Synthesis and spectroscopic properties of new boron subphthalocyanine complexes and a heteronuclear phthalocyanine complex*

A. Yu. Tolbin,[a] M. O. Breusova,[a] V. E. Pushkarev,[b] and L. G. Tomilova[a,b]*

[a]Department of Chemistry, M. V. Lomonosov Moscow State University,
1 Leninskie Gory, 119992 Moscow, Russian Federation.
Fax: +7 (495) 939 0290. E-mail: tom@org.chem.msu.su
[b]Institute of Physiologically Active Compounds, Russian Academy of Sciences,
1 Severnyi proezd, 142432 Chernogolovka, Moscow region, Russian Federation.
Fax: +7 (496) 785 7024

New boron μ-chloro- and μ-alkoxyhexabutylsubphthalocyanines were synthesized. A heteronuclear complex containing both the phthalocyanine and subphthalocyanine fragments was prepared. The spectroscopic properties of these compounds were studied.

Key words: phthalocyanine, subphthalocyanine, heteronuclear complex, synthesis.

In the last decade, boron subphthalocyanine complexes have attracted considerable attention.[1—7] Subphthalocyanines are lower homologs of phthalocyanines consisting of three isoindoline fragments.[2,3] Their 14π-electron aromatic system is characterized by a distorted geometry, which is responsible for their second- and third-order nonlinear optical properties.[4,5]

Earlier,[8,9] numerous subphthalocyanine derivatives have been synthesized. However, their μ-oxy complexes with organic molecules containing the phthalocyanine fragment remained unknown. We expected that such molecules could exhibit unique optical properties.

The aim of the present study was to synthesize the previously unknown boron subphthalocyanine complexes and the heteronuclear phthalocyanine—spacer—subphthalocyanine complex and investigate their spectroscopic properties.

Results and Discussion

Initially, we attempted to synthesize symmetrical hexabutyl-substituted boron subphthalocyanine **1** according to a standard procedure by heating 4,5-dibutylphthalodinitrile in α-chloronaphthalene at 240 °C.[2] However, due to the high reaction temperature, the reaction afforded predominantly polymeric products, whereas the target compound was obtained in a yield of at most 10%. The reaction in refluxing *o*-dichlorobenzene (*o*-DCB), in which the reaction temperature was lowered to 180 °C, produced the target compound in substantially higher yield. In complex **1**, the chlorine atom in the axial position is easily replaced by alkoxy groups in high yield (Scheme 1).

The mass spectra of subphthalocyanines **1** and **2a,b** have molecular ion peaks ($[M]^{+\bullet}$) and the characteristic fragment ions $[M - Cl]^+$ for **1** and $[M - OR]^+$ for **2a,b** with unique isotope splitting.

In the ^{1}H NMR spectra of the compounds synthesized, the signals for the aromatic protons appear as a singlet (6 H) at δ 8.2—8.3 and the signals for the aliphatic protons are observed at δ 1.2—3.3. The ^{11}B NMR spectra of compounds **1** and **2a,b** show singlets for the boron atoms. In the spectra of alkoxy-substituted complexes **2a,b**, these signals are shifted downfield by ~10 ppm compared to those in the spectrum of **1**.

The absorption spectra of subphthalocyanines **1** and **2a,b** were studied. Their shape and character correspond to those of analogs described in the study.[2] The Q band of complex **1** is bathochromically shifted by 5—6 nm compared to this band of compounds **2a,b**. The electronic absorption spectrum of compound **1** is shown as an example in Fig. 1.

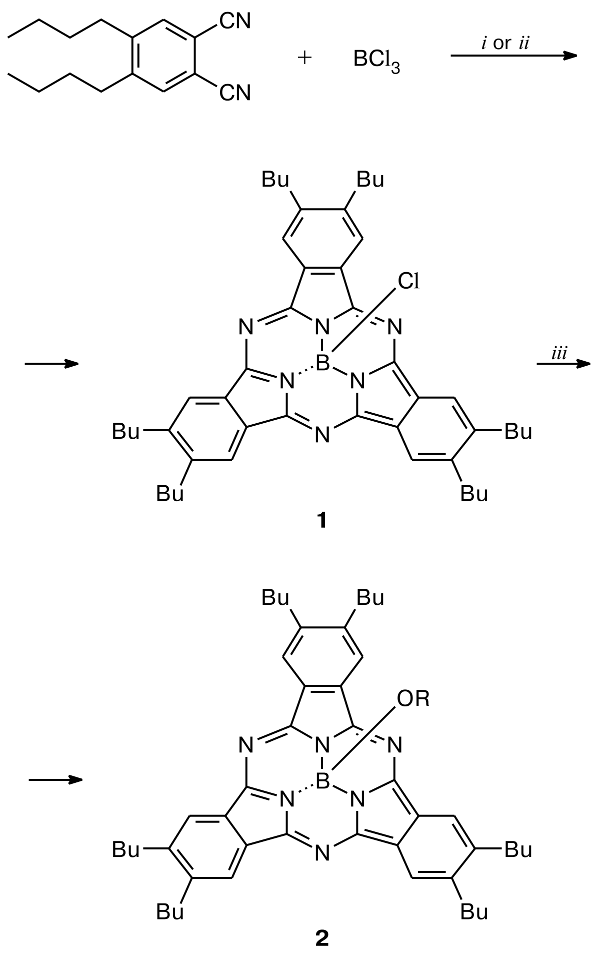
The reaction of subphthalocyanine **1** with phthalocyanine complex **3**, which was synthesized according to a procedure described in our earlier study,[10] produced the corresponding heteronuclear complex **4** (Scheme 2). The course of the reaction was monitored by TLC. After completion of the reaction, the mixture was purified from traces of unconsumed compound **1** and products of its partial destruction by gel permeation chromatography on BioBeads S-X1.

---

* Dedicated to Academician N. S. Zefirov on the occasion of his 70th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 2020—2023, September, 2005.

Scheme 1



R = Me (**a**), Et (**b**)

i. α-Chloronaphthalene, 240 °C, 30 min, yield 9%. *ii.* *o*-DCB, 180 °C, 10 min, yield 88%. *iii.* ROH/THF, 64—65 °C, 25—30 min.

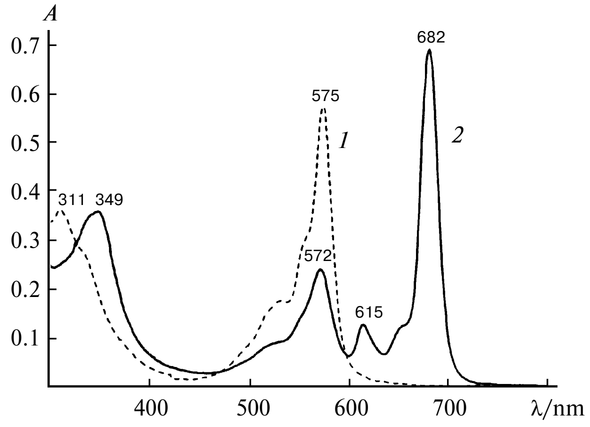


Fig. 1. Electronic absorption spectra of complex **1** (*1*) and heteronuclear complex **4** (*2*) in THF.

Attempts to use basic solvents and raise the temperature in the synthesis of compound **4** led exclusively to decomposition of complex **1**. The use of lower-boiling solvents, such as THF, benzene, or dioxane, instead of toluene substantially increased the reaction time. Therefore, toluene is the solvent of choice for this reaction. A substantial increase in the reaction time in the synthesis of **4** compared to **2a,b** can be attributed to both the concentration factor and the possible steric hindrance caused by the phthalocyanine macrocycle.

The MALDI-TOF mass spectrum of heteronuclear complex **4** contains the molecular ion peaks ($[M]^{+\bullet}$) and the characteristic fragment ions ($[M - C_{56}H_{68}BN_6O^\bullet]^+$ and $[M - C_{56}H_{63}N_8OZn^\bullet]^+$). The peaks of all ions are characterized by isotope splitting corresponding to the natural isotopic abundance. The molecular ion peak of compound **4** is shown as an example in Fig. 2.

In the ^{1}H NMR spectrum of compound **4**, the singlet for the aromatic protons of the subphthalocyanine macrocycle (6 H) is shifted downfield by δ 0.3—0.4 compared to that in the spectra of compounds **2a,b**. The multiplets for the protons of the phthalocyanine ring and the spacer are observed at δ 8.8—9.3 (9 H) and 7.6—8.0 (4 H), respectively. The singlets for the benzylic protons are observed at δ 4.8 and 5.2 (2 H each), the distance between these signals being almost twice shorter than that in the starting complex **3**. The signals for the aliphatic protons are observed at δ 1.1—3.2 (108 H). The ^{11}B NMR spectrum of complex **4** shows a singlet at δ –15.25, which is slightly shifted upfield compared to that observed in the spectra of **2a,b**.

The electronic absorption spectrum of heteronuclear complex **4** is indicative of the presence of both the phthalocyanine and subphthalocyanine components in the complicated molecule. The intensity of the band belonging to the subphthalocyanine fragment in compound **4** is almost three times lower than that in the spectrum of complex **1** at the same concentration ($2.9 \cdot 10^{-5}$ mol L^{-1}), and this

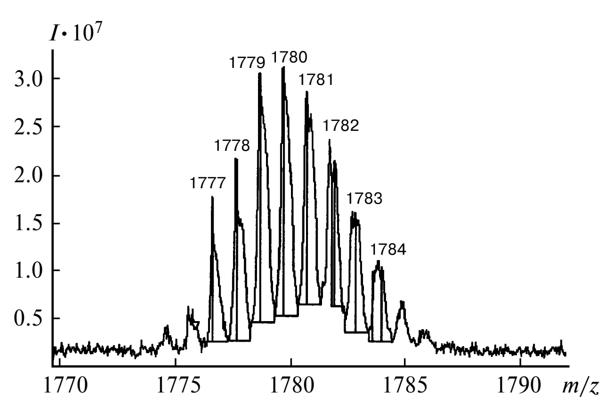
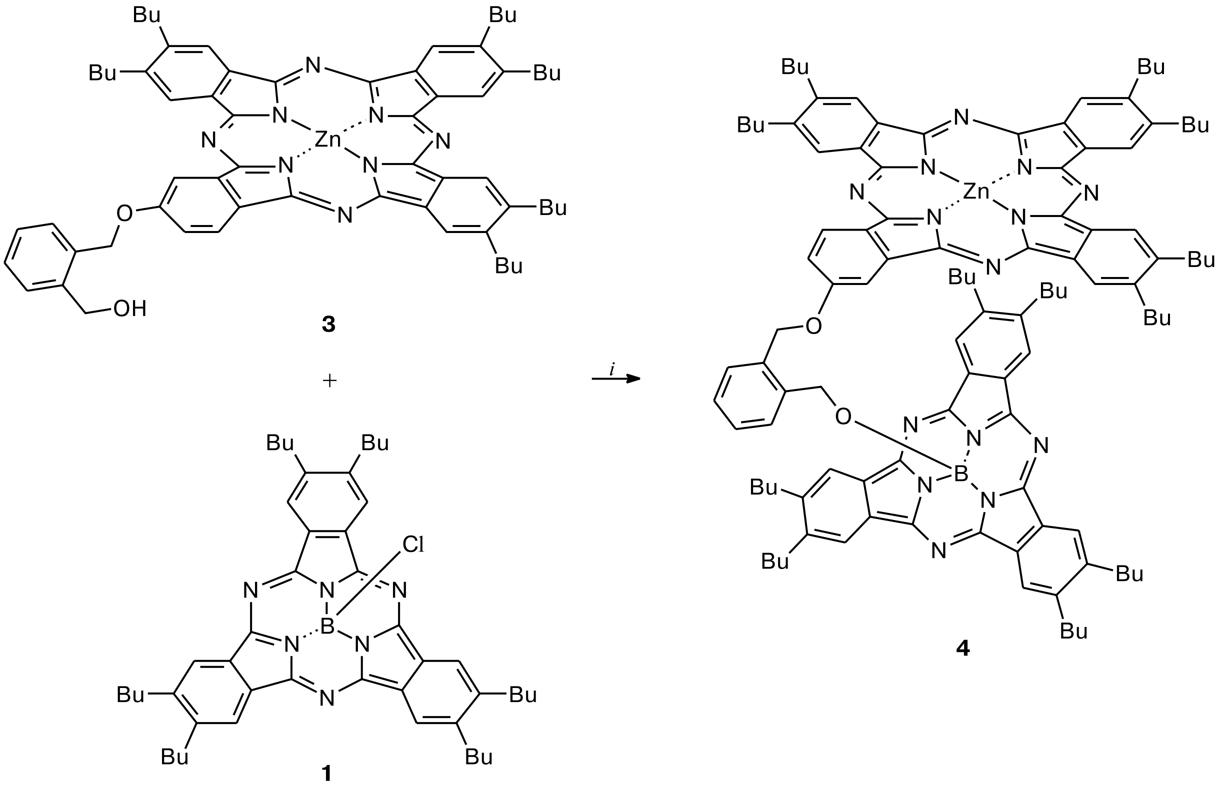


Fig. 2. Molecular ion peak of heteronuclear complex **4** (MALDI-TOF mass spectrum).

Scheme 2



i. Toluene, 110 °C, 16 h.

band is slightly (by 3 nm) hypsochromically shifted. The phthalocyanine band is also shifted by 3 nm compared to that in the spectrum of compound **3**, but the shift is bathochromic. The subphthalocyanine band in the spectrum of complex **4** is also bathochromically shifted by 2—3 nm compared to that of compounds **2a,b**. A change in the nature of the solvents has virtually no effect on the character of the electronic absorption spectrum of heteronuclear complex **4** and the relative intensities of the phthalocyanine and subphthalocyanine bands. The electronic absorption spectrum of compound **4** in THF is shown as an example in Fig. 1.

Compound **4** is stable in most organic solvents at temperatures no higher than 120 °C. In the presence of acids, for example, of CH_3COOH, the ether bond in **4** is cleaved virtually immediately even at room temperature to give the starting phthalocyanine **3** and boron subphthalocyanine containing the OH group in the axial position, which was demonstrated by mass spectrometry. The same virtually complete destruction occurs during chromatography on silica gel or aluminum oxide. Hence, complex **4** was isolated by gel permeation chromatography.

To summarize, we synthesized boron subphthalocyanine complexes **1** and **2a,b** in high yields. Heteronuclear phthalocyanine—spacer—subphthalocyanine complex **4**, which has no analogs in the literature, was synthesized for the first time.

Experimental

The ^{1}H NMR spectra were recorded on a Bruker AM-300 instrument operating at 300.13 MHz. The electronic absorption spectra (EAS) were measured on a Helios-α spectrophotometer in 0.5 cm quartz cells in THF, benzene, acetone, or pyridine. The mass spectra were recorded on an Autoflex II instrument (MALDI-TOF without a matrix). Column chromatography was performed on silica gel 60 (40—63 μm; Merck) and BioBeads SX-1 (BioRad). All solvents were purified according to standard procedures immediately before use. Commercial BCl_3 (1 *M* solution in hexane, Aldrich) was used without additional purification. 4,5-Diutylphthalodinitrile was prepared according to a procedure described earlier.[11]

Boron μ-chloro-(2,3,9,10,16,17-hexabutylsubphthalocyanine) (1). A solution of 4,5-dibutylphthalodinitrile (100 mg, 0.417 mmol) in *o*-DCB (5 mL) was cooled to +5 °C followed by the addition of BCl_3 (0.2 mL, 0.200 mmol). The reaction mixture was stirred for 10 min under argon, heated to 180 °C, kept at this temperature for 15 min, and then cooled to room temperature. The solvent was distilled off *in vacuo*, and compound **1** was extracted with hexane. The yield was 88 mg (88%). MS, m/z (I_{rel} (%)): 766 $[M]^{+\bullet}$ (21), 731 $[M - Cl]^+$ (100). ^{1}H NMR ($CDCl_3$), δ: 1.05 (t, 18 H, $C\underline{H}_3CH_2CH_2CH_2$, J = 7.2 Hz);

1.51—1.53 (m, 12 H, $CH_3C\underline{H}_2CH_2CH_2$); 1.55—1.57 (m, 12 H, $CH_3CH_2C\underline{H}_2CH_2$); 3.0 (t, 12 H, $CH_3CH_2CH_2C\underline{H}_2$, $J = 7.2$ Hz); 8.53 (s, 6 H, Ar). ^{11}B NMR ($CDCl_3$), δ: −25.00 (s, 1 B). EAS (THF), λ_{max}/nm (logε): 311 (4.56), 575 (4.76).

Boron μ-methoxy-(2,3,9,10,16,17-hexabutylsubphthalocyanine) (2a). Methanol (5 mL) was added to a solution of subphthalocyanine **1** (15 mg, 0.019 mmol) in THF (5 mL). The reaction mixture was refluxed for 25 min. After completion of the reaction, the solvents were evaporated *in vacuo*, and the residue was chromatographed on silica gel with the use of benzene as the eluent. The yield was 14 mg (95%). MS, *m/z* (I_{rel} (%)): 762 $[M]^{+\bullet}$ (100), 747 $[M - CH_3]^+$ (50), 731 $[M - OCH_3]^+$ (28). ^{1}H NMR ($CDCl_3$), δ: 1.11 (t, 18 H, $C\underline{H}_3CH_2CH_2CH_2$, $J = 7.4$ Hz); 1.50—1.53 (m, 12 H, $CH_3C\underline{H}_2CH_2CH_2$); 1.54 (s, 3 H, OCH_3); 1.56—1.58 (m, 12 H, $CH_3CH_2C\underline{H}_2CH_2$); 2.95 (t, 12 H, $CH_3CH_2CH_2C\underline{H}_2$, $J = 7.5$ Hz); 8.52 (s, 6 H, Ar). ^{11}B NMR ($CDCl_3$), δ: −14.77 (s, 1 B). EAS (THF), λ_{max}/nm (logε): 308 (4.58), 569 (4.77).

Boron μ-ethoxy-(2,3,9,10,16,17-hexabutylsubphthalocyanine) (2b) was synthesized analogously to compound **2a** with the use of EtOH. The yield of compound **2b** was 20 mg (98%). MS, *m/z* (I_{rel} (%)): 776 $[M]^{+\bullet}$ (100), 731 $[M - OC_2H_5]^+$ (31). ^{1}H NMR ($CDCl_3$), δ: 1.10 (t, 18 H, $C\underline{H}_3CH_2CH_2CH_2$, $J = 7.0$ Hz); 1.51—1.53 (m, 12 H, $CH_3C\underline{H}_2CH_2CH_2$); 1.54—1.55 (m, 5 H, OC_2H_5); 1.56—1.58 (m, 12 H, $CH_3CH_2C\underline{H}_2CH_2$); 2.90 (t, 12 H, $CH_3CH_2CH_2C\underline{H}_2$, $J = 7.2$ Hz); 8.54 (s, 6 H, Ar). ^{11}B NMR ($CDCl_3$), δ: −14.91 (s, 1 B). EAS (THF), λ_{max}/nm (logε): 309 (4.57), 570 (4.78).

Boron [zinc(9´,10´,16´,17´,23´,24´-hexabutylphthalocyanine-2´-oxymethyl-*o*-benzyloxy)]-(2,3,9,10,16,17-hexabutylsubphthalocyanine) (4). Compound **1** (7 mg, 0.009 mmol) was added to a solution of compound **3** (8 mg, 0.007 mmol) in toluene (5 mL). The reaction mixture was refluxed for 15.5 h and then concentrated *in vacuo*. Complex **4** was isolated by chromatography on BioBeads S-X1 in a yield of 12 mg (91%). MS, *m/z* (I_{rel} (%)): 1780 $[M]^{+\bullet}$ (7), 927 $[M - C_{56}H_{68}BN_6O^\bullet]^+$ (48), 851 $[M - C_{56}H_{63}N_8OZn^\bullet]^+$ (100). ^{1}H NMR ($CDCl_3$+Py-d_5), δ: 1.05—3.35 (m, 108 H, C_4H_9); 4.80 and 5.15 (both s, 2 H each, $C\underline{H}_2$); 7.32—7.89 (m, 4 H, Ar); 8.57 (s, 6 H, Ar); 8.84—9.24 (m, 9 H, Ar). ^{11}B NMR ($CDCl_3$), δ: −15.25 (s, 1 B). EAS (THF), λ_{max}/nm (logε): 349 (4.55), 572 (4.38), 615 (4.10), 682 (4.83).

We thank E. V. Shulishov (N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences) for recording NMR spectra.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 05-03-33202) and the International Science and Technology Center (ISTC, Grant 1526).

References

1. N. Kobayashi, T. Ishizaki, K. Ishii, and H. Konami, *J. Am. Chem. Soc.,* 1999, **121**, 9096.
2. M. Geyer, F. Plenzig, J. Rauschnabel, M. Hanack, and T. Torres, *Synthesis,* 1996, 1139.
3. C. G. Claessens, D. Gonzalez-Rodriguez, and T. Torres, *Chem. Rev.,* 2002, **102**, 835.
4. M. A. Diaz-Garcia, F. Agullo-Lopez, A. Sastre, and T. Torres, *J. Phys. Chem.,* 1995, **99**, 14988.
5. G. Rojo, A. Hierro, M.A. Diaz-Garcia, and T. Torres, *Appl. Phys. Lett.,* 1997, **70**, 1802.
6. A. Weitmeyer, H. Kliesch, and D. Woehrle, *J. Org. Chem.,* 1995, **60**, 4900.
7. S. Kudrevich, N. Brasseur, C. La Madeleine, S. Gilbert, and J. E. van Lier, *J. Med. Chem.,* 1997, **40**, 3897.
8. T. Fukuda, M. M. Olmstead, W. S. Durfee, and N. Kobayashi, *Chem. Commun.,* 2003, 1256.
9. D. Gonzalez-Rodrigues, T. Torres, D. M. Guldi, J. Rivera, and L. Echegoyen, *Org. Lett.,* 2002, **4**, 335.
10. A. Yu. Tolbin, L. G. Tomilova, and N. S. Zefirov, *Izv. Akad. Nauk, Ser. Khim.*, 2005, 2036 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 2099].
11. E. A. Cuellar and T. J. Marks, *J. Inorg. Chem.,* 1981, **20**, 3766.

Received July 20, 2005