

Spectral Properties of Phenylbenzopyrylium Salts in Solutions as a Result of Their Nucleophilic Solvation*

by A.D. Roshal^{1**}, D.Yu. Minayev², Yu.F. Pedash³ and A.I. Novikov⁴

¹Physical Organic Chemistry Department, Institute of Chemistry, Kharkov National University, 4 Svoboda sqr., 61077, Kharkov, Ukraine

²Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, Great Britain

³Theoretical Chemistry Department, Institute of Chemistry, Kharkov National University, 4 Svoboda sqr., 61077, Kharkov, Ukraine

⁴Department of Chemistry, Kharkov Military University, 6 Svoboda sqr. 61022, Kharkov, Ukraine

(Received October 20th, 2001; revised manuscript April 4th, 2002)

A dependence of spectral properties of 2-phenylbenzopyrylium (PBP) salts in solutions on the solvent nucleophilicity is presented. A simple solvate complex model for quantum chemical estimation of the nucleophilic solvation influence on band positions in absorption and fluorescence PBP salt spectra is proposed. Quantum yield changes of the PBP salts in solvents of different nucleophilicity are explained as due to the influence of nucleophile solvation on the efficiency of the intersystem crossing in PBP cations. Two ways of this influence are proposed: the *direct* one, due to energy changes in S_1 and T_1 levels, and the *indirect* one, due to an increase or decrease of spin-orbital interaction efficiency, caused by changes of the structural rigidity of solvated PBP cations.

Key words: 2-phenylbenzopyrylium salts, flavylum salts, nucleophilic solvation, absorption spectra, fluorescence spectra, intersystem crossing

2-Phenylbenzopyrylium salts (PBP) are widely used (*e.g.* as laser dyes [1] and in food industry [2]). Various derivatives of PBP salts – anthocyanines and anthocyanidines are widespread in nature as plant dyes. Besides, positions of long-wavelength absorption bands in the spectra of new synthesized phenylbenzopyrylium salts are used for prognostic purposes – in prediction of chemical stability of the PBP cations [3,4,5]. Some PBP salts display photochromic properties [6].

The phenomenon of solvatochromism is typical of most PBP salts [7]. The same behavior of their fluorescence spectra, the long-wave-length shift of emission maxima and the quantum yield decrease in transition from dichloromethane to acetonitrile solutions [7] has also been found.

The noticeable quenching of fluorescence of some PBP salts, whose lateral phenyl is capable to rotate freely around the ordinary bond with a benzopyrylium moiety, and absence of similar effect of PBP with phenyl ring hindered, urged [7] to conclude, that the cause of a decrease in the fluorescence quantum yield is the forma-

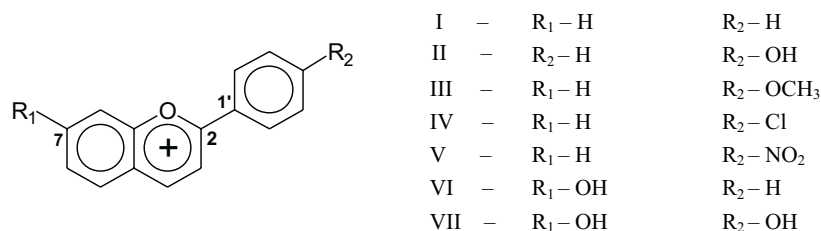
* Presented at the 1st Russian-Ukrainian-Polish Conference on Molecular Interactions in Gdańsk, June 2001, (Poland).

** E-mail: Alexandre.D.Rochal@univer.kharkov.ua; Fax: 38-057-245-71-30

tion of twisted intramolecular charge transfer (TICT) state. This phenomenon can also be characterized in the disruption of the π -conjugation and planarity in PBP cations. According to [7], the TICT state results from electron density shift from the lateral phenyl radical (especially when it contains electron-donor substituents) towards the positively charged benzopyrylium moiety. Further TICT insights were developed in [8,9] concerning dimethylamino substituted PBP salts, where the interplay of lateral phenyl rotating state and "classical" TICT one, due to dimethylamino group twisting, was considered. It is also worth noting that an explanation of luminescent properties based on the TICT state model can be found in numerous papers, concerning other classes of pyrylium compounds (*e.g.* triphenylpyrylium salts [10,11,12]).

Our earlier interpretation of the nature of electronic transitions in the absorption spectra of benzopyrylium salts [13] and the quantitative estimation of the interfragmental charge transfer [14,15] have shown that most PBP salts can be classified into two main groups based on the different origin of long-wave-length absorption and emission bands.

The first group consists of compounds, which have electron-donating substituents only in the benzopyrylium moiety. The low-energy electronic transition of these substances is located mainly in the benzopyrylium fragment; the interfragmental charge transfer in such PBP cations is low. The fluorescent quantum yield of such PBP salts depends slightly on the solvent polarity and can show not only a decrease when going from dichloromethane to acetonitrile, but – on the contrary – it can even increase.



PBP salts of another group possess electron-donor substituents in the lateral phenyl cycle (especially in its 2' and 4' positions) and, independently of the nature and number of substituents in the benzopyrylium moiety, demonstrate the $S_0 \rightarrow S_1$ transition with a significant interfragmental charge transfer. It is a group of compounds that displays significant dependence of the fluorescent quantum yield on the solvent polarity. This last group also includes unsubstituted 2-phenylbenzopyrylium cation.

For "classical" TICT compounds [16], the increase of solvent polarity resulted in a growing stabilization of the higher polar charge transfer state. Our investigation of spectral properties of some of the above-mentioned PBP salts in 16 different solvents [17] gave rise to doubts about the existence of any correlation between spectral properties of these compounds and the polarity of solvents used.

The energy decrease of the long-wave-length electronic transition and increase of the fluorescence quantum yield (ϕ_f) of PBP salts was observed not only in non-polar

dichloromethane, 3-chloropropene and dibromobenzene, but in polar benzoic acid esters, as well as in benzonitrile. On the contrary, the maximum hypsochromic shift of the long-wave-length absorption band and considerable lowering of ϕ_{fl} were observed not only in polar acetone and acetonitrile, but also in low-polar dioxane and tetrahydrofuran. No correlation of the absorption maximum and fluorescence positions (ν_{abs} , ν_{fl}), Stokes shifts ($\Delta\nu_{St}$) and ϕ_{fl} with the dielectric constant, polarity or Lippert function [18] were detected. However, we found quite satisfactory correlation between ν_{abs} and ϕ_{fl} and the solvent nucleophilicity (B) characterizing the electron-donor ability of the solvent molecules [19].

The observations mentioned led to the assumption that both the solvatochromic effects and fluorescent properties of the PBP salts are determined by the same factor – the nucleophilic solvation, *i.e.* the interaction of electron-donor solvent molecules and the positively charged benzopyrylium cation. In this connection we propose an alternative model of photophysical processes to describe spectral behavior of PBP salts. However, our model does not exclude the TICT state being formed in several PBP salts. In our opinion, both an increase and decrease of the fluorescence intensity of the PBP salts is due to the nucleophilic solvation effect on the efficiency of intersystem crossing stipulated by the spin-orbital interaction, and on the related mobility of the benzopyrylium and phenyl moieties in the cations studied.

The present paper is devoted to theoretical and experimental backgrounds of the nucleophilic solvation effect on the spectral properties of PBP salts.

EXPERIMENTAL

The benzopyrylium perchlorates were synthesized according to the methods described in [20]. The absorption and emission spectra of those salts were measured at 20°C using spectrophotometer “Hitachi U3210” and spectrofluorimeter “Hitachi F4010”. Spectroscopy grade solvents were additionally purified and dried by means of the methods described elsewhere [21,22]. The fluorescent quantum yield was determined using fluoresceine in carbonate buffer at pH = 9.93 ($\phi = 0.90$) as a standard [23]. PBP perchlorate concentration did not exceed $5 \cdot 10^{-6}$ mol/l to avoid self-association of the cations.

The molecular geometry optimization of PBP cations and their complexes with solvent molecules was carried out by semi-empirical PM3 method (MOPAC 6.0 program package). The calculation of singlet and triplet energy levels, the matrix elements of spin-orbital coupling operator and also energy and intensity of electronic transitions in their absorption spectra was performed according to the CNDO/S CI scheme (15 singly excited configurations were taken for construction of 15×15 CI matrix) [24]. In our calculations traditional single-center contributions were included in the evaluation of spin-orbital interaction. The calculations of double- and triple-centered integrals, taking into account single- and double-electron interactions were also carried out. The intersystem crossing rate constants k_{ST} (s^{-1}) were evaluated by using:

$$k_{ST} = 3.95 \cdot 10^{11} \sum_i | \langle S_1 | \hat{H} | T_i \rangle |^2 \cdot e^{-\frac{E_{S_1} - E_{T_i}}{5000}} = 3.95 \cdot 10^{11} \sum \beta_{ii}^2 F_{ii} \quad (1)$$

where $| \langle S_1 | \hat{H} | T_i \rangle |$ and β_{ii} are matrix elements of spin-orbital coupling operator, E_{S_1} – the energy of singlet S_1 -state (cm^{-1}), E_{T_i} – energies of all the underlying triplet levels, F_{ii} – the Franck-Condon factor including the overlap between S_1 and T_i states, where intersystem transition occurs. (1) was deduced from the empirical dependence of F on ΔE [25].

Radiative rate constants k_r were calculated using (2) [26,27]:

$$k_r = 1.5 \cdot f \cdot E_{S_1}^2 \quad (2)$$

The parameters necessary for calculation of k_r , the S_1 -state energy (cm^{-1}) and oscillator strength of $S_0 \rightarrow S_1$ electronic transitions were estimated by means of the CNDO/S CI method.

Theoretical fluorescence quantum yields were calculated using the traditional equation

$$\phi = \frac{k_f}{k_f + k_{ST}} \quad (3)$$

considering the intersystem crossing to be the main radiationless process, taking place in PBP cations.

RESULTS AND DISCUSSION

Nucleophilic solvates computer simulation. The spatial structure calculation of solvate complexes of *I–VIII* PBP have been performed using the “supermolecule” method, which requires computer geometry optimization of the complex containing the molecule under study and several solvent molecules [28,29]. An example of the starting geometry is presented in Fig. 1a. Eight solvent molecules were arranged around a PBP cation equally spaced (6 Å) from the C2 atom of benzopyrylium moiety (taking into account the fact that up to 33 percent of the total positive charge of cations investigated was located in it). Solvent molecules were placed below and above the plane of benzopyrylium moiety and were oriented by their nucleophilic centers towards the center of positive charge localization of the PBP cation.

Final geometry of the solvate complexes after the optimization procedure is presented in Fig. 1b. Two solvent molecules were arranged on the axis at a right angle to the plane of the benzopyrylium cation at a distance of 3.0–3.5 Å from it. Positions of other solvent molecules either remained unchanged, or were moved off at a distance of 6–10 Å from the cation. The same results were obtained for all nucleophilic solvents given below Fig. 4. In the case of a non-nucleophilic solvent (*e.g.* dichloromethane) no noticeable changes in distance between solvent molecules and the PBP cation were observed. Thus, no solvate complex was formed, which was analogous to that presented in Fig. 1b.

In further calculations we considered the solvate structure similar to that presented in Fig. 1b as the starting model for both ground and excited state calculations. The model presented has several disadvantages: it does not take into account the influence of all other solvent molecules in the higher solvate layers, macroscopic polar properties of the solvent, and effects of hydrogen bonding (in the case of hydroxy-substituted PBP cations), *etc.* However, in the proposed model there are positive features. It enables calculations of electronic spectra of solvated PBP cations, using a reasonable quantity of singly excited configurations. It also makes possible to estimate the spin-orbital coupling of the solvated cations. Moreover, such a simple model enables us to evaluate the re-solvation of excited PBP cations and the influence of solvent molecules on the charge transfer, while cations are being excited. The comparison of our theoretical results with the experimental solvatochromic effects presented

Table 1. Absorption and fluorescence characteristics of PBP salts in solvents of various nucleophilicity.

Solvents	B	I			II			III			IV			V			VI			VII			
		ν_{abs}	ν_{fl}	$\Delta\nu_{\text{St}}$	ν_{abs}	ν_{fl}	$\Delta\nu_{\text{St}}$	ν_{abs}	ν_{fl}	$\Delta\nu_{\text{St}}$	ν_{abs}	ν_{fl}	$\Delta\nu_{\text{St}}$	ν_{abs}	ν_{fl}	$\Delta\nu_{\text{St}}$	ν_{abs}	ν_{fl}	$\Delta\nu_{\text{St}}$	ν_{abs}	ν_{fl}	$\Delta\nu_{\text{St}}$	
dichloro- methane	23	24880	22173	2707	21900	19600	2300	21552	19724	1828	24570	22422	1997	19979	22422	20040	2381	21100	19720	1380			
3-chloro- propene	40	24880	22095	2785	21900	19531	2369	21552	19569	1982	24752	22422	2179	20056	22422	19802	2620	20940	19480	1460			
ethyltri- fluoroacetate	100	25220	22321	2899	22440	19540	2900	22472	19608	2864	25189	22883	2616	21509	22883	19841	3042	21320	19700	1620			
acetonitrile	160	25340	22168	3172	22396	19140	3257	22727	19531	3196	25445	23256	3074	22385	23256	19417	3838	21335	19560	1775			
acetone	224	25580	21519	4061	22523	19300	3222	22727	19455	3272	25445	23256	3321	22227	23256	19305	3951	21380	19460	1920			
benzonitrile*	155	24760	21760	3000	21680	19340	2340	21520	19580	1940	24592	22380	2212	20380	22371	19659	2712	21144	19540	1604			

* ν_{abs} – position of the long-wave-length absorption maxima, ν_{fl} – positions of the fluorescent maxima, $\Delta\nu_{\text{St}}$ – Stokes shifts (cm^{-1}).

** Benzonitrile has practically the same nucleophilicity as acetonitrile, though it is unable to the nucleophilic solvation of aromatic cations [30,31].

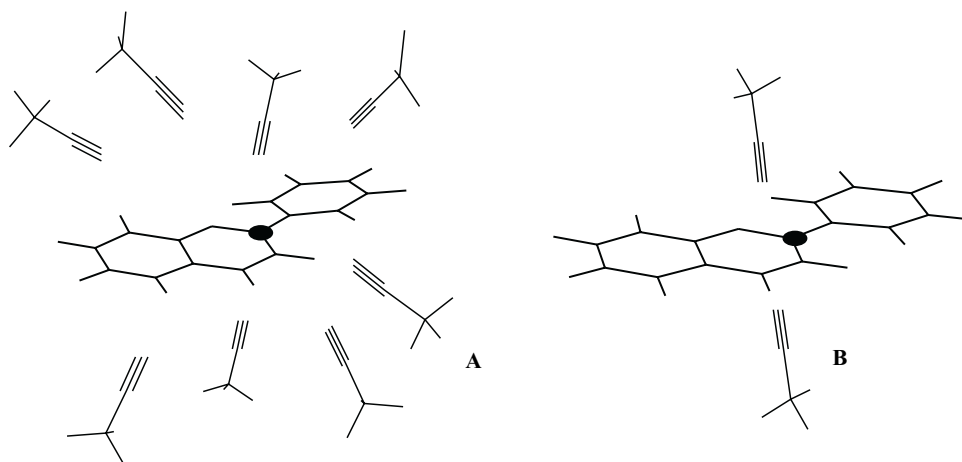


Figure 1. Geometry (before and after optimizing) of the PBP cation solvated by the acetonitrile molecules. The center of the positive charge, C₂ atom, is marked by a black solid circle.

in this paper shows a wide applicability of the proposed solvation model to the description of spectral properties of PBP salts investigated in solvents of various nucleophilicity.

We have used the charge value of negatively charged nucleophilic atoms of solvent molecules in solvate complexes (Q_N) as a theoretical measure of nucleophilicity. It should be noted that Q_N values were well correlated with the empirical nucleophilicity parameter B (see Fig. 2a). Theoretical evaluation of the formation enthalpy is as follows:

$$\Delta H_{Solv} = \Delta H_f^C - (\Delta H_f^{PBP} + 2\Delta H_f^S) \quad (4)$$

where ΔH_f^C is calculated formation enthalpy of the solvate complex, ΔH_f^{PBP} and ΔH_f^S are the same for a PBP cation and a free solvent molecule. Our calculations demonstrate that formation of solvate complexes can be considered to be the energetically favorable process: for all the compounds under study the $-\Delta H_{Solv}$ value ranges from 11.8 to 14.5 kcal/mol.

We have found that formation of such solvate complexes results in increasing the positive charge in the benzopyrylium moiety (Q_{BP}) and, particularly, – in its electrophilic center – C2 atom (Table 2). The bond between the benzopyrylium moiety and the lateral phenyl ring in solvated PBP cations is of a lower order compared with non-solvated ones (Table 3). The increase of solvent nucleophilicity (Fig. 2b) results in increasing Q_{BP} , however, the plot of Q_{BP} versus Q_N is not linear and a saturation of high Q_N values is typical for it. In our opinion, this fact is an evidence of the limited capability of the π -electron system of PBP cations to redistribute electron density due to the influence of external nucleophilic agent.

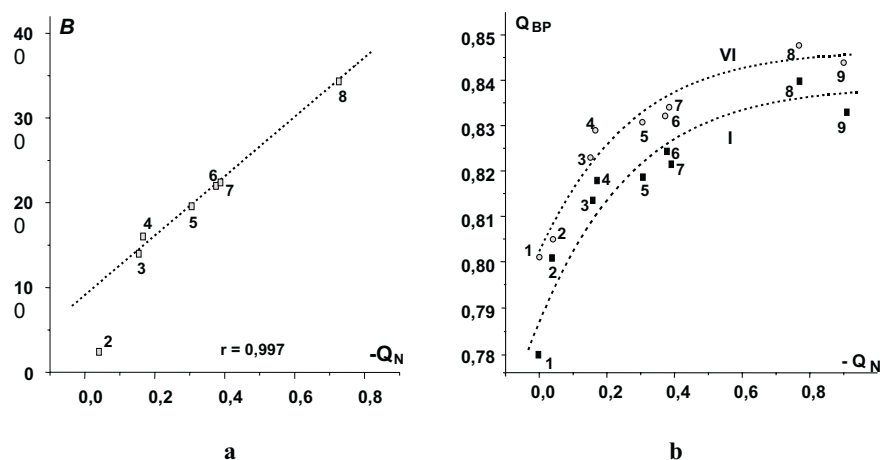


Figure 2. Comparison of the experimental and theoretical nucleophilicity solvent parameters – B and Q_N (a). Plot of the benzopyrylium moiety (Q_{BP}) positive charge against the theoretical nucleophilicity solvent parameter, deduced with the account of polarization effect (Q_N) (b). Used solvents and model nucleophilic molecules: 1 – without solvent (in vacuum), 2 – dichloromethane, 3 – HCN, 4 – acetonitrile, 5 – $\text{CH}_3\text{-O-CH}_3$, 6 – formaldehyde, 7 – acetone, 8 – dimethylsulfoxide, 9 – H_3PO_4 .

The electronic excitation of PBP salts leads to a significant charge transfer from the lateral phenyl and/or from donor substituents in the C_7 position towards the benzopyrylium moiety. It results in the disappearance of the electrophilic center in the C_2 atom and in the increase of the positive charge on C_7, C_1' atoms and on the hydrogen atoms of hydroxy groups (if present in the investigated molecule). The redistribution of electronic density in the excited state under nucleophilic solvation conditions causes the migration of solvent molecules in the direction opposite to the electron density shift in the cations, towards the regions of higher localization of the positive charge (Fig. 3). The presence of nucleophilic solvent molecules in the vicinity of the new center of the positive charge of the excited PBP cations results in its additional stabilization. This statement is the consequence of the comparison of ΔH_f values between solvated and non-solvated PBP ions in Frank-Condon and relaxed S_1 -states (Table 2). Thus, for non-solvated **II** and **VI** cations, the decrease of excited state energy, caused by the intramolecular structural relaxation is only 1.3–3.5 kcal/mol, while the same values for the cations solvated by acetonitrile molecules are much higher, *i.e.* 12.3–25.7 kcal/mol.

If the excited state charge transfer in PBP cations is mainly of a phenyl-benzopyrylium interfragmental nature, the nucleophilic solvation results in more significant decrease of the order of the interfragmental bond. As to the **II** and **VII** compounds, we can conclude that π -conjugation between the phenyl and pyrylium moieties decreases significantly, until its complete disappearance. In the case of solvated **VI** cation (and its OCH_3 -derivative), the excited state charge transfer is predominantly of an intrafragmental nature. In this case, the order of the interfragmental bond discussed even increases slightly.

Table 2. The enthalpies of formation of the PBP cations non-solvated and solvated by the acetonitrile molecules (calculated by PM3 method)*.

	S_0		S_1 (non-relaxed)				S_0 (non-relaxed)				$\Delta E_{S_0 \rightarrow S_1}^{**}$	ΔH_{Solv}	$\Delta E_{S_1 \rightarrow S_0}^{**}$
	ΔH_f^C	$\Delta H_f^{PBP} + 2\Delta H_f^S$	ΔH_{Solv}^C	ΔH_f^C	$\Delta H_f^{PBP} + 2\Delta H_f^S$	ΔH_{Solv}^C	ΔH_f^C	$\Delta H_f^{PBP} + 2\Delta H_f^S$	ΔH_{Solv}^C	ΔH_f^C			
I	234.7	247.7	-13.0	318.4	328.3	-9.9	315.8	326.8	-11.0	318.4	328.3	-9.9	-1.1
II	187.5	199.7	-12.2	268.0	276.9	-8.9	242.3	273.4	-31.1	200.6	204.4	-3.8	-27.3
III	194.0	206.1	-12.1	273.7	282.4	-8.7	246.4	278.5	-32.1	215.6	210.8	-4.8	-27.3
IV	228.9	241.9	-13.0	308.7	316.5	-7.8	303.6	313.7	-10.1	239.6	245.5	-6.0	-4.1
V	234.7	249.7	-15.0	320.2	332.4	-12.2	—	—	—	—	—	—	—
VI	185.9	200.3	-14.5	268.3	278.0	-9.7	256.0	276.7	-20.7	192.5	202.3	-9.8	-10.9
VII	140.9	152.7	-11.8	219.3	228.1	-8.8	198.5	226.7	-28.2	156.0	155.0	+1.0	-29.1

* The enthalpy of formation of the acetonitrile molecule isolated is 23.3 kcal/mol.

**Spectral shifts predicted.

Table 3. Interfragmental excited state charge transfer and benzopyrylium–phenyl bond orders in the PBP cations*.

	Charge values on the phenyl cycle		Charge transfer upon excitation		Benzopyrylium–phenyl bond orders	
	$Q_{S_0}^{Ph}$	$Q_{S_1}^{Ph}$	$\Delta Q_{S_0 \rightarrow S_1}$	$\delta Q_{S_0 \rightarrow S_1}$	$P_{S_0}^{BP \rightarrow Ph}$	$P_{S_1}^{BP \rightarrow Ph}$
I						
without solvent	0.218	0.489	0.271	124	1.107	1.177
in acetonitrile	0.177	0.596	0.419	237	1.086	1.107
II						
without solvent	0.261	0.626	0.365	140	1.159	1.084
in acetonitrile	0.208	0.966	0.758	364	1.119	0.983
III						
without solvent	0.267	0.652	0.385	144	1.165	1.070
in acetonitrile	0.213	0.963	0.750	352	1.123	0.995
IV						
without solvent	0.221	0.644	0.423	191	1.122	1.084
in acetonitrile	0.183	0.713	0.530	290	1.088	1.046
V						
without solvent	0.165	0.347	0.182	110	1.062	1.234
in acetonitrile	0.132	0.138	0.006	5	1.045	1.180
VI						
without solvent	0.201	0.349	0.148	74	1.094	1.272
in acetonitrile	0.166	0.203	0.037	22	1.072	1.279
VII						
without solvent	0.240	0.532	0.292	122	1.141	1.137
in acetonitrile	0.196	0.785	0.589	301	1.107	0.988

* $\Delta Q_{S_0 \rightarrow S_1}$ is a value of charge transferred between the lateral phenyl cycle and benzopyrylium moiety upon electronic excitation; $\delta Q_{S_0 \rightarrow S_1}$ is fraction of charge transferred between the fragments upon excitation, determined as ratio $\Delta Q_{S_0 \rightarrow S_1}$ in the lateral phenyl cycle to its total charge in the ground state ($Q_{S_0}^{Ph}$): $\delta Q_{S_0 \rightarrow S_1} = \Delta Q_{S_0 \rightarrow S_1} / Q_{S_0}^{Ph} \cdot 100(\%)$. (%)

The analysis of the bond order changes upon the electronic excitation of PBP cations enables us to conclude that for PBP ions with interfragmental charge transfer the relative mobility of its fragments grows in the S_1 state. Other molecules, characterized by the intrafragmental charge transfer, have to become more planar and more rigid in their excited state.

Nucleophilic solvation and solvatochromic features of PBP salts. Our theoretical data presented in Table 3 enable us to estimate the energy difference between the non-relaxed S_0 state and that of S_1 of both solvated and non-solvated PBP cations. We assumed that the energy difference of non-solvated cations should be $E_{S_0 \rightarrow S_1} = \Delta H_f^{PBP, S_1 (non-relax)} - \Delta H_f^{PBP, S_0}$ and that of solvated ones

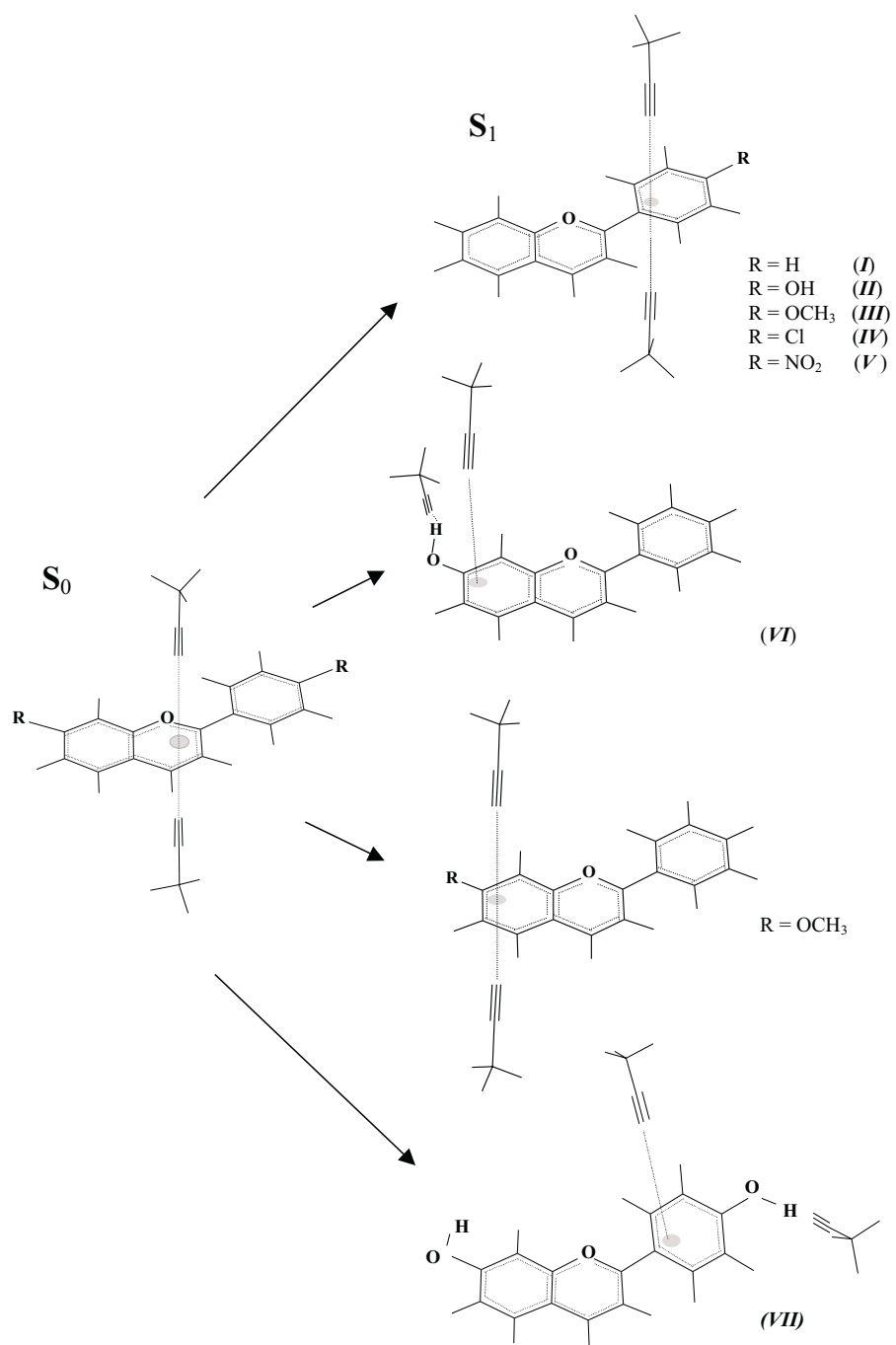


Figure 3. Shift of the acetonitrile molecules in the solvate PBP complexes upon excitation.

$E_{S_0 \rightarrow S_1}^{\text{Solv}} = \Delta H_f^{C,S_1(\text{non-relax})} - \Delta H_f^{C,S_0}$. In addition, assuming that the enthalpy of acetonitrile molecule formation in solvates both in their ground and excited states is the same ($\Delta H_f^{S,S_0} = \Delta H_f^{S,S_1}$), we determine that the energy difference between the solvated cations in their S_0 and S_1 -states is higher by $\Delta H_{\text{Solv}}^{S_1,\text{non-relax}} = \Delta H_{\text{Solv}}^{S_0}$, as compared with that of the non-solvated cations. In real solvates the solvent molecules are polarized. Since in the ground state the positive charge in PBP cations is more localized, than in the excited state, the polarity and consequently the enthalpy of solvate acetonitrile molecules formation in the S_0 -state ($\Delta H_f^{S,S_0}$) should be higher. This assumption is supported by our calculations: Q_N values for solvent molecules in solvates are higher when the PBP cation is in the S_0 -state and lower when being excited. Thus, in the real solvate, where $\Delta H_f^{S,S_0} > \Delta H_f^{S,S_1}$, the difference $\Delta H_{\text{Solv}}^{S_1,\text{non-relax}} - \Delta H_{\text{Solv}}^{S_0}$ and, consequently, the energy difference of solvated and non-solvated PBP cations in their S_0 and S_1 states is higher, taking into account the polarization effects of the solvent molecules. The energy difference obtained in the S_0 and S_1 states of PBP cations non-solvated and solvated by nucleophilic solvents (Table 2, Fig. 4) clearly shows that in exchanging low nucleophilic solvents for highly nucleophilic ones the energy of $S_0 \rightarrow S_1$ transition should increase. This is expected to manifest itself as the nucleophilicity stipulated hypsochromic shift of the long-wave-length absorption band in the PBP salts spectra. The increase of the solvent nucleophilicity (Q_N , B) results in growing $\Delta H_{\text{Solv}}^{S_1,\text{non-relax}} - \Delta H_{\text{Solv}}^{S_0}$ difference and, consequently, the hypsochromic shifting in the absorption spectra.

Since the solvent molecules are kept close to the PBP cations, owing to the positive charge in their benzopyrylium moiety, it is evident that the stability of the solvate

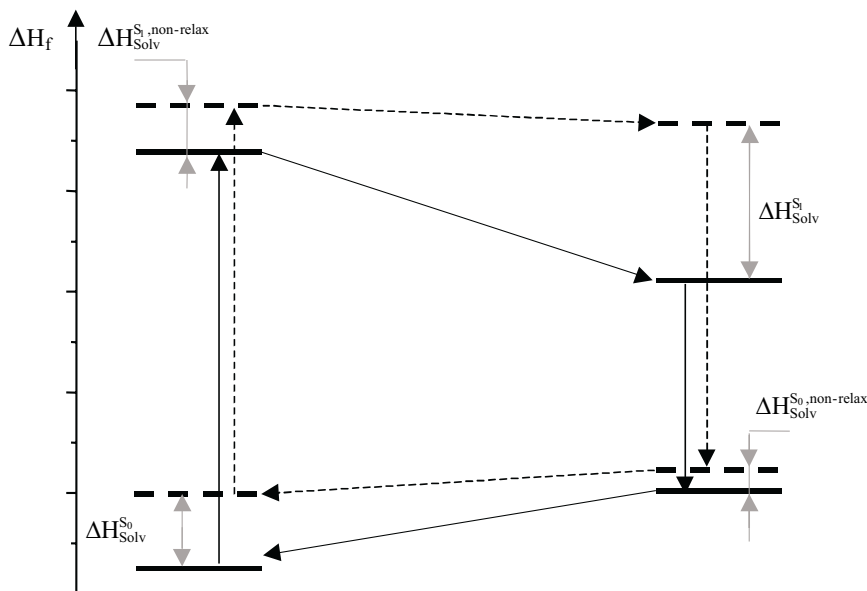


Figure 4. Calculated enthalpies of formation for the solvated and non-solvated PBP cations in the four level Neperent-type diagram (data for compound II are presented).

complex and the observed hypsochromic shift of the long-wave-length absorption band could be determined by Q_{BP} values. Our calculations have shown a linear correlation between the energy of $S_0 \rightarrow S_1$ electronic transition and the Q_{BP} value. This fact clarifies the similarity of the $E_{S_0 \rightarrow S_1}$ plot versus Q_N (Fig. 5a,d) and the plot of Q_{BP} against Q_N (Fig. 2b).

The experimental plots of $E_{S_0 \rightarrow S_1}$ versus solvent nucleophilicity B are similar to the theoretical (Fig. 5a,d). This proves our assumption that spectral properties of PBP salts in solutions are determined mainly by their nucleophilic solvation. Besides, it confirms the possibility of application of the above-discussed simplified solvate model to describe the optical properties of PBP salts in nucleophilic solvents.

The effect of nucleophilic solvation on the fluorescence spectra of PBP salts can be numerically expressed as energy difference of solvated and non-solvated PBP cations, formed in the relaxed excited state and non-relaxed ground one. As pointed out above, the motion of the solvent molecules towards the new nucleophilic centres of the excited PBP cation stabilizes the excited solvate. In this case, $\Delta H_{Solv}^{S_1}$ values are high enough and vary from 11.0 to 31.1 kcal/mol. Corresponding $\Delta H_{Solv}^{S_0, non-relax}$ values

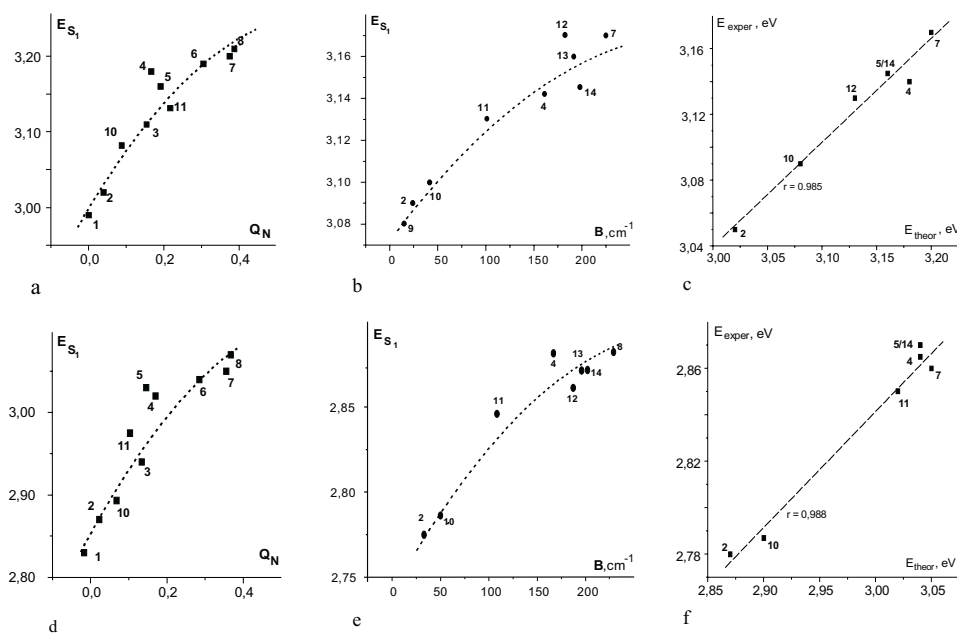


Figure 5. Plots of the electronic transition $S_0 \rightarrow S_1$ energy against the solvent nucleophilicity: a and d are theoretical data E_{S_1} against Q_N for **I** and **VI** correspondingly, b and e are experimental data E_{S_1} against B value, c and f – correlation between theoretical and experimental energies of $S_0 \rightarrow S_1$ electronic transitions. Used solvents and model nucleophilic molecules: 1 – without solvent (in vacuum), 2 – dichloromethane, 3 – HCN, 4 – acetonitrile, 5 – CH_3-O-CH_3 , 6 – formaldehyde, 7 – acetone, 8 – dimethylsulfoxide, 9 – chloroform, 10 – 3-chloropropene, 11 – ethyltri-fluoracetate, 12 – ethylacetate, 13 – butylacetate, 14 – dioxane.

for the non-relaxed S_0 state are lower, ranging from -3.8 to 9.9 kcal/mol. The data for compound **VII**, whose $\Delta H_{\text{Solv}}^{S_0, \text{non-relax}}$ is higher than 0, have appeared to be very interesting, as the non-solvated cation is more energetically favorable, than the solvated one. The resulting difference is negative; hence the $S_1 \rightarrow S_0$ transition energy of solvated PBP cation is lower than that of the non-solvated one. This corresponds to the bathochromic shift of the emission band, when solvent nucleophilicity increases. As the polarity of solvent molecules near the excited PBP cation is lower than that of the cation in the non-relaxed S_0 state, the bathochromic shift obtained in the experiment should be lower than that presented in Table 2.

The experimental data on PBP salts solvatochromism (Fig. 6) confirm our theoretical conclusions that the solvent nucleophilicity causes red shifts in emission spectra. Besides, no correlation between $E_{S_1 \rightarrow S_0}$ and other solvent parameters (dielectric constant, polarity, and polarizability) have been found, with the exception of chlorine substituted compound **IV**, for which the solvent nucleophilicity growth results in a hypsochromic shift of the emission band.

Since the nucleophilic solvation leads to the absorption and emission bands shift in opposite directions to each other, the described solvent effects can also be seen in increasing Stokes shifts ($\Delta\nu_{\text{St}}$) of PBP salts. In non-nucleophilic solvents (dichloromethane, chloroform, 3-chloropropene) the $\Delta\nu_{\text{St}}$ values for all the salts under study do

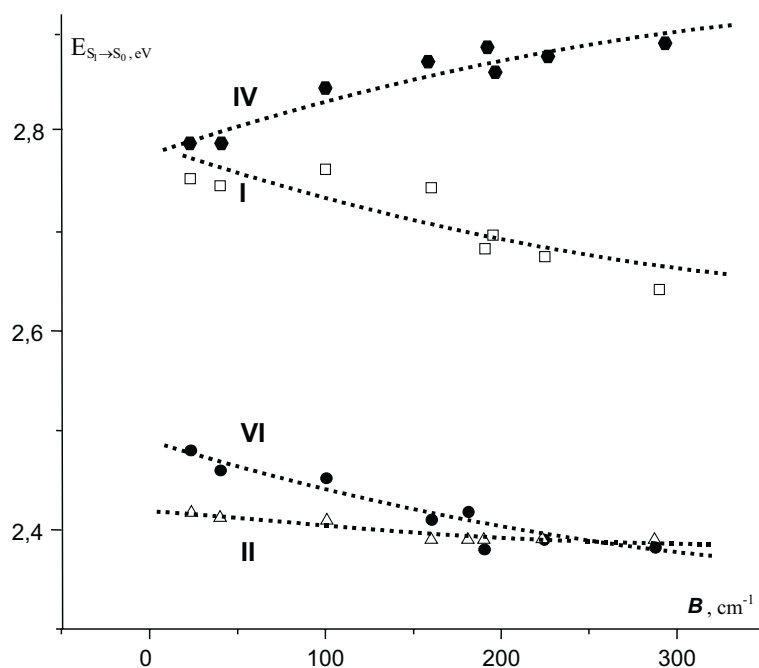


Figure 6. Plot of the long-wave-length band maximum positions in PBP-salt fluorescence spectra against the solvent nucleophilicity. Solvents used (as the nucleophilicity increase): chloroform, 3-chloropropene, ethyltrifluoroacetate, acetonitrile, ethylacetate, butylacetate, acetone, tetrahydrofuran.

not exceed 2300–2500 cm^{-1} . In the nucleophilic non-aromatic solvents, where B is higher than 150 cm^{-1} , the Stokes shift values increase up to 3300–4000 cm^{-1} .

Summing up both theoretical and experimental results presented above, we can conclude that spectral properties of PBP salts are mainly determined by the interaction between the solvent molecules and electrophilic centers of the dyes studied and by stabilization of electron density localization, which is typical of PBP salts in their S_0 and S_1 states, owing to the influence of solvent molecules. As a result, the nucleophilic solvation leads to more significant lowering of energy of the S_0 state in comparison with the non-relaxed excited $S_1^{\text{non-relax}}$ state and the relaxed one in respect of the non-relaxed ground $S_0^{\text{non-relax}}$ relax state. It causes the hypsochromic shifts observed in absorption and, consequently, the bathochromic shifts in the PBP salts fluorescence spectra.

In addition to the correspondence of the theoretical and experimental data, used as arguments in support of our solvation model, there are some other facts confirming our description of the spectral behavior of PBP salts. Neither solvatochromism nor solvatofluorochromism for PBP salts were observed in the aromatic solvents, even in those exhibiting high nucleophilicity: benzonitrile, ethylbenzoate, dibenzyl ether and pyridine. The same behavior was found elsewhere for several cationic cyanine dyes, whose interaction with solvent molecules was studied by means of the NMR method [30,31]. The solvation of organic cations in the aromatic solvents appeared to be mainly of the dispersion rather than the nucleophilic type.

The influence of nucleophilic solvation upon fluorescence quantum yields of PBP salts.

1. ***Spin-orbital interaction effect.*** Our calculations carried out for isolated PBP cations have shown the $\pi\pi^*$ origin of their lowest singlet and triplet excited states. This fact allows us to relate the compounds investigated to the V spectral-luminescent group according to the classification of Nurmukhametov-Plotnikov-Shigorin [26,32,33].

The singlet and triplet states of the $n\pi^*$ and $\sigma\pi^*$ type are of higher energy than low $\pi\pi^*$ type excited states. Therefore, very efficient intersystem crossing processes between the states of different orbital nature [25,33] (El-Sayed rule [34]) do not influence PBP salts emission properties. In some cases, the increase in the intersystem crossing efficiency between high energy states of the $n\pi^*$, $\sigma\pi^*$ and $\pi\pi^*$ type in PBP salts can be enhanced by excitation to higher singlet levels. In this case, the quantum yields sometimes tend to decrease [33]. The only exception among the investigated PBP salts is nitro substituted compound V. Its lowest unoccupied molecular orbital of the n-type is located on the NO_2 fragment. Because of the $n\pi^*$ origin of the S_1 state of cation V, the intersystem crossing is more efficient and, as a result, nitro-substituted PBP salts do not fluoresce. Another channel of radiationless deactivation, owing to the internal conversion $S_1 \rightarrow S_0$, is also unlikely, because of the $S_0 \rightarrow S_1$ transition energy in the PBP salts spectra exceeds by 1.5 eV “critical value”. Only in the case of lower $S_0 \rightarrow S_1$ transition energy the internal conversion becomes the main source of radiationless dissipation for most organic compounds [35,36]. The main reason of relatively low quantum yields of the fluorescent compounds belonging to the V spec-

tral group is the intersystem crossing process between their S_1 ($\pi\pi^*$) state and the underlying triplet ones, which are also of $\pi\pi^*$ origin. Such intersystem crossing rate constants are usually lower or equal to the radiation rate constants (k_f) [37]. If we assume the intersystem crossing to be the main radiationless deactivation channel of the excited molecules of PBP salts ($k_d \approx k_{ST}$), it is possible to evaluate the fluorescence quantum yields by using equation (3). Such an approach was successfully applied to the adequate theoretical description of the luminescent properties of several oxazolic fluorophores [33,38]. In our case, the analysis of fluorescent PBP salts properties should include besides the structural and energy levels of PBP cation, its interaction with nucleophilic solvents discussed in the previous section of this paper. We thus decided to analyse the spin-orbital interaction in the above-mentioned solvate complexes using the same solvation models and its effect on the fluorescence of PBP salts. Another important factor directly connected with the nucleophilic solvation of the investigated compounds is the growing molecular lability owing to decreasing the interfragmental bond order in the solvated S_1 state. The influence of this effect on the quantum efficiency of the PBP salt emission will be discussed below.

2. Substituents influence on spectral properties of PBP salts. Our calculations carried out for non-solvated cations revealed that the quantity of triplet states, the energy of which is lower than that of fluorescent S_1 level, varies from 3 to 5 depending on the nature and positions of substituents in PBP cations. In all cases the triplet T_1 and T_2 levels lie far apart from S_1 , hence the intercrossing conversion is insignificant and does not influence the fluorescent properties of PBP cations. The relative arrangement of S_1 and the nearest triplet levels of **I**, **II**, **VI**, **VII** are illustrated in Fig. 7. In the remaining salts studied, except **V**, their excited energy levels are similarly located. The calculated β_{ii}^2 and F_{1i} parameters (Eq. 1) determining the rate of the intersystem crossing are listed in Table 4. The analysis of Schemes given in Fig. 7 and the numerical data in Table 4 show that intersystem crossing efficiency in **II**, **III**, **VII** excited PBP cations substituted in the lateral phenyl ring is due to the interaction of S_1 and T_3 states. **II** and **III** are characterized by relatively low β_{ii}^2 values and by the high energy gap between S_1 and T_3 levels. In the case of **VII**, S_1 and T_3 states are arranged fairly close to each other, but their matrix element of the spin-orbital coupling operator is typically low. As a result, k_{ISC} values calculated for these cations are comparable with k_f , this fact being responsible for high emission efficiency, $\phi \approx 0.3-0.7$, in dichloromethane. For PBP cations, which are substituted only in benzopyrylium moiety (e.g. **VI**), the most effective intersystem crossing is expected to be between S_1 and two triplet levels, T_3 and T_4 . The energy gap between S_1 and T_4 is low, however rather high β_{ii}^2 values result in $10^8 \text{ s}^{-1} k_{ISC}$ (intersystem crossing rate constants). Thus, fluorescence efficiency of these compounds is comparable to that of **II** and **III**. The unsubstituted **I** PBP cation, unlike the above compounds, is characterized by more effective spin-orbital interaction between its fluorescent state and underlying triplet levels. The main contribution to the intersystem crossing rate is stipulated by three triplet levels: T_3-T_5 . The most important of them (up to 63 per cent of the total ISC efficiency) is the $S_1 \rightarrow T_3$ radiationless channel. Finally, the radiationless decay rate for **I**

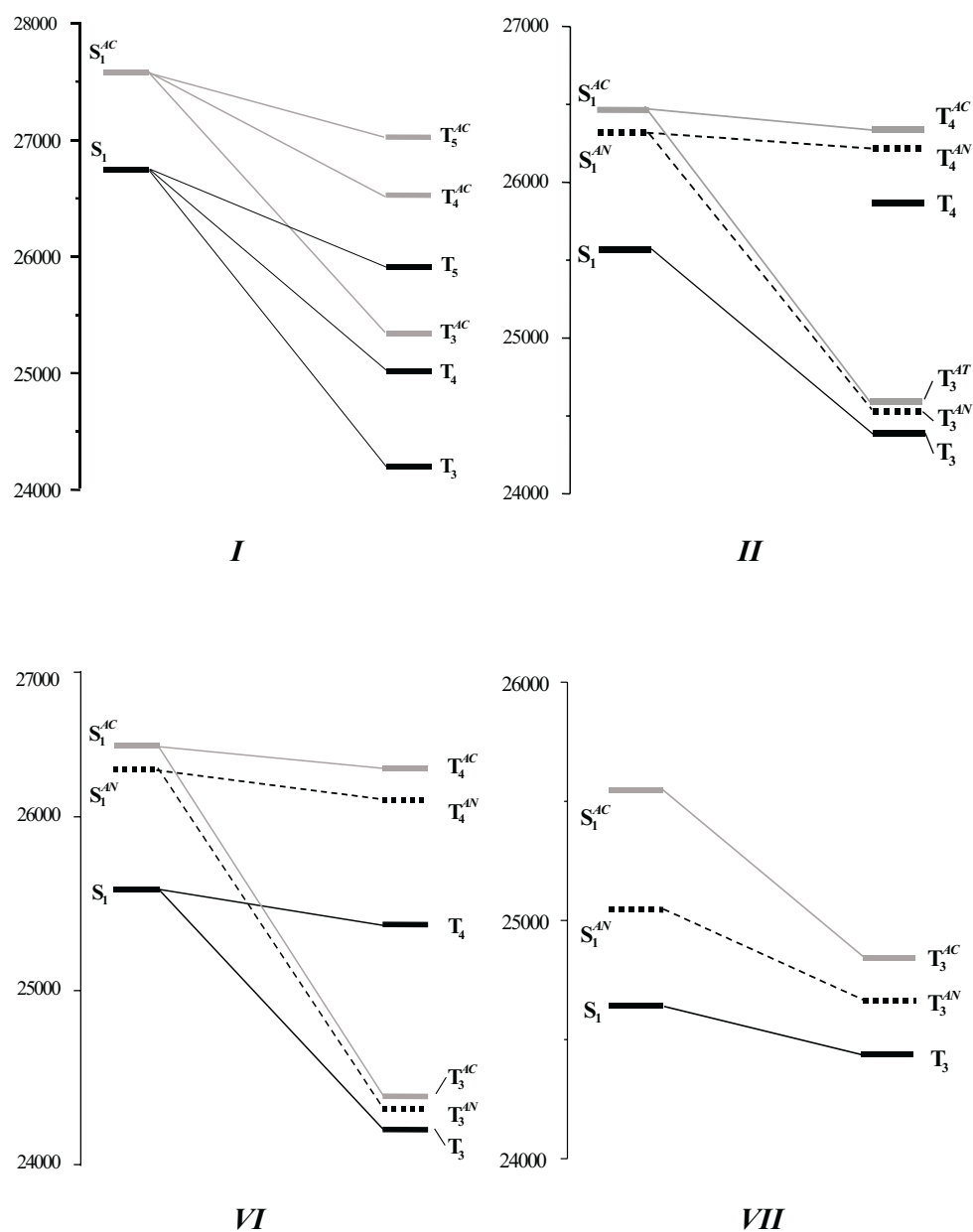


Figure 7. Calculated energies of several lowest excited singlet and triplet levels of the *I*, *II*, *VI*, *VII* PBP cations and energies PBP cation solvates in acetonitrile (S^{AC} , T^{AC}) and acetone (S^{AN} , T^{AN}).

compound exceeds the emission rate by almost one order of magnitude, while the theoretical fluorescence quantum yield is not more than 0.1. The experimental *I–IV*, *VI*, *VII* quantum yields in dichloromethane (Table 4), *i.e.* without nucleophilic solvation,

correspond to our theoretically predicted estimation. Moreover, theoretical and experimental conformity of the ϕ value for chlorine substituted **IV** allows us to propose the analogous scheme of primary photophysical processes.

Table 4. Calculated quantum yields of the PBP salts for the media of various nucleophilicity*.

Cation	Solvent	B	F _{ii}	$\beta_{ii}^2 \cdot 10^3$	$k_d \cdot 10^{-8}$	f	$K_r \cdot 10^{-8}$	ϕ	ϕ_{exp}							
I	Dichloromethane	23	0.61 (S ₁ -T ₃)	2.23	28.94	0.698	3.08	0.10	0.14							
			0.71 (S ₁ -T ₄)	1.94												
			0.85 (S ₁ -T ₅)	5.40												
	Acetonitrile	160	0.63 (S ₁ -T ₃)	4.02	29.59	0.676	3.14	0.09	0.10							
			0.73 (S ₁ -T ₄)	0.27												
			0.88 (S ₁ -T ₅)	5.41												
Acetone	224	0.64 (S ₁ -T ₃)	4.06	32.50	0.673	3.17	0.09	0.08								
		0.80 (S ₁ -T ₄)	0.15													
		0.89 (S ₁ -T ₅)	6.19													
II	Dichloromethane	23	0.79 (S ₁ -T ₃)	1.94	6.05	0.897	3.05	0.33	0.17							
			Acetonitrile	160						0.70 (S ₁ -T ₃)	1.93	27.29	0.873	3.17	0.10	0.003
										0.98 (S ₁ -T ₄)	5.67					
	Acetone	224			0.68 (S ₁ -T ₃)	1.90	28.64	0.872	3.20	0.10	0.004					
			0.98 (S ₁ -T ₄)	6.08												
			VI	Dichloromethane	23	0.76 (S ₁ -T ₃)						0.60	7.89	0.756	2.80	0.26
0.97 (S ₁ -T ₄)	1.59															
Acetonitrile	160	0.68 (S ₁ -T ₃)				0.64	6.57	0.739	2.91	0.31	0.23					
		0.96 (S ₁ -T ₄)		1.28												
		Acetone		224	0.66 (S ₁ -T ₃)	0.70						6.22	0.731	2.90	0.32	0.22
0.95 (S ₁ -T ₄)	1.17															
VII	Dichloromethane		23		0.96 (S ₁ -T ₃)	0.42	1.59	0.915	3.39	0.68	0.85					
		Acetonitrile		160	0.89 (S ₁ -T ₃)	0.58						2.04	0.910	3.58	0.64	0.04
					Acetone	224										

*Parameter names see in formulae 1–3.

3. The influence of nucleophilic solvation on intersystem crossing in PBP cations.

As the solvent relaxation rate exceeds the intersystem crossing rate by several orders of magnitude [39], we have used optimized molecular geometries of structurally and solvent relaxed solvates for evaluation of radiationless singlet-triplet transition efficiency. On the analogy of our substituent effect investigation, only the nearest to fluorescent state T₃-T₅ triplet levels have been taken into account. The energy changes of the above triplet states for **I**, **II**, **VI**, **VII** influenced by nucleophilic solvation due to acetonitrile and acetone molecules are shown in Fig. 7. According to our findings, the solvation is not only responsible for energy changes in the interacting singlet and triplet levels; it possesses an individual sensitivity to solvent effects. It also results in

changing spin-orbital coupling efficiency (β_{ii}^2) and intensity of the long-wavelength absorption band determining changes in k_f values. The calculated F_{ii} , β_{ii} and f parameters for several PBP cations in acetone and acetonitrile are listed in Table 4. The analysis of our theoretical data enables us to predict changes in fluorescence efficiency of the investigated PBP salts caused by the solvent nucleophilicity. Therefore, we expect compound **I** to further decrease in its low quantum yield in nucleophilic solvents. The calculated **VI** and **VII** quantum yields do not depend on surrounding nucleophilicity, because their intersystem rate constants do not change significantly during nucleophilic solvation. The compound **II** of all discussed above is the most representative. As clearly seen in Fig. 7b, the inversion of the excited S_1 and T_4 levels is caused by a solvation. This results in a significant increasing of spin-orbital coupling: in this case the predicted rise of k_{ISC} should be about 5 times of its magnitude. In such a case the fluorescence quantum yield is expected to lose 30 per-cent of its initial value in the non-nucleophilic solvents. The experimental data obtained for **I** and **IV** compounds confirm our theoretical prediction. The low quantum yield of **I** in dichloromethane noticeably decreases in nucleophilic solvents, while **IV** compound shows a tendency to increase ϕ when the solvent nucleophilicity increases. As far as **II**, **III** and **VI** are concerned, quantum yields decrease while changing solvents from non-nucleophilic to nucleophilic ones. Moreover, for **II** and **III** cations the fluorescence efficiency value is lower than that predicted in our theoretical evaluations (inversion of S_1 and T_4 excited levels). The analysis of the π -electron structure and π -electron density redistribution in solvated **II**, **III** and **VII** PBP cations in the excited state predicts noticeable lowering or disappearing of π -conjugation between their benzopyrylium and lateral phenyl moieties. Hence, a significant decrease of quantum yields of these compounds in solvents of high nucleophilicity is supposed to be caused by a decrease in their molecule rigidity in the S_1 state, as well.

4. Rigidity of solvated PBP cations and spin-orbital interaction. The intersystem crossing rate constants have been calculated for the planar model structures of solvated PBP cations listed in Table 4. In the true cations the lateral phenyl ring participates in rotational vibrations around the single bond connecting it with benzopyrylium moiety. Thus, the total time of PBP cation existence in non-planar geometry exceeds that of the planar geometry. The above-mentioned non-planarity of excited PBP cations causes a significant increase of the spin-orbit interaction between the S_1 state and lower triplet one. In non-planar molecules the $\pi\sigma$ contribution to the interacting levels grows, which results in the dramatic increasing of β_{ii} values. Finally, the more the amplitude of the rotational vibrations, the higher is the k_{ISC} rate constants and the lower their quantum yields. Our model calculations for **II** (Fig. 8) show that the increase of the angle between benzopyrylium and phenyl moieties planes (Θ) from 0° to 20° affords a 4–5 times k_{ISC} increase and decrease in fluorescence quantum yield from 0.33 to 0.001. For $\Theta = 50^\circ$ k_{ISC} is 90 times higher than that corresponding to a planar molecule, while ϕ is 66 times lower. The assumption that intermolecular lability is an important factor determining quantum yield values is confirmed by Hauke [7]. Even in non-nucleophilic and low polar dichlorometane

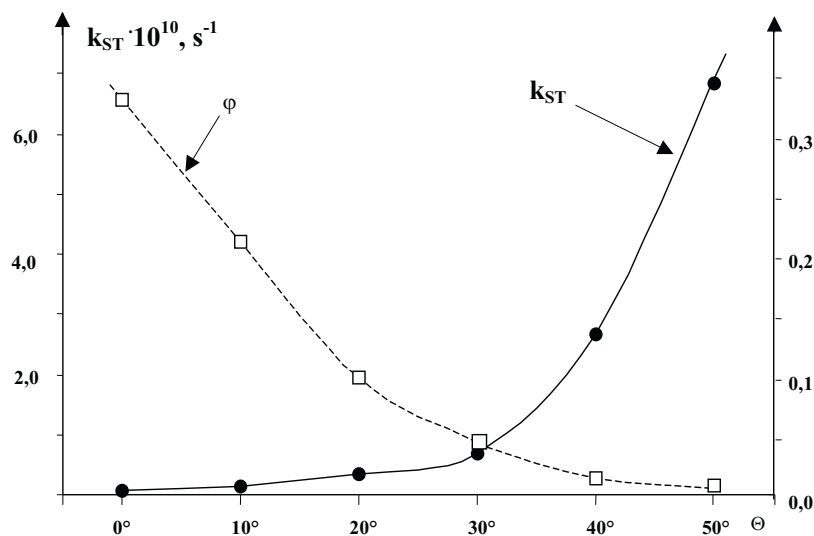


Figure 8. Plot of calculated intersystem crossing rate constant and fluorescence quantum yield (compound **II**) against the torsional angle between the benzopyrylium and lateral phenyl moieties.

quantum yields of rigid PBP cations, where rotational high amplitude motion is impossible or hindered, are usually higher in comparison with those of non-rigid compounds exhibiting similarities to π -electron structures. Apparently, the main factor, capable of decreasing the amplitude and frequency of the rotational vibrations discussed, is the π -conjugation between benzopyrylium and phenyl moieties which can be quantitatively characterized by the order of interfragmental single bond. As shown in Table 3, the nucleophilic solvation can result in noticeable changing of the bond orders of the excited investigated cations.

Some increase of the interfragmental single-bond order in the excited state of **VI** leads to an increase of molecular rigidity and lowering of rotational vibration amplitude. Further increase in the order of the bond mentioned and, consequently, of **VI** PBP cation rigidity takes place under the influence of nucleophilic solvation. As a result, the increase of the fluorescence quantum yield of **VI** is observed in moving to more nucleophilic solvents.

The significant decrease of the π -order of the interfragmental bond in **I** and **IV** PBP cations, and moreover, actual disappearance of the π -order of this bond for **II**, **III** and **VII** cations emphasize the dramatic lowering of their ability to fluoresce in nucleophilic solvents.

The probable lack of π -conjugation between benzopyrylium and phenyl moieties in several PBP cations can cause the rotation of the lateral phenyl ring at the 90° angle and the formation of TICT-like structures. It was not our purpose to investigate such a possibility here, though, it should be noted that if such conformation could be formed, it should be of a non-fluorescent nature owing to the extremely high probability of spin-orbital interaction.

CONCLUSIONS

Results of this paper show that the use of even simplest models for PBP cations with solvent molecules enable to describe and predict sufficiently correctly changes in the spectral parameters of the compounds investigated in media of various nucleophilicity. The analysis of our theoretical and experimental data urged us to propose the following mechanism of solvent nucleophilicity influence on the spectral properties of PBP salts:

- The formation of complexes with a nucleophilic solvent results in additional stabilizing of the relaxed S_0 and S_1 states, and is responsible for the hypsochromic shift observed in absorption spectra and for the bathochromic shift in the fluorescence spectra.
- The quantum yield changes in different nucleophilicity media are controlled by the efficiency of the intersystem crossing in PBP cations under the influence of nucleophilic solvation. There are two ways of such influence: the *direct* one stipulated energy changes in S_1 and T_1 levels, and *indirect* one resulting from the increase or decrease of spin-orbital interaction efficiency, caused by changes in the structure rigidity of solvated PBP cations. In both cases the intersystem crossing rate constant depends on the nature and position of substituents, that determine the direction of PBP cations charge transfer in the excited state.

Finally, we would like to note that the described mechanisms can be widely used and, hence be applied to describe the spectral properties of any other aromatic cations.

REFERENCES

1. Michailov N., Deligeorgiev T. and Tyutyulkov N., *Opt. Quant. Electronics*, **18**, 19 (1986).
2. Timberlake C.F. and Bridle P., Anthocyanins. in: Developments in Food Colours, Ed. Applied Science, London 1980, pp. 115–149.
3. Amic D. and Trinajstic N., *Bull. Soc. Chim. Belge*, **100**, 527 (1991).
4. Davidovic-Amic D., Amic D. and Trinajstic N.J., *Chem. Soc. Perkin Trans.*, **2**, 1933 (1992).
5. Lietz H., Hauke G., Czerney P. and John B., *J. prakt. Chem.*, **338**, 725 (1996).
6. Pina F., Melo M.J., Maestri M., Ballardini R. and Balzani V., *J. Am. Chem. Soc.*, **119**, 5556 (1997).
7. Hauke G., Czerney P., Igney C. and Hartmann H., *Ber. Bunsenges. Phys. Chem.*, **93**, 805 (1989).
8. Czerney P., Graneß G., Brickner E., Vollmer F. and Rettig W., *J. Photochem. Photobiol. A: Chem.*, **89**, 31 (1995).
9. Rettig W., Majenz W., Lapouyade R. and Hauke G., *J. Photochem. Photobiol. A: Chem.*, **62**, 415 (1992).
10. Markovichi D., Sigal H., Ecoffet C., Millié Ph., Charra F., Fiorini C., Nunzi J.M., Strzelecka H., Veber M. and Jallabert C., *Chem. Phys.*, **182**, 69 (1994).
11. Lampre I., Marguet S., Markovitsi D., Delysse S. and Nunzi J.M., *Chem. Phys. Lett.*, **272**, 496 (1997).
12. Lahmadi F., Valat P., Simalty M. and Kosannyi J., *J. Res. Chem. Intermed.*, **21**, 807 (1995).
13. Roshal A.D., Grigorovich A.V., Minayev D.Yu. and Egorova S.I., *Funct. Mat.*, **4**, 584 (1997).
14. Luzanov A.V., *Usp. Khim.*, **49**, 2086 (1980).
15. Mitina V.G., Ivanov V.V., Ponomariov O.A., Sleta L.A. and Shershukov V.M., *Mol. Eng.*, **6**, 249 (1996).
16. Rotkiewicz K., Grellman K.H. and Grabowski Z.R., *Chem. Phys. Lett.*, **19**, 315 (1973).
17. Roshal A.D., Minajev D.Y., Koval V.L. and Novikov A.I., *Opt. Spectr.*, **85**, 772 (1998).
18. Lippert E., *Z. phys. Chem.*, **B.6**, 125 (1956).

19. Koppel I.A. and Payu A.I., *Reactivity of Organic Compounds*, **11**, 121 (1974).
20. Czreny P. and Hartmann H., *J. prakt. Chem.*, **323**, 505 (1983).
21. Weissberger A., Proskauer E.S., Riddik J.A. and Toops E.E., *Organic Solvents: Physical Properties and Methods of Purification*, Interscience Publishers Inc., NY, London, 1955, 519 p.
22. *The Methods of Preparation of High Purity Solvents*, NIITEKHIM Edit., Moscow, 1986, p. 7, (in Russian).
23. Rabek G.F., *Experimental Methods in Photochemistry and Photophysics*, Part. 2, John Wiley & Sons Ed., Chichester-NY-Brisbane-Toronto-Singapore, 1982, p. 775.
24. Pedash Yu.F., Umansky V.E. and Ponomariov O.A., *Funct. Mat.*, **4**, 138 (1997).
25. Muldahmetov Z.M., Minayev B.F. and Ketsle G.A., *Optic and Magnetic Properties of the Triplet State*, Nauka, Alma-Ata, 1983, (in Russian).
26. McGlynn S.P., Azumi T. and Kinoshita M., *Molecular Spectroscopy of the Triplet State*, Prentice Hall Ed., Englewood Cliffs, 1969.
27. Shigorin D.N., *Russian J. Phys. Chem.*, **51**, 1115 (1977).
28. Sheyhet I.I. and Simkin B.Y., *J. Strukt. Khim.*, **29**, 84 (1988).
29. Simkin B.Y. and Sheyhet I.I., *Quantum Chemical and Statistical Solution Theory: Calculation Methods and Their Applications*, Moscow, Khimija, 1989, 79–83.
30. Ishchenko A.A., Svidro V.A. and Derevianko N.A., *Dyes and Pigments*, **10**, P. 85 (1989).
31. Wöhnert M., Dähne S. and Radeaglia R., *Adv. Mol. Relax. Interact. Processes*, **11**, 263 (1977).
32. Shigorin D.N., *Russian J. Phys. Chem.*, **51**, 1115 (1977).
33. Mayer G.V., *Photophysical Processes in Organic Molecules and Their Laser Generate Capacity*, Ed. of Tomsk University, Tomsk, 1992, 265 p. (in Russian).
34. El-Sayed M.A., *J. Phys. Chem.*, **69**, 1294 (1965).
35. Plotnikov V.G. and Dolgih V.A., *Opt. Spectr.*, **43**, 882 (1977).
36. Yermolayev V.L. and Sveshnikova E.B., *Acta Phys. Polon.*, **34**, 771 (1968).
37. Plotnikov V.G. and Dolgih V.A., *Opt. Spectr.*, **44**, 450 (1978).
38. Pedash Yu.F., Babich E.N. and Ponomariov O.A., *Opt. Spekr.*, **69**, 313 (1990).
39. Gard S.K. and Smyth T.P., *J. Phys. Chem.*, **69**, 1294 (1965).