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Synthesis and Spectroscopic Study of *tert*-Butyl-Substituted Benzoporpyrazines with Fused 1,2,5-Thiadiazole Fragments

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Abstract—Cross cyclotetramerization of 1,2,5-thiadiazole-3,4-dicarbonitrile and 4-*tert*-butylphthalodinitrile in the presence of magnesium butoxide gave a mixture of symmetric and asymmetric porphyrazine magnesium(II) complexes. One of these, ($2^{2(3)}$,$7^{2(3)}$,$12^{2(3)}$-tri-*tert*-butyltribenzo[*b*,*g*,*l*][1,2,5]thiadiazolo[3,4-*q*]-5,10,15,20-tetraazaporphyrinato)magnesium(II) (MgSBBB), was isolated by column chromatography and was treated with trifluoroacetic acid to obtain the corresponding free ligand (H_2SBBB). The effect of the mode of heteroring fusion on the electronic absorption spectra of tribenzoporphyrazines was studied.

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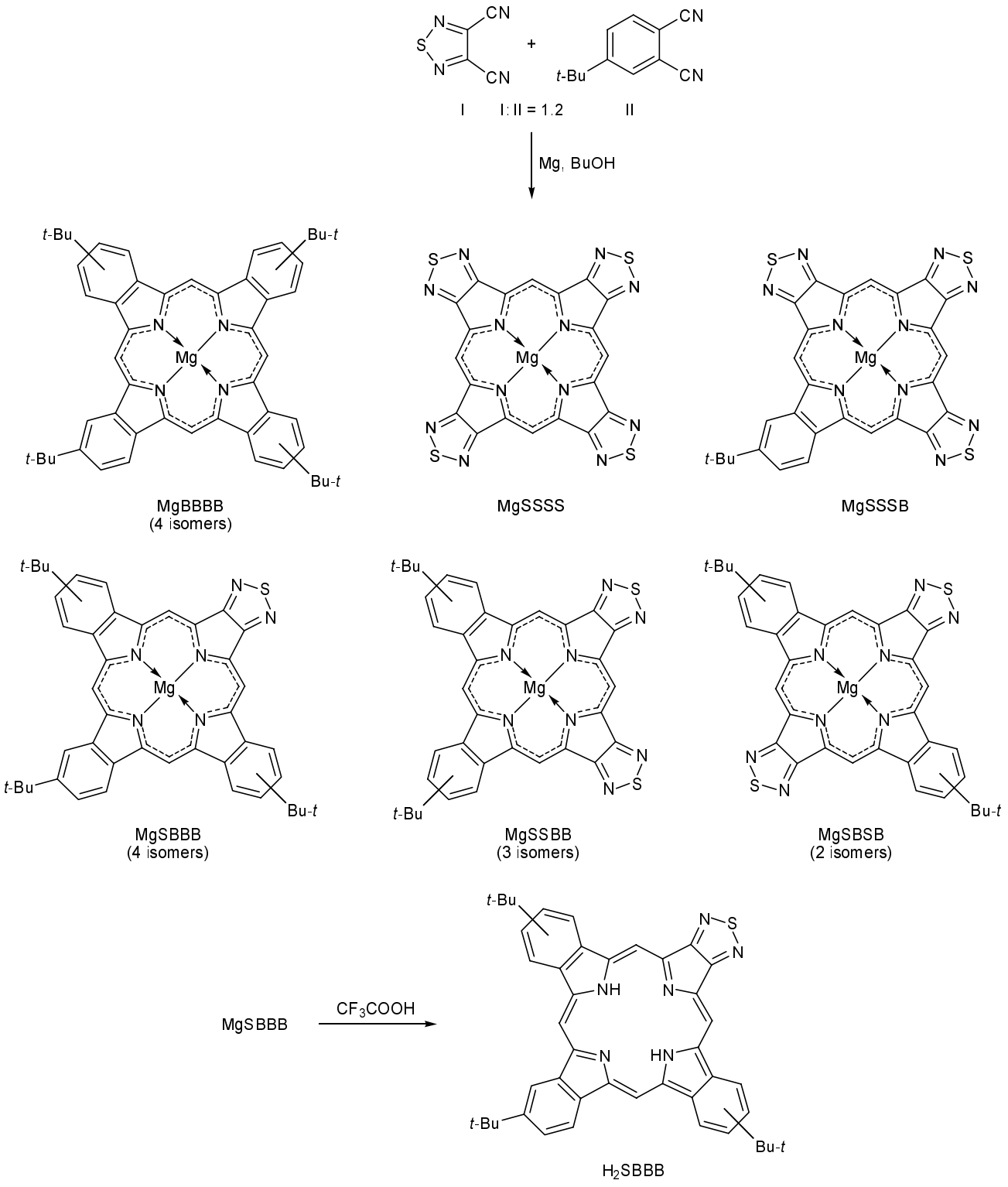
Heteroring fusion strongly affects physicochemical properties of the porphyrazine macroring [1]. We were the first to synthesize porphyrazines having a fused 1,2,5-thiadiazole fragment, tetra(1,2,5-thiadiazolo)porphyrazine H_2SSSS and its complexes with transition metals [2, 3]. Distortion of symmetric structure of the porphyrazine macroring as a result of introduction of different substituents into the β-positions of four pyrrole rings induces polarization of the macrocyclic π-chromophore; such structural modification is important from the viewpoint of obtaining compounds which may be promising as materials for nonlinear optics and liquid crystals [4]. We recently synthesized a series of pentyloxy-substituted 1,2,5-thiadiazolobenzoporphyrazines which were characterized by a very strong polarization of the π-system ("push–pull" effect) [5, 6]. In addition, asymmetric *tert*-butyl-substituted tribenzoporphyrazines with fused pyridine [7], pyrazine [8], and thiophene fragments [9] were reported. Taking into account that the electronic effects intrinsic to pentyloxy and *tert*-butyl groups are strongly different, the influence of the mode of heteroring fusion on the physicochemical properties of asymmetric tribenzoporphyrazines could be analyzed only in a series of compounds having similar substituents in the benzene rings. In the present work we synthesized for the first time *tert*-butyl-substituted 1,2,5-thiadiazolobenzoporphyrazines and studied their spectral properties.

Asymmetric porphyrazines were synthesized by cross condensation of the corresponding dinitriles, 1,2,5-thiadiazole-3,4-dicarbonitrile (**I**) and 4-*tert*-butylphthalodinitrile (**II**), in the presence of magnesium butoxide (Scheme 1). Here, apart from symmetric porphyrazine magnesium complexes MgBBBB and MgSSSS [where $BBBB^{2-}$ and $SSSS^{2-}$ are dianions derived from *tert*-butyl-substituted phthalocyanine and tetra(1,2,5-thiadiazolo)porphyrazine, respectively], four low-symmetry porphyrazine magnesium complexes could be formed, MgSBBB (1:3), *cis*-MgSSBB and *trans*-MgSBSB (2:2), and MgSSSB (3:1).

From the statistical viewpoint, provided that the ratio of the initial dinitriles is equimolar and that their reactivities are similar, the tetramerization process followed by cyclocondensation should give rise to 25% of each of the 1:3, 3:1, and *cis*-2:2 porphyrazines (ABBB, AAAB, and AABB), while the fraction of each symmetric porphyrazine and *trans*-2:2 isomer should be smaller by a factor of 3 (8.33%). Taking into account the results of recent studies on the mechanism of formation of porphyrazine macroring, according to which the cyclocondensation involves two dimeric units [10, 11], the major product should be *cis*-2:2 porphyrazine (27.8%), the fraction of asymmetric 1:3 and 3:1 porphyrazines should be 22.2% each, symmetric porphyrazines should be formed in an amount of 11.2% each, and only 5.6% of *trans*-2:2 isomer should be obtained. Although the fraction of each porphyrazine depends to some extent on the molar ratio of the initial dinitriles and their reactivity, in any case a mixture of products is formed.

Scheme 1.



Insofar as dinitrile **II** is less accessible, dinitriles **I** and **II** were taken at a molar ratio of ~1.2:1. We thus succeeded in considerably reducing the fraction of symmetric phthalocyanine complex MgBBBB and increasing the fraction of 1,2,5-thiadiazole-fused benzoporphyrazine complexes. Complexes MgBBBB, MgSBBB, MgSSBB, and MgSBSB are readily soluble in benzene; they were separated from poorly soluble

MgSSSB and insoluble MgSSSS by extraction of the dry residue obtained by removal of the solvent from the reaction mixture. Increase in the number of fused heterocyclic fragments reduces both the solubility of the corresponding magnesium complexes and their chromatographic mobility. Chromatographic separation of the benzene extract gave symmetric phthalocyanine MgBBBB in the first fraction, asymmetric 1:3 porphyrazine complex MgSBBB was eluted with addition of 5% of acetone, 2:2 porphyrazine complexes MgSSBB and MgSBSB were isolated using 10% of acetone, while 3:1 porphyrazine complex MgSSSB was not isolated (it could not be washed off even on addition of pyridine to the eluent). The composition of the magnesium complexes isolated by chromatography was confirmed by their elemental analyses. In all cases, the complexes were isolated as hydrates, which is consistent with the known ability of magnesium complexes to coordinate water molecule (as axial ligand). The mass spectra of the products isolated from the second and third fractions contained the molecular ion peaks with *m*/*z* 713 and 665, respectively; these values were in agreement with those calculated for the magnesium complexes with 1:3 and 2:2 porphyrazines. Thus the analytical and mass spectral data unambiguously confirmed the structure of the 1:3 porphyrazine complex; however, these data are insufficient to distinguish between isomeric 2:2 porphyrazine complexes, *cis*-MgSSBB and *trans*-MgSBSB.

It should be noted that all the isolated complexes, except for MgSSSB, are not individual compounds but mixtures of isomers (randomers) differing by the position of the *tert*-butyl group (4 isomers for MgBBBB and MgSBBB, 3 isomers for MgSSBB, and 2 isomers for MgSBSB); we failed to separate these mixtures into particular isomers, for they were characterized by very similar chromatographic mobilities. The NMR spectra turned out to be weakly informative for unambiguous determination of their structure, including differentiation between the *cis* and *trans* isomers. In all cases, the ^{1}H NMR spectra contained a broadened signal at δ 1.8–1.9 ppm from the *tert*-butyl protons and complex multiplets in the regions δ 8.0–8.5 and 8.6–9.5 ppm from protons in the β- and α-positions of the fused benzene rings (intensity ratio 9:1:2).

On the other hand, the position of the *tert*-butyl group only slightly influenced the π-chromophore symmetry; therefore, all randomers of a complex with a definite composition (MgBBBB, MgSBBB, MgSSBB, or MgSBSB) showed almost identical absorption patterns in the electronic spectra. However, the number of heterocyclic fragments and the site of their junction with the macroring are important factors determining the electronic properties of the latter. Therefore, electronic absorption spectra can be used to distinguish

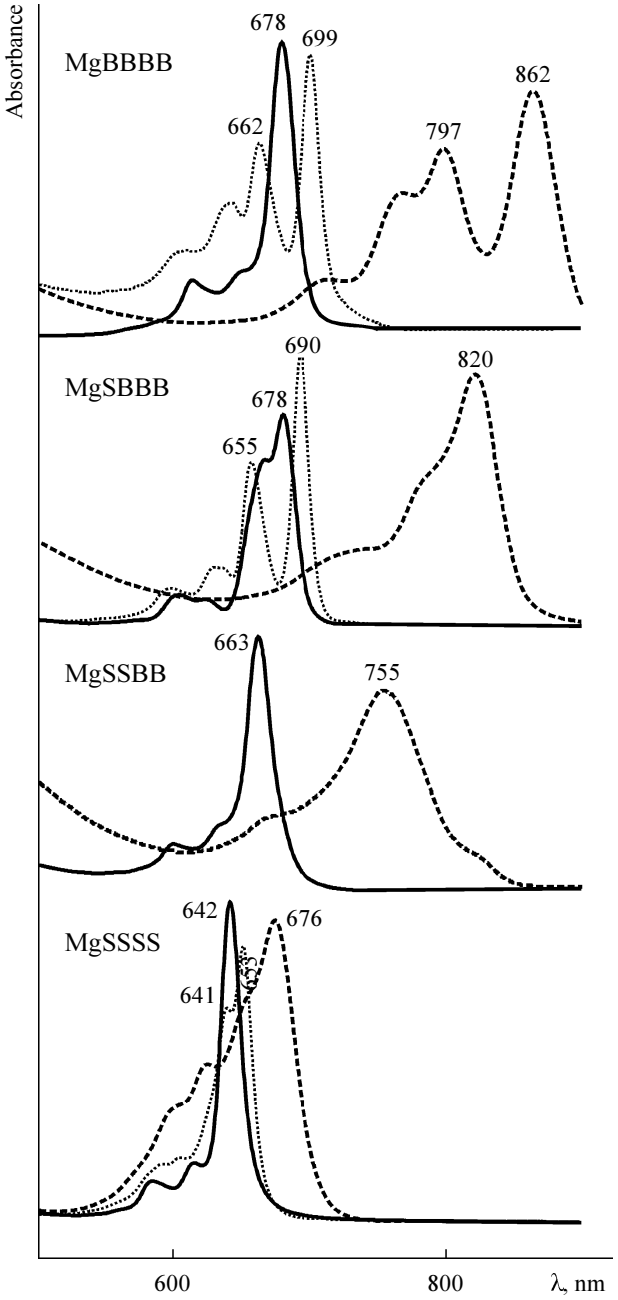


Fig. 1. Visible region of the electronic absorption spectra of magnesium complexes isolated by chromatography: MgBBBB (first fraction), MgSBBB (second fraction), MgSSBB (third fraction) in DMF and pure MgSSSS in pyridine (solid curves). The electronic absorption spectra of the corresponding metal-free compounds in methylene chloride (H_2BBBB, H_2SBBB) and chlorobenzene (H_2SSSS) are shown with dotted curves, and the electronic absorption spectra in 96% H_2SO_4 are shown with dashed curves.

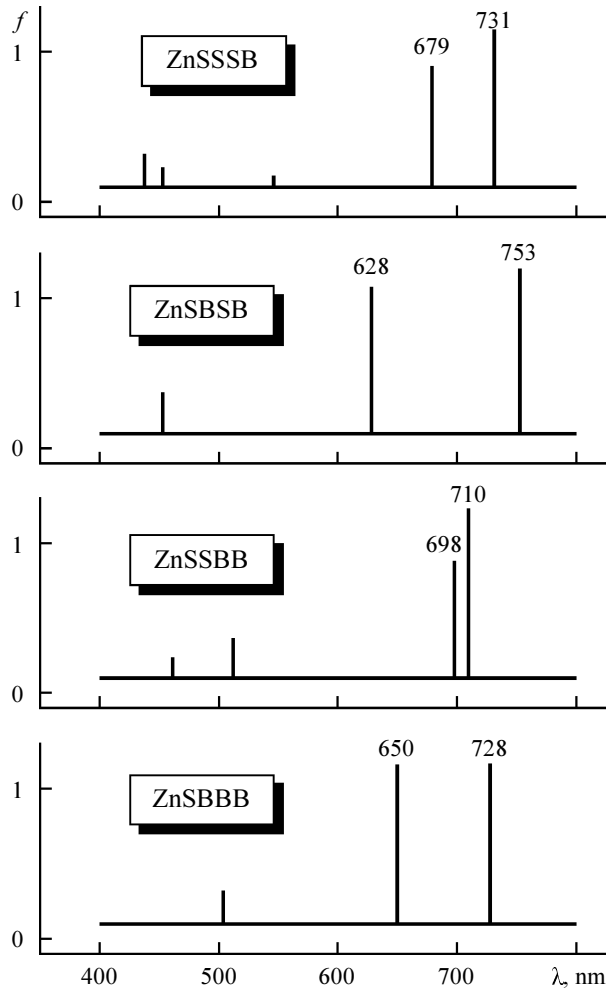


Fig. 2. Calculated electronic absorption spectra of zinc complexes of benzoporphyrazines with fused 1,2,5-thiadiazole fragments (ZINDO/S calculations of the structures optimized by the AM1 method).

between complexes of porphyrazines having different structures, including *cis* and *trans* isomers. Figure 1 (solid curves) shows the electronic absorption spectra of the magnesium complexes isolated by chromatography, as well as of MgSSSS obtained from dinitrile **I** according to the procedure described in [2].

The electronic absorption spectrum of the first fraction containing symmetric MgBBBB was identical to the spectrum of [tetra-(*tert*-butyl)phthalocyaninato]-magnesium(II) [12]. Symmetric complexes MgBBBB and MgSSSS displayed in the electronic absorption spectrum a narrow *Q*-band in the visible region (λ_{max} 678 and 642 nm, respectively), which is typical of porphyrazine complexes with a D_{4h} symmetry of the π-chromophore. The *Q*-band in the spectrum of MgSBBB isolated from the second fraction was split into two components (λ_{max} 678 and 665 nm) due to the lack of LUMO degeneration intrinsic to C_{2v} symmetry of the π-chromophore (the C_2 axis passes through the nitrogen atoms in the pyrrole rings fused to benzene and heterocyclic fragments). The 2:2 porphyrazine complex isolated from the third fraction was characterized by an unsplit but somewhat broadened *Q* band.

Isomeric 2:2 porphyrazines have different symmetries of the π-chromophore: *cis*-MgSSBB has a C_{2v} symmetry with the C_2 axis passing through the opposite *meso*-nitrogen atoms which are located between two benzene and two heterocyclic fragments, respectively; *trans*-MgSBSB has a D_{2h} symmetry with two C_2 axes each passing through the opposite *meso*-nitrogen atoms. Therefore, *cis*-MgSSBB and *trans*-MgSBSB should be characterized by different electronic absorption spectra. Only two publications are available from the literature on the electronic absorption spectra of 2:2 heteroring-fused benzoporphyrazine complexes. Fukuda and Kobayashi [13] reliably described a nickel(II) complex with *cis*-di(1,4-diphenylbenzo)di(diethylpyrazino)porphyrazine which showed an unsplit *Q* band with its maximum at λ 680 nm in the electronic absorption spectrum. Maizlish et al. [8] synthesized a copper(II) complex with *trans*-di(4-*tert*-butylbenzo)di(pyrazino)porphyrazine whose electronic absorption spectrum contained a clearly split *Q* band with its long-wave maximum at λ 647 (DMF) or 704 nm (H_2SO_4). More information is available on the experimental electronic absorption spectra of complexes derived from 2:2 porphyrazines having two isoindole fragments and two pyrrole rings substituted at the β-positions or fused to other aromatic carbocyclic residues (such as naphthalene and anthracene) (see, e.g., [14–16]). In all cases, *cis* isomers showed an unsplit or weakly broadened *Q* band, whereas the *Q* band of *trans* isomers was split to an appreciable extent, and its long-wave component was displaced to the red region. On the other hand, the degree of splitting of the *Q* band in the spectra of *trans*-fused porphyrazine complexes depends on the electronic nature of the fused fragments; for example, splitting of the *Q* band in the spectrum of the cobalt(II) complex of *trans*-di(1,4-diphenylbenzo)-7,8,17,18-tetrapropylporphyrazine is almost imperceptible [14].

We performed a theoretical analysis of the effect of the structure of an asymmetric porphyrazine macroring on the electronic absorption spectrum using zinc complexes as example. For this purpose, the structures of complexes ZnSBBB, ZnSSBB, ZnSBSB, and ZnSSSB were optimized at the AM1 level, and their electronic absorption spectra were calculated in terms of the

ZINDO/S approximation. The theoretical spectra thus obtained are shown in Fig. 2. It is seen that the splitting of the *Q* band is minimal for the *cis*-2:2 complex (ZnSSBB) and maximal for *trans*-2:2 (ZnSBSB) and that in the latter case the red shift of the long-wave component is the largest. The *Q* band in the spectra of the 1:3 (ZnSBBB) and 3:1 complexes (ZnSSSB) is split to a greater extent than for ZnSSBB but to a smaller extent than for ZnSBSB. Thus, the theoretical data suggest that complexes of benzoporphyrazines with fused 1,2,5-thiadiazole rings should be characterized by different electronic absorption spectra.

On the basis of the theoretical data and available experimental absorption spectra of 2:2 porphyrazine complexes we presumed that the product isolated from the third fraction contains mainly *cis*-MgSSBB. This is not surprising, for the fraction of the *cis* isomer should be greater by a factor of 3–5 than the fraction of the corresponding *trans* isomer (in keeping with the statistical data; see above). According to the spectral data, the fraction of *trans*-MgSBSB should not exceed 5–10%.

The electronic absorption spectra of the isolated magnesium complexes essentially changed in going from neutral to acid medium. In concentrated sulfuric acid, all these compounds showed a strong red shift of the *Q* band (Fig. 1, dashed curve): λ_{max} 820 nm for MgSBBB ($\Delta\nu$ = 2550 cm^{-1}) and 755 nm for MgSSBB ($\Delta\nu$ = 1840 cm^{-1}). It is known that magnesium complexes of porphyrazines readily undergo demetalation even in the presence of carboxylic acids [2, 17, 18], which leads to splitting of the *Q* band and shift of its long-wave component by 500–1000 cm^{-1}. However, the red shift observed in H_2SO_4 results mainly from acid–base interaction, i.e., protonation of the *meso*-nitrogen atoms in the porphyrazine macroring [19]. It is interesting that the red shift observed for MgSBBB and MgSSBB in H_2SO_4 is much smaller than the corresponding shift for phthalocyanine complex MgBBBB (3150 cm^{-1}) but greater than for MgSSSS (780 cm^{-1}). Presumably, the basicity of the *meso*-nitrogen atoms (i.e., their ability to take up a proton) depends on the number of fused 1,2,5-thiadiazole fragments. Therefore, the obtained magnesium porphyrazine complexes can readily be identified by their electronic absorption spectra in concentrated sulfuric acid even though the positions of their *Q* bands in the spectra recorded in a neutral solvent differ only slightly.

Solutions of the complexes in sulfuric acid gradually lose their color on storage. Apart from fast demetalation and protonation, the macroring undergoes hydrolytic decomposition, especially in the presence of water [18]. Therefore, reprecipitation of magnesium complex from sulfuric acid gives the corresponding metal-free compound in a lower yield, as compared to treatment with trifluoroacetic acid. By the action of trifluoroacetic acid on MgSBBB we obtained 87% of H_2SBBB whose composition was confirmed by elemental analysis and mass spectrometry.

Maxima of the long-wave *Q* band component in the electronic absorption spectra of porphyrazines

Porphyrazine	Solvent	$\lambda(Q_y)$, nm	$\lambda(Q_x)$, nm	$\Delta E(Q)$, cm^{-1}	Reference
H_2BBBB ≡ H_2Pc(*t*-Bu)$_4$	Toluene	662	699	800	[12]
H_2(^{3,4}Th)BBB	$CHCl_3$	692	727	700	[9]
H_2(^{2,3}Py)BBB	CH_2Cl_2	659	688	640	[7]
H_2SBBB	CH_2Cl_2	656	690	750	
H_2SSSS	CH_2Cl_2	636	649	315	

Metal-free porphyrazine H_2SBBB showed in the electronic absorption spectrum (Fig. 1, dotted curve) a much greater splitting of the *Q* band ($\Delta\nu$ = 750 cm^{-1}), as compared to the corresponding magnesium complex (MgSBBB), though both compounds have similar symmetries of the π-chromophore. Increased splitting originates from differentiation of the energies of the two lowest unoccupied π*-MOs, one of which is strongly contributed by the pyrrole nitrogen atoms in the opposite isoindole fragments and is destabilized, and the other is stabilized due to contributions of the isoindole and thiadiazolopyrrole nitrogen atoms. According to the AM1 calculations, the 22,24-H_2SBBB tautomer is more stable than 21,23-H_2SBBB by 17.4 kJ/mol: their heats of formation are 1483.2 and 1500.8 kJ/mol, respectively. Comparison of the experimental electronic absorption spectrum with the calculated parameters of the *Q* band of 22,24-H_2SBBB (λ_{max} 714 and 659 nm, $\Delta\nu$ = 1400 cm^{-1}) and 21,23-H_2SBBB (λ_{max} 789 and 665 nm, $\Delta\nu$ = 2360 cm^{-1}) also unambiguously indicates that the former prevails. Interestingly, localization of protons at the more electron-donor isoindole fragments in hexa(pentyloxy)-substituted porpyrazine was proved by the X-ray diffraction data [5, 6].

In order to analyze electronic interactions between the fused 1,2,5-thiadiazole ring and porpyrazine macroring it was interesting to compare the electronic absorption spectrum of H_2SBBB with those of related

porphyrazines (see table). It is seen that replacement of one benzene ring in *tert*-butyl-substituted phthalocyanine $H_2Pc(t\text{-}Bu)_4 \equiv H_2BBBB$ by 1,2,5-thiadiazole fragment (H_2SBBB) leads to a blue shift of the *Q* band, especially of its long-wave component (by 200 cm^{-1}), and reduces its splitting (to 750 cm^{-1}). If all four benzene rings are replaced (H_2SSSS), the blue shift increases more than 5-fold (by 1100 cm^{-1}), and the magnitude of splitting decreases more than twofold (to 315 cm^{-1}). These data indicate that π electrons in the 1,2,5-thiadiazole rings are conjugated with the porphyrazine macroring π-system to a weaker extent, as compared to benzene rings. This is the result of π-deficient character of the 1,2,5-thiadiazole ring and its general electron-acceptor effect. An analogous pattern is observed for $H_2(^{2,3}Py)BBB$ which contains a fused pyridine ring. By contrast, fusion of a thiophene ring at the C^3–C^4 bond [$H_2(^{3,4}Th)BBB$] leads to a considerable red shift of the *Q* band (by 550 cm^{-1}), i.e., replacement of two carbon atoms in thiophene by nitrogen atoms (in going to 1,2,5-thiadiazole) changes the electronic nature of the heteroring from π-excessive to π-deficient; as a result, the HOMO energy decreases by 750 cm^{-1} relative to the LUMO energy.

EXPERIMENTAL

($2^{2(3)}$,$7^{2(3)}$,$12^{2(3)}$-Tri-*tert*-butyltribenzo[*b*,*g*,*l*][1,2,5]-thiadiazolo[3,4-*q*]-5,10,15,20-tetraazaporphyrinato)-magnesium(II) (MgSBBB). Metallic magnesium, 0.24 g (0.01 mol), was dissolved in 25 ml of *n*-butanol on heating at the boiling point (the reaction was initiated by adding a crystal of I_2). 4-*tert*-Butylphthalodinitrile, 0.2 g (1.1 mmol), and 1,2,5-thiadiazole-3,4-dicarbonitrile [2], 0.19 g (1.4 mmol), were added to the resulting slurry-like suspension of magnesium butoxide, and the mixture was heated for 8 h under reflux. The solvent was evaporated from the dark green mixture, 20 ml of 50% aqueous acetic acid was added to the dry residue to remove excess magnesium butoxide, and the mixture was thoroughly stirred for 1.5 h. The precipitate was filtered off, washed with several portions of water, dried, and extracted with benzene in a Soxhlet apparatus. The solvent was removed from the extract, and the residue was subjected to chromatography on aluminum oxide to obtain three fractions: the first was eluted with benzene, the second, with benzene–acetone (20:1), and the third, with benzene–acetone (10:1). According to the electronic absorption spectra, the first fraction contained [tetra(4-*tert*-butyl)-phthalocyaninato]magnesium(II), $MgBBBB \equiv MgPc(t\text{-}Bu)_4$ (λ_{max} = 678 nm). The second fraction was subjected to repeated chromatographic purification to isolate 19 mg (4.2%) of $MgSBBB \cdot H_2O$. Mass spectrum: *m*/*z* 713 $[M - H_2O]^+$. Electronic absorption spectrum (CH_2Cl_2), λ_{max}, nm (D/D_{max}): 291 (0.35), 358 (0.73), 611 (0.20), 623 sh, 671 sh, 682 (1.00), 732 sh. Found, %: C 65.57; H 5.33; N 18.83; S 4.06. $C_{40}H_{36}MgN_{10}S \cdot H_2O$. Calculated, %: C 65.71; H 5.24; N 19.16; S 4.38. The third fraction contained ($2^{2(3)}$,$7^{2(3)}$-di-*tert*-butyldibenzo[*b*,*g*]di[1,2,5]thiadiazolo[3,4-*l*,*q*]-5,10,15,20-tetraazaporphyrinato)magnesium(II) hydrate ($MgSSBB \cdot H_2O$). Yield 4 mg (0.9%). Electronic absorption spectrum (CH_2Cl_2), λ_{max}, nm (D/D_{max}): 353 (1.00), 605 (0.25), 667 (1.00), 730 sh. Mass spectrum: *m*/*z* 665 $[M - H_2O]^+$. Found, %: C 56.48; H 4.02; N 24.33; S 9.06. $C_{32}H_{24}MgN_{12}S_2 \cdot H_2O$. Calculated, %: C 56.27; H 3.84; N 24.61; S 9.39. The residue obtained after extraction with benzene contained a mixture of (2^2-*tert*-butylbenzo[*b*]tri[1,2,5]-thiadiazolo)[3,4-*g*,*l*,*q*]-5,10,15,20-tetraazaporphyrinato)magnesium(II) (MgSSSB) and tetra[1,2,5]thiadiazolo[3,4-*b*,*g*,*l*,*q*]-5,10,15,20-tetraazaporphyrinato)-magnesium(II) (MgSSSS) which we failed to separate.

$2^{2(3)}$,$7^{2(3)}$,$12^{2(3)}$-Tri-*tert*-butyltribenzo[*b*,*g*,*l*][1,2,5]-thiadiazolo[3,4-*q*]-5,10,15,20-tetraazaporphyrin (H_2SBBB). A 15-mg (0.02-mmol) portion of $MgSBBB \cdot H_2O$ was dissolved in 3 ml of trifluoroacetic acid, and the solution was left overnight. The mixture was then poured into water, the precipitate was separated by centrifugation, washed with water, dried, and dissolved in benzene, and the solution was subjected to chromatography on aluminum oxide. Removal of the solvent from the eluate gave 12 mg (87%) of H_2SBBB. Electronic absorption spectrum (CH_2Cl_2), λ_{max}, nm (D/D_{max}): 295 (0.30), 353 (0.39), 598 (0.12), 630 (0.20), 635 sh, 657 (0.59), 693 (1.00). Mass spectrum: *m*/*z* 691 $[M]^+$. Found, %: C 69.75; H 5.72; N 19.88; S 4.49%. $C_{40}H_{38}N_{10}S$. Calculated, %: C 69.54; H 5.54; N 20.27; S 4.64%.

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