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SYNTHESIS OF MONO- AND DISUBSTITUTED TETRA(tert-BUTYL)PORPHYRAZINES

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Bromination of tetra(tert-butyl)porphyrazine by N-bromosuccinimide in chloroform results in the formation of mono- and dibromides, substitution for the bromine atoms of which produced the corresponding cyano, phenoxy, phenylthio, styryl, phenylethynyl and piperidino derivatives. From the monobromide and 2,2-bis(p-hydroxyphenyl)propane, the dimeric porphyrazine 2,2-bis[p-tetra(tert-butyl)porphyrazyloxyphenyl]propane was similarly obtained.

Interest in asymmetric mono- and disubstituted porphyrazines (PA), as in the case of porphyrins and phthalocyanines, is due, in particular, to the possibility of their use in simulating photosynthesis processes, obtaining metal-complex catalysts covalently attached to the support, building ordered groups of molecules by the Langmuir–Blodgett method, etc. These compounds certainly are also of independent interest in the study of the relationship between the structure and their electronic absorption spectra. A common method of synthesis of porphyrazines by the template tetramerization of mono- and disubstituted 1,2-dicyanoethylene (mainly their cis isomers) assumes the formation of only tetra- and octasubstituted derivatives [1]. As in the case of porphyrins, porphyrazines with different degrees of substitution (including mono- and disubstituted ones) can be obtained by reactions of substitution in the macroring, and also by mixed condensation of dicyanoethylenes of different structures, which usually give a complex mixture of products. Previously, we studied the nitration of tetra(tert-butyl)porphyrazine (H_2PA^t) [2], which led to the formation of mono- to tetranitro-H_2PA^t, depending on the reaction conditions.

In order to develop a universal method of synthesizing previously unavailable mono- and disubstituted porphyrazines, use may also be made of substitution of various groups for bromine atoms in the corresponding bromoporphyrazines [3]. The possibility of brominating the macroring of porphyrazines was shown in [3, 4]. The bromination of unsubstituted porphyrazine with bromine in acetic acid formed the corresponding tetrabromide [4]. In the series of porphyrins where this reaction was studied in more detail [5-9], the degree and position of the substitution were shown to be determined by the structure of the porphyrin, nature of the brominating agent and solvent, etc.

The subject chosen for our study was H_2PA^t (I) [10], in which the presence of four tert-butyl groups provides for increased solubility of the bromine derivatives in organic solvents. On the other hand, because of the decrease in the number of free β-carbon atoms of the H_2PA^t molecule in comparison to the unsubstituted analogue, identification of the reaction was monitored by means of TLC on silufol.

It was noted that the reaction of equimolar amounts of compound I′ (randomer of type I – 2,7,12,17-tetra(tert-butyl)H_2PA [II]) and N-bromosuccinimide at 20-25°C, there is formed a mixture of 47% of the monobromo derivative N 3-bromo-2,7,12,17-tetra(tert-butyl)H_2PA (II′) – and 24% of a mixture of the dibromo derivatives (III′) with bromine atoms at the adjacent or opposite pyrrole fragments of the molecule. In the presence of twice the amount of N-bromosuccinimide, the yield of dibromide III′ increases to 62%, while the yield of monobromide II′ drops to 14%. Tetrabromo-H_2PA^t (IV′) is formed in 81% yield in the presence of a 10-20-fold excess of N-bromosuccinimide in boiling chloroform.

The reaction of compound I″ (mixture of randomers of types III and IV – 2,8,13,18- 2,8,13,17-tetra(tert-butyl)H_2PA in accordance with [11]) with a 12.5-fold excess of N-bromosuccinimide in chloroform at 20-25°C formed a mixture of 51.5% of monobromo-H_2PA^t (II″) and 39% of dibromo-H_2PA^t (III″).

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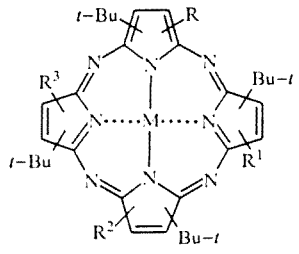
In brominated H_2PA^t II and III, the closeness of the bulky tert-butyl groups increases the lability of the bromine atoms in the substitution reactions, so that it is possible to obtain several mono- and disubstituted derivatives in sufficiently high yields [1].



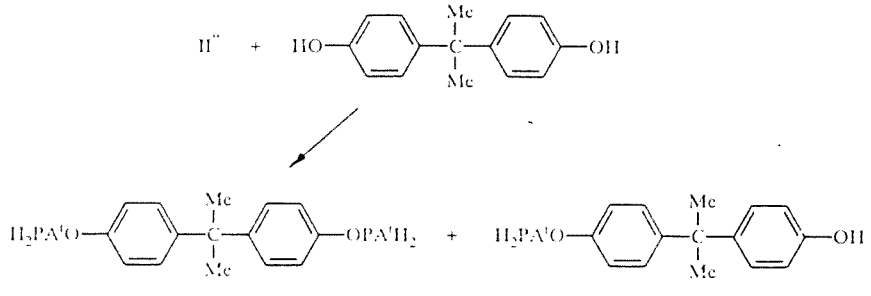
II–XVII

II—V, IX—XVI M = 2H, VI—VIII, XVII M = Cu, $R^1 = R^2 = R^3 = H$; II, VI R = Br; V R = CN; IX R = $C_5H_{10}N$; X R = C_6H_5O; XIa,b R = *p*-$C_8H_{17}C_6H_4O$; XII R = C_6H_5S; XV R = $C_6H_5CH{=}CH$; XVII R = $C_6H_5C{\equiv}C$; III R(R^1) = R^2(R^3) = H, R^1(R) = R^3(R^2) = Br; XIII R^1(R) = R^3(R^2) = C_6H_5S; VII R = R^1 = H, $R^2 = R^3$ = CN; VIII R = R^2 = H, $R^1 = R^3$ = CN; IV R = $R^1 = R^2 = R^3$ = Br

Using this scheme, one can obtain mixtures of randomers as well as the individual mono- and disubstituted porphyrazines, which are necessary for studying fine spectral effects and also for modelling biological objects.

Reaction of monobromide II′ with CuCN in boiling DMFA (the Rosenmund–von Braun reaction) for 3 h forms 75% of monocyano-$CuPA^t$ (V) along with 5.5% of monobromo-$CuPA^t$ (VI). Under analogous conditions, dibromide III was used to obtain a mixture of 78% of dicyano-$CuPA^t$ and 20% of mononitrile V; this showed that under the reaction conditions, in addition to the substitution of bromine atoms, their partial elimination also takes place. The dicyano derivative of $CuPA^t$ was separated chromatographically on silica gel into two fractions – with adjacent (VII, 68%) and opposite (VIII, 10%) positions of the cyano groups.

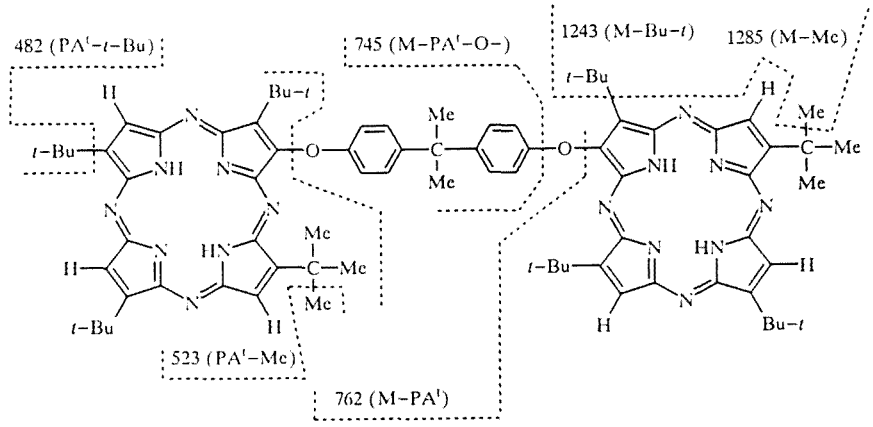
Some monosubstituted PA^t were also obtained by nucleophilic substitution reactions of the bromine atom in monobromide II. When nucleophilic agents such as aniline or sodium ethoxide in DMFA were used, no substitution products were obtained – only elimination of bromine atoms took place. From monobromide II′ and pipiridine, monopipiridino-H_2PA^t (IX) was obtained in 79% yield along with 3% of the debromination product. Compound II′ reacting with sodium phenate under analogous conditions forms only 26.5% of monophenoxy-H_2PA^t (X), 11.5% of compound I′, and an appreciable amount of more strongly polar compounds of unknown structure, whereas with sodium p-octylphenate, mono(p-octylphenoxy)-H_2PA^t was obtained in 16.5% yield and was chromatographically separated into two groups of randomers XIa and XIb. The substitution of a phenylthio group for bromine was carried out directly with thiophenol in the presence of K_2CO_3. In addition to monophenylthio-H_2PA^t (XII, 13%), a substitution product (XIII, 30.6%) was obtained, formation of which was probably due to a partial occurrence of side reactions under the reaction conditions. In accordance with the scheme indicated above, the dihydroxy- and diamino-containing components are used as nucleophiles, dimeric PA linked by hydrocarbon bridges can also be obtained. Indeed, the reaction of monobromide II″ with 2,2-bis(p-hydroxyphenyl)propane (bisphenol A) in the presence of K_2CO_3 in DMFA gave a mixture of two groups of isomers of 2,2-bis[p-tert-butyl)porphyrazoxyphenyl]propane (XIVa, b; yields, 16% and 22%, respectively), which are the first representatives of covalently-bonded PA. Simultaneously formed in this reaction are monosubstitution products (XVa, b) in yields of 9% and 13%, respectively.



XIV a, b XV a, b

The structure of compounds XIVa, b and XVa, b was determined from data of ultimate analysis and mass spectra. Thus, the electron impact mass spectrum of compounds XIVa, b, recorded at a temperature of injection of the substance into the ion source of 500-570°C, shows a peak of the molecular ion (M^+) of mean intensity 1300 (19%).* Also present in the region of the molecular ion and peaks of low intensity (~1%), 1285 and 1243, formed when a methyl and a tert-butyl group become detached from the M^+ ion. Of maximum intensity in the spectrum is the 762 ion peak (100%). Corresponding to the elimination of the H_2PA^t fragment from the M^+ ion, and the weaker ion peak of 745 (19%) corresponds to the detachment of the element H_2PA^t-OH. In the region of mean masses, several peaks of medium and high intensity are recorded. Thus, the ion peak 538 (72%) is due to H_2PA^t, and the peaks 523 (51%), 482 (14.5%), and 368 (77%) correspond to the successive detachment from H_2PA^t of respectively, the methyl group and one and three tert-butyl groups.

Additional and important information on the structure of compounds XIVa,b is also provided by fragments recorded in the region of low masses. Thus, the ions 213 (59%), 135 (46%), 119 (65%), 107 (29%), and 94 (69%) are formed when the bridge portion of the original molecule splits, and they pertain to $(C_6H_4CMe_2C_6H_4OH + H)^+$, $Me_2CC_6H_4OH$, $Me_2CC_6H_5$, $C_6H_5CH_2OH$, and C_6H_5OH. A characteristic feature of the mass-spectrometric behavior of dimer XIVa and XIVb is the appearance of a molecule ion peak at very high injection temperatures, ~500°C, whereas characteristic fragment ions are formed at appreciably lower temperatures (200-250°C). This is probably due to the fact that at high temperatures in small volume of the ionization chamber, ion-molecular or bimolecular reactions may take place which correspond to stabilization of the molecular ion.



The spectra of compounds XVa and XVb contain the maximum peak of the molecular ion (M^+) 765 (100%). In addition, the characteristic ion peaks 750 (16%) and 671 (14%) are observed, which are formed by the detachment from M^+ of the methyl group and phenol, respectively. The ion peak (H_2PA^t, 538, 25%), in contrast to the spectrum of the dimer XIVa, b, has an appreciably lower intensity. The spectrum of compound XVa, b contains the fragments peaks 523 (12%), 508 (7%), and 367 (69%), which respectively correspond to the detachment of one and two methyl groups from the H_2PA^{t+} ion.

There are reports in the literature [12, 13] on the condensation of olefins with brominated and iodinated aromatic compounds in the presence of palladium complexes with the formation of β-substituted styrenes. By analogy with the synthesis of p-carboxystilbene [12], reaction of monobromide II″ with styrene in the presence of palladium catalyst and triethylamine in boiling DMFA (3 h) formed a mixture of 41% of monostyryl-H_2PA^t (XVI) and 23% of H_2PA^t.

Reaction of monobromide II″ and copper phenylacetylide under conditions analogous to those used in the synthesis of the cyano derivatives V, VII, VIII formed the copper complex monophenylethynyl-PA^t (XVII).

Thus, the above results indicate extensive possibilities of using mono- and disubstituted H_2PA^t in the synthesis of previously unknown mono- and difunctional derivatives of H_2PA^t.

Asymmetric monosubstitution and disubstitution in H_2PA^t leave their electronic absorption spectra practically unchanged, and only cause an irregular bathochromic shift of the Q_1 and Q_2 bands (Table 1). The maximum shift of the Q_1 band is 10 nm for compound XII, and the shift of the Q_2 band is 37 nm for compound XVI. Furthermore, the internal $\Delta\nu$

*Given here and below are the values of m/z.

between them for these compounds is constant (2000 cm^{-1}) and similar to that for the tetrasubstituted analogs tetra(butoxy)- and tetra(amyloxy)-H_2PA^t [14]. Only in the case of mono- and disubstituted phenylthio-H_2PA^t XII, XIII does this interval decrease to 1100 cm^{-1} and 1700 cm^{-1}, respectively, apparently as a result of a stronger perturbing influence of the phenylthio substituents on the orbitals responsible for the Q_2 band. The greatest changes occur in the electronic absorption spectra of the phenylethynyl compound XVII, in which, in addition to the splitting spectra of the phenylethynyl compound XVII, in which, in addition to the splitting of the Q band, a "transfer" of the intensities of the Q_1 and Q_2 bands is also observed, in contrast to other analogs.

The transition from symmetric tetra- and octasubstituted H_2PA^t, containing electron-acceptor substituents, to the less symmetric mono- (II, V) and disubstituted PA (III, VII, VIII) is manifested spectroscopically most clearly in the case of their metal complexes. Thus, in the absorption spectrum of monocyano-$CuPA^t$ XII, in contrast to the tetrasubstituted analog [15], the long-wavelength band Q is, as a result of a lowering of the molecular symmetry, represented as a doublet at 606 nm and 576 nm. The appearance of the spectrum of copper dicyano-H_2PA^t depends on the relative positions of the cyano groups in the macroring. Thus, compound VII in the visible region shows a single band at 598 nm, whereas in compound VIII the doublet is at 627 nm and 568 nm, which in accordance with the oscillator model of electronic transitions makes it possible to classify compound VIII as an isomer with an opposite arrangement of cyano groups.

EXPERIMENTAL

The electronic absorption spectra of solutions of the synthesized compounds were measured with a Hitachi-356 spectrophotometer; the mass spectra of several were obtained with a Finnigan MAT-4615 mass spectrometer with an INCOS-2000 automatic data processing system; the ionizing voltage was 70 eV, and the injection temperature, 70-570°C.

Data of ultimate analysis of the compounds obtained for C, H, and N correspond to the calculated values.

Metal-free 3-Bromo-(II'), 3,8(13)-Dibromo-(III') and 3,8,13,18-Tetra-2,7,12,17-bromotetra(tert-butyl)porphyrazine (IV'). **A.** A solution of 0.05 g (0.093 mmole) of tetra-2,7,12,17-(tert-butyl)porphyrazine (I') and 0.018 g (0.1 mmole) of bromosuccinimide in 30 ml of chloroform is kept for 10-12 h at 20-25°C, the solvent is driven off, and the residue is washed with 100 ml of hot water and dried in air. The reaction mixture is then applied by the "dry method" to a column packed with silica gel (40/100), is eluted with hexane, and two fractions are separated: fraction 1 – 0.02 g (31%) of dibromide III' with R_f 0.76 (SiO_2, hexane); fraction 2 – 0.028 g (49%) of monobromide II' with R_f 0.58 (SiO_2, hexane).

B. A solution of 0.05 g (0.093 mmole) of compound I' and 0.035 g (0.2 mmole) of bromosuccinimide in 30 ml of chloroform is kept for 10-12 h at 20-25°C, and the reaction product is chromatographed as in method A. The products obtained are 0.04 g (62%) of dibromide and 0.008 g (14%) of monobromide II'.

C. A solution of 0.10 g (0.18 mmole) of compound I' and 0.53 g (2.98 mmole) of bromosuccinimide in 50 ml of chloroform is boiled for 5 h and cooled, and the precipitate is filtered off and washed with 100 ml of hot water, then recrystallized from chloroform; 0.13 g (80.5%) of tetrabromide IV' is obtained.

D. A solution of 0.10 g (0.18 mmole) of compound I" and 0.40 g (2.25 mmole) of bromosuccinimide in 200 ml of chloroform is kept for 10-12 h at 20-25°C, the solvent is driven off, the residue is chromatographed on silica gel in a 1:2 benzene–hexane system, and two fractions are separated: fraction 1 – 0.50 g (39%) of dibromide III" with R_f 0.74 (SiO_2, 2:1 hexane–benzene); fraction 2 – 0.59 g (51.5%) of monobromide II" with R_f 0.36 (SiO_2, 2:1 hexane–benzene).

Compounds II" and III" were identified by mass-spectrometric analysis.

Copper 3-Cyano-2,7,12,17-tetra(tert-butyl)porphyrazine (V). A mixture of 0.10 g (0.162 mmole) of monobromide II' and 0.04 g of CuCN in 10 ml of DMFA is boiled for 3 h, cooled, decanted into 100 ml of water, and the precipitate is separated, dried in air, and chromatographed in silica gel, the elution being successively carried out with hexane and benzene; 0.005 g (5.5%) of copper 3-bromo-2,7,12,17-tetra(tert-butyl)porphyrazine (VI) with R_f 0.4 (SiO_2, hexane) and 0.076 g (75%) of compound V with R_f 0.87 (SiO_2, benzene) are isolated.

Copper 3,13-dicyano- (VII) and 3,8-Dicyano-2,7,12,17-tetra(tert-butyl)porphyrazine (VIII). A mixture of 0.10 g (0.14 mmole) of dibromide II' and 0.054 g of CuCN in 20 ml of DMFA is stirred for 3 h with boiling, cooled, treated in the manner used for compound V, chromatographed on silica gel with a 1:1 mixture of benzene–hexane, and three fractions are isolated: fraction 1 – 0.025 g (28%) of copper complex VI, R_f 0.65 (SiO_2, 1:1 benzene–hexane); fraction 2 – 0.051 g (55%) of compound VII, R_f 0.22 (SiO_2, 1:1 benzene–hexane); fraction 3 – 0.01 g (11%) of compound VIII, R_f 0.13 (SiO_2, 1:1 benzene–hexane).

TABLE 1. Electronic Absorption Spectra of Mono- and Disubstituted Tetra(tert-butyl)porphyrazines in Benzene

Compound	λ_{max} (log ε) [relative intensity]	$\Delta\nu_{Q_1-Q_2}$, cm^{-1}
II	623 (4.88), 558 (4.74), 524 sh (4.15), 342 (4.84)	1870
IIIa, b	624 (4.74), 565 (4.60), 528 sh (4.06), 346 (4.80)	1670
V	602 (4.92), 574 (4.77), 524 sh (4.01), 336 (4.74)	865*
VII	627 (4.92), 563 (4.58), 341 (4.71)	1820
VIII	598 [1.0], 540 [0.16], 342 [0.62]	—
IX	624 (4.60), 554 (4.44), 336 (4.68)	2025
X	627 (4.81), 557 (4.44), 340 (4.80)	2000
XIa	627 (4.86), 557 (4.65), 340 (4.88)	2000
XIb	627 (4.83), 557 (4.63), 340 (4.85)	2000
XII	624 [1.0], 584 [0.88], 332 [1.3]	1100
XIII	624 [1.0], 564 [0.7], 332 [1.27]	1700
XIVa	624 [1.0], 554 [0.53], 332 [1.04]	2025
XIVb	624 [1.0], 554 [0.61], 332 [1.11]	2025
XVa	624 [1.0], 554 [0.63], 332 [1.15]	2025
XVb	624 [1.0], 554 [0.61], 332 [1.11]	2025
XVI	630 (4.70), 562 (4.55), 340 (4.80)	1920
XVII	602 [1.0], 580 [1.29], 338 [1.0]	630*

*The quantity $\Delta\nu\ Q_0 - Q_1$ is in cm^{-1}.

3-(N-Piperidino)-2,7,12,17-tetra(tert-butyl)porphyrazine (IX). A mixture of 0.10 g (0.144 mmole) of monobromide II′ and 2 ml of piperidine in 10 ml of DMFA is boiled for 1 h, cooled, decanted into 100 ml of water, and the precipitate is separated, dried in air, and chromatographed on silica gel by successively eluting with hexane and a 1:1 hexane–benzene mixture; 0.02 g of compound I′ (the product of reduction of compound II′) and 0.08 g (79%) of IX, R_f 0.83 (SiO_2, 1:1 hexane–benzene) are obtained.

3-Phenoxy-2,8-13,18(17)-tetra(tert-butyl)porphyrazine (X). A mixture of 0.20 g (0.37 mmole) of porphyrazine II″ and 0.50 g (4.3 mmole) of sodium phenate in 20 ml of DMFA is boiled for 6 h, cooled, decanted into 100 ml of water, the precipitate is separated, and the purification is carried out on silufol plates (150 × 150 mm) in a 1:25 ethyl acetate–hexane system. Two fractions are isolated: fraction 1 – 0.02 g (11.5%) of the initial porphyrazine II″, R_f 0.47 (SiO_2, 1:25 ethyl–hexane); fraction 2 – 0.054 g (26.5%) of compound X, R_f 0.44 (SiO_2, 1:25 ethyl acetate–hexane).

3-(p-Octylphenoxy)-2,8,13,18- and 2,8,13,17-Tetra(tert-butyl)porphyrazine (XIa, b). A mixture of 0.20 g (0.37 mmole) of monobromide II″ and 0.50 g (2.24 mmole) of sodium p-octylphenate in 20 ml of DMFA is boiled for 5 h, treated and purified as in the case of compound X, and two fractions are isolated: fraction 1 – 0.03 g (12%) of compound XIa, R_f 0.52 (SiO_2, 1:25 ethyl acetate–hexane); fraction 2 – 0.01 g (4%) of compound XIb, R_f 0.44 (SiO_2, 1:25 ethyl acetate–hexane).

Mono-3-(XII) and Di-3,7(12)-(phenylthio)-2,8,13,18(17)-tetra-(tert-butyl)porphyrazine (XIII). A mixture of 0.20 g (0.32 mmole) of monobromide II″, 0.5 ml of thiophenol, and 0.02 g of K_2CO_3 in 20 ml of DMFA is stirred for 1 h at 100°C, treated in the manner of compound X, chromatographed on silica gel (40/100) with benzene, and two fractions are isolated: fraction 1 – 0.027 g (13%) of monosulfide XII, R_f 0.64 (SiO_2, benzene); fraction 2 – 0.11 g – mixture of two compounds which is separated on silufol plates (150 × 150 mm) in a 1:25 ethyl acetate–hexane system. The products obtained are 0.005 g (3%) of porphyrazine I″ (the reduction product of II″) and 0.075 g (31%) of disulfide XIII with R_f 0.45 (SiO_2, 1:25 ethyl acetate–hexane).

2,2-Bis{p-[tetra(tert-butyl)porphyrazoxylphenyl]propane (XIVa, b) and p-[2-(4[1]-Hydroxyphenyl)propylphenoxy]tetra-(tert-butyl)porphyrazine (XVa, b). A mixture of 0.31 g (0.57 mmole) of monobromide II″, 0.06 g of 2,2-bis(p-hydroxyphenyl)propane, and 0.034 g of K_2CO_3 in 30 ml of DMFA is boiled for 5 h, cooled, and decanted into water, the precipitate is separated, washed with 100 ml of water, dried, and chromatographed on silica gel with benzene, and five fractions are isolated: fraction 1 – 0.04 g (15%) of porphyrazine I″, R_f 0.57 (SiO_2, benzene); fraction 2 – 0.052 g (16%) of dimer XIVa with R_f 0.32 (SiO_2, benzene); fraction 3 – 0.073 g (22%) of dimer XIVb with R_f 0.21 (SiO_2, benzene); fraction 4 – 0.035 g (9%) of monomeric porphyrazine XVa with R_f 0.08 (SiO_2, benzene); M^+ 762; fraction 5 – 0.05 g (13%) of monomeric porphyrazine XVb with R_f 0.05 (SiO_2, benzene), M^+ 762.

3-(β-Styryl)-2,8,13,18(17)-tetra(tert-butyl)porphyrazine (XVI). A mixture of 0.2 g (0.32 mmole) of monobromide II″, 0.5 ml of freshly distilled styrene, 0.005 g of palladium acetate, 0.023 g (0.088 mmole) of triphenylphosphine, and 0.5 ml of triethylamine in 15 ml of DMFA is boiled for 3 h, cooled, and decanted into 100 ml of water, the only sediment is separated, purification is carried out on silufol plates (150 × 150 mm) in a 1:25 ethyl acetate–hexane system, and two fractions are isolated: fraction 1 – 0.04 g (23%) of porphyrazine I; fraction 2 – 0.085 g (41%) of compound XVI, R_f 0.4 (SiO_2, 1:25 ethyl acetate–hexane).

Copper 3-(Phenylethynyl)-2,8,13,18(17)-tetra(tert-butyl)porphyrazine (XVII). As in the case of porphyrazine V from 0.10 g (0.16 mmole) of monobromide II″ and 0.085 g (0.52 mmole) of copper phenylacetylide in 15 ml of DMFA, there is obtained 0.094 g (81%) of copper complex XVII with R_f 0.2 (silufol, 1:1 benzene–petroleum ether).

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