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Synthesis and Spectral Properties of 1,2,5-Thiadiazolo-, 1,2,5-Selenadiazolo-, and Benzo-Fused β-Phenyl-Substituted Porphyrazines

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Abstract—Cross cyclotetramerization of *trans*-2,3-diphenylbutanedinitrile with 1,2,5-thia(selena)diazole-3,4-dicarbonitriles or phthalodinitrile in the presence of magnesium butoxide gave mixtures of Mg(II) porphyrazine complexes which were treated with trifluoroacetic acid to isolate unsymmetrical hexaphenyl-substituted 1,2,5-thia(selena)diazolo- and benzo-fused porphyrazines together with diphenyltribenzoporphyrazine. Their ^{1}H NMR and electronic absorption spectra (in the UV and visible regions) were recorded. The effect of benzene and heteroring fusion on the electronic and steric structure and spectral properties of porphyrazine derivatives was studied in terms of the molecular orbital perturbation theory and semiempirical quantum-chemical calculations (AM1, PM3, ZINDO/S, CNDO/S).

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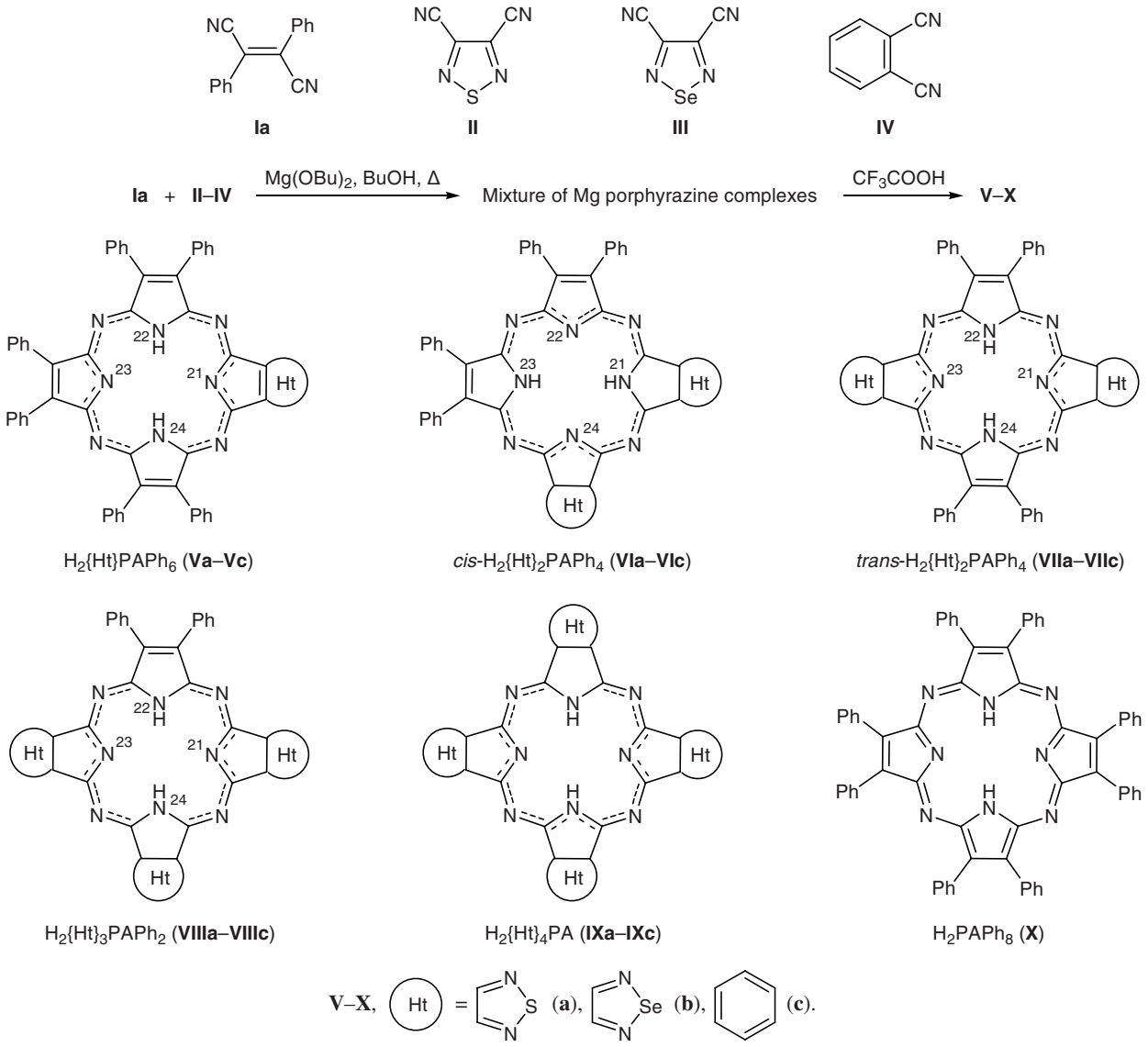
Fusion of various heterorings considerably affects physical and chemical properties of porphyrazines (PA) [1]. We previously synthesized tetra(1,2,5-thiadiazolo)porphyrazine ($H_2\{SN_2\}_4PA$) [2], its selenium-containing analog $H_2\{SeN_2\}_4PA$ [3], and benzoporphyrazines with fused 1,2,5-thiadiazole [4–6] or 1,2,5-selenadiazole fragments [4]. Like phthalocyanine H_2Pc, these compounds possess a 42π-electron chromophore, and they may be regarded as heteroelement-containing analogs of phthalocyanine. In the present work we synthesized porphyrazines with a contracted 30π-electron chromophore, namely hexa-β-phenylporphyrazines having only one fused 1,2,5-thiadiazole, 1,2,5-selenadiazole, or benzene ring, and examined how the nature of the fused ring affects their spectral parameters. The relations between the size and symmetry of π-electron chromophore and spectral parameters were studied using porphyrazines having different numbers of fused benzene rings.

The most convenient and widely used method for the synthesis of porphyrazine derivatives is based on template condensation of maleonitrile or phthalonitrile with a metal salt, which is carried out by heating the reactants in melt or in a high-boiling solvent [1, 7, 8]. Metal-free porphyrazines are usually obtained by demetalation of the corresponding Mg(II) complexes which are synthesized by either direct fusion of a dinitrile {e.g., *trans*-2,3-diphenylbutanedinitrile (**Ia**) [9] or phthalonitrile (**IV**) [10]} with magnesium or template cyclotetramerization of a dinitrile in alcohol in the presence of magnesium alkoxide (Linstead procedure [11]). Porphyrazines having four fused 1,2,5-thia(selena)diazole rings are obtained as Mg(II) complexes $Mg\{XN_2\}_4PA$ by cyclotetramerization of 1,2,5-thia(selena)diazole-3,4-dicarbonitrile **II** or **III** in the presence of magnesium propoxide or butoxide in the corresponding alcohol [2, 3]. In order to synthesize hexa-β-phenylporphyrazines **Va**–**Vc** having only one fused hetero (or benzene) ring, cross template cyclocondensations of dinitrile **Ia** with heterocyclic dinitriles **II** and **III** or phthalodinitrile (**IV**) in the presence of magnesium butoxide in butanol was performed (Scheme 1).

Taking into account that cross cyclocondensation of two different dinitriles A and B could give rise to

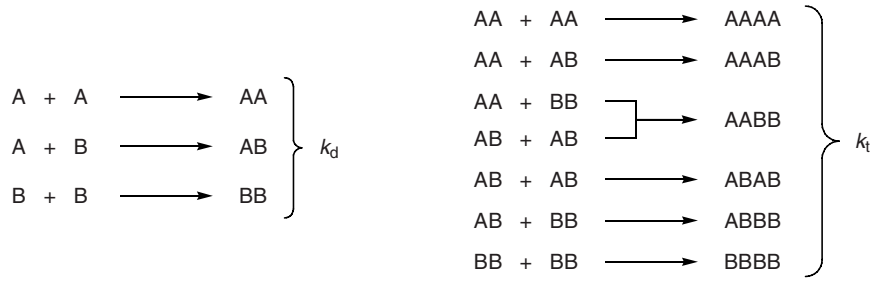
Scheme 1.



a mixture of two symmetric porphyrazines AAAA and BBBB and four porphyrazines with a lower symmetry (AABB, ABAB, AAAB, ABBB), we examined the reaction in more detail with a view to find optimal conditions for the formation of hexa-β-phenylporphyrazines having only one fused ring. It is most likely that the porphyrazine macroring is formed in two steps. In the first step, condensation of two dinitrile molecules gives a dimer, and next follows intermolecular cyclization of two dimeric units [12, 13].

In terms of the above mechanism, we performed kinetic and statistical analysis of the cross cyclocondensation (Scheme 2). Provided that dinitriles A and B are equally reactive (rate constant k_d) in the processes leading to dimeric structures AA, AB, and BB and that the latter are equally reactive in the subsequent cyclocondensation with formation of structures AAAA, AABB, ABAB, AAAB, ABBB, and BBBB (rate constant k_t), porphyrazine ABBB should be formed with the maximal yield (18.5%) at a dinitrile B-to-A ratio of 3:1 (Fig. 1). However, the fractions of the other low-symmetry porphyrazines should also be significant (19.4% of AABB, 7.4% of ABAB, and 4.7% AAAB), and the fractions of symmetric structures BBBB and AAAA should be 46.6% and 3.5%, respectively. As shown in Fig. 1, the yield of ABBB begins to exceed the yields of all other low-symmetry porphyrazines starting from a B:A ratio of 4:1, and the value B:A = 7:1 seems to be optimal for the synthesis and isolation of ABBB. Although the yield of symmetric structure

Scheme 2.



BBBB reaches 68%, the theoretical yield of target structure ABBB (16.3%) is greater than the overall yield of the other products (15.5%).

Taking into account the above stated, we performed cross cyclocondensation using 4–7-fold excess of dinitrile **Ia** with respect to dinitrile **II**–**IV**. At a **Ia**-to-**II**–**IV** ratio of 4:1, the yield of porphyrazines **Va**–**Vc** (after demetalation) was 3–4% calculated on the overall amount of initial dinitriles and 4–5% calculated on the minor dinitrile. Insofar as at the given reactant ratio the maximal theoretical yield of structure ABBB is 18.3% (23% on the minor dinitrile), the experimental yield is 16–22% of the theoretical value. In the reaction of dinitrile **Ia** with selenadiazole **III** at a ratio of 7:1 we isolated 4.7% of $H_2\{SeN_2\}PAPh_6$ (**Vb**), the conversion of **III** being 9.4%; these values constitute 29% of the theoretically possible ones (16.3 and 33%, respectively).

The overall yield of magnesium(II) porphyrazine complexes in joint condensation of two different dinitriles ranged from 90 to 95%, and their demetalation was also characterized by a high yield (about 90%). Therefore, the considerably lower yield of hexaphenylporphyrazines **Va**–**Vc**, as compared to the theoretical

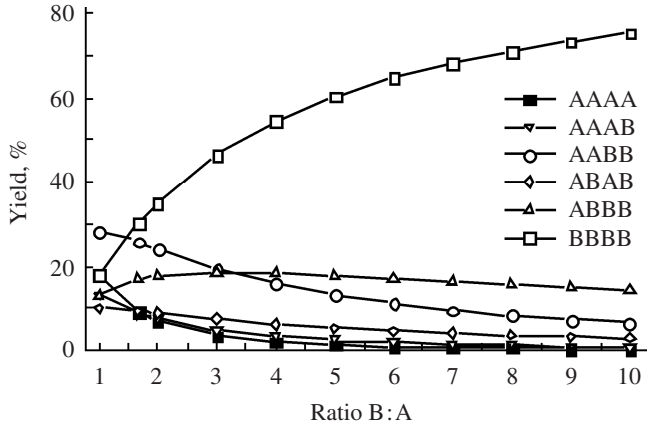
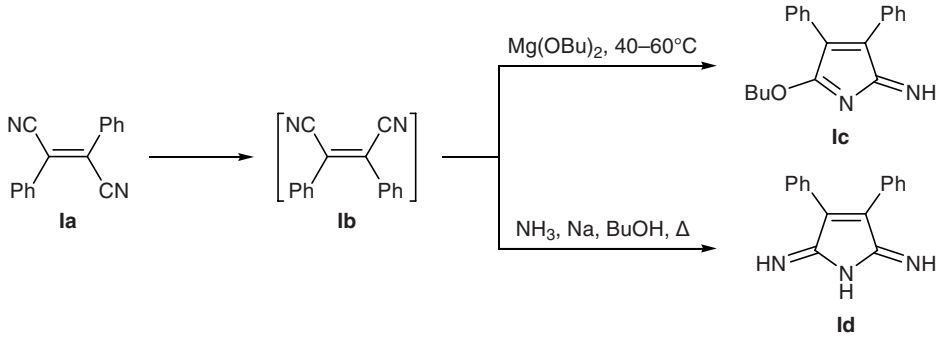


Fig.1. Plot of the yield of porphyrazines versus the dinitrile A–B ratio in the cross condensation according to Scheme 2.

value, is likely to result from different reactivities of the initial dinitriles, which were assumed to be similar while estimating the theoretical yield. The reactivity of dinitriles is determined by both polarization of the C≡N bond (which depends on the charges on the nitrogen and carbon atoms) and steric structure of their molecules. The results of PM3 quantum-chemical calculations showed that the cyano groups in heterocyclic dinitriles **II** and **III** should be more reactive in the cyclotetramerization process than those in phthalodinitrile (**IV**): the C≡N bonds in molecules **II** and **III** are polarized more strongly, and the nitrogen atoms are electron-deficient (Table 1). On the other hand, closure of pyrrole ring fused to a five-membered heteroring is expected to involve greater steric hindrances than in the formation of isoindole fragment from phthalodinitrile [8]. The cyano groups in dinitrile **Ia** are least polarized, and their *trans* configuration is unfavorable for pyrrole ring closure. Therefore, the cyclocondensation should be preceded by transformation of *trans*-dinitrile **Ia** into *cis* isomer **Ib** (Scheme 3); this process is accompanied by increase in the polarization of the cyano groups (Table 1).

Theoretically, only 5–10% of dinitrile **II**–**IV** [**II**–**IV**-to-**Ia** ratio 1:(4–7)] should give rise to symmetric porphyrazines **IXa**–**IXc**. In fact, the yield of porphyrazines **IX** was 40–60%. Increased yield was also observed for diphenylporphyrazines **VIIIa**–**VIIIc** having three fused rings. At a **Ia**–**IV** ratio of 4.3:1, the conversion of phthalodinitrile (**IV**) into tribenzoporphyrazine **VIIIc** was 24%, and the overall yield of the latter was 6.1% against theoretical values of 12 and 3.2%, respectively. Under these conditions, the yield of tetraphenyl derivatives **VIa**–**VIc** and **VIIa**–**VIIc** and especially of hexaphenylporphyrazines **Va**–**Vc** is lower than that expected theoretically. Thus dinitriles **II**–**IV**, despite their small fraction in the reaction mixture [ratio 1:(4–7) with respect to **Ia**] are consumed mainly for their self-condensation rather than for the reaction with dinitrile **Ia**, and the latter gives rise to a larger

Scheme 3.



amount of symmetric ocaphenylporphyrazine (**X**) (70–80%) than it is expected at the given initial dinitrile ratio (55–70%).

When dinitrile **Ia** was added to a suspension of magnesium butoxide, the mixture was kept for 10–20 min at 40–60°C, and the other (more reactive) dinitrile was then added, the relative yield of the corresponding hexaphenylporphyrazine slightly increased, while the yield of symmetrically fused product **IX** decreased. Presumably, in the first step dinitrile **Ia** undergoes isomerization into *cis*-dinitrile **Ib** which reacts with magnesium butoxide to give intermediate 5-butoxy-3,4-diphenyl-2*H*-pyrrol-2-imine (**Ic**) (Scheme 3), as was reported for phthalodinitrile under analogous conditions [12, 14]. Even better results were obtained when dinitrile **Ia** was converted into more reactive dihydropyrrole-2,5-diimine **Id** according to [15]. For this purpose, gaseous ammonia was bubbled through a suspension of compound **Ia** in butanol in the presence of a catalytic amount of sodium butoxide at moderately elevated temperature. Diimine **Id** was not isolated from the reaction mixture but was added together with dinitrile **III** to a suspension of magnesium butoxide. In this case, at a **Ia**-to-**III** ratio of 7:1, the experimental yield of hexa-β-phenylporphyrazine **Vb** increased up to the theoretical value (overall yield 16.3%, yield calculated on **III** 33%).

Apart from optimization of conditions for joint condensation of dinitriles **Ia** and **II–IV**, the problem related to separation of the porphyrazine mixture thus formed turned out to be equally important. Symmetrically fused porphyrazines **IXa–IXc** and their Mg(II) complexes are very poorly soluble in noncoordinating organic solvents (CH_2Cl_2, $CHCl_3$, benzene), and they are separated from the other products by Soxhlet extraction with those solvents. Symmetric Mg(II)–octaphenylporphyrazine ($MgPAPh_8$) is readily separated from the soluble magnesium complexes by chromatography on aluminum oxide using chloroform as eluent. Unsymmetrical porphyrazine magnesium complexes cannot be separated in such a way; therefore, their mixture was subjected to demetalation by treatment with trifluoroacetic acid, followed by repeated chromatography. The first fraction contained a small amount of octaphenylporphyrazine H_2PAPh_8 (**X**), hexa-β-phenylporphyrazines **Va–Vc** were eluted in the second fraction, and the third fraction contained a mixture of *cis*- and *trans*-tetra-β-phenylporphyrazines **VIa–VIc** and **VIIa–VIIc**. Isomers **VI** and **VII** are characterized by very similar R_f values in thin-layer chromatography on silica gel. Dibenzoporphyrazines **VIc** and **VIIc** were identified by electronic absorption spectroscopy (see below). We failed to find conditions for preparative separation of *cis* and *trans* isomers **VI** and **VII** by column chromatography. Di-β-phenylporphyrazines **VIIIa** and **VIIIb** having three fused 1,2,5-thia- or 1,2,5-selenadiazole fragments are poorly soluble and are partially separated together with symmetric products **IXa** and **IXb** by Soxhlet extraction and filtration. The remaining (dissolved) part of **VIIIa** and **VIIIb** is retained in the chromatographic column; the chromatographic mobility of compounds **VIIIa** and **VIIIb** is so low that they cannot be eluted with chloroform containing methanol or even with pyridine or dimethylformamide. By contrast, di-β-phenyltribenzoporphyr-

Table 1. Polarization of the C≡N bond in dinitriles **I–IV** according to PM3 calculations

Dinitrile	Charges on atoms		Polarization of the C≡N bond $\Delta\delta = \lvert\delta_C - \delta_N\rvert$
	C	N	
Ia	–0.096	–0.056	0.040
Ib	–0.125	–0.024	0.101
II	–0.108	0.022	0.130
III	–0.116	0.024	0.140
IV	–0.114	–0.028	0.086

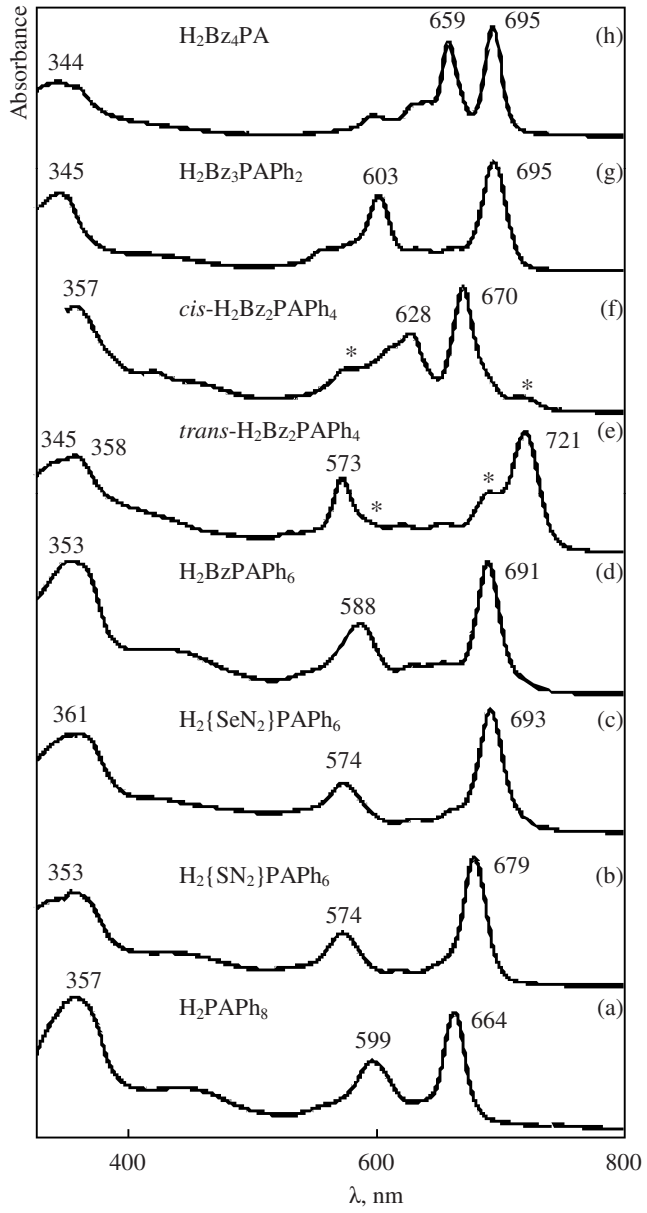


Fig. 2. Electronic absorption spectra of fractions isolated by chromatographic separation of mixtures of β-phenyl-substituted porphyrazines in methylene chloride: (a) H_2PAPh_8 (**X**, first fraction); (b) $H_2\{SN_2\}PAPh_6$ (**Va**), (c) $H_2\{SeN_2\}PAPh_6$ (**Vb**), and (d) $H_2\{Bz\}PAPh_6$ (**Vc**) (second fraction); (e) *trans*-$H_2\{Bz\}_2PAPh_4$ (**VIIc**) and (**f**) *cis*-$H_2\{Bz\}_2PAPh_4$ (**VIc**) (third fraction); (g) $H_2\{Bz\}_3PAPh_2$ (**VIIIc**, fourth fraction); (h) phthalocyanine H_2Pc [$H_2\{Bz\}_4PA$] (**IXc**) in chlorobenzene. Absorption bands marked with an asterisk correspond to impurities of other porphyrazines.

azine $H_2\{Bz\}_3PAPh_2$ (**VIIIc**) is characterized by fairly high solubility and chromatographic mobility; it was successfully isolated by column chromatography (in the fourth fraction).

The purity of porphyrazines isolated by column chromatography was checked by electronic absorption spectroscopy. Their electronic absorption spectra showed strong dependence on the nature and position of the fused fragments, as well as on the size of the macrocyclic π-chromophore (Fig. 2). Porphyrazines **Va–Vc** and tribenzoporphyrazine **VIIIc** were also characterized by elemental analyses and ^{1}H NMR spectra.

In the ^{1}H NMR spectra of β-phenyl-substituted porphyrazines, protons in the β-phenyl groups resonate as multiplets at δ 8.0–8.5 (*o*-H), 7.5–7.6 (*m*-H), and 7.7–7.9 ppm (*p*-H). Protons in the *ortho* positions appear most closely to the macroring and are deshielded more strongly by the π-electron ring current; therefore, their signals are differentiated to a greater extent than signals from the *para*- and *meta*-protons. In the spectra of $H_2\{SeN_2\}PAPh_6$ (**Vb**) and $H_2\{Bz\}PAPh_6$ (**Vc**) separate doublets are observed from *ortho*-protons in different phenyl groups. Protons in the α-positions of fused benzene rings in compounds **Vc** and **VIIIc** suffer the maximal effect of π-electron ring current in the porphyrazine macroring, and their signal is located most downfield (δ 8.8–9.2 ppm); signals from the corresponding β-protons appear at δ 7.9–8.2 ppm. The inner NH protons are strongly shielded by π-electron ring current; their broadened signals are observed at δ –1.7 to –2.2 ppm.

The electronic absorption spectra of unsymmetrical porphyrazines, as well as of symmetric derivatives, octaphenylporphyrazine and phthalocyanine, contain strong bands arising from π–π* transitions in the macroring (Fig. 2). In keeping with the Gouterman four-orbital theory [16], two strong absorption bands (Q_1 and Q_2) in the visible region (λ 570–730 nm) may be assigned to electron transitions from the HOMO to LUMO and LUMO-1. Vibrational satellites of the Q_1 and Q_2 bands have low intensity. Broadened Soret band in the UV region (λ 340–360 nm) corresponds to transitions from the HOMO-1 to LUMO and LUMO-1; it is characterized by considerable contribution of electronic excitations other than HOMO-1 → LUMO, LUMO-1 (see, e.g., [17]).

Figure 2 (a–d) shows that extension of macrocyclic chromophore from 26 π-electrons in H_2PAPh_8 to 30 π-electrons upon fusion of one aromatic fragment (1,2,5-thiadiazole, 1,2,5-selenadiazole, or benzene) leads to increased splitting of the *Q*-bands: from 1630 cm^{-1} for H_2PAPh_8 (**X**) to 2690 cm^{-1} for $H_2\{SN_2\}$-$PAPh_6$ (**Va**), 2990 cm^{-1} for $H_2\{SeN_2\}PAPh_6$ (**Vb**), and 2540 cm^{-1} for $H_2\{Bz\}PAPh_6$ (**Vc**). This is the result of hypsochromic shift of the Q_2 component by 730, 730,

and 330 cm^{-1} and bathochromic shift of the Q_1 component by 330, 660, and 590 cm^{-1}, respectively (hereinafter, the shifts are given relative to H_2PAPh_8). The Soret band maximum shifts by 330 cm^{-1} toward higher frequencies for $H_2\{SN_2\}PAPh_6$ and $H_2\{Bz\}PAPh_6$ and by 690 cm^{-1} toward lower frequencies for $H_2\{SeN_2\}$-$PAPh_6$. Variations in the electronic absorption spectra with increase in the number of fused benzene rings in β-phenyl-substituted porphyrazines $H_2\{Bz\}_nPAPh_{8-2n}$ (**Vc**–**IXc**) are fairly similar to those observed for structurally related β-aryl-substituted porphyrazines, β-(3-trifluoromethylphenyl)benzoporphyrazines $H_2\{Bz\}_nPA$-$(3\text{-}CF_3C_6H_4)_{8-2n}$ [18] and β-(4-*tert*-butylphenyl)(4,5-dioctyloxybenzo)porphyrazines $H_2\{4,5\text{-}(C_8H_{17}O)_2Bz\}_n$-$PA(4\text{-}t\text{-}BuC_6H_4)_{8-2n}$ [19, 20]. The chromophoric fragment in isomeric tetra-β-phenyldibenzoporphyrazines, *cis*- and *trans*-$H_2\{Bz\}_2PAPh_4$, has the same number of π-electrons (34); however, the electronic absorption spectra of fractions isolated by thin-layer chromatography on silica gel differed considerably (Fig. 2e, f). The fraction with R_f 0.90 is characterized by red shift of the Q_1 band (λ_{max} 721 nm) and blue shift of the Q_2 band (λ_{max} 573 nm), so that splitting of the Q band is fairly large (3580 cm^{-1}); strong splitting (~1050 cm^{-1}) is also observed for the Soret band (λ_{max} 345 and 358 nm). By contrast, the fraction with R_f 0.88 displayed a weak splitting of the Q-band (990 cm^{-1}; λ_{max} 670 and 628 nm for Q_1 and Q_2, respectively), while the Soret band was not split. Theoretical analysis (see below) and comparison with published data [18–20] allowed us to assign the fraction with R_f 0.90 to *trans* isomer **VIIc**, and that with R_f 0.88, to *cis*-**VIc**.

Further extension of the chromophore fragment to 38 π-electrons in tribenzoporphyrazine **VIIIc** and 42 π-electrons in phthalocyanine (**IXc**) almost does not affect the position of the Q_1 band as compared to benzoporphyrazine **Vc** but is accompanied by red shift of the Q_2 band maximum to λ 603 and 659 nm for compounds **VIIIc** and **IXc**, respectively. As a result, splitting of the Q bands decreases to 2200 cm^{-1} in the spectrum of **VIIIc** [which is slightly smaller than in the spectrum of **Vc** (2540 cm^{-1})] and to 780 cm^{-1} in the spectrum of **IXc**. The Soret maxima in the spectra of tri- and tetrabenzoporphyrazines are displaced by ~1000 cm^{-1} toward higher frequencies relative to that in the spectrum of octa-β-phenylporphyrazine **X** having no fused rings.

On a qualitative level, the observed shifts of the Q-band maxima may be interpreted in terms of the perturbation theory as applied to π-molecular orbitals. Fusion of an aromatic ring should change the energies

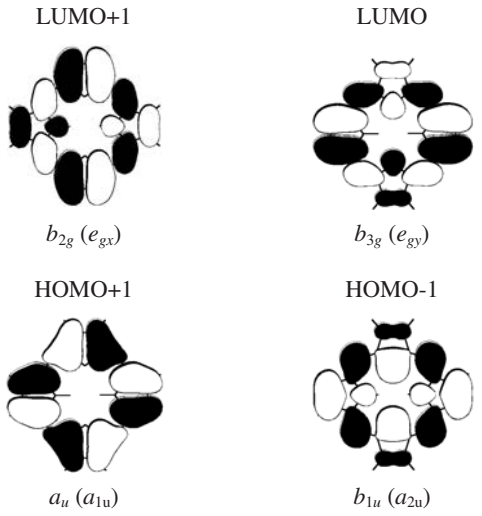


Fig. 3. Structure of the frontier molecular orbitals of parent porphyrazine H_2PA (D_{2h} symmetry). In parentheses are given the theoretical group designations for the D_{4h} symmetry group.

of molecular orbitals, including the highest occupied and lowest unoccupied molecular orbitals responsible for electronic absorption patterns. Fusion affects primarily the contribution of atomic orbitals of the pyrrole β-carbon atoms. Figure 3 shows the structure of frontier π-molecular orbitals of porphyrazine (H_2PA) having a D_{2h} symmetry (ZINDO/S or CNDO/S calculations). It is seen that the LUMO-1 b_{2g} should be sensitive to annelation to 2*H*-pyrrole rings, and the LUMO b_{3g}, to 1*H*-pyrrole rings (inner NH protons are located along the horizontal axis). The HOMO a_u elec-

Table 2. Gas-phase heats of formation (ΔH_f) of fused porphyrazines according to PM3 and AM1 calculations

Porphyrazine	NH tautomer	ΔH_f, kJ/mol		
		β-H		β-Ph
		PM3	AM1	AM1
$H_2\{SeN_2\}PA$	21,23	927		
	22,24	904		
$H_2\{SN_2\}PA$	21,23	993	1386	2029
	22,24	972	1364	2004
$H_2\{Bz\}PA$	21,23	920	1215	1858
	22,24	910	1211	1851
trans-$H_2\{Bz\}_2PA$	21,23	967	1257	1686
	22,24	947	1247	1672
cis-$H_2\{Bz\}_2PA$		956	1252	1679
$H_2\{Bz\}_3PA$	21,23	1004	1295	1509
	22,24	993	1289	1501

tron density on the β-carbon atoms in 1*H*-pyrrole rings is higher than on C^{β} in 2*H*-pyrrole rings. The main contributions to the HOMO-1 b_{1u} are those of the *meso*-nitrogen atoms and nitrogen atoms in the 2*H*-pyrrole rings.

1,2,5-Thia(selena)diazole fragments in molecules $H_2\{SN_2\}PA$ and $H_2\{SeN_2\}PA$ contain electronegative nitrogen atoms and are π-deficient; therefore, fusion of such heterorings reduces the energy of π-molecular orbitals, the HOMO a_u being stabilized to a lesser extent than the LUMO b_{3g} but to a greater extent than the LUMO-1 b_{2g}. Increased splitting of the *Q* band in electronic absorption spectra indicates greater stabilization of the LUMO rather than LUMO-1. Smaller distance between the Q_1 and Q_2 maxima corresponds to lesser stabilization of the HOMO as compared to the LUMO but greater as compared to the LUMO-1. Larger bathochromic shifts of the Q_1 and Soret bands in the electronic spectrum of the selenium-containing derivative suggest stronger relative stabilization of the LUMO. A probable reason is smaller contribution to the conjugation system of selenium $4d_{\pi}$ orbitals compared to sulfur $3d_{\pi}$ orbitals.

Fusion of benzene rings destabilizes π-molecular orbitals, especially those in which the contributions of π-atomic orbitals of the β-carbon atoms are considerable. Therefore, increased splitting of the *Q* band in the spectrum of benzoporphyrazine **VIIc** may be attributed to increased energy of the LUMO-1, and bathochromic shift of the Q_1 band, to somewhat weaker destabilization of the HOMO, the LUMO energy changing insignificantly. Fusion of the second benzene ring at the *trans* position may be expected to further destabilize the HOMO and LUMO-1, which should lead to increased splitting of the *Q* band as a result of bathochromic shift of its long-wave component Q_1. By contrast, *cis*-fusion increases the HOMO and LUMO energies, which should be accompanied by an additional hypsochromic shift of the Q_1 component and hence weaker splitting of the *Q* band. Taking into account the above stated, the TLC fractions with R_f 0.90 and 0.88 (Fig. 2e, f) may be identified, respectively, as *trans*-dibenzoporphyrazine **VIIc** (λ_{max} 721 and 573 nm for Q_1 and Q_2; $\Delta\nu = 3580$ cm^{-1}) and its *cis* isomer **VIc** (λ_{max} 670 and 628 nm for Q_1 and Q_2; $\Delta\nu = 990$ cm^{-1}). Fusion of the third benzene ring to the *trans* isomer increases the energies of both HOMO and LUMO, and to the *cis* isomer, the energies of the HOMO and LUMO-1. Therefore, the *Q* band in the electronic absorption spectrum of tribenzoporphyrazine **VIIIc** (Fig. 2g) is split more weakly ($\Delta\nu$ = 2200 cm^{-1}), and bathochromic shift of its Q_1 component is smaller than that observed for *trans*-dibenzoporphyrazine **VIIc** but greater than the corresponding shift for *cis* isomer **VIc**. Finally, exhaustive benzene ring fusion [phthalocyanine (**IXc**)] leads to increase in both HOMO and LUMO energies, and splitting of the *Q* band becomes smaller due to bathochromic shift of its short-wave component Q_2 (Fig. 2h).

Additional information on the structure of fused porphyrazine derivatives, which is helpful for interpretation of their spectral parameters, can be obtained by quantum-chemical calculations. We performed semiempirical AM1, PM3, CNDO/S, and ZINDO/S calculations for parent porphyrazine H_2PA, its benzo- and 1,2,5-thiadiazolo-fused derivatives containing different numbers of fused rings, and their β-phenyl-substituted derivatives. The existence of different NH tautomers of porphyrazines having one, two (*trans* isomers), and three fused rings was also taken into account. The heats of formation of their molecules in the gas phase are given in Table 2 (the structures were optimized by the AM1 and PM3 methods). Figure 4 illustrates the effect of 1,2,5-thiadiazole and benzene ring fusion on the energies of frontier π-molecular orbitals of most stable tautomers, and Figure 5 shows theoretical electronic absorption spectra in the region of *Q* band maxima, calculated by the ZINDO/S and CNDO/S methods for AM1-optimized structures.

The data in Table 2 show that in all cases 22,24-NH tautomer is more stable than the corresponding 21,23-NH tautomer ($\Delta\Delta H_f$ = 10–25 kJ/mol). The calculated *Q*-band splittings (Fig. 5) for 22,24-NH tautomers are consistent with the experimental data (Fig. 2), while those calculated for 21,23-NH tautomers are considerably lower. The ^{1}H NMR spectra of porphyrazines **Va**–**Vc** contain one signal from NH protons, while tribenzoporphyrazine $H_2\{Bz\}_3PAPh_2$ (**VIIIc**) displays two NH signals. These findings indicate that in all cases at 293 K the most stable are 22,24-NH tautomers in which the maximal number of β-phenyl groups reside on the 1*H*-pyrrole rings (four in **Va**–**Vc** and two in **VIIIb**; see Scheme 1) while aromatic heterorings or benzene rings are fused to the 2*H*-pyrrole fragments (two of three in **VIIIb**). The presence of only one NH signal in the ^{1}H NMR spectra of **Va**–**Vc** may also be rationalized in terms of fast interconversion of the 21,23- and 22,24-NH tautomers. However, taking into account the presence of two NH signals in the spectrum of $H_2\{Bz\}_3PAPh_2$ (**VIIIb**) and published data for pentyloxy-substituted [1,2,5]thiadiazolotribenzoporphyrazine which was shown to exist as the only

22,24-NH tautomer over a broad temperature range (210–300 K) [5], such interpretation seems to be less appropriate. Thus the results of quantum-chemical calculations in combination with the experimental electronic absorption and ^{1}H NMR spectra indicate that the most stable is 22,24-NH tautomer.

As shown in Fig. 4, fusion of electron-withdrawing 1,2,5-thiadiazole fragment actually stabilizes all frontier π-molecular orbitals, while benzene ring fusion destabilizes them.

Concerning calculations of the excited states, the following must be noted. Initially, CNDO/S and ZINDO/S calculations of electronic absorption spectra of the compounds under study were performed using standard sets of parameters. The predicted trends in variation of the Q_1 and Q_2 transitions and Q_2–Q_1 splitting for structures having different numbers of fused benzene rings were consistent with the experimental data (the results obtained by the CNDO/S and ZINDO/S methods differed insignificantly). In particular, the data for dibenzoporphyrazines were reproduced especially well: the strongest splitting of the *Q* band and the largest bathochromic shift of the Q_1 component are observed for the *trans* isomer, while the *cis* isomer is characterized by the lowest values of these parameters. Nevertheless, the calculations were not free from some disadvantages typical of porphyrins on the whole [17]. On the one hand, the energies of transitions Q_1 and Q_2 to the two lowest excited singlet states (S_1 and S_2) are systematically underestimated with respect to the experimental data. On the other hand, the calculated energies of transitions to other states with higher energies are overestimated. This applies primarily to transitions in the near UV region, i.e., to the Soret band. According to the calculations, the Soret band covers at least six $S_0 \rightarrow S_i$ transitions (where i = 3–8) with fairly high probabilities (cf. PM3 and ZINDO/S calculations of the electronic absorption spectra of benzoporphyrazine zinc complexes [20]).

In order to improve agreement between the calculated and experimental electronic absorption spectra we changed some parameters in the CNDO/S and ZINDO/S approximations. In particular, raising the π–π overlap parameter from the common value 0.585 to 0.67 resulted in increased energies of Q_1 and Q_2 transitions so that the latter better matched the experimental data (Fig. 5). On the other hand, the transitions $S_0 \rightarrow S_i$ (i = 3, 4, 5, 6, 7, 8) were simultaneously displaced to even shorter wavelengths.

Optimization of parameters involved in CNDO/S and ZINDO/S calculations to achieve quantitative

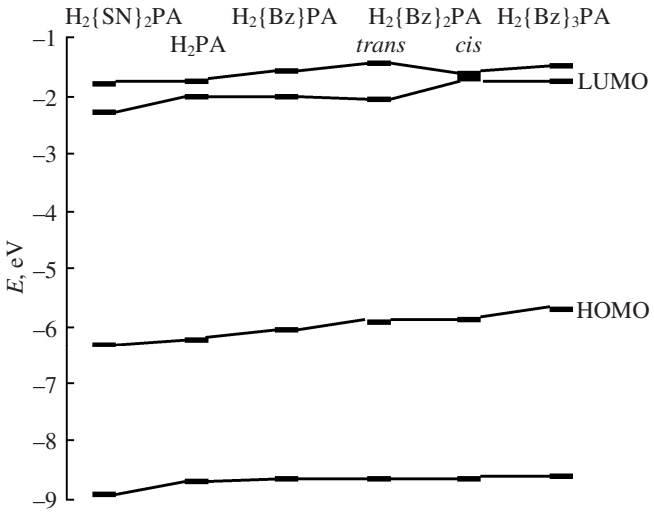


Fig. 4. Calculated (ZINDO/S) energies of frontier π-molecular orbitals of fused porphyrazines having no substituents in the β-positions.

reproduction of experimental electronic absorption spectra of porphyrin and porphyrazine derivatives constitutes a separate problem. In addition, this problem is considerably complicated by a number of factors. For example, the experimental spectrum in the UV region (Fig. 2) looks like a broad diffuse band with no distinct maxima. Calculations of the low-symmetry fused porphyrazine derivatives showed that their excited states

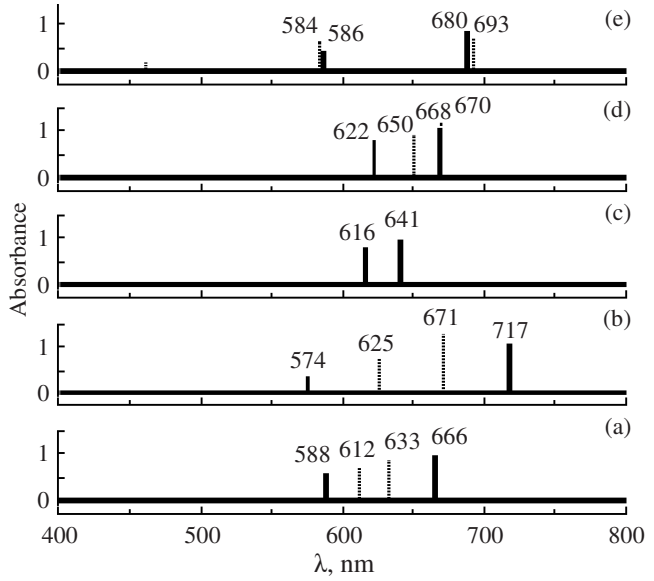


Fig. 5. Theoretical electronic absorption spectra of β-phenyl-substituted porphyrazines with fused benzene rings: (a) **Vc**, (b) **VIc**, (c) **VIIc**, (d) **VIIIc**, and (e) 1,2,5-thiadiazole derivative **Va** (ZINDO/S calculations). Bold solid lines correspond to the 22,24-NH tautomers, and hashed lines, to the 21,23-NH tautomers.

S_i (i = 3, 4, 5, 6, 7, 8) include a number of configurations. For structurally related molecules having an inversion center, the S_i states (i = 3, 4, 5, 6, 7, 8) are B_1, B_2 N_1, and N_2 with u-symmetry and two states with g-symmetry [21–24].

EXPERIMENTAL

The electronic absorption spectra were measured in the range from λ 350 to 900 nm on a Hitachi U-2000 spectrophotometer from solutions with a concentration of 10^{-6} to 10^{-5} M. The ^{1}H NMR spectra were recorded at 293 K on a Bruker AC-200 spectrometer operating at 200.13 MHz from solutions in chloroform-*d*. At a porphyrazine concentration of 0.005 to 0.01 M, all ^{1}H NMR signals were broadened due to strong intermolecular association. Resolved signals were observed only from dilute solutions (c < 0.002 M).

7,8,12,13,17,18-Hexaphenyl[1,2,5]selenadiazolo-[3,4-*b*]-5,10,15,20-tetraazaporphyrin $H_2\{SeN_2\}$-$PAPh_6$ (Vb). *a*. Metallic magnesium, 0.24 g (0.01 mol), was dissolved in 25 ml of boiling butan-1-ol (the reaction was initiated by adding a small crystal of iodine), 1 g (4.3 mmol) of diphenylfumaronitrile (**Ia**) and 0.112 g (0.6 mmol) of 1,2,5-selenadiazole-3,4-dicarbonitrile (**III**) were added to the resulting porridge-like suspension of magnesium butoxide, and the mixture was heated for 8 h under reflux. The solvent was distilled off from the dark green mixture, the dry residue was treated with 20 ml of 50% aqueous acetic acid to remove excess magnesium butoxide (the mixture was stirred for 1.5 h), and the precipitate was filtered off, washed with several portions of water, dried, and extracted with chloroform in a Soxhlet apparatus. The extract containing a mixture of soluble Mg(II)–porphyrazine complexes was subjected to chromatography on aluminum oxide to separate the main part of the Mg(II)–octaphenylporphyrazine complex (about 500 mg, 41%). A fraction containing unsymmetrical Mg(II)–porphyrazine complexes was evaporated, the residue was dissolved in 5 ml of trifluoroacetic acid, the solution was left overnight and evaporated, and the residue was washed with water until neutral washings, dried, dissolved in chloroform, and subjected to chromatography on aluminum oxide. The first fraction contained octaphenylporphyrazine, and the second fraction was subjected to repeated chromatography to isolate 50 mg (9%) of $H_2\{SeN_2\}PAPh_6$.

b. Dinitrile **Ia**, 1 g, was added to 20 ml of butan-1-ol, a catalytic amount (10 mg) of metallic sodium was added, and dry ammonia was bubbled through the mixture over a period of 2 h on heating at the boiling point. A suspension of magnesium butoxide in 25 ml of butan-1-ol (preliminarily prepared from 0.24 g of magnesium) and 0.112 g (0.6 mmol) of 1,2,5-selenadiazole-3,4-dicarbonitrile (**III**) were added, and the mixture was heated for 2 h under reflux. The product was isolated as described in *a*. Yield 175 mg (33%), R_f 0.79 (CH_2Cl_2, Silufol). ^{1}H NMR spectrum, δ, ppm: 8.76 m (2H, *o*-H), 8.33 m (10H, *o*-H), 7.70 m (6H, *p*-H), 7.54 m (12H, *m*-H), –1.70 br (2H, NH). Found, %: C 71.20; H 3.77; N 16.08. $C_{52}H_{32}N_{10}Se$. Calculated, %: C 71.31; H 3.68; N 15.99. *M* 875.85.

7,8,12,13,17,18-Hexaphenyl[1,2,5]thiadiazolo-[3,4-*b*]-5,10,15,20-tetraazaporphyrin $H_2\{SN_2\}PAPh_6$ (Va) was synthesized and isolated as described above for $H_2\{SeN_2\}PAPh_6$ (method *a*) from 1 g (4.3 mmol) of dinitrile **Ia** and 0.135 g (1.0 mmol) of 1,2,5-thiadiazole-3,4-dicarbonitrile (**II**). Yield 40 mg (5%), R_f 0.91 (CH_2Cl_2, Silufol). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.15–8.35 m (12H, *o*-H), 7.70 m (6H, *p*-H), 7.54 m (12H, *m*-H), –2.24 br (2H, NH). Found, %: C 75.22; H 3.70; N 17.19; S 3.95. $C_{52}H_{32}N_{10}S$. Calculated, %: C 75.34; H 3.89; N 16.90; S 3.87. *M* 828.95.

7,8,12,13,17,18-Hexaphenylbenzo[*b*]-5,10,15,20-tetraazaporphyrin $H_2\{Bz\}PAPh_6$ (Vc) and 17,18-diphenyltribenzo[*b*,*g*,*l*]-5,10,15,20-tetraazaporphyrin $H_2\{Bz\}_3PAPh_2$ (VIIIc). Cross condensation of 1 g (4.3 mmol) of dinitrile **Ia** and 0.125 g (1.0 mmol) of phthalodinitrile (**IV**) was performed as described above for the synthesis of $H_2\{SeN_2\}PAPh_6$ (**Vb**), method *a*. Chromatographic separation of the extract on aluminum oxide using chloroform as eluent gave 4 fractions. By repeated chromatography of the second fraction we isolated 30 mg (4%) of compound **Vc**, R_f 0.94 (benzene, Silufol). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 9.15 m (2H, α-H), 8.79 d (4H, *o*-H), 8.42 d (4H, *o*-H), 8.25–8.35 m (4H, *o*-H), 8.03 m (2H, β-H), 7.80–7.95 m (6H, *p*-H), 7.55 m (12H, *m*-H), –1.34 br (2H, NH). Found, %: C 82.30; H 4.63; N 13.78. $C_{56}H_{36}N_8$. Calculated, %: C 81.93; H 4.42; N 13.65. *M* 820.95.

The third fraction contained *cis*- and *trans*-tetraphenyldibenzoporphyrazines $H_2\{Bz\}_2PAPh_4$ which we failed to separate by column chromatography [R_f 0.88 and 0.90 (benzene, Silufol). By repeated chromatography of the fourth fraction (Al_2O_3, benzene) we isolated 50 mg (6%) of compound **VIIIc**, R_f 0.70 (benzene, Silufol). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.82 m (2H, α-H), 8.70 m (4H, α-H), 8.24 d (4H, *o*-H), 8.15 m

(4H, β-H), 7.93 m (2H, β-H), 7.64 m (2H, *p*-H), 7.52 m (4H, *m*-H), –1.68 br (1H, NH), –2.24 br (1H, NH). Found, %: C 77.84; H 4.07; N 18.22. $C_{40}H_{24}N_8$. Calculated, %: C 77.91; H 3.92; N 18.17. *M* 616.68.

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