Synthesis and Separation of Structural Isomers of 2(3),9(10),16(17),23(24)-Tetrasubstituted Phthalocyanines

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Abstract: The 2(3),9(10),16(17),23(24)-tetrasubstituted metalphthalocyanines **1**–**7** (M = In, Ni, Zn) were synthesized, as mixtures of four different structural isomers, from the corresponding 4-alkoxy-1,2-dicyanobenzenes and the appropriate metal salts. Separation of the four structural isomers was successfully achieved on a C_{30} alkyl phase by high-performance liquid chromatography (HPLC). The determination of the point groups of the structural isomers was carried out for **1** and **3**, the composition of the structural isomers of **4**–**7** was accomplished by comparing their retention times and UV/Vis spectra with the data of **1** and **3**. For the phthalocyanines **8**–**10** and the naphthalocyanines **11** and **12** only the C_{4h} and D_{2h} isomers could be separated.

Keywords: HPLC · isomer separation · NMR spectroscopy · phthalocyanines

Introduction

Phthalocyanines (Pcs) and metalphthalocyanines have been investigated for many years owing to their high thermal stability and facile accessibility, as well as their wide application fields.[1, 2] Even today, phthalocyanines are widely used as dyes and catalysts; recently they have also found applications in many fields of material sciences, for example, as chemical sensors, Langmuir–Blodgett films, liquid crystals, in nonlinear optics, and as carrier-generation materials in near-IR or in photodynamic cancer therapy.[1, 2] Peripherally alkyl- or alkyloxy-substituted phthalocyanines are soluble in common organic solvents, among which tetrasubstituted phthalocyanines have been found to be more soluble than the corresponding octasubstituted phthalocyanines, because of their lower degree of order in the solid state.[3] Depending on the position of the substitutents in the precursor phthalonitriles or the corresponding isoindolines [1(4)- or 2(3)-], two structurally different tetrasubstituted systems, the 1(4),8(11),15(18),22(25)- or 2(3),9(10),16(17),23(24)- tetrakis-substituted phthalocyanines are possible.[1] In a statistical condensation reaction of the corresponding substituted phthalonitrile and a metal salt with a suitable solvent, four structural isomers are formed in the 1(4)- and 2(3)-series.[4] The symmetries for 2(3)-tetrasubstituted phthalocyanines are shown in Figure 1.

The separation and characterization of these structural isomers by chromatographic methods (MPLC, HPLC) was described by us first in 1993 for the separation of the C_{2v} and C_s isomers of 2(3)-tetra-*tert*-butylphthalocyaninatonickel.[5] In the same year we separated all four structural isomers of 1(4),8(11),15(18),22(25)-tetrakis[(2-ethylhexyloxy)phthalocyaninato]nickel(II).[6] In a more detailed work we reported in 1999 on the formation and distribution of the structural isomers of 1(4)- and 2(3)-tetraalkyloxy-substituted metal and metal-free phthalocyanines under different reaction conditions.[7] In contrast to the 1(4)-tetraalkyloxy-substituted structural isomers which exhibit a perpendicular arrangement of the substituents to the macrocycle,[8] the structural isomers of the 2(3)-tetraalkoxy-substituted phthalocyanines, for example, **1**–**10**, are much more difficult to separate, both by MPLC and HPLC. For the first time we were able to achieve a separation of the structural isomers of 2(3)-tetraalkyloxy-substituted phthalocyanines with HPLC by applying special nitrophenyl phases linked by a spacer to the silica surface.[9] The separation was possible because the large norbornyloxy group was used as substituent in the Pcs. The determination of the symmetry of the four isomers (D_{2h}, C_{4h}, C_{2v}, C_s) was carried out by a combination of ^{1}H NMR, ^{13}C DEPT NMR, IR, and UV/Vis spectroscopy.[9]

In the present work, we report the separation of all four structural isomers of different metal and metal-free 2(3),9(10),16(17),23(24)-tetrakis(alkenyloxy)-substituted phthalocyanines (**1**–**7**) by HPLC. The separation of the Pcs **8**–**10** with the shorter ethyl-, the *tert*-butyl-, or a cyclic substituent was successful only for the D_{2h} and C_{4h} isomers. In the case of the two 3(4),12(13),21(22),30(31)-tetrasubstituted indium naphthalocyanines **11** and **12** it was only possible to

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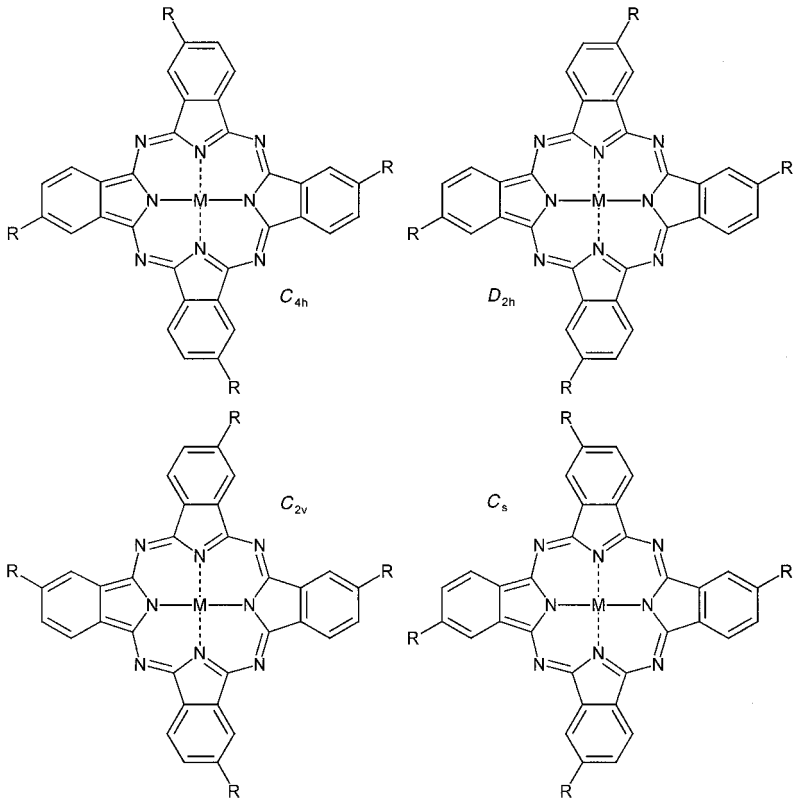


Figure 1. The four structural isomers of 2(3),9(10),16(17),23(24)-tetrasubstituted phthalocyanines. R = alkyl group; M = metal.

separate the D_{2h} and C_{4h} isomers. All separations were carried out on a C_{30} column; the structural isomers were characterized in terms of their symmetry by ^{1}H NMR and UV/Vis spectroscopy.[6, 9] The C_{30} column was chosen, because it has a high shape selectivity and loading capacity and was successfully used before for the separation of stereoisomers of Vitamin A derivatives[10] or carotenoids, for example, β-carotene.[11] To obtain the NMR spectra of the four structural Pc isomers, an on-line coupling of HPLC and NMR spectroscopy was employed;[12] this allows the separation and characterization of the isomers in a comparatively short time.

Results and Discussion

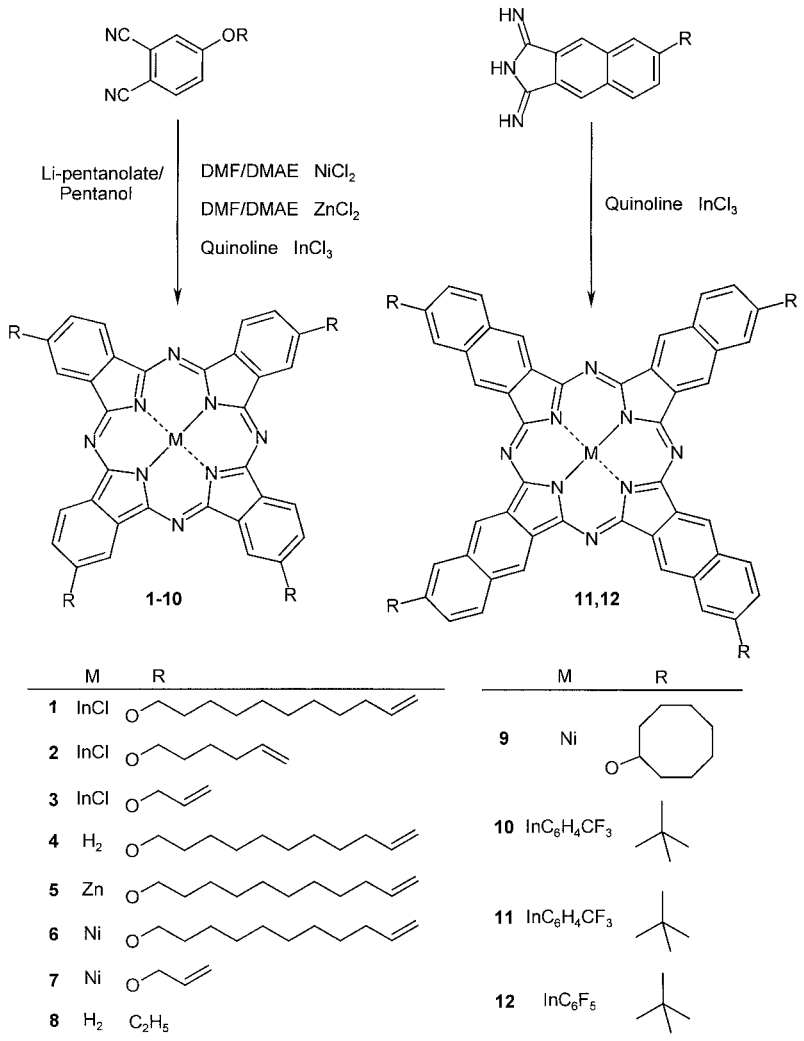
The syntheses of the investigated 2(3)-tetraalkoxy-substituted phthalocyanines **1**–**10** and the 3(4)-tetrasubstituted naphthalocyanines **11** and **12** are shown in Scheme 1. To obtain the 4-alkoxyphthalonitriles or the corresponding diiminoisoindolines[13] the appropriate 4-nitrophthalonitriles were treated with the corresponding alcohols. In the case of the alkenyloxy-substituted phthalocyanines **1**–**7**, different length of the substituent was chosen to verify, if the planned separation of the structural isomers depends on the length of the alkenyloxy chains. The 2(3)-tetrakis-substituted phthalocyanines **1**–**7** were obtained in yields between 12.8% and 65%.[13] For the preparation of **8** and **9** the corresponding ethyl- and cyclooctyloxy-substituted phthalonitriles were used.[3, 9] The axially 2(3)-*tert*-butyl-substituted indium phthalocyanine **10** and 3(4)-*tert*-butyl-substituted indium naphthalocyanines **11** and **12** were synthesized first by treating indium(III) chloride with the corresponding *tert*-butyl-substituted diiminoisoindolines to form the tetra-*tert*-butyl-substituted phthalo- and naphthalocyanine indium(III) chlorides. In a second step the axial chloride in *t*-Bu_4PcInCl and *t*-Bu_4NcInCl were converted to **10**–**12** by reaction with the appropriate Grignard reagents at room temperature in good yields.[14]

All 2(3)-tetrasubstituted phthalocyanines **1**–**10** and 3(4)-tetrasubstituted naphthalocyanines **11** and **12** were formed as four structural isomers.[1, 2, 4] The mixture of the structural isomers were characterized by ^{1}H NMR, ^{13}C NMR, IR, and UV/Vis spectroscopy, and mass spectrometry.[6, 9] To obtain good resolved ^{1}H NMR spectra a dilute solution in $CDCl_3$ (~3 mg per 0.5 mL) was used. However, 2(3)-tetrasubstituted phthalocyanines and 3(4)-tetrasubstituted naphthalocyanines exhibit broad signals in the ^{1}H NMR spectra, as known in general for many substituted phthalocyanines;[9] this not only causes difficulties for the characterization of the phthalocyanines, it also prevents the determination of the symmetry of these molecules. The broad signals and their high-field shift in the ^{1}H NMR spectra could be due to aggregation of the molecules in solution and the very short relaxation times T_1 and T_2 for phthalo- and naphthalocyanines. This problem has been solved using very dilute solutions of phthalocyanines for ^{1}H NMR measurements.

A complete separation of all four structural isomers D_{2h}, C_{2v}, C_s, and C_{4h} (cf. Table 1 and Figure 2) of compounds **1**–**7** was achieved by HPLC with a C_{30} stationary phase. The separation process of the isomers occurs as a result of the hydrophobic interaction between the dissolved molecules and the long C_{30} alkyl chains of the stationary phase. Table 1 shows the retention times of the 2(3)-tetrasubstituted phthalocya-

Abstract in German: *Die Synthese von neuen 2,3-tetraalkenyloxy substituierten Phthalocyaninen mit verschieden langen Alkenylketten und unterschiedlichen Zentralmetallen, sowie die Separierung der vier Strukturisomere mittels HPLC (C_{30}-Phase) ist Thema dieser Arbeit. Charakterisierung der einzelnen Isomere erfolgte durch ^{1}H NMR- und UV/Vis-Spektroskopie. Die Untersuchung des sterischen Einflusses der Substituenten sowie der Einfluß des Zentralmetalls auf den Trennprozess und die Isomerenzusammensetzung ist hierbei von besonderem Interesse.*

  0947-6539/01/0711-2460 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 11



Scheme 1. Synthesis of 2(3),9(10),16(17),23(24)-tetrasubstituted phthalocyanines **1**–**10** and naphthalocyanines **11** and **12**.

Table 1. Retention times t [min] of the complete separated Pcs **1**–**7** with the C_{30} phase and the used eluent mixture.

Pc	Eluent $CHCl_3$/acetone	C_{4h} (C_4) t [min]	C_{2v} (C_2) t [min]	C_s t [min]	D_{2h} (D_2) t [min]
1	80:20	10.32	11.41	14.20	30.40
2	70:30	16.12	17.38	20.04	31.10
3	65:35	18.45	20.40	22.30	35.10
4	70:30	20.47	23.08	25.02	40.50
5	70:30	12.23	13.58	16.48	34.30
6	60:40 → 100:0[a]	11.25	14.49	22.50	53.40
7	80:20 → 100:0[a]	16.51	18.40	20.20	43.12

[a] After the elution of the C_s isomer the eluent was changed to pure $CHCl_3$ to obtain the D_{2h} isomer.

nines **1**–**7**. The HPLC separations of **1** and **3** are shown in Figure 2. For the tetrasubstituted phthalocyanines **8**–**10** and naphthalocyanines **11** and **12** a successful separation was only possible for the D_{2h} and C_{4h} isomers; this is comparable to the results reported in our previous work.[9] In the case of the indium phthalocyanines **1**–**3** and **10** and naphthalocyanines **11** and **12**, the symmetry of the isomers is reduced because of their axial substituent due to the loss of the mirror plane to D_2, C_2, C_s, and C_4 symmetry.

The peripheral substitutents in the Pcs play the most important role in the separation of the structural isomers by HPLC. A good separation of the isomers depends on the length, or the bulk of the alkoxy substituent. Normally, if the chain length is short as in the case of $PcH_2(Et)_4$ (**8**), or if the compound possesses cyclic substitutents as in [Ni{Pc(c-$C_8H_{15}O)_4$}] (**9**), the C_{2v} and C_s isomers are not separated completely from each other. Compounds **8** and **9** show a distinct shoulder for the C_{2v} isomer in the common C_{2v}/C_s peak of the HPLC chromatograms.

The expected statistical distribution for the 2(3)-tetrasubstituted phthalocyanines is 12.5% D_{2h}, 12.5% C_{4h}, 25% C_{2v}, and 50% C_s (for the determination of the point groups, vide infra). Whether the statistical distribution always occurs for **1**–**10** or if the nature of the side chains influence the statistical distribution must be taken into consideration. As shown in Table 2 for the 2(3)-tetrasubstituted phthalocyanines **1** and **4**–**6**, substituted with the long undec-10-enyloxy chains, the statistical distribution has changed. The formation mechanism of these 2(3)-substituted phthalocyanines does not follow the expected statistically controlled route and resembles rather the formation of 1(4)-substituted phthalocyanines.[7] The steric hinderance of the alkenyloxy-substitutend phthalonitriles determines the composition of the structural isomers of 2(3)-tetrasubstituted phthalocyanines, during the condensation process of the four isoindolines units to form the macrocycle.[7] However, the statistical distribution is valid for the other 2(3)-tetraalkenyloxy-substituted phthalocyanines **2**, **3**, and **7** (Table 2), which contain substituents with shorter chain length. For the incompletely separated isomers of the substituted phthalocyanines **8**–**10**, the peak area of both isomers D_{2h} and C_{4h} are the same. The integration of the unseparated peak, which represents the C_{2v} and C_s isomers, includes 75% of the total amount of all isomers and indicates the expected statistical distribution.

Another important point is the dependence of the separation of the structural isomers **1**–**7** on the central atoms. Compounds **1** and **4**–**6** contain the same alkenyloxy substituent ($OC_{11}H_{21}$), but differ in their central metals, which in particular play an important role for the solubility of the macrocyclic systems.[1] The more soluble systems, like

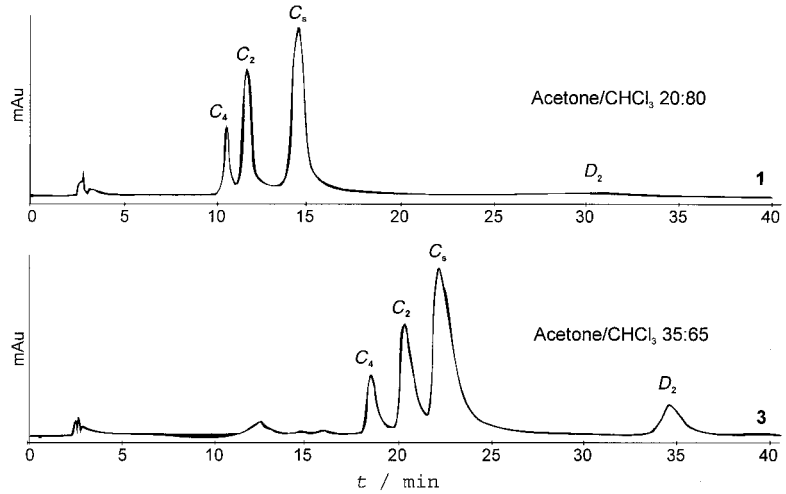


Figure 2. Separation of **1** and **3** with a C_{30} phase. Flow: 1 mL min^{-1}; eluent: $CHCl_3$ and acetone; wavelength for detection: 358 nm; room temperature.

$[InCl\{Pc(C_{11}H_{21}O)_4\}]$ (**1**) and $PcH_2(C_{11}H_{21}O)_4$ (**4**), can be easily separated and show shorter retention times than the 2(3)-tetrasubstituted nickel phthalocyanines **5** and **6**. The central atoms in **1** and **4**–**6** have nearly no influence on the separation of the structural isomers. To obtain a good separation in every case only the polarity of the eluent mixture must be changed (cf. Table 1).

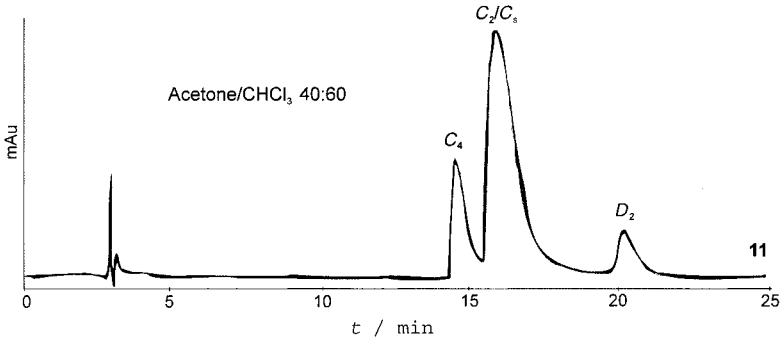


Figure 3. Separation of **11** with a C_{30} phase. Flow: 1 ml min^{-1}; eluent: $CHCl_3$ and acetone; wavelength for detection: 358 nm; room temperature.

The separation of the axially substituted 3(4)-tetra-*tert*-butylindium naphthalocyanines **11** and **12** into their structural isomers was achived successfully for the D_2 and C_4 isomers also on a C_{30} column; the C_2/C_s isomers were not separated. The elution order of the structural isomers is the same as in the case of the phthalocyanines **1**–**10**. Integration of the peak area of the unseparated C_2/C_s isomers comprises 75% of the total amount of all isomers; the peak area of D_2 and ocassionally also C_4 amounts to 12.5%. The formation of the axially substituted indium naphthalocyanines **11** and **12** with the expected statistical composition resembles the mechanism of formation of the indium phthalocyanines **10**. Figure 3 shows the chromatogram of **11**. The main difference between the phthalocyanine **10** and the naphthalocyanine **11** for the separation of the structural isomers are the broader peaks in the chromatogram of the naphthalocyanine system. The retention times of the phthalocyanines and naphthalocyanines **8**–**12** are given in Table 3.

The measurements of the ^{1}H NMR spectra were done by very fast and successfully employed HPLC/NMR on-line coupling techniques.[12] For the determination of the point groups, the ^{1}H NMR spectra were recorded by the *stopped-flow* method (cf. Figure 4). In the *stopped-flow* mode the valves of the sample unit switch and the chromatographic run were stopped as soon as the maximum of the peak is in the flow cell (indicated by UV detector); the spectra were then recorded. Another method to obtain the ^{1}H NMR spectra is to record a *continuous-flow* spectra (cf. Figure 5). The acquisition of on-line *continuous-flow* NMR spectra results in a two-dimensional contour plot of ^{1}H NMR signals of the separated structural isomers (x axis = ^{1}H chemical shift) against the retention times (y axis). In this experiment there is only a short time available for accumulation of transients and therefore for exposure of a ^{1}H NMR spectra. Figure 5 shows the two-dimensional continuous-flow contour plot of $[InCl\{Pc(C_{11}H_{21}O)_4\}]$ (**1**). As eluent for the separation and detection, a solvent mixture of acetone and chloroform, containing 10% $CDCl_3$ for the lock signal, with solvent suppres-

Table 2. Percentage distribution of the structural isomers of Pc **1**–**7** achieved with the eluent mixture given in Table 1.

Pc	C_{4h}	C_{2v}	C_s	D_{2h}
1	11.5	25.0	59.0	4.5
2	12.3	25.4	50.3	12.0
3	12.4	24.8	51.0	11.8
4	11.0	22.0	61.5	5.5
5	11.5	24.5	58.5	5.5
6	11.0	23.0	60.2	5.8
7	12.2	25.3	50.2	12.1

Table 3. Retention times t [min] of the partial separated phthalocyanines **8**–**10** and naphthalocyanines **11** and **12** with the C_{30} phase and the used eluent mixture.

Pc/Nc	Eluent	C_{4h} (C_4) t [min]	C_{2v} (C_2)/C_s t [min]	D_{2h} (D_2) t [min]
8	$CHCl_3$/acetone 60:40	30.35	32.40	39.10
9	$CHCl_3$/acetone 80:20	5.00	5.60	8.20
10	acetone/methanol 70:30	13.70	15.00	18.00
11	$CHCl_3$/acetone 60:40	14.55	15.58	20.30
12	$CHCl_3$/acetone 60:40	18.20	20.00	25.00

0947-6539/01/0711-2462 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 11

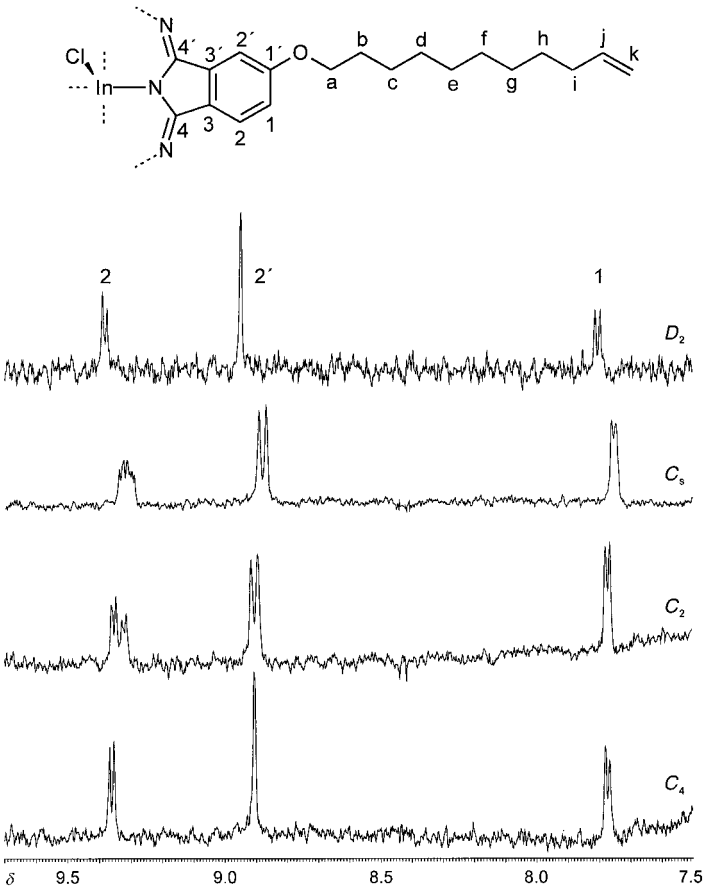


Figure 4. ^{1}H NMR spectra (600 MHz, 300 K) of the aromatic region of the separated pure isomers **1a–d** measured by *stopped-flow* NMR spectroscopy.

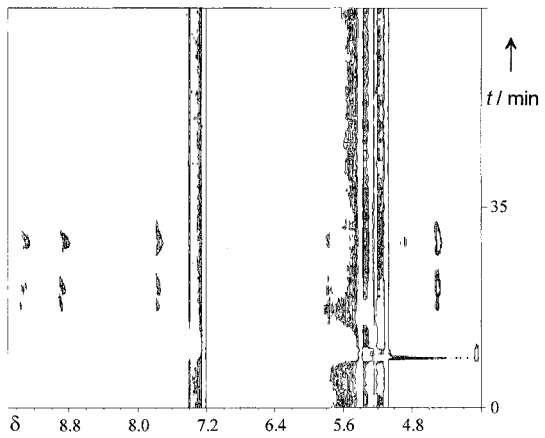


Figure 5. ^{1}H NMR *continuous-flow* spectra (contour plot, 600 MHz) of the chromatographic separation (shown in Figure 2) of the structural isomers of **1a–d** in acetone/$CHCl_3$ (containing 10% of $CDCl_3$).

sion was used. The concentration of the D_{2h} isomer was too low to be detected in the continuous-flow spectra, but the other three isomers could be clearly identified by only one measurement.

For the determination of the point group of the separated structural isomers of the 2(3)-tetrasubstituted phthalocyanines **1–3** only the aromatic region of the recorded proton NMR spectra was used. The described spectroscopic method for the separation and structural elucidation of composition mixtures enabled us to obtain highly resolved spectra in a short time. The determination of the composition of the structural isomers of **4–7** was done by comparison of the retention times of HPLC and their UV spectra with the data of the separated isomers of **1–3**.

The aromatic region of the recorded ^{1}H NMR spectra of the phthalocyanines **1** and **3** is used to determine the point group of the four succsessfully separated structural isomers. Each phthalocyanine contains four isoindolines units.[9] The splitting of the pattern can be explained through a short point-group discussion. Figure 4 shows the typical pattern of the aromatic protons for compound **1**: H2 ($^3J_{Hab} = 8.8$ Hz) is a doublet, H1 ($^3J_{Hba} = 8.8$ Hz) is also a doublet, and H2′ appears as a singlet. In the cases of the D_{2h} and C_{4h} isomers, all isoindolines units are equal and the pattern of the aromatic protons is shown only once. The C_{2v} isomer has two different units that leads to a double signal pattern. In the case for the C_s isomer, all four units are different and the pattern of the aromatic protons appears four times for this isomer. Due to the low chemical shift difference of the aromatic protons of the four units of the C_s isomer, a signal overlap occurs in the spectrum. To determine the point groups of the D_{2h} and C_{4h} isomers that have nearly identical ^{1}H NMR spectra (Figure 4), the UV/Vis spectra were recorded in $CHCl_3$. Figure 6a shows

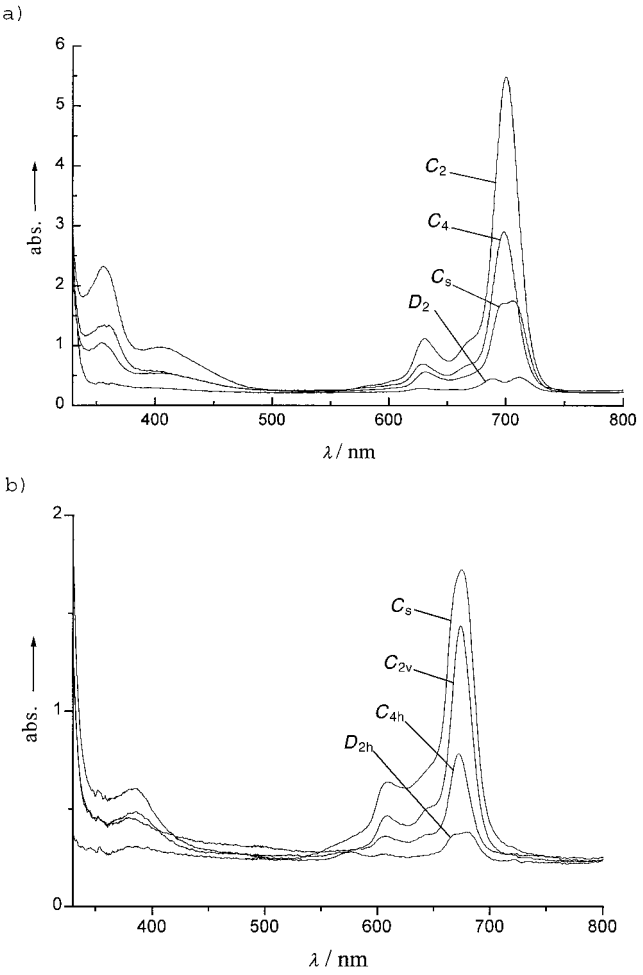


Figure 6. UV/Vis spectra of the structural isomers of a) **1** and b) **6** in $CHCl_3$.

the UV/Vis spectra of all four structural isomers of **1**. The spectrum with the split Q-band, $\Delta = 23$ nm, is assigned to the D_2 symmetry and the C_s isomer also shows a small splitting of the Q-band with $\Delta = 9.5$ nm. Only the indium phthalocyanines **1**–**3** show the splitting of the C_s isomer and a lower extinction of the Q-band relative to, for example, the nickel phthalocyanine **6** (compare Figure 6b). The split Q-band in the D_2 symmetry is due to the symmetry reduction, which necessarily means that the phthalocyanines must be planar and the peripheral substituents do not hinder each other. As theoretically predicted, the C_4 isomer of **1** shows the smallest width of the Q-band. The maxima of the C_2 and C_4 isomers at 699.5 nm for **1** are almost equivalent to the D_2 and C_s isomers and represent a mixture of 2(3)-tetrasubstituted phthalocyanines. Tables 4 and 5 show the ^{1}H NMR and UV/Vis data of the separated structural isomers **1** and **3**.

Table 4. Spectroscopic data for the separated structural isomers of **1** (assignment according to Figure 5).

	C_4	C_2	C_s	D_2
^{1}H NMR[a]				
H2	9.36 (d, $J = 8.8$ Hz)	9.35 (d, $J = 7.8$ Hz), 9.32 (d, $J = 7.8$ Hz)	9.32 (m)	9.38 (d, $J = 8.8$ Hz)
H2′	8.90 (s)	8.91 (s), 8.89 (s)	8.89 (s), 8,87 (s).	8.95 (s)
H1	7.77 (d, $J = 8.8$ Hz).	7.76 (d, $J = 7.8$ Hz).	7.75 (d, $J = 8.8$ Hz)	7.80 (d, $J = 8.8$ Hz)
UV/Vis ($CHCl_3$) [nm]	698.5, 667, 630. 395, 357	700.5, 667, 631, 406, 356	706, 692, 666.5, 632, 396, 355	712, 689, 630, 352

[a] 600 MHz, 300 K, only aromatic region.

Table 5. Spectroscopic data for the separated structural isomers of **3** (assignment according to Figure 5).

	C_4	C_2	C_s	D_2
^{1}H NMR[a]				
H2	9.73 (d, $J = 8.1$ Hz)	9.68 (d, $J = 8.1$ Hz) 9.65 (d, $J = 8.1$ Hz)	9.67 (m)	9.63 (d, $J = 8.1$ Hz)
H2′	9.28 (s)	9.26 (s), 9.24 (s)	9.25 (s), 9.23 (s)	9.23 (s)
H1	8.21 (d, $J = 8.1$ Hz)	8.18 (d, $J = 8.1$ Hz)	8.19 (d, $J = 8.1$ Hz)	8.11 (d, $J = 8.1$ Hz)
UV/Vis ($CHCl_3$) [nm]	699, 664, 630.5, 395.5, 356	696, 661, 626.5, 396, 356	702.5, 696.5, 665, 630, 396.5, 355	710, 687.5, 627, 355

[a] 600 MHz, 300 K, only aromatic region.

Conclusion

In conclusion, we have shown that all four structural isomers of 2(3)-tetraalkenyloxy-substituted phthalocyanines **1**–**7** can be separated by HPLC with a C_{30} phase. Separation of two (D_{2h} and C_{4v}) of the four isomers with a short alkyl substituent **8** (R = ethyl), cyclic- **9** (R = *c*-C_8H_{16}) or *tert*-butyl-substituted system **10**, and the naphthalocyanines **11** and **12** were also achieved successfully. The determination of the symmetry of the four structural isomers was carried out by a combination of ^{1}H NMR measurements and UV/Vis spectroscopy. The ^{1}H NMR spectra (**1**, **3**) of the isomers were recorded by employing the on-line coupling of HPLC and NMR spectroscopy with solvent suppression. Due to the low concentration of the pure isomer of the phthalocyanine in the detection cell, aggregation of the molecules, which leads to band broadening and a high field shift of the aromatic signals, is low.

Experimental Section

General: All reactions were carried out under dry nitrogen and all solvents were dried according to standard methods. Commercially available reagents were used as purchased. The 4-substituted 1,2-dicyanobenzenes were synthesized according to reported procedures. NMR spectra were recorded on Bruker ARX250 spectrometer. The chemical shifts in these spectra were measured relative to partially deuterated solvent, which were recorded relative to TMS. The UV/Vis spectra were taken in $CHCl_3$ using a Perkin–Elmer Lamda2 spectrometer and IR spectra on a Bruker IFS48. FD mass spectra were obtained on a Varian MAT711A. Elemental analyses were caried out using a Carlo Erba elemental analyzer 1106.

HPLC were carried out by using Beckmann System Gold (Autosampler 507, programmable solvent module 126 and diode array detector module 168) and Kornlab systems (Mastercron4 high-performance pump, Dynamax absorbance detector module UV-1 and Gilson fraction collector Model 201). All separations were performed on a ProntoSIL C_{30} column (Bischoff Chromatography Leonberg Germany, 3 μm particle size, 200 Å pore diameter, 250 × 4.6 mm), flow rate 1 mL min^{-1} at 358 nm (B band for phthalocyanines) and room temperature.

The HPLC–NMR experiments were conducted on a Bruker AMX600 spectrometer equiped with a Bruker peak sampling unit (BPSU-12) interface and controlled by Bruker HyStar software. For HPLC an HP1100 system (Hewlett–Packard GmbH) equipped with a binary pump G1312A and a UV detector G1314A was used. The separations were carried out with a mobile phase of a mixture of acetone and $CHCl_3$ (consisting 10% of $CDCl_3$) at room temperature. The stopped-flow ^{1}H NMR and the continuous-flow two-dimensional H,H NMR spectra were recorded at 300 K by using an inverse LC-NMR probe head with a 120 μL detection cell. To suppress the intense solvent signals of acetone and $CHCl_3$ shaped pulses for low-power presaturation (rectangular pulses with a length of 100 ms) were created for 1.6 s before applying the first 90° pulse.

The synthesis of phthalocyanines **6** and **8**–**10** and the naphthalocyanines **11** and **12** have been reported elsewhere.[6, 9, 13, 14]

General procedure for the synthesis of phthalocyanines 2–5 and 7: 1,2-Dicyano-4-alkyloxybenzene (0.02 mol) and a metal salt (0.006 mol of $NiCl_2$, $ZiCl_2$, or $InCl_3$) were dissolved in the absolute solvent (50 mL: DMF/DMAE, pentanole or quinoline) with five drops of DBU. The mixture was heated under reflux for serveral hours (Table 6). After the reaction the solvent was distilled in the cases of **2** and **3** and in the cases of **4**, **5**, and **7** the reaction mixture was diluted in methanol/water (90:10) and filtered. The residue was purified by chromatography over silica gel as shown in Table 6 and recrystallized two times from dichloromethane/methanol/water.

Table 6. Experimental data for the preparation of the Pcs **2**–**5** and **7**.

Pc	Reaction time [h]	Solvent	Solvent for chromatography	Yield [%]
2	10	quinoline	CH_2Cl_2/THF 20:1	12.8
3	10	quinoline	CH_2Cl_2/THF 20:1	65.0
4	1	Li-pentanolate/pentanol	CH_2Cl_2/THF 20:1	25.4
5	16	DMF/DMAE 2:1	CH_2Cl_2/THF 20:1	38.4
7	16	DMF/DMAE 2:1	CH_2Cl_2/THF 10:1	37.4

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[Tetrakis(hex-5-enyloxy)phthalocyaninato]indium(III) chloride (2): Dark green powder; MS (FD): *m*/*z*: 1334.7 $[M]^+$; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 8.27$ (m, 4H), 7.78– 6.9 (m, 8H), 5.84 (m, 4H), 5.09 – 4.93 (m, 8H), 3.99 (br, 8H), 2.12 – 1.95 (m), 1.61 – 1.0 (m); ^{13}C{^{1}H} NMR ($CDCl_3$, 62.9 MHz): $\delta = 161.4$ (m), 150.9 (m), 139.2, 138.8 (m), 129.5 (m), 123.4 (m), 119.1 (m), 114.2 (m), 104.6 (m), 68.8 (m), 33.9, 29.7 (m), 26.3; IR (KBr): $\tilde{\nu} = 3074$ (s), 2924 (s), 2835 (s), 1641 (s), 1607 (s), 1487 (s), 1468 (m), 1387 (s), 1339 (s), 1244 (s), 1121 (m), 1094 (s), 1049 (s), 908 (m), 827 (s), 743 cm^{-1} (m); UV ($CHCl_3$): $\lambda = 701$, 631, 403, 358 nm; elemental analysis calcd (%) for $C_{76}H_{96}N_8O_4InC$: C 68.33, H 7.24, N 8.39; found C 68.15, H 7.43, N 8.37.

[Tetrakis(undec-10-enyloxy)phthalocyaninato]indium(III) chloride (3): Dark green powder; MS (FD): *m*/*z*: 1334.7 $[M]^+$; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 8.27$ (m, 4H; H2), 7.78– 6.9 (m, 8H; H2′, H1), 5.84 (m, 8H; Hj), 5.09 – 4.93 (m, 4H; Hk), 3.99 (br, 8H; Ha), 2.12 – 1.95 (m, Hi, Hb), 1.61 – 1.0 (m, Hc – Hh); ^{13}C{^{1}H} NMR ($CDCl_3$, 62.9 MHz): $\delta = 161.4$ (C1′), 150.9 (C4,C4′), 139.2 (Cj), 138.8 (C3′), 129.5 (C3), 123.4 (C2), 119.1 (C2′), 114.2 (Ck), 104.6 (C1), 68.8 (Ca), 33.9 (Cb), 29.7 – 29.0 (Cc – Ch), 26.3 (Ci); IR (KBr): $\tilde{\nu} = 3074$ (s), 2924 (s), 2835 (s), 1641 (s), 1607 (s), 1487 (s), 1468 (m), 1387 (s), 1339 (s), 1244 (s), 1121 (m), 1094 (s), 1049 (s), 908 (m), 827 (s), 743 cm^{-1} (m); UV ($CHCl_3$): $\lambda = 701$, 631, 403, 358 nm; elemental analysis calcd (%) for $C_{76}H_{96}N_8O_4InCl$: C 68.33, H 7.24, N 8.39; found C 68.15, H 7.43, N 8.37.

Tetrakis(undec-10-enyloxy)phthalocyanine (4): Dark blue-green powder; MS (FD): *m*/*z*: 1186.5 $[M]^+$; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 7.95 – 7.75$ (m, 4H; H2), 7.31 – 7.21 (m, 4H; H2′), 7.05 – 6.83 (m, 4H; H1), 5.69 – 5.85 (m, 4H; Hj), 5.12 – 4.99 (m, 8H; Hk), 4.03 (m, 8H; Ha), 2.46 (br, 8H; Hi), 2.01 (br, 8H; Hb), 1.69 – 1.49 (m, 48H; Hc – Hh), – 4.73 to – 5.12 (m, 2H; N–H); ^{13}C{^{1}H} NMR ($CDCl_3$, 62.9 MHz): $\delta = 160.2$ (C1′), 146.8 (C4,C4′), 139.2 (Cj), 136.6 (C3′), 127.9 (C3), 122.5 (C2), 117.5 (C2′), 114.3 (Ck), 103.9 (C1), 68.3 (Ca), 33.9 (Cb), 31.0 – 29.1 (Cc – Ch), 26.4 (Ci); IR (KBr): $\tilde{\nu} =$ 3296 (m), 3076 (s), 2924 (s), 2853 (m), 1641 (s), 1612 (s), 1504 (m), 1487 (m), 1389 (m), 1242 (s), 1121 (m), 1099 (m), 1024 (s), 910 (m), 833 (m), 748 cm^{-1} (s); UV ($CHCl_3$): $\lambda = 704$, 667.5, 646, 607, 388, 341 nm; elemental analysis calcd (%) for $C_{76}H_{98}N_8O_4$: C 76.86, H 8.32, N 9.43; found C 75.63, H 8.26, N 8.46.

[Tetrakis(undec-10-enyloxy)phthalocyaninato]zinc (5): Violet powder; MS (FD): *m*/*z*: 1248.7 $[M]^+$; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 8.86 – 8.74$ (m, 4H; H2), 8.39 – 8.31 (m, 4H; H2′), 7.53 – 7.41 (m, 4H; H1), 5.93 – 5.81 (m, 4H; Hj), 5.08 – 4.94 (m, 8H; Hk), 4.46 (t, 8H; Ha), 2.13 (br, 8H; Hi), 1.82 (br, 8H; Hb), 1.62 – 1.49 (m, 48H; Hc – Hh); ^{13}C{^{1}H}-NMR ($CDCl_3$, 62.9 MHz): $\delta = 161.7$ (C1′), 152.7 (C4,C4′), 141.2 (C3′), 139.8 (Cj), 132.4 (C3), 123.8 (C2), 118.0 (C2′), 114.7 (Ck), 106.2 (C1), 69.3 (Ca), 34.8 (Cb), 30.8 – 30.1 (Cc – Ch), 27.4 (Ci); IR (KBr): $\tilde{\nu} = 3074$ (s), 2924 (s), 2853 (s), 1728 (s), 1641 (s), 1607 (s), 1491 (s),1468 (m), 1389 (m), 1339 (s), 1279 (s), 1240 (s), 1121 (s), 1094 (s), 1051 (s), 908 (m), 825 (s), 743 cm^{-1} (m); UV ($CHCl_3$): $\lambda = 680.5$, 613.5, 350.5 nm; elemental analysis calcd (%) for $C_{76}H_{96}N_8O_4Zn$: C 72.97, H 7.73, N 8.96; found C 70.46, H 7.47, N 8.75.

[Tetrakis(prop-2-enyloxy)phthalocyaninato]nickel (7): Dark blue-green powder; MS (FD): *m*/*z*: 794.2 $[M]^+$; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta =$ 6.95 – 6.23 (m, 12H; H2, H2′, H1), 6.04 (br, Hb), 5.44 – 5.25 (br, 8H; Hc), 4.17 (br, 8H; Ha); ^{13}C{^{1}H} NMR ($CDCl_3$, 62.9 MHz): $\delta = 157.7$ (C1′), 140.6 (C4,C4′), 135.2 (C3′), 133.3 (Cb), 126.9 (C3), 120.4 (C2), 117.2 (Cc), 116.3 (C2′), 101.2 (C1), 68.6 (Ca); IR (KBr): $\tilde{\nu} = 3074$ (s), 2918 (s), 1722 (s), 1647 (s), 1610 (s), 1533 (m), 1481 (s), 1414 (s), 1352 (m), 1273 (m), 1240 (s), 1124 (s), 1096 (s), 1063 (s), 1016 (m), 955 (s), 820 (s), 750 cm^{-1} (m); UV ($CHCl_3$): $\lambda = 672$, 618.5, 380, 328 nm; elemental analysis calcd (%) for $C_{44}H_{32}N_8O_4N$: C 66.44, H 4.05, N 14.09; found C 65.67, H 4.10, N 12.74.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (Graduiertenkolleg "Chemie in Interphasen") for financial support of this work.

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Received: November 15, 2000 [F2872]