Russian Journal of General Chemistry, Vol. 75, No. 3, 2005, pp. 468–472. Translated from Zhurnal Obshchei Khimii, Vol. 75, No. 3, 2005, pp. 504–508.

Unsymmetrical Pentoxy-Substituted Porphyrazines

I. Yu. Nikolaev, E. V. Kudrik, V. P. Kulinich, and G. P. Shaposhnikov

Ivanovo State University of Chemical Technology, Ivanovo, Russia

Received September 29, 2003

Abstract — The reactions of 3,6-dipentoxyphthalonitrile (A) in the 1-pentanol–magnesium pentylate medium with phthalonitrile, 2,3-di(methylsulfanyl)-2-butenedinitrile, and 2,3-dihydro-1,4-dithiin-5,6-dicarbonitrile (B) were performed. Unsymmetrically substituted porphyrazines A_3B were prepared and studied. The influence of the structure of fragment B on the spectral characteristics of the porphyrazines was examined.

Much attention is given today to unsymmetrically substituted porphyrazines, which are very promising for various branches of science and engineering [1–4]. The main route to unsymmetrically substituted porphyrazines is random condensation of two *o*-dinitriles or 1,3-diiminoisoindolines in various molar ratios. The reaction in all cases yields a mixture of all the possible porphyrazines, which are usually separated chromatographically. The product separation is often the most difficulty step; therefore, active efforts are made to develop procedures for selective synthesis of unsymmetrically substituted porphyrazines [5–7].

We reported previously [8] that 3,6-didecyloxyphthalonitrile can be used for selective synthesis of ABAB-type phthalocyanines. 3,6-Dipentoxyphthalonitrile **I** does not form the corresponding symmetrical octasubstituted phthalocyanine in the reaction with magnesium pentylate in 1-pentanol. At the same time, in the presence of another dinitrile containing no bulky substituents, e.g., 2,3-di(methylsulfanyl)-2-butenodinitrile, a mixture of unsymmetrically substituted porphyrazines is formed.

To find the causes of such a behavior of **I**, it was heated in 1-pentanol in the presence of magnesium pentylate; after removing the solvent, the precipitate was treated with acetic acid and purified by column chromatography (Al_2O_3, eluent benzene). We recovered the starting 3,6-dipentoxyphthalonitrile **I**, as judged from the IR data and comparison of the melting points of **I** before and after the attempted reaction (cf. [9]). Thus, dinitrile **I** does not undergo closure of the isoindole ring with the formation of the corresponding alkoxy derivatives. Apparently, for the porphyrazine ring to be formed, the magnesium ion should coordinate four dinitrile molecules. With **I**, such a coordination is apparently impossible because of steric interactions between bulky substituents in positions 3 and 6. On adding another dinitrile containing no bulky substituents, the formation of fairly stable 1 : 4 complexes becomes possible, and the porphyrazine ring is formed around the metal cation.

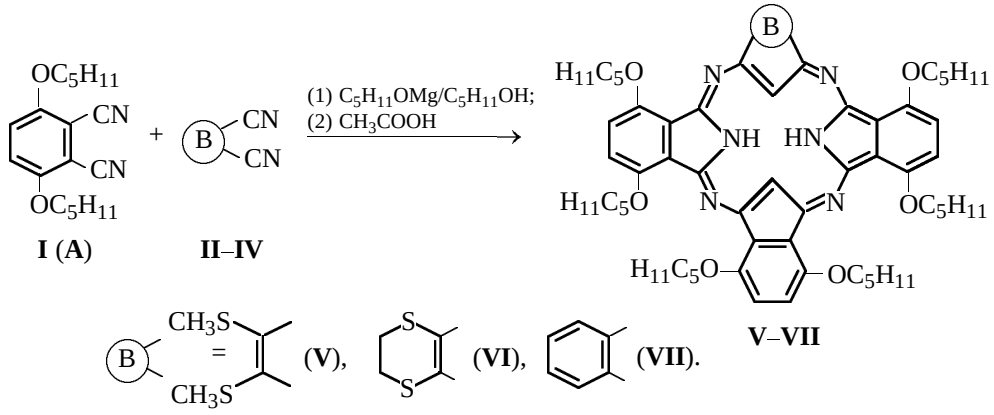
The absence of octasubstituted phthalocyanines in the reaction products considerably simplifies the chromatographic separation of the product mixture, because the A_3B products are in all cases the most mobile. The synthesis was performed in accordance with the scheme shown below under the conditions excluding formation of octapentoxyphthaloxyanine.

We were able to isolate pure only the compound A_3B. Chromatographic separation of A_2B_2 isomers was difficult because of their similar polarity and solubility. Porphyrazines AB_3 were not isolated because of their low solubility in organic solvents. The composition and structure of the compounds were determined by elemental analysis, ^{1}H NMR and electronic spectroscopy, and mass spectrometry.

Compound **V** gives eight groups of signals in the ^{1}H NMR spectrum. A singlet at 7.3 ppm corresponds to six protons of phenyl fragments. In the range 4.0–4.1 ppm, there is a triplet corresponding to 12 α-methylene protons; under the influence of electron-withdrawing fragment B, this signal can be split in two components with a 1 : 2 intensity ratio. The absence of splitting in the spectrum of **V** shows that the electron densities on all the six α-CH_2 groups are close. Six –SCH_3 protons give a singlet at 3.35 ppm. The β-CH_2 protons give a multiplet at 1.75–1.85 ppm, and the γ- and δ-CH_2 protons, a multiplet at 1.7–1.3 ppm. The highest-field signals are those of terminal CH_3 groups (a multiplet at 1.0–0.9 ppm).

Unsymmetrically substituted porphyrazines A_3B have characteristic electronic absorption spectra. In particular, metal-free compounds A_3B in the long-wave (*Q*) range exhibit three bands. The majority of authors assign the longest-wave component to a

1070-3632/05/7503-0468



charge-transfer transition from the donor fragment of the molecule to the fragment acting as electron acceptor. This hypothesis is indirectly confirmed by comparison of the spectral characteristics of hexapentoxy-substituted porphyrazines A_3B containing fragments B with pronounced electron deficiency (1,2,5-thia- and 1,2,5-selenadiazole rings [10]) with the related porphyrazines prepared for the first time in this study, in which the electron density on fragments B widely varies.

Comparison of the structures of porphyrazines **V** and **VI** suggests that their electronic absorption spectra should be similar, because the electron-donor properties of two methylsulfanyl groups and the dithiacyclohexene fragment differ insignificantly. However, actually the spectra of these compounds strongly differ. The spectrum of **VI** consists of six bands, three of which are in the *Q* range (Figs. 1, 2). Also, the spectrum contains a strong Soret band and two charge-transfer bands at 430 and 513 nm. The band at 513 nm is also characteristic of symmetrical ethylenedithio-substituted porphyrazines [11].

The spectrum of **V** is essentially different, especially in the *Q* range (Fig. 2). The spectrum is two-band, with the disappearance of the longest-wave component and substantial hypsochromic shift of the main absorption bands. The main difference between **V** and **VI** is that in compound **VI** the sulfur atoms are linked with a CH_2–CH_2 bridge, whereas in **V** the two SCH_3 groups are relatively autonomous and mobile. It seemed reasonable that the differences in the spectra are due to deviation of the SCH_3 groups from the macroring plane, and the longest-wave band in the spectrum of **VI** is due to the charge transfer from the sulfur atoms to the lowest unoccupied molecular orbital of the molecule, to which all the four isoindole fragments make contributions, as in the case of symmetrically substituted porphyrazines.

To confirm this hypothesis, we performed quantum-chemical calculations of **V** and **VI** (AM1 [12], full optimization of all the geometric parameters). As both compounds can exist as two tautomers differing in the mutual location of NH protons, we initially compared the energy characteristics of the tautomers

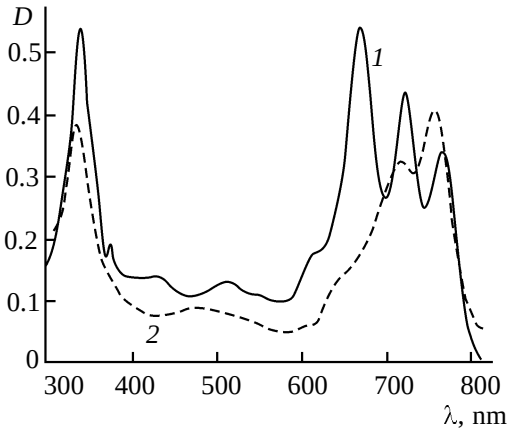


Fig. 1. UV spectra of (*1*) **VI** and (*2*) **VII**.

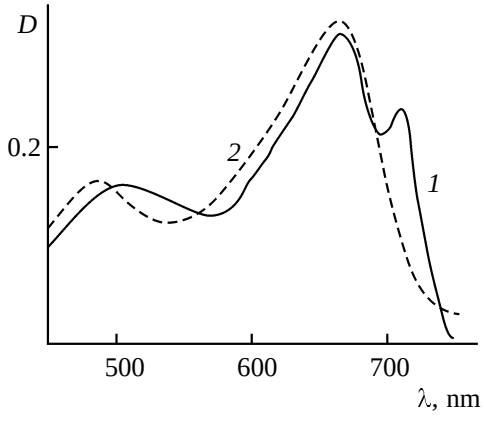


Fig. 2. UV spectra of (*1*) **V** and (*2*) **VIII**.

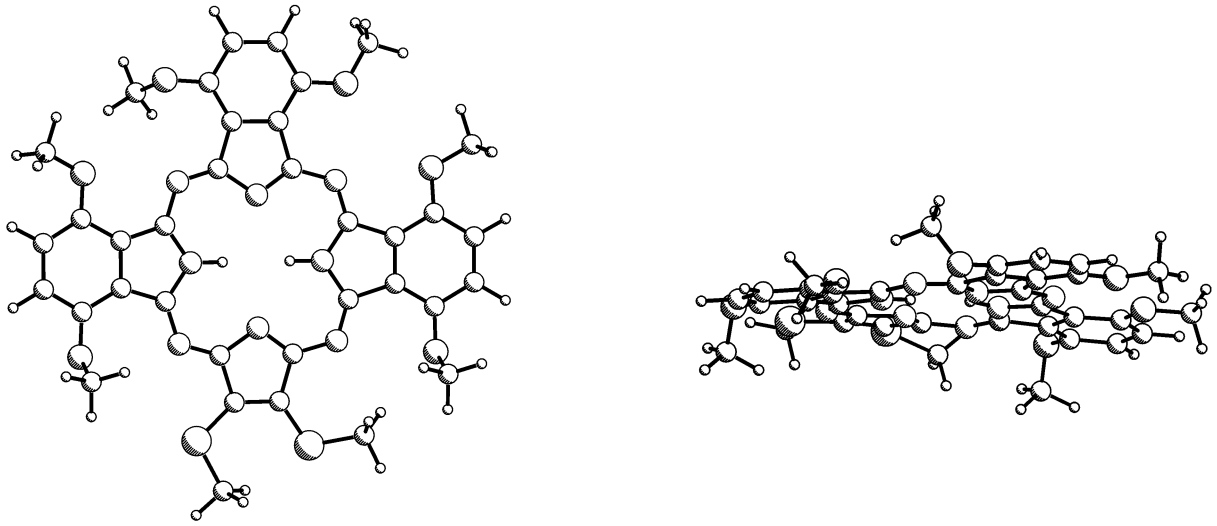


Fig. 3. PLUTO plot of **V**.

and, in what follows, used for comparison the data for the most stable tautomers.

Figure 3 shows the PLUTO plot of **V**. The macrorings of both molecules are planar to within 2°, and the deviation of one of the SCH_3 groups from the plane does not exceed 6°. In **VI**, both sulfur atoms are in the same plane. The bond lengths and bond angles in both macrocycles virtually coincide. Thus, the deviation of the SCH_3 groups from the macroring plane cannot be responsible for the differences between the electronic spectra of **V** and **VI**. Published data on the spectral characteristics of the related compounds, in combination with the results of this study, show that the decisive factor is the electronic structure of the electron-withdrawing fragment B.

To check this assumption, we prepared phthalocyanine **VII** using unsubstituted phthalonitrile as a source of fragment B. Figure 1 shows that, as the electron-withdrawing properties of fragment B are enhanced, the relative intensity of the longest-wave absorption band increases; however, this band remains appreciably weaker than in the spectra of porphyrazines with strongly electron-withdrawing fragments.

Since metal complexes (except magnesium complexes) of unsymmetrical porphyrazines synthesized in this study cannot be prepared directly and the absorption spectra of phthalocyanine complexes differ essentially from those of the metal-free compounds, we prepared nickel complex **VIII** by the reaction of **V** with excess nickel acetate in DMF. The reaction progress was monitored spectrophotometrically by the disappearance of the longest-wave absorption band from the spectrum of the reaction mixture. The composition of **VIII** was confirmed by elemental analysis. The electronic absorption spectrum of **VIII** significantly differs from that of **V** (Fig. 2). In the *Q* range, there is only one band, which is characteristic of symmetrical phthalocyanines. The spectral changes in going from **V** to **VIII** are due to an increase in the symmetry of the occupied molecular orbitals, whereas the symmetry of the molecule as a whole remains unchanged.

Thus, 3,6-dipentoxyphthalonitrile can be used for selective synthesis of a series of unsymmetrically substituted porphyrazines A_3B differing in the structure of fragment B. The electronic absorption spectra of these compounds depend only on the electronic effect of fragment B.

EXPERIMENTAL

The ^1H NMR spectra were taken on Bruker WH-400 and Bruker AMD-300 spectrometers. The mass spectra were recorded on VG-ZAB-HF-2F/AMO604 and Varian M-700 devices. The electronic absorption spectra were measured on Specord M-40 and Hitachi U-2000 spectrometers at room temperature in the range 300–900 nm and on a Specord UV-Vis spectrometer in the range 300–750 nm.

3,6-Dipentoxyphthalonitrile I. A mixture of 10 g of 3,6-dihydroxyphthalonitrile, 45.13 ml of 1-bromopentane, 34.5 g of K_2CO_3, and 50 ml of DMF was stirred at 100°C for 20 h. Then the mixture was cooled and diluted with water; the precipitate was filtered off, recrystallized from DMF, and dried at room temperature. Yield 18 g (96%), mp 177°C. IR spectrum, ν, cm^{-1}: 3096 (C_{Ar}–H), 3032 (C_{Alk}–H), 2936 (C_{Alk}–H), 2304 (C≡N), 1528 (C=C), 1416, 1336, 1220, 1116 (C_{Ar}–O), 1080 (C_{Alk}–O), 832.

Found, %: C 71.83; H 8.17; N 9.40. $C_{18}H_{24}N_2O_2$. Calculated, %: C 71.97; H 8.05; N 9.33.

2,3-Di(methylsulfanyl)-2-butenodinitrile **II** and 2,3-dihydro-1,4-dithiin-5,6-dicarbonitrile **III** were prepared and purified as described in [13, 14].

1,2-Di(methylsulfanyl)tri[6,7;11,12;16,17-(3,6-dipentoxy)benzo]tetraazaporphine V. A mixture of 1 g of dinitrile **I** and 0.57 g of 2,3-di(methylsulfanyl)-2-butenedinitrile **II** was added to a system 1-pentanol–magnesium pentylate prepared by dissolving 0.5 g of Mg in 30 ml of 1-pentanol. The mixture was refluxed with stirring for 6 h. After cooling, the mixture was evaporated to dryness, and the residue was dissolved in 20 ml of acetic acid and stirred at room temperature for 1 h. The solution was diluted with water, and the precipitate was filtered off, washed with water (to pH 7), and dried at 100°C. The resulting product was dissolved in benzene and chromatographed on a column packed with Al_2O_3 (eluent benzene–hexane, 1 : 1). The eluate was evaporated, and the residue was dissolved in benzene and chromatographed on plates for preparative TLC (silica gel L 5/20, 20% $CaSO_4$), eluent benzene–CCl_4, 1 : 1. The substance forming the main colored band on the plate was extracted with benzene and chromatographed again on a column with Al_2O_3. Elution with hexane allowed complete removal of the residual dinitrile **I**, and the target product **V** was eluted with hexane–benzene, 1 : 1. Porphyrazine **V** was obtained as a violet powder; yield 83 mg (7%). Electronic absorption spectrum (benzene), λ_{max}, nm (*D*): 506 (0.117), 666 (0.168), 710 (0.132). ^{1}H NMR spectrum (CD_2Cl_2), δ, ppm: 0.9–1.0 m (18H, CH_3), 1.3–1.7 m (24H, γ- and δ-CH_2), 1.75–1.85 m (12H, β-CH_2), 3.35 s (6H, SCH_3), 4.0–4.1 m (12H, α-CH_2), 7.3 s (6H, C_{Ar}). Found, %: C 67.05; H 7.59; N 10.5; S 6.01. $C_{60}H_{80}N_8O_6S_2$. Calculated, %: C 67.13; H 7.52; N 10.44; S 5.97.

1,2-(Ethylenedisulfanyl)tri[6,7;11,12;16,17-(3,6-dipentoxy)benzo]tetraazaporphine VI. A mixture of 1 g of dinitrile **I** and 0.56 g of 2,3-dihydro-1,4-dithiin-5,6-dicarbonitrile **III** was added to the system 1-pentanol–magnesium pentylate prepared by dissolving 0.5 g of Mg in 30 ml of 1-pentanol. The mixture was refluxed with stirring for 6 h. After cooling, 20 ml of 50% acetic acid and 20 ml of acetone were added, and the mixture was allowed to stand for 30 min. The precipitate was filtered off, washed with water, dried, and dissolved in 20 ml of trifluoroacetic acid; the solution was stirred for 30 min at room temperature and poured into water. The precipitate that formed was filtered off and dried at 60°C. The crude product was dissolved in benzene and chromatographed on a column packed with Al_2O_3 (eluent benzene), with the subsequent precipitation of **VI** from the benzene solution by slow diffusion of acetone vapor into the solution. The precipitate was filtered off and dried at room temperature. Porphyrazine **VI** was obtained as blue-green needle-like crystals; yield 56 mg (4.7%). Electronic absorption spectrum (benzene), λ_{max}, nm: 339, 430, 513, 670, 722, 767. Mass spectrum (*m*-nitrobenzyl alcohol), *m/z*: 1072 $[M + H]^+$. Found, %: C 67.20; H 7.41; N 10.39; S 6.63. $C_{60}H_{78}N_8O_6S_2$. Calculated, %: C 67.26; H 7.34; N 10.46; S 5.98.

1,4,8,11,15,18-Hexapentoxyphthalocyanine VII. A mixture of 1 g of dinitrile **I** and 3.84 g of phthalonitrile was added to the system 1-pentanol–magnesium pentylate prepared by dissolving 0.5 g of Mg in 30 ml of 1-pentanol. The mixture was refluxed for 6 h and filtered; the filtrate was diluted with 20 ml of 50% acetic acid, and 10 min later 200 ml of acetone was added. The precipitate was filtered off, dried, and treated with 20 ml of CF_3COOH for 1 h. The solution in trifluoroacetic acid was diluted with water, and the precipitate was filtered off, washed with water, and dried. The resulting product was dissolved in benzene and chromatographed on a column packed with Al_2O_3 (eluent benzene). Phthalocyanine **VII** was obtained as a blue-green powder; yield 97 mg (8.5%). Electronic absorption spectrum (benzene), λ_{max}, nm (*D*): 332 (1.76), 482 (0.41), 648 (0.58), 716 (1.49), 759 (1.87). Mass spectrum (*m*-nitrobenzyl alcohol), *m/z*: 1032 $[M + H]^+$. Found, %: C 72.08; H 7.76; N 10.71. $C_{62}H_{78}N_8O_6$. Calculated, %: C 72.20; H 7.62; N 10.86.

1,2-Di(methylsulfanyl)tri[6,7;11,12;16,17-(3,6-dipentoxy)benzo]tetraazaporphinatonickel VIII. A 10-mg portion of **V** was dissolved in 10 ml of DMF, and 16 mg of nickel acetate was added. The mixture was refluxed with stirring for 6 h, after which it was cooled and diluted with water. The precipitate was filtered off, washed with water, dried, dissolved in benzene, and chromatographed on a column packed with Al_2O_3 (eluent benzene). Yield 7.4 mg (70%). Electronic absorption spectrum, λ_{max}, nm (*D*): 486 (0.206); 664 (0.411). Found Ni, %: 5.15. $C_{60}H_{78}N_8 \cdot NiO_6S_2$. Calculated Ni, %: 5.19.

REFERENCES

1. Napier, A. and Hart, J.P., *Electroanal.*, 1998, vol. 8, no. 11, p. 1006.
2. Torre G. de la, Vazquez, P., Agullo-Lopez, F., and Torres, T., *J. Mater. Chem.*, 1998, vol. 8, no. 8, p. 1671.
3. Liu, S.G., Liu, Y.Q., Xu, Y., Zhu, D.B., Yu, A.C., and Zhao, X.S., *Langmuir*, 1998, vol. 14, no. 3, p. 690.

4. Aladib, Z., Clarkson, G.J., McKeown, N.B., Treacher, K.E., Glecson, H.F., and Stennet, A.S., *J. Mater. Chem.*, 1998, vol. 8, no. 11, p. 2371.

5. Torre, G. de la, Martinez-Diaz, M.V., Ashon, P.R., and Torres, T., *J. Org. Chem.*, 1998, vol. 63, no. 24, p. 8888.

6. Maya, E.M., Vazquez, P., and Torres, T., *Chem. Eur. J.*, 1999, vol. 5, no. 7, p. 2004.

7. Maya, E.M., Garsia, C., Garsia-Frutos, E.M., Vazquez, P., and Torres, T., *J. Org. Chem.*, 2000, vol. 65, no. 9, p. 2733.

8. Kudrik, E.V., Nikolaev, I.Yu., and Shaposhnikov, G.P., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2000, no. 12, p. 2062.

9. Cook, M.J., Dunn, A.J., Howe, S.D., and Thomson, A.J., *J. Chem. Soc., Perkin Trans. 1*, 1988, no. 8, p. 2453.

10. Kudrik, E.V., Bauer, E.M., Ercolani, K., Chiesi-Vila, A., Rizzoli, C., Gabercorn, A., and Stuzhin, P., *Mendeleev Commun.*, 2001, no. 2, p. 45.

11. Shaposhnikov, G.P., Kulinich, V.P., Osipov, Yu.M., and Smirnov, R.P., *Khim. Geterotsikl. Soedin.*, 1986, no. 9, p. 1276.

12. Dewar, M.J.S., Zoebisch, E.G., Healy, E.F., and Stewart, J.J.P., *J. Am. Chem. Soc.*, 1985, vol. 107, no. 13, p. 3902.

13. Wolf, W., Degener, E., and Petersen, S., *Angew. Chem.*, 1960, vol. 72, no. 24, p. 963.

14. Simons, H.E., Vest, R.D., Blomström, D.C., Roland, J.R., and Cairns, T.L., *J. Am. Chem. Soc.*, 1962, vol. 84, no. 21, p. 4146.