Inorg. Chem. **1993**, *32*, 1259–1265

Structure and Conformation of Photosynthetic Pigments and Related Compounds. 5.[1] Structural Investigation of Nickel(II) Bacteriopetroporphyrins Related to the Bacteriochlorophylls c and d: Evidence for Localized Conformational Distortion in the c-Series

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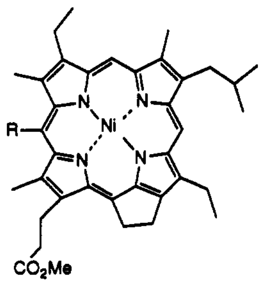
Received July 14, 1992

The structural investigation of three bacteriopetroporphyrins related to bacteriochlorophylls c and d reveals a localized distortion of the porphyrin macrocycle in the c-series at the meso-substituted C(20) position. This presents a structural rationale for the differences observed in reactivity and absorption spectra between bacteriochlorophylls bearing a C(20) methyl group and those without. The crystal structures determined for the Ni(II) bacteriopetroporphyrins present the first such analysis for geoporphyrins derived from bacteriochlorophylls of the green sulfur bacteria. Crystal data **1**; $C_{38}H_{44}N_4NiO_2$, $M_r = 647.5$, triclinic, $P\bar{1}$, $a = 10.449(3)$ Å, $b = 12.469(4)$ Å, $c = 14.622(8)$ Å, $\alpha = 64.93(3)°$, $\beta = 72.37(4)°$, $\gamma = 68.50(3)°$, $V = 1580.7(11)$ Å^3, $Z = 2$, $D_X = 1.360$ Mg·m^{-3}, λ(Mo Kα) = 0.710 69 Å, $\mu = 0.654$ mm^{-1}, $F(000) = 688$, 130 K, $R = 0.056$ for 4566 reflections with $I > 3\sigma(I)$; **2**, $C_{37}H_{42}N_4NiO_2$, $M_r = 633.5$, triclinic, $P\bar{1}$, $a = 9.581(3)$ Å, $b = 12.365(5)$ Å, $c = 14.429(7)$ Å, $\alpha = 110.03(3)°$, $\beta = 95.82(3)°$, $\gamma = 101.34(3)°$, $V = 1548.0(11)$ Å^3, $Z = 2$, $D_X = 1.359$ Mg·m^{-3}, λ(Mo Kα) = 0.710 69 Å, $\mu = 0.667$ mm^{-1}, $F(000) = 672$, 130 K, $R = 0.042$ for 5452 reflections with $I > 3\sigma(I)$; **3**; $C_{36}H_{40}N_4NiO_2$, $M_r = 619.4$, triclinic, $P\bar{1}$, $a = 8.248(4)$ Å, $b = 11.487(7)$ Å, $c = 16.164(8)$ Å, $\alpha = 93.28(5)°$, $\beta = 91.11(4)°$, $\gamma = 100.42(4)°$, $V = 1503.1(13)$ Å^3, $Z = 2$, $D_X = 1.369$ Mg·m^{-3}, λ(Mo Kα) = 0.710 69 Å, $\mu = 0.686$ mm^{-1}, $F(000) = 656$, 130 K, $R = 0.059$ for 5269 reflections with $I > 2\sigma(I)$.

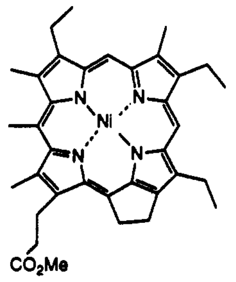
Introduction

The bacteriochlorophylls c, d and e present a unique class of photosynthetic chromophores which function as accessory pigments in the Chlorobiaceae and Chloroflexaceae.[2] Their basic chemistry and structures resemble those of other metallophorbins.[3] Main differences compared with the chlorophylls of higher plants are found in the absence of the 13^2-carbomethoxy group, the presence of a 3^1-hydroxyethyl group, and the remarkable variability found in the substituents at position 8 and 12.[4] The main structural variation found is that the bacteriochlorophylls d (**1**) have an unsubstituted C-20 position while bacteriochlorophylls c (**2**) and e bear a C(20) methyl group. Bacteriochlorophylls e are distinguished by having an aldehyde function at position 8.

The role of the C(20) methyl gruop has been under some scrutiny. The methyl group present in the c and e series is responsible for red shifted absorption bands compared with those in the d series, and several chemical studies have shown red shifted absorption bands upon meso-substitution of chlorins.[5,6] Recently it was discovered that such spectroscopic differences are used by Chlorobiaceae to facilitate adaptation to low light conditions by methylating bacteriochlorophyll d and changing the antenna pigments to those of the c-series, thus being better able to utilize the light energy.[7]



1 R = CH_3
2 R = H



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Besides such use in nature, meso-substituted chlorins have been found to readily undergo ring opening at the substituted meso-position.[8-10] It has been postulated that steric strain, imposed on the macrocycle by the substituent, is responsible for this. The ease with which chlorins undergo electrophilic substitution at the C(20) meso-position[11,12] has been used to infer

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the possibility of biological substitution reactions in the catabolism of chlorophylls.[13]

A detailed structural analysis of the bacteriochlorophyllides would give valuable information on the aggregation properties and might reveal structural differences between the C(20) substituted and unsubstituted bacteriochlorophylls. Considerable time and effort have been expended by our and other laboratories in crystallization attempts of the bacteriopheophorbides c and e and their metal complexes. However, all attempts to obtain satisfactory crystals of meso-substituted bacteriopheophorbides c or e have failed so far. Only structures of free base bacteriopheophorbides d are known,[14] while the aggregation properties in solution have been studied in some detail.[15] We decided therefore to turn our attention to structurally related compounds which might be easier to crystallize. Previous work[16] on the synthesis of bacteriopetroporphyrins related to the bacteriochlorophylls of green sulfur bacteria had provided us with several derivatives of high purity of which ultimately we were able to crystallize two bacteriochlorophyll c (**1**, **3**) and one bacteriochlorophyll d (**2**) related Ni(II) methyl 13^1-deoxophytoporphyrin type derivatives.

Bacteriopetroporphyrins are formed on a geological time scale from chlorophylls which have survived the normal catabolic pathways.[17] Petroporphyrins related to the bacteriochlorophylls have been isolated from immature Messel oil shale.[18] Structural analyses of geoporphyrins are scarce, the only structures published being those of nickel and vanadyl complexes related to chlorophyll a.[19,20]

We report here the structural analysis of compounds **1**–**3**, which constitutes the first structural analysis of geoporphyrins related to the bacteriochlorophylls of the Chlorobiaceae and Chloroflexaceae.

Experimental Section

All compounds were prepared and characterized as described previously.[16] Absorption spectra were recorded with a Hewlett Packard 8450A spectrophotometer in methylene chloride solution.

Structure Determination of 1. Red plates of **3** were grown by slow diffusion of a concentrated solution of the compound in methylene chloride into *n*-hexane. The crystals were immersed in hydrocarbon oil, a single crystal selected (1.0 × 0.8 × 0.2 mm), mounted on a glass fiber and placed in the low-temperature N_2 stream.[21] A Siemens R3m/V automatic diffractometer with a graphite monochromator and equipped with a locally modified Siemens LT device and Mo Kα radiation ($\lambda = 0.7107$ Å) was used. Cell parameters were determined from 19 reflections with $21° \leq 2\theta \leq 25°$. $F(000) = 688$, $\mu = 0.654$ mm^{-} The intensities were measured in the range $0 < 2\theta < 55°$ at 130 K using the ω scan technique. Octants collected: $+/-h,+/-k,+l$. The data collection was performed using a constant scan speed of 58.29° min^{-1} in ω and a scan range of 1.90°. Two standard reflections were measured every 198 reflections and showed no variation in intensity during the data collection. Of the 6968 independent reflections collected 4566 were considered observed with $I > 3.0\sigma(I)$. The intensities were corrected for Lorentz and polarization effects. An absorption correction was applied using the program XABS,[22] extinction was disregarded. The structure was solved via Patterson Synthesis using the SHELXTL PLUS program system, version 5.[23] The refinement was carried out by full-matrix least-squares on F using the same program system. The function minimized was $\sum w(F_o - F_c)^2$. Hydrogen atoms were included at calculated positions by using a riding model (C–H distance 0.96 Å, N–H distance 0.90 Å, $U_{iso} = 0.04$). Calculations were carried out on a Vax-station 3200. The final cycle of refinement on $|F|$ included 406 variable parameters and converged with $R = 0.056$, $R_w = 0.083$ and $S = 0.82$. All non-hydrogen atoms were refined with anisotropic thermal parameters. The weighting scheme used was $w^{-1} = \sigma^2(F) + 0.0079F^2$. Largest $\Delta/\sigma = 0.039$, largest difference peak = 0.61 eÅ^{-3}, and largest difference hole = –0.65 Å^{-3}. If not otherwise stated, the same procedure was used for the determination of the other crystal structures.

Structure Determination of 2. Red parallelepipeds were crystallized by slow diffusion of methanol into a solution of the porphyrin in methylene chloride, crystal size 1.1 × 0.5 × 0.36 mm. Cell constants were refined from 22 reflections with $23° \leq 2\theta < 26°$. Data collection was performed at 130 K on a Siemens R3m/V diffractometer with Mo Kα radiation ($\lambda = 0.7107$ Å), range $0 < 2\theta < 55°$, scan speed 58.29°/min, scan range 2.00°, ω-scan, $F(000) = 672$. Octants collected: $+/-h,+/-k,+l$. A total of 7113 independent reflections were collected of which 5452 were considered observed with $I > 3.0\sigma(I)$. Data were corrected for absorption,[22] with extinction disregarded. Structure solution was via Patterson synthesis. The final cycle of refinement included 397 independent parameters and converged with $R = 0.042$, $R_w = 0.061$, $S = 1.08$. H atoms were included using the riding model described for **3**. Weighting scheme $w^{-1} = \sigma^2(F) + 0.0018F^2$, and $\Delta/\sigma = 0.002$. Final difference Fourier synthesis: $-0.50 \leq \Delta\rho \leq 0.60$ e Å^{-3}.

Structure Determination of 3. Red parallelepipeds were obtained by crystallization from methylene chloride/*n*-hexane, crystal size 0.51 × 0.38 × 0.19 mm. Cell constants were refined from 22 reflections with $21° \leq 2\theta \leq 26°$. Data collection was performed at 130 K on a Siemens R3m/V diffractometer with Mo Kα radiation ($\lambda = 0.7107$ Å, range $0 < 2\theta < 55°$, scan speed 29.30°/min, scan range 2.00°, ω-scan, $F(000) = 656$. Octants collected: $+/-h,+/-k,+l$. A total of 6900 independent reflections were collected of which 5269 were considered observed with $I > 2.0\sigma(I)$. Data were collected for absorption,[22] with extinction disregarded. Structure solution was via Patterson synthesis. The final cycle of refinement included 388 independent parameters and converged with $R = 0.059$, $R_w = 0.077$, $S = 1.40$. H atoms were included using the riding model described for **3**. Weighting scheme $w^{-1} = \sigma^2(F) + 0.0010F^2$, and $\Delta/\sigma = 0.315$. Final difference Fourier synthesis: $-0.44 \leq \Delta\rho \leq 0.54$ e Å^{-3}.

Results and Discussion

The molecular structures and labelling schemes for compounds **1**–**3** are displayed in Figures 1–3. Crystal data for all three compounds are given in Table I, while Tables II–IV list the isotropic temperature factors and potential parameters for the non-hydrogen atoms.

All three compounds show the typical S_4-ruffling effect often observed in Ni(II) porphyrins.[24] This is characterized by alternating displacement of the four meso-carbons above and

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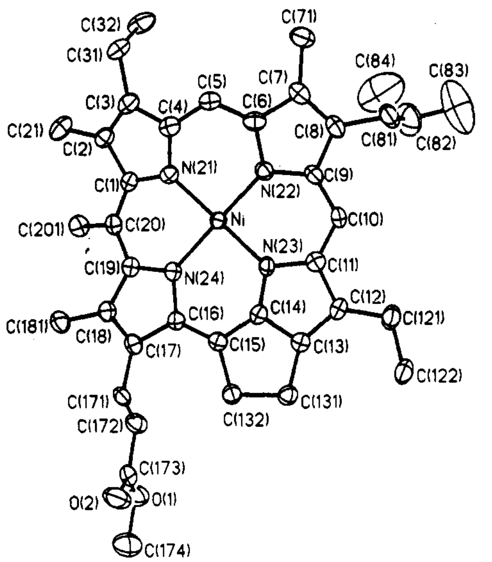

Figure 1. Computer-generated plot of **1** with labelling scheme used. Ellipsoids are drawn for 50% occupancy. Hydrogen atoms have been omitted for clarity.

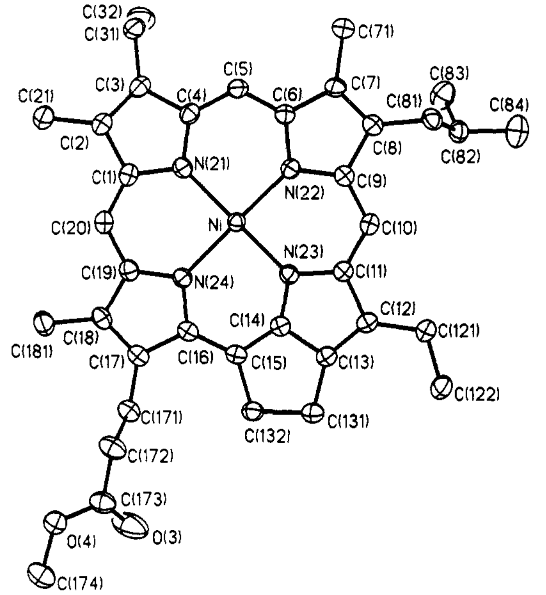

Figure 2. Computer-generated plot of **2** with labelling scheme used. Ellipsoids are drawn for 50% occupancy. Hydrogen atoms have been omitted for clarity.

below the nitrogen plane and a concomitant out-of-plant rotation of the pyrrole rings. The overall degree of ruffling is about the same in both c-derivatives **1** and **3**, while the d-derivative **2** shows only moderate ruffling. Such a different degree of overall ruffling has been observed in a number of Ni(II) tetrapyrroles.[24,25] The individual pyrrole rings are all planar; the largest deviations from planarity being <0.02 Å.

The degree of ruffling is best seen in the angles of the pyrrole rings with the mean plane of the molecules and the pyrrole tilt angles. Selected bond lengths and bond angles for the 26 atoms of the phorbin macrocycle are compiled in Tables V and VI. For **1** the angles of the pyrroles to the 4N-plane are 18.1, 13.2, 8.9 and 14.8° (rings I–IV). The tilt angles between neighboring pyrroles are 22.3, 18.3, 12.5, and 25.7°. The corresponding values for compound **3** are 15.7, 10.4, 8.8, and 15.6° for the angles pyrrole to 4N-plane and 22.6, 11.8, 16.1, and 21.5° for the pyrrole tilt angles. The relative planar macrocycle of **2** becomes evident by the small average angle between neighboring pyrroles of 5.6° and angles of individual pyrroles with the 4N-plane of 4.1, 5.2, 2.8, and 3°.

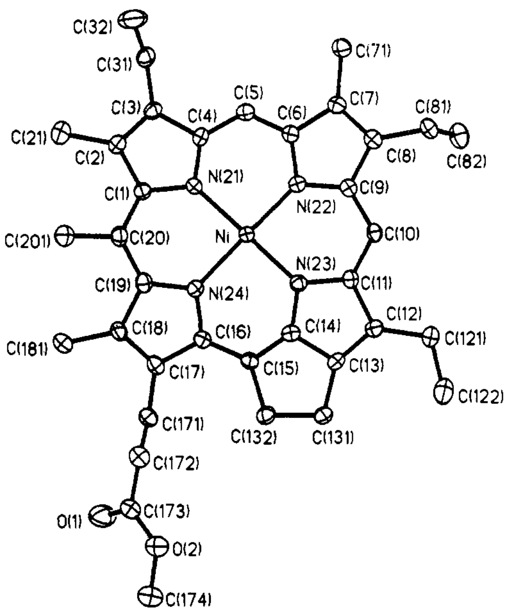

Figure 3. Computer-generated plot of **3** with labelling scheme used. Ellipsoids are drawn for 50% occupancy. Hydrogen atoms have been omitted for clarity.

Table I. Crystal Data and Data Collection Parameters for Compounds **1–3**

	1	2	3
chem formula	$C_{38}H_{44}N_4NiO_2$	$C_{37}H_{42}N_4NiO_2$	$C_{36}H_{40}N_4NiO_2$
mol wt	647.5	633.5	619.4
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	10.449(3)	9.581(3)	8.248(4)
b, Å	12.469(4)	12.365(5)	11.487(7)
c, Å	14.662(8)	14.429(7)	16.164(8)
α, deg	64.93(3)	110.03(3)	93.28(5)
β, deg	72.37(4)	95.82(3)	91.11(4)
γ, deg	68.50(3)	101.34(3)	100.42(4)
V, Å^3	1580.7(11)	1548.0(11)	1503.1(13)
Z	2	2	2
D_{calcd}, Mg·m^{-3}	1.360	1.359	1.369
μ(Mo Kα), mm^{-1}	0.654	0.667	0.686
λ, Å	0.710 69	0.710 69	0.710 69
T, K	130	130	130
R	0.056	0.042	0.059
R_w	0.083	0.061	0.077
S	0.82	1.08	1.40

Compounds **1** and **3** show clearly the C(20) methyl substituent. Since these compounds were prepared by derivatization of bacteriochlorophyll c isolated from *Prosthecochloris aestuarii*, the present structures clearly confirm the substitution pattern previously proposed by spectroscopic means.[3] Compound **1** has been shown by Ocampo et al.[18] to occur in Messel oil shale. The synthetic material used here has been shown to be identical with the material isolated from oil shale[16] and thus structure **2** unambiguously proves the "bacterio" character of the petroporphyrins and further substantiates their formation from bacteriochlorophyll d. Bacteriopetroporphyrins c or e have not yet been isolated.

The methyl-substituent at C(20) induces a localized increase in conformational distortion. Figure 4 shows the deviations of the macrocycle atoms from the least-squares planes of the four nitrogen atoms in all three compounds. The three meso-positions 5, 10, and 15 in **1** show an average deviation of 0.38 Å, while the C(20) is displaced by 0.59 Å. In compound **3** the methyl bearing carbon is displaced by 0.64 Å compared to 0.33 Å for the other

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Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{Å}^2 \times 10^3$) for **1**

atom	*x*	*y*	*z*	*U*(eq)[a]
Ni	2246(1)	2621(1)	464(1)	22(1)
N(21)	4238(3)	2066(3)	60(3)	26(1)
N(22)	2443(3)	2418(3)	1800(2)	27(1)
N(23)	293(3)	3205(3)	860(2)	25(1)
N(24)	2004(3)	2837(3)	−890(2)	24(1)
C(1)	4973(4)	1628(3)	−728(3)	26(2)
C(2)	6473(4)	1262(3)	−721(3)	29(2)
C(21)	7681(4)	733(5)	−1431(4)	45(2)
C(3)	6607(4)	1539(4)	35(3)	32(2)
C(31)	7930(4)	1327(4)	384(4)	37(2)
C(32)	8376(5)	68(4)	1170(4)	50(2)
C(4)	5228(4)	1976(4)	545(3)	30(2)
C(5)	4946(4)	2121(4)	1482(3)	30(2)
C(6)	3666(4)	2244(4)	2099(3)	30(2)
C(7)	3412(5)	2141(4)	3148(3)	33(2)
C(71)	4511(5)	1900(5)	3728(4)	48(2)
C(8)	2038(5)	2235(4)	3499(3)	33(2)
C(81)	1274(5)	2048(5)	4577(3)	45(2)
C(82)	1017(8)	778(6)	5133(5)	71(3)
C(83)	363(11)	510(8)	6194(6)	127(7)
C(84)	2280(10)	−251(8)	5067(8)	146(7)
C(9)	1414(4)	2473(4)	2654(3)	29(2)
C(10)	8(4)	2859(4)	2650(3)	29(2)
C(11)	−538(4)	3271(3)	1780(3)	28(2)
C(12)	−2008(4)	3869(4)	1680(3)	29(2)
C(121)	−3159(4)	4191(4)	2500(3)	38(2)
C(122)	−4571(4)	4874(5)	2164(4)	43(2)
C(13)	−2029(4)	4138(3)	673(3)	26(2)
C(131)	−2959(4)	4654(4)	−98(3)	30(2)
C(132)	−1915(4)	4514(4)	−1097(3)	30(2)
C(14)	−626(4)	3729(3)	206(3)	24(1)
C(15)	−472(4)	3914(3)	−803(3)	25(2)
C(16)	809(4)	3497(3)	−1349(3)	24(2)
C(17)	1115(4)	3517(3)	−2376(3)	26(2)
C(171)	127(4)	4209(4)	−3132(3)	30(2)
C(172)	−646(5)	3409(4)	−3159(3)	37(2)
C(173)	−1706(5)	4111(5)	−3850(3)	37(2)
C(174)	−3251(7)	3938(7)	−4632(5)	74(4)
C(18)	2446(4)	2807(3)	−2532(3)	28(2)
C(181)	3170(5)	2608(5)	−3537(3)	41(2)
C(19)	3001(4)	2383(3)	−1613(3)	26(2)
C(20)	4379(4)	1663(3)	−1470(3)	27(2)
C(201)	5214(4)	904(4)	−2137(3)	34(2)
O(1)	−2240(4)	3351(3)	−3959(3)	56(2)
O(2)	−2042(4)	5196(4)	−4271(3)	57(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

three meso-positions. The meso-carbons in **2** are displaced by an average of 0.10 Å. The higher degree of distortion for the C(20) meso-carbon also becomes evident when the skeletal deviations are displayed in a linear fashion (Figure 5). The effect of the meso-substituent can easily be seen by its larger displacement compared with the other three meso-positions. The fact that the displacement of the meso-carbon C20 and C5 in **1** differ by only 14% might reflect the lower flexibility of phytoporphyrin type molecules compared to phytochlorins and clearly indicates the necessity for further studies on the corresponding chlorophyllides.

However, similar distortion effects have been observed in a number of mono- and di-meso-substituted porphyrin derivatives. Compounds bearing a bulky meso substituent, such as 2,2-bis(ethoxycarbonyl)vinyl,[26a] between β-ethyl groups exhibit considerable ring distortion, which becomes large when a formyl group is introduced at the neighboring meso-positions.[26b] A comparative analysis of several mono- and di-meso-acrolein-substituted Ni(II) porphyrins showed that the substituted positions are displaced up to 54% more than the unsubstituted ones.[27]

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{Å}^2 \times 10^3$) for **2**

atom	*x*	*y*	*z*	*U*(eq)[a]
Ni	2154(1)	4296(1)	477(1)	22(1)
N(21)	1428(2)	3126(2)	1043(1)	26(1)
N(22)	3817(2)	5032(2)	1576(1)	24(1)
N(23)	2879(2)	5453(2)	−61(1)	24(1)
N(24)	476(2)	3567(2)	−674(1)	25(1)
C(1)	217(3)	2174(2)	643(2)	27(1)
C(2)	23(3)	1517(2)	1305(2)	29(1)
C(21)	−1192(3)	445(2)	1107(2)	36(1)
C(3)	1099(3)	2084(2)	2115(2)	29(1)
C(31)	1325(3)	1829(2)	3057(2)	36(1)
C(32)	579(3)	2537(3)	3854(2)	51(1)
C(4)	1977(3)	3080(2)	1947(2)	27(1)
C(5)	3202(3)	3844(2)	2596(2)	27(1)
C(6)	4085(3)	4753(2)	2416(2)	25(1)
C(7)	5406(3)	5522(2)	3077(2)	27(1)
C(71)	5973(3)	5485(2)	4073(2)	35(1)
C(8)	5992(2)	6268(2)	2632(2)	25(1)
C(81)	7369(3)	7229(2)	2982(2)	29(1)
C(82)	7194(3)	8494(2)	3457(2)	33(1)
C(83)	6566(4)	8679(3)	4416(2)	47(1)
C(84)	8660(4)	9364(3)	3650(3)	55(1)
C(9)	4991(3)	5963(2)	1704(2)	24(1)
C(10)	5164(3)	6578(2)	1068(2)	26(1)
C(11)	4156(3)	6356(2)	238(2)	25(1)
C(12)	4257(3)	7007(2)	−436(2)	26(1)
C(121)	5508(3)	8046(2)	−280(2)	31(1)
C(122)	5345(3)	8608(2)	−1058(2)	39(1)
C(13)	3040(3)	6468(2)	−1153(2)	26(1)
C(131)	2254(3)	6454(2)	−2117(2)	30(1)
C(132)	867(3)	5408(2)	−2399(2)	30(1)
C(14)	2236(3)	5537(2)	−906(2)	25(1)
C(15)	974(3)	4897(2)	−1576(2)	26(1)
C(16)	96(3)	3927(2)	−1464(2)	25(1)
C(17)	−1233(3)	3147(2)	−2104(2)	27(1)
C(171)	−2040(3)	3263(2)	−3003(2)	30(1)
C(172)	−1696(3)	2513(3)	−3999(2)	37(1)
C(173)	−2562(3)	2640(2)	−4867(2)	36(1)
C(174)	−4091(4)	1612(3)	−6439(2)	64(2)
C(18)	−1651(3)	2289(2)	−1734(2)	29(1)
C(181)	−2977(3)	1263(2)	−2123(2)	37(1)
C(19)	−605(3)	2564(2)	−843(2)	27(1)
C(20)	−714(3)	1901(2)	−240(2)	28(1)
O(1)	−2661(4)	3545(2)	−4943(2)	82(1)
O(2)	−3243(2)	1594(2)	−5564(1)	48(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Several meso-linked porphyrin dimer structures have been described which formally are mono-meso-substituted metalloporphyrins.[28] In all cases conformational distortion of the substituted part of the molecule was observed. A Ni(II) porphyrin, [5,5′-ethylenebis(octaethylporphyrinato)]nickel(II) showed displacements for the nonsubstituted meso-carbons of 0.5 Å from the mean plane, while the carbon bearing the substituent showed a displacement of 0.82 Å.[28b] Such drastic differences have not been observed in mono-meso-substituted free-base porphyrins.[29] Similar distortion effects have been observed in 5,15-disubstituted metalloporphyrins[30a] while the corresponding free bases showed again a much lesser degree of distortion.[30b]

The fact that the distortion is due to steric interaction of the meso-substituent and neighboring β-pyrrole substituents can be seen by comparison with the structure of (5,10,15,20-tetrame-

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Table IV. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for **3**

atom	*x*	*y*	*z*	*U*(eq)[a]
Ni	1939(1)	2483(1)	3635(1)	17(1)
N(21)	44(4)	1979(3)	2903(2)	18(1)
N(22)	705(4)	1948(3)	4589(2)	19(1)
N(23)	3786(4)	3001(3)	4359(2)	20(2)
N(24)	3257(4)	3036(3)	2672(2)	19(1)
C(1)	5(5)	1762(3)	2048(2)	21(1)
C(2)	−1679(5)	1333(3)	1755(2)	25(1)
C(21)	−2349(6)	1096(4)	870(3)	39(2)
C(3)	−2645(5)	1280(3)	2422(2)	22(1)
C(31)	−4465(5)	867(4)	2443(3)	27(1)
C(32)	−4967(6)	−451(4)	2283(3)	50(2)
C(4)	−1556(4)	1635(3)	3139(2)	18(1)
C(5)	−2041(5)	1458(3)	3943(2)	20(1)
C(6)	−968(4)	1524(3)	4611(2)	19(1)
C(7)	−1425(5)	1117(3)	5413(2)	21(1)
C(71)	−3130(5)	518(3)	5633(3)	25(1)
C(8)	−19(5)	1288(3)	5890(2)	21(1)
C(81)	187(5)	981(3)	6777(2)	24(1)
C(82)	45(6)	1970(4)	7427(3)	34(1)
C(9)	1288(4)	1835(3)	5384(2)	18(1)
C(10)	2880(4)	2254(3)	5681(2)	20(1)
C(11)	4071(4)	2862(3)	5197(2)	19(1)
C(12)	5719(5)	3456(3)	5475(2)	21(1)
C(121)	6386(5)	3507(3)	6354(2)	25(1)
C(122)	8103(6)	4227(4)	6452(3)	40(2)
C(13)	6411(5)	3959(3)	4796(2)	21(1)
C(131)	7956(5)	4655(3)	4464(2)	25(1)
C(132)	7501(5)	4775(3)	3636(2)	27(1)
C(14)	5212(4)	3669(3)	4131(2)	20(1)
C(15)	5748(5)	4080(3)	3397(2)	21(1)
C(16)	4792(5)	3770(3)	2673(2)	20(1)
C(17)	5276(5)	4003(3)	1849(2)	24(1)
C(171)	6739(5)	4881(4)	1601(3)	28(1)
C(172)	8218(5)	4338(4)	1357(3)	34(1)
C(173)	9608(5)	5273(4)	1083(3)	35(1)
C(174)	12435(6)	6025(5)	1194(3)	47(2)
C(18)	4102(5)	3328(4)	1331(2)	25(1)
C(181)	4128(6)	3324(4)	395(3)	38(1)
C(19)	2842(5)	2724(3)	1845(2)	23(1)
C(20)	1376(5)	2001(3)	1561(2)	25(1)
C(201)	1304(6)	1415(4)	691(3)	39(2)
O(1)	9445(4)	6013(4)	596(2)	57(1)
O(2)	11034(4)	5200(3)	1429(2)	40(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

thylporphyrinato)nickel(II).[31] This porphyrin has only meso-substituents and no β-pyrrole substituents and shows an essentially planar macrocycle with similar deviations from planarity for all four meso-positions. The structure of the corresponding chlorin which has a ruffled macrocyclic exhibits similar displacements for all four meso-positions, too.

Only two cases of meso-substituted free-base chlorins are known: the dimer 20,20′-ethylenebis(2,3,7,8,12,13,17,18-*trans*-octaethylchlorin)[32] and 5,10-dimethyloctaethylchlorin.[33] In both cases no significant differences are observed for the displacement of the substituted and unsubstituted meso-positions although the macrocycle clearly shows ring puckering which leads to an out-of-plane position for the substituents. In the case of the dimethylchlorin this was also interpreted as evidence for structural differences between bacteriochlorophylls c and d.[33] The fact that no significant differences are observed for the meso-positions can be explained by the high conformational flexibility of free base chlorins which leads to an even distribution of the conformational strain induced by the substituents (evidenced by ring distortion) over the macrocycle. It should also be noted that the situation becomes more complicated in the case of the chlorophylls due to the presence of the isocyclic pentanone ring V. Ring V already induces asymmetric distortion as evidenced by nonequal displacement of the meso-carbons, e.g. in the structure of Ni(II) methyl pyropheophorbide a.[34] However in the light of the above mentioned evidence, the presence of an additional C20 methyl substituent should lead to a significantly larger displacement of the meso-carbon involved. In the same context it is clear that the presence of the saturated ring IV in chlorophylls should lead to overall larger displacements of the meso-carbons than observed in the present bacteriopetro*porphyrin* derivatives.

Table V. Selected Bond Lengths (Å) in **1**–**3**

	1	**2**	**3**
Ni–N(21)	1.925(3)	1.943(3)	1.924(3)
Ni–N(22)	1.926(4)	1.951(2)	1.932(3)
Ni–N(23)	1.892(3)	1.901(2)	1.889(3)
Ni–N(24)	1.964(4)	2.005(2)	1.984(30)
N(21)–C(1)	1.380(6)	1.388(3)	1.389(5)
N(21)–C(4)	1.370(7)	1.380(3)	1.375(5)
N(22)–C(6)	1.388(7)	1.383(4)	1.380(5)
N(22)–C(9)	1.387(5)	1.389(3)	1.385(5)
N(23)–C(11)	1.379(5)	1.398(3)	1.393(5)
N(23)–C(14)	1.353(6)	1.355(3)	1.353(5)
N(24)–C(16)	1.405(5)	1.399(4)	1.389(4)
N(24)–C(19)	1.390(5)	1.381(3)	1.385(5)
C(1)–C(2)	1.464(6)	1.454(4)	1.448(5)
C(1)–C(20)	1.384(7)	1.375(3)	1.386(5)
C(2)–C(3)	1.346(8)	1.352(3)	1.351(6)
C(3)–C(4)	1.431(5)	1.456(4)	1.445(5)
C(4)–C(5)	1.387(7)	1.372(3)	1.382(5)
C(5)–C(6)	1.365(5)	1.384(4)	1.373(5)
C(6)–C(7)	1.432(7)	1.441(3)	1.436(5)
C(7)–C(8)	1.349(6)	1.361(4)	1.358(5)
C(8)–C(9)	1.440(7)	1.451(3)	1.441(5)
C(9)–C(10)	1.369(6)	1.382(4)	1.381(5)
C(10)–C(11)	1.372(7)	1.371(3)	1.382(5)
C(11)–C(12)	1.463(6)	1.458(4)	1.457(5)
C(12)–C(13)	1.370(6)	1.361(3)	1.357(5)
C(13)–C(14)	1.420(5)	1.426(4)	1.429(5)
C(14)–C(15)	1.361(6)	1.373(3)	1.354(5)
C(15)–C(16)	1.375(5)	1.391(4)	1.391(5)
C(16)–C(17)	1.429(6)	1.440(3)	1.424(5)
C(17)–C(18)	1.359(5)	1.355(4)	1.365(5)
C(18)–C(19)	1.438(7)	1.442(3)	1.446(5)
C(19)–C(20)	1.414(5)	1.383(4)	1.391(5)
C(20)–C(201)	1.507(7)		1.519(6)

The substituent effect can also be delineated by inspection of the relevant C_a–C_m–C_a bond angles. The unsubstituted meso-positions in **2** have C_a–C_m–C_a bond angles with an average of 124.1(2)°. C(15), with the fused five-membered ring, has a slightly smaller C_a–C_m–C_a angle of 120.8(2)°. This effect of ring V can also be seen in compounds **1** and **3**, which have C_a–C_m–C_a angles of 121.0(4)° and 120.9(3)°. However, the C(20) meso-bridge shows a bond angle of 121.7(4)° in **1** and 122.7(3)° in **3**, while the unsubstituted positions have values between 122 and 125°. Differences of 4° between substituted and unsubstituted positions have been found recently in a number of mono- and diacrolein-substituted Ni(II) porphyrins.[27] The fact that these values are somewhat smaller in the case of the bacteriopetroporphyrins can be attributed to the effect of ring V.

The influence of ring V is also apparent in the metal–nitrogen bond lengths. The average Ni–N bond lengths in rings I, II, and IV is 1.938(4) Å, 1.966(2) Å and 1.947(3) Å in compounds **1**–**3**, respectively. Compared to this, the bond lengths between Ni and

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Table VI. Selected Bond Angles (deg) in **1**–**3**

	1	**2**	**3**
N(21)–Ni–N(22)	91.7(2)	90.6(1)	91.9(1)
N(21)–Ni–N(23)	178.5(2)	179.3(1)	179.0(1)
N(22)–Ni–N(23)	87.8(2)	88.7(1)	87.9(1)
N(21)–Ni–N(24)	89.4(2)	91.0(1)	89.5(1)
N(22)–Ni–N(24)	178.8(1)	178.3(1)	178.6(1)
N(23)–Ni–N(24)	91.1(1)	89.6(1)	90.7(1)
Ni–N(21)–C(1)	128.6(3)	127.6(2)	128.1(2)
Ni–N(21)–C(4)	125.9(3)	127.5(1)	126.1(2)
C(1)–N(21)–C(4)	105.4(3)	104.8(2)	105.5(3)
Ni–N(22)–C(6)	126.6(3)	127.8(2)	126.9(2)
Ni–N(22)–C(9)	128.7(3)	128.2(2)	128.6(2)
C(6)–N(22)–C(9)	104.6(4)	104.0(2)	104.4(3)
Ni–N(23)–C(11)	132.6(3)	131.7(2)	132.8(2)
Ni–N(23)–C(14)	123.8(3)	125.3(1)	123.9(3)
C(11)–N(23)–C(14)	103.5(3)	103.0(2)	103.3(3)
Ni–N(24)–C(16)	128.0(3)	130.1(2)	128.4(2)
Ni–N(24)–C(19)	127.0(3)	125.7(2)	126.3(2)
C(16)–N(24)–C(19)	104.9(4)	104.1(2)	105.2(3)
N(21)–C(1)–C(2)	109.6(4)	110.8(2)	109.5(3)
N(21)–C(1)–C(20)	124.4(3)	125.3(3)	124.0(3)
C(2)–C(1)–C(20)	125.6(4)	123.9(2)	126.3(3)
C(1)–C(2)–C(3)	106.5(4)	106.6(2)	107.6(3)
C(2)–C(3)–C(4)	107.2(4)	106.9(2)	106.5(3)
N(21)–C(4)–C(3)	111.1(4)	110.8(2)	110.7(3)
N(21)–C(4)–C(5)	124.7(4)	125.2(2)	125.3(3)
C(3)–C(4)–C(5)	123.7(5)	124.0(2)	123.2(3)
C(4)–C(5)–C(6)	124.6(5)	124.3(2)	124.1(3)
N(22)–C(6)–C(5)	123.8(5)	124.3(2)	124.2(3)
N(22)–C(6)–C(7)	111.1(4)	111.5(2)	111.2(3)
C(5)–C(6)–C(7)	125.1(5)	124.2(2)	124.6(3)
C(6)–C(7)–C(8)	106.5(5)	107.1(2)	106.9(3)
C(7)–C(8)–C(9)	107.7(4)	106.0(2)	106.5(3)
N(22)–C(9)–C(8)	109.9(4)	111.5(2)	111.0(3)
N(22)–C(9)–C(10)	124.6(4)	125.1(2)	125.3(3)
C(8)–C(9)–C(10)	125.0(4)	123.4(2)	123.5(3)
C(9)–C(10)–C(11)	123.0(4)	123.3(2)	122.0(3)
N(23)–C(11)–C(10)	122.1(4)	122.8(2)	122.2(3)
N(23)–C(11)–C(12)	111.8(4)	111.6(2)	111.5(3)
C(10)–C(11)–C(12)	126.1(4)	125.6(2)	126.3(3)
C(11)–C(12)–C(13)	104.5(3)	105.0(2)	105.1(3)
C(12)–C(13)–C(14)	106.7(4)	106.9(2)	107.0(3)
N(23)–C(14)–C(13)	113.5(4)	113.5(2)	113.1(3)
N(23)–C(14)–C(15)	132.5(3)	132.8(2)	133.0(3)
C(13)–C(14)–C(15)	113.9(4)	113.8(2)	113.9(3)
C(14)–C(15)–C(16)	121.0(4)	120.8(2)	120.9(3)
N(24)–C(16)–C(15)	122.0(4)	121.2(2)	121.7(3)
N(24)–C(16)–C(17)	110.0(3)	110.7(2)	110.8(3)
C(15)–C(16)–C(17)	127.7(4)	128.1(2)	127.0(3)
C(16)–C(17)–C(18)	107.4(4)	107.1(2)	106.8(3)
C(17)–C(18)–C(19)	107.4(4)	106.7(2)	107.2(3)
N(24)–C(19)–C(18)	110.1(3)	111.4(2)	109.7(3)
N(24)–C(19)–C(20)	124.2(4)	125.6(2)	128.6(3)
C(18)–C(19)–C(20)	125.6(4)	123.1(2)	125.8(3)
C(1)–C(20)–C(19)	121.7(4)	124.7(2)	122.7(3)
C(19)–C(20)–C(201)	119.1(5)		118.3(4)
C(1)–C(20)–C(201)	119.3(3)		118.9(3)

the nitrogen in ring III (for **1**–**3**) are shorter with 1.892(3), 1.901(2), and 1.889(3) Å. The slightly larger values for **2** are due to the smaller degree of ring ruffling observed in this compound. Similar shortenings of the metal–nitrogen bond involving the pyrrole with the fused five-membered ring have been observed in the structures of Ni(II) deoxophylloerythrin and vanadyl deoxophylloerythroetioporphyrin.[19,20] The average metal–nitrogen bond lengths have intermediate values between those observed in the S_4-ruffled (1.929(3) Å) and planar (1.958(2) Å) form of Ni(II) octaethylporphyrin.[35]

The phorbin molecules form layers in the crystal with the propionic acid ester groups and ring V pointing away from each other in different layers. There is no evidence for π–π interactions or close intermolecular interactions. The Ni–Ni distances are 5.975 Å in the crystal of **1**, 5.839 Å in **2**, and 8.004 Å in **3**. The shortest nonbonding interaction in the crystal of **1** is 4.995 Å between the oxygen atoms in neighboring propionic acid ester groups. Thus the observed conformational distortion effects are not due to intermolecular interactions.

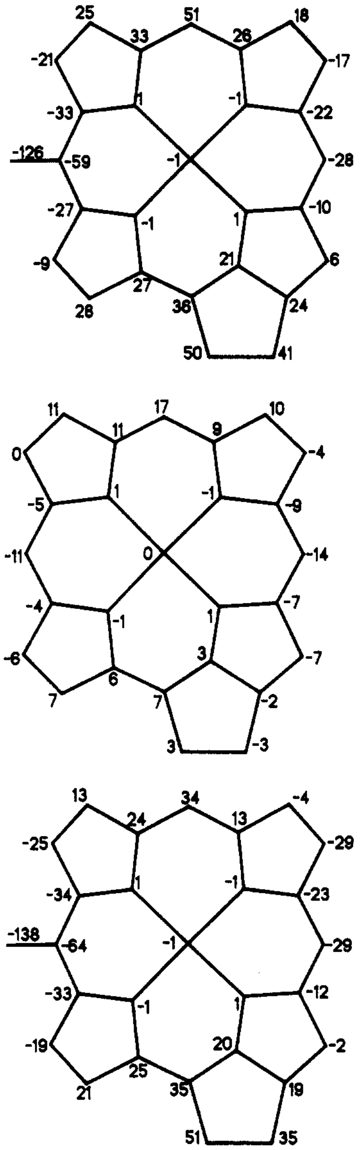

Figure 4. Deviations from the least-squares plane of the four nitrogen atoms in **1**–**3** (from top to bottom (Å × 10^2)).

In several cases remarkable differences have been observed in the reactivity of meso-substituted chlorins versus unsubstituted ones. Zinc and magnesium complexes of the bacteriopheophorbides c and e, 20-((trifluoroacetoxy)methyl)pheophorbide a and 20-(chloromethyl)pheophorbide a readily undergo photooxidation to give photobilins via oxoniachlorin intermediates.[8-10] The increased steric strain in the vicinity of the substituted meso-position in phorbins presents a simple rational for the observed differences in reactivity between substituted and unsubstituted chlorins.

Figure 6 shows the absorption spectra of the 8-isobutyl-12-ethylbacteriopetroporphyrins c (**1**) and d (**2**). The C(20)-substituted compound **1** exhibits a shift of 12 nm toward longer wavelengths in the red region. The magnitude of this shift resembles closely those observed in natural pigments of the c and d series of bacteriochlorophylls.[36] Thus the effect of meso-substitution on the absorption spectra is about the same in the metalloporphyrins described here and the corresponding met-

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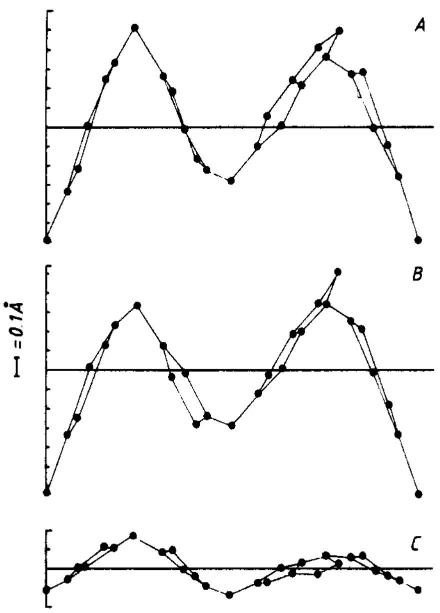

Figure 5. Linear display of the skeletal deviations from the least squares plane of the four nitrogen atoms in **1** (A), **3** (B), and **2** (C).

allochlorins. The fact that the absorption differences are being retained in the bacteriopetroporphyrins indicates that these compounds can serve as valid model compounds for the bacteriochlorophylls.

Similar spectroscopic differences between unsubstituted and mono-meso-substituted porphyrins and chlorins have been observed in a number of octaethylporphyrin and octaethylchlorin derivatives and meso-halogenated chlorophylls.[5,6]

The question of conformational distortion of porphyrins and associated red shifts in the absorption spectra is currently under active scrutiny.[14b,37,38] Dodecasubstituted porphyrins have been shown to exhibit severe conformational distortions with the β-pyrrole carbons being displaced up to 1.2 Å from the mean plane of the molecule.[38] A clear correlation between conformational distortion and physicochemical properties, such as redox potential and spectra has been shown.[14b] For example, INDO/s calculations showed for highly substituted porphyrins that ring puckering results in destabilization of the π-system and raising of the HOMO. The smaller energy gap between HOMO and LUMO gives a concomitant red shift of the absorption band.[14b] The increasing body of information on the conformation of mono- and disubstituted porphyrins indicates that the conformation of pigments can be finetuned by the successive introduction of substituents. Thus, spectral differences between the bacteriochlorophylls of the c, d, and e series can be explained on the basis of localized conformational distortion in the meso-substituted series. However, more detailed studies of the substitution effects in chlorophylls are needed and are the focus of ongoing research in our laboratory.

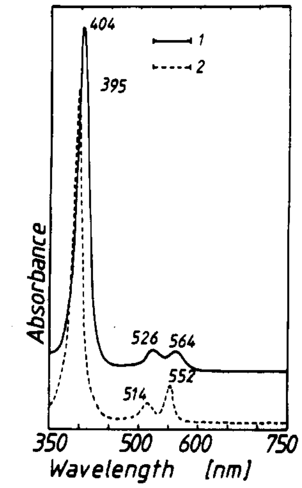

Figure 6. Absorption spectra of compounds **1** and **2** in methylene chloride. The baselines have been adjusted arbitrarily to avoid overlap.

Acknowledgment. This work was supported by grants from the Deutsche Forschungsgemeinschaft (Se543/1-1) and the National Science Foundation (K.M.S.; CHE-90-01381). We wish to thank one of the reviewers for stimulating criticism and helpful suggestions.

Supplementary Material Available: Listings of complete bond lengths, bond angles, anisotropic thermal parameters, and hydrogen coordinates (12 pages). Ordering information is given on any current masthead page.

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