PHOTOPHYSICS OF PHENOXAZINE AND ITS FLUOROSUBSTITUTED ANALOG

O.N. Chaikovskaya, I.V. Sokolova, Yu.P. Morozova, and A.N. Nikonova

*V.P. Kuznetsov Siberian Physicotechnical Scientific—Research Institute
at the State University, Tomsk*

Spectral behaviors of the luminescence of phenoxazine and its fluorosubstituted analog are compared using the methods of quantum chemistry and electron spectroscopy. Fluorination causes a displacement of the absorption bands towards longer wavelengths. The fluorine atoms were shown to be inactive directly in the process of a charge transfer in a molecule, giving rise only to the electron—acceptor induction effect on the intermolecular processes. This results in changing the molecular geometry and its acid—based properties.

At present a lot of data can be found in the literature on the influence of substitution of hydrogen atoms for the fluorine atoms in the molecules of organic compounds on their biological activity, photochemical resistance, and color. However, it should be noted that in spite of a considerable progress, photophysical properties of the fluorinated molecules are yet purely studied. Cyanine dyes with the fluorinated substitutes in the heterocyclic cores are investigated best of all.[1] One of the topical problems of the molecular spectroscopy now is the relation of the optical characteristics of molecules to their chemical structure. This resulted from an extensive use of the polyatomic molecules as the components of active media for lasers operating on vapors and solutions of organic compounds. This, in turn causes the necessity of seeking for synthesizing of new molecular structures effective for lasing.

Phenoxazines make a vast class of laser dyes. Investigation of the spectral behavior of the luminescence of phenoxazine (Ph—3) and its fluorosubstituted analog (Ph—Ph—1) was carried out using the quantum chemistry methods (the method of partial ignorance of the differential overlap with the spectroscopic parameterization and the electrostatic potential method (ESPM)) and the electron spectroscopy method. The structure formulas of phenoxazines are presented in Fig. 1. The investigated dyes were synthesized at the Institute of Organic Chemistry (Novosibirsk) under T.N. Gerasimova's supervision. Figure 2 shows the diagram of the energy levels of the molecules under study. Experimentally observed characteristics of the transition $S_0 \rightarrow S_1$ in these compounds are best of all calculated using our version of the calculational algorithm we have obtained assuming a plane geometry of molecules with a fracture of the central ring. This method was first proposed by Artyukhov[2,3] for xanthine dyes. This group of dyes can be classified according to Nurmukhametov—Plotnikov—Shigorin's classification as the V—type of compounds. Since on the ends of molecules there are strong donor—acceptor groups, they can have strong dipole moments (see Fig. 1).

Orbital nature of the first excited state of the molecules is the same and it can be treated to be of $\pi\pi*$ type. This state is formed by the molecular orbitals localized mainly on the nitrogen atoms of the central ring and of the diethylamine group. Distribution of the charges over the atoms taking part in formation of the S_1 state is shown in Fig. 1. One can see from this figure that for the

transition from S_0 to S_1 state there occurs an electron density transfer from nitrogen of the diethylamine group and carbonyl oxygen to the atoms of nitrogen and oxygen of the ring with the prevailing charge transfer from nitrogen atom of diethylamine group to the heterocyclic nitrogen. Because of the central ring fracture there appears the σ— and π—type of mixing in the orbital nature of the highest excited states which is characteristic of the nonplanar molecules.[5] The problem of difference between the molecules Ph—3 and Ph—Ph—1 should be considered in more detailed. Three atoms of fluorine that substitute three atoms of hydrogen in the Ph—3 molecule make the difference between these molecules. Fluorination process results in the displacement of the absorption bands towards longer wavelengths as well as in the redistribution of the electron density among heteroatoms.
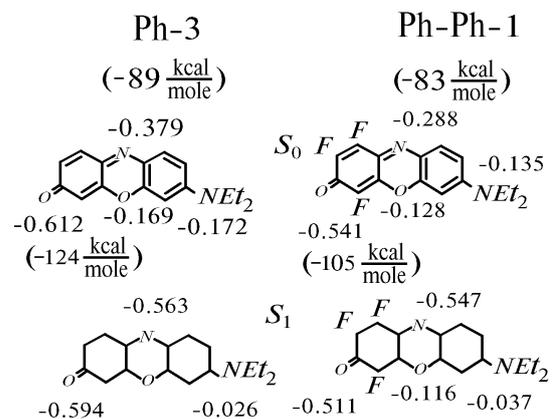

FIG. 1. *Structure formulas of the molecules of phenoxazines and distribution of the electron density (minima of values of the electrostatic potential are given in parenthesis).*

It should be noted that in this case the fluorine atoms affect slightly the absorption spectrum in comparison with the dyes in which the fluorine atoms are incorporated into a polymethine chain and behaves like an electron—donor substituent.[1] It is obvious that in the Ph—Ph—1 molecule the fluorine atoms do not take part in the process of a charge transfer within a molecule directly but their

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electron—acceptor induction effect on the intramolecular processes in its turn results in changing the spectral characteristics of the molecule (see Table I). In this paper the constants of the rates of the intramolecular processes κ_r, κ_{S_1}, κ_{S_0}, κ_{ST} were estimated out following the technique developed by Plotnikov and Mayer.[7,8]

TABLE I. *Spectral characteristics of the phenoxazine luminescence (λ_l is the wavelength of the dye lasing when pumped with an eximer laser emitting at the wavelength of 308 nm and φ is the quantum yield of luminescence).*

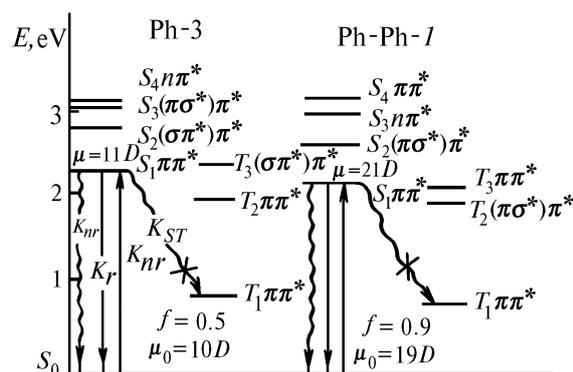| Molecules	κ_r, s^{-1}	κ_{S_1, S_2}, s^{-1}	κ_{ST}, s^{-1}	φ	λ_{le}, nm	E_{eff}, %
Quantum—chemical calculation						
Ph—3	$1.2 \cdot 10^8$	$2 \cdot 10^7$	$0.3 \cdot 10^{-3}$	0.2		
Ph—Ph—1	$2 \cdot 10^8$	$3 \cdot 10^7$	$0.33 \cdot 10^{-3}$	0.07		
Experiment						
Ph—3 in ethanol	$1.8 \cdot 10^8$ (Ref. 6)	$8 \cdot 10^8$ (Ref. 6)	—	0.27	655	15
Ph—Ph—1 in ethanol	$1.2 \cdot 10^8$ (Ref. 6)	$1.7 \cdot 10^9$ (Ref. 6)	—	0.08	668	3
Ph—3 in toluene	—	—	—	0.6	617	10^{-3}
Ph—Ph—1 in toluene	—	—	—	0.3	654	13

FIG. 2. *Diagram of intramolecular processes in the molecules under study. E is the energy of electron states, μ is the dipole moment in the Debye units, and f is the oscillator strength.*

Proceeding from the aforementioned, one can state that the processes of light absorption and deactivation occur in these molecules as follows: the maxima of an absorption spectrum are formed by $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, and $S_0 \rightarrow S_9$ transitions then a fast process of an internal conversion $S_n \rightsquigarrow \rightarrow S_1$ occurs. Since the constant of intercombination conversion is considerably less than the constants of radiative atomic decay and internal conversion and also taking into account a comparatively low quantum yield of the fluorescence, one can conclude that the main way of the S_1—state deactivation in phenoxazines is due to the process of internal conversion $S_1 \rightsquigarrow \rightarrow S_0$. However, the $\sigma-$ and $\pi-$ displaced T states close to S_1 state do not exclude the processes of the $S \rightsquigarrow \rightarrow T$ conversion.

Some disagreement between the experimental and calculational values of the quantum yields of the fluorescence of the Ph—Ph—1 substance can result from changing the molecule conformation which is not taken into account in calculations. The geometry of the Ph—Ph—1 molecule becomes more plane than the geometry of the Ph—3 molecule due to introduction of the fluorine atoms.

The use of the ESP method made it possible to determine the most probable places for accepting the protons by phenoxazines in the ground and excited states. For the Ph—3 and Ph—Ph—1 molecules the most deep minima of the electrostatic potentials can be observed near the oxygen atoms of the C=O group and nitrogen atoms of the ring (see Fig. 1). These results make it possible to assume that the formation of hydrogen bonds or complexes with the proton transfer can be performed at these centers. The results show that the fluorination of molecules leads to a decrease of the electrostatic potentials on the carbonyl oxygen and ring nitrogen, i.e., the probability of protolytic reactions descreases at these centers. Thus, the process of incorporating the fluorine atoms into a molecule changes not only its geometry but also the acid—based properties of a molecule that, in its turn, results in changing the spectral characteristics of luminescence of the dyes (see Table II).

TABLE II. *Positions of maxima of the absorption bands (λ_a) and fluorescence (λ_f) of the Ph—3 and Ph—Ph—1 molecules in different solvents.*

Solvent	Ph—3		Ph—Ph—1	
	λ_a, nm	λ_f, nm	λ_a, nm	λ_f, nm
Toluene	500	605	540	635
Ethanol	560	635	570	650
Propanol	555	630	570	650
Isopropanol	550	625	570	650
Butanol	555	650	575	670
Cyclohexane	490	570	520	585
Dimethylsylphoxide	555	640	540	630

When accepting protons the phenoxazines take larger dipole moments in the S_0 and S_1 states and there occurs a redistribution of the electron density among the heteroatoms in a molecule what decreases the charge on the oxygen atoms of the C=O group and on the nitrogen atoms of the diethylamine group. For the Ph—3 molecule there occurs a growth of the oscillator strength of the $S_0 \rightarrow S_1$ transition from 0.5 to 0.8, while for the Ph—Ph—1 molecule it decreases from 0.9 to 0.7. The orbital nature of the S_1 state does not change and remains to be of $\pi\pi*$ type. Molecular orbitals taking part in formation of this state are localized on the nitrogen atoms of the ring and diethylamine group. The contribution coming from carbonyl oxygen becomes negligible.

The solvatochromic effect, in the case of these molecules is determined by their ability to form the hydrogen bonds. The base property (ability to accept a proton) of the heteroatoms involved in the end groups depends on the lightness with which the cloud of the pair of undivided electrons of these atoms is allowed to be a part of a common oscillating π—electron system.[9] Since the molecular orbital of n—type of a phenoxazine molecule accepting a proton mostly localized on the oxygen atom of the C = O group is deeper the accepted proton takes the C = O group out of coupling with the rest molecule what decreases the base ability of this group. This, in turn, increases the base property of the ring nitrogen. Thus, in real situation, depending on a solvent, the complex H^+ ... O=C< in its excited state, can strengthen or, on the contrary, decay.

Analysis of data obtained based on quantum–chemical calculations has revealed lowering of the ability of the fluorinated–molecules to the formation of the H–type bonds.

Decrease of the intermolecular interaction activity at fluorination is experimentally observed as a decrease of the quantum yield of fluorescence of a Ph–Ph–1 molecule in a nonplanar solvent compared to that in a polar solvent.

Thus, it becomes clear that the fluorination stabilizes molecular systems. However, the use of phenoxazines as active media of dye lasers requires proper matching of a solvent. It would be better to use phenoxazines in polar solvents, while its fluorinated analog in nonpolar solvents. Photochemistry of these molecules is needed for additional studies.

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