# Synthesis of a Bisdienophilic Phthalocyanine and of Precursors for Repetitive Diels-Alder Reactions Based on Hemiporphyrazines and Phthalocyanines

**Patrick Stihler, Bernd Hauschel, and Michael Hanack***

Institut für Organische Chemie, Universität Tübingen,
Auf der Morgenstelle 18, D-72076 Tübingen, Germany
Fax: (internat.) +49(0)-7071/295244
E-mail: hanack@uni-tuebingen.de
WWW: http://www.uni-tuebingen.de/hanack/index.html

Received November 14, 1996

**Keywords:** Unsymmetrical phthalocyanines / Hemiporphyrazines / Macrocyclic bisdienes and bisdienophiles / Diels-Alder reactions / Ladder polymers / Cycloaddition / Macrocycles

---

The specific synthesis of a metal-free bisdienophilic phthalocyanine **3**, suitable for repetitive Diels-Alder reactions, is reported. This was achieved by condensation of 1,3,3-trichloro-6/7-nitroisoindolenine (**1**) and 4,9-dibutoxy-2,3,5,8-tetrahydro-1,3-diimino-1*H*-5,8-epoxybenz[*f*]isoindoline (**2**). The ability of **3** to undergo Diels-Alder reactions was tested by reaction with an excess of 1,2,3,4-tetraphenylcyclopentadienone (**5**). Experimental data of the hemiporphyrazines **9**, **10**, and **11**, which can be used as precursors for the synthesis of ladder polymers, are also given in the Experimental Section.

---

## Introduction

Some conjugated ladder polymers show, in addition to high thermal and chemical stability, nonlinear optical properties and electrical conductivity[1]. MO calculations based on extended Hückel theory indicate that a fully conjugated, planar metallophthalocyanine polymer should exhibit intrinsic conductivity[2]. To date, the best method of obtaining conjugated ladder polymers with high structural regularity has been the repetitive Diels-Alder reaction[3]. The monomers used for such a reaction also allow the stepwise synthesis of defined oligomers. Suitable macrocyclic monomers for a repetitive Diels-Alder reaction are, for example, hemiporphyrazines (Hps) and phthalocyanines (Pcs), which contain two opposite-faced dienophilic fragments (compare **3** and **7** in Schemes 1 and 3a)[4]. The Hp system is more easily accessible than the corresponding Pc system[5] because the starting compounds in a typical Hp synthesis – a substituted diiminoisoindoline and an aromatic diamine, e.g. 2,6-diaminopyridine – mainly form the corresponding hemiporphyrazine, e.g. **7**. However, Hps show instability towards strong protonic acids due to their imine-like nature.

Some Diels-Alder monomers based on Hps that can be used as bisdienes, bisdienophiles, and diendienophiles have previously been synthesized[4b,4c,6]. We have reported the preparation of ladder-type oligomers from such monomers by performing subsequent Diels-Alder reactions[4e,6]. Pcs could be likewise employed in a similar approach. Their major advantage compared to the Hps is their higher chemical stability arising from the fully delocalized 18-$\pi$ electron system. Pcs such as **3** have hitherto only been accessible by the statistical condensation of equimolar amounts of two differently substituted phthalodinitriles or diiminoisoindolines (**A**) and (**B**)[7]. During such a synthesis, all possible combinations (**AAAA**, **AAAB**, **AABB**, **ABAB**, **ABBB**, **BBBB**) are generally formed[7c]. The separation of these products by common chromatographic methods is not easy due to their tendency to form aggregates[8,9]. Normally, the desired **ABAB** phthalocyanine ($D_{2h}$ symmetry) is obtained in less than 5% yield after separation. One method of reducing the number of possible combinations is to attach bulky substituents such as phenyl groups at the 3,6- or 3,4,5,6-positions of reacting component **B** (as phthalodinitrile or diiminoisoindoline), e.g. to use 3,6-diphenylphthalodinitrile or 3,4,5,6-tetraphenylphthalodinitrile[7,10].

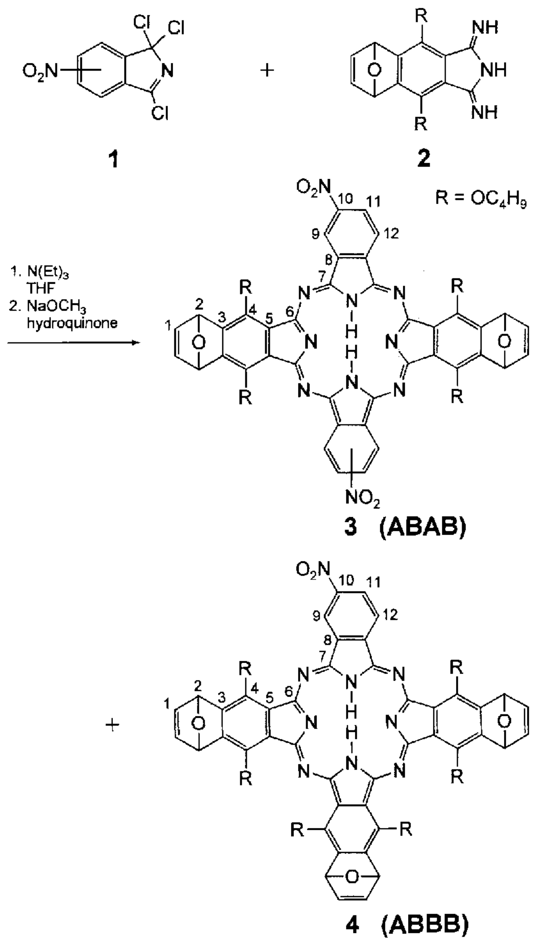
Herein, we present a more direct method for the synthesis of bisdienophilic Pcs such as **3** (**ABAB**). The obtained yields of the desired bifunctional Pcs are much higher than those achievable using the statistical approach. Moreover, the isolation of **3** is easier compared with the separation of a statistical mixture, since only one additional Pc (compare Scheme 1) is formed as a minor by-product.

We also report on the preparation of Pc **6** (Scheme 2), which is a precursor for a reactive bisdiene. We have recently prepared similar reactive bisdienes starting from Hps **9**, **10**, and **11**[6a]. For example, when **9** was refluxed in toluene (Scheme 3a, 3b) loss of CO and 1,2,3,4-tetraphenylbenzene (TPB) occurred, leading to an isobenzofuran derivative[6a]. A similar in-situ generated intermediate from **6** could be trapped in the presence of dienophiles (e.g. **3**)[6a,11].

## Results and Discussion

The synthesis of the **ABAB**-type Pc **3** was accomplished by a cross-condensation of the diiminoisoindoline **2** with an equimolar amount of 1,3,3-trichloro-6/7-nitroisoindolenine **1** (Scheme 1), following a procedure first reported by Young and Onyebuagu[12]. **1** was obtained by chlorination of 4-nitrophthalimide with $PCl_5$ in *o*-dichlorobenzene[12]. The diiminoisoindoline **2** was synthesized by treating the corresponding phthalodinitrile with ammonia and sodium in methanol[4b]. The cross-condensation of **1** and **2** was carried out in dry THF in the presence of triethylamine at 0–20°C.

Scheme 1. Reaction of diiminoisoindoline **2** with **1**



As mentioned above, the statistical condensation of two differently substituted diiminoisoindolines generally furnishes six Pcs. However, the condensation of **1** and a substituted diiminoisoindoline should give only the **ABAB**-type Pc. The reason for the exclusive formation of a single Pc is that **1** cannot undergo self-condensation, while self-condensation of **2** is clearly suppressed because of the low reaction temperature (0–20°C) used.

In contrast to the reported results with 1,3,3-trichloro-6/7-nitroisoindolenine and monoaryloxy- or monoalkyloxy-substituted diiminoisoindolines [e.g. 6-(*p*-*tert*-butylphenoxy)-, 6-(*p*-cumylphenoxy)-, and 6-isobutoxy-1,3-dihydro-1,3-diiminoisoindolines][12], we obtained two macrocyclic condensation products **3** (**ABAB**) and **4** (**ABBB**) (Scheme 1). However, Pc **3** was the major product (**3**/**4** ≈ 92%:8%). The formation of **4** may have been due to traces of water in the reaction mixture, resulting in partial hydrolysis of **1**. A slight loss of **1** in this way would upset the stoichiometric balance of **1** and **2**, and under conditions where **2** was in excess, the formation of Pc **4** as a by-product would be expected.

The separation of **3** and **4** was carried out using HPLC for analytical purposes and by preparative thin-layer chromatography (PTLC).

The HPLC method allows not only a separation of **3** and **4**, but also a partial separation of the constitutional isomers of **3**. Pc **3** should be present as a mixture of four isomers due to the possible *syn* or *anti* orientations of the epoxy bridges and the different positions of the nitro substituents. The presence of such constitutional isomers is confirmed by HPLC and by NMR spectroscopy.

The $^1$H-NMR spectrum of pure **3** exhibits two broad signals due to the NH protons at very high field ($\delta$ = −6.15 and −5.75). The NH protons exist in two different positions relative to the four nitrogen atoms of the porphyrazine system. Due to the non-equivalence of the neighbouring pyrrole rings, two signals can be seen. The resonances of 1-H and 2-H appear as singlets at $\delta$ = 7.24, 7.25, 7.38 and $\delta$ = 6.15, 6.17, 6.30, respectively. The apparent multiplets are in fact overlapped singlets. This was evident from the 400 MHz $^1$H-NMR spectrum. The resonances of 11-H and 12-H of **3** appear as multiplets due to the presence of constitutional isomers, but also due to the ABX spin system. The signal of 9-H appears as three resonances ($\delta$ = 8.80, 8.87, and 8.94), owing to the presence of the aforementioned isomers (Figure 1a). The resonances of the OCH$_2$ protons form a multiplet at $\delta$ = 4.45. This multiplet is due to the diastereotopy of the OCH$_2$ protons and the existence of four constitutional isomers. The OCH$_2$ protons are magnetically non-equivalent and form an ABX$_2$ spin system with the adjacent CH$_2$ protons. The existence of four constitutional isomers is also evident from the $^{13}$C-NMR spectrum. For example, the methyl groups of the butyloxy side-chains are seen as four discrete signals.

The $^1$H-NMR spectrum of **4** also shows a multiplet due to the OCH$_2$ protons and multiplets due to 1-H and 2-H (at $\delta$ = 7.34–7.39 and $\delta$ = 6.36–6.52, respectively). An obvious difference between **3** and **4** is seen in the different couplings and shapes of the multiplets due to 9-H, 11-H, and 12-H (Figure 1).

The UV/Vis spectra of **3** and **4** (recorded in chloroform) show the typical phthalocyanine pattern with the Q-bands at 723.5 nm and 734.5 nm, respectively. Mainly the π-π* transitions of the 18-π electron system are seen. The Q-band of **4** shows a bathochromic shift (Figure 2) compared to **3**, due to the different substitution patterns.

The Diels-Alder reaction of the bisdienophilic phthalocyanine **3** with 2.5 equiv. of 1,2,3,4-tetraphenylcyclopentadienone (**5**), in toluene at 65°C under nitrogen atmosphere, afforded the bisadduct **6** (yield 59%) (Scheme 2). The reaction was monitored by TLC (silica gel, CHCl$_3$).

The bisadduct **6** was obtained as a mixture of at least four constitutional isomers since the starting material **3** consisted of an isomeric mixture. It has been reported that only *exo* attack occurs during the addition of tetracyclone to 1,4-epoxynaphthalene[13]. This was also confirmed in the case of the Hps **9**, **10**, and **11**[6a]. The $^1$H-NMR spectrum of **6** shows broad signals and no clear multiplicity could be recognized. This is due to aggregation phenomena of **6** in

Figure 1. Multiplets of the aromatic protons in the $^1$H-NMR spectra of a) Pc **3** ($CD_2Cl_2$), b) Pc **4** ($CDCl_3$)

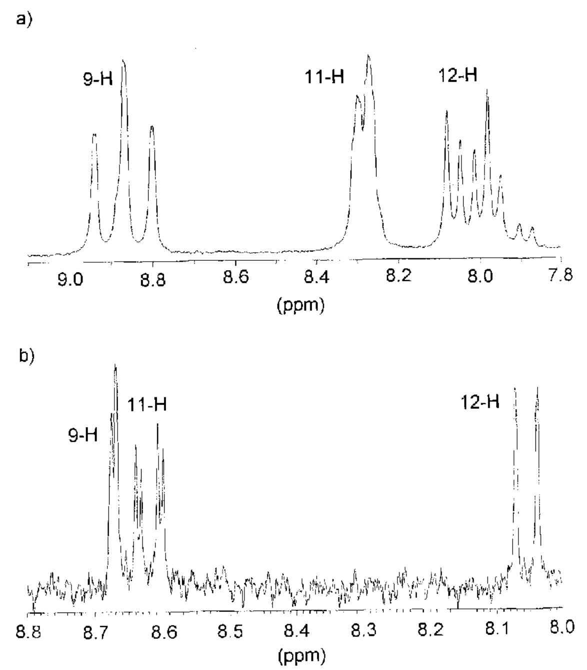
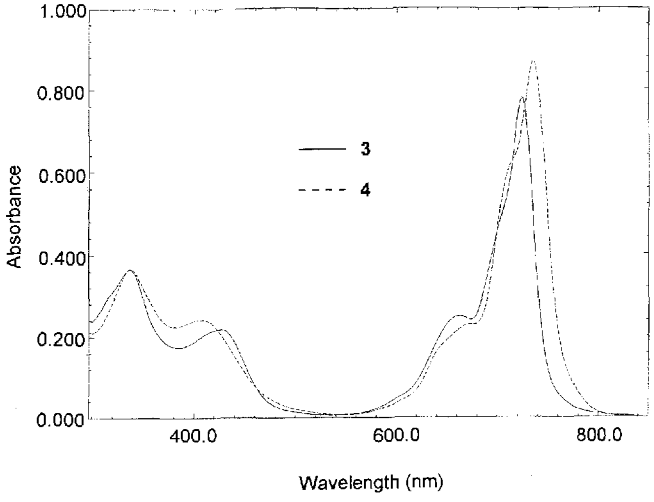
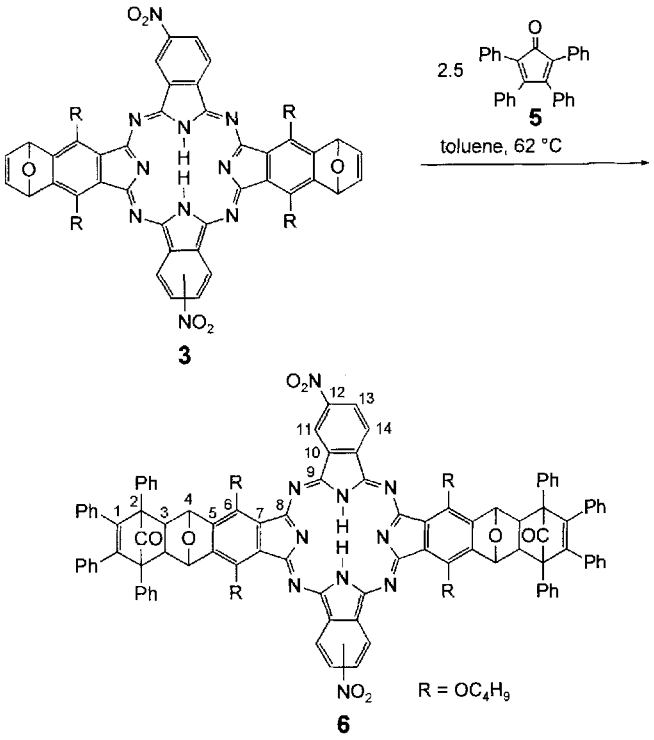


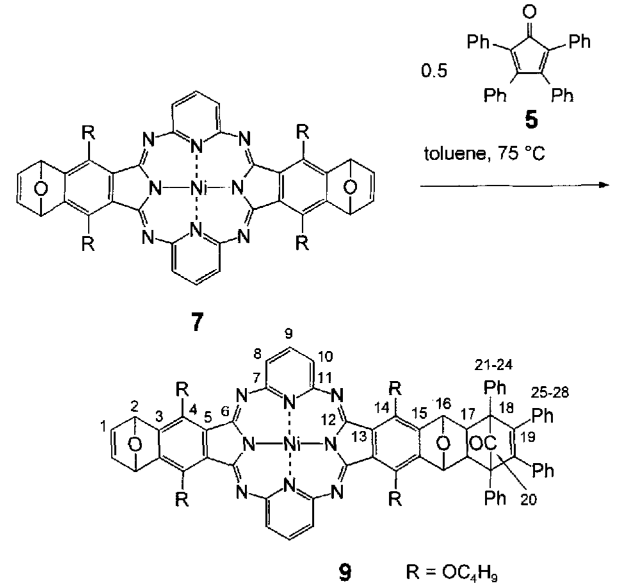
Figure 2. UV/Vis spectra of **3** and **4** in chloroform ($c = 10^{-5}$ mol l$^{-1}$)



Scheme 2. Reaction of Pc **3** with excess tetracyclone **5**



Scheme 3a. Synthesis of the HpNi complex **9**



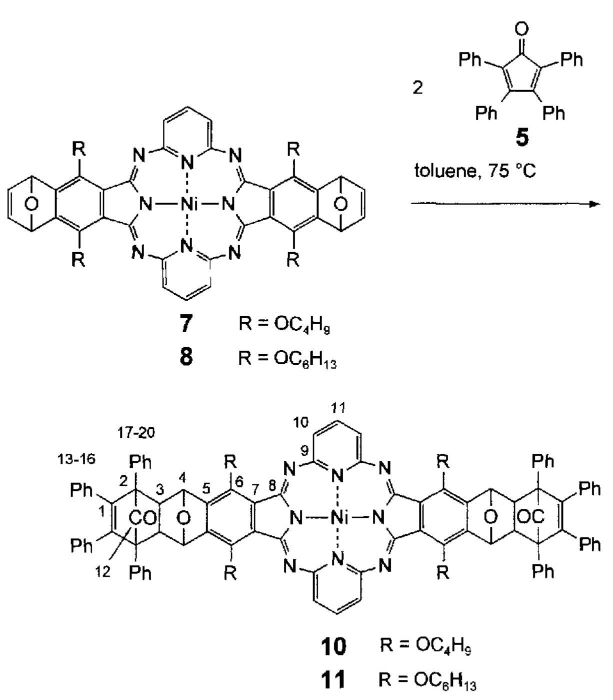
solution. To increase the resolution of the signals, $^1$H-NMR spectra were measured at elevated temperatures. The thermal instability of **6** limited the temperature to 60°C. At temperatures higher than 80°C, **6** starts to lose CO and 1,2,3,4-tetraphenylbenzene, resulting in the formation of reactive intermediates (isobenzofuran derivatives), which will be the starting materials for further Diels-Alder reactions.

The $^1$H-NMR spectrum at 60°C shows relatively good resolution in the aromatic region, although the aliphatic part still appears as broad signals without discernable multiplicity. At this temperature, the signal of 3-H appears as a broad peak at $\delta = 3.64$.

Additional signals characteristic of tetracyclone adducts appear in the $^{13}$C-NMR spectrum at $\delta = 48.3$ (C-3), $\delta = 65.03$ (C-2), and $\delta = 196.2$ (CO). In the FD-MS spectrum of **6**, two fragment peaks at $m/z = 1383.3$ and $m/z = 976.1$ can be seen. These peaks are due to the loss of CO and 1,2,3,4-tetraphenylbenzene, whereby the corresponding isobenzofuran fragments are generated. All the given data confirm the proposed structure **6**.

The mentioned Hps **9**, **10**, and **11** were synthesized in a similar manner to Pc **6**. The spectroscopic and analytical data are given in the Experimental Section. We have already described the preparation and reactions of these compounds[6a,11,14].

Scheme 3b. Synthesis of the HpNi complexes **10** and **11**



We are presently working on the preparation of the Pc trimer **12** (Scheme 4) by addition of **3** (excess) to the intermediate generated from **6**. The Pc trimer **12** is a starting compound for the stepwise synthesis of higher ladder-type oligomers.

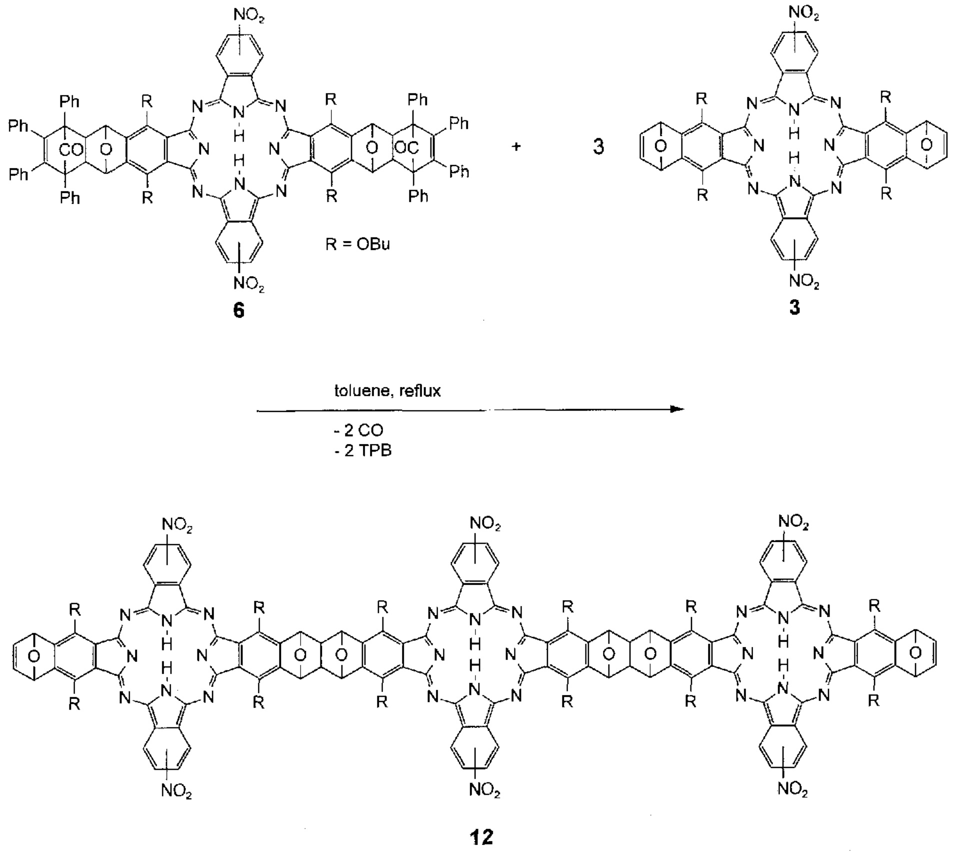
## Experimental Section

The following compounds were prepared as described in the literature: 4,9-Dibutoxy-2,3,5,8-tetrahydro-1,3-diimino-1*H*-5,8-epoxybenz[*f*]isoindoline (**2**)[4b], 1,3,3-trichloro-6/7-nitroisoindolenine (**1**)[12]. – FT-IR: Bruker IFS 48. – UV/Vis: Shimadzu UV-2101 PC. – NMR: Bruker AC 250 ($^1$H: 250.1 MHz, $^{13}$C: 62.9 MHz). – MS: Finnigan ISQ 70; Varian MAT 711A (modified by AMD Intectra). – Elemental analyses: Carlo Erba Elemental Analyser 1106.

*Synthesis of* **3** *and* **4**: To a solution of **2** (0.36 g, 1.02 mmol) in dry THF (60 ml) was added 0.45 ml of triethylamine (3.06 mmol). The mixture was cooled to approximately 0°C in an ice/salt bath and then a solution of **1** (0.27 g, 1.02 mmol) in dry THF (30 ml) was added dropwise over a period of 15 min. The mixture was stirred for 1 h at 0°C, and then allowed to warm slowly to room temperature overnight. The mixture was then filtered to remove the triethylamine hydrochloride. The filtrate was returned to the reaction vessel, hydroquinone (0.11 g, 1.02 mmol) and sodium methoxide (0.154 g, 3.06 mmol) were added and the resulting mixture was refluxed under nitrogen for 6 h. After cooling to room temperature, the solvent was removed from the filtrate. The green fraction was separated from the residue by column chromatography on silica gel using chloroform/ethyl acetate (3:1) as eluent. The purified green fraction consisting of **3** and **4** was separated by HPLC or PTLC.

*Separation by HPLC:* Beckman system Gold 5:1; column: self made[9b], 200 × 4 mm, (*o*-nitrophenyl)quinoline phase; 5 µm; elu-

Scheme 4. Synthesis of the Pc trimer **12**



ent: THF/*n*-hexane (4:6); pressure: 100 bar; flow rate: 1.5 ml $min^{-1}$; peak detection: 330 nm. Retention times ($R_t$) of the different fractions: $R_t$ = 2.59 min (fraction 1, **4**), $R_t$ = 4.24 min (fraction 2, **3**, constitutional isomer), $R_t$ = 6.68 min (fraction 3, **3**, constitutional isomer), $R_t$ = 7.03 min (fraction 4, **3**, constitutional isomer).

The HPLC chromatogram shows only partial resolution of the constitutional isomers of **3**. Assuming that **3** and **4** have the same extinction coefficients, the chromatogram indicates that the product mixture consists of 8.1% **4** and 91.9% **3**.

*Separation by PTLC:* preparative TLC with concentration zone 4 × 20 cm, 20 × 20 cm plate, thickness 1 mm, silica gel 60 $F_{254}$, Merck: $R_f$ = 0.57 (fraction 1, **4**), $R_f$ = 0.32 (fraction 2, **3**).

*Yields:* 40 mg (15.3%) of **3** and 4 mg (1.3%) of **4** (**3**/**4** ≈ 92.2%: 7.8%).

*1,6,17,22-Tetrabutyloxy-2,5,18,21-tetrahydro-2,5,18,21-diepoxynaphtho[b,l]-11/12,27-dinitrodibenzo[g,q]-34H,36H-porphyrazine* (**3**): IR (KBr): $\tilde{\nu}$ = 3273 $cm^{-1}$, 3050, 2959, 2935, 2872, 1602, 1579, 1526, 1495, 1339, 1286, 1144, 1076, 874, 839, 739. – UV/Vis ($CHCl_3$): $\lambda_{max}$ (lg ε) = 723.5 nm (4.89), 662 (4.40), 425.5 (4.34), 336.5 (4.56). – $^1H$ NMR ($CD_2Cl_2$): δ = −6.15, −5.75 (2 s, br, 2H, NH), 1.23 (m, 12H, $CH_3$), 1.83 (m, 8H, $CH_2$), 2.17 (m, 8H, $CH_2$), 4.45 (m, 8H, $OCH_2$), 6.15, 6.17, 6.30 (3 s, 4H, 2-H), 7.24, 7.25, 7.35, 7.38 (4 s, 4H, 1-H), 7.83–8.13 (m, 2H, 12-H), 8.20–8.37 (m, 2H, 11-H), 8.80–8.94 (m, 2H, 9-H). – $^{13}C$ NMR ($CDCl_3$): δ = 14.07, 14.18, 14.28, 14.37 ($CH_3$), 19.67, 19.74, 19.85, 19.95 ($CH_2$), 32.95 ($CH_2$), 73.65, 73.80, 73.84 ($OCH_2$), 81.34 (C-2), 117.20, 117.24 (C-9), 121.41, 121.55 (C-12), 123.50, 123.69, 123.84, 123.99 (C-11), 138.03, 138.20, 138.40, 138.59, 138.77, 139.00, 141.48, 141.52, 142.08, 142.56 (C-5, C-6, C-8), 142.84, 142.90, 142.93 (C-1), 144.55, 144.63, 144.88, 144.99 (C-3, C-4), 148.12, 148.19 (C-10), 154.1, 154.29, 154.77, 154.94 (C-7). – MS (FAB), *m/z*: 1025.2 (100) [$M^+$]. – $C_{56}H_{52}N_{10}O_{10}$ (1025.09): calcd. C 65.62, H 5.11, N 13.66; found C 63.08, H 5.50, N 12.2.

*1,6,10,15,19,24-Hexabutyloxy-2,5,11,14,20,23-hexahydro-2,5,11,14,20,23-triepoxynaphtho[b,g,l]-29-nitrobenzo[q]-34H,36H-porphyrazine* (**4**): IR (KBr): $\tilde{\nu}$ = 3051 $cm^{-1}$, 2961, 2932, 2873, 2862, 1612, 1557, 1532, 1467, 1385, 1286, 1119, 1076, 800. – UV/Vis ($CHCl_3$): $\lambda_{max}$ (lg ε) = 734.5 nm (4.94), 714.5, 671 (4.36), 405.5 (4.38), 338 (4.56). – $^1H$ NMR ($CDCl_3$): δ = −4.72 (s, br, NH), 1.01 (m, 18H, $CH_3$), 1.98 (m, 12H, $CH_2$), 2.34 (m, 12H, $CH_2$), 4.76–5.19 (m, 12H, $OCH_2$), 6.36–6.52 (m, 6H, 2-H), 7.34–7.39 (m, 6H, 1-H), 8.06 (m, 1H, 12-H), 8.62 (m, 1H, 11-H), 8.67 (m, 1H, 9-H). – MS (FAB), *m/z*: 1190.2 (10) [$M^+$].

*$PcH_2$* **6** *(Tetracyclone Bisadduct):* 40.2 mg (0.0392 mmol) of **3** and 37.68 mg (0.098 mmol) of tetracyclone **5** were dissolved in 200 ml toluene under nitrogen. The reaction mixture was then stirred for 26 h at 65 °C. After evaporation of the solvent, the mixture was separated by preparative TLC on silica gel using chloroform/ethyl acetate (10:1) as eluent. $R_f$ = 0.69 (fraction 1, bisadduct **6**). **6** was obtained in a yield of 41.3 mg (58.7%). – IR (KBr): $\tilde{\nu}$ = 3274 $cm^{-1}$, 3058, 3036, 2957, 2935, 2878, 1776, 1603, 1576, 1529, 1494, 1339, 1286, 1144, 1028, 696. – UV/Vis ($CHCl_3$): $\lambda_{max}$ (lg ε) = 720 nm, 652, 407, 339.5. – $^1H$ NMR ($C_6D_6$): δ = −3.84 (br, 2H, NH), 1.35 (br, 12H, $CH_3$), 1.94 (br, 8H, $CH_2$), 2.41 (br, 8H, $CH_2$), 3.64 (br, 4H, 3-H), 4.25–5.26 (br, 8H, $OCH_2$), 6.45–6.95 (m, 4H, 4-H), 6.95–8.24 (m, 40H, $H_{arom}$), 8.38 (br, 2H, 14-H), 8.59 (br, 2H, 13-H), 9.17 (br, 2H, 11-H). – $^{13}C$ NMR ($C_6D_6$): δ = 14.56 ($CH_3$), 19.98 ($CH_2$), 33.63 ($CH_2$), 48.33 (C-3), 65.03 (C-2), 74.35 ($OCH_2$), 80.99 (C-4), 127.83, 128.21, 128.71, 130.11, 130.48, 130.69, 135.73, 135.93, 136.43 ($C_{arom}$), 139.50 (C-1), 155.42 (C-9), 196.2 (CO). – MS (FD), *m/z*: 1795.5 (100) [$M^+$], 1383.3 (52) [$M^+$ – CO – TPB], 976.1 (19) [$M^+$ – (2 × CO) – (2 × TPB)]. – $C_{114}H_{92}N_{10}O_{12}$ (1794.0): calcd. C 76.31, H 5.17, N 7.81; found C 73.68, H 5.33, N 7.35.

*HpNi* **9** *(Tetracyclone Monoadduct):* 110 mg (0.12 mmol) of **7** and 23 mg (0.06 mmol) of 1,2,3,4-tetraphenylcyclopentadienone (**5**) were dissolved in 15 ml of toluene under nitrogen atmosphere. The reaction mixture was then stirred for 5 h at 75 °C. After evaporation of the solvent, the mixture was separated by column chromatography on silica gel using $CH_2Cl_2$/ethyl acetate (5:1) as eluent; $R_f$ = 0.96 (fraction 1, bisadduct **10**), $R_f$ = 0.77 (fraction 2, monoadduct **9**), $R_f$ = 0.39 (fraction 3, starting material **7**). The separation afforded 48 mg of **9** (62%) and 11 mg of **10** (11%) as green solids. – IR (KBr): $\tilde{\nu}$ = 3057 $cm^{-1}$, 3028, 2957, 2932, 2870, 1778, 1663, 1614, 1578, 1539, 1489, 1435, 1393, 1335, 1205, 1157, 698. – $^1H$ NMR ($CDCl_3$): δ = 0.95 (t, *J* = 7.3 Hz, 6H, $CH_3$), 0.99 (t, *J* = 7.3 Hz, 6H, $CH_3$), 1.42–1.64 (m, 8H, $CH_2$), 1.67–1.95 (m, 8H, $CH_2$), 3.14 (s, 2H, H-17), 3.99–4.35 (m, 8H, $OCH_2$), 5.92 (s, 2H, H-2), 5.96, 5.97 (2 s, 2H, H-16), 6.51 (m, 4H, H-8,10), 6.84–7.01 (m, 10H, H-26–28), 7.02 (s, 2H, H-1), 7.27–7.48 (m, 10H, H-22–24), 7.47 (dd, *J* = 7.3 Hz, 2H, H-9). – $^{13}C$ NMR ($CDCl_3$): δ = 13.9, 14.0 ($CH_3$), 19.1, 19.2 ($CH_2$), 32.1, 32.2 ($CH_2$), 46.6 (C-17), 64.3 (C-18), 74.5, 75.0 ($OCH_2$), 79.7 (C-16), 80.7 (C-2), 120.2, 120.5 (C-8,10), 126.8, 127.4, 127.5, 128.2, 129.6, 129.8 (C-22–24, C-26–28), 129.1 (C-5), 130.0 (C-13), 135.0, 135.2 (C-21,25), 138.7 (C-19), 139.4 (C-9), 142.6 (C-1), 143.4 (C-15), 144.2, 144.4 (C-4,14), 145.7 (C-3), 155.5, 155.8 (C-6,12), 158.4, 158.6 (C-7,11), 196.2 (C-20). – MS (FD), *m/z* (%): 891.5 (100) [$M^+$ – CO – TPB]. – $C_{79}H_{70}N_8NiO_7$ (1302.2): calcd. C 72.87, H 5.42, N 8.61; found C 72.74, H 5.88, N 8.18.

*HpNi* **10** *(Tetracyclone Bisadduct):* 80 mg (0.087 mmol) of **7** and 68 mg (0.177 mmol) of tetracyclone **5** were dissolved in 15 ml of toluene under nitrogen atmosphere. The mixture was stirred at 70–75 °C until no more **7** could be detected by TLC (silica gel, $CH_2Cl_2$/ethyl acetate, 4:1; 24–48 h). Chromatographic work-up on silica gel with $CH_2Cl_2$/ethyl acetate (5:1) as eluent furnished 132 mg (90%) of **10**. – IR (KBr): $\tilde{\nu}$ = 3057 $cm^{-1}$, 3028, 2957, 2932, 2870, 1778, 1663, 1612, 1576, 1539, 1489, 1435, 1393, 1204, 1161, 696. – $^1H$ NMR ($CDCl_3$): δ = 0.99 (t, *J* = 7.3 Hz, 12H, $CH_3$), 1.59 (m, 8H, $CH_2$), 1.86 (m, 8H, $CH_2$), 3.13 (s, 4H, H-3), 4.27 (t, *J* = 6.5 Hz, 8H, $OCH_2$), 5.96 (s, 4H, H-4), 6.56 (d, *J* = 7.6 Hz, 4H, H-10), 6.82–7.00 (m, 20H, H-14–16), 7.25–7.49 (m, 22H, H-11, H-18–20). – $^{13}C$ NMR ($CDCl_3$): δ = 14.0 ($CH_3$), 19.3 ($CH_2$), 32.4 ($CH_2$), 46.6 (C-3), 64.3 (C-2), 75.0 ($OCH_2$), 79.7 (C-4), 120.4 (C-10), 126.8, 127.4, 127.5, 128.2, 129.6, 129.8 (C-14–16, C-18–20), 130.0 (C-7), 135.0, 135.2 (C-13,17), 138.7 (C-1), 139.5 (C-11), 143.4 (C-5), 144.3 (C-6), 155.6 (C-8), 158.4 (C-9), 196.2 (C-12). – MS (FD); *m/z* (%): 864.1 (58) [$M^+$ – (2 × CO) × (2 × TPB) – 1], 382.4 (100) [TPB]. – $C_{108}H_{90}N_8NiO_8$ (1686.6): calcd. C 76.91, H 5.38, N 6.64; found C 75.69, H 5.51, N 6.21.

*HpNi* **11** *(Tetracyclone Bisadduct):* Compound **11** was prepared as described for **10**. Reaction of 150 mg (0.146 mmol) **8** with 113 mg (0.294 mmol) of tetracyclone **5** gave 231 mg (88%) of **11**. – IR (KBr), $\tilde{\nu}$ = 3057 $cm^{-1}$, 3030, 2953, 2930, 2858, 1778, 1663, 1612, 1576, 1539, 1489, 1435, 1393, 1204, 1161, 1020, 698. – $^1H$ NMR ($CDCl_3$): δ = 0.87 (t, *J* = 7.0 Hz, 12H, $CH_3$), 1.34 (m, 16H, $CH_2$), 1.56 (m, 8H, $CH_2$), 1.87 (m, 8H, $CH_2$), 3.14 (s, 4H, H-3), 4.28 (m, 8H, $OCH_2$), 5.88 (s, 4H, H-4), 6.57 (d, *J* = 7.6 Hz, 4H, H-10), 6.85–7.01 (m, 20H, H-14–16), 7.27–7.49 (m, 22H, H-11, H-18–20). – $^{13}C$ NMR ($CDCl_3$): δ = 14.0 ($CH_3$), 22.6 ($CH_2$), 25.8 ($CH_2$), 30.3 ($CH_2$), 31.7 ($CH_2$), 46.6 (C-3), 64.3 (C-2), 75.4 ($OCH_2$), 79.7 (C-4), 120.6 (C-10), 126.8, 127.4, 127.5, 128.2, 129.6, 129.8 (C-14–16, C-18–20), 130.1 (C-7), 135.0, 135.2 (C-13,17), 138.7 (C-1), 139.4 (C-11), 143.4 (C-5), 144.3 (C-6), 155.7 (C-8), 158.4 (C-9), 196.1 (C-12). – MS (FD); *m/z* (%): 1799.1 (100) [M$^+$]. – $C_{116}H_{106}N_8NiO_8$ (1798.9): calcd. C 77.45, H 5.94, N 6.23; found C 78.73, H 6.15, N 6.70.

---

[1] [1a] M. Kertesz, G. Frapper, S. Y. Hong, Y. S. Lee, O.-K. Kim, *Synth. Met.* **1993**, *57*, 4344–4349. – [1b] C.-S. Wang, *Trends Polym. Sci.* **1993**, *1*, 199–205. – [1c] M. Kertesz, *Macromolecules* **1995**, *28*, 1475–1480. – [1d] L. Yu, M. Chen, L. R. Dalton, *Chem. Mater.* **1990**, *2*, 649–659.

[2] P. Gomez-Romero, Y.-S. Lee, M. Kertesz, *Inorg. Chem.* **1988**, *27*, 3672–3675.

[3] [3a] A.-D. Schlüter, *Adv. Mater.* **1991**, *3*, 282–291. – [3b] S. Wegener, K. Müllen, *Macromolecules* **1993**, *26*, 3037–3040.

[4] [4a] C. Feucht, T. Linßen, M. Hanack, *Chem. Ber.* **1994**, *127*, 113–117. – [4b] M. Rack, B. Hauschel, M. Hanack, *Chem. Ber.* **1996**, *129*, 237–242. – [4c] D. Ruff, S. Fiedler, M. Hanack, *Synth. Met.* **1995**, *69*, 579–580. – [4d] T. Linßen, K. Dürr, M. Hanack, A. Hirsch, *J. Chem. Soc., Chem. Commun.* **1995**, 103–104. – [4e] B. Hauschel, P. Stihler, M. Hanack, *Trends Polym. Sci.* **1996**, *4*, 348–354.

[5] [5a] M. Hanack, M. Lang, *Adv. Mater.* **1994**, *6*, 819–833. – [5b] M. Hanack, K. Haberroth, M. Rack, *Chem. Ber.* **1993**, *126*, 1201–1204.

[6] [6a] B. Hauschel, D. Ruff, M. Hanack, *J. Chem. Soc., Chem. Commun.* **1995**, 2449–2451. – [6b] M. Rack, M. Hanack, *Angew. Chem.* **1994**, *106*, 1712–1715; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1646–1648. – [6c] P. Stihler, Ph. D. Thesis, Universität Tübingen, in preparation.

[7] [7a] T. Linßen, M. Hanack, *Chem. Ber.* **1994**, *127*, 2051–2057. – [7b] T. Linßen, Ph. D. Thesis, Universität Tübingen, **1995**. – [7c] G. Schmid, M. Sommerauer, M. Geyer, M. Hanack in *Phathalocyanines: Properties and Applications* (Eds.: C. C. Leznoff, A. B. P. Lever) Vol. 4, VCH, Weinheim, **1996**, p. 5.

[8] W. A. Nevin, W. Liu, S. Greenberg, M. R. Hempstead, S. M. Maruccio, M. Melnik, C. C. Leznoff, A. B. P. Lever, *Inorg. Chem.* **1987**, *26*, 891–899.

[9] [9a] M. Hanack, G. Schmid, M. Sommerauer, *Angew. Chem.* **1993**, *105*, 1540–1542; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1422–1424. – [9b] M. Sommerauer, C. Rager, M. Hanack, *J. Am. Chem. Soc.* **1996**, *118*, 10085–10093.

[10] [10a] J. Jang, M. R. Van de Mark, *J. Heterocycl. Chem.* **1995**, *32*, 1521–1524. – [10b] N. Kobayashi, T. Ashida, T. Osa, *Chem. Lett.* **1992**, 2031–2339.

[11] B. Hauschel, P. Stihler, M. Hanack, *Synth. Met.* **1996**, in press.

[12] J. G. Young, W. Onyebuagu, *J. Org. Chem.* **1990**, *55*, 2155–2159.

[13] [13a] J. Luo, H. Hart, *J. Org. Chem.* **1988**, *53*, 1341–1343. – [13b] T. Vogel, K. Blatter, A.-D. Schlüter, *Makromol. Chem. Rapid Commun.* **1989**, *10*, 427–430.

[14] M. Hanack, B. Hauschel, P. Stihler, M. Rack, T. Linßen, *Mat. Res. Soc. Symp. Proc.* **1996**, *413*, 465–470.

[96246]