Synthesis and Separation of Structural Isomers of Tri-*tert*-butylsubphthalocyaninatophenylboron(III)

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Tri-*tert*-butylsubphthalocyaninatophenylboron(III) is synthesized from phthalodinitrile and triphenylboron, whereby a mixture of two structural isomers is obtained; these isomers, with C_3- and C_1-symmetry, are separated by HPLC and characterized by ^{1}H NMR spectroscopy.

Subphthalocyanines **1** (X = Cl, Br, F) recently became increasingly interesting due to the fact that they can be used as precursors for the synthesis of unsymmetrically substituted phthalocyanines.[1–8] As in the case of phthalocyanines, unsubstituted subphthalocyanines **1** (X = Cl, Br, F) are practically insoluble in common organic solvents. On the other hand, the tri-*tert*-butyl-substituted subphthalocyanine Bu^t_3SubPcBBr is soluble in organic solvents, exhibiting similarity with tetra-*tert*-butyl-substituted phthalocyaninato analogues.

Recently we described for the first time a new subphthalocyanine **1** (X = Ph) in which the axial substituent is a phenyl group.[7]

We have now prepared the corresponding tri-*tert*-butyl-substituted derivative Bu^t_3SubPcBPh and report here also on the successful chromatographic separation and spectroscopic characterization of its two possible structural isomers (C_1 and C_3) (Scheme 1). The first chromatographic separation of the four possible structural isomers (C_{4h}, D_{2h}, C_{2v} and C_s) of a tetra-substituted phthalocyanine was carried out in our group recently.[9,10]

A mixture of tri-*tert*-butylsubphthalocyanines, Bu^t_3SubPcBCl and Bu^t_3SubPcBPh, both soluble in common organic solvents, starting from *tert*-butylphthalodinitrile and dichlorophenylborane in chloronaphthalene as solvent at 230 °C is prepared first. As a side reaction, chlorination of the macrocycle by chlorine generated from $PhBCl_2$ under the reaction conditions is observed. The mixture of subphthalocyanines obtained is difficult to separate and purify. A careful HPLC-analysis shows, beside the chlorinated products, four peaks, which we assign to the two isomers of Bu^t_3SubPcBCl and Bu^t_3SubPcBPh, respectively.

The preparation of only one subphthalocyanine, with a phenyl group as axial substituent, would facilitate the separation of the isomers. For this purpose triphenylboron as the boron-reagent and naphthalene instead of 1-chloronaphthalene as solvent are used. By this approach the unwanted chlorination of the macrocycle is avoided.

The reaction of *tert*-butylphthalodinitrile and BPh_3 (Scheme 1) is carried out in naphthalene at 218 °C. The obtained product Bu^t_3SubPcBPh is prepurified by column chromatography on deactivated Al_2O_3 using toluene as the eluent.

The reaction of *tert*-butylphthalodinitrile with BPh_3 can lead to two structural isomers with the point group symmetry C_3 and C_1, respectively (Scheme 1), whereby in the mixture four magnetically nonequivalent isoindolenine units should be observable. The C_3-isomer contains only one magnetically equivalent isoindolenine whereas the C_1-isomer has three nonequivalent isoindolenine units.

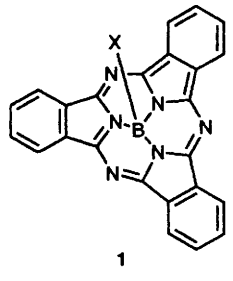
If the four signals for the *tert*-butyl group do not overlap, one should find one signal for the C_3-isomer and three signals with equal intensity for the C_1-isomer. The ^{1}H NMR spectrum of the prepurified Bu^t_3SubPcBPh shows four singlets for the *tert*-butyl groups. This proves that two structural isomers were formed.

The separation of the C_3- and C_1-isomers is carried out by HPLC,† the peak detection was done by a UV-detector in the region λ 190–600 nm. The HPLC chromatogram shows two completely separated peaks, which were collected by preparative HPLC‡ (fraction A and fraction B).

The ^{1}H NMR spectra of both fractions show three signals (δ 5.748–5.786, 6.517–6.581, 6.624–6.695) with an integration ratio of 2 : 2 : 1 for the protons of the axial phenyl group. The position of the *tert*-butyl group has no influence on these signals.

The ^{1}H NMR spectrum of fraction A (250 MHz, C_6D_6)§ exhibits signals at δ 1.312, 5.748–5.786, 6.517–6.581, 6.624–6.695, 7.604–7.644, 8.839–8.875, 9.050–9.059 with an integration ratio of 27 : 2 : 2 : 1 : 3 : 3 : 3. In the region of the *tert*-butyl group only one signal (δ 1.312) is found. The aromatic protons appear as a doublet of doublets for the H^1 proton with $^3J_{2,1}$ 8.2–8.5 Hz, $^4J_{3,1}$ 1.5–1.8 Hz, a doublet of doublets for the H^2 proton with $^3J_{1,2}$ 8.2–8.5 Hz, $^5J_{3,2}$ 0.6–0.9 Hz and a doublet of doublets for the H^3 proton, $^4J_{1,3}$ 1.8 Hz, $^5J_{2,3}$ 0.6 Hz (Scheme 1). This confirms that fraction A contains the pure C_3-isomer.

The ^{1}H NMR spectrum of fraction B (250 MHz, C_6D_6)§ shows signals at δ 1.301–1.329, 5.748–5.786, 6.517–6.581, 6.624–6.695, 7.615–7.677, 8.854–8.897, 9.053–9.058 with an integration ratio of 27 : 2 : 2 : 1 : 3 : 3 : 3. For the *tert*-butyl group three signals (δ 1.301, 1.316, 1.329) with the same intensity are observed. In the aromatic region two doublets of doublets for the H^1 proton with an integration ratio of 1 : 2 are found, in addition to two doublets of doublets with the same integration



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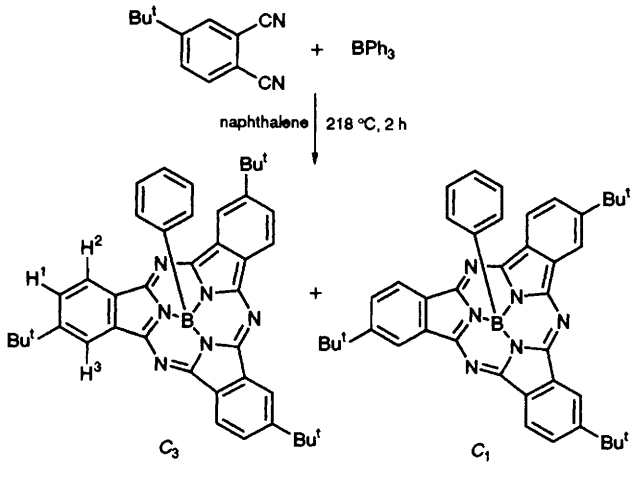

Scheme 1

ratio for the H^2 proton. Due to the overlap of the expected two doublets of doublet, the signal for H^3 shows only one doublet. The signals of the *tert*-butyl group and the aromatic protons respectively prove that fraction B contains the pure C_1-isomer.

In summary we have described for the first time the synthesis and HPLC-separation of the structural isomers of a trisubstituted subphthalocyanine, Bu^t_3SubPcBPh. The point groups are determined unequivocally by ^1H NMR spectroscopy.

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Footnotes

† Beckmann system Gold 5.1: column; Macherey-Nagel, ET 250/8/4, Nucleosil $5NO_2$: solvent; hexane–toluene (1:1): sample collection, 1.5 ml min^{-1}

‡ Harley Systems Peakmaster, Sepacon Peakmaster Auto Interface: column; Macherey-Nagel VarioPrep ET250/21, Nucleosil 100-$5NO_2$: solvent; hexane–toluene (2:3); sample collection, 26 ml min^{-1}

§ Isomer **1**: ^1H NMR (C_6D_6) δ 1.312 (s, 27H), 5.748–5.786 (dd, 2H), 6.517–6.581 (m, 2H), 6.624–6.695 (tt, 1H), 7.604–7.644 (dd, 3H), 8.839–8.875 (dd, 3H), 9.050–9.059 (dd, 3H). Isomer **2**: ^1H NMR (C_6D_6) δ 1.301–1.329 (3s, 27H), 5.748–5.786 (dd, 2H), 6.517–6.581 (m, 2H), 6.624–6.695 (tt, 1H), 7.615–7.677 (2 dd, 3H), 8.854–8.897 (2 dd, 3H), 9.053–9.058 (d, 3H)

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