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Study of Luminescence Properties of Cyclic and Acyclic Thiadiazole-Containing Compounds

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Abstract—Luminescence properties of thiadiazole-containing compounds of cyclic and acyclic structure have been investigated. All compounds are characterized by fluorescence in the region 500–600 nm. The highest quantum yield of luminescence in the studied series is exhibited by acyclic product of the ABA type (where A is thiadiazole cycle, B is isoindole cycle) with *N*-pentylthiadiazoline fragments.

Keywords: luminescence/fluorescence, thiadiazole-containing compounds, macroheterocycles

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Photoluminescence has found wide application in technique, analytical chemistry, photochemistry and chemical kinetics for investigation of excited states and fast chemical reactions, in photobiology and medicine for investigation of properties of biological objects [1]. From this point of view, phthalocyanines and porphyrins are the most studied compounds [2–10].

Only limited number of publications concerns the luminescent properties of macroheterocyclic compounds containing a system from substituted pyrrole and heterocycluc fragments and metal complexes based thereon [11–16].

First results of investigation [13, 15] revealed that macroheterocycles showed moderate quantum yields of fluorescence (φ). For example, the fluorescence quantum yield of the solution of compound **I** in *N,N*-dimethylformamide is 0.052 [13], which is slightly higher than that of the nonsubstituted porphyrin (0.043) [17] but by one order of magnitude lower than that of nonsubstituted phthalocycnine (0.546) in the presence of oxygen [18] (Scheme 1).

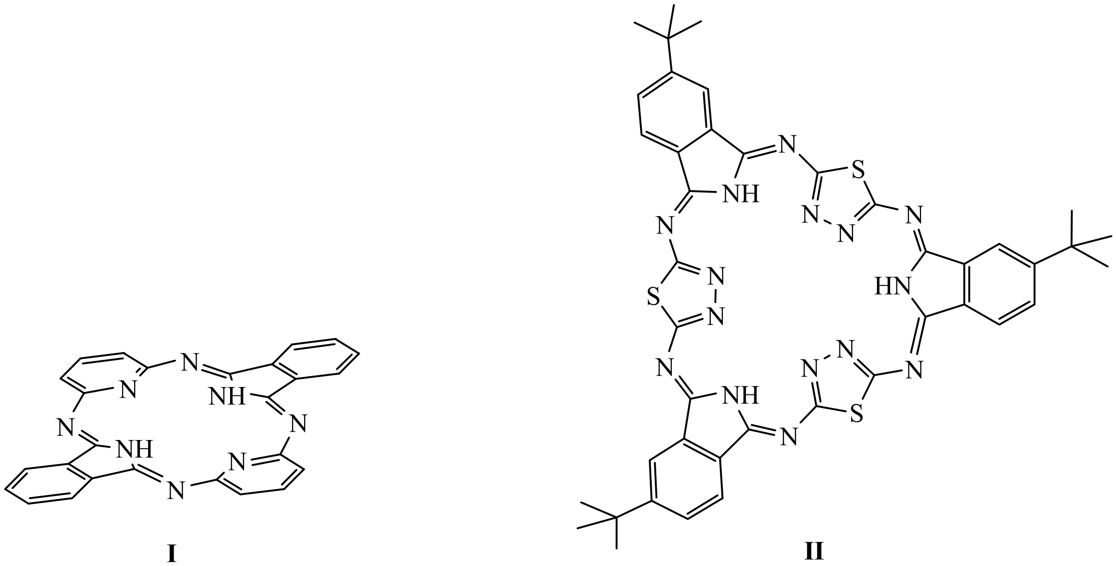
Earlier [12, 15], it was shown that substituted macroheterocycles of the ABABAB type possessed fluorescence properties. For macroheterocycle **II** [15] and its complexes with lanthanum and neodymium, molecular fluorescence in the visible region extinguished due to the heavy atom effect [19].

In continuation of these studies, we have synthesized three-link products of the ABA and macroheterocycles of the ABBB types by the reaction of the corresponding 3-alkyl-5-amino-2-imino-1,3,4-thiadiazolines with 1,1-dimethoxy-3-iminoisoindoline [20–22]. The synthesized compounds contain the 1,3,4-thiadiazole motif. It is known that some derivatives of 2,5-diamino-1,3,4-thiadiazole are used as optical bleachers, scintillation activators and absorbents of UV light [23] (Scheme 2).

Spectral fluorescence studies have shown that the solutions of 1,3,4-thiadiazole-containing three-link products of the ABA type and macroheterocycles of the ABBB type fluoresce under the action of UV light [19]. It prompted the beginning of the studies in this field [19, 24].

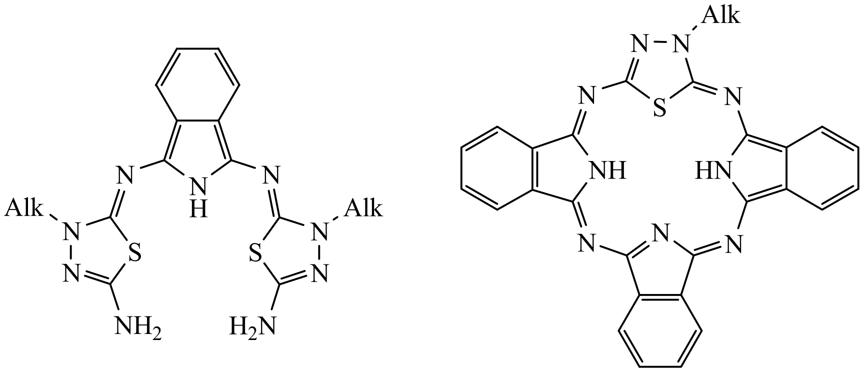
The investigation of the fluorescence properties of compounds **III–VIII** is of interest in two aspects. On the one hand, three-link products of the ABA type **III–V** are acyclic analogs of macroheterocycles of the ABBB type **VI–VIII**, which allows the examination of the effect of cyclization on their emission properties.

Scheme 1.



I **II**

Scheme 2.



III–V **VI–VIII**

Alk = C_5H_{11} (**III, VI**), $C_{10}H_{21}$ (**IV**), $C_{12}H_{25}$ (**V, VII**), $C_{15}H_{31}$ (**VIII**).

On the other hand, all compounds have one or two sulfur atoms, which allows correlating the properties of the cyclic compounds with those of phthalocycnines that have no sulfur atom in the molecule.

The spectral luminescence characteristics of the synthesized compounds are given in the table. From the data presented in the table and on Fig. 1 it is seen that the maxima in the absorption spectra of compounds **III–VIII** have close positions; the same is true for the emission spectra. All studied ligands are characterized by the fluorescence in the visible range of the spectrum, with the band maxima showing a red shift at the elongation of the hydrocarbon chain of the substituent in three-link products **III–V** ($\Delta\lambda$ = 32 nm for **V** (Alk = $C_{12}H_{25}$) relative to **III** (Alk = C_5H_{11}). In contrast, the fluorescence bands of macroheterocycles **VI–VIII** suffer a blue shift: $\Delta\lambda$ = 44 nm for **VII** (Alk = $C_{15}H_{31}$) as compared to its shorter-chain analog **VI** (Alk = C_5H_{11}).

The obtained results are indicative of the fact that the increase in the number of methylene links in the alkyl substituents substantially affects the structure of acyclic compounds **III–V** leading to strong deviation of the molecule from planarity and, as a consequence, to red shift of the emission band.

For the cyclic analogs, it is not easy to explain the blue shift in the emission spectrum only from the viewpoint of the structure of the molecule. Apparently, Spectral luminescence characteristics of the solutions of the studied compounds in methanol[a]

Ligand	$\lambda_{Qx(0,0)}$, nm	Fluorescence bands, $\lambda_{Qx(0,0)}$, nm	Stokes shift, Δλ, nm	φ_x
ABA (**III**)	490	534	44	0.180
ABA (**IV**)	494	564	70	0.025
ABA (**V**)	496	566	70	0.026
ABBB (**VI**)	499	586	87	0.013
ABBB (**VII**)	499	582	83	0.016
ABBB (**VIII**)	475	542	67	0.021
Compound **I**	350 [13]	675 [13]	325	0.052 [13]
Phthalocyanine	698 [26]	704 [27]	6	0.546 [18]

[a] $T = 298$ K, $c = 10^{-5}$ mol/L; error of determination of quantum yields is 10%.

in this case, intermolecular interactions and the solvation of compounds **VI–VIII** differing in lipophilicity play the role.

We have determined the dependence of the value of the Stokes shift (Δλ) on the character and the degree of distortion of macrocycles and their acyclic analogs. On going from **III** to **IV** the shift is changed by 26 nm due to a larger distortion of planarity; with further elongation of the aliphatic chain, its value remains constant.

In the case of macrocycles, the Stokes shift should be only slightly dependent on the peripheral substituents because of the absence of substantial conformational reorganization in the S_1-state. Thus, on the similar transition from **V** to **VI**, the Stokes shift remains practically constant, although for the pentadecyl fragment in **VIII** the Stokes shift is changed by 20 nm as compared to the shortest amyl derivative **V**. In our opinion, as in the aforementioned case, this is due only to intermolecular interactions.

With elongation of the hydrocarbon chain of the substituent the quantum yield of fluorescence of the three-link acyclic compounds **III–V** in solutions is reduced (see the table, Fig. 2). The maximum quantum yield was reached for compound **III,** the product of the ABA type with 3*N*-pentylthiadiazoline fragment (φ_x = 0.180). For compounds characterized by a high degree of nonplanarity due to steric interactions of the macrocyclic fragments with bulky alkyl groups large variations in the spectral luminescence properties of the singlet states at 298 K in solutions are caused by dynamic relaxation of the macrocycle to the conformation most preferable by energy. Apparently, with elongation of the alkyl substituent, this effect is

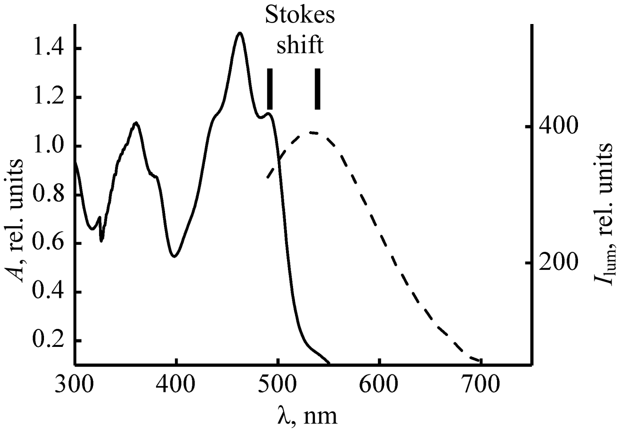


Fig. 1. Electron absorption and emission spectra of compound **III** ($c = 10^{-5}$ mol/L, MeOH).

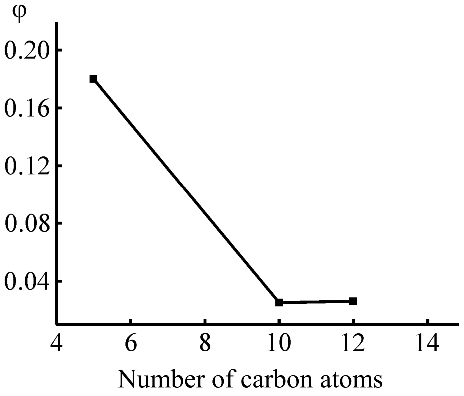


Fig. 2. Dependence of quantum yield on the length of the aliphatic chain of substituents in compounds **III–V**.

superimposed with the increase of the number of vibrational states of the molecule, leading to further drop in intensity of radiation.

This effect should be expected for the formation of cyclic structures of the ABBB type (macrocycles **VI–VIII**). However, with elongation of the alkyl chain in the thiadiazoline fragments the value of φ_x increases, although not significantly. This is consistent with the published data on alkyl-substituted porphyrins [28]. Comparative analysis of the results obtained for macrocycles **VI–VIII** and the data for phthalocyanine (see the table) shows that, due to the presence of the 1,3,4-thiadiazoline fragment in the macrocycle the maximum of emission of these compounds is suffers a blue shift by more than 100 nm. Such a sharp increase in the position of the excited singlet state level S_1 is determined, most probably, by a significant reduction of the symmetry and planarity of the molecule.

Therefore, we have first examined the luminescence properties of the thiadiazole-containing compounds of both cyclic and acyclic structure. The acyclic three-link product of the ABA type with *N*-pentylthiadiazoline fragments was found to show the maximum quantum yield of luminescence at room temperature in the series of the studied compounds.

EXPERIMENTAL

Spectra of excitation and of molecular luminescence were recorded on a Fluorolog FL 3-22 and Horiba Jobin Yvon instruments (xenon lamp, 450 Wt) using quartz cells of 1 cm thickness. Methanol was used as a solvent. For calculations, the zinc complex of tetraphenylporphyrin was used as a standard [25].

Relative quantum yields of fluorescence were calculated by a standard formula

$$\varphi_x = \varphi_0 \times I_x/I_0 \times A_0/A_x,$$

where φ_x is the quantum yield of the studied sample; φ_0 is quantum yield of the standard; I_x and I_0 are integral intensities of fluorescence of the sample and the standard, respectively; A_x and A_0 are optical densities in the maxima of the excitation bands of the sample and the standard, respectively. Processing of the spectra and calculations were performed using the OriginPro 7.5® program.

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