Structural Investigations on Mono- and Di-Acrolein Substituted Ni(II) Porphyrins and a Ni(II) Benzochlorin. Model Compounds for Photosensitizers in Photodynamic Therapy

Mathias O. Senge*, Maria da Graça H. Vicente, Sean R. Parkin, Håkon Hope, and Kevin M. Smith

Department of Chemistry, University of California, Davis, CA 95616,
United States of America

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The structures of four Ni complexes and a free base related to tetrapentanoporphyrin (TC_7P) and octaethylporphyrin (OEP) have been determined by X-ray crystallograpic methods. The Ni(II) complexes exhibit considerable S_4-ruffling induced by coordination hole contraction due to the low spin Ni(II). The degree of conformational distortion is enhanced by one or two additional acrolein substituents at the *meso* positions. The steric strain imposed by interaction of the *meso* substituent with the neighboring β-pyrrole substituents leads to a significant displacement from the mean plane of the molecule of the *meso* carbon(s) involved. Increasing non-planarity of the macrocycles is correlated with shifts to longer wavelenghts in the absorption spectra. Ring closures of the acrolein group to afford benzochlorin type pigments results in further bathochromic shifts and a very non-planar molecular conformation. Long wavelength absorbing pigments such as benzochlorins are useful photosensitizers for photodynamic therapy and thus one criterion for a good photosensitizer might be its conformational distortion. Crystal data – **3.** $C_{40}H_{46}N_4 \cdot CH_2Cl_2$, $M_r = 667.7$, triclinic, $P\bar{1}$, $a = 7.776(5)$ Å, $b = 8.556(4)$ Å, $c = 14.509(8)$ Å, $\alpha = 73.96(1)°$, $\beta = 82.04(2)°$, $\gamma = 82.58(2)°$, $V = 914.5(9)$ Å^3, $Z = 1$, $D_x = 1.212$ Mg/m^3, (MoKα) $\lambda = 0.71069$ Å, $\mu = 0.209$ mm^{-1}, $F(000) = 356$, 130 K, $R = 0.082$ for 2217 reflections with $I > 1.5\sigma(I)$. **Ni4.** $C_{44}H_{40}N_4NiO \cdot CH_2Cl_2$, $M_r = 770.4$, triclinic, $P\bar{1}$, $a = 11.283(3)$ Å, $b = 11.800(4)$ Å, $c = 15.871(7)$ Å, $\alpha = 79.28(3)°$, $\beta = 88.95(2)°$, $\gamma = 62.41(1)°$, $V = 1838.8(11)$ Å^3, $Z = 2$, $D_x = 1.391$ Mg/m^3, (MoKα), $\mu = 0.715$ mm^{-1}, $F(000) = 804$, 130 K, $R = 0.072$ for 5309 reflections with $I > 2.0\sigma(I)$. **Ni5.** $C_{46}H_{28}N_4NiO_2 \cdot CH_2Cl_2$, $M_r = 812.4$, triclinic, $P\bar{1}$, $a = 8.959(4)$ Å, $b = 14.420(7)$ Å, $c = 15.471(5)$ Å, $\alpha = 102.73(4)°$, $\beta = 101.83(4)°$, $\gamma = 92.01(5)°$, $V = 1901.3(14)$ Å^3, $Z = 2$, $D_x = 1.419$ Mg/m^3, (MoKα), $\mu = 0.679$ mm^{-1}, $F(000) = 836$, 130 K, $R = 0.059$ for 4197 reflections with $I > 1.75\sigma(I)$. **Ni7.** $C_{43}H_{45}N_4NiO_2 \cdot CH_2Cl_2$, $M_r = 793.5$, triclinic, $P\bar{1}$, $a = 8.948(3)$ Å, $b = 13.855(3)$ Å, $c = 15.451(3)$ Å, $\alpha = 82.43(2)°$, $\beta = 78.79(2)°$, $\gamma = 81.24(2)°$, $V = 1846.7(8)$ Å^3, $Z = 2$, $D_x = 1.427$ Mg/m^3, (CuKα) $\lambda = 1.54178$ Å, $\mu = 2.448$ mm^{-1}, $F(000) = 834$, 126 K, $R = 0.09$ for 4039 reflections with $I > 2.0\sigma(I)$. **Ni8.** $C_{42}H_{48}N_4NiO$, $M_r = 683.6$, monoclinic, $P2_1/n$, $a = 15.168(6)$ Å, $b = 14.796(3)$ Å, $c = 15.983(4)$ Å, $\beta = 97.17(3)°$, $V = 3552(2)$ Å^3, $Z = 4$, $D_x = 1.278$ Mg/m^3, (MoKα), $\mu = 0.584$ mm^{-1}, $F(000) = 1456$, 130 K, $R = 0.042$ for 5904 reflections with $I > 2.5\sigma(I)$.

Introduction

In recent years numerous studies have been performed on the structure and conformation of tetrapyrrolic pigments [1]. Main points of interest are the analysis of the conformational flexibility of the porphyrin macrocycle and the significant distortion that can be imposed by steric contraints, the central metal ion, and crystal packing effects [2–8]. Special attention has been given to the fact that non-planar porphyrins, derived by steric overload of the porphyrin periphery with bulky substituents, might serve as a model for the modulation of the physical properties of these pigments *in vivo* [9–13]. A distinct conformational nonplanarity of the chromophores is observed in the crystal structures of a bacterial photosynthetic antenna complex [14] and the photosynthetic reaction center [15]. Such flexibility has been observed also in a series of bacteriopheophorbide d derivatives [16] and compounds related to chlorophyll a [17, 18].

With their severe saddle-shaped conformation, Ni-porphyrins have attracted wide interest as

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* Reprint requests to Dr. M. O. Senge.

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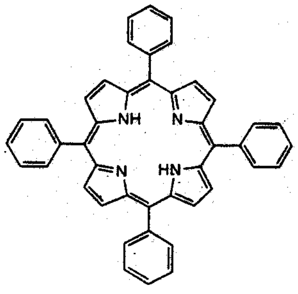
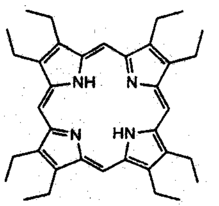
models for studies on conformationally distorted porphyrins [1]. Historically, X-ray structural analyses of Ni-porphyrins pointed first to the existence of non-planar conformations in porphyrins [19−21]. Biologically, Ni-porphyrins are related to the corrins of chromophore F430, involved in methanogenesis [6, 22−24].

Most of the structural analyses performed so far have been restricted to the use of "simple" porphyrin ligands such as tetraphenylporphyrin **1** or octaethylporphyrin **2.** The influence of one or two additional substituents at the *meso*-bridging carbons on the conformation of the central macrocycle has been studied in some detail in free-base porphyrins [25, 26] or porphyrins with an almost planar core [27, 28]. We were interested in the influence of additional *meso*-substituents on the conformation of Ni-porphyrins, which already have an S_4-ruffling induced by the Ni-ion. As the object of our study we have chosen derivatives of the tetrapentanoporphyrin **3** with one or two acrolein groups at neighboring *meso*-positions **4, 5** and the corresponding octaethylderivatives **6, 7.** Chromophores of this type might be useful as potential percursors for the synthesis of covalently linked porphyrin dimers by reductive coupling [29, 30], as model compounds for photosynthetic reaction centers, and as precursors for the preparation of benzochlorins. Benzochlorins such as **8** can be prepared by acid catalyzed cyclization of the acrolein side chain of *e.g.* **7** onto the adjacent pyrrole subunit *β*-position [30]. Due to their long-wavelength absorption maxima these types of chromophores have been shown to be important sensitizers for photodynamic therapy (PDT) of tumors [30−32]. PDT involves the selective retention of a photosensitizer in tumor tissue and its ability to be activated by penetrating light [33]. In order to investigate the influence of the different side groups on the core conformation of these model compounds we have undertaken a structural analysis of the compounds **3, Ni4, Ni5, Ni7,** and **Ni8,** a benzochlorin type porphyrin.



1



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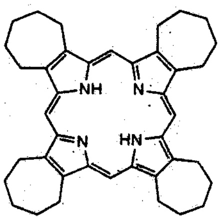

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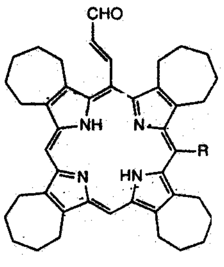
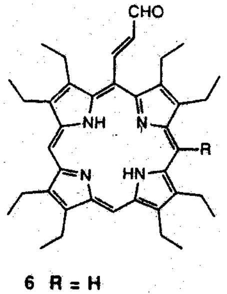
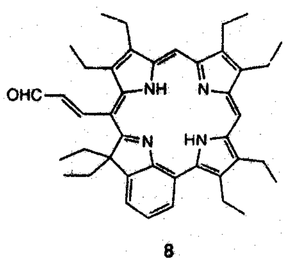


4 R = H
5 R = CH=CH-CHO



6 R = H
7 R = CH=CH-CHO



8

Experimental

All compounds were prepared and characterized as described previously [30].

Structure determination of 3

Red plates of **3** were grown by slow diffusion of a concentrated solution of the compound in methylene chloride into *n*-hexane. A single crystal (0.325×0.15×0.08 mm, D_x = 1.212 Mg/m³) was mounted on a Syntex P2_1 automatic diffractometer with a graphite monochromator and equipped with a locally modified Syntex LT-1 device. MoKα radiation (λ = 0.717 Å) was used. Cell parameters were determined from 18 reflections with 18° ≤ 2θ ≤ 23°. The compound ($C_{40}H_{46}N_4 \cdot CH_2Cl_2$, FW 667.7) crystallizes in the triclinic space group P$\bar{1}$ with the cell parameters: a = 7.776(5) Å, b = 8.556(4) Å, c = 14.509(8) Å, α = 73.69(2)°, β = 82.04(2)°, γ = 92.58(2)°, V = 914.4(9) Å³, Z = 1, F(000) = 356, μ = 0.209 mm^{-1}. The intensities were measured in the range 2θ = 0−55° at 130 K using the ω-scan technique; octants collected: $+/-h$, $+/-k$, $+l$. The data collection was performed using a constant scan speed of 3.97°/min in ω and a scan range of 1.4°. Two standard reflections were measured every 198 reflections and showed no significant variation in intensity during the data collection. Of the 4157 independent reflections collected 2217 were considered observed with $I > 1.5\sigma(I)$. The intensities were corrected for Lorentz and polarization effects. An absorption correction was applied using the Program XABS [34], extinction was disregarded. The structure was solved with direct methods using the SHELXTL PLUS program system, version 5 [35]. The refinement was carried out by full-matrix least-squares on F using the same program system. The function minimized was $\Sigma w(F_o - F_c)^2$. 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) except for the solvent molecule. Calculations were carried out on a Vax-station 3200. The final cycle of refinement on $|F|$ included 227 variable parameters and converged with R = 0.082, wR = 0.091 and S = 1.30. All nonhydrogen atoms were refined with anisotropic thermal parameters. The solvent molecule was refined with a total occupancy of 50% and the chloride atoms were treated as disordered over two positions with equal occupancy, each. The weighting scheme used was $w^{-1} = \sigma^2(F) + 0.0015\,F^2$. Largest Δ/σ 0.077, largest difference peak 0.56 eÅ^{-3}, largest difference hole −0.41 eÅ^{-3}. If not otherwise stated the same procedure was used for the determination of the other crystal structures.

Structure determination of Ni 4

$C_{43}H_{40}N_4NiO \cdot CH_2Cl_2$, FW = 793.5, dark blue plate, 0.6×0.4×0.22 mm, triclinic, P$\bar{1}$, a = 11.283(3) Å, b = 11.800(4) Å, c = 15.871(7) Å, α = 79.28(3)°, β = 88.95(2)°, γ = 62.41(1)°, V = 1838.8(11) Å^3, Z = 2, D_x = 1.391 Mg/m^3, μ = 0.679 mm^{-1}, F(000) = 836. Cell constants from 19 reflections with 22° ≤ 2θ ≤ 24°. Data collection at 130 K on a Siemens R3m/V diffractometer with MoKα radiation (λ = 0.7107 Å), 2θ range 0–55°, scan speed 29.30°/min, scan range 1.70°, ω-scan. Octants collected: $+/-h$, $+/-k$, $+l$, 8459 independent reflections of which 5309 were considered observed with $I > 2.0\sigma(I)$. Absorption correction according to ref. [34], extinction disregarded. Structure solution *via* Patterson synthesis. Atom C74 was treated as disordered over two positions (0.60, 0.40 occupancy), C52 was refined similarily with equal occupancy for the split positions. The solvent molecule was refined as disordered over two positions with occupancies of 0.7 and 0.3. The final cycle of refinement included 509 independent parameters and converged with R = 0.072, wR = 0.079, S = 1.36. H atoms were included using the riding model described for **3**. Weighting scheme $w^{-1} = \sigma^2(F) + 0.0008\,F^2$, Δ/σ 0.003, final difference Fourier synthesis: $-0.77 \leq \Delta\varrho \leq 0.67$ eÅ^{-3}.

Structure determination of Ni 5

$C_{46}H_{48}N_4NiO_2 \cdot CH_2Cl_2$, FW = 812.4, dark blue plate, 0.32×0.24×0.16 mm, triclinic, P$\bar{1}$, a = 8.959(4) Å, b = 14.420(7) Å, c = 15.471(5) Å, α = 102.73(4)°, β = 101.83(4)°, γ = 92.01(5)°, V = 1901.3(14) Å^3, Z = 2, D_x = 1.419 Mg/m^3, μ = 0.715 mm^{-1}, F(000) = 804. Cell constants from 21 reflections with 18° ≤ 2θ ≤ 21°. Data collection at 130 K on a Siemens R3m/V diffractometer with MoKα radiation (λ = 0.7107 Å), 2θ range 0–49°, scan speed 6.01°/min, scan range 2.10°, ω-scan. Octants collected: $+/-h$, $+/-k$, $+l$, 6336 independent reflections of which 4197 were considered observed with $I > 1.75\sigma(I)$. Absorption correction according to ref. [34], extinction disregarded. Structure solution *via* Patterson synthesis. The solvent molecule was refined with 50% occupancy. The final cycle of refinement included 502 independent parameters and converged with R = 0.0585, wR = 0.0506, S = 1.31. All atoms were refined with anisotropic thermal parameters. H atoms were included using the riding model mentioned for **3**. Weighting scheme $w^{-1} = \sigma^2(F) + 0.0002\,F^2$, Δ/σ 0.020, final difference Fourier synthesis: $-0.50 \leq \Delta\varrho \leq 0.52$ eÅ^{-3}

Structure determination of Ni 7

$C_{43}H_{45}N_4NiO_2 \cdot CH_2Cl_2$, FW = 793.5, red parallelpiped, 0.2×0.11×0.03 mm, triclinic, P$\bar{1}$, a = 8.948(3) Å, b = 13.855(3) Å, c = 15.451(3) Å, α = 82.43(2)°, β = 78.79(2)°, γ = 81.24(2)°, V = 1846.7(8) Å^3, Z = 2, D_x = 1.427 Mg/m^3, μ = 2.448 mm^{-1}, F(000) = 834. Cell constants from 22 reflections with 39° ≤ 2θ ≤ 64°. Data collection at 120 K on a Siemens P4/RA (rotating anode) diffractometer with CuKα radiation (λ = 1.54178 Å), 2θ range 0–108.5°, scan speed 29.30°/min, scan range $+/-2.00°$ plus Kα separation, $\theta-2\theta$ scan. Octants collected: $+/-h$, $+/-k$, $+l$, 4535 independent reflections of which 4039 were considered observed with $I > 2.0\sigma(I)$. Absorption correction according to ref. [34], extinction correction with $\chi = -0.0120(11)$, where $F^* = F[1+0.002\,\chi\,F^2/\sin(2\theta)]^{-1/4}$. Structure solution *via* Patterson synthesis. Atom C82 was treated as disordered over two positions (0.42, 0.58 occupancy), determined by refinement of occupancies, O1 was refined similarily to 0.73 and 0.27 occupancy for the split positions. The final cycle of refinement included 465 independent parameters and converged with R = 0.09, wR = 0.173, S = 0.70. Except for the disordered positions and the solvent molecule all non H atoms were refined with anisotropic thermal parameters. H atoms were included using the riding model mentioned above with U_{iso} = 1.2 times U of (non H atom). Weighting scheme $w^{-1} = \sigma^2(F) + 0.0664\ F^2$, Δ/σ 0.155, final difference Fourier synthesis: $-0.70 \leq \Delta\varrho \leq 1.19$ eÅ^{-3}.

Structure determination of **Ni8**

$C_{42}H_{48}N_4NiO$, FW = 683.6, dark blue hexagonal plate, 1.62×1.45×0.51 mm, monoclinic, $P2_1/n$, a = 15.168(6) Å, b = 14.796(3) Å, c = 15.983(4) Å, β = 97.17(3)°, V = 3552(2) Å^3, Z = 4, D_x = 1.278 Mg/m^3, μ = 0.584 mm^{-1}, F(000) = 1456. Cell constants from 18 reflections with $21° \leq 2\theta \leq 23°$. Data collection at 130 K on a Siemens R3m/V diffractometer with MoKα radiation (λ = 0.7107 Å), 2θ range 0–55°, scan speed 58.29°/min, scan range 1.80°, ω-scan. Octants collected: $+/-h$, $+k$, $+l$, 8204 independent reflections, of which 5904 were considered observed with $I > 2.5\sigma(I)$. Absorption correction according to ref. [34], extinction disregarded. Structure solution *via* Patterson synthesis. The final cycle of refinement included 434 independent parameters and converged with R = 0.0419, wR = 0.0597, S = 1.21. All non H atoms were refined with anisotropic thermal parameters. H atoms were included using the riding model mentioned for **3**. Weighting scheme $w^{-1} = \sigma^2(F) + 0.0015\ F^2$, Δ/σ 0.020, final difference Fourier synthesis: $-0.40 \leq \Delta\varrho \leq 0.38$ eÅ^{-3}.

Results and Discussion

Table I gives the atomic positional parameters for the 5-(2-formylvinyl)-Ni(II)TC$_7$P complex while Table II contains interatomic distances and angles for **Ni4**, **Ni5**, and **Ni7**. Figure 1 shows a view of the molecule with the numbering scheme.

Table I. Atomic coordinates [× 10^4] and equivalent isotropic displacement coefficients [A^2 × 10^3] for [5-(2-formylvinyl)-2:3,7:8,12:13,17:18-tetrapentanoporphyrinato]-nickel(II) **Ni4**.

Atom	x	y	z	U_{eq}*
Ni	148(1)	2690(1)	4387(1)	18(1)
N(21)	1189(3)	3560(3)	3988(2)	19(2)
N(22)	-421(3)	2879(4)	3210(2)	22(2)
N(23)	-945(3)	1875(3)	4787(1)	21(2)
N(24)	254(4)	2483(3)	5555(2)	20(2)
C(1)	1659(4)	4160(4)	4461(3)	21(2)
C(2)	2274(5)	4815(4)	3922(3)	21(2)
C(21)	2897(4)	5640(4)	4176(3)	27(2)
C(22)	4309(4)	5215(5)	3906(3)	28(2)
C(23)	4448(6)	5575(5)	2959(2)	33(3)
C(24)	4063(4)	4908(5)	2363(3)	31(3)
C(25)	2596(4)	5237(5)	2336(3)	32(3)
C(3)	2219(5)	4584(5)	3126(3)	26(2)
C(4)	1576(5)	3761(5)	3173(2)	22(2)
C(5)	1323(5)	3268(5)	2495(3)	26(2)
C(51)	2344(7)	2803(6)	1892(4)	49(3)
C(52)	3555(10)	2355(10)	1925(6)	26(5)
C(53)	4265(7)	1731(8)	1166(5)	76(4)
C(6)	201(5)	3053(5)	2482(2)	25(2)
C(7)	-516(6)	3060(5)	1725(3)	32(3)
C(71)	-248(5)	3372(6)	797(3)	47(4)
C(72)	-1474(6)	4322(6)	209(4)	70(4)
C(73)	-2419(7)	3818(9)	-11(4)	88(5)
C(74)	-3270(7)	3937(7)	750(4)	41(5)
C(75)	-2584(6)	2772(6)	1471(3)	53(4)
C(8)	-1562(6)	2881(6)	2008(3)	36(3)
C(9)	-1486(4)	2739(5)	2930(3)	27(2)
C(10)	-2269(5)	2355(5)	3456(3)	26(2)
C(11)	-1990(4)	1904(5)	4334(3)	22(2)
C(12)	-2633(4)	1277(5)	4865(3)	24(2)
C(121)	-3827(4)	1130(5)	4598(3)	31(2)
C(122)	-4676(4)	1594(5)	5176(3)	31(2)
C(123)	-4743(5)	792(5)	6072(3)	34(3)
C(124)	-3715(4)	811(5)	6663(3)	32(2)
C(125)	-2278(4)	108(5)	6429(3)	29(2)
C(13)	-1961(5)	823(4)	5643(3)	24(2)
C(14)	-908(5)	1196(4)	5593(2)	20(2)
C(15)	-64(5)	1016(5)	6273(3)	23(2)
C(16)	683(5)	1661(4)	6263(2)	23(2)
C(17)	1318(5)	1740(5)	7012(3)	28(2)
C(171)	1525(6)	908(5)	7893(2)	39(3)
C(172)	1120(5)	1633(6)	8633(3)	43(3)
C(173)	1995(6)	2236(5)	8810(3)	43(3)
C(174)	1798(6)	3429(5)	8164(3)	38(3)
C(175)	2378(5)	3171(6)	7309(3)	37(3)
C(18)	1694(5)	2680(5)	6765(3)	28(2)
C(19)	1357(4)	3133(4)	5849(3)	21(2)
C(20)	1713(5)	3975(5)	5337(3)	21(2)
O(1)	5546(8)	1435(8)	1237(5)	44(4)

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

The structure of the molecule is strikingly nonplanar and shows the typical S_4-ruffling of Ni porphyrins (Fig. 3). The saddle conformation is typical for non-planar Ni porphyrins and is characterized by an alternating displacement of the four *meso*-carbons above and below the nitrogen plane and a concomitant out-of-plane rotation of the pyrrole rings. In **Ni3** the *meso* carbons exhibit an average displacement of 0.59 Å from the nitrogen plane, and the pyrrole rings are tilted by an average of 17.5° out of the plane of the nitrogens. The average angle between neighboring pyrrole rings is 25.15°. The conformational distortion observed in

Table II. Selected bond lengths [Å] and bond angles [°] in the three acrolein substituted Ni porphyrins **Ni4**, **Ni5**, and **Ni7**. Averages are given for the core regions which are not appreciably influenced by the substitution pattern.

	Ni4	**Ni5**	**Ni7**
Ni−N	1.924(4)	1.916(4)	1.901(4)
$N-C_\alpha$	1.376(6)	1.377(6)	1.375(6)
$C_\alpha-C_\beta$	1.442(7)	1.447(7)	1.449(8)
$C_\beta-C_\beta$	1.349(7)	1.363(7)	1.371(8)
C(1)−C(20)	1.367(6)	1.363(7)	1.408(7)
C(4)−C(5)	1.400(8)	1.411(6)	1.410(8)
C(5)−C(6)	1.403(9)	1.409(6)	1.398(7)
C(9)−C(10)	1.376(8)	1.400(7)	1.407(7)
C(10)−C(11)	1.387(6)	1.412(7)	1.392(7)
C(14)−C(15)	1.373(7)	1.373(6)	1.377(7)
C(15)−C(16)	1.371(9)	1.386(7)	1.396(7)
C(19)−C(20)	1.372(8)	1.390(7)	1.369(6)
N−Ni−N adj	90.03(2)	90.03(2)	90.00(2)
N−Ni−N opp	178.4(1)	178.2(2)	178.7(2)
$Ni-N-C_\alpha$	127.3(3)	127.2(3)	126.9(3)
$N-C_\alpha-C_\beta$	110.4(4)	110.4(4)	110.4(4)
$N-C_\alpha-C_\alpha$	105.3(3)	105.6(4)	106.0(4)
$C_\alpha-C_\beta-C_\beta$	107.0(4)	106.7(4)	106.7(4)
N(21)−C(1)−C(20)	123.8(5)	124.1(5)	122.1(4)
C(2)−C(1)−C(20)	125.1(6)	125.8(4)	125.2(4)
N(21)−C(4)−C(5)	123.7(6)	122.9(4)	123.1(4)
C(3)−C(4)−C(5)	126.5(4)	127.1(5)	127.1(5)
C(4)−C(5)−C(6)	120.0(5)	120.7(4)	121.2(5)
N(22)−C(6)−C(5)	122.7(4)	121.8(4)	122.6(5)
C(5)−C(6)−C(7)	126.6(4)	127.6(5)	127.5(5)
N(22)−C(9)−C(10)	124.9(4)	123.6(4)	124.1(4)
C(8)−C(9)−C(10)	124.0(6)	125.1(4)	124.3(4)
C(9)−C(10)−C(11)	124.2(5)	120.2(4)	120.4(4)
N(23)−C(11)−C(10)	123.5(5)	122.6(4)	122.2(5)
C(10)−C(11)−C(12)	125.1(5)	127.0(4)	127.4(5)
N(23)−C(14)−C(15)	124.0(5)	123.6(4)	124.2(5)
C(13)−C(14)−C(15)	125.1(4)	125.2(5)	123.3(5)
C(14)−C(15)−C(16)	123.5(4)	124.0(5)	122.9(5)
N(24)−C(16)−C(15)	124.2(4)	124.1(4)	123.6(4)
C(15)−C(16)−C(17)	124.7(4)	124.3(5)	125.0(4)
N(24)−C(19)−C(20)	124.8(4)	122.8(4)	124.0(4)
C(18)−C(19)−C(20)	125.3(6)	125.5(4)	126.4(4)
C(1)−C(20)−C(19)	124.1(6)	124.6(4)	123.6(4)

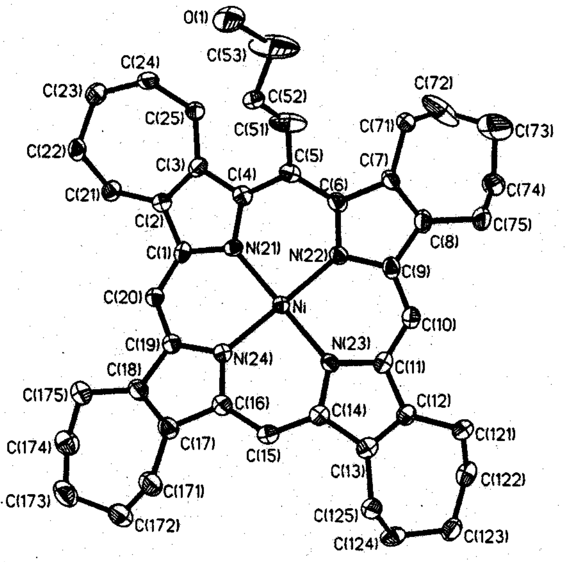


Fig. 1. View of the molecular structure of [5-(2-formylvinyl)-tetrapentanoporphyrinato]nickel(II) **Ni4**. Ellipsoids are drawn for 50% occupancy.

numerous Ni porphyrins [1] has been attributed to the fact that S_4-ruffling allows the ligand system to decrease the dimension of the inner coordination sphere and thus strengthen the coordinative bond with those metal ions, whose radius is too small for the coordination space of planar porphyrin ligands [2, 36].

While the overall pattern of conformational distortion is quite comparable to those of other known Ni tetrapyrroles, it is rather intriguing to note the effect of additional *meso* substituents. An acrolein substituent at C5 results in a localized increase in conformational distortion. Figure 10 shows the deviations of the macrocycle atoms from the least-squares-plane of the four nitrogen atoms in all complexes studied here. The unsubstituted *meso* carbons deviate by an average 0.52 Å from the mean plane while the carbon bearing the substituent is displaced by 0.77 Å. In NiOEP, which bears no additional *meso* substituents, the *meso* carbons are evenly displaced by 0.51 Å. A similar effect was observed in the structure of 5,5′-ethylenebis-(octaethylporphyrinato)nickel(II), which can be considered a mono-*meso* substituted NiOEP. While the non-substituted *meso* carbons are displaced 0.5 Å from the mean plane the carbon bearing the substituent shows a displacement of 0.82 Å [38].

This localized distortion in the macrocycle can also be seen in di-*meso* substituted porphyrins. Figure 2 shows the molecular structure of the $NiTC_7P$ **Ni4** bearing two acrolein groups at C5 and C10. Table III lists the atomic parameters; the respective bond lengths and angles are compiled in Table II.

The overall pattern of the molecular structure is about the same as that observed for the mono-substituted complex **Ni3**. The core is characterized by the Ni atom coordinated in a square planar fashion to the four pyrrole nitrogens. The average

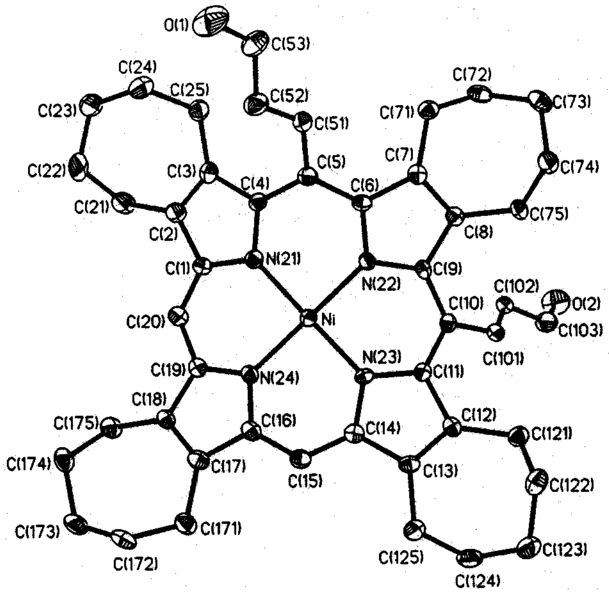


Fig. 2. View of the molecular structure of [5,10-di-(2-formylvinyl)-tetrapentanoporphyrinato]nickel(II) **Ni5**. Ellipsoids are drawn for 50% occupancy.

Ni−N bond length is 1.914 Å and is thus slightly shorter than in **Ni3**, where the average bond length is 1.924 Å. The small Ni(II) ion causes a considerably ruffled conformation of the macrocycle (Fig. 4). The macrocycle is much more distorted than in the corresponding mono-substituted complex. This is demonstrated by the angle between adjacent pyrrole rings of 28.9°, compared to 25.2° in **Ni3**, and an average angle between the pyrroles and the nitrogen plane of 20.4°, compared to 17.5° in **Ni3**. The mean displacement of the *meso* carbon is 0.72 Å in **Ni4** and 0.59 Å in **Ni3** (also see Fig. 10).

Although the introduction of a second bulky substituent at a *meso* position results in a generally more non-planar macrocycle, the effect of the sub-

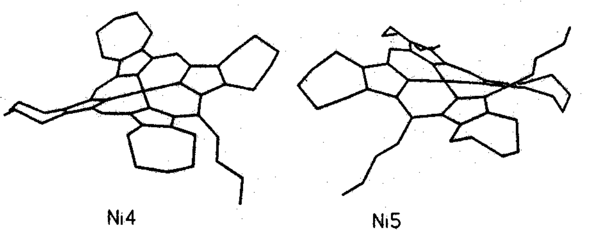


Fig. 3. Side view of the mono- and di-acrolein substituted Ni(II) tetrapentanoporphyrins **Ni4** and **Ni5**.

Table III. Atomic coordinates [× 10⁴] and equivalent isotropic displacement coefficients [Å^2 × 10^3] for [5,10-di-(2-formylvinyl)-2:3,7:8,12:13,17:18-tetrapentanoporphyrinato]nickel(II) **Ni5**.

Atom	*x*	*y*	*z*	U_{eq}*
Ni	8754(1)	9707(1)	6561(1)	20(1)
N(21)	8164(5)	8507(3)	6785(3)	24(2)
N(22)	10063(4)	10036(3)	7748(2)	21(2)
N(23)	9408(4)	10900(3)	6351(3)	21(2)
N(24)	7384(4)	9394(3)	5390(3)	22(2)
C(1)	6849(6)	7917(3)	6337(3)	23(2)
C(2)	6787(6)	7105(3)	6727(3)	29(2)
C(21)	5501(6)	6325(4)	6469(4)	42(2)
C(22)	6006(7)	5312(4)	6248(4)	48(2)
C(23)	6815(7)	4946(4)	7048(4)	52(3)
C(24)	8393(7)	5456(3)	7531(4)	43(2)
C(25)	8392(6)	6496(3)	7996(3)	33(2)
C(3)	8111(6)	7165(3)	7359(3)	26(2)
C(4)	8978(6)	8037(3)	7383(3)	22(2)
C(5)	10373(6)	8430(3)	7985(3)	26(2)
C(51)	11494(6)	7802(3)	8288(3)	30(2)
C(52)	11737(6)	6962(3)	7827(4)	36(2)
C(53)	12875(6)	6392(3)	8228(4)	38(2)
C(6)	10716(5)	9426(3)	8266(3)	22(2)
C(7)	11596(5)	9969(3)	9138(3)	22(2)
C(71)	12322(6)	9570(3)	9934(3)	26(2)
C(72)	12512(6)	10264(3)	10855(3)	30(2)
C(73)	13840(6)	11025(3)	11100(3)	34(2)
C(74)	13872(6)	11542(3)	10340(3)	34(2)
C(75)	12308(6)	11750(3)	9856(3)	30(2)
C(8)	11433(5)	10910(3)	9145(3)	23(2)
C(9)	10502(5)	10943(3)	8271(3)	19(2)
C(10)	10301(5)	11766(3)	7934(3)	21(2)
C(101)	10155(6)	12695(3)	8509(3)	26(2)
C(102)	9546(6)	12844(3)	9243(3)	26(2)
C(103)	9341(6)	13797(3)	9687(3)	38(2)
C(11)	10075(5)	11705(3)	6993(3)	20(2)
C(12)	10448(5)	12456(3)	6554(3)	22(2)
C(121)	11477(6)	13360(3)	7000(3)	28(2)
C(122)	12438(6)	13641(3)	6372(3)	35(2)
C(123)	11572(7)	14144(4)	5672(3)	44(2)
C(124)	10000(7)	13677(3)	5188(3)	39(2)
C(125)	9941(6)	12589(3)	4886(3)	32(2)
C(13)	9933(5)	12100(3)	5651(3)	23(2)
C(14)	9240(5)	11150(3)	5526(3)	22(2)
C(15)	8317(5)	10625(3)	4735(3)	26(2)
C(16)	7377(6)	9822(3)	4685(3)	25(2)
C(17)	6161(6)	9387(3)	3908(3)	27(2)
C(171)	5807(6)	9693(3)	3025(3)	33(2)
C(172)	5521(6)	8882(3)	2178(3)	33(2)
C(173)	4068(6)	8233(4)	2007(3)	40(2)
C(174)	4095(6)	7566(3)	2654(3)	35(2)
C(175)	4023(6)	8056(3)	3622(3)	32(2)
C(18)	5396(6)	8690(3)	4166(3)	24(2)
C(19)	6184(5)	8696(3)	5079(3)	21(2)
C(20)	5888(6)	8039(3)	5572(3)	25(2)
O(1)	13138(5)	5602(3)	7855(3)	63(2)
O(2)	8773(5)	14020(3)	10344(2)	55(2)

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

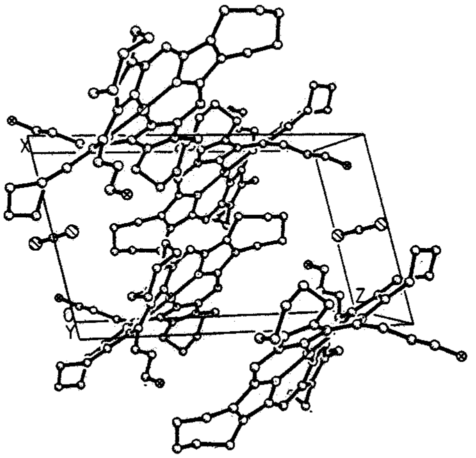


Fig. 4. View of the packing in the unit cell of [5,10-di-(2-formylvinyl)-tetrapentanoporphyrinato]nickel(II) **Ni5**.

stituents is mainly a localized displacement of the *meso* carbon involved. The two unsubstituted *meso* carbons are displaced by 0.55 Å while a value of 0.89 Å is found for C(5) and C(10) bearing the acrolein groups.

An example of how the NiTC$_7$P molecules pack in the unit cell is given for **Ni4** in Fig. 4. The compound crystallizes with one molecule of methylene chloride, situated on a crystallographic inversion point. The porphyrin macrocycles form layers of molecules with the acrolein side chains oriented into the space between the layers. The solvent molecules are situated in holes between neighboring layers. This prevents effectively any close contacts between the porphyrin macrocycles. Nevertheless, porphyrins in adjacent layers are oriented so that two of their pyrrole rings overlap. The effect of this π stacking is not very pronounced; no intermolecular contacts less than 4 Å are observed. The absence of close contacts also validates the interpretation of the conformational distortion in the compounds, described here as caused by the metal effect of the Ni(II) ion and steric effects imposed by the substituents and not due to packing effects in the crystal.

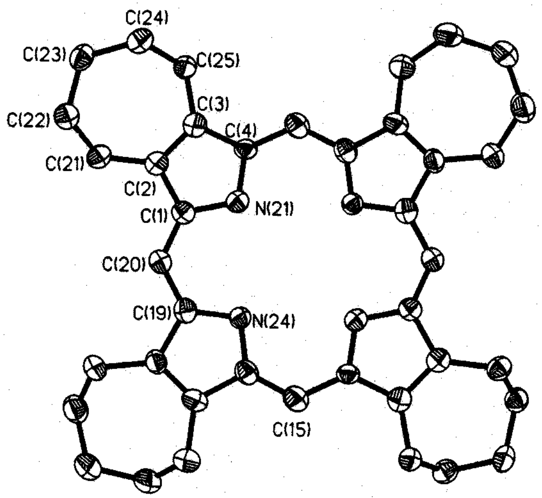


Fig. 5. The molecular structure of 2:3,7:8,12:13,17:18-tetrapentanoporphyrin **3**. Ellipsoids are drawn for 50% occupancy.

Table IV. Atomic coordinates [× 10^4] and equivalent isotropic displacement coefficients [Å^2 × 10^3] for tetra-

Atom	x	y	z	U$_{eq}$*
N(21)	2664(5)	6356(5)	− 410(3)	32(2)
N(24)	3960(5)	4317(5)	1378(3)	31(2)
C(1)	1180(7)	6414(6)	221(3)	33(2)
C(2)	− 149(7)	7416(6)	− 329(4)	33(2)
C(21)	−1993(7)	7770(6)	49(4)	36(2)
C(22)	−2558(7)	9593(7)	− 112(4)	39(2)
C(23)	−2777(7)	10511(7)	−1154(4)	40(2)
C(24)	−1122(7)	10658(7)	−1850(4)	40(2)
C(25)	− 277(7)	9071(6)	−2074(3)	36(2)
C(3)	605(7)	7935(6)	−1256(4)	34(2)
C(4)	2355(7)	7254(6)	−1307(3)	31(2)
C(15)	6390(7)	2615(7)	2135(4)	40(2)
C(16)	4714(7)	3353(7)	2162(4)	35(2)
C(17)	3541(7)	3203(7)	3039(4)	37(2)
C(171)	2603(8)	1274(8)	4663(4)	56(3)
C(172)	3978(8)	2305(8)	4026(4)	50(2)
C(173)	918(8)	2221(8)	4965(4)	54(3)
C(174)	− 242(8)	3000(8)	4181(4)	50(2)
C(175)	420(7)	4437(7)	3408(4)	45(2)
C(18)	2039(7)	4085(7)	2784(4)	34(2)
C(19)	2320(7)	4754(6)	1740(4)	34(2)
C(20)	1040(7)	5695(6)	1190(3)	34(2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U$_{ij}$ tensor.

For comparative purposes the structure of the corresponding parent porphyrin, 2:3,7:8,12:13,17:18-tetrapentanoporphyrin **3**, was determined. Figure 5 shows the molecular structure and Tables IV and V list the atomic coordinates, isotropic thermal parameters and selected bond lengths and angles, respectively. The compound crystallizes with one molecule of methylene chloride of solvation and with the porphyrin macrocycle situated on a crystallographic inversion point. The seven-membered rings are alternately displaced above and below the porphyrin plane

Table V. Bond lengths [Å] and angles [°] in the tetrapentanoporphyrin **3**.

N(21)–C(1)	1.375(6)	N(21)–C(4)	1.351(6)
N(24)–C(16)	1.363(6)	N(24)–C(19)	1.357(6)
C(1)–C(2)	1.436(7)	C(1)–C(20)	1.365(7)
C(2)–C(21)	1.486(7)	C(2)–C(3)	1.368(7)
C(21)–C(22)	1.526(8)	C(22)–C(23)	1.521(7)
C(23)–C(24)	1.517(7)	C(24)–C(25)	1.528(8)
C(25)–C(3)	1.496(7)	C(3)–C(4)	1.410(7)
C(4)–C(15A)	1.427(7)	C(15)–C(16)	1.374(8)
C(15)–C(4A)	1.427(7)	C(16)–C(17)	1.445(7)
C(17)–C(172)	1.488(7)	C(17)–C(18)	1.345(7)
C(171)–C(172)	1.515(8)	C(171)–C(173)	1.525(9)
C(173)–C(174)	1.505(8)	C(174)–C(175)	1.509(8)
C(175)–C(18)	1.494(7)	C(18)–C(19)	1.460(7)
C(19)–C(20)	1.391(7)		
C(1)–N(21)–C(4)	110.1(4)	C(16)–N(24)–C(19)	104.3(4)
N(21)–C(1)–C(2)	106.9(4)	N(21)–C(1)–C(2)	125.9(5)
C(2)–C(1)–C(20)	127.2(5)	C(1)–C(2)–C(21)	125.8(4)
C(1)–C(2)–C(3)	106.7(4)	C(21)–C(2)–C(3)	127.4(5)
C(2)–C(21)–C(22)	113.3(4)	C(21)–C(22)–C(23)	114.7(5)
C(22)–C(23)–C(24)	116.2(4)	C(23)–C(24)–C(25)	115.7(5)
C(24)–C(25)–C(3)	113.3(5)	C(2)–C(3)–C(25)	125.4(5)
C(2)–C(3)–C(4)	108.7(4)	C(25)–C(3)–C(4)	125.9(4)
N(21)–C(4)–C(3)	107.6(4)	N(21)–C(4)–C(15A)	123.9(4)
C(3)–C(4)–C(15A)	128.5(4)	C(16)–C(15)–C(4A)	126.8(5)
N(24)–C(16)–C(15)	124.7(5)	N(24)–C(16)–C(17)	111.9(4)
C(15)–C(16)–C(17)	123.3(5)	C(16)–C(17)–C(172)	125.7(5)
C(16)–C(17)–C(18)	106.4(4)	C(172)–C(17)–C(18)	127.9(5)
C(172)–C(171)–C(173)	115.5(5)	C(17)–C(172)–C(171)	116.1(5)
C(171)–C(173)–C(174)	115.7(5)	C(173)–C(174)–C(175)	116.1(5)
C(174)–C(175)–C(18)	116.3(5)	C(17)–C(18)–C(175)	129.2(5)
C(17)–C(18)–C(19)	105.7(4)	C(175)–C(18)–C(19)	124.9(4)
N(24)–C(19)–C(18)	111.7(4)	N(24)–C(19)–C(20)	124.7(4)
C(18)–C(19)–C(20)	123.6(5)	C(1)–C(20)–C(19)	128.2(5)

and assume the thermodynamically favored chair conformation. Similar conformations are observed for the cycloheptene rings in the corresponding Ni complexes **Ni3** and **Ni4**. Thus any possibility of steric strain from the bulky substituents is minimized. The macrocycle is essentially planar with a mean deviation from the plane of the four nitrogens of 0.012 Å (compare Fig. 10).

Figure 7 shows a view of the diacrolein-NiOEP **Ni7**. The unique 5,10-disubstitution pattern had earlier been predicted on the basis of proton and ^{13}C NMR studies [30]. Structural parameters for this compound are summarized in Tables VI and II. This molecule has the same substitution pattern as compound **Ni5**, with the exception that the substituents at the β-pyrrole carbons are not cyclized. The conformation is characterized by the same ring puckering as observed above. The Ni–N bond lengths have an average value of 1.901 Å and

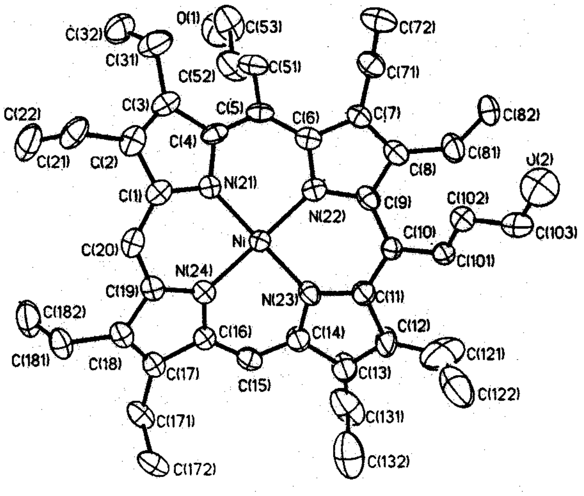


Fig. 6. The molecular structure of [2,3,7,8,12,13,17,18-octaethyl-5,10-di-(2-formylvinyl)-porphyrinato]nickel(II) **Ni7**. Ellipsoids are drawn for 50% occupancy.

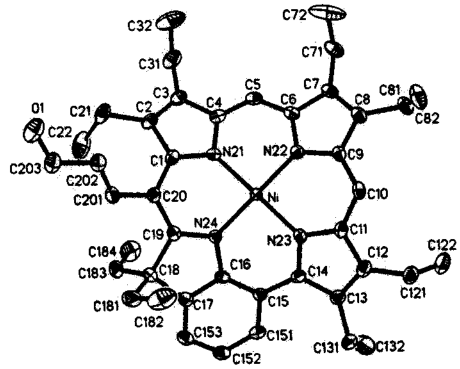


Fig. 7. View of the molecular structure of [20-(2-formylvinyl)-2,3,7,8,12,13,17,17-octaethylbenzochlorinato]-nickel(II) **Ni8**. Ellipsoids are drawn for 50% occupancy.

thus are somewhat shorter than in the corresponding $\mathrm{NiTC_7P}$. The mean displacement from the plane of the four nitrogen atoms are 0.79 Å for the *meso* carbons, 0.39 Å for C_a, and 0.31 Å for C_b. The macrocycle is thus more distorted than the ruffled form of NiOEP, where the relevant values are 0.51, 0.30, and 0.21 Å [37]. The non-planarity of the molecule is again best described by the angles between neighboring pyrrole rings, 35.8° and the angle between pyrrole rings and the nitrogen plane, 21.3°. In NiOEP these values are 14.2° and 28.4° [37]. **Ni7** thus shows much larger deviations from planarity and a concomitant larger out-of-plane rotation of the pyrrole rings compared to NiOEP (tetragonal form). As in the case of the $\mathrm{TC_7P}$ **Ni5** the two *meso* substituents results in an asymmetric displacement of the unsubstituted and substituted *meso* carbons. The mean displacement is 0.9 Å for carbons bearing an acrolein group, while the unsubstituted *meso* carbons are displaced by 0.55 Å from the nitrogen plane. This difference between substituted and unsubstituted *meso* carbons is thus much more pronounced for the OEP derivative than for the corresponding tetrapentanoporphyrins. This has to be due to the effect of ring closure at the *β*-substituents, which to a certain degree prevents the localized distortion in a given dipyrrole unit.

Table VI. Atomic coordinates [× 10^4] and equivalent isotropic displacement coefficients [$Å^2 \times 10^3$] for [2,3,7,8,12,13,17,18-octaethyl-5,10-di-(2-formylvinyl)-porphyrinato]nickel(II) **Ni7**.

Atom	*x*	*y*	*z*	U_{eq}*
Ni	2170(1)	4970(1)	1365(1)	28(1)
N(21)	924(4)	6177(3)	1575(3)	29(1)
N(22)	2242(5)	4725(3)	2594(3)	32(1)
N(23)	3434(5)	3755(3)	1175(3)	36(1)
N(24)	2143(5)	5236(3)	123(3)	30(1)
C(1)	− 67(5)	6707(3)	1056(3)	33(2)
C(2)	− 862(5)	7553(3)	1449(4)	42(2)
C(21)	−2073(5)	8252(3)	1038(4)	51(2)
C(22)	−1483(7)	9018(4)	363(4)	70(3)
C(3)	− 319(6)	7608(3)	2189(3)	38(2)
C(31)	− 820(7)	8384(3)	2832(4)	61(3)
C(32)	− 165(10)	9311(4)	2570(5)	83(4)
C(4)	838(6)	6723(3)	2270(3)	34(2)
C(5)	1641(6)	6410(4)	2978(3)	34(2)
C(51)	1972(7)	7181(4)	3483(4)	49(2)
C(52)	2997(9)	7729(5)	3189(5)	70(3)
C(53)	3411(4)	8430(3)	3682(5)	77(3)
C(6)	2204(5)	5422(4)	3165(3)	32(2)
C(7)	2673(6)	4950(4)	3973(3)	39(2)
C(71)	2886(5)	5416(4)	4768(3)	47(2)
C(72)	1490(6)	5597(5)	5435(3)	62(3)
C(8)	2840(6)	3958(4)	3914(3)	41(2)
C(81)	3520(7)	3205(4)	4587(3)	52(2)
C(82)	5099(8)	2744(8)	4309(7)	59(4)
C(9)	2575(6)	3833(4)	3058(3)	36(2)
C(10)	2924(6)	2938(3)	2679(3)	36(2)
C(101)	2466(7)	2045(4)	3215(3)	42(2)
C(102)	1266(7)	2035(4)	3884(3)	45(2)
C(103)	817(7)	1158(4)	4393(3)	63(3)
C(11)	3541(7)	2921(4)	1782(3)	47(2)
C(12)	4589(11)	2120(5)	1351(4)	93(3)
C(121)	5343(9)	1174(5)	1790(5)	107(4)
C(122)	4275(10)	534(7)	1643(5)	104(4)
C(13)	5247(9)	2548(5)	496(4)	77(3)
C(131)	6683(7)	2152(5)	− 123(4)	87(3)
C(132)	6043(10)	1529(6)	− 616(5)	101(4)
C(14)	4342(7)	3505(4)	393(4)	52(2)
C(15)	4306(6)	4055(4)	− 416(3)	43(2)
C(16)	3179(5)	4849(3)	− 546(3)	28(2)
C(17)	2834(5)	5283(3)	−1399(2)	32(2)
C(171)	3751(5)	5039(3)	−2295(3)	42(2)
C(172)	3292(7)	4200(4)	−2623(3)	52(2)
C(18)	1550(5)	5918(3)	−1228(3)	33(2)
C(181)	739(6)	6610(3)	−1887(3)	44(2)
C(182)	1346(8)	7557(4)	−2102(5)	68(3)
C(19)	1121(5)	5906(3)	− 275(3)	32(2)
C(20)	− 13(5)	6529(3)	174(3)	35(2)
O(1)	4613(7)	8802(6)	3439(5)	98(3)
O(2)	− 195(5)	1154(4)	5060(3)	80(1)

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

Acid-catalyzed cyclization of one of the acrolein side chains of **Ni7** leads to the formation of a benzene moiety at ring IV. The molecule thus obtained, **Ni8**, is formally a chlorin, *i.e.* has one "reduced" pyrrole ring. These compounds are therefore termed benzochlorins. The reduced character of ring IV becomes evident by comparison of the C(17)−C(18) bond lengths, 1.501 Å in the case of the benzochlorin and 1.341 Å in the corresponding diacrolein-porphyrin **Ni7**. The utility of compounds like this in PDT becomes evident by the large red shift in the red absorption band. The step from the diacrolein-porphyrin to the monoacrolein benzochlorin results in a 110 nm red shift of the long wavelength absorption band (Table IX) [30]. Ring closure of one of the acrolein sidechains in diacrolein-TC_7P to the corresponding benzochlorin results in a 68 nm shift.

The molecular structure of the Ni(II) benzochlorin **Ni8** is shown in Fig. 7. Table VII gives the atomic coordinates, and Table VIII lists the bond lengths and angles. As in the case of the other Ni porphyrins the molecule has a square-planar coordination about the Ni atom. The Ni−N bond lengths range from 1.898(2) to 1.923(2) Å with the longest bond length involving the N atom of ring III. Normally the reduced ring exhibits the longest Ni−N bond length [18, 39]. An explanation for this unusual behavior can be found in the presence of the benzene ring fused on to the reduced ring. This effectively prevents the formation of the typical half-chair conformation for reduced pyrroles in Ni-hydroporphyrins [2]. The mean deviation from planarity for the reduced ring is only 0.025 Å compared to 0.14 Å for the other pyrrole rings. The effect of the fused benzene ring can also be seen in the aromatic character of the C(16)−C(17) bond with a length of 1.397 Å compared to 1.548 Å for the C(18)−C(19) bond.

Table VII. Atomic coordinates [× 10^4] and equivalent isotropic displacement coefficients [$Å^2 \times 10^3$] for [20-(2-formylvinyl)-2,3,7,8,12,13,17,17-octaethylbenzochlorinato]nickel(II) **Ni8**.

Atom	*x*	*y*	*z*	U_{eq}*
Ni	6902(1)	86(1)	1075(1)	15(1)
N(21)	6093(1)	118(1)	1890(1)	19(1)
N(22)	6149(1)	869(1)	362(1)	18(1)
N(23)	7125(1)	24(1)	243(1)	19(1)
N(24)	7637(1)	− 706(1)	1790(1)	18(1)
C(1)	6246(2)	− 90(2)	2726(2)	20(1)
C(2)	5407(2)	− 97(2)	3093(1)	24(1)
C(21)	5225(2)	− 400(2)	3959(1)	33(1)
C(22)	5462(3)	−1378(2)	4159(2)	56(1)
C(3)	4761(1)	102(2)	2453(2)	24(1)
C(31)	3769(1)	163(2)	2481(2)	36(1)
C(32)	3482(2)	1075(2)	2783(3)	59(1)
C(4)	5179(2)	283(2)	1715(2)	21(1)
C(5)	4787(2)	679(2)	996(2)	22(1)
C(6)	5263(2)	1029(2)	382(1)	20(1)
C(7)	4931(1)	1658(2)	− 267(2)	24(1)
C(71)	3975(1)	1965(2)	− 463(2)	32(1)
C(72)	3771(2)	2791(2)	64(3)	70(2)
C(8)	5633(2)	1912(2)	− 659(1)	24(1)
C(81)	5633(2)	2579(1)	−1370(1)	31(1)
C(82)	6124(2)	3450(2)	−1066(2)	43(1)
C(9)	6383(2)	1406(2)	− 282(1)	20(1)
C(10)	7202(2)	1364(2)	− 564(1)	23(1)
C(11)	7819(2)	698(2)	− 343(1)	21(1)
C(12)	8549(2)	491(2)	− 793(2)	24(1)
C(121)	8894(2)	1100(2)	−1433(2)	29(1)
C(122)	8415(2)	1020(2)	−2326(2)	39(1)
C(13)	8851(2)	− 342(2)	− 529(2)	24(1)
C(131)	9610(2)	− 833(2)	− 861(2)	33(1)
C(132)	9295(2)	−1460(2)	−1587(2)	55(1)
C(14)	8327(2)	− 617(2)	122(1)	20(1)
C(15)	8493(2)	−1368(2)	689(1)	19(1)
C(151)	9014(2)	−2131(2)	528(2)	23(1)
C(152)	9327(2)	−2729(2)	1156(2)	26(1)
C(153)	9159(2)	−2595(2)	1987(2)	26(1)
C(16)	8231(2)	−1321(2)	1499(1)	18(1)
C(17)	8600(2)	−1894(2)	2144(2)	23(1)
C(18)	8317(1)	−1585(2)	2964(1)	24(1)
C(181)	9129(2)	−1252(2)	3537(2)	38(1)
C(182)	9522(2)	− 367(2)	3276(2)	51(1)
C(183)	7863(2)	−2353(2)	3381(2)	33(1)
C(184)	7081(2)	−2796(2)	2854(2)	44(1)
C(19)	7658(2)	− 830(2)	2631(1)	19(1)
C(20)	7079(2)	− 398(20)	3120(1)	21(2)
C(201)	7335(2)	−2877(2)	4017(2)	24(1)
C(202)	7094(2)	412(2)	4473(2)	25(1)
C(203)	7327(2)	449(2)	5377(2)	31(1)
O(1)	7042(1)	1003(2)	5840(1)	40(1)

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

The molecule shows the typical S_4-ruffling of the macrocycle (Fig. 8). This becomes evident in the large angles between neighboring pyrroles. The respective values are: 25.8°, 27.2°, 30.3°, 34.7°, and 42.5°. These are fairly large angles for nonplanar Ni tetrapyrroles, *e.g.* the corresponding angles in Ni(II) tetramethylchlorin are 21.7 to 28.6° [39].

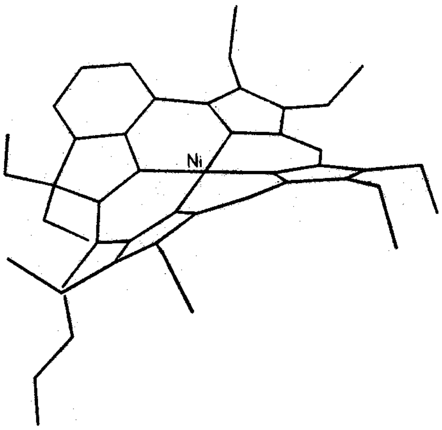


Fig. 8. Side view of the [20-(2-formylvinyl)-2,3,7,8,12,13,17,17-octaethylbenzochlorinato]nickel(II) molecule **Ni8**.

Table VIII. Bond lengths and bond angles [°] in [20-(2-formylvinyl)-2,3,7,8,12,13,17,17-octaethylbenzochlorinato]-nickel(II) **Ni8** [Å].

Ni−N(21)	1.898(2)	Ni−N(22)	1.903(2)
Ni−N(23)	1.923(2)	Ni−N(24)	1.899(2)
N−C_α unsat	1.377(3)	N−C_α sat	1.377(3)
C_α−C_β unsat	1.427(4)	C_α−C_β sat	1.473(4)
C_β−C_β unsat	1.358(3)	C_β−C_β sat	1.501(3)
C(1)−C(20)	1.414(3)	C(4)−C(5)	1.359(3)
C(5)−C(6)	1.389(3)	C(9)−C(10)	1.376(4)
C(10)−C(11)	1.375(3)	C(14)−C(15)	1.435(3)
C(15)−C(16)	1.404(3)	C(19)−C(20)	1.402(3)
N−Ni−N adj	90.0(1)	N−Ni−N opp	178.9(1)
Ni−N−C_α	126.9(2)	N−C_α−C_β unsat	110.3(2)
N−C_α−C_β sat	111.7(2)	N−C_α−C_α sat	105.6(2)
N−C_α−C_α unsat	107.8(2)	C_α−C_β−C_β	106.9(2)
C(2)−C(1)−C(20)	126.2(2)	N(21)−C(4)−C(5)	124.1(2)
C(3)−C(4)−C(5)	125.8(2)	C(4)−C(5)−C(6)	123.2(2)
N(22)−C(6)−C(5)	123.3(2)	C(5)−C(6)−C(7)	125.9(2)
N(22)−C(9)−C(10)	123.1(2)	C(8)−C(9)−C(10)	126.1(2)
C(9)−C(10)−C(11)	124.2(2)	N(23)−C(11)−C(10)	123.6(2)
C(10)−C(11)−C(12)	124.8(2)	N(23)−C(14)−C(15)	121.4(2)
C(13)−C(14)−C(5)	127.1(2)	N(24)−C(16)−C(15)	127.4(2)
C(15)−C(16)−C(17)	121.1(2)	N(24)−C(19)−C(18)	112.0(2)
N(24)−C(19)−C(20)	123.6(2)	C(18)−C(19)−C(20)	124.0(2)
C(1)−C(20)−C(19)	119.0(2)		

The large value of 42.5° between the pyrrole rings III and IV, is due to the effect of the fused benzene ring which tends to increase the steric strain on this part of the molecule. The benzene ring itself is planar with a deviation of 0.035 Å from planarity. Figure 9 shows the packing in the unit cell, which is characterized by the formation of closely spaced layers of macrocycles. The acrolein groups of neighboring molecules are oriented toward each other to minimize the space required for a single molecule; nevertheless there are no unusual short intermolecular distances less than 4 Å.

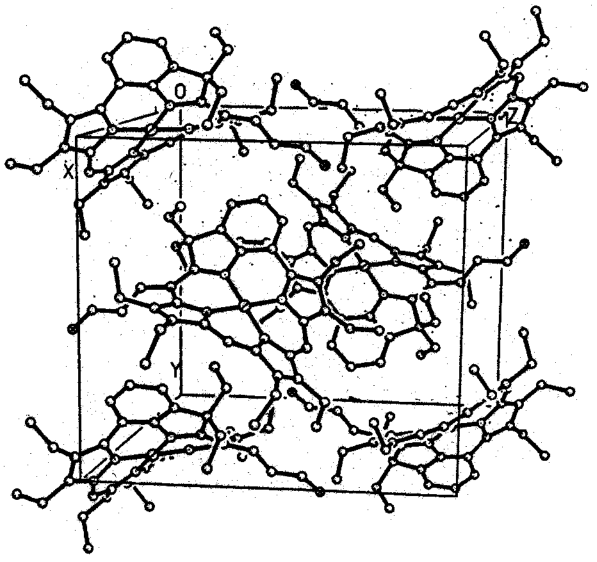


Fig. 9. View of the unit cell of [20-(2-formylvinyl)-2,3,7,8,12,13,17,17-octaethylbenzochlorinato]nickel(II) **Ni8**.

The degree of non-planarity does not differ from that observed in the Ni(II) diacrolein-OEP (Fig. 10). The puckering of the molecule as described by the mean deviation from the plane of the four *meso*-carbons is 0.78 Å for the benzochlorin and 0.79 Å for the diacrolein-OEP. Nevertheless, the conformational distortion is more evenly distributed in the benzochlorin. The values of displacement of the *meso*-carbons from the nitrogen plane are −0.75, 0.74, −0.84, and 0.78 for the benzochlorin while in the di-*meso* substituted compound **Ni7** the respective values are 0.89, −0.9, 0.51, and −0.59 Å, with the larger deviations observed for the substituted *meso*-carbons. The fused benzene ring seems to prevent a localized distortion of parts of the molecule in order to release the steric strain imposed by the substituents. Rather the distortion is evenly distributed over the whole macrocycle in the benzochlorin.

A general comparison of the conformational distortion of the tetrapyrroles studied here is shown in Fig. 11, which displays the skeletal deviations from the mean nitrogen plane. All Ni complexes show a high degree of ring puckering with

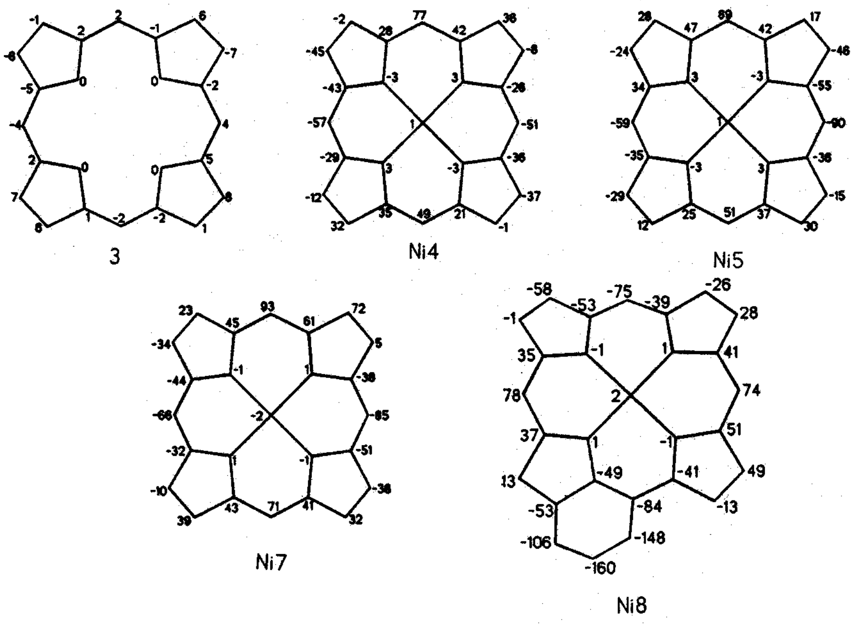


Fig. 10. Displacement of the macrocycle atoms from the least square plane of the four nitrogen atoms.

concomitant rotation of the single pyrrole rings out of the mean plane of the molecule. The effect of the *meso* substituents can easily be seen by the larger displacement of the substituted *meso*-carbons, compared with the unsubstituted ones. This effect can be illustrated very well by inspection of the relevant $C_a-C_m-C_a$ bond angles. In the free-base porphyrin **3** this angle is 127.5°. The introduction of Ni into the macrocycle leads to an average value of 124.3° for the unsubstituted *meso* carbons in the Ni tetrapentanoporphyrins and of 120.3° for the substituted *meso* carbons. The smaller values are in accord with the increased steric strain on these parts of the macrocycle. In the disubstituted NiOEP **Ni7** the mean bond angle for unsubstituted carbons is 123.3° compared to 120.8° for substituted ones. In contrast the Ni benzochlorin **Ni8** shows a more even distribution of the conformational distortion due to the influence of the fused benzene ring.

Table IX lists the absorption maxima of the compounds studied. It is apparent that increasing substitution at the *meso* positions induces a shift in the absorption maxima toward longer wavelengths. Since the substitution is directly correlated

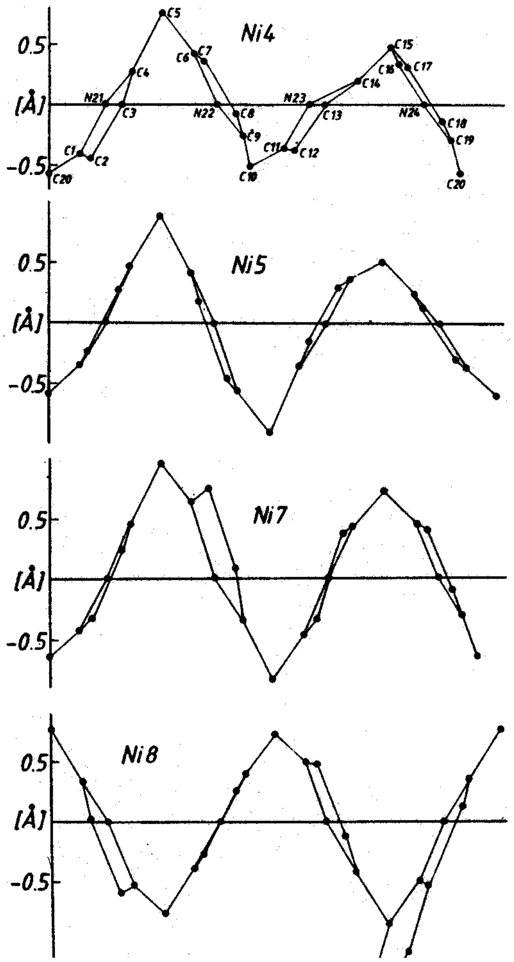


Fig. 11. Linear display of the deviations of the macrocycle atoms from a plane defined by the four nitrogen atoms.

Table IX. Main absorption maxima in methylene chloride of some of the compounds investigated [nm].

Compound	Absorption maxima	
Ni 4	542	608
Ni 5	478	640
Ni 6	406	582
Ni 7	458	616
Ni 8	444	726

with the degree of non-planarity in the molecules it is obvious that the bathochromic shift correlates with the conformational distortion of the macrocycle in question. For dodecasubstituted porphyrins it has been shown by INDO/s calculations that ring puckering results in destabilization of the π system and raising of the HOMO resulting in a smaller energy gap between HOMO and LUMO and a concomitant red shift of the absorption band [16]. Pigments with long wavelength absorption maxima are potentially suitable for photodynamic therapy, because light of longer wavelengths penetrates tissue farther and thus allows better treatment of larger tumors. Besides questions of membrane transport, uptake, and solubility, one of the requirements for a good photosensitizer in PDT is thus a molecule with a high degree of conformational distortion, allowing for red-shifted absorption bands. Since it has been shown that dimers generally are better compounds for PDT than the corresponding monomers [33], useful candidates for further studies should be dimers which are comprised of a monomer with a highly distored macrocycle as described here and another one bearing functional groups enhancing the solubility and membrane transport properties of the photosensitizer.

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Details of all structure determinations can be obtained on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-W-7514 Eggenstein-Leopoldshafen, Germany, by quoting the deposit number CSD 56239, the authors and the journal citation.

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