Synthesis, Separation and Characterization of the Structural Isomers of Octa-*tert*-butylphthalocyanines and Dienophilic Phthalocyanine Derivatives

Salomé Rodríguez-Morgade and Michael Hanack*

Abstract: Octa-*tert*-butylphthalocyaninatonickel(II) (**4**) was synthesized from 3,5-di-*tert*-butylphthalonitrile (**1**) and nickel acetate. A nonstatistical mixture of the four structural isomers **4a–d** was obtained. The isolation of the structural isomers **4a–d** by preparative HPLC (MPLC) allowed their unequivocal identification and characterization by spectroscopic techniques. Moreover, a new family of *tert*-butyl-substituted phthalocyanines **6–10** containing dienophilic functionalities were prepared by condensation of 3,5-di-*tert*-butylphthalonitrile (**1**) with 6,7-dicyano-1,4-epoxy-1,4-dihydronaphthalene (**5**). The separation of the phthalocyanines **6–10** and of some of their structural isomers was accomplished by normal column chromatography. The structural isomers were characterized by spectroscopic methods in terms of their symmetry.

Keywords
dienophiles · isomer separation · macrocyclic ligands · monomers · phthalocyanines

Introduction

Phthalocyanines (Pc) and their metal complexes[1] (PcM) are the best-known derivatives of tetraazaporphyrins. These coloured macrocyclic compounds are not only of theoretical interest as heteroaromatic systems, but are also of wide practical importance because of their thermal stability, chemical resistivity, and their electrical, optical or liquid-crystalline properties.[2–4] However, the low solubility of the Pc ring system in common organic solvents represents a considerable problem, which reduces their usefulness. The solubility can be increased by introducing, for example, alkyl and alkoxy substituents at peripheral positions in the Pc framework. Because of their lower degree of order in the solid state, tetrasubstituted Pc's are more soluble than the corresponding symmetrical octasubstituted compounds.[1–3] The use of these compounds, for example, in nonlinear optics or as macrocyclic monomers for the synthesis of conjugated ladder polymers, demands the preparation of substituted phthalocyanines as single structural isomers with the appropriate symmetry, bearing donor–acceptor substituents,[8] and diene or dienophilic functionalities, respectively.[6, 7, 9, 10]

The synthesis of unsymmetrically substituted phthalocyanines constitutes a difficult problem. These compounds have, with few exceptions, been synthesized by tetramerization of the corresponding substituted phthalonitriles or derivatives.[1–3] The lack of selectivity of this reaction means that mixtures of Pc's with all possible orientation patterns for the substituents are obtained. Thus, the self-condensation of an unsymmetrically substituted phthalonitrile yields phthalocyanine derivatives as statistical mixtures of structural isomers.[11] Similarly, in a statistical condensation of two differently substituted phthalonitriles A and B, six possible phthalocyanines are expected: two phthalocyanines containing identical subunits AAAA and BBBB, and the four mixed phthalocyanines AAAB, BBBA, AABB, and ABAB.[11–13]

The problem of the poor regioselectivity in the synthesis of nonidentically substituted phthalocyanines, together with the low solubility of these macrocycles, must be overcome if utilization of these compounds in new molecular materials is to be achieved. Recently we reported for the first time the separation by chromatography of pure Pc structural isomers.[14] Furthermore, there are very few examples where single structural isomers have been successfully prepared by using diverse substrates and procedures.[15–20] In these cases, electronic effects that favour single-isomer formation[16, 18] or steric constrains that prevent the attainment of particular isomers[15, 16, 19, 20] have been suggested. Literature precedents demonstrate that substitution of phthalonitrile derivatives by bulky groups in the *ortho* position can change the isomer distribution in a mixed condensation of two differently substituted phthalic subunits, towards the formation of the less congested phthalocyanines, as a result of steric interactions during cyclization.[21]

Our interest in the synthesis of conjugated ladder polymers stabilized with metallophthalocyanine subunits[6, 7, 10] led us to study diverse strategies for the preparation of phthalocyanine monomers with the appropriate symmetry pattern ABAB, suit-

[*] Prof. Dr. Dr. h.c. M. Hanack, Dr. S. Rodríguez-Morgade
Lehrstuhl für Organische Chemie II, Universität Tübingen
Auf der Morgenstelle 18, D-72076 Tübingen (Germany)
Fax: Int. code +(7071)29-5244
e-mail: hanack@uni-tuebingen.de

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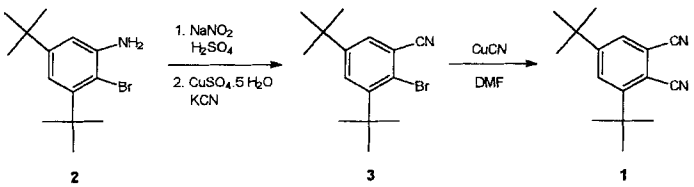
0947-6539/97/0307-1042 $ 17.50+.50/0

able for use as bisdienes or bisdienophiles.[7, 13] Based on previous work,[1–3] we envisaged that a phthalonitrile bearing two bulky substituents would be able to confer the desired solubility in organic solvents to the target phthalocyanines, and that derivatives with at least one of the substituents in the *ortho* position would be good candidates for our purposes. By substituting the 3- and 5-positions of the phthalonitrile with the sterically demanding *t*Bu group (**1**, component A), we expected to be able to suppress formation of the AAAB and AABB phthalocyanine isomers in the condensation with a second appropriate phthalonitrile (B) (**5** in Scheme 2). Herein we describe the synthesis of **1** (Scheme 1) and its self-condensation with $Ni(OAc)_2$ to form the PcNi compounds **4** (Figure 1), and its mixed-condensation with phthalonitrile **5**, which carries a dienophilic functionality (Scheme 2). All the obtained phthalocyanines and a large number of their structural isomers were separated by high-pressure liquid chromatography (HPLC), medium-pressure liquid chromatography (MPLC) or common column chromatography. The structural isomers were unambiguously characterized by spectroscopic methods.

Results and Discussion

3,5-Di-*tert*-butylphthalonitrile (**1**) had been prepared previously in a synthesis involving the reaction of 2,4-di-*tert*-butylcyclopentadienone[22] with a mixture of dichloromaleodinitrile and dichlorofumarodinitrile[23] as the key step. However, this method is laborious and only marginal yields (<1%) are achieved, owing to the low yield of the cycloaddition of the dienone and the multistep procedure required for the preparation of the cyclopentadienone itself. Furthermore, no thorough characterization of **1** (only melting point and the elemental analysis) was given.

Our synthesis of **1** (Scheme 1) follows a stepwise method in which the readily available aniline **2**[24] is converted into the corresponding cyanide **3**[24] by diazotization and transformation of the diazonium compound by means of the Sandmeyer reaction.[25] Bromocyanide **3** was easily converted into the phthalonitrile **1** in a Rosenmund–von Braun reaction with copper cyanide in DMF.



Scheme 1. Synthesis of **1**.

Self-condensation of 1: The self-condensation of **1** was carried out by treatment with an excess nickel acetate in *n*-pentanol at 139 °C, in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).[26] The reaction was monitored by TLC until all starting material had reacted (4 days). This comparatively long reaction time, probably due to the steric hindrance of the substituent at the *ortho* position of the dinitrile **1**, was found to be necessary to drive the reaction to completion. However, the yield of phthalocyanine obtained (86%) was higher than the yields normally reported for phthalocyanines substituted at the *ortho* positions of the benzene ring.[1, 27] CNDO calculations for the metal-free phthalocyanines **4** (cf. Figure 1) showed a reduced planarity for the C_s, C_{2v} and D_{2h} isomers, owing to the steric interactions between proximal *t*Bu groups.

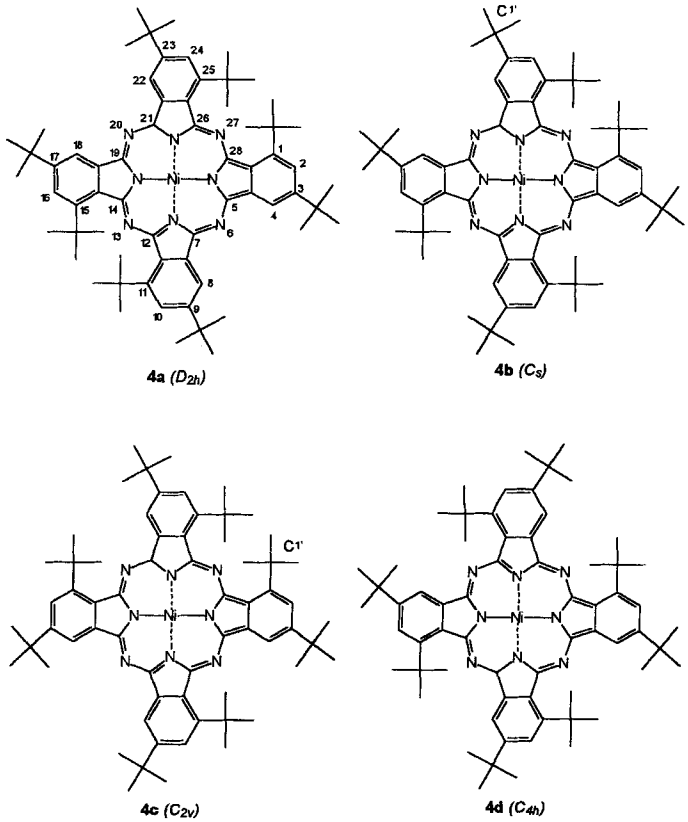


Figure 1. The four structural isomers of **4**.

The separation of the octa-*t*Bu-PcNi structural isomers of **4** (Figure 1) was achieved analytically by HPLC. The HPLC chromatogram of compound **4** is shown in Figure 2. This shows that phthalocyanine **4** consists of a mixture of 2% D_{2h}, 69% C_s,

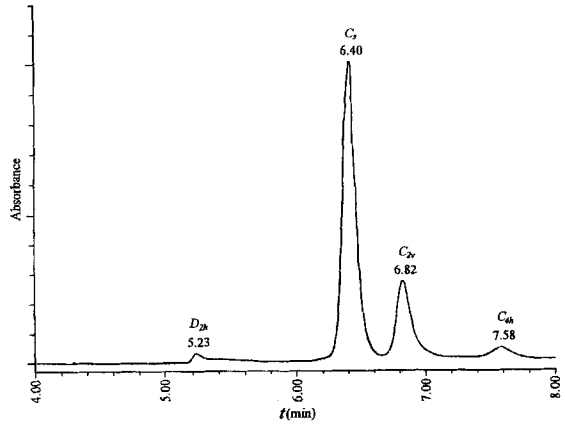


Figure 2. HPLC chromatogram of octa-*t*Bu-PcNi (**4**). Column, (*o*-nitrophenyl)-quinoline-modified silica gel; flow, 1.5 mL min^{-1}; peak detection 340 nm.

Table 1. ^{1}H NMR data of the four structural isomers of [(tBu)$_8$PcNi] (**4**) [a].

	D_{2h}	C_s	C_{2v}	C_{4h}
δ(H^a)	9.17 (d, ^4J = 2.5 Hz, 4H)	9.54 (d, ^4J = 2.5 Hz, 1H) 9.46 (d, ^4J = 2.5 Hz, 1H) 9.40 (d, ^4J = 2.5 Hz, 1H) 9.34 (d, ^4J = 2.5 Hz, 1H)	9.52 (d, ^4J = 2.5 Hz, 2H) 9.34 (d, ^4J = 2.5 Hz, 2H)	9.61 (d, ^4J = 2.5 Hz, 4H)
δ(H^b)	8.01 (d, ^4J = 2.5 Hz, 4H)	8.19 (d, ^4J = 2.5 Hz, 1H) 8.16 (d, ^4J = 2.5 Hz, 1H) 8.12 (m, 2H)	8.17 (d, ^4J = 2.5 Hz, 2H) 8.10 (d, ^4J = 2.5 Hz, 2H)	8.22 (d, ^4J = 2.5 Hz, 4H)
δ(o-tBu) [b]	–	2.36, 2.35 (2s, 18H), R^8, R^{15}	2.33 (s, 18H), R^8, R^{18}	2.41 (s, 36H), R^1, R^8, R^{15}, R^{22}
δ(o-tBu) [c]	1.94 (s, 36H), R^1, R^{11}, R^{15}, R^{25}	2.03 (s, 9H), 2.00 (s, 9H), R^1, R^{25}	2.00 (s, 18H), R^1, R^{25}	–
δ(m-tBu)	1.67 (s, 36H), R^3, R^9, R^{17}, R^{23}	1.74 (s, 9H), 1.72 (s, 18H), 1.71 (s, 9H), R^3, R^{10}, R^{17}, R^{23}	1.73 (s, 18H), 1.69 (s, 18H), R^3, R^{10}, R^{16}, R^{23}	1.74 (s, 36H), R^3, R^{10}, R^{17}, R^{24}

[a] 250 MHz, $CDCl_3$, 25 °C. [b] Nonproximal. [c] Proximal.

23% C_{2v} and 6% C_{4h} isomers. The isolation of the four isomers on a preparative scale by MPLC allowed the unequivocal characterization of the D_{2h}, C_s, C_{2v} and C_{4h} isomers (**4a–d**) by spectroscopic techniques.

The structures of the isomers were established by comparing the number of distinct aromatic protons H^a and H^b in the ^{1}H NMR spectra (see Figure 3) with the expected patterns for each symmetry and by examining the different shifts of the tBu groups attached to the benzene rings. The weak aggregation observed for **4** is remarkable and allows the NMR spectra to be recorded at normal concentrations, in contrast to other substituted phthalocyanines that we have previously investigated.[14c] The ^{1}H NMR data are listed in Table 1.

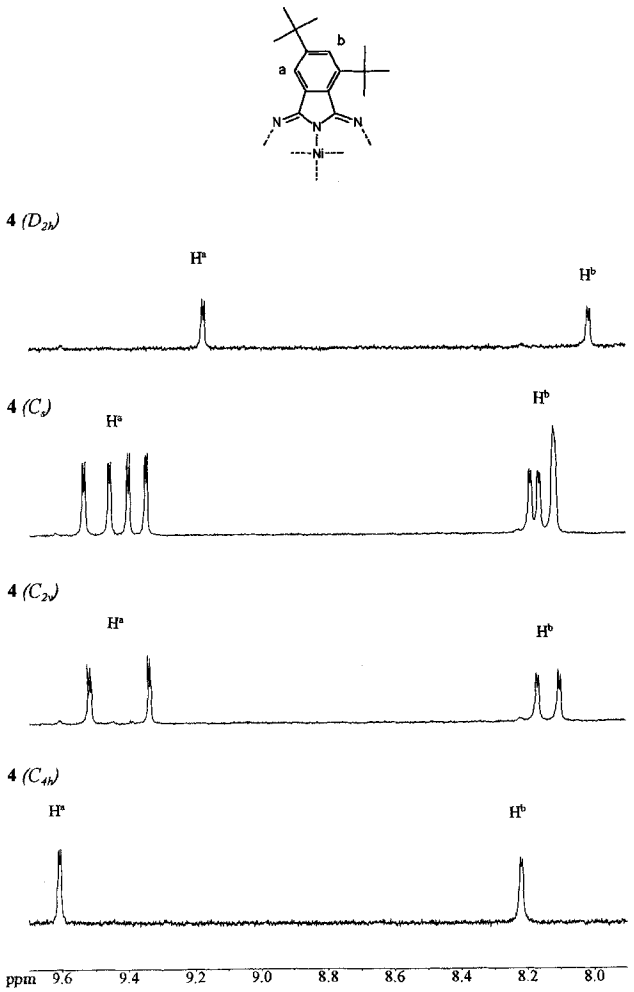


Figure 3. Aromatic region in the ^{1}H NMR spectra of the four separated structural isomers of phthalocyanine **4** (250 MHz, $CDCl_3$, 25 °C).

Two sets of signals are observed in the aromatic region, in the range δ = 9.6–9.1 corresponding to the H^a protons, which are strongly deshielded by the phthalocyanine core, and in the range δ = 8.2–8.0 corresponding to the H^b protons.[14] Figure 3 shows the ^{1}H NMR spectra of the four isomers of **4** in the aromatic region. The C_s isomer exhibits four different doublets of equal intensity for the H^a protons. Two more doublets, again of the same intensity as the first four, together with a broad signal of twice the intensity, correspond to the H^b protons. The isomer with C_{2v} symmetry shows two doublets of equal intensity for the H^a protons, and two doublets corresponding to the H^b protons. In the spectra of the D_{2h} and C_{4h} isomers, again, only two types of aromatic protons can be distinguished, one doublet corresponding to the H^a protons and one to the H^b protons, with an integral ratio of 1:1.

In the aliphatic regions, three sets of signals are clearly observed. The tBu groups located at the *meta* position of the benzene ring appear at around δ = 1.7. The proximal and nonproximal o-tBu groups can also be clearly distinguished, since the electron density around proximal o-tBu protons is greater, and the corresponding signals in ^{1}H NMR are thus shifted to higher field. Proximal tBu groups appear at $\delta \approx 2.0$, and nonproximal tBu groups at $\delta \approx 2.4$ (Figure 4). In this way, the D_{2h} and the C_{4h} isomers can readily be identified. The C_{4h} isomer shows two signals tBu, at δ = 1.74 and 2.41, and the D_{2h} isomer two tBu signals at δ = 1.67 and 1.94.

The ^{13}C NMR spectra of the C_s and C_{2v} isomers are in agreement with the proposed structures. The C_s isomer shows four signals corresponding to the C^a carbons and four assigned to the C^b carbons (see Experimental Section). Moreover, it is possible to observe seven different signals due to the quaternary tBu carbons C$^{1'}$. The C_{2v} isomer exhibits the two signals expected for the two equivalent C^a carbons, and two signals in the range of the C^b carbons, while in the aliphatic region, the presence of four nonequivalent tBu moieties is indicated by four different C$^{1'}$ carbons.

The UV/Vis spectrum of the least congested C_{4h} isomer exhibits the smallest width of the Q-band (13.5 nm at half-width).

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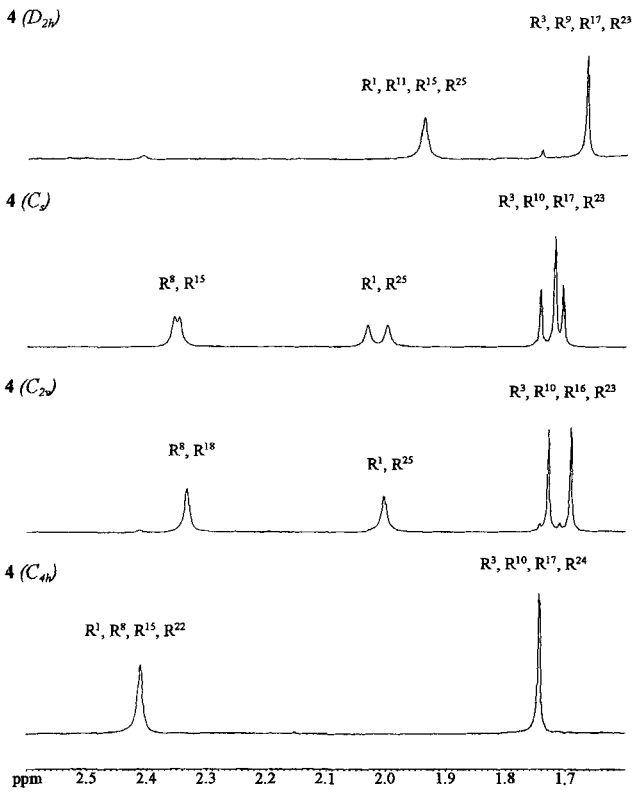


Figure 4. Aliphatic region in the ^{1}H NMR spectra of the four separated structural isomers of phthalocyanine **4** (250 MHz, $CDCl_3$, 25 °C).

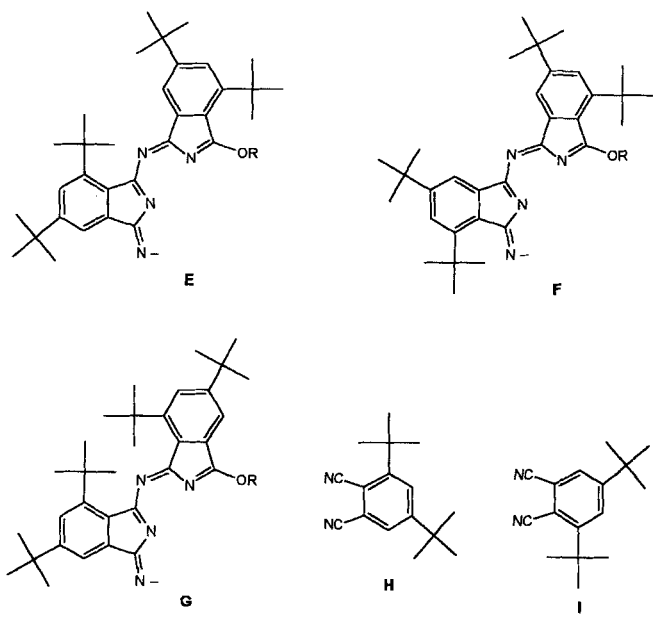


Figure 5. Dimeric species in the first oligomerization step of the self-condensation of phthalonitrile **1**.

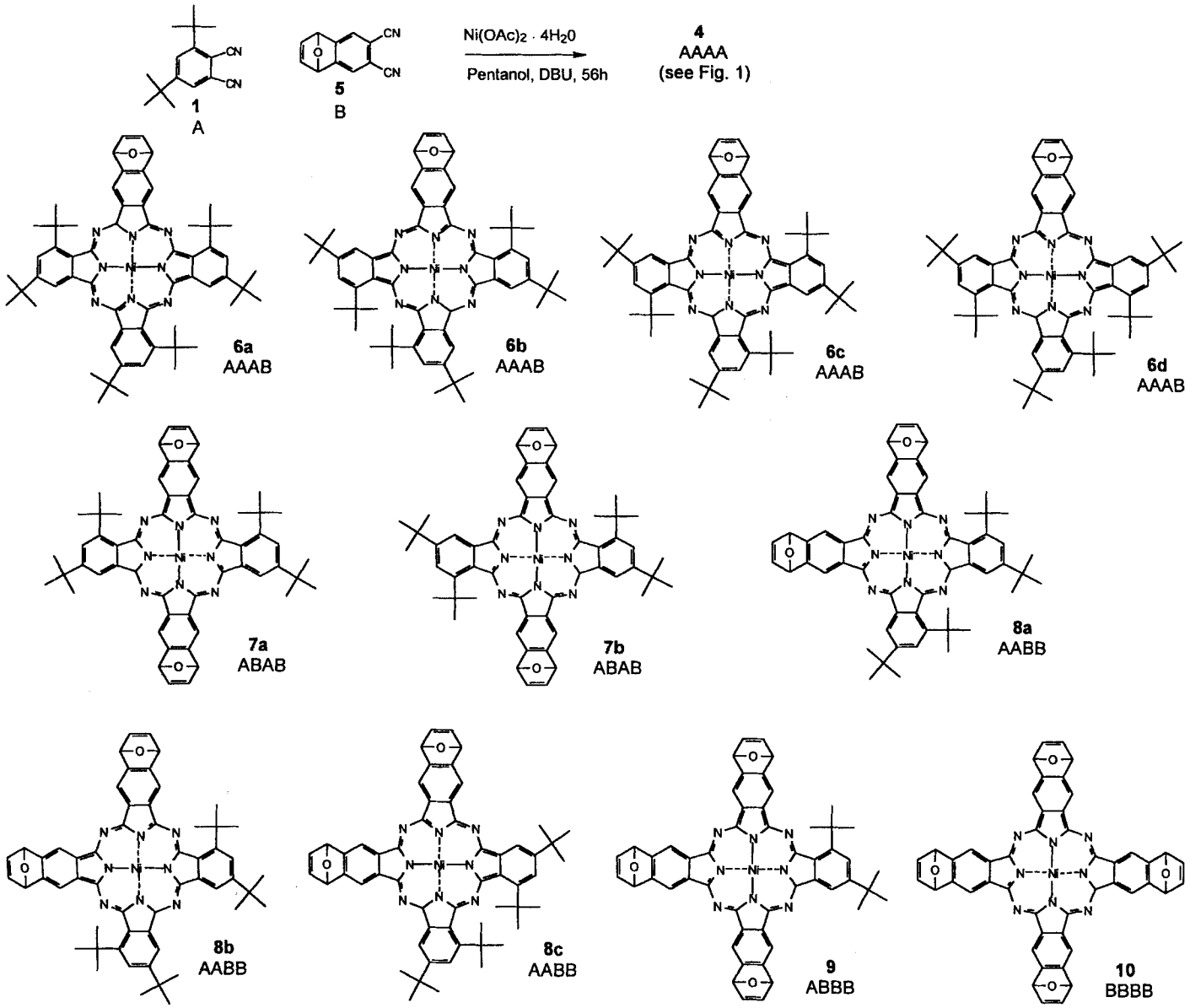
The C_s and C_{2v} isomers turn out to be electronically identical, and the Q-bands are broadened and shifted to higher wavelength (by 15 nm) with respect to the C_{4h} isomer. The broadening is even more pronounced in the case of the D_{2h} isomer: the width at half-width of 51.5 nm for the Q-band confirms the assigned structure.[14]

The distribution obtained for the structural isomers of **4** differs considerably from the statistical ratio, which should be 50% C_s, 25% C_{2v}, 12.5% D_{2h} and 12.5% C_{4h}.[11] There are some precedents in the literature where only the less congested C_{4h} isomers are obtained.[15, 16, 19] However, the reasons for the preferential formation of a given isomer remain unclear.[16] It is worth noting that, in our case, the most (D_{2h}) and least (C_{4h}) congested isomers are formed as very minor components (2% and 6%, respectively). In addition, the highly congested D_{2h} isomer is very unstable and decomposes completely after some weeks.

The formation of the different isomers **4a–d** from **1** can be rationalized as follows: According the postulated mechanism for the formation of the phthalocyanine ring system in the presence of a base,[26, 28] three dimeric species—**E**, **F**, and **G** (Figure 5)—would be produced in the first step of the reaction. The lack of a template effect at the beginning of the formation of the phthalocyanine system has been previously suggested.[20, 28] Taking into account the nonequivalence of the two cyano groups in **1**, due to the 3,5-di-*tert*-butyl substitution,[18] we expect species **E** and **F** to be preferred (Figure 5). Because strong steric interactions disfavour the formation of dimers **E** and **G** and electronic effects additionally disfavour the formation of **G**,[18] the dimer **F** might be formed selectively in the first oligomerization step. This would explain the observed final ratio of isomers: The dimerization of **F** in the presence of nickel as template or its condensation with two phthalonitrile subunits in the two possible orientations **H** and **I** (Figure 5) could yield the D_{2h}, C_s and C_{2v} isomers. The formation of the D_{2h} isomer is very unfavourable because it is highly congested, as demonstrated by its instability. Consequently, the combination of the **F** species with two phthalonitrile moieties would give preferentially a mixture of the C_s and C_{2v} isomers in a ratio of 3:1, which is in agreement with the experimental results. Likewise, formation of minor amounts of species **E** in the first step of the reaction would afford the C_{4h} isomer as a by-product.

In order to obtain further information about the self-condensation of **1**, the reaction in the absence of the metal ion was attempted. The treatment of a phthalonitrile with lithium alkoxide at low temperatures has been reported to yield single isomers of Pc derivatives.[15, 16] Under these conditions a lithiated phthalocyanine is obtained, which can be converted into the metal-free analogue. However, reaction of **1** in the presence of lithium octanolate in *n*-octanol at 100 °C for four days gave no phthalocyanine. A cyclization with the substituents directed toward each other is evidently not possible in the absence of a template effect. The fact that **F** cannot undergo ring closure without producing steric hindrance might explain the observed result. Although based on known theories, the mechanism proposed here is only tentative. A more definitive explanation of the isomer ratio would require further mechanistic studies.

Condensation of 1 with 5 (Scheme 2): The mixed condensation of dinitrile **5**[10a] with **1** (3 equiv) was carried out with nickel acetate in *n*-pentanol in the presence of DBU for 56 h (Scheme 2). Phthalonitrile **5** turned out to be more reactive than **1** and, to a large extent, underwent self-condensation after some hours. It was therefore necessary to add **5** periodically until all the phthalonitrile **1** had reacted (see Experimental Section). Moreover, in order to reduce self-condensation of the di-*t*Bu deriva-



Scheme 2. Mixed-condensation of **1** and **5**.

tive **1** in the absence of **5**, an equimolecular amount of nickel acetate with respect to the amount of **5** was added with each portion of the latter. Under these conditions, a mixture composed of all possible structures was obtained (Scheme 2).

Pc **10**,[10] produced by self-condensation of phthalonitrile **5**, was separated from the other Pc's by extraction of the *tert*-butyl-substituted derivatives with dichloromethane. Separation of the phthalocyanines **4**, **6**, **7**, **8** and **9** (order of elution) was accomplished by chromatography on silica gel, with toluene, chloroform, and chloroform/tetrahydrofuran as eluents (see Experimental Section), and their unequivocal characterization was achieved by MS, NMR, IR, UV/Vis and elemental analysis. Only very minor amounts of the AAAA pattern **4** (<0.5%) was observed. In contrast to our original assumption, similar yields were obtained for the AAAB (**6**) and ABAB (**7**) structures (Table 2). Furthermore, the ratio of AABB phthalocyanines **8** to the desired ABAB compounds **7** was about 3:1. The most congested isomers **6b** and **6d** (AAAB form) and **8c** (AABB structure) were obtained as the major isomers for their respective distribution patterns.

Table 2. Mixed-condensation of **1** and **5**.

Pc	Method 1 [a] Yield (%)	Method 2 [a] Yield (%)	Pc	Method 1 [a] Yield (%)	Method 2 [a] Yield (%)
4	<0.5	–	**7a+7b**	4	2
6a	1	3	**8a+8b**	6 [b]	5
6b	1.5 [b]	–	**8c**	7 [b]	–
6c	1 [b]	6	**9**	19	19
6d	3	–	**10**	19	15

[a] Method 1: pentanol, DBU, 139 °C, 56 h. Method 2: 1) lithium octanolate, 1-octanol/THF, 60 °C, 36 h; 2) $Ni(OAc)_2$, Pentanol, 139 °C, 4 h. [b] Within the limit of error of ^1H NMR.

The reaction of **1** and **5** in octanol, in the presence of lithium octanolate at 60 °C, and further metalation of the obtained free Pc's with nickel acetate in *n*-pentanol afforded a mixture of the AAAB (**6a–d**), ABAB (**7a,b**), AABB (**8a–c**), ABBB (**9**) and BBBB (**10**) phthalocyanines. Under these conditions, no

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phthalocyanines with the *t*Bu groups pointing toward each other (**6b**, **6d** and **8c**) were obtained (Table 2).

Strictly speaking, phthalocyanine **7a** exists as a mixture of two stereoisomers, differing in the relative *syn* and *anti* configurations of the oxo bridges attached to the B subunit.[7, 10] Thus, four isomers are expected for compound **7**, six for **8** and three for **9**. In order to simplify the analysis, we will refer only to the isomerism associated with the *t*Bu groups.

The structures were established by comparison of their spectroscopic data with those of related derivatives which we previously reported[7, 10] and with those of the phthalocyanines **4**. In addition, a 2D-NMR HMQC experiment for the **6d** isomer allowed the assignments of most of the signals. The following different types of signals are observed in the NMR spectra of all the obtained phthalocyanine structures: In ^{1}H NMR, there are three groups of signals in the aromatic region, one of which lies in the range $\delta = 9.6-9.1$, assigned to the H^a and H^c protons (see Figure 6).[7] As in the phthalocyanines **4**, the H^b protons appear in the range $\delta = 8.2-8.0$. The third group of signals lies in the range $\delta = 7.5-7.0$ and corresponds to the H^e protons.[7] Moreover, all spectra show a group of signals in the range $\delta = 6.4-6.0$, which is assigned to the H^d protons.[7] The procedure used for the assignment of the *t*Bu signals for compounds **4** can be applied in this case too (see Figure 7). The ^{13}C NMR spectra of phthalocyanines **6**, **7**, **8** and **9** exhibit very characteristic signals for the C^e carbons in the range $\delta = 143.4-142.6$, and the *t*Bu-substituted *ortho* and *meta* aromatic carbon atoms appear in the ranges $\delta = 141.6-139.6$ and $\delta = 132.2-131.5$, respectively. As in phthalocyanines **4**, the C^a and C^b carbons can be distinguished at $\delta = 117.6-116.2$ and 126.2–125.6, respectively, while the C^c signals are observed at $\delta = 114.1-112.1$. The quaternary carbons of the epoxy ring are found at $\delta = 136.5-134.0$, and the C^d carbons of the same ring at $\delta = 83.0-82.2$. In the aliphatic region, the $C^{1'}$ quaternary carbons of the *t*Bu groups are observed at $\delta = 37.8-35.6$. Proximal substituents appear at $\delta = 32.6-32.3$ and nonproximal *o*-*t*Bu groups at $\delta = 30.9-30.6$. In addition, a group of signals between $\delta = 32.0-31.7$ is assigned to the *meta* substituents of the benzene rings.

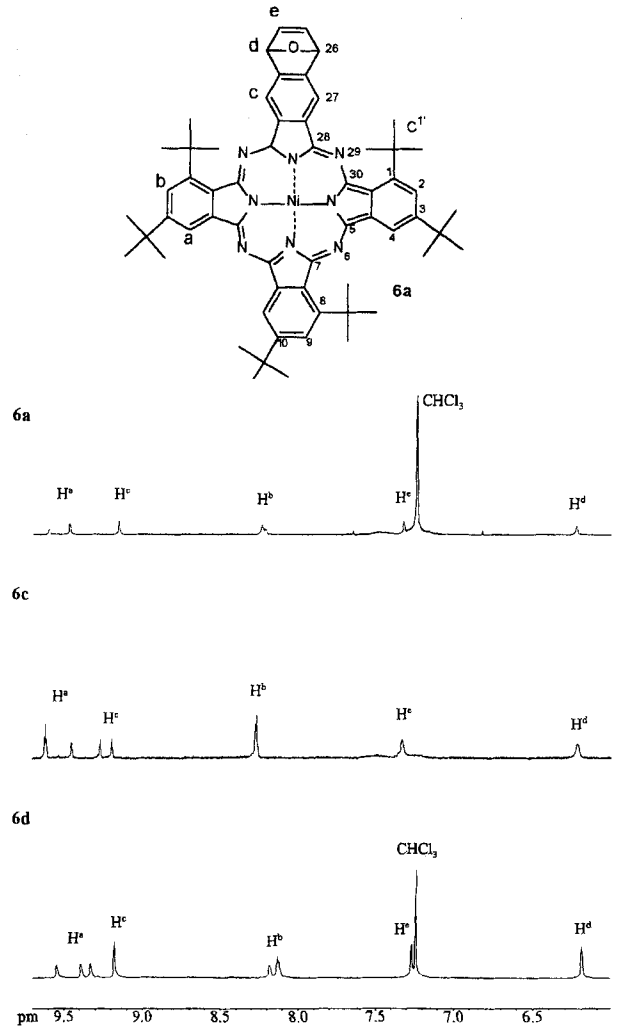

Figure 6. Aromatic region in the ^{1}H NMR spectra of the isolated isomers **6a**, **6c** and **6d** (250 MHz, 25 °C; **6a** and **6d** in $CDCl_3$; **6c** in CD_2Cl_2).

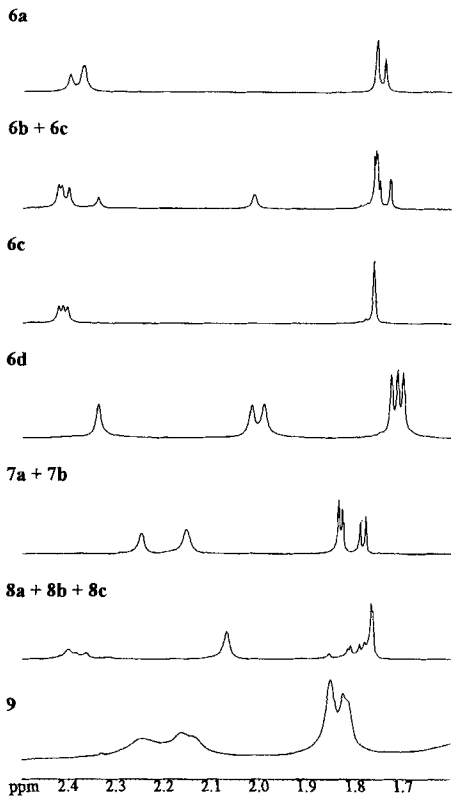

Figure 7. Aliphatic region in the ^{1}H NMR spectra of the mixed phthalocyanines (250 MHz, 25 °C; **6a**, **6d**, **9** in $CDCl_3$; **6b**+**6c**, **7a**+**7b**, **8a**+**8b**+**8c** in CD_2Cl_2).

AAAB isomers (6): Compound **6** was obtained as a mixture of the four structural isomers **6a**, **6b**, **6c** and **6d** (Table 2). The isomers **6a** and **6d** were isolated by standard column chromatography. The relative ratio of **6b** and **6c** was calculated by integration of the signals of the *t*Bu groups in the ^{1}H NMR spectrum before recrystallization. Since **6b** (metal-free) was not formed in the absence of a template, compound **6c** (metal-free) could also be isolated from this reaction, thus allowing a clear characterization of all isomers. The UV/Vis spectra of the isomers **6a** and **6c** show a small splitting of the Q-band of 9 and 6 nm, respectively, while the Q-band of **6d** is red-shifted by 8 nm with respect to the former isomers. In the MS spectra the peaks corresponding to the molecular ions at $m/z = 972/974$ demonstrate the presence of the structures (**6a**–**6d**).

Figure 6 shows the ^{1}H NMR spectra of the isolated Pc's **6a**, **6c** and **6d** in the aromatic region. Phthalocyanine **6a** exhibits two doublets corresponding to the H^a protons at $\delta = 9.46$ and 9.59 (in a 2:1 ratio); the former is assigned to the H^{11} and H^{15} protons (for numbering, see Figure 1). The two equivalent H^c protons appear as a broad singlet at $\delta = 9.15$. The three H^b protons are observed at $\delta = 8.24$–8.21. Two broad singlets at $\delta = 7.32$ and $\delta = 6.22$ correspond to the H^e and H^d protons, respectively. In the aliphatic region two types of nonproximal *o*-*t*Bu groups are observed (Figure 7), at $\delta = 2.37$ and 2.40 in a ratio 2:1; the former is assigned to the equivalent R^1 and R^{18} *t*Bu groups. The *meta* substituents appear at $\delta = 1.76$ (R^{10} and R^{16}) and 1.74 (R^3) in a ratio of 2:1. Compound **6c** shows three doublets for the H^a protons and two different singlets corresponding to the magnetically nonequivalent H^c protons at $\delta = 9.26$ and 9.19. The three *t*Bu groups at the *ortho* position (R^1, R^8 and R^{15}) appear as three singlets in the range of the nonproximal groups. The NMR data of phthalocyanine **6b** were taken from the mixture of **6b** and **6c**. Three different doublets for H^a protons and three additional doublets for H^b protons are observed. The nonequivalent H^c signals appear as two broad singlets at $\delta = 9.18$ and 9.09. In the aliphatic region the neighbouring substituents R^{11} and R^{15} are observed at $\delta = 2.01$, while the nonproximal *o*-*t*Bu group R^1 appears as a singlet at $\delta = 2.34$ (Figure 7). In ^{13}C NMR **6b** exhibits two signals due to the C^e carbons and two signals for the C^c carbons. Compound **6d** shows three distinct doublets due to the H^a protons, and only one singlet at $\delta = 9.17$, which is assigned to the equivalent H^c protons. Two proximal *t*Bu groups at $\delta = 2.02$ and 1.99, corresponding to the R^4 and R^8 substituents, are clearly observed, while the nonproximal R^{15} moiety appears at $\delta = 2.34$. In ^{13}C NMR phthalocyanine **6d** exhibits three signals in the range of the C^a carbons and three signals in the range of the C^b carbons. Only one signal for the equivalent C^e carbons and one for the C^d carbons are detected. In the aliphatic region, five different quaternary carbons corresponding to the six $C^{1'}$ carbons are observed.

ABAB isomers (7): Phthalocyanine **7** consists of a mixture of the structural isomers **7a** and **7b** (Table 2). All spectroscopic data were taken from the mixture of these compounds. Thus, the MS spectrum shows the expected molecular ion peak at $m/z = 926$, 928. A split Q-band (26.5 nm) in the UV/Vis spectrum is in agreement with the proposed ABAB structure. The ^{1}H NMR spectrum shows the characteristic signals for H^a, H^b, H^c, H^d and H^e protons (see Figure 6 for labels). Two types of signals corresponding to the *t*Bu groups are observed. The *o*-*t*Bu substituents appear in the typical range of nonproximal groups at $\delta = 2.26$ and 2.16 (Figure 7), in agreement with the ABAB structure; four different singlets correspond to the *m*-*t*Bu substituents. In ^{13}C NMR spectrum seven signals for the $C^{1'}$ quaternary carbons are detected: these correspond to the four $C^{1'}$ carbons of the nonproximal *o*-*t*Bu groups and four $C^{1'}$ carbons of the *m*-*t*Bu groups.

AABB isomers (8): Phthalocyanine **8** proved to be a mixture of the structural isomers **8a**, **8b** and **8c** (Table 2) obtained in a yield of 6% for the **8a,b** isomers and 7% for the **8c** isomer (determined by integration of the signals due to the *t*Bu groups in the ^{1}H NMR spectrum before recrystallization). However, the nontemplate reaction afforded only the less congested **8a** and **8b** isomers. The spectroscopic data are in good agreement with the proposed structures. The MS spectrum exhibits the expected peak at $m/z = 926/928$ corresponding to the molecular ion. The UV/Vis spectrum shows the characteristic Q-band at 671.0 nm. In ^{1}H NMR, the signals corresponding to the H^a, H^b, H^c, H^d and H^e (see Figure 6 for labels) are clearly distinguished. A singlet at $\delta = 2.07$ (Figure 7), which is assigned to the R^4 and R^8 proximal *o*-*t*Bu groups of **8c**, confirms unequivocally the proposed AABB structure. The presence of the proximal *ortho* substituents is also observed in the ^{13}C NMR spectrum through a signal at $\delta = 32.60$. Moreover, seven magnetically different $C^{1'}$ quaternary carbons are distinguished.

ABBB isomers (9): Phthalocyanine **9** was obtained as the major mixed-phthalocyanine form in both the template and nontemplate reactions (Table 2). This compound proved to be less soluble than the other *t*Bu-substituted phthalocyanines described here, and it showed a larger tendency to aggregate. The MS (FAB) spectrum exhibits the expected peak corresponding to the $[M+H^+]$ ion at $m/z = 881/883$, in accordance with an ABBB structural pattern. The characteristic Q-band in the UV/Vis spectrum appears at 663.5 nm. The ^{1}H NMR spectrum shows signals at $\delta = 9.1$–8.4, corresponding to one H^a and six H^c protons, and signals at $\delta = 8.21$ and 8.13 corresponding to the H^b protons (see Figure 6 for labels). Different signals in the range $\delta = 6.4$–6.0, assigned to the six H^d protons, are observed. In the aliphatic region the nonproximal *o*-*t*Bu group appears as three broad singlets at $\delta = 2.33$, 2.19 and 2.16; the *m*-*t*Bu signals are observed at $\delta = 1.85$, 1.82 and 1.81. The nonproximal *o*-*t*Bu group is also distinguished in the ^{13}C NMR spectrum through a signal at $\delta = 30.86$; a signal at $\delta = 32.03$ is assigned to the *m*-*t*Bu.

Distribution of isomers: It is difficult to explain the relative amounts of nonidentically substituted phthalocyanines obtained, because of the number of different intermediates involved in a statistical condensation of two differently substituted phthalonitriles. Theoretically, a mixed-condensation of two phthalonitriles A and B would give a statistical distribution of the isomers, depending on the molar ratio of A and B.[29] However, these percentages are strongly affected by the different natures of the starting phthalonitriles. In our case, the formation of phthalocyanines containing a larger amount of the B moieties is due to the higher reactivity of phthalonitrile **5** in comparison to **1**, leading to a higher yield of the ABBB form **9**, even if an excess **1** is used. On the other hand, the nonsymmetrical substitution of 3,5-di-*tert*-butylphthalonitrile (**1**) gives rise to different numbers of isomers. Thus, four isomers are obtained for phthalocyanine **4**, four isomers for **6**, four isomers for **7**, six isomers for **8** and three isomers for **9**. A higher number of isomers means a higher number of combinations for the phthalodinitrile units and, consequently, a higher yield of this phthalocyanine (e.g. **4**, **6** etc.). It is remarkable that the most congested isomers with proximal *t*Bu groups were not obtained in the nontemplate reaction. This result, which is in accordance with that obtained in the self-condensation of **1**, indicates that a cyclization in which the *t*Bu groups point toward each other is impracticable under these conditions.

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0947-6539/97/0307-1048 $ 17.50+.50/0 Chem. Eur. J. 1997, 3, No. 7

Conclusion

We have prepared octa-*tert*-butylphthalocyanine derivatives and a variety of new soluble phthalocyanines bearing dienophilic functionalities and *t*Bu substituents in the *ortho* and *meta* positions of the benzene ring. The weak aggregation of these systems in solution allowed the unequivocal identification of the isomers and a detailed study of their spectroscopic properties. The use of some of the obtained soluble dienophilic phthalocyanines as substrates in Diels–Alder polymerizations for the synthesis of conjugated ladder polymers is in progress.[6]

Experimental Section

General: Reactions were performed under dry nitrogen, and all solvents were purified according to standard methods. NMR spectra were recorded on Bruker ARX 250, IR spectra on a Bruker IFS 48, mass spectra on a Variant MAT 711, and UV/Vis spectra on Shimadzu UV-2102 PC spectrometers. Elemental analyses were carried out using a Carlo Erba elemental analyzer 1106. HPLC were conducted using Beckmann System Gold (Autosampler 507, programmable solvent module 126 and diode array detector module 168) and Kronlab systems (Mastercron 4 high performance pump, Dynamax absorbance detector module UV-1 and Gilson fraction collector Model 201). Melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. Compound **2** was prepared by literature procedures[24] starting from commercially available 3,5-di-*tert*-butylaniline.

2-Bromo-1-cyano-3,5-di-*tert*-butylbenzene (3): Concentrated sulfuric acid (4.6 mL) was added gradually and with stirring to a solution of 2-bromo-3,5-di-*tert*-butylaniline (**2**) (3 g, 10.55 mmol) in acetic acid (4.2 mL) and water (4.2 mL). The mixture was heated to complete solution and then cooled down to 0 °C in an ice bath. The aniline sulfate thus obtained was diazotized with $NaNO_2$ (1.11 g, 16.1 mmol) in water (2.5 mL) at 0 °C, by adding the nitrite solution dropwise within about 15 min. Stirring was continued for additional 15 min at 0 °C until a yellow-clear solution was obtained. The solution of the catalyst was prepared as follows: $CuSO_4 \cdot 5H_2O$ (3.15 g, 12.6 mmol) was dissolved in water (7.8 mL), and ice (5.25 g) was added. With vigorous stirring, a solution of KCN (3.42 g, 52.6 mmol) in water (7.8 mL) was added. The temperature of the mixture was kept below 20 °C to prevent excessive formation of $Cu_2(CN)_2$. A voluminous precipitate was first produced and then a light-brown solution. $NaHCO_3$ (7.02 g, 83.5 mmol) and toluene (7.8 mL) were added to this solution. The mixture was heated at 50 °C, and the solution of the diazonium compound added dropwise with vigorous stirring within about 20 min. After addition of toluene (200 mL), the organic layers were separated, washed with a solution of NaOH (2N) and with water, and dried. A second extraction was performed with diethyl ether, and the ethereal layers were washed with NaOH (2N) and with water, and dried. The combined organic layers were filtered and evaporated, and the crude product was chromatographed on silica gel using a mixture of hexane and dichloromethane (5:4) as eluent. Yield: 1.64 mg (53%), m.p. 98 °C (lit.[24] 97.5–98.5 °C). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.61$ (d, $^4J = 2.4$ Hz, 1H), 7.44 (d, $^4J = 2.4$ Hz, 1H), 1.46 (s, 9H, $C(CH_3)_3$), 1.24 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (250 MHz, $CDCl_3$): $\delta = 150.89$, 149.18, 129.66, 129.58, 121.49, 118.80, 118.67, 37.50, 34.97 (2C$^{1'}$), 30.00, 29.67 (2C$^{2'}$); IR (KBr): $\tilde{\nu} = 3001$, 2964, 2872, 2230 (CN), 1585, 1479, 1466, 1418, 1396, 1365, 1271, 1256, 1232, 1200, 1176, 1143, 1028, 891 cm^{-1}; MS (70 eV, EI): $m/z = 293$, 295 [M^+], 278, 280, 250, 252.

3,5-Di-*tert*-butylphthalonitrile (1): CuCN (636.6 mg, 7.1 mmol) was added to a solution of **3** (1.39 g, 4.7 mmol) in DMF (25 mL), and the mixture was heated under N_2 at 153 °C for 27 h. After cooling, the reaction mixture was poured in a concentrated ammonia solution (50 mL), and the blue suspension was left overnight under a current of air. The green solid was filtered, washed with water until pH = 7 and dried. The crude product was extracted with dichloromethane in a Soxhlett for 24 h. After evaporation of the solvent the residue was chromatographed on silica gel using as eluent a mixture of dichloromethane and hexane 2:1. Yield 1.05 g (78%), m.p. 134–136 °C (lit[23] 131–132 °C). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.74$ (d, $^4J = 1.8$ Hz, 1H), 7.64 (d, $^4J = 1.8$ Hz, 1H), 1.56 (s, 9H, $C(CH_3)_3$), 1.33 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (250 MHz, $CDCl_3$): $\delta = 156.97$, 155.46, 149.18, 129.00, 127.80, 118.67, 116.86, 116.57, 111.14, 36.37, 35.74 (2C$^{1'}$), 30.80, 30.07 (2C$^{2'}$); IR (KBr): $\tilde{\nu} = 2963$, 2910, 2873, 2226 (CN), 1593, 1483, 1466, 1410, 1400, 1369, 1267, 1240, 1213, 903 cm^{-1}; MS (70 eV, EI): $m/z = 240$ [M^+], 225, 197.

Self-condensation of 1—template reaction: A mixture of **1** (200 mg, 0.84 mmol), nickel acetate tetrahydrate (100 mg, 0.40 mmol) and DBU (four drops) in *n*-pentanol (12 mL) was heated at 139 °C under nitrogen for 4 d. The cooled green solution was poured into methanol/water (5:1; 70 mL), and the suspension was centrifuged. The filtrate was removed and the solid was resuspended in methanol, filtered and dried. The purification of the crude product was performed by column chromatography on silica gel using hexane/dichloromethane 2:1 as eluent. Further recrystallization from dichloromethane/methanol gave **4** as a green powder. Yield 192 mg (86%). MS (FD): $m/z = 1020$, 1022 [$M + H^+$], 1019, 1021 [M^+]; $C_{64}H_{80}N_8Ni$ (1020.08): calcd C 75.36%, H 7.90%, N 10.98%; found C 75.42%, H 7.99%, N 10.70%.

The isomers **4** were separated by HPLC. Column: (*o*-nitrophenyl)quinoline-modified silica gel; [14c] 1.5 mL min^{-1}. Eluent gradient: 0 min, 100% hexane; 1 min, 75% hexane/25% chloroform; 5 min, 20% hexane/80% chloroform. The isomers were purified by preparative HPLC: portions of 10 mg of phthalocyanine **4** in 10 mL of eluent were transferred to the preparative column (250 mm × 16 mm, with a precolumn 30 mm × 16 mm). Column: (*o*-nitrophenyl)quinoline-modified silica gel;[14c] 14 mL min^{-1}; eluent: 0.05% THF in hexane.

(1,3,9,11,15,17,23,25-Octa-*tert*-butylphthalocyaninato)nickel(II) (4a): ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 9.17$ (d, $^4J = 2.5$ Hz, 4H^a), 8.01 (d, $^4J = 2.5$ Hz, 4H^b), 1.94 (s, 36H, $C(CH_3)_3$, R^1, R^{11}, R^{15}, R^{25}), 1.67 (s, 36H, $C(CH_3)_3$, R^3, R^9, R^{17}, R^{23}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 708.0 (0.530), 680.5 (0.309) sh (Q-band), 635.0 (0.125), 365.0 (0.220), 341.0 (0.309), 299.0 nm (0.455); MS (FD): $m/z = 1020$, 1022 [$M + H^+$], 1019, 1021 [M^+].

(1,3,8,10,15,17,23,25-Octa-*tert*-butylphthalocyaninato)nickel(II) (4b): ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 9.54$ (d, $^4J = 2.5$ Hz, 1H^a), 9.46 (d, $^4J = 2.5$ Hz, 1H^a), 9.40 (d, $^4J = 2.5$ Hz, 1H^a), 9.34 (d, $^4J = 2.5$ Hz, 1H^a), 8.19 (d, $^4J = 2.5$ Hz, 1H^b), 8.16 (d, $^4J = 2.5$ Hz, 1H^b), 8.12 (brs, 2H^b), 2.36, 2.35 (2s, 18H, $C(CH_3)_3$, R^8, R^{15}), 2.03, 2.00 (2s, 18H, $C(CH_3)_3$, R^1, R^{25}), [1.74 (s, 9H), 1.72 (s, 18H), 1.71 (s, 9H), $C(CH_3)_3$, R^3, R^{10}, R^{17}, R^{23}]; ^{13}C NMR (250 MHz, $CDCl_3$): $\delta = 152.58$, 152.45, 151.74, 151.67, 149.23, 149.17, 148.49, 148.45, 147.34, 147.23, 146.88, 146.80, 146.47, 145.96, 145.03, [140.67, 140.63, 140.06, 140.05, 132.11, 131.85, 131.38, 131.18 (C^1, C^3, C^8, C^{10}, C^{15}, C^{17}, C^{23}, C^{25})], [125.97, 125.81, 125.51, 125.33 (4C^b)], [117.08, 116.90, 116.65, 116.38 (4C^a)], [37.64, 37.61, 37.56, 35.95, 35.90, 35.68, 35.65 (8C$^{1'}$)], 32.29 (CH_3, R^1, R^{25}), 31.87, 31.80, 31.74 (CH_3, R^3, R^{10}, R^{17}, R^{23}), 30.74, 30.63 (CH_3, R^8, R^{15}); IR (KBr): $\tilde{\nu} = 2959$, 2905, 2867, 1614, 1560, 1485, 1464, 1393, 1362, 1267, 1113, 996 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 693.5 (135 500), 661.5 (33 000) sh, 623.5 (25 000), 365.0 (33 000) sh, 341.5 (46 500), 299.0 nm (56 500); MS (FD): $m/z = 1020$, 1022 [$M + H^+$], 1019, 1021 [M^+].

(1,3,8,10,16,18,23,25-Octa-*tert*-butylphthalocyaninato)nickel(II) (4c): ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 9.52$ (d, $^4J = 2.5$ Hz, 2H^a), 9.34 (d, $^4J = 2.5$ Hz, 2H^a), 8.17 (d, $^4J = 2.5$ Hz, 2H^b), 8.10 (d, $^4J = 2.5$ Hz, 2H^b), 2.33 (s, 18H, $C(CH_3)_3$, R^8, R^{18}), 2.00 (s, 18H, $C(CH_3)_3$, R^1, R^{25}), [1.73 (s, 18H), 1.69 (s, 18H), $C(CH_3)_3$, R^3, R^{10}, R^{16}, R^{23}]; ^{13}C NMR (250 MHz, $CDCl_3$): $\delta = 152.59$, 151.63, 149.20, 148.43, 148.24, 146.62, 146.38, 145.63, [140.46, 140.11, 131.84, 131.30 (C^1, C^3, C^8, C^{10}, C^{16}, C^{18}, C^{23}, C^{25})], [125.94, 125.37 (4C^b)], [116.87, 116.71, (4C^a)], [37.61, 37.56, 35.94, 35.68, (8C$^{1'}$)], 31.20 (CH_3, R^1, R^{25}), 31.86, 31.73 (CH_3, R^3, R^{10}, R^{16}, R^{23}), 30.69 (CH_3, R^8, R^{18}); IR (KBr): $\tilde{\nu} = 2961$, 2905, 2867, 1614, 1562, 1483, 1461, 1446, 1393, 1364, 1271, 1130, 1113, 1053, 1022, 996 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 694.0 (136 000), 660.5 (30 000) sh, 624.0 (24 000), 367.0 (20 000) sh, 340.0 (34 000), 300.5 nm (42 000); MS (FD): $m/z = 1020$, 1022 [$M + H^+$], 1019, 1021 [M^+].

(1,3,8,10,15,17,22,24-Octa-*tert*-butylphthalocyaninato)nickel(II) (4d): ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 9.61$ (d, $^4J = 2.5$ Hz, 4H^a), 8.22 (d, $^4J = 2.5$ Hz, 4H^b), 2.41 (s, 36H, $C(CH_3)_3$, R^1, R^8, R^{15}, R^{22}), 1.74 (s, 36H, $C(CH_3)_3$, R^3, R^{10}, R^{17}, R^{24}; IR (KBr): $\tilde{\nu} = 2958$, 2942, 2899, 2865, 1612, 1564, 1533, 1483, 1462, 1390, 1359, 1320, 1268, 1203, 1133, 1115, 1092, 1022, 964 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 679.0 (147 166), 649.5 (24 666), 610.5

(23500), 361.5 (42333), 337.0 (69166), 295.5 nm (90166); MS (FD): m/z = 1020, 1022 [$M+H^+$], 1019, 1021 [M^+].

Self-condensation of 1—nontemplate reaction: A solution of lithium octanolate was prepared by heating lithium (12 mg, 1.7 mmol) in dry *n*-octanol (1.8 mL) at 170 °C. The solution gel was cooled to 50 °C, and **1** (100 mg, 0.42 mmol) dissolved in THF (0.6 mL) was added. After 1 h of heating at 60 °C under nitrogen, no reaction was observed. The temperature was raised to 100 °C and kept under these conditions for 4 d, but no colour change was observed.

Mixed-condensation of 1 with 5—template reaction: 3,5-Di-*tert*-butylphthalonitrile (**1**) (300 mg, 1.25 mmol) and 6,7-dicyano-1,4-epoxy-1,4-dihydronaphthalene (**5**) (81 mg, 0.42 mmol) were dissolved in *n*-pentanol (25 mL) and nickel acetate tetrahydrate (104 mg, 0.42 mmol) and DBU (0.5 mL) were added. The mixture was heated at 139 °C under nitrogen and, after 15 h, the same amounts of **5** (81 mg, 0.42 mmol) and nickel acetate tetrahydrate (104 mg, 0.42 mmol) were added. After heating for 12 h **5** (40 mg, 0.21 mmol) and $Ni(OAc)_4 \cdot 4H_2O$ (52 mg, 0.21 mmol) was added again. The resulting mixture was heated for other 17 h and afterward **5** (40 mg, 0.21 mmol) and $Ni(OAc)_4 \cdot 4H_2O$ (52 mg, 40 mmol) were added. The solution was heated for 12 h and, after cooling, it was poured into MeOH/H_2O (5:1; 120 mL) and centrifuged. The filtrate was removed, and the solid was resuspended in methanol and filtered. The blue-green powder obtained was extracted with dichloromethane for 24 h. The remaining solid was extracted with methanol for 4 d affording 61 mg (19%) of compound **10**.[10a] The solution of dichloromethane was evaporated and dried, giving a mixture of **4**, **6**, **7**, **8** and **9**. The separation of these phthalocyanines was carried out by column chromatography on silica gel, using toluene, chloroform and chloroform/tetrahydrofuran 50:1 as eluents. Compounds **4**, **6a**, **6b**+**6c** and **6d** were separated in the toluene fractions, **7** was obtained from the chloroform fractions, and **8** and **9** were separated in the chloroform/THF fractions. Phthalocyanines **4**, **6**, **7** and **8** were recrystallized from dichloromethane/methanol. Compound **9** was recrystallized from chloroform/methanol. Compound **4** was obtained in a yield of 1 mg (0.3%).

(1,3,8,10,16,18-Hexa-*tert*-butyl-tribenzo[b,g,l]-23,26-dihydro-23,26-epoxynaphtho[q]porphyrazinato)nickel(II) (6a): Blue-green powder, yield 4 mg (1%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 9.59 (d, ^4J = 1.4 Hz, 1H^a, H^4), 9.46 (d, ^4J = 1.4 Hz, 2H^a, H^{11}, H^{15}), 9.15 (s, 2H^c), 8.24–8.23 (m, 2H^b), 8.21 (d, ^4J = 1.4 Hz, 1H^b), 7.32 (s, 2H^c), 6.22 (s, 2H^d), 2.40, (s, 9H, $C(CH_3)_3$, R^8), 2.37 (s, 18H, $C(CH_3)_3$, R^1, R^{18}), 1.76 (s, 18H, $C(CH_3)_3$, R^{10}, R^{16}), 1.74 (s, 9H, $C(CH_3)_3$, R^3); IR (KBr): $\tilde{\nu}$ = 2959, 2905, 2866, 1614, 1564, 1529, 1483, 1467, 1446, 1427, 1393, 1360, 1277, 1130, 1115, 1069 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 678.0 (78500), 669.0 (81000) (splitted Q-band), 604.5 (15500), 364.5 (15500) sh, 340.5 (22500), 298.5 (28500), 271.0 nm (22500); MS (FD): m/z = 973, 975 [$M+H^+$], 972, 974 [M^+]; $C_{60}H_{66}N_8NiO$ (973.93): calcd C 74.00%, H 6.83%, N 11.51%; found C 74.25%, H 6.96%, N 11.32%.

6b + **6c**: Blue-green powder, yield 10 mg (2.5%). ^{13}C NMR (250 MHz, $CDCl_3$): δ = 152.93, 152.85, 152.51, 152.16, 152.00, 150.25, 150.07, 149.89, 149.46, 149.29, 149.24, 148.83, 148.59, 148.55, 148.44, 148.03, 147.70, 146.84, 145.05, 144.24, [143.17, 143.14, 143.07, 143.01 (4C^e)], [141.58, 141.17, 140.56, 140.39, 140.36, 139.84, 132.00, 131.96, 131.91, 131.78 (C^1, C^3, C^8, C^{10}, C^{15}, C^{17} of **6c** and C^1, C^3 C^9, C^{11}, C^{15}, C^{17} of **6b**)], [136.50, 136.22, 135.40, 135.22 (2C^{22a}, 2C^{26a})], [126.10, 126.06, 126.01, 125.98, 125.80, 125.69 (6C^b)], [117.54, 117.24, 116.86, 116.83, 116.23, 116.21 (6C^a)], [114.01, 113.93, 113.77, 113.71 (4C^c)], [82.74, 82.70, 82.67 (4C^d)], [37.74, 37.66, 37.59, 37.48, 35.99, 35.98, 35.94, 35.68 (12C$^{1'}$)], 32.39 32.31 (CH_3, R^{11}, R^{15} of **6b**), 31.84, 31.74, 31.71 (CH_3, R^3, R^{10}, R^{17} of **6c** and R^3 R^9, R^{17} of **6b**), 30.77, 30.74, 30.66 (CH_3, R^1, R^8, R^{15} of **6c** and R^1 of **6b**); IR (KBr): $\tilde{\nu}$ = 2957, 2903, 2866, 1612, 1564, 1529, 1485, 1469, 1444, 1427, 1391, 1375, 1362, 1279, 1202, 1132, 1115, 1080, 1022, 964 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 679.5 (139666), 669.5 (127333) sh (broad Q-band), 607.5 (26000), 368.5 (29000) sh, 337.5 (45333), 299.0 (55666), 271.5 nm (44666); MS (FD): m/z = 973, 975 [$M+H^+$], 972, 974 [M^+]; $C_{60}H_{66}N_8NiO$ (973.93): calcd C 74.00%, H 6.83%, N 11.51%; found. C 73.68%, H 6.72%, N 11.52%. The data of **6c** are given below.

(1,3,9,11,15,17-Hexa-*tert*-butyltribenzo[b,g,l]-23,26-dihydro-23,26-epoxynaphtho-[q]porphyrazinato)nickel(II) (6b) (taken from the mixture of **6b** and **6c**): ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 9.46 (d, ^4J = 1.7 Hz, 1H^a), 9.42 (d, ^4J = 1.7 Hz, 1H^a), 9.41 (d, ^4J = 1.7 Hz, 1H^a), 9.18 (brs, 1H^c), 9.09 (brs, 1H^c), 8.24 (d, ^4J = 1.7 Hz, 1H^b), 8.18 (d, ^4J = 1.7 Hz, 1H^b), 8.17 (d, ^4J = 1.7 Hz, 1H^b), 7.33–7.30 (m, 2H^c), 6.18 (brs, 2H^d), 2.34 (s, 9H, $C(CH_3)_3$, R^1), 2.01, (s, 18H, $C(CH_3)_3$, R^{11}, R^{15}), [1.756, 1.734, 1.732 (3s, 27H, $C(CH_3)_3$, R^3, R^9, R^{17})].

(2,4,8,10,15,17-Hexa-*tert*-butyl-tribenzo[b,g,l]-23,26-dihydro-23,26-epoxynaphtho-[q]porphyrazinato)nickel(II) (6d): Blue-green powder, yield 12 mg (3%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 9.54 (d, ^4J = 1.8 Hz, 1H^a), 9.39 (d, ^4J = 1.8 Hz, 1H^a), 9.33 (d, ^4J = 1.8 Hz, 1H^a), 9.17 (s, 2H^c), 8.17 (d, ^4J = 1.8 Hz, 1H^b), 8.13 (d, ^4J = 1.8 Hz, 1H^b), 8.11 (d, ^4J = 1.8 Hz, 1H^b), 7.27 (s, 2H^c), 6.20 (s, 2H^d), 2.34, (s, 9H, $C(CH_3)_3$, R^{15}), [2.02 (s, 9H,), 1.99 (s, 9H), $C(CH_3)_3$, R^4, R^8)], [1.73, (s, 9H), 1.71, (s, 9H), 1.70, (s, 9H), $C(CH_3)_3$, R^2, R^{10}, R^{17}]; ^{13}C NMR (250 MHz, $CDCl_3$): δ = 152.75, 152.07, 151.95, 150.31, 150.28, 149.52, 149.27, 148.51, 147.62, 147.46, 147.00, 146.13, 146.11, 145.27, [143.11 (C^e)], [140.87, 140.30, 140.22, 131.71, 131.69, 131.45 (C^2, C^4, C^8, C^{10}, C^{15}, C^{17})], [135.82, 135.73 (C^{22a}, C^{26a})], [125.90, 125.80, 125.70 (3C^b)], [116.96, 116.74, 116.26, (3C^a)], [114.01, 113.99, (C^c)], 82.65 (C^d), [37.65, 37.59, 35.95, 35.71, 35.68 (6C$^{1'}$)], 32.29, 32.27 (CH_3, R^4, R^8), 31.85, 31.74, 31.71 (CH_3, R^2, R^{10}, R^{17}), 30.69 (CH_3, R^{15}); IR (KBr): $\tilde{\nu}$ = 2959, 2905, 2868, 1612, 1562, 1535, 1514, 1485, 1444, 1425, 1393, 1362, 1281, 1200, 1113, 1101, 996 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 688.0 (86400), 618.5 (16600), 369.0 (17600) sh, 338.0 (27800), 302.0 (33800) 271.0 nm (27800); MS (FD): m/z = 973, 975 [$M+H^+$], 972, 974 [M^+]; $C_{60}H_{66}N_8NiO$ (973.93): calcd C 74.00%, H 6.83%, N 11.51%; found C 74.23%, H 6.88%, N 11.71%.

(1,3,18,20-Tetra-*tert*-butyl-dibenzo[b,l]-9,12,25,28-tetrahydro-9,12,25,28-diepoxynaphtho[g,q]porphyrazinato)nickel(II) (7a) and **(1,3,17,19-tetra-*tert*-butyl-dibenzo[b,l]-9,12,25,28-tetrahydro-9,12,25,28-diepoxynaphtho[g,q]-porphyrazinato)nickel(II) (7b)**: Blue-green powder, yield 23 mg (4%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ = [9.30 (d, ^4J = 1.3 Hz), 9.21 (d, ^4J = 1.3 Hz), 9.16–8.82 (8m), 2H^a and 4H^e], 8.22 (d, ^4J = 1.3 Hz), 8.19 (m), 2H^b], 7.40, 7.35, 7.33, 7.31 (4m, 4H^e), 6.36, 6.33, 6.31, 6.27 (4brs, 4H^d), [2.26, (brs, 9H), 2.16 (brs, 9H,), $C(CH_3)_3$, R^1, R^{20} of **7a** and R^1, R^{17} of **7b**)], [1.84, 1.83 (2s, 9H), 1.80, 1.78 (2s, 9H), $C(CH_3)_3$, R^3, R^{18} of **7a** and R^3, R^{19} of **7b**)]; ^{13}C NMR (250 MHz, $CDCl_3$): δ = 152.16, 151.98, 150.38, 150.36, 150.29, 150.21, 150.15, 150.13, 150.06, 149.96, 149.93, 149.83, 148.32, 148.17, 148.13, 148.02, 146.61, 146.43, 144.50, 143.55, [143.21, 143.18, 143.15, 143.11 (C^e)], 139.64, 139.58, [136.05, 136.03, 136.00, 135.39 (C^{8a}, C^{12a}, C^{24a}, C^{28a})], [125.92, 125.89, 125.72, 125.65 (C^b)], [116.57, 116.45 (C^a)], [114.56, 114.54, 114.50, 114.47, 113.94, 113.55, 113.42 (C^c)], 82.94, 82.89, 82.80, 82.75 (C^d), [37.44, 37.38, 37.31, 37.26, 35.96, 35.94, 35.90 (C$^{1'}$)], [32.04, 32.01, 31.98, 31.95 (CH_3, R^3, R^{18} of **7a** and R^3 R^{19} of **7b**)], [30.81, 30.78, 30.74, 30.61 (CH_3, R^1, R^{20} of **7a** and R^1, R^{17} of **7b**)]; IR (KBr): $\tilde{\nu}$ = 2957, 2902, 2867, 1612, 1564, 1528, 1483, 1462, 1414, 1391, 1375, 1359, 1350, 1317, 1281, 1151, 1126, 1112, 1096, 870, 847 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 683.5 (96666), 657.0 (109000) (split Q-band), 627.0 (28333), 595.0 (21666), 370.5 (24666), 334.0 (38666), 299.5 (47666), 270.5 nm (43333); MS (FD): m/z = 927, 929 [$M+H^+$], 926, 928 [M^+]; $C_{56}H_{52}N_8NiO_2$ (927.77): calcd C 72.50%, H 5.65%, N 12.08%; found C 72.38%, H 5.63%, N 12.40%.

(1,3,8,10-Tetra-*tert*-butyl-dibenzo[b,g]-16,19,25,28-tetrahydro-16,19,25,28-diepoxynaphtho[l,q]porphyrazinato)nickel(II) (8a), **(1,3,9,11-tetra-*tert*-butyl-dibenzo[b,g]-16,19,25,28-tetrahydro-16,19,25,28-diepoxynaphtho[l,q]porphyrazinato)nickel(II) (8b)** and **(2,4,8,10-tetra-*tert*-butyl-dibenzo[b,g]-16,19,25,28-tetrahydro-16,19,25,28-diepoxynaphtho[l,q]porphyrazinato)nickel(II) (8c)**: Blue-green powder, yield 75 mg (13%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ = [9.52–9.25, 8.96–8.84 (m), 8.61 (brs), 8.55 (brs), 2H^a and 4H^e], [8.29–8.24 (m), 8.21 (d, ^4J = 1.7 Hz) 2H^b], 7.31–7.19 (m, 4H^e), 6.13, 6.11, 6.06, 6.02 (4brs, 4H^d), [2.40, 2.39, 2.36, 2.32 (4brs, 8.3H), $C(CH_3)_3$, R^1, R^8 of **8a** and R^1, R^{11} of **8b**)], [2.07, (brs, 9.7H), $C(CH_3)_3$, R^4, R^8 of **8c**)], [1.86, 1.82, 1.81, 1.79, 1.78, 1.77, 1.76 (7s, 18H) $C(CH_3)_3$, R^3, R^{10} of **8a**, R^3, R^9 of **8b** and R^2, R^{10} of **8c**)]; ^{13}C NMR (250 MHz, $CDCl_3$): δ = 152.72, 152.48, 152.44, 152.39, 152.16, 151.92, 149.83, 149.69, 149.48, 149.40, 149.30, 149.24, 148.49, 148.40, 148.26, 147.46–146.00, [143.43–142.63 (C^e)], [140.61, 140.50, 140.46, 140.37, 132.15, 131.94, 131.82, 131.78, 131.58, 131.53 (C^1, C^3, C^8, C^{10} of **8a**, C^1, C^3, C^9, C^{11} of **8b** and C^2, C^4, C^8, C^{10} of **8c**)], [135.36–134.09 (C^{15a}, C^{19a}, C^{24a}, C^{28a})], [126.21, 126.16, 126.07, 125.73 (C^b)], [117.63, 117.55, 117.50, 117.13, 116.74, 116.43 (C^a)], [113.56–112.46 (C^c)], [82.49,

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0947-6539/97/0307-1050 $ 17.50+.50/0 Chem. Eur. J. 1997, 3, No. 7

82.32 (C^d)], [37.76, 37.66, 37.62, 37.48, 37.45, 35.94, 35.68 ($C^{1'}$)], 32.60 (CH_3, R^4, R^8 of **8c**), [32.02, 31.98, 31.94, 31.86, 31.82 (CH_3, R^3, R^{10} of **8a**, CH_3, R^3, R^9 of **8b** and R^2, R^{10} of **8c**)], [30.87, 30.83, 30.79 (CH_3, R^1, R^8 of **8a** and R^1, R^{11} of **8b**)]; IR (KBr): $\tilde{\nu}$ = 2959, 2905, 2868, 1612, 1564, 1528, 1485, 1423, 1393, 1362, 1281, 1180, 1171, 1101, 964, 849 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 671.0 (159000) (Q-band), 641.0 (34333) sh, 604.0 (26666), 371.0 (26666) sh, 335.5 (44333), 301.0 (53000), 272.0 nm (51000); MS (FD): m/z = 927, 929 [$M+H^+$], 926, 928 [M^+]; $C_{56}H_{52}N_8NiO_2$ (927.77): calcd C 72.50%, H 5.65%, N 12.08%; found C 72.72%, H 5.77%, N 12.18%.

(1,3-Di-*tert*-butyl-dibenzo[b]-9,12,18,21,27,30-hexahydro-9,12,18,21,27,30-triepoxynaphtho[g,l,q]porphyrazinato)nickel(II) (**9**): Blue powder, yield 70 mg (19%). ^1H NMR (250 MHz, $CDCl_3$): δ = 9.1–8.4 (7m, 7H, 1 H^a and 6 H^c), 8.21, 8.13 (2m, 1 H^b), 7.5–7.00 (m, H^e), 6.4–6.0 (8brs, 6 H^d), [2.33, 2.19, 2.16 (3brs, 9H, $C(CH_3)_3$, R^1], [1.85, 1.82, 1.81 (3brs, 9H, $C(CH_3)_3$, R^3)]; ^{13}C NMR (250 MHz, $CDCl_3$): δ = 152.2–149.0, 143.4–142.8 (C^e), 135.3–134.0 (C^{8a}, C^{12a}, C^{17a}, C^{21a}, C^{26a}, C^{30a})], [125.92, 125.87 (C^b)], 113.8–112.1 (C^c), 82.9–82.2 (C^d), [37.40, 37.27, 35.9 (broad) ($C^{1'}$)], 32.03 (CH_3, R^3), 30.86 (CH_3, R^1); IR (KBr): $\tilde{\nu}$ = 3006, 2957, 2905, 2868, 1612, 1528, 1483, 1410, 1392, 1281, 1182, 1151, 1140, 1097, 870, 849, 694 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 663.5 (148444), 630.5 (41333) sh, 597.5 (32000), 375.0 (30888), 334.0 (57111), 301.5 (67111), 270.5 nm (70000); MS (FAB): m/z = 881, 883 [$M+H^+$]; $C_{52}H_{38}N_8NiO_3$ (881.62): calcd C 70.84%, H 4.34%, N 12.71%; found. C 71.19%, H 4.40%, N 13.13%.

Mixed-condensation of 1 with 5—nontemplate reaction: Li (12 mg, 1.7 mmol) was added to dry *n*-octanol (1.8 mL), and the mixture was heated under nitrogen at 170 °C until a solution gel was obtained. The solution of lithium octanolate was cooled to 50 °C, and a solution of phthalonitrile **1** (50 mg, 0.21 mmol) and **5** (20 mg, 0.10 mmol) in THF (0.6 mL) added. The temperature was raised to 60 °C and after 16 h **5** (20 mg, 0.10 mmol) was added again. The solution was heated at 60 °C for 20 h, and afterwards cooled and quenched with a mixture of methanol/water (10 mL; 1:1). The organic fraction was extracted with dichloromethane, washed with water, and after evaporation of the dichloromethane, the octanol was distilled off at reduced pressure. The residue was resuspended in methanol (15 mL), filtered, dried and used in the next step without further purification. The green solid obtained (43 mg) was dissolved in *n*-pentanol (3 mL) and, after addition of nickel acetate tetrahydrate (104 mg, 0.42 mmol), the mixture was heated at 139 °C for 4 h. The solution was cooled, poured into methanol/water (5:1), and the resulting suspension was centrifuged. After removing the filtrate, the solid was resuspended in methanol, filtered and dried. The phthalocyanines thus obtained were separated and purified using the same procedure as described above. The yields are given in Table 2.

(1,3,8,10,15,17-Hexa-*tert*-butyl-tribenzo[b,g,l]-23,26-dihydro-23,26-epoxynaphtho[q]porphyrazinato)nickel(II) (**6c**): ^1H NMR (250 MHz, CD_2Cl_2): δ = 9.62 (d, ^4J = 1.7 Hz, 1 H^a), 9.61 (d, ^4J = 1.7 Hz, 1 H^a), 9.45 (d, ^4J = 1.7 Hz, 1 H^a), 9.26 (brs, 1 H^c), 9.19 (brs, 1 H^c), 8.28–8.26 (m, 3 H^b), 7.33 (s, 2 H^e), 6.21 (brs, 2 H^d)], [2.43, (s, 9H), 2.42 (s, 9H), 2.41 (s, 9H), $C(CH_3)_3$, R^1, R^8, R^{15})], [1.768, 1.764, 1.762 (3s, 27H), $C(CH_3)_3$, R^3, R^{10}, R^{17}]; IR (KBr): $\tilde{\nu}$ = 2957, 2901, 2868, 1612, 1564, 1529, 1483, 1469, 1444, 1427, 1391, 1375, 1360, 1279, 1130, 1115, 1101, 1022, 964 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 677.0 (47250), 671.0 (48250) (split Q-band), 640.0 (9250) sh, 605.0 (9000), 369.0 (8500) sh, 337.5 (13500), 297.5 (16500) 271.0 nm (12500); MS (FD): m/z = 973, 975 [$M+H^+$], 972, 974 [M^+]; $C_{60}H_{66}N_8NiO$ (973.93): calcd C 74.00%, H 6.83%, N 11.51%; found C 73.77%, H 6.70%, N 11.79%.

Acknowledgements: This work was carried out within the scope of Human Capital and Mobility Programme funded by European Community, Brussels. We thank these authorities for the financial support and Christine Rager for her help in preparing the manuscript.

Received: January 27, 1997 [F 586]

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