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Conformationally Distorted Chlorins via Diimide Reduction of Nonplanar Porphyrins

Mathias O. Senge,* Werner W. Kalisch and Steffen Runge

Institut für Organische Chemie (WE02), Fachbereich Chemie, Freie Universität Berlin, Takustr. 3, D-14195 Berlin, Germany

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Abstract: Tetraphenylporphyrins with varying degree of β-ethyl substitution were reduced with diimide to the respective chlorins. Increasing nonplanarity of the parent porphyrins led to successively more instable chlorins and the most nonplanar chlorins that could be isolated, were based on a tetra-β-ethyl-tetra-*meso*-phenyl-macrocycle. Depending on the substituent pattern different isomers were formed and crystal structure analysis showed the chlorins to possess varying degrees of conformational distortion depending on the degree of peripheral substitution and the localization of the pyrrolenine ring. Highly substituted free base chlorins exhibited a larger degree of ring distortion than their parent porphyrins.

INTRODUCTION

One of the most fascinating recent developments in porphyrin chemistry has been the study of nonplanar macrocycle conformations.[1] The conformational flexibility of porphyrins has emerged as one of the most intriguing potentially regulating factors for fine-tuning the physicochemical properties of a tetrapyrrole macrocycle in vivo.[2] Tetrapyrroles with different macrocycle conformations differ with regard to their redox chemistry, photophysics and reactivity[3] and conformational divergence would account for the observation that chemically similar chromophores can catalyze quite different reactions when bound to different protein complexes. Indeed, more and more examples of nonplanar porphyrins are identified in pigment-protein crystal structures.[1b,4]

Synthetic work has concentrated on the preparation of nonplanar tetrapyrroles in which different macrocycle conformations are brought about by sterically overloading the porphyrin periphery. Examples widely studied in this context include porphyrins with bulky *meso*-substituents (e.g. **6**),[3b,5] and especially dodecasubstituted porphyrins such as octaethyltetraphenylporphyrin (**8**).[6,7] These compounds often show striking degrees of nonplanarity with displacements of individual atoms from the mean-plane often exceeding 1 Å. Despite their importance in photosynthesis, no specifically designed nonplanar chlorins have been studied in this context and most studies have so far concentrated on the preparation of nonplanar porphyrins. The only crystallographically studied examples include some mono *meso*-substituted pheophorbide derivatives related to bacteriochlorophyll c[8] and a 5,10-dimethyl substituted octaethylchlorin.[9] A notable exception are the wide ranging studies by Eschenmoser on the conformation of highly reduced corphinoids related to vitamin B_{12} and

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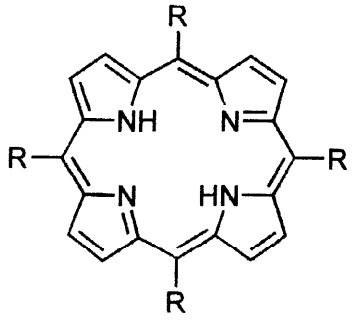
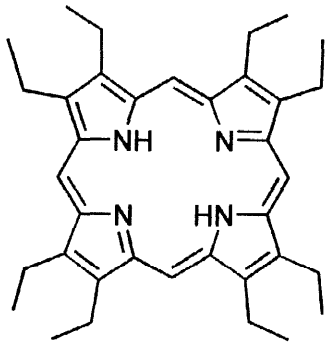
factor F_{430}.[10] However, these studies concentrated on the influence of the reduction (e.g. in hexahydroporphyrins) and did not attempt to access specific conformations via peripheral substitution. The degree of reduction in these compounds was much higher than that found in chlorophylls (dihydroporphyrins) or bacteriochlorophylls (tetrahydroporphyrins).



1 R = Ph
2 R = $CH_2CH_2CH_2CH_3$
3 R = $CH_2CH(CH_3)_2$
4 R = $CH(CH_3)_2$
5 R = $CH(CH_2CH_3)_2$
6 R = $C(CH_3)_3$



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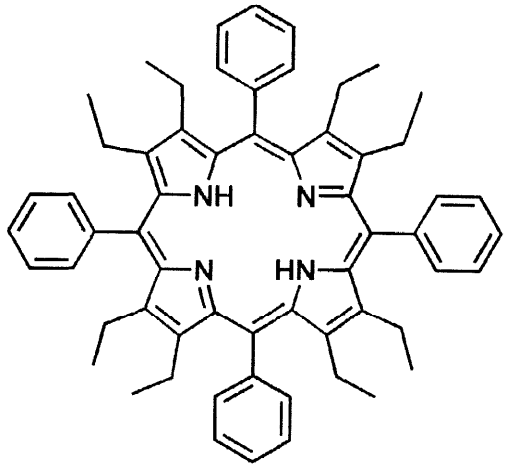

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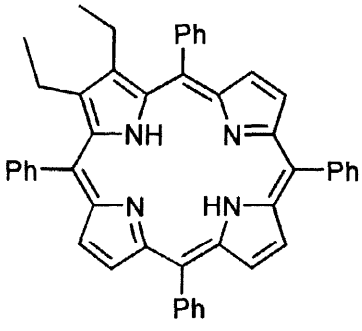
Since it has become more apparent that the conformational flexibility indeed plays a role in intact photosynthetic pigment-protein complexes,[4,11] the need arises for a comparative study of highly substituted porphyrins and chlorins. Such a study requires the preparation of chlorins closely related to the nonplanar porphyrins for which a wealth of analytical data has been accumulated. In addition, it should be noted that while tetra-pyrrole macrocycles in pigment-protein complexes have nonplanar conformations, the degree of distortion is less than that observed in the highly substituted porphyrins employed in model studies so far. Thus, appropriate objects of studies would be chlorins with an intermediate degree of nonplanarity for which porphyrin counterparts exist for comparison. We have recently described a series of porphyrins with increasing degree of nonplanarity induced by adding successively more β-ethyl groups to the basic tetraphenylporphyrin macrocycle (**1**).[12] Depending on



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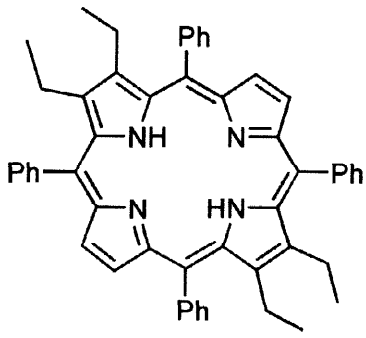

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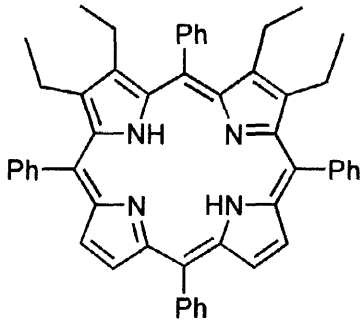

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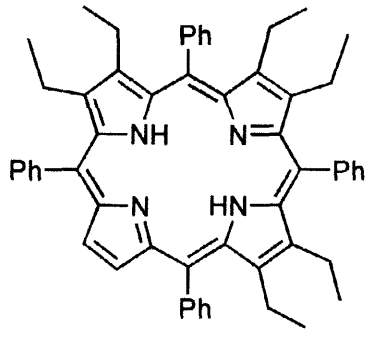

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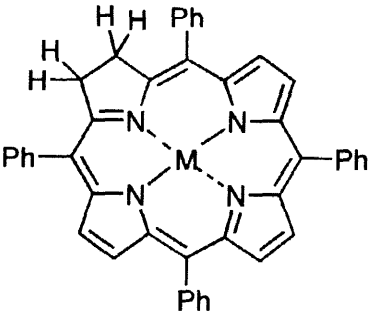
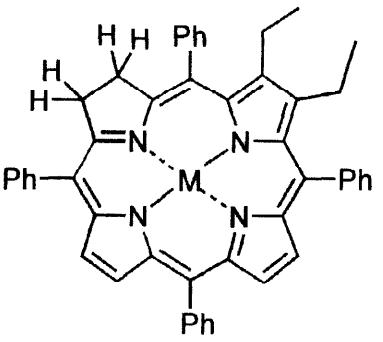
the substituent pattern these porphyrins showed increasing macrocycle distortions in the order: **1** < **9** < **10** < **11** < **12** < **8**. Synthesis of the respective chlorins would yield a series of conformationally designed chlorins with graded degree of nonplanarity. In this contribution, we describe our attempts to prepare conformationally distorted chlorins from these and other nonplanar porphyrins.

RESULTS AND DISCUSSION

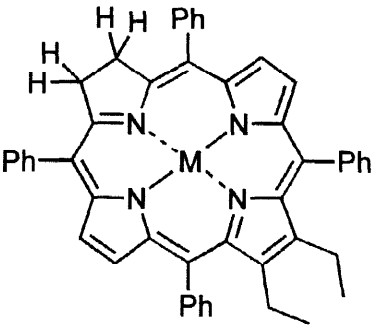
While addition reactions with the formal pyrrole double bond have been known for some time,[13] only few methods have gained practical importance for the reduction of porphyrins. Treatment with sodium in isoamylalcohol[14] gives *trans*-chlorins in low yield while OsO_4[15] has been used to prepare *cis*-2,3-dihydroxychlorins. Both reagents are able to react with β-substituted and unsubstituted pyrrole rings and would give a large number of different regioisomers upon reaction with e.g. **9**-**12**. The third possible reagent, *in situ* generated diimide,[16] gives chlorins from β-unsubstituted porphyrins in good yields. Recently, a new method has been described by Smith and coworkers, which utilizes active methylene compounds for the preparation of cyclopropachlorins and chlorins; however, this method is only applicable to β-nitro-tetraphenylporphyrins.[17] In the present study, we concentrated on using the diimide method for the preparation of the desired chlorins. This method gives the highest yields with *meso*-aryl porphyrins and shows selectivity for β-unsubstituted pyrrole rings. First, we utilized the series of porphyrins **1** < **9** < **10** < **11** < **12** < **8** for our experiments. With the exception of **8**, all porphyrins have at least one β-unsubstituted pyrrole ring and should thus be amenable for diimide reduction.



13 M = 2H
14 M = Zn(II)



15 M = 2H
17 M = Zn(II)

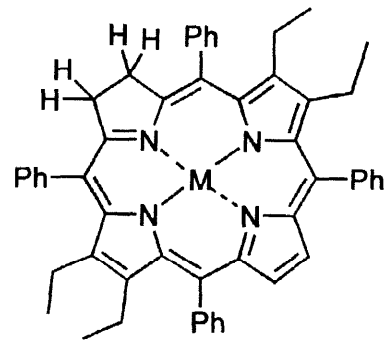


16 M = 2H
18 M = Zn(II)

Reduction of tetraphenylporphyrin (**1**) with diimide has been described in the literature and gave the respective tetraphenylchlorin **13** in 70 % yield.[16b] Treatment of **9** with the same procedure gave two isomeric chlorin fractions which were easily separated via column chromatography. The main product (46 %) was identified as the tetrapyrrole **15** in which reduction occurred at the pyrrole ring next to the diethyl-substituted pyrrole. The second, minor product (7 %) was the isomer **16**, where reduction proceeded in the pyrrole ring opposite to the diethylpyrrole unit. Both chlorins show a strong tendency towards reoxidation to the starting

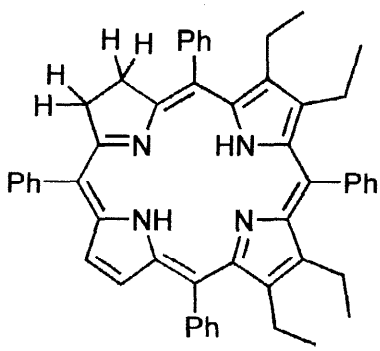
porphyrin **9**. The electronic absorption spectra of both compounds showed a typical chlorin band at 652 nm (in CH_2Cl_2) for **15** and at 664 nm for **16**, respectively. Contrary to this bathochromic shift for the long wavelength Q-band of the more symmetric chlorin **16**, the Soret band of **16** (413 nm) showed a hypsochromic shift compared to **15** (421 nm). Heating of compound **15** in vacuo at 200 °C yielded a compound with a typical chlorin UV/vis spectrum (λ_{max} = 418 and 645 nm). Unfortunately, all attempts to characterize this compound failed.

Reaction of **10** with diimide should yield only one isomer and indeed, chlorin **19** was obtained in 30 % yield as the sole product. Compound **19** was even more prone to reoxidation than **15** or **16** and could only be separated from the starting material via thin layer chromatography. Simple treatment with air reoxidized this chlorin to **10**.



19 M = 2H
20 M = Zn(II)

As reaction product for the reduction of **11**, we expected only the product **21**. Nevertheless, the situation proved to be more complicated and three different products (**21-23**) were found. The main product of the reduction was the bacteriochlorin **23**, which was formed in approx. 50 % yield. The yield is only an estimate since the product **21** is so unstable that most of it was lost during TLC purification and only 3 % could be isolated in pure form. The high, initial yield of **23** with reduction occurring at a substituted and an unsubstituted pyrrole ring is remarkable; variation of the reaction condition did not give any substantial changes in the product distribution. Thus, formation of **23** is not due to excess reducing agent but perhaps a result of the high conformational distortion present in **11**, which might aid attack at a diethyl-substituted ring. The expected product **21** was again prone to reoxidation and was obtained only in minute amounts (3.2 %). The preference for reduction of **11** at substituted pyrrole rings becomes evident when the third product is taken into account. This was identified as the chlorin **22**, where reduction again proceeded at a substituted pyrrole ring. Compound **22** was much more stable than **23** and was isolated in a yield of 19 %.



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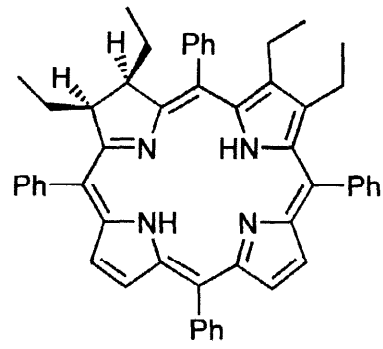

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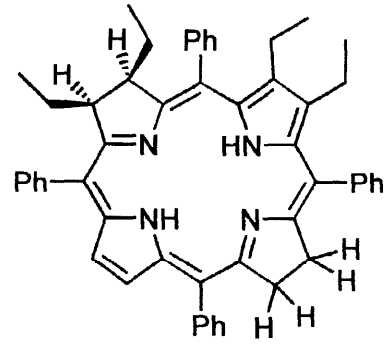


23

All attempts to convert the more nonplanar porphyrins **12** or **8** to the respective chlorins failed. The reaction products were too instable and could not be isolated. Reduction experiments with **12** gave the in situ formation a compound with absorption bands at 440 and 685 nm. However, the exact constitution of this the product is unknown. In general, the stability of the chlorins decreased significantly with increasing distortion of the macrocycle.

Table 1. Comparison of the Soret and long-wavelength absorption bands of the relevant β-ethylporphyrins and hydroporphyrins in CH_2Cl_2 with 1 % triethylamine.

Substituent pattern	no β-ethyl	2,3-diethyl	2,3,12,13-tetraethyl	2,3,7,8-tetraethyl	2,3,7,8,12,13-hexaethyl
Porphyrins	**1** 417, 647	**9** 420, 645	**10** 426, 649	**11** 433, 672	**12** 444, 685
Chlorins	**13** 416, 652	**15** 421, 652 **16** 413, 664	**19** 422, 657	**21** 431, 677 **22** 427, 663	(440, 685)
Bacteriochlorins	-	-	-	**23** 377, 755	-

The main absorption maxima of the new chlorins and the respective parent porphyrins are compiled in Table 1. A comparison of the UV/vis spectra shows that with increasing degree of β-ethyl substitution the absorption bands become progressively more shifted bathochromically. One of the recurring results of the work on nonplanar tetrapyrroles is a direct correlation of red-shifted absorption bands with the degree of macrocycle distortion.[2b] On the basis of the absorption maxima the same ordering of putative macrocycle distortion in solution (from left to right in Table 1) is observed for the chlorins as was described by us for the respective porphyrins.[12] This includes the difference between **19** and **21**, the latter showing significant bathochromic shifts compared to the former. Both have the same number of substituents, however, the substituent pattern in **21** gives rise to more steric hindrance than the one in **19**. Chlorin **22**, in which reduction involved a substituted pyrrole ring showed hypsochromically shifted absorption bands compared to **21**. Thus, when chlorins with the same reduction pattern are considered electronic absorption spectroscopy provides again a rough estimate of the relative conformation.

In order to gain unambiguous information about the conformation we tried to crystallize all relevant chlorins and prepared the zinc complexes **17** (from **15**), **18** (from **16**) and **20** (from **19**) for comparative investigation of metallo chlorins. Due to their relative instability no metal derivatives were prepared from the other chlorins. Table 2 lists the relevant structural information for the crystallized chlorins and metallo chlorins and compares selected conformational parameters with those of related porphyrins. Two compounds [**20(MeOH)** and **21**] showed crystallographically imposed disorder of the reduced pyrrole ring over all positions and only averaged overall structural data are presented for these two compounds. Depending on the crystallization conditions, the zinc complexes contained different axial ligands. Two different forms could be crystallized for **17**, one with an axial methanol [**17(MeOH)**] and one without (**17**). Compound **20** crystallized with an axial methanol [**20(MeOH)**].

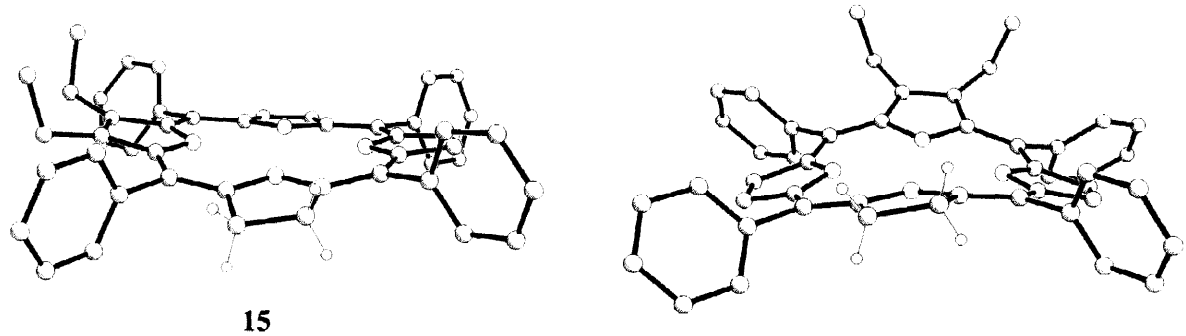
Relevant data for the description of nonplanar tetrapyrrole conformations are the Δ24 value (the average deviation of all 24 macrocycle atoms from their least-squares plane), which is a measure of the overall degree of nonplanarity, the displacements of the C_b-positions (large in saddle-distorted porphyrins) and the C_m-positions (large in ruffled porphyrins) from the 4N-plane. An inspection of these values shows that almost all chlorins exhibit a higher degree of conformational distortion than the respective parent porphyrins.

Table 2. Structural parameters for the chlorins studied by X-ray crystallography and comparison with the relevant porphyrins.

	Δ24 [a]	C_b-displacements, Å [c]							C_m-displacements, Å [c]					Pyrrole tilt angle, deg. [c]				
			Quadrant											Quadrant				
		av.	N21			N22 [b]	N23 [b]	N24 [b]	av.	C5	C10	C15	C20	av.	N21	N22	N23	N24
			av. [b]	C2	C3													
Free base porphyrins and chlorins																		
1 [18,d,e]	0.05	0.06	0.03			0.09	*	*	0.04	0.05	0.03	*	*	4.0	6.6	1.4	*	*
1 [19,f]	0.19	0.14	0.14			*	*	*	0.38	0.38	*	*	*	11.9	11.9	*	*	*
9 [12]	0.10	0.19	0.29			0.04	0.15	0.29	0.05	0.06	0.03	0.05	0.06	4.3	6.8	0.5	3.1	6.7
15	0.22	0.36	0.36	0.22	0.49	0.40	0.41	0.27	0.10	0.05	0.01	0.14	0.18	9.1	10.0	9.7	9.1	7.5
16	0.33	0.63	0.41	0.55	0.27	0.66	0.80	0.59	0.13	0.20	0.07	0.15	0.10	15.0	11.0	15.7	19.0	14.2
10 [12]	0.29	0.61	0.64			0.59	0.62	0.57	0.04	0.01	0.05	0.05	0.06	15.0	16.3	14.1	15.9	13.7
11 [12]	0.38	0.76	0.93			1.24	0.57	0.31	0.12	0.18	0.03	0.04	0.20	20.4	25.1	33.7	14.8	7.8
21 [f,g]	0.45	0.88	-	-	-	-	-	-	0.18	-	-	-	-	22.3	-	-	-	-
22	0.31	0.57	0.77	0.49	1.05	0.66	0.49	0.37	0.16	0.21	0.10	0.18	0.15	15.2	22.2	16.7	11.5	10.2
Zinc(II) porphyrins and chlorins																		
Zn1(H_2O) [20]	0.01	0	0			*	*	*	0	0	*	*	*	0	0	*	*	*
Zn1 [21,d]	0.05	0.21	0.34			0.08	*	*	0.15	0.17	0.12	*	*	6.5	9.1	3.1	*	*
14(pyr) [22,e]	0.06	0.10	0.16	0.20	0.11	0.07	0.13	0.02	0.04	0.08	0.03	0	0.05	3-6				
Zn9(MeOH) [12]	0.06	0.12	0.24			0.11	0.09	0.03	0.02	0.01	0.01	0	0.05	3.1	6.3	3.0	2.3	0.7
17	0.36	0.69	0.58	0.75	0.41	0.87	0.83	0.49	0.15	0.22	0.17	0.02	0.18	16.9	15.3	21.8	19.5	11.0
17(MeOH)	0.06	0.13	0.08	0.06	0.09	0.09	0.25	0.09	0.06	0.03	0.14	0.01	0.05	3.4	1.8	3.1	6.4	2.2
Zn10(pyr) [12]	0.28	0.54	0.35			0.61	0.68	0.50	0.20	0.33	0.14	0.19	0.15	15.0	10.5	16.9	18.4	14.0
20(MeOH) [12,g]	0.27	0.55	-	-	-	-	-	-	0.06	-	-	-	-	11.3	-	-	-	-

[a] Δ24 = average displacement of the 24 macrocycle atoms from their least-squares plane. [b] Average of two C_b-atoms. [c] Values are given relative to the least-squares plane of the four nitrogen atoms. [d] Triclinic modification. [e] Data relative to the 24 macrocycle atom plane [f] Tetragonal modification. [g] Due to crystallographically required disorder of the reduced ring only average values are given. * Generated by symmetry operation.

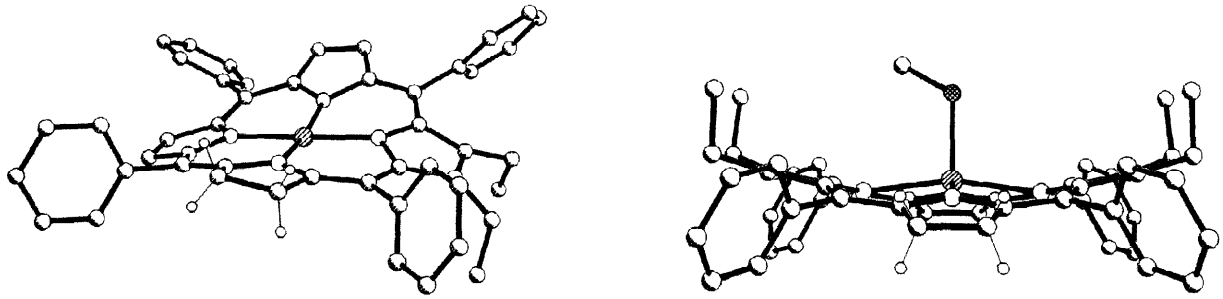
Note that according to IUPAC rules porphyrins are numbered with ethyl substituents starting in 2,3-positions while simple chlorins are always numbered with the additional hydrogen atoms in position 2 and 3.



15 16

Figure 1. View of the molecular structures of **15** and **16** in the crystal. Only selected hydrogen atoms are shown for clarity.

The structures of the two isomeric chlorins from the reduction of **9** are shown in Figure 1. The two chlorins **15** and **16** show average deviations from planarity for the 24 macrocycle atoms of 0.22 and 0.23 Å, respectively. Thus, both chlorins are more nonplanar than the respective parent porphyrin **9** (Δ24 = 0.10 Å) and positioning of the reduced unit opposite of the diethyl-substituted pyrrole in **16** leads to a more nonplanar conformation. Interestingly, the diethylchlorin **16** is already more nonplanar than the respective tetraethylporphyrin **10**. Overall, the conformation of these and other chlorins presented here can be described as a saddle conformation. This is evidenced by the significant displacements of the C_b-positions and an alternating tilt of individual pyrrole rings above and below the mean plane. Some degree of ruffling is present in all compounds as shown by the significant C_m-displacements.[23] Based on the limited number of structures presented here, there seems to be a slight tendency towards larger C_m-displacements with increasing overall macrocycle distortion in the sterically encumbered chlorins.



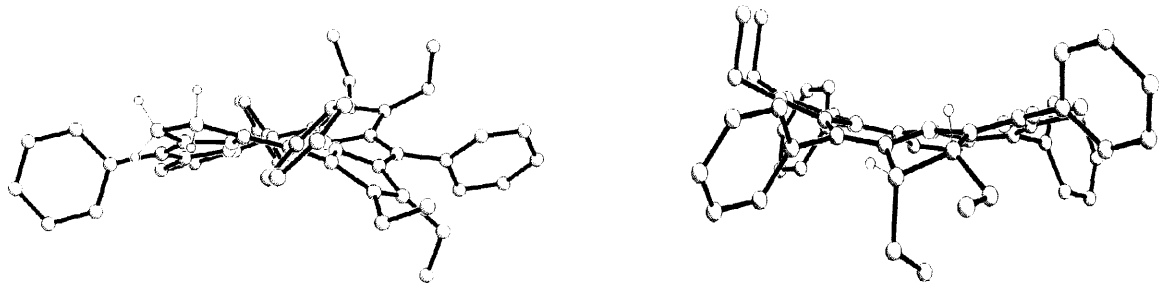
17 **20(MeOH)**

Figure 2. View of the molecular structures of **17** and **20(MeOH)** in the crystal. Only selected hydrogen atoms are shown for clarity.

The molecular structures of two zinc chlorins are shown in Figure 2. Here the differences between the parent porphyrins and chlorins are much smaller. For example, **17(MeOH)** (Δ24 = 0.06 Å) shows almost the same degree of distortion than the related porphyrin **Zn9(MeOH)** (Table 2), while **20(MeOH)** (Δ24 = 0.27 Å) even shows slightly less distortion than **Zn10(pyr)** (Δ24 = 0.28 Å). Insertion of zinc appears to counteract the conformational effect of reduction. However, a clear analysis of this phenomenon will have to await the

analysis of more metal complexes. As was noted by us for the respective porphyrins,[12] the diethyltetrapyrrole macrocycle has a considerable degree of conformational flexibility. The structure of the axially uncoordinated zinc complex **17** (shown in Figure 2, Δ24 = 0.36 Å) is much more distorted than the almost planar zinc chlorin which bears an axial methanol ligand (**17(MeOH)**, Δ24 = 0.06 Å). In fact, **17** shows larger displacements than the sterically more hindered **20(MeOH)**. Thus, the relative degree of conformational distortion in sterically encumbered chlorins can not be predicted as easily as in the respective porphyrin series. There, the degree of nonplanarity always followed the number of β-ethyl substituents, i.e. the number of peripheral points of steric hindrance.

The place of reduction significantly influences the conformation. Structural investigation of **21** and **22** (Figure 3) shows that chlorin **21** (Δ24 = 0.45 Å) is more nonplanar than its parent porphyrin **11** (Δ24 = 0.38 Å). On the other hand, compound **22** (Δ24 = 0.31 Å), where reduction involved an ethyl substituted C_b-C_b-bond, is much less distorted than chlorin **16** (Δ24 = 0.33 Å), which has only one β-ethyl-substituted pyrrole ring, or it's isomer **21**. Thus, reduction of unsubstituted pyrrole rings leads to higher conformational distortion while reduction of β-ethyl-substituted pyrrole rings leads to slight decrease in conformational distortion compared to the porphyrin. Reduction of ethyl-substituted pyrrole rings effectively moves the β-ethyl groups farther out of the plane of the molecule and thus further minimizes β-ethyl-*meso*-phenyl steric interactions.



21 **22**

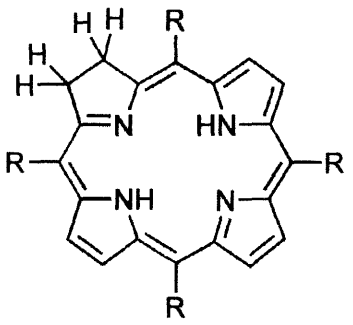
Figure 3. View of the molecular structures of **21** and **22** in the crystal. Only selected hydrogen atoms are shown for clarity.

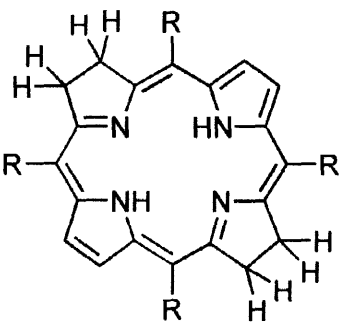
Another point of interest concerned the asymmetry of the distortion modes in nonplanar chlorins. For the parent porphyrins we had shown, that the distortion is localized to a large degree in areas of the macrocycle bearing the β-ethyl groups. This holds true to some extent for the chlorins. Again, β-ethyl substituted pyrrole rings and the reduced rings show the largest deviations from planarity. However, the differences between individual quadrants of the macrocycle have become smaller than in the respective porphyrins. Presumably, the higher conformational flexibility of chlorins allows more redistribution of steric strain throughout the tetrapyrrole system.

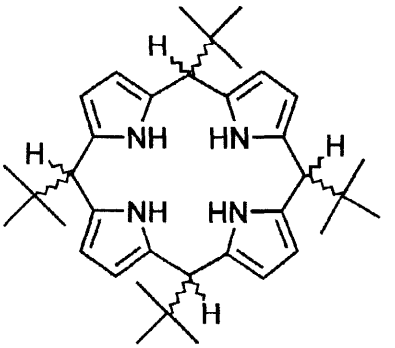
The individual structural characteristics like bond lengths and angles, especially those involving the pyrrolenine ring are comparable to those of other chlorins[9,23,24] if the known effects of saddle distortion on structural parameters are taken into account.[6b12,23] Similar results are obtained upon comparison of the coordination about the zinc centers in the metallo chlorins with literature data.[22,23,25] Other results of the crystal structure determinations agree with observations made before for nonplanar porphyrins. One example is the

tendency towards inclusion of solvent molecules in the cavities formed in the crystal by the more nonplanar chlorins. Since the overall molecular shape of the chlorins is similar to those of their parent porphyrins, similar crystal packing arrangements are observed for both.

We also investigated the reactivity of β-unsubstituted porphyrins bearing *meso*-alkyl substituents of different steric bulk. As pointed out above, highly hindered systems such as **6** exhibit severely ruffled conformations.[5] Thus, compounds **2-6** were subjected to a diimide reduction and we hoped to gain access to purely ruffled chlorins which would be interesting compounds for comparison with the nonplanar chlorins described above. Reduction of porphyrins with no or small degrees of conformational distortion (**2-5**) proceeded smoothly and in each case gave two products - the respective chlorin and bacteriochlorin (**2** --> **24** + **25**; **3** --> **26** + **27**; **4** --> **28** + **29**; **5** --> **30** + **31**). The ratio of chlorin to bacteriochlorin formed was approximately 2 : 1 in each case under the reaction conditions used. All chlorins in this series were extremely prone to reoxidation. Compounds **24** and **26** were so instable that they could only be handled for short periods immediately after the synthesis and often-decayed under argon on the way to the respective analysis. In difference to the results with tetraphenylporphyrin we never observed the formation of isobacteriochlorins upon reduction of tetra-*meso*-alkylporphyrins.







24 R = $CH_2CH_2CH_2CH_3$
26 R = $CH_2CH(CH_3)_2$
28 R = $CH(CH_3)_2$
30 R = $CH(CH_2CH_3)_2$

25 R = $CH_2CH_2CH_2CH_3$
27 R = $CH_2CH(CH_3)_2$
29 R = $CH(CH_3)_2$
31 R = $CH(CH_2CH_3)_2$

32

A different result was obtained upon reduction of the highly ruffled porphyrin **6**. Shortly after formation of diimide the reaction mixture immediately turned brown and the sole reaction product was the fully reduced porphyrinogen **32**. Due to the ruffled distortion with large displacements of the *meso*-carbons in **6**[5] any chemical attack at the *meso*-carbons is greatly facilitated and atypical reactions to nonporphyrin type products have been observed in several cases for this porphyrin.[5,26] Thus, the high reactivity of **6** makes it unlikely that a severely ruffled nonplanar chlorin can be prepared via any direct reduction attempt.

EXPERIMENTAL

General

All chemicals used were of analytical grade and purified before use by distillation. Methylene chloride was dried before use by filtration through basic aluminum oxide (grade I); methanol was dried by refluxing over magnesium turnings followed by distillation. All manipulations involving nonplanar chlorins were

performed under a purified argon atmosphere by using modified Schlenk techniques and dried and degassed solvents. Melting points are uncorrected and were measured with a Reichert Thermovar apparatus. Silica gel 60 (Merck) or basic alumina (Alfa) (usually Brockmann Grade III, i. e. deactivated with 7.5% water) were used for column chromatography. Analytical thin-layer chromatography (TLC) was carried out using Merck silica gel 60 plates or alumina 60 (neutral, fluorescence indicator F_{254}) plates (precoated sheets, 0.2 mm thick). Reactions were monitored by TLC and spectrophotometry and were carried out in dimmed light. Proton NMR spectra were recorded at a frequency of 250 MHz (AC 250) or 500 MHz (Bruker, AMX 500). All chemical shifts are given in ppm and have been converted to the δ scale and are referenced against the TMS signal as internal standard. Electronic absorption spectra were recorded with a Specord S10 (Carl Zeiss) spectrophotometer using dichloromethane as solvent. Mass spectra were obtained using a Varian MAT 711 mass spectrometer. Elemental analyses were performed with a Perkin-Elmer 240-analyzer.

Reduction of 2,3-Diethyl-5,10,15,20-tetraphenylporphyrin

A mixture of 280 mg (0.42 mmol) **9** and 2.08 g (15 mmol) potassium carbonate in 10 ml β-picoline were heated to reflux. Over the course of 6 h 620 mg (3.3 mmol) tosylhydrazine were added in small portions. After TLC control showed no further reaction the mixture was diluted with 150 ml methylene chloride and washed with water, 10 % hydrochloric acid, water, and 5 % sodium hydrogencarbonate solution. The organic solvents was evaporated in the cold and dried in high vaccum. Column chromatography on basic alumina (Brockmann grade III) with toluene/n-hexane (1:1, v/v) yielded 120 mg (0.18 mmol, 42 %) **15** as the most unpolar product, 50 mg (0.075 mmol, 18 %) unchanged **9**, and 20 mg (0.03 mmol, 7 %) **16**. Recrystallizaton under inert conditions from dichloromethane/*n*-hexane or /methanol gave purple crystals for both products.

7,8-Diethyl-5,10,15,20-tetraphenylchlorin, (**15**). M.p. >325 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = -1.53, -0.81 (each s, 2H, NH), 0.93, 0.96 (each t, ^{3}J = 7.5 Hz, 6H, CH_2CH_3), 2.57, 2.70 (each q, ^{3}J = 7.5 Hz, 4H, CH_2CH_3), 3.99 (m, 4H, CH_2CH_2), 7.55-7.69 (m, 12H, H_m, $H_{p\text{-}Ph}$), 7.82-7.86, 8.03-8.09 (each m, 8H, $H_{o\text{-}Ph}$), 8.04, 8.13, 8.29, 8.48 (each d, ^{3}J = 5 Hz, 4H, 12-, 13-, 17-, 18-H); UV/Vis (CH_2Cl_2 + 1% NEt_3): λ_{max} (lg ε) = 421 nm (5.37), 522 (4.66), 554 (4.59), 599 (4.52), 652 (4.74); UV/Vis (CH_2Cl_2 + 1% TFA): λ_{max} (lg ε) = 443 nm (5.20), 548 (3.68), 596 (3.93), 654 (4.50); MS (80 eV); m/z (%): 672 (100) [M^+], 336 (19) [M^{2+}]; HRMS [$C_{48}H_{40}N_4$]: calcd. 672.3253, found 672.3251; [$C_{48}H_{40}N_4$•0.5 CH_3OH, 688.89 g mol^{-1}]: anal. calcd. C 84.56, H 6.15, N 8.13, found. C 84.57, H 5.82, N 7.87.

12,13-Diethyl-5,10,15,20-tetraphenylchlorin, (**16**). M.p. 313 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = -1.48 (s, 2H, NH), 0.79 (t, ^{3}J = 7.5 Hz, 6H, CH_2CH_3), 2.44 (q, ^{3}J = 7.5 Hz, 4H, CH_2CH_3), 4.06 (s, 4H, CH_2CH_2), 7.62-7.70 (m, 12H, H_m, $H_{p\text{-}Ph}$), 7.84-7.86, 8.13-8.15 (each m, 8H, $H_{o\text{-}Ph}$), 8.05, 8.38 (each d, ^{3}J = 5 Hz, 4H, 7-, 8-, 17-, 18-H); UV/Vis (CH_2Cl_2 + 1% NEt_3): λ_{max} (lg ε) = 373sh nm (4.62), 413 (5.20), 517 (4.18), 546sh (3.96), 610 (3.68) 664 (4.50); UV/Vis (CH_2Cl_2 + 1% TFA): λ_{max} (lg ε) = 448 nm (5.31), 549 (4.00), 593 (4.20), 649 (4.53); MS (80 eV); m/z (%): 672 (100) [M^+], 336 (13) [M^{2+}]; HRMS [$C_{48}H_{40}N_4$]: calcd. 672.3253, found. 672.3257; [$C_{48}H_{40}N_4$, 672.87 g mol^{-1}]: anal. calcd. C 85.68, H 5.99, N 8.33, found C 85.68, H 6.00, N 8.21.

Reduction of 2,3,12,13-Tetraethyl-5,10,15,20-tetraphenylporphyrin

A mixture of 50 mg (0.07 mmol) **10**, 80 mg (0.4 mmol) tosylhydrazine and 140 mg (1.03 mmol) potassium carbonate in 5 ml dry β-picoline was heated to reflux for 2.5 h. After cooling to room temperature the solution was taken up in dichloromethane and washed repeatedly with 5 % aq. hydrochloric acid and water. The organic phase was dried over baisc alumina and concentrated in the cold. The product was isolated via preparative thin layer chromatography on alumina plates eluting with neat toluene. The fastest running, green

fraction was scraped off, extracted with dichloromethane and recrystallized under dry conditions from CH_2Cl_2/*n*-hexane yielding 15 mg (0.12 mmol, 30 %) blue **19**. A second, more polar fraction contained 20 mg (0.16 mmol, 40 %) starting material.

7,8,17,18-Tetraethyl-5,10,15,20-tetraphenylchlorin, (**19**). M.p. 325 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (s, 2H, NH), 0.80, 0.81 (each t, ^{3}J = 7.5 Hz, 12H, CH_2CH_3), 2.48, 2.61 (each q, ^{3}J = 7.5 Hz, 8H, CH_2CH_3), 3.77 (s, 4H, CH_2CH_2), 7.57-7.68 (m, 12H, H_m, $H_{p\text{-}Ph}$), 7.85-7.88, 8.05 (each m, 8H, $H_{o\text{-}Ph}$), 7.90 (s, 2H, 12-, 13-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 17.34, 19.05, 19.45, 110.21, 121.48, 126.39, 127.44, 127.65, 127.99, 130.08, 130.66, 132.70, 133.67, 137.07, 137.28, 142.19, 142.35, 142.99, 152.75, 167.11; UV/Vis (CH_2Cl_2 + 1% NEt_3): λ_{max} (lg ε) = 426 nm (5.25), 527 (4.09), 565 (3.86), 604 (3.78), 657 (4.43); UV/Vis (CH_2Cl_2 + 1% TFA): λ_{max} (lg ε) = 450 nm (5.23), 667 (4.62); MS (80 eV); m/z (%): 728 (100) [M^+], 700 (29) [$M^+ - C_2H_4$], 364 (34) [M^{2+}]; HRMS [$C_{52}H_{48}N_4$]: calcd. 728.3879, found 728.3889; [$C_{52}H_{48}N_4$•0.75CH_2Cl_2, 792.68 g mol^{-1}]: anal. calcd. C 79.73, H 6.29, N 7.07, found. C 79.96, H 6.37, N 6.84.

Reduction of 2,3,7,8-Tetraethyl-5,10,15,20-tetraphenylporphyrin

Compound **11** (310 mg, 0.43 mmol), 1.2 g (8.7 mmol) potassium carbonate and 480 mg (2.6 mmol) tosylhydrazine were dissolved in 10 ml β-picoline and heated to reflux. After 2 and 4 h, respectively another 75 mg were added and heating under reflux was continued for a total of 6 h. The reaction mixture was taken up in dichloromethane and washed once with water, once with 10 % aq. HCl, again with water and finally with 5 % aq. sodium hydrogen carbonate solution. After removal of the solvent *in vacuo* in the cold the mixture was first chromatographed on a basic aluminium oxide column (Brockmann grade III). Elution with neat toluene yielded two fractions which were each subjected to another chromatographic purification step. The more unpolar fraction could be separated by column chromatography on basic alumina. Elution with CH_2Cl_2/*n*-hexane (1:1, v/v) gave the stable **21** (10 mg, 0.014 mmol, 3.2 %) and the instable bacteriochlorin **23** (10 mg, 0.013 mmol, 3 %). TLC of the crude fraction prior to column chromatography showed the content of the bacteriochlorin to be about 50 %. Thus, most of the bacteriochlorin decayed during the chromatographic work up. The second, polar fraction from the first column chromatographic step contained starting material (50 mg, 0.07 mmol, 16 %) and **22** (60 mg, 0.08 mmol, 19 %) which were separated via preparative thin layer chromatography on neutral alumina oxide plates using toluene as eluant. Compound **22** shows a tendency towards oxidation to **11**. All products were recrystallized under inert conditions from CH_2Cl_2/*n*-hexane or CH_2Cl_2/CH_3OH.

2,3,7,8-Tetraethyl-5,10,15,20-tetraphenylchlorin, (**21**). Purple crystals, M.p. 273 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = -1.22 (s, 1H, NH), -0.77 (t, ^{3}J = 7.5 Hz, 3H, CH_2CH_3), -0.62 (s, 1H, NH), 0.73, 0.78, 0.80 (each t, ^{3}J = 7.5 Hz, 9H, CH_2CH_3), 0.87-0.97 (m, 2H, $CHCH_2CH_3$), 1.39-1.51, 1.54-1.63 (each m, 2H, $CHCH_2CH_3$), 1.99, 2.41 (each m, 2 H, CCH_2CH_3), 2.82 (m, 2H, CCH_2CH_3), 4.84 (m, 2H, $CHCH_2CH_3$), 7.56-7.73, 8.05-8.16 (each m, 20H, H_{Ph}), 8.08, 8.20, 8.23, 8.36 (each d, ^{3}J = 5 Hz, 4H, 12-, 13-, 17-, 18-H); UV/Vis (CH_2Cl_2 + 1% NEt_3): λ_{max} (lg ε) = 427 nm (5.28), 531 (4.11), 565 (4.04), 609 (3.88), 663 (4.39); UV/Vis (CH_2Cl_2 + 1% TFA): λ_{max} (lg ε) = 450 nm (5.12), 665 (4.43); MS (80 eV); m/z (%): 728 (100) [M^+], 364 (14) [M^{2+}]; HRMS [$C_{52}H_{48}N_4$]: calcd. 728.3879, found 728.3871; [$C_{52}H_{48}N_4$•0.5CH_3OH, 745 g mol^{-1}]: anal. calcd. C 84.64, H 6.76, N 7.52, found. C 84.19, H 6.62, N 7.12.

7,8,12,13-Tetraethyl-5,10,15,20-tetraphenylchlorin, (**22**). Purple crystals, M.p. 322 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = -1.20, -0.49 (each s, 2H, NH), 0.39, 0.41, 0.55, 0.69 (each t, ^{3}J = 7.5 Hz, 12H, CH_2CH_3), 2.01, 2.25, 2.37, 2.41 (each q, ^{3}J = 7.5 Hz, 8H, CH_2CH_3), 3.83 (m, 4H, CH_2CH_2), 7.53-7.74, 7.83-7.93, 8.12,-8.24 (each m, 20H, H_{Ph}), 7.87, 8.29 (each d, ^{3}J = 5 Hz, 2H, 17-, 18-H); UV/Vis (CH_2Cl_2 + 1% NEt_3): λ_{max} (lg ε)

= 431 nm (5.19), 534 (4.09), 570 (3.98), 621 (3.81), 677 (4.41); UV/Vis (CH_2Cl_2 + 1% TFA): λ_{max} (lg ε) = 458 nm (5.21), 662 (4.44); MS (80 eV); m/z (%): 728 (100) [M^+], 364 (18) [M^{2+}]; HRMS [$C_{52}H_{48}N_4$]: calcd. 728.3879, found 728.3868; [$C_{52}H_{48}N_4$•0.5CH_3OH, 745 g mol^{-1}]: anal. calcd. C 84.64, H 6.76, N 7.52, found. C 84.94, H 6.78, N 7.47.

2,3,7,8-Tetraethyl-5,10,15,20-tetraphenylbacteriochlorin, (**23**). Red-gray powder, M.p. 235 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = -1.32, -1.06 (each s, 2H, NH), -0.59, 0.71, 0.76 (each t, ^{3}J = 7.5 Hz, 12H, CH_2CH_3), 0.88, 1.41, (each m, 4H, CH_2), 1.91, 2.09 (each m, 2H, CH_2CH_3), 2.68 (m, 2H, CH_2CH_3), 3.97 (s, 4H, CH_2CH_2), 4.29, 4.79 (each m, 2H, $CHCH_2CH_3$, 2-, 3-H), 7.42-8.02 (each m, 22H, H_{ph}, 17-, 18-H); UV/Vis (CH_2Cl_2 + 1% NEt_3): λ_{max} (lg ε) = 368sh nm (4.78), 377 (4.82), 418 (4.31), 522 (4.23), 538sh (4.10), 742 (4.52), 755sh (4.43); UV/Vis (CH_2Cl_2 + 1% TFA): λ_{max} (lg ε) = 396 nm (4.68), 433sh (4.42), 650 (4.12), 812 (4.38); MS (80 eV); m/z (%): 730 (100) [M^+], 365 (15) [M^{2+}]; HRMS [$C_{52}H_{48}N_4$]: calcd. 730.4036, found 730.4036.

Metallation

Zinc(II) insertion was performed by preparation of a saturated solution of the chlorin in THF (e.g. 10 mg chlorin), followed by addition of 80 mg potassium carbonate and 40 mg zinc(II) bromide. The mixture was stirred for 30-60 min and the solvent removed *in vacuo*. The residue was taken up in a small amout of dichloromethane and filtered through potassium carbonate followed recrystallization from CH_2Cl_2/n-hexane. Use of a conventional extraction step with water for purification of the crude product often led to demetallation and should be avoided.

(7,8-Diethyl-5,10,15,20-tetraphenylchlorinato)zinc(II), (**17**). M.p. >325 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.93, 0.94 (t, ^{3}J = 7.5 Hz, 6H, CH_2CH_3), 2.41, 2.54 (each q, ^{3}J = 7.5 Hz, 4H, CH_2CH_3), 3.94 (s, 4H, CH_2CH_2), 7.54-7.67 (m, 12H, H_m, $H_{p\text{-}Ph}$), 7.76-7.80, 7.97-8.01 (each m, 8H, $H_{o\text{-}Ph}$), 7.89, 7.97, 8.17, 8.33 (each d, ^{3}J = 5 Hz, 4H, 12-, 13-, 17-, 18-H); UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 419 nm (5.38), 578 (4.00), 620 (4.55); MS (80 eV); m/z (%): 734 (100) [M^+], 367 (9) [M^{2+}]; HRMS [$C_{48}H_{38}N_4Zn$]: calcd. 734.2388, found 734.240; [$C_{48}H_{38}N_4Zn$•0.25CH_3OH, 744.25 g mol^{-1}]: anal. calcd. C 77.87, H 5.28, N 7.53, found. C 77.88, H 5.20, N 6.93.

(12,13-Diethyl-5,10,15,20-tetraphenylchlorinato)zinc(II), (**18**). M.p. >320 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.74 (t, ^{3}J = 7.5 Hz, 6H, CH_2CH_3), 2.36 (q, ^{3}J = 7.5 Hz, 4H, CH_2CH_3), 3.71 (s, 4H, CH_2CH_2), 7.51-7.63 (m, 12H, H_m, $H_{p\text{-}Ph}$), 7.01-7.14, 7.73-7.76, (each m, 8H, $H_{o\text{-}Ph}$), 7.25, 7.94 (each d, ^{3}J = 5 Hz, 4H, 7-, 8-, 17-, 18-H); UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 450 (5.24), 579 (3.89), 621 (4.44); MS (80 eV); m/z (%): 734 (100) [M^+], 690 (12) [M^+ - C_3H_8], 367 (10) [M^{2+}]; HRMS [$C_{48}H_{38}N_4Zn$]: calcd. 734.2388, found 734.2368.

(7,8,17,18-Tetraethyl-5,10,15,20-tetraphenylchlorinato)zinc(II), (**20**). M.p. >325 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.79, 0.81 (each t, ^{3}J = 7.5 Hz, 12H, CH_2CH_3), 2.28, 2.41 (each q, ^{3}J = 7.5 Hz, 8H, CH_2CH_3), 3.73 (s, 4H, CH_2CH_2), 7.33-7.64 (m, 14H, H_m, $H_{p\text{-}Ph}$, 12-, 13-H), 7.89-7.91 (each m, 8H, $H_{o\text{-}Ph}$), 7.25, 7.94 (each d, ^{3}J = 5 Hz, 4H, 7-, 8-, 17-, 18-H); UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 422 nm (5.32), 621 (4.43); MS (80 eV); HRMS [$C_{48}H_{38}N_4Zn$]: calcd. 734.2388, found 734.2391.

Reduction of 5,10,15,20-Tetraalkylporphyrins

A mixture of 0.47 mmol (approx. 0.25 g) of the respective porphyrin and 11.0 g anhydrous potassium carbonate in 40 ml pyridine was heated to reflux. Then a solution of 8.5 g (45.6 mmol) of tosylhydrazine in 40

ml pyridine was added. The mixture was heated under reflux for 2 h (15 min for compound **6**), cooled to room temperature and neutralized with aq. HCl (10%). The mixture was diluted with 200 ml dichloromethane and was washed neutral with water. The organic layer was dried over Na_2SO_4 and evaporated to dryness. The residue was purified via column chromatography on silica gel first using CH_2Cl_2/n-hexane to elute the bacteriochlorin and then using CH_2Cl_2 for the chlorin. Final purification of the bacteriochlorins necessitated a recrystallization step to remove coeluting *p*-toluenesulfonic acid.

5,10,15,20-Tetra(n-butyl)chlorin, (**24**). Yield 100 mg (0.19 mmol, 40 %) red-purple crystals from CH_2Cl_2/n-hexane; M.p. > 300 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = -1.55 (s, 2H, NH), 1.07-1.15 (t, J = 7.3 Hz, 12H, $CH_2CH_2CH_2CH_3$), 1.67-1.80 (sext, J = 7.3 Hz, 8H, $CH_2CH_2CH_2CH_3$), 2.22-2.24 (quint, J = 7.3 Hz, 4H, $CH_2CH_2CH_2CH_3$), 2.35-2.50 (quint, J = 7.3 Hz, 4H, $CH_2CH_2CH_2CH_3$), 4.05-4.12 (t, J = 7.3 Hz, 4H, $CH_2CH_2CH_2CH_3$), 4.48 (s, 4H, CH_2CH_2), 4.65-4.75 (t, J = 7.3 Hz, 4H, $CH_2CH_2CH_2CH_3$), 8.90-8.95 (d, J = 4.9 Hz, 2H, $H_{ß\text{-pyrrol}}$), 9.15 (s, 2H, $H_{ß\text{-pyrrol}}$), 9.25 - 9.27 (d, J = 4.9 Hz, $H_{pyrrole}$); UV/vis (CH_2Cl_2): λ_{max} (rel. ε) = 372 nm (0.36), 410 (0.47), 434 (1.0), 530 (0.11), 555 (0.11), 600 (0.05), 654 (0.23); MS (40 eV); m/z (%): 536 (47) [M^+], 493 (28) [M^+ - C_3H_7].

5,10,15,20-Tetra(n-butyl)bacteriochlorin, (**25**). Yield: 60 mg (0.11 mmol, 24 %) green crystals from CH_2Cl_2/n-pentane; M.p. 212-215 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = - 1.53 (s, 2H, NH), 1.08-1.14 (t, J = 7.3 Hz, 12H, $CH_2CH_2CH_2CH_3$), 1.66-1.80 (sext, J = 7.3 Hz, 8H, $CH_2CH_2CH_2CH_3$), 2.03-2.15 (quin, J = 7.6 Hz, 8H, $CH_2CH_2CH_2CH_3$), 3.93-3.99 (t, J = 8.7 Hz, 8H $CH_2CH_2CH_2CH_3$), 4.30 (br s, 8H, CH_2CH_2), 8.71 (br s, 4H, $H_{pyrrole}$); UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 369 nm (4.99), 534 (4.58), 731 (4.84); MS (40 eV); *m/z* (%): 538 (100) [M^+], 495 (13) [M^+ - C_3H_7], 452 (3) [M^+ - 2x C_3H_7], 426 (4) [M^+ - 2x C_3H_7 - C_2H_2].

5,10,15,20-Tetra(2-methyl-propyl)chlorin, (**26**). Yield: 100 mg (0.19 mmol, 40 %) red-purple crystals from CH_2Cl_2/n-pentane; M.p. > 300 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = -1.68 (s, 2H, NH), 1.07-1.18 (m, 24H, $CH_2CH(CH_3)2$), 2.35-2.74 (m, 4H, $CH_2CH(CH_3)2$), 4.14-4.53 (m, 8H, $CH_2CH(CH_3)2$), 4.61-4.63 (m, 4H, CH_2CH_2), 8.99-9.01 (d, J = 5.1 Hz, 2H, $H_{pyrrole}$), 9.15-9.20 (q, J = 4.4 Hz, 2H, $H_{pyrrole}$), 9.26-9.27 (d, J = 2.5 Hz, 2H, $H_{pyrrole}$). UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 372 nm (4.45), 410 (5.34), 431 (5.27), 529 (3.91), 556 (4.13), 593 (3.50), 650 (4.31).

5,10,15,20-Tetra(2-methyl-propyl)bacteriochlorin, (**27**). Yield: 60 mg (0.11 mmol, 24 %) green crystals from CH_2Cl_2/n-pentane; M.p. 240-245 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = -1.21 (s, 2H, NH), 1.02-1.05 (d, J = 6.5 Hz, 24 H, $CH_2CH(CH_3)_2$), 2.31-2.40 (m, 4H, $CH_2CH(CH_3)_2$), 3.94-3.96 (d, J = 7.0 Hz, 8H, $CH_2CH(CH_3)_2$), 4.36 (s, 8H, CH_2CH_2), 8.68 (s, 4H, $H_{pyrrole}$); UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 370 nm (5.34), 535 (4.75), 736 (4.83); MS (40 eV); m/z (%): 538 (100) [M^+], 495 (30) [M^+ - C_3H_7], 452 (13) [M^+ - 2x C_3H_7]; HRMS [$C_{36}H_{50}N_4$]: calcd. 538.4036, found 538.4042.

5,10,15,20-Tetra(iso-propyl)chlorin, (**28**). Yield: 150 mg (0.31 mmol, 60 %) red-purple crystals from CH_2Cl_2/n-pentane; M.p. > 300 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = -0.32 (s, 2H, NH), 1.89-1.92 (d, 12H, $CH(CH_3)_2$), 2.13-2.15 (d, 12H, $CH(CH_3)_2$), 4.08-4.17 (quint, J = 7.4 Hz, 2H, $CH(CH_3)_2$), 4.95-5.06 (quint, J = 7.4 Hz, 2H, $CH(CH_3)_2$), 4.26 (s, 4H, CH_2CH_2), 8.83-8.85 (d, J = 5.7 Hz, 2H, $H_{pyrrole}$), 9.02 (s, 2H, $H_{pyrrole}$), 9.08-9.10 (d, J = 5.7 Hz, 2H, $H_{pyrrole}$); UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 378 nm (4.33), 419 (5.02), 532 (3.84), 562 (3.81), 606 (3.54), 661 (4.08); MS (40 eV); m/z (%): 480 (76) [M^+], 465 (66) [M^+ -CH_3], 437 (8) [M^+ -C_3H_7]; HRMS [$C_{32}H_{40}N_4$]: calcd. 480.3253, found 480.3264.

5,10,15,20-Tetra(iso-propyl)bacteriochlorin, (**29**). Yield: 70 mg (0.14 mmol, 28 %) green crystals from CH_2Cl_2/n-pentane; M.p. 250-253 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.08 (s, 2H, NH), 1.29 (m, 24H, $CH(CH_3)_2$), 4.01-4.11 (m, 4H, $CH(CH_3)_2$), 4.27 (s, 8H, CH_2CH_2), 8.70 (s, 4H, $H_{pyrrole}$); UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 358 nm (4.56), 369 (4.68), 377 (4.68), 541 (3.95), 746 (4.29); MS (40 eV); m/z (%): 482 (100) [M^+], 467 (22) [M^+ - CH_3], 439 (8) [M^+ - C_3H_7]; HRMS [$C_{32}H_{42}N_4$]: calcd. 482.3410, found 482.3666.

5,10,15,20-Tetra(1-ethyl-propyl)chlorin, (**30**). Yield: 130 mg (0.22 mmol, 52 %) red-purple crystals from CH_2Cl_2/n-pentane; M.p. > 300 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = -0.58 (s, 2H, NH), 0.93-0.99 (t, J = 7.4 Hz, 12H, $CH(CH_2CH_3)_2$), 1.01-1.07 (t, J = 7.4 Hz, 12H, $CH(CH_2CH_3)_2$), 2.47-2.91 (m, 16H, $CH(CH_2CH_3)_2$), 3.91 (br s, 2H, $CH(CH_2CH_3)_2$), 4.45 (s, 4H, CH_2CH_2), 4.59-4.65 (quin, J = 8.2 Hz, 2H, $CH(CH_2CH_3)_2$), 8.98-9.00 (d, J = 4.9 Hz, 2H, $H_{pyrrole}$), 9.19 (s, 2H, $H_{pyrrole}$), 9.25-9.27 (d, J = 4.9 Hz, 2H, $H_{pyrrole}$); UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 415 nm (5.35), 436 (5.19), 534 (4.33), 561 (4.33), 603 (4.13), 659 (4.54); MS (40 eV); m/z (%): 592 (100) [M^+], 563 (49) [M^+ - C_2H_5], 536 (6) [M^+ - 2x C_2H_4], 505 (6) [M^+ - 3x C_2H_5]; HRMS [$C_{40}H_{56}N_4$]: calcd. 592.4505, found 592.4515.

5,10,15,20-Tetra(1-ethyl-propyl)bacteriochlorin, (**31**). Yield: 40 mg (0.067 mmol, 16 %) green crystals from CH_2Cl_2/n-pentane; M.p. 263-270 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = -0.26 (s, 2H, NH), 0.85-0.91 (t, J = 7.4 Hz, 24H, $CH(CH_2CH_3)_2$), 2.33-2.53 (m, 16H, $CH(CH_2CH_3)_2$), 3.67 (br s, 4H, $CH(CH_2CH_3)_2$), 4.18 (s, 8H, CH_2CH_2), 8.66 (s, 4H, $H_{pyrrole}$); UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 360 nm (4.91), 371 (5.02), 377 (4.67), 543 (4.72), 749 (4.43); - MS (40 eV); m/z (%): 594 (100) [M^+], 565 (17) [M^+ -C_2H_5], 523 (73) [M^+ -C_5H_{11}]; HRMS [$C_{40}H_{58}N_4$]: calcd. 594.4661, found 594.4678.

5,10,15,20-Tetra(tert-butyl)porphyrinogen, (**32**). Yield: 40 mg (0.074 mmol, 16 %) yellow crystals from CH_2Cl_2/n-pentane; M.p. 233-235 °C; - ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.99 (s, 36H, $C(CH_3)_3$), 3.50 (s, 4H, C_m-H), 5.90-5.91 (d, J = 2.5 Hz, 8H, $H_{pyrrole}$), 7.40 (s, 4H, NH); ^{13}C NMR ($CDCl_3$): δ = 28.6 ($C(CH_3)_3$), 34.7 ($C(CH_3)_3$), 49.6 (C_m), 105.5 (C_b), 129.0 (C_a); UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 231 nm (4.66); MS (40 eV); m/z (%): 540 (1) [M^+], 525 (3) [M^+ -CH_3],483 (100) [M^+ -C_4H_9]; HRMS [$C_{36}H_{52}N_4$]: calcd. 540.4192, found 540.4183.

Crystallography[27]

X-ray quality crystals were grown by slow diffusion of methanol or n-hexane into a concentrated solution of the chlorins in dichloromethane. The crystals were removed from solution and covered with a layer of Paraton N®. A suitable single crystal was selected, attached to a glass fiber and immediately placed into the low-temperature nitrogen stream as described by Hope.[28] Data sets for compounds **15** and **17** were collected with the use of a Siemens P4 diffractometer with an attached Siemens rotating anode (Ni filtered Cu-K_α radiation, λ = 1.541 78 Å) and equipped with a locally modified LT2 low-temperature device. The data set for **15(MeOH)** was collected on a Siemens R3m/V diffractometer (Mo-K_α radiation, λ = 0.710 69 Å) equipped with a graphite monochromator. Cell parameters were determined from 20-25 automatically centered reflections in the range 20° < 2 θ < 25°. Intensity data for **16**, **20**, **21**, and **22** were collected with a Syntex $P2_1$ diffractometer (graphite monochromatted Cu-K_α radiation, λ = 1.541 78 Å) equipped with a low-temperature device. Cell parameters for all data collections performed with Cu-K_α radiation were determined from 20-25 automatically centered reflections in the range 40° < 2θ < 60°. During all data collections two standard reflections were measured every 198 reflections and showed in all cases only statistical variation of the intensities (< 2 %). The intensities were corrected for Lorentz and polarization effects. In all structure refinements an absorption correction was applied using the program *XABS2*,[29] while extinction effects were disregarded.

The free base structures were solved by Direct Methods while structures of the zinc(II) complexes were solved via Patterson synthesis, followed by structure expansion using the *SHELXTL PLUS* program system installed on a PC clone.[30] The structures of **15**, **16**, and **21** were solved with the program *SHELXS86*[31a] and refined with the program *XL-93*.[31b] The other structures were solved with newer versions of Sheldrick's programs.[32] Missing atoms and/or solvent molecules were located in subsequent difference Fourier maps. Refinements were carried out by full-matrix least-squares on $|F^2|$ using the same program system. Hydrogen atoms were included at calculated positions using a riding model with C-H = 0.96 Å and N-H = 0.9 Å. No hydrogen atoms were included for disordered positions, Unless otherwise stated, all nonhydrogen atoms were refined with anisotropic thermal parameters.

Data for **15**. $C_{48}H_{40}N_4$, irregular shaped green crystals from CH_2Cl_2/n-hexane, crystal size 0.1 x 0.1 x 0.08 mm, T = 126K, FW = 672.84, triclinic, P $\bar{1}$, a = 10.933(4), b = 12.946(5), c = 13.496(5) Å, α = 96.20(3), β = 90.24(3), γ = 109.72(3)°, V = 1786.1(11) $Å^{-3}$; Z = 2, μ = 0.564 mm^{-1}, D_{calcd} = 1.251 $g.cm^{-3}$, 4714 independent reflections, 3030 reflections with F > 4.0σ(F), 356 parameters, θ_{max} = 56.43°, R1 [F > 4.0σ(F)] = 0.0845, wR2 (all data) = 0.2418.

Data for **16.** $C_{48}H_{40}N_4$, brown parallelepipeds CH_2Cl_2/CH_3OH, crystal size 0.52 x 0.35 x 0.33 mm, FW = 672.84, T = 126K, monoclinic, $P2_1/n$, a = 17.064(3), b = 10.858(2), c = 21.362(4) Å, β = 113.11(3)°, V = 3640.5(13) $Å^{-3}$; Z = 4, μ = 0.553 mm^{-1}, D_{calcd} = 1.228 $g.cm^{-3}$, 4917 independent reflections, 4144 reflections with F > 4.0σ(F), 471 parameters, θ_{max} = 57.14°, R1 [F > 4.0σ(F)] = 0.0507, wR2 (all data) = 0.1373.

Data for **17**. $C_{48}H_{38}N_4Zn \bullet 0.5CH_2Cl_2$, red parallelepipeds from CH_2Cl_2/n-hexane, crystal size 0.6 x 0.12 x 0.12 mm, FW = 778.66, T = 129K, triclinic, P $\bar{1}$, a = 10.813(6), b = 12.436(8), c = 16.119(10) Å, α = 103.99(5), β = 98.64(5), γ = 101.26(5)°, V = 2018(2) $Å^{-3}$; Z = 2, μ = 1.745 mm^{-1}, D_{calcd} = 1.282 $g.cm^{-3}$, 5327 independent reflections, 3905 reflections with F > 4.0σ(F), 497 parameters, θ_{max} = 56.35°, R1 [F > 4.0σ(F)] = 0.1173, wR2 (all data) = 0.3893. The structure contained a heavily disordered methylene chloride of solvation which was refined with 50 % occupancy and isotropic thermal parameters. Some residual electron density (1.461 e. $Å^{-3}$) was located 1.3 Å distant from the central Zn atom.

Data for **17(MeOH)**. $C_{49}H_{42}N_4OZn$, blue parallelepipeds from CH_2Cl_2/CH_3OH, crystal size 0.80 x 0.58 x 0.28 mm, FW = 768.24, T = 298K, triclinic, P $\bar{1}$, a = 12.188(7), b = 13.631(9), c = 13.714(8) Å, α = 84.00(5), β = 72.47(5), γ = 64.74(4)°, V = 1964(2) $Å^{-3}$; Z = 2, μ = 0.668 mm^{-1}, D_{calcd} = 1.299 $g.cm^{-3}$, 9019 independent reflections, 7236 reflections with F > 4.0σ(F), 497 parameters, θ_{max} = 27.50°, R1 [F > 4.0σ(F)] = 0.0475, wR2 (all data) = 0.1316.

Data for **20(MeOH)**. $C_{53}H_{50}N_4OZn \bullet CH_2Cl_2 \bullet CH_3OH$, irregular shaped blue crystals from CH_2Cl_2/CH_3OH, crystal size 0.8 x 0.8 x 0.7 mm, FW = 905.86, T = 126K, tetragonal, $P4_2/ncm$, a = 19.153(4), b = 19.153(4), c = 13.019(6) Å, V = 4776(3) $Å^{-3}$; Z = 4, μ = 1.576 mm^{-1}, D_{calcd} = 1.260 $g.cm^{-3}$, 1585 independent reflections, 1439 reflections with F > 4.0σ(F), 161 parameters, θ_{max} = 56.85°, R1 [F > 4.0σ(F)] = 0.0851, wR2 (all data) = 0.2243. Crystallographically required disorder of the reduced pyrrole ring, the axial methanol and the solvent molecules. Residual electron density (1.504 e. $Å^{-3}$) was located in the solvent region.

Data for **21**. $C_{52}H_{48}N_4$, green parallelepipeds from CH_2Cl_2/n-hexane, crystal size 0.52 x 0.38 x 0.22 mm, FW = 728.94, T = 126K, triclinic, P $\bar{1}$, a = 10.642(6), b = 13.061(11), c = 15.733(7) Å, α = 113.34(5), β = 91.99(4), γ = 99.34(6)°, V = 1964.4(22) $Å^{-3}$; Z = 2, μ = 0.548 mm^{-1}, D_{calcd} = 1.229 $g.cm^{-3}$, 5317 independent

reflections, 3552 reflections with F > 4.0σ(F), 472 parameters, θ_{max} = 57.03°, R1 [F > 4.0σ(F)] = 0.1041, wR2 (all data) = 0.2856. The pyrrolenine was found to be disordered over two positions. C72 was disordered over two positions and refined with occupancies of 0.65 and 0.44, respectively. C104 and C105 each were refined as disordered over two positions with equal occupancies.

Data for **22**. $C_{52}H_{48}N_4 \bullet 1.75CH_2Cl_2 \bullet 0.5CH_3OH$, brown blocks from CH_2Cl_2/CH_3OH, crystal size 0.8 x 0.7 x 0.32 mm, FW = 893.59, T = 129K, triclinic, P $\bar{1}$, a = 13.281(4), b = 13.734(4), c = 14.559(5) Å, α = 112.09(2), β = 99.42(2), γ = 99.26(2)°, V = 2354.7(12) $Å^{-3}$; Z = 2, μ = 2.344 mm^{-1}, D_{calcd} = 1.260 $g.cm^{-3}$, 6117 independent reflections, 5040 reflections with F > 4.0σ(F), 578 parameters, θ_{max} = 56.06°, R1 [F > 4.0σ(F)] = 0.1081, wR2 (all data) = 0.3040. The structure contained several disordered solvent molecules which could not be modelled satisfactory. Three sites were found for methylene chlorides which were refined with total occupancies of 1, 0.5, and 0.25, respectively. A methanol molecule of solvation was refined with 50 % occupancy. Some residual electron density (1.003 e. $Å^{-3}$) was located in the solvent region.

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