To calculate the ring-current shifts we have adopted the double-dipole model of Abraham et al.[15] The contribution of the porphyrin macrocycle to the ring-current shift is treated as the sum of the contributions of four pentagons and four hexagons. The current loops are replaced by equivalent magnetic dipoles, located at 0.64 Å above and below the center of the polygons. The total ring-current shift of a nucleus is given by

$$\Delta\delta_i = \sum_{i=1}^{8}\mu_H(1 - 3\cos^2\theta_{ik})/r_{ik} + \sum_{i=1}^{8}\mu_P(1 - 3\cos^2\theta_{ik})/r_{ik} + \sum_{i=1}^{8}\mu_A(1 - 3\cos^2\theta_{ik})/r_{ik}$$

where μ_H, μ_P, and μ_A are the dipole moments of the hexagons, the pentagons and the aryl groups, respectively, r_{ik} is the distance of the nucleus i to the origin of the dipole moment and θ_{ik} is the angle between the vector r_{ik} and the normal to the polygon k.

At short distances between a proton and the neighboring porphyrin the equivalent dipole approximation is no longer valid. The ring-current shift is then given by

$$\Delta\delta = \Delta\delta_d g_d[b(d^2 - z^2) + c(d^4 - z^4)]$$

where $\Delta\delta_d$ and g_d are the shift and the gradient of the shift at the close range boundary at $z = d$, b and d are −0.64 and 3.6 Å, respectively, and $c = -(1 + bd)/4z$.[15]

The values for the equivalent dipoles were taken from those previously used for the tetraphenylporphyrins ZnTPP and H_2TPP, viz. $\mu_H = 17.1$ Å^3, $\mu_P = 19.3$ Å^3, and $\mu_A = 27.6$ Å^3.[16]

The coordinates of the porphyrins were taken from the X-ray data of H_2TPP.[17] The aryl substituent groups were assumed to be perpendicular to the porphyrin plane.

For the calculation of the conformation of the porphyrin molecules, the position and orientation of the anthraquinone and dimethylaniline groups with respect to the porphyrin plane were optimized. A computer program was used to vary systematically the x and y distances in the plane of the porphyrin ring and the z distance perpendicular to the plane in 0.1-Å steps. Also the orientation of both substituents was varied by rotating around the main axes of the molecule. The $N(CH_3)_2$ groups were assumed to be coplanar with the phenyl group. The calculated ring-current shifts yielding optimal agreement with the experimental shifts are given in Table III.

Table III. Experimental and Calculated $\Delta\delta$ Values of the Porphyrins 8a and 8b in $CDCl_3$ Solution at 213 K

	8a		8b	
	$\Delta\delta_{exp}$[a]	$\Delta\delta_{calcd}$[b]	$\Delta\delta_{exp}$	$\Delta\delta_{calcd}$
H1′	2.22	2.27	3.89	3.86
H3′	3.23	3.23	0.99	0.99
H4′	5.20	5.09	1.64	1.45
H5′	1.39	1.60	0.65	0.82
H6′	0.39	0.43	0.40	0.50
H7′	0.39	0.43	0.81	0.69
H8′	0.93	0.88	3.79	3.46
H2″,H6″	2.15	2.15	2.33	2.33
H3″,H5″	3.32	3.38	3.76	3.76
$N(CH_3)_2$	2.42	2.37	2.82	2.82

[a] $\Delta\delta$:δ(proton in 2-R-benzaldehyde) − δ(proton in porphyrin). [b] The root mean square error is 0.10 ppm for the anthraquinone protons. A translation of 0.1 Å from the calculated conformation induces a 2-fold increase of the root mean square error for these protons.

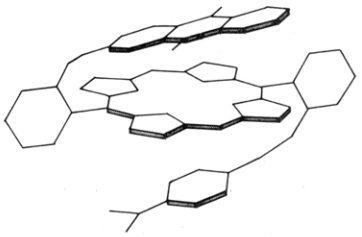


Figure 3. Calculated conformation of **8a**.

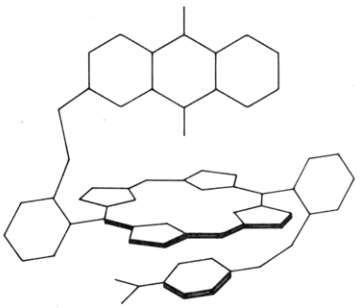


Figure 4. Calculated conformation of **8b**.

The calculated conformations for **8a** and **8b** are given in Figures 3 and 4; **8a** has a "type I conformation"[18] in which the planes of the donor and acceptor groups are practically parallel to the porphyrin plane. The plane-to-plane distance between porphyrin and anthraquinone is 3.2 Å. The angle between the two planes is 17°, and the anthraquinone is nearly coplanar with the porphyrin plane. The dimethylaniline group has a plane-to-plane distance of 3.0 Å, and the plane of the molecule makes an angle of 24° with the porphyrin plane.

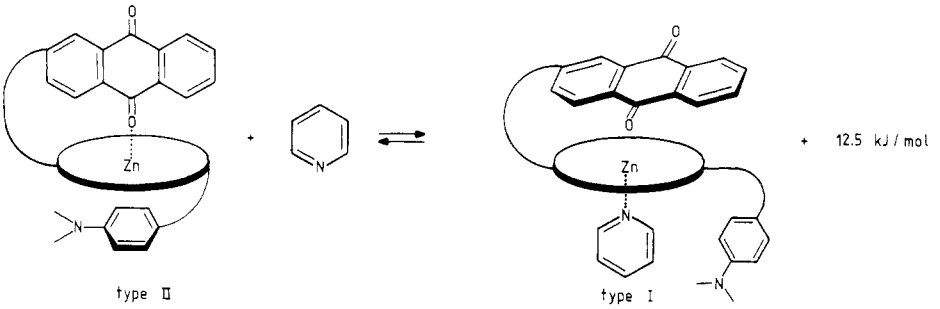
For **8b** the situation is more complicated. The conformation is best described as an average of two conformations (I and II). Conformation I is similar to the coplanar conformation of **8a**, whereas in conformation II the anthraquinone plane has a perpendicular orientation with respect to the porphyrin plane (the angle between the planes of the dimethylaniline group and the porphyrin is 6°). The distance between the center of the anthraquinone

(15) Abraham, R. J.; Smith, K. M.; Goff, D. A.; Lai, J.-J. *J. Am. Chem. Soc.* **1982**, *104*, 4332.
(16) Abraham, R. J.; Bedford, G. R.; McNellie, D.; Wright, B. *Org. Magn. Reson.* **1980**, *14*, 418.
(17) Silvers, S. J.; Tulinsky, A. *J. Am. Chem. Soc.* **1967**, *89*, 3331.
(18) In the following we designate the type of conformation with the A group parallel to the porphyrin plane as I, and with the A group perpendicular to the porphyrin plane as II. Thus I and II may be used for different compounds.

Table IV. ^{1}H Chemical Shifts of 8b in $CDCl_3$ Solution in the Presence of Deuteriated Pyridine

total molar equiv of pyridine added	H1′	H3′	H4′	H8′	H2″,H6″	H3″,H5″	$N(CH_3)_2$	calcd % of II
	5.39	6.58	5.92	5.46	5.20	2.89	0.30	
0.2	5.46	6.48	5.80	5.57	5.25	2.98	0.37	55
0.8	5.68	6.18	5.38	5.93	5.45	3.39	0.74	44
1.4	5.88	5.93	5.01	6.23	5.60	3.73	1.03	35
3.0	6.13	5.55	4.52	6.64	5.86	4.19	1.44	23
4.5	6.27	5.37	4.26	6.85	5.96	4.44	1.66	16
6.2	6.35	5.26	4.11	6.97	6.05	4.58	1.78	12
7.7	6.40	5.18	4.00	7.06	6.10	4.68	1.87	10
9.3	6.44	5.13	3.93	7.12	6.13	4.74	1.93	9
12.5	6.48	5.07	3.86	7.20	6.17	4.82	1.99	7
15.5	6.51	5.03	3.80	7.25	6.20	4.87	2.04	6
20.0	6.63	4.86	3.58	7.27	6.30	5.08	2.22	0

Scheme II. Ligand Exchange of Anthraquinone and Pyridine in 8b



and the porphyrin plane is 5.6 Å and the anthraquinone makes an angle of 90° with the porphyrin. The distance between the Zn atom of the porphyrin and the O atom of the anthraquinone is 2.9 Å. Evidently, in this conformation ligation of the Zn atom by the O atom of the anthraquinone group is well possible. The best fit of the calculated with the experimental ring-current shifts is obtained when we assume that **8b** exists for 82% in conformation II and for 18% in conformation I.

The behavior of **8b** toward pyridine gave another proof for intramolecular coordination. It is to be expected that the addition of a good ligand like pyridine will result in an exchange reaction in which the carbonyl group of anthraquinone is replaced by pyridine. Therefore, we added known amounts of deuteriated pyridine to a solution of **8b** in $CDCl_3$ and measured the NMR spectrum after each addition. In Table IV δ values are given for the protons, whose chemical shifts change most upon the pyridine addition.

We found that the chemical shifts of the anthraquinone protons gradually move toward values nearly equal to those of **8a** in $CDCl_3$. The protons of the dimethylaniline group, however, move to lower field. On account of this effect we propose that the zinc derivative **8b** is initially in the coordinated conformation II and that the addition of pyridine leads eventually to a conformation of type I in which the anthraquinone plane is about parallel to the porphyrin plane, just as in **8a**, but in which the dimethylaniline group has been pushed away from its original parallel position by a ligand pyridine molecule (Scheme II).

It is possible to calculate the percentages of conformation II and I, present in the mixture, from the δ values of H1′, H3′, H4′, H8′, by taking the δ values of **8b** with excess (20 equiv) of pyridine for those of pure conformation I and the corrected δ values of **8b**[19] for those of pure conformation II. The results of these calculations, which assume that the measured chemical shift is a time-averaged value for the two conformations, are given in Table II. As the initial concentration of **8b** is known (9.6×10^{-3} mol/L), the equilibrium constant K can be obtained: $K = 150$ L/mol, which leads to a value for ΔG at 27 °C: $\Delta G = -12.5$ kJ/mol (−3.0 kcal/mol). This value is in reasonable agreement with the ΔG value for coordination of zinc tetraphenylporphyrin by pyridine at 25 °C: $\Delta G = -5.0$ kcal/mol, given in the literature.[20] When we assume the same ΔG value for coordination of pyridine with our compound **8b** and moreover neglect the differences in van der Waals interactions between the porphyrin and the anthraquinone and dimethylaniline parts, it follows that ΔG for coordination of zinc by the anthraquinone group is about −2 kcal/mol. The literature[20] reports for coordination of zinc in tetraphenyl porphyrin by the CO group in 1,1,3,3-tetramethylurea at 25 °C: $\Delta G = -2.5$ kcal/mol.

For the dianthraquinone zinc porphyrin **8d** we did not investigate the effect of pyridine. The ^{1}H NMR spectra of **8c** and **8d** show some minor deviations from those of **8a** and **8b**, but on the whole the pattern is very much alike. Therefore, we assume for these compounds the same conformations: for **8c** a conformation with parallel planes and for **8d** a conformation in which the anthraquinone groups are perpendicular to the porphyrin plane. As zinc is strictly five-coordinate[21] and as we find only one set of signals for the anthraquinone protons in **8d** with about the same $\Delta\delta$ values as in **8b**, we believe that both anthraquinone groups are in a perpendicular position, forming two partial carbonyl–Zn bonds. Introduction of zinc into the bis(dimethylanilino)-substituted porphyrin **8e** leads to an increase in upfield shift for the sulfonylphenyl protons in **8f**, especially for H3″, H5″, and $N(CH_3)_2$. The higher $\Delta\delta$ values are partially explained by the increase in ring current on metalation of the porphyrin;[22] in ad-

(19) According to the ring-current calculations, **8b** exists at 213 K for 82% in conformation II and for 18% in conformation I. Correction for the presence of 18% of I gave the following δ values for "pure" conformation II: H1′, 4.54; H3′, 7.75; H4′, 7.64; H8′, 3.91.

(20) Hambright, P. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier Scientific: Amsterdam, 1975; p 261.

(21) Leighton, P.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1984**, 854.

Table V. Upfield Shift for the Tosyl Protons of 6b at Various Temperatures in $CDCl_3$

temp, K	Δδ H2′,H6′	Δδ H3′,H5′
323	1.89	2.79
301	2.04	3.07
278	2.17	3.31
258	2.29	3.51
243	2.37	3.64
228	2.47	3.87
218	2.56	4.05

Scheme III. Conformational Equilibrium for 6b

Folded conformation ⇄ nonfolded conformations
ΔG = +2.9 kJ/mol at 28 °C (0.7 kcal/mol)
ΔH = +14.7 kJ/mol (3.5 kcal/mol)
ΔS = +9.5 eu

dition, ligation of the zinc atom by the lone pair on nitrogen will probably be responsible for the increased folding.

Low-Temperature NMR Measurements. A large upfield shift for a compound in solution does not prove that the compound exists in only one (folded) conformation. There may as well be an equilibrium between several conformations, interconverting rapidly on the NMR time scale. To solve this question we measured NMR spectra at various temperatures for the tosylates **6a–c** and for **8a** and **8b**. For **6a** and **6c** the chemical shifts did not change upon lowering the temperature to −60 °C. Compound **6b** showed an increase of the upfield shift of the tosyl protons when the solution was cooled (Table V); the signals remained sharp. Cooling below −55 °C was impossible as the solvent started to solidify.

On account of these results we assume for **6b** an equilibrium between folded and nonfolded conformations; lower temperatures favor the conformations with the lower H values, in our case evidently the folded conformation(s). By assuming that the $\Delta\delta$ values found for **6b** at −55 °C correspond to those of the folded conformation and that the $\Delta\delta$ values reported for the long chain compound **6e** are characteristic for a nonfolded conformation, we were able to determine the equilibrium constant K at various temperatures, from which the ΔG,ΔH,ΔS values shown in Scheme III were calculated.

These values are upper limits. Upon cooling below −55 °C the δ values of **6b** will probably continue to move upfield, resulting in larger $\Delta\delta$ values for the folded conformation and thus lower absolute values for ΔH and ΔS. The positive ΔH and ΔS values agree with the idea of an attractive interaction and restricted motion in the folded conformation, mentioned before. Moreover, the values agree with values found for some sulfones (ΔH = +10.8 kJ/mol, ΔS = +3.5 eu) and carbamates (ΔH = +14.7 kJ/mol, ΔS = +10 eu).[10]

The fact that **6a** does not show a temperature dependence of the chemical shift can be explained by the presence of only one, folded conformation at room temperature. Calculation of the ring-current shifts of **6a** by the method described before gave a good fit with the measured δ values for a folded conformation, in which the tosyl rings lie nearly parallel (<36° deviation) to the porphyrin plane on 3.1 Å vertical distance; the displacement of the center of the phenyl ring from the porphyrin center is 0.8 Å along the axis C5–C15 and 1.7 Å in the perpendicular direction (C10–C20). The folded form of

(22) Scheer, H.; Katz, J. J. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier Scientific: Amsterdam, 1975; p 459.

Scheme IV. Conformational Equilibrium for 8b

I ⇄ II
ΔH = −6.2 kJ/mol (−1.5 kcal/mol)
ΔS = −4.4 eu
ΔG = −0.8 kJ/mol (−0.2 kcal/mol) at 30 °C

Scheme V. Conformational Equilibrium for 8a

I ⇄ II
ΔH = +17.2 kJ/mol (4.1 kcal/mol)
ΔS = +10 eu
ΔG = +4.3 kJ/mol (1.0 kcal/mol) at 27 °C

6a has slightly lower upfield shifts than the folded form of **6b** (i.e. **6b** at −55 °C), probably because the flexible chain in the latter compound allows a closer proximity of the tosyl group to the center of the porphyrin ring current.

To explain the absence of a temperature effect for the longer chain compound **6c** we assume that the folded and nonfolded conformations of **6c** are energetically equivalent (ΔH = 0); the contribution of the folded conformations present in the equilibrium will be responsible for the overall upfield shift. For **6d** and **6e** we also assume an equilibrium of conformations; due to the longer distance from the porphyrin system the resulting upfield shift will be smaller.

The short-chain compounds **8a–f** might be expected to behave like **6a**, i.e. no NMR temperature effect. Significant changes, however, were observed upon cooling or heating of solutions of **8a** and **8b**, mainly on the chemical shifts of the anthraquinone protons. For the zinc compound **8b** some protons (H1′, H7′, H8′) move to higher field upon cooling, others (H3′, H4′, H5′) to lower field; no broadening or splitting of signals was observed. Evidently, this is due to an equilibrium between the differently folded forms (I and II) in this case. We assume that at room temperature **8b** exists to a small extent in the not-coordinated form, with the anthraquinone group parallel to the porphyrin plane (I), and that the equilibrium shifts in the direction of the intramolecularly coordinated conformation (II) upon lowering of the temperature. It is possible to calculate the percentages of I and II present at various temperatures, when we take the δ values for the free base **8a** at −60 °C (Table VI) for those of conformation I and the corrected δ values of **8b** at −60 °C, which we used in the ligand exchange experiment,[19] for those of conformation II. From the calculated percentages of I and II equilibrium constants can be obtained at various temperatures, from which ΔG, ΔH, and ΔS values for the equilibrium can be calculated. In this way we found the values given in Scheme IV.

For the free base **8a**, only a slight change occurs on cooling, which can be explained by assuming that a minor amount of the perpendicular type II conformation is present at room temperature in solution. By similar calculations as carried out for **8b**, the values shown in Scheme V were obtained for **8a**. Evidently in the zinc compound **8b** the perpendicular conformation II is favored because of coordination with zinc, in spite of the slightly more rigid structure required for this bonding. On the other hand, the parallel conformation I is favored in the free base **8a**, because of a favorable van der Waals interaction, in spite of the more rigid structure required.

From the ΔG values for the equilibrium I ⇄ II in the two compounds **8a** and **8b** we can calculate an approximate ΔG value for intramolecular ligand formation: about −1.2 kcal/mol. We assume in this approximation that conformation I in **8a** and **8b** has the same G value. The calculated value, −1.2 kcal/mol, is somewhat lower than the value obtained from the ligand exchange experiment

Table VI. ^{1}H NMR δ Values for 8b and 8a in $CDCl_3$ Solution at Various Temperatures

temp, K	H1′	H3′	H4′	H5′	H6′	H7′	H8′	H2″,H6″	H3″,H5″	calcd % of II[a]
8b										
213	4.91	7.26	6.86	7.68	7.49	7.08	4.54	5.21	2.82	82
243	5.12	6.95	6.44	7.62	7.50	7.14	4.94	5.21	2.84	71
260	5.18	6.81	6.25	7.60	7.49	7.17	5.15	5.22	2.83	67
273	5.26	6.75	6.16	7.57	7.49	7.18	5.26	5.20	2.85	64
303	5.40	6.58	5.93	7.54	7.48	7.22	5.46	5.20	2.88	58
335	5.50	6.46	5.76	7.50	7.49	7.25	5.66	5.20	2.92	53
343	5.53	6.43	5.72	7.49	7.49	7.25	5.70	5.20	2.94	42
8a										
213	6.58	5.02	3.30	6.94	7.50	7.50	7.40	5.39	3.26	
223	6.57	5.06	3.38	6.94	7.49	7.49	7.38	5.37	3.25	2.5
233	6.56	5.10	3.46	6.93	7.47	7.47	7.35	5.35	3.24	2.5
243	6.55	5.15	3.54	6.93	7.46	7.46	7.32	5.34	3.24	3.5
263	6.53	5.23	3.68	6.93	7.44	7.44	*b*	5.31	3.24	5.5
283	6.51	5.30	3.81	6.92	7.42	7.42	*b*	5.30	3.25	7.5
300	6.51	5.36	3.90	6.93	7.41	7.41	7.22	5.29	3.27	8.5

[a] δ values used in the calculation of the percentage of II: pure conformation I, H-1′ 6.58; H-3′ 5.02; H-4′ 3.30; H-8′ 7.40; pure conformation II, H-1′ 4.54; H-3′ 7.75; H-4′ 7.64; H-8′ 3.91; [b] Under $CHCl_3$ peak.

Table VII. ^{1}H NMR Upfield Shifts Δδ in $CDCl_3$ Solution for Compounds 6s–x

		Δδ	
compd	R	H2′,H6′	H3′,H5′
6s	$OCOC_6H_4$(4′-Me)	1.34	0.90
6t	$O(CH_2)_2OCOC_6H_4$(4′-Me)	1.06	0.78
6u	$O(CH_2)_2SO_2C_6H_4$(4′-Me)	0.91	1.25
6v	$O(CH_2)_2SOC_6H_4$(4′-Me)	1.41	1.26
6w	$O(CH_2)_2SC_6H_4$(4′-Me)	0.62	0.66
6x	$O(CH_2)_3C_6H_4$(4′-Me)	0.39	0.72

(−2.0 kcal/mol); in view of the many approximations we had to make in our calculations, this is hardly surprising.

Influence of the Connecting Chain. In order to answer the question whether the sulfonyloxy group is essential for the folding of the molecule, we synthesized a series of compounds **6s–x** with different groups in the connecting chain (ester, sulfonyl, sulfinyl, thio, methylene group). The upfield shifts for H2′, H6′, and for H3′, H5′ are given in Table VII.

We assigned the lower field signals to H2′ and H6′ in analogy with the assignment for **6a–r**. When we assume that the slight variation in chain length does not influence the comparison between the groups, the results indicate that the folding tendency decreases by replacement of the sulfonyloxy group by other groups. Even if the assignment of H2′,H6′ and H3′,H5′ would have to be reversed this conclusion holds. The effect can be explained by the strongly electron withdrawing properties of the sulfonyloxy group, leading to more charge transfer interaction. However, the geometric requirements of the groups concerned may also play a role.

Toluene Solutions. All porphyrins mentioned until here were studied in $CDCl_3$ solution as their solubility in other solvents was too low. A methyl-*n*-butylporphyrin analogue of **8a**:**8g** proved considerably more soluble in organic solvents so that we could study the ^{1}H NMR spectra in toluene, which was used for photophysical measurements.[14] As the spectrum of **8g** in $CDCl_3$ was found to be identical with that of **8a**, apart from the alkyl signals (Table II), the replacement of ethyl by *n*-butyl groups evidently does not influence the conformation. The results of the NMR measurements in deuteriated toluene at various temperatures are given in Table VIII.

The protons of the anthraquinone and dimethylaniline groups absorb at 0.2–0.4 ppm lower field in toluene than in $CDCl_3$. The δ values of the aldehyde reference compounds in toluene, however, also differ considerably from those in $CDCl_3$ due to interaction with the aromatic solvent molecules. Thus, determination of upfield shifts due to the porphyrin ring current is impossible and Δδ values are useless, as the ring-current contributions of the solvent are not known. However, whether we compare the δ values of **8g** in toluene with the δ values of the reference aldehydes in toluene or with those in $CDCl_3$, in both cases the Δδ values obtained are lower than those obtained for **8g** in $CDCl_3$ solution.[23] The effect of the temperature on the chemical shifts seems to be the same as that found for **8a** in $CDCl_3$, e.g. at increasing temperatures H1′ moves to higher field while H3′ and H4′ move to lower field. On the basis of these facts, we propose that in toluene solution **8g** exists as a mixture of conformation I, conformation II, and (possibly) nonfolded conformations.

Table VIII. δ Values for Some Protons of 8g in Deuteriated Toluene at Various Temperatures

	δ (ppm)				
temp, K	H1′	H3′	H4′	H2″,H6″	H3″,H5″
213	7.07	5.37	3.74	5.88	
233	7.02	5.47	3.92	5.82	3.39
263	6.98	5.59	4.15	5.77	3.43
293	6.95	5.68	4.30	5.73	3.46
300	6.94	5.69	4.34	5.70	3.46
333	6.93	5.73	4.41	5.70	3.48
353	6.93	5.75	4.45	5.69	3.49
363	6.92	5.77	4.49	5.68	3.51
373	6.92	5.80	4.52	5.68	3.52

Experimental Section

Melting points are uncorrected. The ^{1}H NMR spectra of the porphyrins were recorded on a 300-MHz Bruker CPX-300 spectrometer; those of the aldehydes mostly on a Varian EM-390 spectrometer, with tetramethylsilane as internal reference. All spectra were measured in $CDCl_3$ solution, concentration of the porphyrins 1 mg/mL or less, of the other compounds about 50 mg/mL. The ^{1}H NMR data of the octamethyl porphyrins **6a–x** are given in Table IX; those of **8a–g** are given under the respective compounds. All integration values were in accordance with the assignment. All porphyrins and aldehydes gave satisfactory C, H, (N) analyses; for some porphyrins, however, we had to assume the presence of 0.1–0.6 mol of $CHCl_3$/mol of porphyrin. The tendency of ortho-substituted 5,15-diphenylporphyrins to form solvates or to occlude solvent molecules, which are difficult to remove, has been described in the literature.[4]

Preparation of the Octamethylporphyrins 6a–x. A. Hexahydroporphyrins 5a–x. Ten millimoles of ortho-substi-

(23) The Δδ values of **8g** in toluene-d_8 (27 °C) on comparing with the standard aldehydes in $CDCl_3$ (in toluene-d_8) are as follows: Δδ for H1′, 1.86 (1.76); H3′, 2.56 (1.99); H4′, 4.16 (3.59); H2″,H6″, 1.84 (1.78); H3″,H5″, 3.12 (2.59). Compare with the Δδ values of **8g** in $CDCl_3$: H1′, 2.27; H3′, 2.93; H4′, 4.65; H2″,H6″, 2.29; H3″,H5″, 3.33.

Table IX. ^{1}H NMR Chemical Shifts of the Porphyrins 6a–x in $CDCl_3$ Solution

	chemical shift, δ[a]										
	CH_3(pyrrole)				mesoaryl				sulfonylaryl		
compd	3,7,13,17	2,8,12,18	H meso	NH	H3	H4	H5	H6	H2′,H6′	H3′,H5′	other protons
6a	2.45	3.50	10.13	−2.99	7.90	7.96	7.70	8.09	5.63	4.36	CH_3, 0.20
6b	2.55	3.54	10.21	*b*	7.28	7.79	7.39	7.73	5.76	4.24	CH_3, 0.16; CH_2, 3.51, 4.26
6c	2.53	3.54	10.21	−2.35	7.26	7.78	7.33	7.71	6.72	6.02	CH_3, 1.59; CH_2, 1.39, 3.05, 4.08
6d	2.51	3.52	10.16	−1.81	7.25	7.75	7.35	7.74	7.06	6.57	CH_3, 1.97; CH_2, 0.54, 1.10, 3.00, 3.94
6e	2.80	3.79	10.43	−0.74	7.61	8.01	7.61	8.01	7.54	7.16	CH_3, 2.42; CH_2, 0.58, 0.66, 0.80, 1.26, 3.39, 4.19
6f	2.40	3.49	10.18	−2.67	8.01	7.93	7.72	8.15	5.73[c]	4.41[c]	
6g	2.44	3.49	10.14	−2.78	7.93	7.93	7.70	8.15	5.71	4.57	H4′, 4.92
6h	2.48	3.47	10.10	−2.53	7.96	7.89	7.71	8.10	5.81	5.16	CH_3, −0.07
6i	2.50	3.49	10.09	−2.71	7.93	7.93	7.72	8.11	5.63	4.48	cyclohexyl, −0.50, −0.09, 0.06 (H_α), 0.46, 0.88, 1.09
6j	2.43	3.49	10.14	−2.73	7.87	7.94	7.66	8.01	5.69	4.16	CH_3, 1.76
6k	2.50	3.49	10.12	*b*	7.92	7.90	7.71	8.25	5.50	3.90	CH_3, 1.45
6l	2.50	3.51	10.06	−3.41	7.92	7.92	7.78	8.31	5.52	4.75	
6m	2.47	3.49	10.11	−2.93	7.98	7.91	7.66	8.13		4.06	CH_3 (*o*), 0.89; CH_3 (*p*), −0.07
6n	2.60	3.50	10.12	−2.66	7.92	7.86	7.61	8.12		6.27	CH (*o*), 3.37; CH (*p*), 2.14; CH_3 (*o*), 0.26; CH_3 (*p*), 0.60
6o	2.55	3.55	10.20	−2.24	7.27	7.78	7.41	7.83	5.99[d]	4.56[d]	CH_2, 3.55, 4.29
6p	2.53	3.54	10.18	*b*	7.30	7.81	7.43	7.81			H2′, 4.32; H4′, 5.00; H5′, 4.05; H6′, 4.61; CH_2, 3.50, 4.22
6q	2.51	3.36	9.87	*b*	7.95	7.95	7.80	8.10	5.62	4.59	H8′,H12′, 5.16;[e] H9′,H11′, 6.29[e]
6r	2.50	3.39	9.85	−2.97	7.94	7.94	7.85	8.14	5.59	4.34	H8′,H12′,4.84; H9′,H11′, 7.27
6s	2.63	3.52	10.16	−2.46	7.86	7.86	7.61	7.99	6.78	6.25	CH_3, 1.73
6t	2.52	3.42	10.10	−2.31	7.36	7.76	7.43	7.76	6.88	6.44	CH_3, 2.15; CH_2, 4.17, 4.32
6u	2.47	3.51	10.14	−2.41	7.34	7.76	7.43	7.76	6.88	6.03	CH_3, 1.36; CH_2, 2.86, 4.35
6v	2.49	3.52	10.13	−2.28	7.39	7.81	7.43	7.84	6.13	6.04	CH_3, 1.68; CH_2, 4.15, 4.59
6w	2.53	3.52	10.15	−2.2	7.23	7.72	7.34	7.75	6.68	6.39	CH_3, 1.25; CH_2, 2.55, 4.13
6x	2.56	3.53	10.16	−2.28	7.24	7.72	7.31	7.94	6.69	6.36	CH_3, 2.13; CH_2, 1.41, 1.75, 3.93

[a] See for numbering of the protons Figure 1. [b] Not determined. [c] *J*(H,F ortho) = 8.3 Hz; *J*(H,F meta) = 4.9 Hz. [d] *J*(H,F ortho) = 8.6 Hz; *J*(H,F meta) = 5.2 Hz. [e] *J*(H,F ortho) = 8.6 Hz; *J*(H, F meta) = 3.7 Hz.

tuted aldehyde **7** were dissolved in 125 mL of methanol with stirring (for **7k,l,q,r,v**, the addition of CH_2Cl_2 was necessary to obtain a solution). Next 10 mmol of 3,3′,4,4′-tetramethyl-2,2′-dipyrrolylmethane (**4**)[5-7] were added and stirred until a solution was obtained. After addition of 0.5 g of *p*-toluenesulfonic acid, the mixture was stirred for 1 h, left at room temperature for 5 h, and kept in the refrigerator overnight. The precipitate was removed by filtration, washed with cold methanol, and dried in vacuo. In cases where a precipitate had not been formed, it could be obtained by removal of the CH_2Cl_2 added in vacuo (**5l,r**). Yields varied from 40 to 84%, but for **5h,l,v** lower yields (20–40%) were obtained.

B. Porphyrins 6a–x. Five millimoles of **5** were dissolved (as much as possible) in 300 mL of tetrahydrofuran (THF). A solution of 18.1 mmol of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in 75 mL of THF was added over a period of 5 min. The mixture was stirred for 1 h at room temperature and left for 1 h. The precipitate formed was filtered off and washed with THF, stirred with $CHCl_3$, filtered off, and dried in vacuo. If necessary the porphyrin was purified further by column chromatography over silica gel, eluent $CHCl_3$ with gradual addition of a few percent ether or ethanol. In case no precipitate had been formed after the reaction, the solvent was evaporated and the solid residue was purified by chromatography as described above. Yields varied from 50 to 75%, but for **6b–e,l,n–p,s,t,w** lower yields were found (8–50%).[24]

Preparation of the Aldehydes 7. Melting points, yields, and ^{1}H NMR data in $CDCl_3$ solution are given in Table X.

A. Aldehydes 7a,b,f–n,r,s. To a mixture of 0.2 mol of the corresponding sulfonyl chloride (or acyl chloride) and 100 mL of dry pyridine a solution of 0.22 mol of 2-hydroxybenzaldehyde (for **7b** 2-(2-hydroxyethoxy)benzaldehyde[25]) in 25 mL of dry pyridine was added over a period of 10 min with stirring at a temperature below −10 °C. Stirring was continued for 2 h at −10 °C, next for 2 h at 0 °C. The mixture was left overnight at room temperature and then poured into ice/water. The precipitate was sucked off, washed with water, and solved in $CHCl_3$. This solution was washed with dilute HCl solution, $NaHCO_3$ solution, and water, dried on $CaCl_2$, and evaporated. The crude product was purified by recrystallization or chromatography.

B. Aldehydes 7c,e,o. To a solution of 0.12 mol of 2-(3-hydroxypropoxy)benzaldehyde[25] (or 2-[(6-hydroxyhexyl)oxy]-benzaldehyde or 2-(2-hydroxyethoxy)benzaldehyde, respectively) in 50 mL of ether and 30 mL of pyridine was added 0.16 mol of the required sulfonyl chloride at a temperature below −30 °C with stirring. After being stirred for another 2 h at −30 °C, the mixture was left overnight at −18 °C and then poured onto ice. The precipitate was sucked off, washed with water, and solved in ether or CH_2Cl_2. This solution was treated as described under A.

C. Aldehydes 7p,t. Compounds **7p** and **7t** were prepared by the same method as described under B except that the reaction was carried out at room temperature in a mixture of pyridine and toluene.

D. Aldehyde 7d. Compound **7d** was prepared from the sodium salt of 2-hydroxybenzaldehyde by a coupling reaction with 1,4-dibromobutane in DMSO (stirring for 16 h at room temperature). By pouring the mixture into water, extraction with ether, washing with water, drying, and evaporation, crude 2-(4-bromobutoxy)-benzaldehyde was obtained, which was purified by chromatography over silica gel, eluent petroleum ether/ethyl acetate, 9:1. The bromobutoxyaldehyde was refluxed with silver tosylate in acetonitrile for 24 h. The silver bromide was filtered off, and the residue obtained from the filtrate by evaporation of the solvent was purified by chromatography over silica gel, gradient elution with petroleum ether/ethyl acetate.

E. Aldehydes 7w,v,u,q,x. Aldehyde 7w was prepared by a coupling reaction of the sodium salt of 2-hydroxybenzaldehyde with 3 equiv of 1,2-dibromoethane in refluxing ethanol during 16 h. The 2-(2-bromoethoxy)benzaldehyde thus obtained was reacted with sodium *p*-(methylthio)phenolate in DMSO for 16 h at room temperature. Dilution with water, extraction with ether, and chromatography over silica gel (eluens petroleum ether/ethyl acetate, 9:1) gave **7w**.

Aldehyde 7v was obtained by addition of a solution of 50 mmol of $NaIO_4$ in 95 mL of water to a solution of 46 mmol of **7w** in 220 mL of absolute ethanol. Stirring for 16 h at room temperature, evaporation of ethanol, dilution with water, extraction with $CHCl_3$,

(24) The yields can probably be improved by dissolving the residue, obtained an evaporation of the solvent, in CH_2Cl_2, followed by addition of methanol/triethyl amine leading to a precipitate (see: Young, R.; Chang, C. K. *J. Am. Chem. Soc.* **1985**, *107*, 898).

(25) Almog, J.; Baldwin, J. E.; Crossley, M. J.; Debernardis, J. F.; Dyer, R. L.; Huff, J. R.; Peters, M. K. *Tetrahedron* **1981**, *37*, 3589.

Table X. Melting Points, Yields of Preparation, and ^1H NMR Chemical Shifts in $CDCl_3$ Solution for the Aldehydes 7a–x

aldehyde	mp, °C	yield, %	δ[a]
7a	60.5–61.5	82	H2′,6′, 7.70; H3′,5′, 7.32; CH_3, 2.45
7b	104.5–105.5	48	H2′,6′, 7.79; H3′,5′, 7.30; CH_3, 2.46; CH_2, 4.40, 4.26
7c	92.5–93	31	H2′,6′, 7.72; H3′,5′, 7.18; CH_3, 2.35; CH_2, 4.25, 4.07, 2.19
7d	65–69	31	H2′,6′, 7.82; H3′,5′, 7.35; CH_3, 2.42; CH_2, 3.9–4.3, 1.85
7e	oil	32	H2′,6′, 7.74; H3′,5′, 7.26; CH_3, 2.41; CH_2, 4.0, 1.1–2.0
7f	55–57	50	H2′,6′, 7.90; H3′,5′, 7.23
7g	56–58.5	95	H2′,6′, 7.84; H3′,5′, 7.36; H4′, 7.54
7h	78–79.5	94	H2′,6′, 7.78; H3′,5′, 7.55; CH_3, 1.42
7i	66–68	64	H2′,6′, 7.76; H3′,5′, 7.35; H(α), 2.59; H(β), 1.84; H(γ), 1.40
7j	68–70	75	H2′,6′, 7.79; H3′,5′, 7.00; OCH_3, 3.90
7k[b]	100.5–102	51	H2′,6′, 7.54; H3′,5′, 6.58; $N(CH_3)_2$, 3.07
7l	122–124	28	H2′,6′, 8.10; H3′,5′, 8.42
7m	115.5–116.5	69	H3′,5′, 7.00; CH_3, 2.53 (o), 2.33 (p)
7n	68.5–69.5	65	H3′,5′, 7.25; CH, 4.02 (o), 2.95 (p); CH_3, 1.25 (o), 1.30 (p)
7o	75–79	50	H2′,6′, 7.98; H3′,5′, 7.26; CH_2, 4.50, 4.33
7p	75–76	32	H2′, 8.75; H4′, 8.52; H5′, 7.80; H6′, 8.25; CH_2, 4.63, 4.11
7q	106.5–107.5	53	H2′,6′, 7.90; H3′,5′, 7.69; H8′,12′, 7.56; H9′,11′, 7.17
7r	146–147	60	H2′,6′, 8.06; H3′,5′, 7.89; H8′,12′, 7.89; H9′,11′, 8.41
7s	79–80	65	H2′,6′, 8.12; H3′,5′, 7.15; CH_2, 2.43
7t	90–92	75	H2′,6′, 7.94; H3′,5′, 7.22; CH_3, 2.40; CH_2, 4.74, 4.43
7u	111.5–112.5	59	H2′,6′, 7.79; H3′,5′, 7.28; CH_3, 2.46; CH_2, 4.50, 3.67
7v	142–142.5	67	H2′,6′, 7.54; H3′,5′, 7.30; CH_3, 2.40; CH_2, 4.47, 3.23
7w	oil	92	H2′,6′, 7.30; H3′,5′, 7.05; CH_3, 2.30; CH_2, 4.15, 3.23
7x	oil	68	H2′,6′, 7.08; H3′5′, 7.08; CH_3, 2.30; CH_2, 3.97, 2.74, 2.12

[a] δ values for the protons of the benzaldehyde ring, 6.8–7.9; for the CHO proton, 10.0–10.5 (**7u**, 9.54). The protons of the sulfonylphenyl ring are indicated by a single accent, e.g. H2′,H3′, etc. [b] δ values in toluene-d_8 solution: H2′,H6′, 7.48; H3′,H5′, 6.05; $N(CH_3)_2$, 2.30.

and chromatography over silica gel (eluens methylenechloride/ethyl acetate) gave **7v**, which was purified by crystallization from ethyl acetate.

Aldehyde 7u was obtained by oxidation of the diethylene acetale of **7w**. A mixture of 30 mmol of **7w**, 90 mmol of ethylene glycol and 0.1 g of *p*-toluenesulfonic acid in 150 mL of toluene was refluxed for 16 h with a Dean-Stark water separator. Dilution with ether and washing with $NaHCO_3$ solution gave the acetal, which was reacted with 60 mmol of *m*-chloroperbenzoic acid in 250 mL of CH_2Cl_2 for 1.5 h. Filtration, evaporation, and chromatography of the residue over silica gel (eluens petroleum ether/ethyl acetate, 1:1) gave pure **7u**.

Aldehyde 7q was prepared by reduction of 4-nitrobiphenyl,[26] followed by a Schiemann reaction leading to 4-fluorobiphenyl.[27] Sulfonation of this compound[28] and refluxing of the sodium salt with $POCl_3$ gave 4-fluoro-4′-(chlorosulfonyl)biphenyl, which was coupled to 2-hydroxybenzaldehyde in the way described under A.

Aldehyde 7x was prepared by reaction of 4-methylbenzaldehyde with malonic acid,[29] followed by reduction with Pd/C and next $LiAlH_4$,[30] leading to 4-(3-hydroxypropyl)toluene. Reaction with PBr_3[31] gave the bromide, which was coupled to 2-hydroxybenzaldehyde in the way described under D for aldehyde **7d**.

Preparation of the Porphyrins 8a–g. Anthraquinone-2-sulfonyl chloride. A mixture of 25.0 g of the sodium salt of anthraquinone-2-sulfonic acid (monohydrate) and 125 mL of $POCl_3$ was refluxed with stirring for 4 h and then poured onto ice. Extraction with $CHCl_3$, washing with water, drying, and evaporation gave 22.3 g (95%) of anthraquinone-2-sulfonyl chloride.

2-[(Anthraquinone-2-sulfonyl)oxy]benzaldehyde. A solution of 22.0 g (72 mmol) of anthraquinone-2-sulfonyl chloride in 250 mL of pyridine was cooled to 0 °C. A solution of 9.7 g (79 mmol) of 2-hydroxybenzaldehyde in 25 mL of pyridine was then added over a period of 5 min; the mixture was stirred for 1 h at 0 °C and for 20 h at room temperature and then poured into ice/water. The oily precipitate was filtered off, solved in $CHCl_3$, washed with water, dilute HCl, water, $NaHCO_3$ solution, and water, and then dried on $CaCl_2$. After evaporation and recrystallization from acetone, 19.9 g (70%) of the aldehyde was obtained, mp 152–153 °C. ^1H NMR ($CDCl_3$): δ 10.10 (s, 1 H, CHO), 8.80 (d, 1 H, H1′), 8.50 (d, 1 H, H4′), 8.25 (dd, 1 H, H3′), 8.33 (m, 2 H, H5′, H8′), 7.89 (m, 3 H, H6, H6′, H7′), 7.63 (ddd, 1 H, H4), 7.42 (ddd, 1 H, H5), 7.24 (dd, 1 H, H3). ^1H NMR (toluene-d_8): δ 10.00 (s, 1 H, CHO), 8.70 (d, 1 H, H1′), 7.93 (d, 1 H, H4′), 7.68 (dd, 1 H, H3′), 8.0 (m, 2 H, H5′, H8′), 7.56 (dd, 1 H, H6), 7.0 (m, 3 H, H6′, H7′, H3), 6.88 (ddd, 1 H, H4), 6.70 (ddd, 1 H, H5).

(3,3′-Diethyl-4,4′-dimethyl-2,2′-dipyrrolyl)methane. This compound was prepared in five steps in 39% overall yield, according to procedures described in the literature, from diethylmalonate and 3-ethyl-2,4-pentanedione,[5] via 2-(ethoxycarbonyl)-4-ethyl-3,5-dimethylpyrrole.[32] The latter compound was coupled to [5,5′-bis(ethoxycarbonyl)-3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrrolyl]methane,[33] which was hydrolyzed and decarboxylated.[34] In this last step, however, a modified procedure was applied. Instead of removing $^2/_3$ of the solvent alcohol, all alcohol was removed after the reaction. Moreover, the resulting mixture was heated with water for 20 h instead of 6 h.

5,15-Bis[2-[(anthraquinone-2-sulfonyl)oxy]phenyl]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (8c). To a solution of 3.92 g (10 mmol) of 2-[(anthraquinone-2-sulfonyl)oxy]benzaldehyde in 75 mL of CH_2Cl_2 and 75 mL of CH_3OH was added 2.30 g (10 mmol) of (3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrrolyl)methane. The mixture was stirred until complete solution. Then 0.5 g of *p*-toluenesulfonic acid was added, and the mixture was stirred for 4 h at room temperature and left overnight in the refrigerator. The precipitate (5.18 g of hexahydroporphyrin) was sucked off, washed with cold CH_2Cl_2/CH_3OH, 1:1, and suspended in 300 mL of THF. A solution of 3.50 g of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in 75 mL of THF was added gradually over a period of 10 min, and the mixture was stirred for 1 h and left for 1 h at room temperature. The precipitate formed was filtered off and washed with THF, yield 3.3 g (56%). ^1H NMR ($CDCl_3$): δ 9.76 (s, 2 H, H10, H20), 8.48 (dd, 2 H, H6), 7.98 (ddd, 2 H, H4), 7.91 (ddd, 2 H, H5), 7.83 (dd, 2 H, H3), 3.81 (dq, 4 H, CH_2), 3.70 (dq, 4 H, CH_2), 2.50 (s, 12 H, CH_3), 1.88 (t, 12 H, ethyl CH_3), −4.20 (s, 2 H, NH); anthraquinone, see Table II.

Zinc Derivative 8d. The zinc derivative **8d** was obtained by adding a solution of 0.5 g of zinc acetate in 10 mL of CH_3OH to a solution of 100 mg of **8c** in 100 mL of $CHCl_3$. The mixture was

(26) Reduction by the method described in *Org. Synth.* **1966**, *46*, 85.
(27) Schiemann, G.; Roselius, W. *Chem. Ber.* **1929**, *62*, 1805.
(28) Sulfonation by the method described in Suzuki, H.; Yamamoto, N. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 289.
(29) Dippy, J. F. J.; Page, J. E. *J. Chem. Soc.* **1938**, 357.
(30) Collins, C. J. *J. Am. Chem. Soc.* **1951**, *73*, 1038.
(31) By the method described in *Houben/Weyl, Methoden der Organischen Chemie*; Georg Thieme Verlag: Stuttgart, 1960; part V/4, p 390.
(32) Paine, J. B., III; Dolphin, D. *J. Org. Chem.* **1985**, *50*, 5598.
(33) In a similar manner as described by Fuhrhop, J.-H.; Smith, K. M. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier Scientific: Amsterdam, 1975; p 764, par. 19.2.2.9.
(34) Young, R.; Chang, C. K. *J. Am. Chem. Soc.* **1985**, *107*, 898.

refluxed for 4 h and then washed with water and evaporated; **8d** was obtained in practically quantitative yield. ^{1}H NMR ($CDCl_3$): δ 9.58 (s, 2 H, H10, H20), 8.43 (dd, 2 H, H6), 8.00 (m, 4 H, H3, H4), 7.89 (ddd, 2 H, H5), 3.57 (m, CH_2), 2.39 (s, 12 H, CH_3), 1.67 (t, 12 H, ethyl CH_3); anthraquinone, see Table II.

5,15-Bis[2-[[[4-(dimethylamino)phenyl]sulfonyl]oxy]-phenyl]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (8e). The porphyrin **8e** was prepared in the same way as **8c** from 1.22 g (4 mmol) of 2-[[[4-(dimethylamino)phenyl]sulfonyl]oxy]-benzaldehyde (dissolved in 25 mL of CH_2Cl_2 and 75 mL of CH_3OH) and 0.92 g of the dipyrrolylmethane (4 mmol). Yield: 49%. ^{1}H NMR ($CDCl_3$): δ 10.11 (s, 2 H, H10, H20), 8.01 (dd, 2 H, H6), 7.94 (dd, 2 H, H3), 7.87 (ddd, 2 H, H4), 7.68 (ddd, 2 H, H5), 3.98 (m, 8 H, CH_2), 2.52 (s, 12 H, CH_3), 1.81 (t, 12 H, ethyl CH_3), −2.93 (s, 2 H, NH); (dimethylamino)phenyl, see Table II.

Zinc Derivative 8f. The zinc derivative **8f** was obtained from **8e** in the way described above for **8d**. ^{1}H NMR ($CDCl_3$): δ 10.09 (s, 2 H, H10, H20), 8.11 (dd, 2 H, H6), 7.88 (m, 4 H, H3, H4), 7.72 (ddd, 2 H, H5), 4.01 (q, 8 H, CH_2), 2.54 (s, 12 H, CH_3), 1.81 (t, 12 H, ethyl CH_3); (dimethylamino)phenyl, see Table II.

5-[2-[(Anthraquinone-2-sulfonyl)oxy]phenyl]-15-[2-[[[4-(dimethylamino)phenyl]sulfonyl]oxy]phenyl]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (8a). The porphyrin **8a** was prepared in the same way as described for **8c**, from 1.57 g (4 mmol) of 2-[(anthraquinone-2-sulfonyl)oxy]benzaldehyde and 1.22 g (4 mmol) of 2-[[[4-(dimethylamino)-phenyl]sulfonyl]oxy]benzaldehyde in 100 mL of CH_2Cl_2/CH_3OH, 3:2, with 1.84 g (8 mmol) (3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrrolyl)methane under the catalytic influence of 0.4 g of *p*-toluenesulfonic acid. After the reaction, 1.3 g of a mixture of hexahydroporphyrins precipitated, consisting mainly of the dianthraquinone compound; by concentration of the mother liquor and subsequent addition of CH_3OH, another 2.05 g was obtained. After oxidation of this latter portion with DDQ, no precipitate was obtained. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2; filtration of the solution and addition of $CH_3OH/N(C_2H_5)_3$, 3:1, gave a precipitate of a mixture of porphyrins. Repeated chromatography over silica gel (eluens CH_2Cl_2/diethyl ether, 98:2) gave pure **8a** in low yield (5–10%). ^{1}H NMR ($CDCl_3$): δ 9.92 (s, 2 H, H10, H20), 8.41 and 8.08 (dd, 2 H, H6), 7.89 (m, 6 H, H3, H4, H5), 4.00 (m, 4 H, CH_2), 3.78 and 3.68 (m, 4 H, CH_2), 2.59 and 2.44 (s, 12 H, CH_3), 1.88 and 1.77 (t, 12 H, ethyl CH_3), −3.41 and −3.64 (s, 2 H, NH); anthraquinone and (dimethylamino)phenyl, see Table II.

Zinc Derivative 8b. The zinc derivative was prepared in the same way as described for **8d**. ^{1}H NMR ($CDCl_3$): δ 9.82 (s, 2 H, H10, H20), 8.42 and 8.02 (dd, 2 H, H6), 7.98 (m, 6 H, H3, H4, H5), 3.92 and 3.63 (m, 4 H, CH_2), 3.78 (m, 4 H, CH_2), 2.46 and 2.43 (s, 12 H, methyl), 1.78 and 1.71 (t, 12 H, ethyl CH_3); anthraquinone and (dimethylamino)phenyl, see Table II.

(3,3′-Di-*n*-butyl-4,4′-dimethyl-2,2′-dipyrrolyl)methane. This compound was prepared in the same way as described for (3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrrolyl)methane, with 3-*n*-butyl-2,4-pentanedione and diethylmalonate. Overall yield for five steps: 37%.

5-[2-[(Anthraquinone-2-sulfonyl)oxy]phenyl]-15-[2-[[[4-(dimethylamino)phenyl]sulfonyl]oxy]phenyl]-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphyrin (8g). The porphyrin **8g** was prepared in the same way as described for **8c** from 0.98 g (2.5 mmol) of 2-[(anthraquinone-2-sulfonyl)-oxy]benzaldehyde and 1.22 g (2.5 mmol) 2-[[[4-(dimethyl-amino)phenyl]sulfonyl]oxy]benzaldehyde in 90 mL of CH_2Cl_2/CH_3OH, 4:5, with 1.43 g (5 mmol) of (3,3′-di-*n*-butyl-4,4′-dimethyl-2,2′-dipyrrolyl)methane and 0.25 g of *p*-toluenesulfonic acid. As the hexahydroporphyrins did not precipitate, the solvent was evaporated, the residue was oxidized with DDQ in THF, and the solvent was again evaporated. The residue was purified by repeated chromatography over silica gel (eluens $CHCl_3$); pure **8g** was obtained in low yield (5–10%). ^{1}H NMR ($CDCl_3$): δ 9.92 (s, 2 H, H10, H20), 8.41 and 8.08 (d, 2 H, H6), 7.90 (m, 6 H, H3, H4, H5), 3.95 (m, 4 H, CH_2), 3.73 and 3.63 (m, 4 H, CH_2), 2.27 and 2.14 (m, 8 H, CH_2), 1.83 (m, 8 H, CH_2), 1.21 and 1.16 (t, 12 H, butyl CH_3), 2.58 and 2.44 (s, 12 H, CH_3); anthraquinone and (dimethylamino)phenyl, see Table II.

Preparation of Other Compounds. The following compounds were prepared according to directions given in the literature: 4-fluorobenzenesulfonyl chloride,[35] 4-*tert*-butylbenzenesulfonyl chloride,[36] 4-cyclohexylbenzenesulfonyl chloride,[36] 4-methoxybenzenesulfonyl chloride,[37] 4-(dimethylamino)-benzenesulfonyl chloride,[38] 2,4,6-trimethylbenzenesulfonyl chloride,[36] 2,4,6-triisopropylbenzenesulfonyl chloride,[39] 4-methylbenzoyl chloride,[41] and 6-bromohexanol.[42] 3-Nitrobenzenesulfonyl chloride was prepared by refluxing the sodium salt of 3-nitrobenzenesulfonic acid with $POCl_3$, removal of excess $POCl_3$ in vacuo, pouring onto ice, extraction with $CHCl_3$, and purification.[40]

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(35) Huntress, E. H.; Carten, F. H. *J. Am. Chem. Soc.* **1940**, *62*, 511.
(36) Huntress, E. H.; Autenrieth, J. S. *J. Am. Chem. Soc.* **1941**, *63*, 3446.
(37) Morgan, M. S.; Cretcher, L. H. *J. Am. Chem. Soc.* **1948**, *70*, 375.
(38) *Houben/Weyl, Methoden der Organischen Chemie*, 4th ed.; Georg Thieme Verlag: Stuttgart, 1955; part IX, p 570.
(39) Newton, A. *J. Am. Chem. Soc.* **1943**, *65*, 2439.
(40) Hodgson, H. H.; Whitehurst, J. S. *J. Chem. Soc.* **1944**, 482.
(41) McElvain, S. M.; Carney, T. P. *J. Am. Chem. Soc.* **1946**, *68*, 2592.
(42) Degering, E. F.; Boatright, L. G. *J. Am. Chem. Soc.* **1950**, *72*, 5137.

Selectivity in the Iodination of Phenol in the Presence of β-Cyclodextrin[1]

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The ratio of products formed in the iodination of phenol and *o*-chlorophenol with I_2/I^- in water solution depends on the pH and buffer concentration. At high pH and high buffer concentration the para/ortho ratio increases. This ratio also increases in the presence of β-cyclodextrin (CD). The kinetics of the iodination reaction was measured for phenol, *o*-iodophenol, *o*-chlorophenol, and *p*-iodophenol, and in all cases the observed rate decreases with the addition of CD. The decrease in the overall rate is due to consumption of the active iodinating species through complexation of I_2, I^-, and I_3^- with CD. The iodination occurs in the bound substrates as well as in the free substrates. The equilibrium constants for the association of the phenols with CD were determined, and it is possible to conclude that the reaction of the bound substrates is faster than that of the free substrates not only for the para position but also for the ortho position. The catalysis is attributed mainly to a microsolvent effect which in the case of the ortho position is counterbalanced by a steric effect.

Cyclodextrins are doughnut-shaped molecules formed by six, seven, or eight glucose units, which are produced by enzymatic degradation of starch. During the last 10 years there has been a growing interest in several aspects

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