Synthesis of alkyl-substituted phosphorus phthalocyanines and triazatetrabenzocorroles

M. O. Breusova,[a,b] 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.ru*
[b]*Institute of Physiologically Active Compounds, Russian Academy of Sciences, 1 Severnyi proezd, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 (495) 913 2113*

New alkyl-substituted phosphorus phthalocyanines and triazatetrabenzocorroles were synthesized. The structures of these complexes were confirmed by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, mass spectrometry, and electronic absorption spectroscopy.

Key words: phthalocyanine, triazatetrabenzocorrole, phosphorus, electronic absorption spectra, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, MALDI-TOF mass spectrometry.

Methods for the synthesis and properties of various metal phthalocyanines having both planar and sandwich structures have been studied in sufficient detail, whereas phthalocyanine complexes with nonmetals have received much less attention. In our previous study,[1] we have investigated boron phthalocyanine complexes. Due to the small radius, boron is prone to form only subphthalocyanine complexes with ligands consisting of three isoindole fragments. Due to the geometric and electronic structures, these complexes exhibit unusual spectroscopic properties allowing their use in new fields of engineering.

The aim of the present study was to synthesize alkyl-substituted phosphorus phthalocyanines and triazatetrabenzocorroles and investigate their spectroscopic properties.

Phosphorus phthalocyanines were synthesized for the first time[2] in 1981. However, data on these compounds are scarce, and many questions remain open.

It was reported that phosphorus can form not only phthalocyanine complexes but also complexes with triazatetrabenzocorroles.[3,4] Initially, it has been hypothesized that the latter compounds are phthalocyanine complexes of trivalent phosphorus.[2] However, further physicochemical studies showed that the complex consists of triazatetrabenzocorrole and pentavalent phosphorus; analogs of this complex are synthesized for both nonmetals (germanium and silicon) and some metals (manganese, iron, and chromium).[5] The electronic structure of triazatetrabenzocorrole, whose "window" radius allows stabilization of the complexing ions in high oxidation states, can favor the use of these compounds in oxidative catalysis.

Results and Discussion

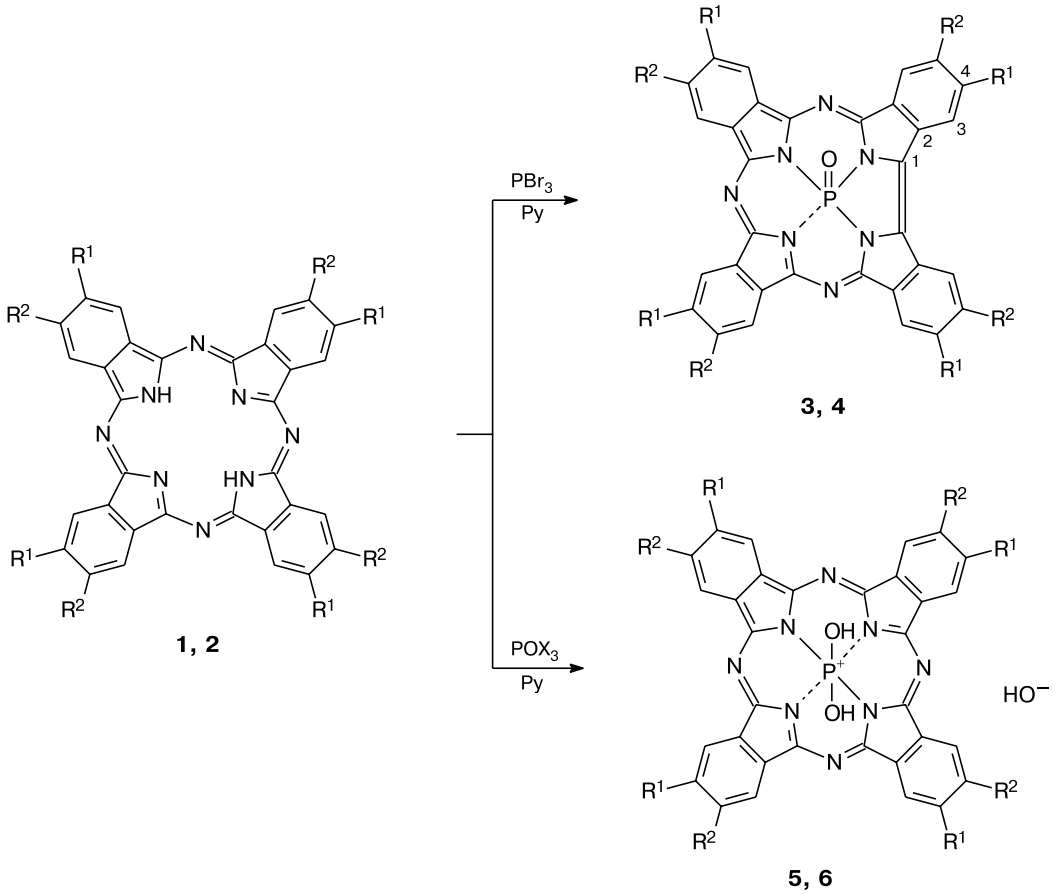
We used metal-free phthalocyanines **1** and **2**, which have been prepared in our earlier study,[6] as the starting compounds for the synthesis of phosphorus phthalocyanine and triazatetrabenzocorrole complexes, respectively. Depending on the nature of the starting phosphorus-containing compound, the reactions give different types of complexes. The reactions of phosphorus(v) oxyhalides produce phthalocyanine complexes, whereas the reactions of phosphorus(III) bromide give triazatetrabenzocorroles (Scheme 1).

In the reaction with PBr_3 for 1.5 h, phthalocyanine **1** undergoes complete conversion to form the only product of the phthalocyanine nature, *viz.*, triazatetrabenzocorrole (**3**). Since compound **3** is poorly soluble in most of organic solvents, investigations of **3** present difficulties. The use of *tert*-butyl-substituted phthalocyanine (**2**) as the starting compound allowed us to substantially increase the solubility of the resulting triazatetrabenzocorrole **4**.

The reaction of phthalocyanine **2** with $POCl_3$ giving rise to compound **6** was completed in 24 h. The yield of the product was 62%. The reaction time in the case of $POBr_3$ decreases to 45 min with a simultaneous increase in the yield of the target product to 75%. The reaction of octabutylphthalocyanine **1** with $POBr_3$ affords phthalocyanine **5** in 48% yield, whereas the reaction with $POCl_3$ does not result in the target complex **5** at all. The suggestion[7] that this is due to lower solubility of the ligand is not quite correct because complete dissolution of the ligand upon the addition of *o*-dichlorobenzene also did not give rise to the target product.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1403—1407, July, 2007.
1066-5285/07/5607-1456

Scheme 1



$R^1 = R^2$ = Bu (**1**, **3**, **5**); R^1 = H, R^2 = Bu^t (**2**, **4**, **6**); X = Br, Cl

An attempt to employ the method that we have developed earlier for the efficient synthesis of metal phthalocyanine complexes,[6,8] *viz.*, in *o*-dichlorobenzene in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), also failed. Apparently, phosphorus phthalocyanine that is formed in the first step is converted into triazatetrabenzocorrole because of the high reducing ability of DBU. Actually, the addition of DBU to a solution of phosphorus phthalocyanine resulted in the quantitative conversion of phthalocyanine into triazatetrabenzocorrole. This process can easily be monitored by following the changes in the electronic absorption spectra. The electronic absorption spectra of phosphorus phthalocyanine complexes **5** and **6** are typical of phthalocyanines. These spectra show a Q band at 680—690 nm and a Soret band at 350—360 nm. The electronic absorption spectrum of compound **5** is exemplified in Fig. 1, *a*.

The position of the Q band of octabutylphthalocyanine **5** correlates well with the corresponding band of symmetrical octapropyl-substituted phosphorus phthalocyanine synthesized earlier.[7] For example, an increase in the length of the substituent in the macroligand by one

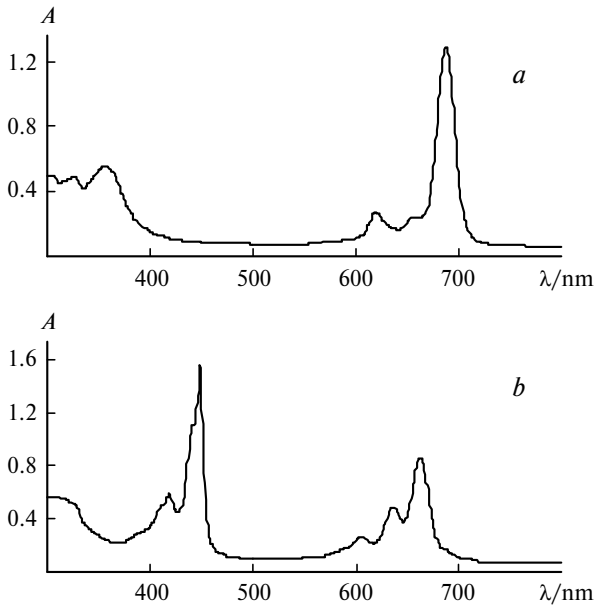


Fig. 1. Electronic absorption spectra of complexes **5** (*a*) and **3** (*b*) in pyridine.

CH_2 group leads to a slight bathochromic shift of the Q band from 684 to 688 nm.

The absence of one *meso*-nitrogen atom in triazatetrabenzocorrole compared to phthalocyanine results in a substantial change in the electronic absorption spectrum characterized by the split Q band and the Soret band, whose intensity is almost twice as high as that of the Q band (Fig. 1, *b*). The Q band is shifted hypsochromically by 30 nm with respect to the corresponding bands in the spectra of phthalocyanines; the Soret band, bathochromically by 100 nm.

The shift of the Soret band to longer wavelengths is apparently attributed to destabilization of the highest occupied MO-1 (a_{2u}) due to elimination of one *meso*-nitrogen atom.[9] The structures of the resulting complexes were confirmed by ^1H, ^{13}C, and ^{31}P NMR spectroscopy and mass spectrometry.

The ^1H NMR spectrum of compound **5** shows a singlet for aromatic protons at δ 9.30 (8 H). Signals for aliphatic protons are observed at δ 1.10—2.90 (72 H).

Since the triazatetrabenzocorrole macrocycle consists of two types of nonequivalent isoindole fragments, the ^1H NMR spectrum of the symmetrically substituted complex should have four signals corresponding to aromatic protons. In the spectrum of octabutyl-substituted triazatetrabenzocorrole **3** in a $CDCl_3$—Py-d_5 system (1 : 1, v/v), the signals in the region of aromatic protons partially overlap, and the spectrum shows three rather than four protons. However, these signals correspond to four types of protons, as evidenced by the integrated intensity ratio (1 : 2 : 1). The spectrum recorded in $CDCl_3$ shows two signals at δ 9.00—9.30 with an integrated intensity ratio of 1 : 1. The signals corresponding to the protons of the alkyl groups, unlike the corresponding signals of butyl-substituted phosphorus phthalocyanine **5**, appear as multiplets (for example, a multiplet instead of a triplet corresponding to the terminal methyl groups is observed at δ 1.10—1.25).

The available ^{13}C NMR spectroscopic data are insufficient for describing the structural features of the compounds under consideration. The optimization of the conditions for recording the NMR spectra allowed us to efficiently use ^{13}C NMR spectroscopy for studying triazatetrabenzocorrole **3**. The introduction of the ^{13}C label at the α-pyrrole positions of the phthalocyanine macrocycle (this procedure has not been described earlier) appeared to be an important factor for the interpretation of the spectra. Thus triazatetrabenzocorrole **3´** was synthesized based on 4,5-dibutylphthalonitrile labeled at the CN groups (the enrichment in the ^{13}C isotope was 10%). The effect of the concentration-dependent aggregation of the complex, which hinders the interpretation of the spectra, was reduced by recording the spectrum at 50 °C. By analogy with the ^1H NMR spectra, four sets of similar signals were observed, which is indicative of the different shielding and reflects the structural features of triazatetrabenzocorrole **3** (Fig. 2).

Evidently, the signals at δ 142.87, 141.14, 137.33, and 119.38 correspond to the labeled C(1) atoms. The signal at δ 119.38 belongs apparently to the strongly shielded

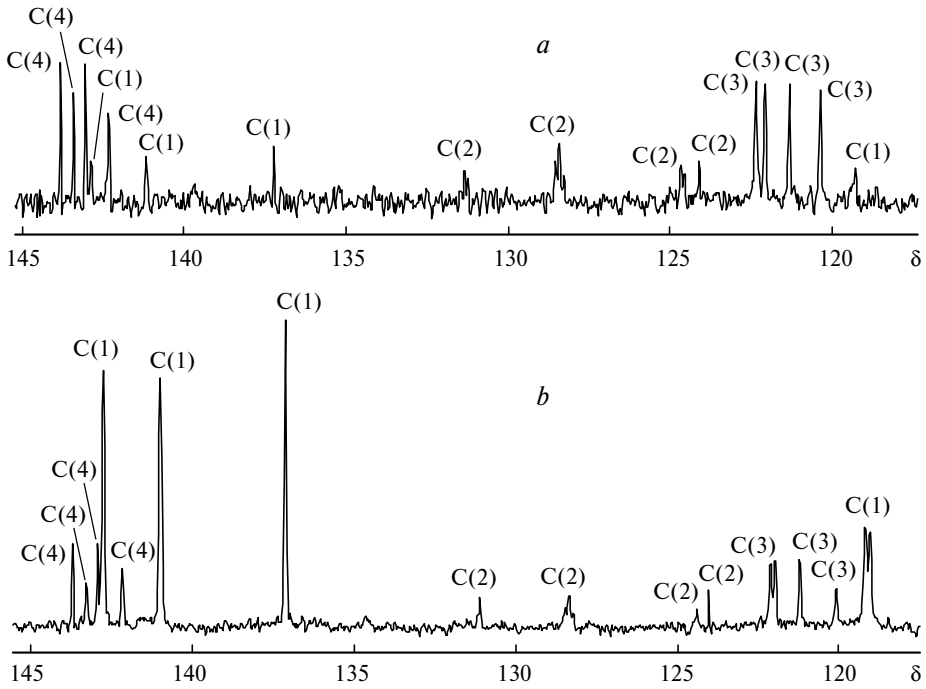


Fig. 2. Aromatic region of the ^{13}C NMR spectra of compound **3** (*a*) and compound **3´** enriched in ^{13}C at the C(1) atom (*b*).

carbon atoms of the C—C bridge. According to the data obtained with the use of the DEPT-135 pulse techniques, the signals for the C(3) atoms appear at δ 122.43, 122.15, 121.41, and 120.46. The signals for the C(4) and C(2) atoms are observed at δ 143.91—142.41 and 131.43—124.20, respectively.

The signals for the phosphorus atoms in the ^{31}P NMR spectra are observed at δ −100 and −200 and depend on the structure of the complex. The position of the signal provides data on the coordination number of phosphorus and its spatial environment.[10,11] For example, the spectra of phosphorus triazatetrabenzocorroles **3** and **4** and phthalocyanines **5** and **6** in the $CHCl_3$—Py system (1 : 1, v/v) show one signal at δ −201 and one signal at δ −189, respectively, which corresponds to the six-coordinate phosphorus atom. This structure of the complexes is confirmed also by MALDI-TOF mass spectra.

The ^{31}P NMR spectrum of triazatetrabenzocorrole **3** in $CDCl_3$ shows, along with the signal at δ −201, a signal at δ −105, whose intensity increases with time. According to the data published earlier, this corresponds to the five-coordinate phosphorus atom[11] and is apparently attributed to the partial protonation of the axial oxygen atom by the solvent in the course of the preparation of a sample, resulting in a change in the coordination number of the complexing ion.[10]

The MALDI-TOF mass spectra of triazatetrabenzocorroles **3** and **4** have peaks of singly charged ions with masses and isotope splitting corresponding to the theoretically calculated parameters (Fig. 3). The mass spectra of phosphorus phthalocyanines **5** and **6** contain not only peaks of singly charged ions with masses corresponding to the molecular weights of the target compounds, but also peaks of the $\{[PcP(OH)_2]OH\}^+$, $[PcP(OH)_2]^+$, and $[PcPO]^+$ ions that are formed due to successive elimination of the hydroxy groups induced by laser ionization, the most intense peaks belonging to $[PcP]^{3+}$. The spectra also have a peak with the molecular mass corresponding to the free ligand, which is produced by dephosphorylation under laser irradiation. Relatively low stability of the complexes to laser radiation is attributed to the small ionic radius of pentavalent phosphorus and, consequently, to its weak bonds with the ligand.

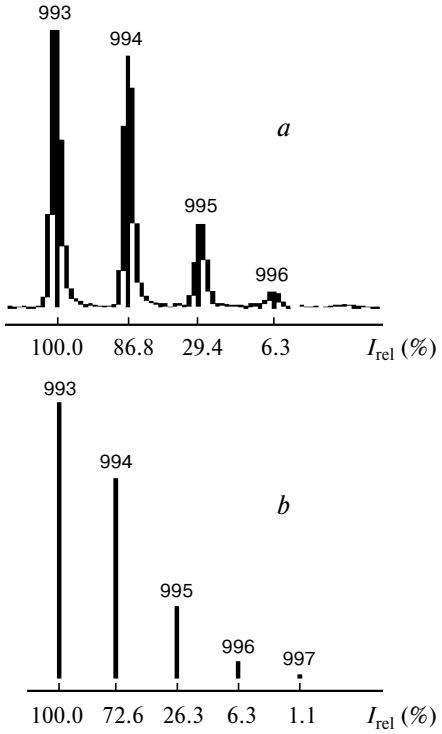


Fig. 3. Experimental (*a*) and calculated (*b*) mass spectra of compound **3**; *m/z* are given.

Experimental

The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AC-300 instrument (300.13 MHz) using $CDCl_3$ and the $CDCl_3$ — Py-d_5 system (1 : 1, v/v) as the solvents. The chemical shifts are given on the δ scale relative to Me_4Si. The matrix-free mass spectra of phthalocyanines and triazatetrabenzocorroles were obtained on an Autoflex II (MALDI-TOF) instrument. The theoretical mass spectra were calculated using the Chem Draw 10.0 program. The electronic absorption spectra were measured on a Helios-α spectrophotometer in solutions at a concentration of ~10^{-5} mol L^{-1} in 0.5- and 1.0-cm quartz cells using pyridine as the solvent. The reaction mixtures were analyzed and the purity of the compounds was checked by TLC on 60 F_{254} silica gel and F_{254} neutral alumina (Merck) plates. Column chromatography was performed on silica gel 60 (40—63 μm, Merck). The starting free ligands were synthesized according to a known procedure.[6] The solvents were purified according to standard procedures immediately before use; $POBr_3$, $POCl_3$, and PBr_3 (Aldrich) were used without additional purification.

Oxophosphoryl-4,5,11,12,18,19,25,26-octabutyltriazatetrabenzocorrole PO[Bu$^n_8$tbc] (3). A solution of PBr_3 (0.2 mL) in pyridine (2 mL) was added to a suspension of phthalocyanine **1** (50 mg, 0.052 mmol) in pyridine (15 mL) under argon. The reaction mixture was stirred at 90—100 °C until the starting ligand was completely consumed (1.5 h, monitoring by TLC, SiO_2, C_6H_6). Then the reaction mixture was cooled to ~20 °C and poured into water. The precipitate that formed was filtered off, thoroughly washed with water and then with methanol (3×30 mL), and dried *in vacuo*. Complex **3** was obtained in a yield of 34.5 mg (67%) as a dark green powder with purple tint. MS, *m/z*: 993 $[M]^+$. ^{1}H NMR ($CDCl_3$), δ: 1.10—1.25 (m, 24 H, CH_3); 3.25—3.45 (m, 16 H, $ArCH_2$); 2.05—2.20 (m, 16 H, $ArCH_2C\underline{H}_2—CH_2$), 1.60—1.80 (m, 16 H, $ArCH_2CH_2—C\underline{H}_2$); 9.21 (s, 2 H, ArH); 9.09 (s, 4 H, ArH); 8.87 (s, 2 H, ArH). ^{13}C NMR ($CDCl_3$), δ: 142.87, 141.14, 137.33, 119.38 (C(1)); 122.43, 122.15, 121.41, 120.46 (C(3)); 143.91, 143.52, 143.14, 142.41 (C(4)); 131.43, 128.51, 124.74, 124.20 (C(2)); 34.19—32.70 (α-CH_2, β-CH_2); 23.50—22.78 (γ-CH_2); 14.32—13.92 (CH_3). ^{31}P NMR ($CDCl_3$—Py-d_5, 1 : 1, v/v), δ: −201.69. UV—Vis (Py), λ_{max}/nm (I_{rel}): 663 (1.0), 637 (0.549), 606 (0.272), 448 (1.780), 418 (0.698).

Oxophosphoryl-4,11,18,25-tetra-*tert*-butyltriazatetrabenzocorrole PO[Bu^t_4tbc] (4). A solution of PBr_3 (0.2 mL) in pyridine (2 mL) was added to a suspension of phthalocyanine **2** (50 mg, 0.068 mmol) in pyridine (15 mL) under argon. The reaction was carried out as described above. Complex **4** was obtained in a yield of 34.8 mg (67%) as a dark green powder with purple tint. MS, *m/z*: 769 $[M]^+$. ^1H NMR ($CDCl_3$), δ: 1.95—2.10 (m, 36 H, CH_3); 8.50—9.35 (m, 12 H, ArH). ^{31}P NMR ($CDCl_3$—Py-d_5, 1 : 1, v/v), δ: −201.69. UV—Vis (Py), λ_{max}/nm (I_{rel}): 658 (1.0), 632 (0.491), 601 (0.242), 445 (1.860), 438 (1.241), 416 (0.629).

Phosphorus(v) 2,3,9,10,16,17,23,24-octabutylphthalocyanine {$P(OH)_2$[Bu^n_8pc]}(OH) (5). Phosphorus oxybromide (1 g, 3.5 mmol) was added to a suspension of phthalocyanine **1** (50 mg, 0.052 mmol) in pyridine (20 mL). The reaction mixture was stirred at 90—100 °C for 1 h (monitoring by TLC on Al_2O_3 in C_6H_6 and by spectrophotometry). After completion of the reaction, the solution was cooled and poured into water. The finely dispersed precipitate was filtered off, thoroughly washed with water, and dried *in vacuo*. Complex **5**, intense blue, was isolated by chromatography on a 2.5×20 cm silica gel column (elution with $CHCl_3$ and then with a 7 : 3 $CHCl_3$—MeOH mixture). The yield was 26 mg (48%). MS, *m/z*: 1042 $[M]^+$, 1025 $[M - OH]^+$, 1007 $[M - OH - H_2O]^+$, 990 $[M - 2\ OH - H_2O]^+$. ^1H NMR ($CDCl_3$), δ: 1.15 (m, 24 H, CH_3); 1.65 (m, 16 H, $ArCH_2$); 1.95 (m, 16 H, $ArCH_2C\underline{H}_2—CH_2$); 2.90 (m, 16 H, $ArCH_2CH_2—C\underline{H}_2$); 9.30 (s, 8 H, ArH). UV—Vis (Py), λ_{max}/nm (I_{rel}): 688 (1.0), 658 (0.187), 620 (0.208), 356 (0.431).

Phosphorus(v) 2,9,16,23-tetra-*tert*-butylphthalocyanine $P(OH)_2$[Bu^t_4pc](OH) (6). *A.* Phosphorus oxychloride (8 mL, 86 mmol) was added dropwise to a solution of phthalocyanine **2** (50 mg, 0.068 mmol) in pyridine (20 mL) under argon. The reaction mixture was refluxed under argon until the ligand was completely consumed (24 h). The reaction mixture was worked up as described above. The yield was 36.5 mg (62%).

B. Phosphorus oxybromide (1 g, 3.5 mmol) was added to a solution of phthalocyanine **2** (50 mg, 0.068 mmol) in pyridine (20 mL) under argon. The reaction mixture was refluxed under argon until the ligand was completely consumed (45 min). The complex was isolated as described above. The yield was 44.1 mg (75%).

MS, *m/z*: 815 $[M]^+$, 798 $[M - OH]^+$, 781 $[M - OH - H_2O]^+$, 763 $[M - 2\ OH - H_2O]^+$. ^1H NMR ($CDCl_3$), δ: 1.95—2.10 (m, 36 H, Bu^t); 7.90—9.30 (m, 12 H, ArH). UV—Vis (Py), λ_{max}/nm (I_{rel}): 677 (1.0), 648 (0.160), 609 (0.185), 353 (0.395).

This study was financially supported by the Presidium of the Russian Academy of Sciences (Program for Basic Research "Directed Synthesis of Organic Compounds with Desired Properties and Design of Materials on Their Basis") and the Russian Foundation for Basic Research (Project No. 05-03-33202).

References

1. A. Yu. Tolbin, M. O. Breusova, V. E. Pushkarev, and L. G. Tomilova, *Izv. Akad. Nauk, Ser. Khim.*, 2005, 2020 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 2083].
2. M. Gouterman, P. Sayer, E. Shankland, and J. P. Smith, *Inorg. Chem.*, 1981, **20**, 87.
3. M. Fujiki, H. Tabei, and K. Isa, *J. Am. Chem. Soc.*, 1986, **108**, 1532.
4. L. Li, L. Subramanian, and M. Hanack, *Chem. Commun.*, 1997, 679.
5. Z. Gross, *J. Biol. Inorg. Chem.*, 2001, **6**, 733.
6. V. E. Pushkarev, M. O. Breusova, E. V. Shulishov, and Yu. V. Tomilov, *Izv. Akad. Nauk, Ser. Khim.*, 2005, 2024 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 2087].
7. L. Li, L. R. Subramanian, and M. Hanack, *Eur. J. Org. Chem.*, 1998, 2759.
8. L. A. Lapkina, V. E. Larchenko, E. O. Tolkacheva, K. I. Popov, N. Yu. Konstantinov, V. M. Nosova, and A. Yu. Tsivadze, *Zh. Neorg. Khim.,* 1998, **43**, 987 [*Russ. J. Inorg. Chem.*, 1998, **43** (Engl. Transl.)].
9. J. Liu, F. Zhang, F. Zhao, Y. Tang, X. Songm, and G. Yao, *J. Photochem. Photobiol. A*, 1995, **91**, 99.
10. J. P. Fox and D. P. Goldberg, *Inorg. Chem.*, 2003, **42**, 8181.
11. J. Mason, *Multinuclear NMR*, Plenum Press, New York, 1987.

Received December 19, 2006;
in revised form March 27, 2007