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INFLUENCE OF TEMPERATURE ON THE FLUORESCENCE DURATION AND ELECTRONIC SPECTRA OF METAL-FREE TETRAPYRROLES IN AN ORGANIC POLYMER

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Spectral and luminescent characteristics and the duration of fluorescence were measured for a series of metal-free tetrapyrroles in polyvinylbutyral solid films at 293 and 77 K. The results provided evidence for the lack of a viscosity factor in the case of the fluorescence enhancement under study, i.e., for the tetrapyrroles showing the enhancement effect in liquid solutions (tetraazaporphine and substituted tetraazachlorin). The fluorescence duration in the film increased insignificantly on lowering the temperature to 77 K. An analysis of the experimental data made it possible to estimate the quantum yields of internal conversion and intersystem crossing for tetraazaporphine and tetraazachlorin, which were the fundamental structures in the tetrapyrrole series.

Keywords: *metal-free tetrapyrroles, absorption spectrum, fluorescence and fluorescence excitation spectrum, duration of fluorescence, effect of fluorescence enhancement.*

Introduction. The fluorescence of metal-free tetraazachlorins (dihydroporphyrazines) in solutions was previously observed to be sharply enhanced at a cryogenic temperature of 77 K [1]. The term "fluorescence enhancement" was introduced by A. N. Terenin, Academician of the USSR Academy of Sciences and used to describe this effect [2]. New data on the influence of temperature on the fluorescence intensity of tetraazachlorins were obtained for two derivatives of hexaphenyltetraazachlorin (HPTAC), unsubstituted tetraazaporphine (H_2TAP) [3], and two derivatives of tribenzotetraazachlorin (H_2TBTAC) [4]. The enhancement that was significant for H_2TAP [3] was practically absent for H_2TBTAC [4].

Molecules of the tetrapyrrole class, including porphyrins and chlorins (heme, chlorophyll, and their derivatives), and their synthetic analogs warrant comprehensive spectral, luminescent, and photophysical studies because they are involved in vital processes and have many practical applications. Research in this area addresses the transformation efficiency of excitation energy by tetrapyrroles as potential photosensitizers. An important issue that must be resolved is whether the fluorescence enhancement of this type of molecules is thermal or thermal-viscous. Both the temperature and viscosity changed upon freezing a solution. The experimental results reported in the present work were obtained to avoid the influence of viscosity (translations and rotations of molecules in a solid polymer matrix that are possible in a liquid medium) on the measured fluorescence duration and spectra.

The goal of the present work was to study the spectral, luminescent, and photophysical properties of tetramethyltr ibenzotetraazachlorin (H_2TBTAC^{tm}, tm = tetramethyl), di(*tert*-butylbenzo)barreleno-substituted tetraazachlorin (H_2TAC^{t}, the letter t indicates the presence of two *t*-butyl groups in the dibenzobarrelene fragment), tetraazaporphine (H_2TAP), and unsubstituted tetraphenylporphine (H_2TPP).

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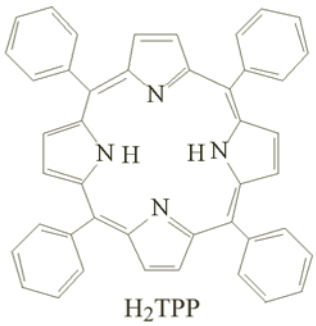
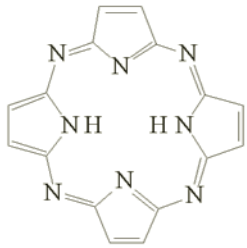


H_2TPP



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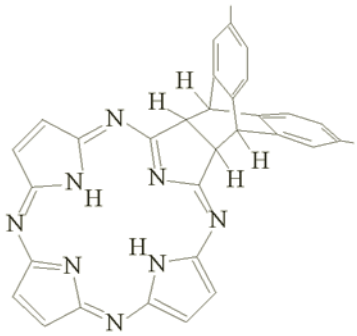
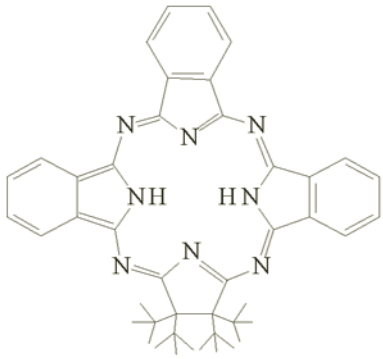


H_2TAC^t



H_2TBTAC^{tm}

Experimental. The studied species were selected for the following reasons. H_2TPP is considered a standard tetrapyrrole with carbon (methine) bridges. The others had tetraaza-substitution. The greatest fluorescence enhancement was obtained for H_2TAC^t [1]. Conversely, the fluorescence of H_2TBTAC^{tm} depended weakly on temperature [4]. An anomalously high efficiency of nonradiative deactivation $S_1 \sim> S_0$ was observed for H_2TAP (like for H_2TAC^t) [5].

H_2TAP and H_2TAC^t were synthesized by the published methods [6, 7]. The dibenzobarrelene motif in the hydrogenated pyrrole ring stabilized the hydrogenated macrocycle against oxidation. The benzo-substituted tetraazachlorin with four methyls on the hydrogenated pyrrole ring incorporating the tribenzotetraazachlorin free base, (H_2TBTAC^{tm}) or 7,7,8,8-tetramethyltribenzo[*b*,*l*,*q*]tetraazachlorin according to the systematic nomenclature, was synthesized by the literature method [8, 9] of mixed condensation of tetramethylsuccinonitrile with phthalonitrile. H_2TBTAC^{tm} was isolated by extraction of the crude product with hot chlorobenzene followed by chromatography over silica gel using $CHCl_3$ eluent. The two methyl substituents on each of the two quaternary C atoms of the hydrogenated pyrrole ring made the compound more resistant to oxidation and much more soluble than phthalocyanine because the methyls were displaced from the plane of the molecule. H_2TPP was taken from laboratory supplies.

Spectral and kinetic studies were performed for the four tetrapyrrole compounds incorporated into solid-state matrices of an organic polymer (polyvinylbutyral, PVB). PVB samples were prepared as thin ($d \approx 0.5$–1.0 mm) films colored by the studied compounds by pouring an EtOH solution of the selected film-forming polymer. EtOH was used as the solvent because PVB and the studied compounds were very soluble in it. The solution was poured onto a horizontal glass substrate that ensured the film had a uniform thickness. The optical density at the absorption band wavelength maxima in the polymer films was 0.2–0.3, which diminished reabsorption during luminescence measurements. The obtained PVB films were stored for a long time (months). Control measurements of the spectral and luminescence parameters of the sample showed that they did not change. It could be expected that diffusion-viscous translations of the molecular fragments, including their reorientation and conformational changes, would be hindered at room temperature in the solid-state medium so that the viscous component of the fluorescence enhancement would be absent.

Electronic absorption spectra were recorded on a Cary 500 Scan UV-Vis NIR spectrophotometer (Varian, USA, Australia). Fluorescence and fluorescence excitation spectra were measured on an updated SDL-2 spectrometric system (LOMO, USSR) consisting of an MDR-12 high-aperture excitation monochromator and an MDR-23 recording monochromator. The excitation source was an XBO 150W/I Xe lamp (Osram, Germany). Fluorescence was recorded using chilled FEU-100 (230–800 nm) and FEU-62 (600–1100 nm) photomultipliers operating in photon-counting mode.

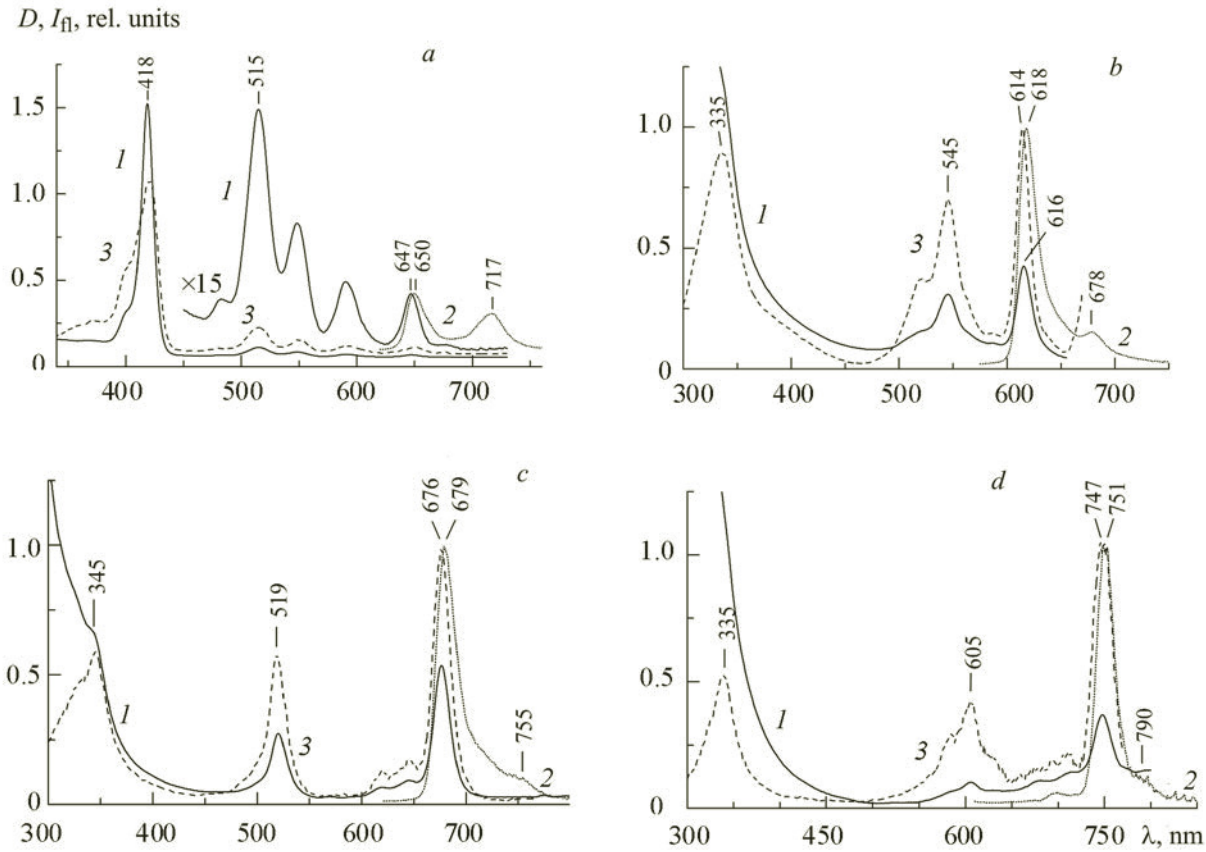


Fig. 1. Absorption (1), fluorescence (2) and fluorescence excitation spectra (3) of H_2TPP (a), H_2TAP (b), H_2TAC^t (c), and H_2TBTAC^{tm} (d) in PVB at 293 K; fluorescence spectra for λ_{ex} = 514 (a), 545 (b), 520 (c), and 605 nm (d); fluorescence excitation spectra for λ_{rec} = 730 (a), 680 (b), 760 (c), and 780 nm (d).

Fluorescence kinetics (and separate spectra) were measured on a Fluorolog-3 multifunctional spectrofluorometer (Horiba Scientific, Japan–USA–France) using a DeltaDiode-314 pulsed excitation source (diode laser, λ_{ex} = 314 nm, $\Delta t \approx 900$ ps, f = 25 MHz). Decay curve parameters [characteristic decay times τ_1 and τ_2 and relative integrated intensities of emission A_1 and A_2 ($A_1 + A_2 = 1$)] were calculated using the DAS6 program (Horiba Scientific).

Polymer samples were chilled in a cryostat based on a quartz Dewar flask with liquid N_2. A sample was mounted on a copper block with holes for excitation and recording of emission that was partially immersed in the liquid N_2. The block holes were situated above the surface of the liquid N_2 to decrease noise from the boiling N_2 during recording of the spectra.

Results and Discussion. *Absorption and fluorescence spectra of the tetrapyrroles in the polymer matrix.* The characteristic electronic absorption spectrum of H_2TAP in the visible region (Fig. 1b, curve 1) could be considered to result from quasi-forbidden transitions $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ upon replacing the methine bridges in unsubstituted porphine (H_2P) by the N atoms because the electronegativity of the bridge atoms (π-centers) was increased. Then, the S_2–S_1 gap was ~2090 cm^{-1}, which was slightly less than that in benzene solution (~2100 cm^{-1}) and noticeably less than in *n*-octane solution (~2350 cm^{-1}) [10]. The region of the electronic $S_1 \leftarrow S_0$-transition in the H_2TAP absorption spectrum had approximate mirror symmetry in the fluorescence spectrum for diffuse spectra in PVB at both room temperature and 77 K.

Figure 1c (curve 1) shows the absorption spectrum of H_2TAC^t in PVB at room temperature. The spectral changes in the visible region after hydrogenation of the pyrrole ring in H_2TAP [in combination with addition of the di(*tert*-butylbenzo) barrelene fragment] consisted of a bathochromic shift of the long-wavelength 0–0-band of the $S_1 \leftarrow S_0$-transition and a hypsochromic shift of the band of the $S_2 \leftarrow S_0$-transition. The S_2–S_1 gap increased from ~2090 to ~4480 cm^{-1} because of these shifts. It is noteworthy that the electronic absorption spectrum of H_2TAC^t differed from that of H_2TAC by small

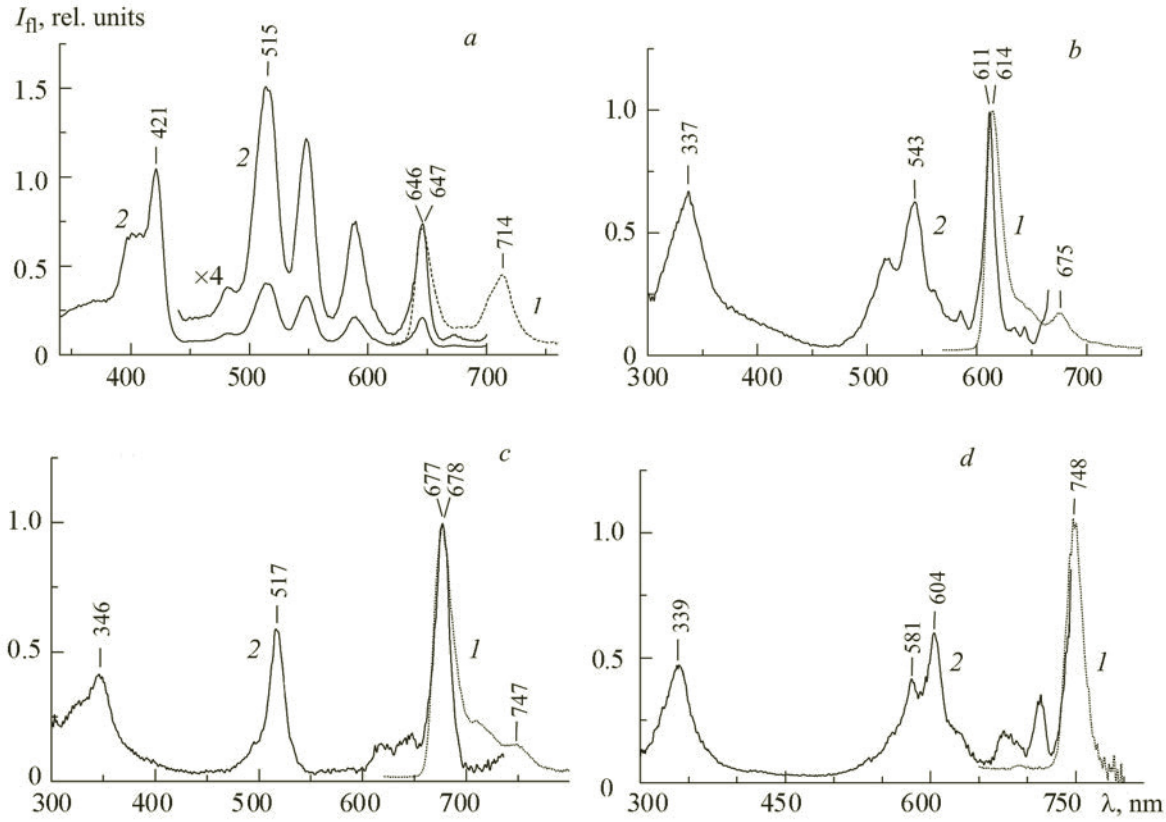


Fig. 2. Fluorescence (1) and fluorescence excitation spectra (2) of H_2TPP (a), H_2TAP (b), H_2TAC^t (c), and H_2TBTAC^{tm} (d) in PVB at 77 K; fluorescence spectra for λ_{ex} = 414 (a), 545 (b), 520 (c), and 605 nm (d); fluorescence excitation spectra for λ_{rec} = 720 (a), 680 (b), and 760 nm (c, d).

TABLE 1. Fluorescence Duration of Tetrapyrroles in PVB for λ_{ex} = 314 nm

Compound	λ_{rec}, nm	T, K	A_1, %	τ_1, ns	A_2, %	τ_2, ns	$\tau_{A_1}^{77} / \tau_{A_1}^{293}$	$\tau_{A_2}^{77} / \tau_{A_2}^{293}$
H_2TPP	650	293	3	3.1	97	12.5	1.68	1.14
		77	5	5.2	95	14.3		
H_2TAP	620	293	45	3.6	55	5.7	1.78	1.68
		77	50	6.4	50	9.6		
H_2TAC^t	680	293	74	2.0	26	3.2	1.75	2.00
		77	84	3.5	16	6.4		
H_2TBTAC^{tm}	750	293	76	2.7	24	4.2	1.41	1.48

Note: τ_1 and τ_2 are characteristic fluorescence decay times; A_1 and A_2, relative integrated intensities of emission ($A_1 + A_2 = 1$).

hypsochromic shifts of the bands [7], i.e., the di(*tert*-butylbenzo)barrelene fragment had an insignificant influence on the electronic structure of the tetraazachlorin macrocycle. The fluorescence and fluorescence excitation bands of H_2TAC^t in PVB (Fig. 2c, curves 1 and 2) narrowed insignificantly upon lowering the temperature to 77 K although the vibrational structure of the spectra was more sharply defined.

Figure 1d (curve 1) shows the absorption spectrum of H_2TBTAC^{tm} in PVB at 293 K. A comparison with the literature showed that changing from a liquid solution to a solid polymer film had practically no effect on the absorption spectrum. The $S_1 \leftarrow S_0$-band in PVB (747 nm) shifted insignificantly relative to its position in chlorobenzene (748 nm) [8], 2-methyltetrahydrofuran (743 nm) [4], and DMSO solutions (745 nm) [4]. An analogous shift was observed for a conglomerate of bands with the main maximum at ~605 nm that belonged to the purely electronic $S_2 \leftarrow S_0$-transition of H_2TBTAC^{tm} according to magnetic circular dichroism [8] and low-temperature polarized fluorescence spectra [4]. Hence, the energy gap S_2–S_1 for H_2TBTAC^{tm} in PVB could be estimated as ~3150 cm^{-1}. The fluorescence spectrum of H_2TBTAC^{tm} in PVB (curve 2) obtained with monochromatic excitation (λ_{ex} = 605 nm) at room temperature had a maximum at 751 nm. Destruction of the mirror symmetry of the absorption spectrum near the $S_1 \rightarrow S_0$-transition and the fluorescence spectrum provided evidence that the molecule rearranged in the excited S_1-state. A Stokes shift of ~70 cm^{-1} was considerably less than for a 2-methyltetrahydrofuran solution (~300 cm^{-1}) [4]. The fluorescence excitation spectrum of H_2TBTAC^{tm} in the PVB film that was obtained with selective recording at λ_{rec} = 780 nm (curve 3) practically coincided with the absorption spectrum of H_2TBTAC^{tm} in PVB (curve 1). This provided evidence that the sample contained mainly the ground-state compound. A weak fluorescence band at 695 nm indicated that the H_2TBTAC^{tm} sample had a trace impurity. It was concluded before that the sample contained a trace amount of H_2Pc [11].

The fluorescence excitation spectrum exhibited vibrational structure upon going from 293 to 77 K. The bands in the visible region narrowed slightly while the Soret band underwent a bathochromic shift without visibly broadening. The complex band near the $S_2 \leftarrow S_0$-transition (~605 nm) practically did not shift upon lowering the temperature to 77 K although its structure was defined better. The spectral and luminescence characteristics of H_2TPP in the polymer film were not discussed but were shown for comparison to a tetrapyrrole with methine bridges.

Temperature influence on fluorescence duration. The main result of the work was the production of a combination of experimental data on the fluorescence duration (τ_f) of the studied metal-free tetrapyrroles in PVB films (Table 1). As a rule, changes of τ_f of molecules under the influence of various factors can be considered proportional to changes of the fluorescence quantum yield.

Experimental studies of the fluorescence duration of the tetrapyrrole molecules in the polymer matrix at room temperature and 77 K showed that the temperature had a small effect. The enhancement effect in liquid solutions increased for τ_f^{77} by 6.3 times for H_2TAC and by 7.4 times for H_2TAC^t in 2-methyltetrahydrofuran [4]. The quantity τ_f^{77} increased by 1.75 times relative to τ_f^{293} for H_2TAC^t in the polymer matrix for the larger component (A_1) and by 2 times for the smaller component (A_2). This meant that neither anchoring of the molecules in the matrix nor limitation of their orientational motion upon freezing could be the main cause of the increased fluorescence duration upon lowering the temperature, i.e., could not be fully responsible for the fluorescence enhancement upon chilling the liquid solutions. Spatial isomerism or a change of intermolecular interactions upon freezing could have been the causes for enhancement of τ_f^{77} for molecules fixed in the polymer matrix.

Table 1 presents the ratios of the fluorescence durations for the main components A_1 and A_2 of the decay laws at the different temperatures: $\tau_{A_1}^{77}/\tau_{A_1}^{293}$ and $\tau_{A_2}^{77}/\tau_{A_2}^{293}$. It can be seen that the increase of τ_f at 77 K was about the same for forms 1 and 2. Apparently, they corresponded to two solvated forms. It is noteworthy that the main component (A_2) of the fluorescence decay law of H_2TPP did not display temperature features ($\tau_{A_2}^{77}$ increased by ~14% upon lowering the temperature). This was typical of tetrapyrroles with carbon bridges.

The question of fluorescence enhancement was contingent on fulfillment of the Ermolaev–Sveshnikova rule [12], according to which the sum of the fluorescence quantum yield (φ_F) and yield from intersystem crossing $S_1 \sim\!\!> T_1$ (φ_{ST}) is close to unity: $\varphi_F + \varphi_{ST} \approx 1$. In fact, strict fulfillment of this rule does not give a basis for seeking fluorescence enhancement. The empirically found condition for fulfillment of the Ermolaev–Sveshnikova rule for tetrapyrroles was $\Delta E_{S_1S_0} > 14{,}000$ cm^{-1} ($\lambda^{00} < 700$ nm, where λ^{00} is the position of the long-wavelength $S_1 \leftarrow S_0$ absorption band). As a rule, the energy of organic molecules is fully determined by the equation: $\varphi_F + \varphi_{ST} + \varphi_{SS} = 1$, where φ_{SS} is the quantum yield of transitions in the $S_1 \sim\!\!> S_0$ channel. Usually, only the physical internal conversion occurs when excitation energy is exchanged only on nuclear vibrations, i.e., when there are no reversible and irreversible photochemical processes in the molecule.

Picosecond absorption spectroscopy found that $\varphi_F + \varphi_{ST} < 1$ for H_2TAP, H_2TAC^t, and two isomers (*cis*- and *trans*-) of tetraazabacteriochlorin (H_2TABC^{tt}) [5]. If this result is expected for hydroporphyrazines (λ^{00} close to 700 nm, $\varphi_{SS} \neq 0$), then an anomaly can be invoked for H_2TAP ($\lambda^{00} \approx 610$ nm). The quantity φ_{SS} for H_2TAP may include reversible photochemical processes besides exchange of excitation energy on nuclear vibrations [5].

Currently, φ_{ST} cannot be measured accurately enough. However, based on the quantum yield for generation of singlet oxygen $^1O_2$ in the $^1\Delta_g$ state not being greater than φ_{ST} ($\varphi_\Delta \le \varphi_{ST}$), we obtain a refined value of φ_{ST}. Therefore, the measured $\varphi_\Delta = 0.47$ for H_2TAP in toluene [3] indicates that the estimated φ_{ST} for H_2TAP of 0.30–0.35 [5] is highly underestimated because φ_{ST} should correspond better to φ_Δ.

Thus, $\varphi_F^{293} = 0.17$ and $\varphi_{SS}^{293} \approx 0.35$ for H_2TAP in toluene [3]. Their sum is 0.52 so that $\varphi_{ST} = 0.48$, i.e., the quantum yield of intersystem crossing $\varphi_{ST} = 0.30$–0.35 [5] is low by ~1.45 times. The quantities τ_F and φ_{ST} for H_2TAC and H_2TAC^t were the same and were treated the same. Parameters for H_2TAC of $\varphi_F = 0.03$ and $\varphi_{ST} = 0.51$ and their sum of 0.54, i.e., $\varphi_{SS} = 0.46$, were obtained by comparing the parameters of H_2TAP and H_2TAC [5] and their estimate. It could be assumed that φ_{ST} and φ_{SS} for these tetrapyrroles were determined with adequate accuracy.

A significant shortening of the triplet-state lifetimes in liquid solutions at room temperature was found for a series of *meso*-phenyl-substituted Pd-octaethylporphyrins [13]. This effect was explained by relaxation of out-of-plane dynamic conformational rearrangements of the Pd-porphyrin macrocycle in the T_1-state and, as a result, an increase of fast nonradiative deactivation of the triple state that reduced the phosphorescence quantum yield and shortened its decay time. Conformational transformations were probably responsible for the changes of τ_F at 77 K that were observed in the present work.

Conclusions. The results provided evidence that a viscous factor was absent for fluorescence enhancement, which was determined exclusively by the temperature. Experimental data confirmed the idea about the quasi-photochemical nature of the low population efficiency of the T_1 level of H_2TAP and hydroporphyrazine [5], which was apparently a temperature-dependent factor.

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