

INFLUENCE OF A SOLVENT ON THE QUANTUM YIELD AND DURATION OF THE FLUORESCENCE OF TETRAAZOPORPHIN

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In view of the discrepancies between the values available in the literature for the photophysical parameters of tetraazaporphin in solutions, we measured its quantum yield and duration of fluorescence in a number of solvents. It has been found that alcohols (isobutanol and isopropanol) quench the fluorescence appreciably. For a solution in toluene — a stable chemically inactive and low-polar solvent — the measured quantum yield of the fluorescence of tetraazaporphin is equal to 0.180 ± 0.015 and its duration is 3.4 ± 0.1 nsec.

Keywords: tetraazaporphin, quantum yield of fluorescence, fluorescence duration.

Introduction. The tetraazaporphin (H_2TAP) molecule, or porphyrazine, is one of the fundamental structures in the porphin series, which is an intermediate between the biologically important class of porphyrins and classical dyes of the type of phthalocyanine, which are finding wide application in various fields of science and technology.

In investigating the effect of hydrogenation of pyrrolic rings in porphyrazine macrocycles on the photophysical properties, in [1, 2] the quantum yield of fluorescence (φ_F) of H_2TAP was measured as a basis for comparison with the data on dihydroderivatives. By comparing our results with the data of earlier investigations [3–6], we found that there were noticeable discrepancies between the values of φ_F measured by various authors and also between the data on durations of fluorescence τ_F . In [3, 4], it was found that $\varphi_F = 0.12$ and $\tau_F = 3.7$ nsec (see also the review [7]), in [5], $\varphi_F = 0.16$ and $\tau_F = 6.4$ nsec; in [6], $\varphi_F = 0.12$. Recently, in [8], the value $\varphi_F = 0.29$ was obtained for H_2TAP , whereas in [1, 2] $\varphi_F = 0.19$ and $\tau_F = 3.3$ nsec.

Since different solvents were used in the works cited, the idea arose that the quantity φ_F of H_2TAP can substantially depend on the nature of the solvent. The aim of the present work is to elucidate this influence and to arrange in an ordered fashion the data on the values of φ_F and τ_F for H_2TAP .

Experimental. Measurements of the quantum yield of fluorescence were performed by a relative method from the ratio between the areas of the fluorescence spectra of an object and a standard determined in terms of "quantum" intensities ($I_\lambda/h\nu$) on an SDL-2 automated spectrofluorimeter (USSR) consisting of an MDR-12 light-transmission excitation monochromator and an MDR-23 registration monochromator. The excitation and registration axes were arranged at an angle of 90° . A DKsSh-120 xenon lamp was used as the source of excitation. The light signal separated by the monochromator was registered with the aid of an FÉU-100 cooled photomultiplier (spectral range 200–800 nm) operating in the regime of photon counting. The spectral sensitivity of the recording monochromator–FÉU system was corrected with the aid of a TRSh 2850 standard ribbon tungsten lamp. The spectral width of the excitation monochromator slit did not exceed 4.8 nm in the entire spectral range studied, and that of the registration monochromator — 2.6 nm in the 400–800-nm range. The absorption spectra were recorded at room temperature on a Cary 500 Scan UV-Vis-NIR spectrophotometer (USA, Australia).

Measurements of τ_F were made by the method of correlated photon counting on a setup assembled on the basis of the complete sets manufactured by Edinburgh Analytical Instruments (Great Britain). In the first series of experiments, we used the light of an nF 900 pulse lamp manufactured by the same firm (the pulse duration determined by the full width at half maximum (FWHM) was $\Delta t = 2.0$ – 2.5 nsec, the exciting-light wavelength $\lambda_{exc} = 337$ nm

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(through the monochromator), the pulse repetition rate $f = 15$ kHz). In the second series of experiments, a PicoQuant PDL 370-nm light diode (Germany) was used ($\Delta t \approx 700$ psec, $f = 2.5$ MHz).

Results and Discussion. We have measured the quantum yield of the fluorescence of H₂TAP in toluene relative to a solution of tetraphenylporphyrin in toluene for which $\phi_F = 0.09$ [9]. The measurements were performed at $\lambda_{exc} = 547$ nm, which corresponds to rather intense absorption bands $Q_y(0,0)$ of both compounds and also at other values of λ_{exc} . The resulting ratio of quantum yields was 2.00 ± 0.06 . For H₂TAP in toluene $\phi_F = 0.180 \pm 0.005$. However, the true accuracy of measurements in this case is determined by the accuracy of the value of ϕ_F of the standard. We assume that the representation $\phi_F = 0.180 \pm 0.015$ will be quite correct.

Using the solution of H₂TAP in toluene as the standard, we performed measurements of the relative values of the fluorescence yield for solutions in isobutanol, in a diethyl ether–light ligroin–isopropanol mixture (5:5:2) (ÉPIP), and in chloroform. For all the solvents, the values of τ_F were measured. These solvents were not selected at random — toluene was used in [1, 2, 6], isobutanol* in [3, 4], EPIP in [5], and chloroform in [8].

The results of measurements of τ_F on excitation by a pulsed lamp and light diode agree qualitatively: for solutions in toluene the values of τ_F are practically the same (3.2 and 3.4 nsec), whereas for solutions in isobutanol a considerable reduction in τ_F is noted. Naturally, in the latter case the value $\tau_F = 1.5$ nsec obtained at an exciting pulse of 700 psec is more reliable. This is confirmed by control measurements on other setups. Table 1 lists the results of the second series of measurements except for the case of EPIP. It is seen that in transition from a solution of H₂TAP in toluene to a solution in chloroform the value of τ_F virtually does not change, i.e., neither quenching nor the flareup of fluorescence was observed. In contrast to this, as already mentioned, the duration τ_F in isobutanol is noticeably short, whereas for EPIP an intermediate value of τ_F was obtained. Probably, the hydroxylic groups of the alcohol molecules (isobutanol and isopropanol, which enters into the composition of EPIP) form hydrogen bonds with bridging nitrogen atoms of the H₂TAP molecules, and these bonds create an additional channel of deactivation of the S_1 state. In EPIP, the content of the OH groups is smaller, which is responsible for the lesser degree of quenching.

The results of measurements of the quantum yield of fluorescence agree with the data on τ_F , but some of the characteristic features should be noted. Table 1 lists the values of the ratio $\tau_F^{rel} = \tau_F/\tau_F^{tol}$ (the superscript tol refers to toluene) and the values of the relative quantum yield of fluorescence $\phi_F^{rel} = \phi_F/\phi_F^{tol}$. As is seen, in isobutanol and EPIP the measured relative quantum yield of fluorescence is much smaller than ϕ_F^{rel} . We attribute this discrepancy to the inaccuracy with which τ_F^{rel} was measured because of the poor solubility of H₂TAP in the solvents mentioned, namely, aggregation of the pigment may occur, i.e., errors in determining the optical density because of the inactive absorption and scattering.

The value of ϕ_F measured in a fresh solution in chloroform practically does not differ from that measured in toluene. However, during storage the intensity of the fluorescence of the solution decreases. This means that the measurement of ϕ_F for chloroform solutions of H₂TAP requires some caution.

An analysis of the data obtained leads to the conclusion that the values $\phi_F = 0.180 \pm 0.015$ and $\tau_F = 3.4 \pm 0.1$ nsec obtained for H₂TAP in toluene, which is a low-polar and chemically inactive solvent, are the most reliable. They agree well with the above-given data of [1, 2], in which another standard was used for determining ϕ_F (a solution of the cresylic violet dye — oxazine-9 — in ethanol). The probabilities that were calculated for the radiative transition $S_1 \rightarrow S_0$ and intercombination conversion $S_1 \rightsquigarrow T_1$ are equal to $k_F = 5.3 \cdot 10^7$ sec⁻¹ and $k_{ST} = 2.4 \cdot 10^8$ sec⁻¹, respectively. In the calculations, we ignored the probability of internal conversion $k_{S_1S_0}$. This was suggested by the data on the good compliance with the Ermolaev–Sveshnikova rule $\phi_F + \phi_T = 1$ [10] for metallophthalocyanines [11, 12], in the structure of which there are also four nitrogen bridges, but the energy interval S_1-S_0 is much smaller than for H₂TAP. (The data for nonmetallic phthalocyanine and its substituents [13–15] are less definite but nevertheless allow the conclusion that the role of the internal conversion is insignificant.)

Table 1 also lists the values of ϕ_F^τ , defined as the product of ϕ_F^{tol} and τ_F^{rel} . Under the assumption that $k_F = \text{const}$, the quantity ϕ_F^τ should be equal to $\phi_F^{rel} = \phi_F/\phi_F^{tol}$. Taking into account the above-mentioned differences in measuring ϕ_F^{rel} , it should be assumed that the values of τ_F^{rel} were determined with a high accuracy. Therefore, the values of ϕ_F^τ should better fit the true values of ϕ_F in the solvents indicated.

*Isobutanol was used in [3, 4] in a series of spectral-luminescent measurements, but unfortunately it was not mentioned for which of the solvents the given values of ϕ_F and τ_F of H₂TAP were obtained.

TABLE 1. Photophysical Parameters of H₂TAP Molecules in Various Solvents

Solvent	τ_F , nsec	τ_F^{rel}	Φ_F^{rel}	Φ_F^τ
Toluene	3.4	1.00	1.00	(0.18)
Isobutanol	1.5	0.45	0.24	0.08
EPIP	2.5	0.73	0.40	0.13
Chloroform	3.3	0.97	0.94	0.17

Note. The measured value of Φ_F for toluene is given in parentheses.

It was noted above that in the case of alcohol-containing solvents the OH groups of the molecules of alcohols may form hydrogen bonds with bridging nitrogen atoms and participate in radiationless deactivation of the S_1 state. A similar role can be played by water impurities, which can also favor aggregation of the H₂TAP molecules, resulting in distortion of the results of measurements of Φ_F .

An important feature of H₂TAP is the relatively low value of Φ_F , which is much lower than, for example, in the magnetic complex MgTAP [3, 4]. According to the data on Φ_F and τ_F from [3, 4], the probability of the intercombination conversion of MgTAP is $k_{ST} = 8.9 \cdot 10^7 \text{ sec}^{-1}$, i.e., for H₂TAP it is 2.7 times higher. In [16] (see also [17]), the increase in the quantum yield of fluorescence in MTAP (M is the diamagnetic light metal) is attributed to the increase in the energy of the triple levels T_3 and T_4 above the fluorescent single level S_1 . It can be assumed that in transition from MTAP (D_{4h} symmetry) to H₂TAP (D_{2h} symmetry) and removal of the orbital degeneracy of the $T_{3,4}$ level (2^3E_u), the T_3 level becomes lower than the S_1 level, and this creates an additional channel of intercombination conversion.

Conclusions. The results of measurements have shown that the values of Φ_F and τ_F in H₂TAP indeed depend noticeably on the nature of the solvent. Such a dependence is untypical of the free bases of porphyrins. For a solution in toluene, which is a stable, chemically inactive, and low-polar solvent, the measured quantum yield of the fluorescence of tetraazaporphin equals 0.180 ± 0.15 , and its duration is 3.4 ± 0.1 nsec.

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