Separation of Structural Isomers of Tetra-*tert*-butylphthalocyaninatonickel(II)

Michael Hanack,* Diya Meng, Anton Beck, Michael Sommerauer and Lakshminarayanapuram R. Subramanian
Institut für Organische Chemie der Universität Tübingen, Auf der Morgenstelle 18, D-7400 Tübingen, Germany

Tetra-*tert*-butylphthalocyaninatonickel is synthesized from phthalic anhydride as well as from phthalodinitrile and nickel chloride, whereby a mixture of four different structural isomers are obtained; two of these isomers, with C_{2v}- and C_s-symmetry are isolated for the first time by HPLC and medium pressure liquid chromatography (MPLC) and characterized.

Owing to their high thermal stability and facile accessibility, metallophthalocyanines and metallonaphthalocyanines have been of great interest in the preparation of organic conductors and semiconductors. Using different main group or transition metals in the centre of the macrocycles, oxygen-bridged, *e.g.* $[Pc(SiO)]_n$ (Pc = phthalocyanine) and other bridged systems with organic ligands, *e.g.* $[Pc(FeL)]_n$ with L = *e.g.* pyrazine, diisocyanobenzene and tetrazine, can be obtained exhibiting good semiconducting properties with and without doping.[1]

The main problem in processing these bridged systems is

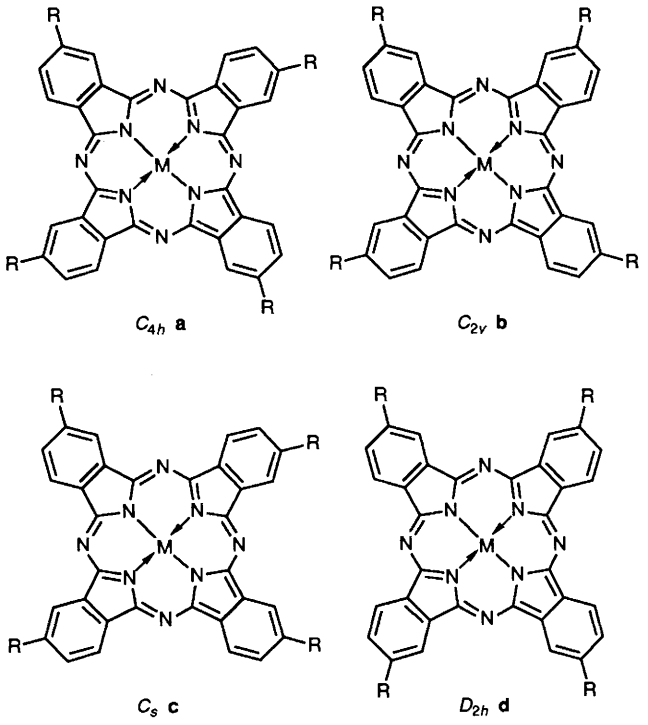

Fig. 1 The structural isomers of tetrasubstituted phthalocyanines, R = Bu^t

their scant solubility in common organic solvents. Since phthalocyanines have attracted interest not only as organic semiconductors but also for their non-linear optical properties and formation of Langmuir–Blodgett films, the solubility problem has becomes a prominent one. Work from different laboratories have shown that the solubility of phthalocyanines in organic solvents can be increased by introducing bulky or long chain substituents in the molecule.[1–3]

However, the formation of metallophthalocyanines from phthalodinitrile and a suitable metal derivative by tetramerization confronts us with the problem of dealing with either tetra- or octa-substituted metallophthalocyanines starting from, *e.g.* 4-substituted or 4,5-disubstituted phthalodinitriles. Tetrasubstituted phthalocyanines were found to be better soluble in common organic solvents,[3] but exist as four structural isomers (Fig. 1). Except in one case,[4] neither serious attempts to separate them, nor to tackle the problem were undertaken.

Clearly, highly-ordered crystals and films of these materials will be more favoured if pure single isomers are used rather than a mixture of different isomers in the detailed study of electrical and optical properties of soluble tetrasubstituted metallophthalocyanines and their bridged oligomers, $[R_4PcML]_n$. Accordingly, we report here for the first time the successful separation of two of the four isomers of tetra-*tert*-butylphthalocyaninatonickel(II) using HPLC and medium pressure liquid chromatography (MPLC) and the determination of their structure by ^{1}H NMR spectroscopy.

It was shown that for the preparation of tetrasubstituted metallophthalocyanines R_4PcM starting from a substituted phthalonitrile[5] or substituted phthalic anhydride,[6] the composition of the isomer mixture depends on the nature of the central metal atom,[7] the solvent and the reaction conditions.[8] By surveying the several synthesis of tetra-*tert*-butylphthalocyaninatometal complexes reported in the literature,[2,4,5,9,10] we could conceive that different isomer mixtures are formed using the same synthetic route depending on the central metal atom.

Very little is known about the separation of the four different isomers of a tetrasubstituted metallophthalocyanine using chromatographic methods, *e.g.* with HPLC[4] or MPLC. Therefore, attempts were made to separate tetrasubstituted phthalocyanines using these methods. Because of their easy availability, high stability and the formation of all four isomers, the separation was carried out with the isomeric tetra-*tert*-butylphthalocyaninatonickel(II), $(Bu^t)_4PcNi$.

In order to study also the influence of the synthetic methods on the formation of the structural isomers, $(Bu^t)_4PcNi$ was prepared starting from 4-*tert*-butylphthalodinitrile[5] and 4-*tert*-butylphthalic anhydride.[6] The two $(Bu^t)_4PcNi$ obtained by either method are $(Bu^t)_4PcNi$ **1** and $(Bu^t)_4PcNi$ **2**, respectively.

The mixture of isomers of $(Bu^t)_4PcNi$ **1** and **2** were characterized by ^{1}H NMR spectra (C_6D_6).† A dilute benzene solution (1.5–2.5 mg per 0.5 ml) was used to obtain good resolved NMR spectra, while high concentration showed broad signals due to aggregation. Moreover, the chemical shifts of the protons are very dependent upon the concentration of the solution. Use of $CDCl_3$ gave a badly resolved spectrum with only four broad signals for the *tert*-butyl group. $CDCl_3$ is not capable of breaking up the molecular structure completely; the molecules continue to be stacked in solution.

According to Fig. 1, the *tert*-butyl substituted PcNi-system has four different isomers, whereby eight magnetically nonequivalent isoindole units should be observable. Structures **a** and **d** contain only one magnetically equivalent isoindole unit, structure **b** contains two and **c** four nonequivalent isoindole units, respectively.

If the eight signals do not overlap one should find four signals with equal intensity for isomer **c** and two signals with equal intensity for isomer **b**, respectively. The ^{1}H NMR spectra of **1** and **2** show eight singlets for the *tert*-butyl groups and the expected intensity of the signals. This is the clearest evidence, which proves that there exist four isomers of $(Bu^t)_4PcNi$ **1** and **2**.

The existence of a mixture of isomers is also confirmed by ^{13}C NMR spectra,† each ^{13}C signal appears as a split signal $(Bu^t)_4PcNi$. Complexes **1** and **2** show intensive absorption bands in the visible and near UV regions.† The low-energy band and the high-energy band are attributed to the π-π^* Q-band and π-π^* Soret band, respectively.

$(Bu^t)_4PcNi$ **1** were prepurified by column chromatography on silica gel using chloroform as the eluent. The separation of the isomers of **1** and **2** was attempted by HPLC‡ and MPLC.§ Both methods are suitable for the separation of the isomers. Preliminary results show that we could enrich the C_s isomer to 93% by HPLC, and the C_s and C_{2v} isomers to 76–84% by MPLC. The peaks in HPLC were detected by a UV-detector in the wave region λ = 190–600 nm. This showed which peaks belong to phthalocyanines, but not to which isomer.

† *Selected spectral data* for **1**: UV–VIS (CH_2Cl_2), λ_{max}/nm 255, 278, 294, 338, 365sh, 610, 645sh, 674. ^{1}H NMR (C_6D_6): δ 1.807, 1.818, 1.823, 1.834, 1.876, 1.880, 1.893, 1.961, (Bu^t), 8.00–8.173 (H_1-arom), 8.703–9.133, 9.413–9.483 (H_2, $H_{2'}$-arom). ^{13}C NMR (C_6D_6): δ 117.85 ($C_{2'}$), 120.58–121.24 (C_2), 129.19 (C_1), 133.00–134.26 (C_3), 135.16–136.58 ($C_{3'}$), 143.34–143.81 (C_4, $C_{4'}$), 150.83–151.29 (C_1).

For **2**: UV–VIS (CH_2Cl_2), λ_{max}/nm 255, 278, 291, 340, 365sh, 610, 648sh, 678. ^{1}H NMR (C_6D_6): δ 1.810, 1.819, 1.823, 1.836, 1.877, 1.883, 1.895, 1.962 (Bu^t), 8.00–8.174 (H_1-arom), 8.706–9.150, 9.415–9.490 (H_2, $H_{2'}$-arom). ^{13}C NMR (C_6D_6): δ 116.88–117.93 ($C_{2'}$), 120.80–121.35 (C_2), 126.25 (C_1), 133.88 (C_3), 134.42 ($C_{3'}$), 143.93 (C_4, $C_{4'}$), 151.37–150.97 (C_1).

‡ Beckman system Gold 5.1; column: Knauer 250 × 20 mm Li Chrosorb Si 60, 7 μm (silica gel, preparative); solvent: hexane (87%), toluene (12%), tetrahydrofuran (THF) (1%); sample collection: 6 ml min^{-1}.

§ Column: 125 × 3 cm packed with Merck 5–40 μm silica gel 60 H using 75% petroleum (b.p. 110–140 °C) and 25% paraffin oil; solvent: hexane–toluene (60:40); pressure: 5 bar, sample collection: 200 ml per fraction 3.5 ml min^{-1}.

Altogether six fractions were collected by preparative HPLC, the sixth fraction was the C_s isomer to an extent of 93%.

In a typical run, $(Bu^t)_4PcNi$ **1** was allowed to separate by MPLC (5 bar) on a silica gel column with hexane–toluene (60:40) as eluent. Nine fractions were collected, and all fractions A to I were numbered in order of their elution from the chromatographic column. The ^1H NMR spectra of fraction A and H reveal that they contain the isomers **b** and **c**, respectively. The fraction B, C, D, E, F, G consisted of different mixtures of isomers.

The ^1H NMR spectrum of fraction A (400 MHz, C_6D_6) exhibits signals at δ 1.802–1.887, 8.041–8.120, 8.979–9.502, with an integration ratio of 36:4:8. In the region of the *tert*-butyl group there are two signals (δ 1.802, 1.861) with equal intensity. On the other hand, in the aromatic region there are two doublets of doublets for each of the magnetically nonequivalent protons H_1 with $^3J_{2,1}$ 8 Hz, $^4J_{2,1}$ 1.5–2 Hz. For H_2 protons two doublets with splitting through $^3J_{1,2}$ 8 Hz and for $H_{2'}$ protons two singlets were observed. This confirms that fraction A is the isomer with C_{2v}-symmetry **b**.

The ^1H NMR spectrum of fraction H (400 MHz, C_6D_6) shows signals at δ 1.819–1.921, 7.991–8.120 and 8.710–9.332 with an integration ratio of 36:4:8. In the *tert*-butyl group region mainly there are four signals (δ 1.836, 1.841, 1.914 and 1.921), with the same intensity. Because the chemical shifts are often dependent on the concentration of the sample, it is not possible to assign all four signals for the *tert*-butyl group to the original mixture. In the aromatic region, instead of the four expected doublets of doublets for four chemical nonequivalent protons H_1, only three groups of peaks in the spectrum were observed. Their integration ratio is 1:1:2, due probably to the overlap of two doublets. The signals of H_2 and $H_{2'}$ protons appear partly together, therefore it is not easy to assign all the protons. However, the signals of the *tert*-butyl group and aromatic protons H_1 do certainly prove that the fraction H consists of the C_s isomer **c**.

In summary, we have shown for the first time the possible separation of isomeric tetrasubstituted metallophthalocyanines containing the same substituents. This is more tedious than the separation of isomeric tetrasubstituted phthalocyanine containing different substituents, which can be carried out by gel-permeation chromatography.[11,12] We will now concentrate our efforts on the separation of the two other isomers and other functionally tetrasubstituted metallophthalocyanines.

Received, 18th May 1992; Com. 2/02569H

References

1 H. Schultz, H. Lehmann, M. Rein and M. Hanack, in *Structure and Bonding 74*, Springer-Verlag, Heidelberg, 1991, p. 41.
2 S. A. Mikhalenko, S. U. Barkanova, O. L. Lebedev and E. A. Lu'yanets, *J. Gen. Chem. UdSSR*, 1971, **41**, 2770.
3 M. Hanack, J. Metz and G. Pawlowski, *Chem. Ber.*, 1982, **115**, 2836; H. Shirai, K. Hanabusa, M. Kitamura and E. Masuda, *Makromol, Chem.*, 1984, **185**, 2537; C. C. Leznoff and T. W. Hall, *Tetrahedron Lett.*, 1982, **23**, 3023; T. W. Hall, S. Greenberg, C. R. McArthur, B. Khouw and C. C. Leznoff, *Nouv. J. Chim.*, 1982, **6**, 653; C. C. Leznoff, S. Greenberg, B. Khouw and A. B. P. Lever, *Can. J. Chem.*, 1987, **65**, 1705; Geigy AG, J. R. French Pat. No. 1 580 683, 1969; *Chem. Abstr.*, 1970, **73**, 100057.
4 S. Gaspard and Ph. Maillard, *Tetrahedron*, 1987, **43**, 1083.
5 A. Beck, K.-M. Mangold and M. Hanack, *Chem. Ber.*, 1991, **124**, 2315.
6 J. Metz, O. Schneider and M. Hanack, *Inorg. Chem.*, 1984, **23**, 1064.
7 M. Hanack, G. Renz, J. Strähle and S. Schmid, *J. Org. Chem.*, 1991, **56**, 3501.
8 S. M. Marcucio, P. I. Svirskaya, S. Greenberg, A. B. P. Lever and C. C. Leznoff, *Can. J. Chem.*, 1985, **63**, 3057.
9 R. Fay and M. Hanack, *Recl. Trav. Chim. Pays-Bas*, 1986, **105**, 427.
10 M. Hanack and P. Vermehren, *Chem. Ber.*, 1991, **124**, 733.
11 Y. Ikeda, H. Konami, M. Hatano and K. Mochizuki, *Chem. Lett.*, 1992, 763.
12 N. Kobayashi, T. Ashida and T. Osa, *Chem. Lett.*, 1992, 2031.