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# SPECTRAL AND LUMINESCENCE PROPERTIES OF DERIVATIVES OF 2-ARYL[9,10]PHENANTHROXAZOLE

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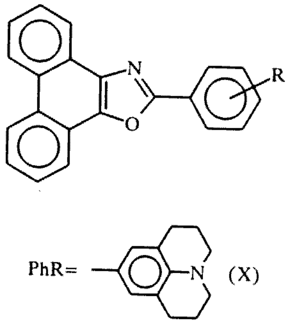
*Certain 2-aryl derivatives of [9,10]phenanthroxazole have been synthesized and their spectral and luminescence properties have been investigated. It has been shown that the introduction of acceptor substituents into the para position of the 2-phenyl radical changes the nature of the fluorescence state, resulting in a nearly twofold increase of the rate constant of fluorescence emission and a 50% increase of the quantum yield of fluorescence. Special features of the spectral and luminescence properties have been examined for derivatives with an intramolecular hydrogen bond (aryl = o-hydroxyphenyl) and with considerable steric hindrance (aryl = 9-anthryl).*

Aryl derivatives of oxazole are finding extensive applications as effective luminophors in the violet and blue range of the spectrum, and also as activating additives in liquid and plastic scintillators [1, 2]. However, there is still a critical problem in increasing the resistance to photodegradation and the radiation resistance of fluorescing compositions based on these compounds [3]. One of the important approaches in solving of this problem is the synthesis of new derivatives of oxazole with larger $\pi$-conjugated systems [3]; from the standpoint of improving the stability, annelation of benzene rings appears to be the most promising, as this will produce molecules with a more rigid structure, frequently having a higher level of fluorescence characteristics [2].

In view of this background, we have synthesized certain derivatives of 2-aryl[9,10]phenanthroxazole and have carried out theoretical and experimental studies of the spectral and luminescence properties of the synthesized compounds.



Here, R, the substituent in the p-position, is H (I), Cl (II), F (III), CN (IV), $COOCH_3$ (V), $NO_2$ (VI), $C_6H_5$ (VII), $OCH_3$ (VIII), $N(CH_3)_2$ (IX), and also compounds in which the $C_6H_5R$ has been replaced by o-hydroxyphenyl (XI) or 9-anthryl (XII).

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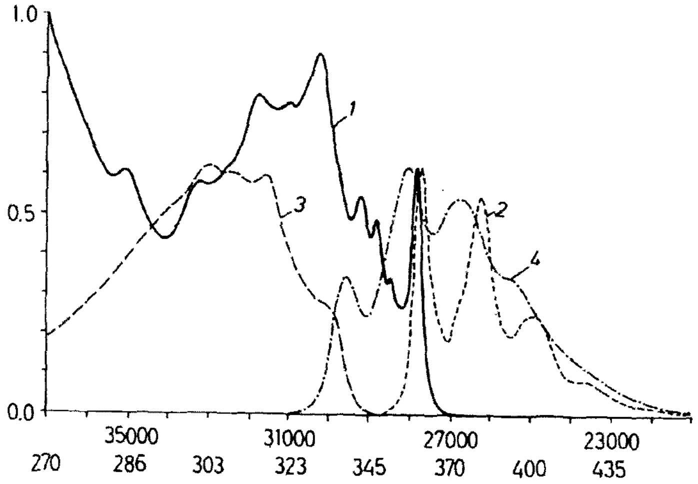


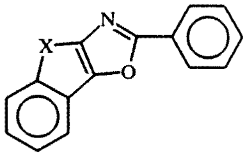
Fig. 1. Absorption and fluorescence spectra of 2-phenyl[9,10]phenanthroxazole (curve 1 for absorption, curve 2 for fluorescence) and 2,5-diphenyloxazole (curve 3 for absorption, curve 4 for fluorescence) in octane. Wavenumbers are in cm$^{-1}$, wavelengths in nm.

If the molecule of 2-phenyl[9,10]phenanthroxazole is represented as the result of annelation of two fragments, namely the phenanthrene and 2-phenyloxazole fragments, we can expect that its spectral properties will be determined by the properties of these basis structures. In order to elucidate the nature of the electronic transitions and describe the genesis of the bands in the absorption spectra of these compounds and the corresponding basis molecules, we have carried out a series of quantum-chemical calculations in the semi-empirical $\pi$-electron approximation PPP CI. For the assignment of transitions and analysis of the redistribution of electron density upon excitation, we used special quantum-chemical indexes: a number defining the localization of electronic excitation on the structurally separated fragments ($L_{fr}$), and numbers defining the intrafragment ($l_A$) and interfragment ($l_{AB}$) charge transfer [4].

The electronic absorption spectra of 2-phenanthroxazole (I) in the 27,000-35,000 cm$^{-1}$ interval consists of a broad band with a distinct vibrational structure (Fig. 1). According to the results of the calculation, this is the envelope of two bands of electronic transitions that are similar in energy and intensity. In Fig. 2 we show calculated absorption spectra of 2-phenyl[9,10]phenanthroxazole, phenanthroxazole, phenanthrene, and 2,5-diphenyloxazole (PPO). This last molecule was included as a model in the possible representation of the molecule I as an analog of PPO with a 5-phenyl radical fixed by a phenylene bridge.

An analysis of the electronic excitation localization numbers shows that the first two electronic transitions in the molecule of 2-phenylphenanthroxazole are largely localized on the oxazolophenanthrene fragment ($L_{fr} > 70\%$). At the same time, the energies and intensities of these transitions are considerably different from the values calculated for the model molecule of phenanthroxazole (Fig. 2). In order to determine the reasons for this discrepancy, we analyzed the energy, symmetry, and character of localization of certain occupied and vacant molecular orbitals that are spectrally important for the molecules of phenanthroxazole and its 2-phenyl derivative. As shown by an analysis of the distribution of the squares of the coefficients in the expansion of the molecular orbitals (MO) on the basis of atomic orbitals (AO), the two highest occupied MO and the two lowest unoccupied MO of phenanthroxazole are weakly perturbed analogs of the corresponding orbitals of the phenanthrene molecule. Accordingly, the long-wave transitions $S_0-S_1$ and $S_0-S_2$ in the spectrum of phenanthroxazole, which are formed with the participation of these MO, should be regarded as weakly perturbed transitions in the spectrum of phenanthrene ($\alpha$- and p-transitions in the nomenclature of Clar [5]). Assignment of the long-wave transitions of 2-phenylphenanthroxazole to the local-phenanthrene type proves to be very arbitrary, in spite of their rather high localization on the phenanthrene fragment and the substantial contribution of the latter to the intrafragment charge transfer ($l_A > 50\%$). This is a consequence of the high localization of the lowest unoccupied orbital of the 2-phenylphenanthroxazole molecule on the 2-phenyloxazole fragment and the relatively high contributions to these transitions from configurations formed with the participation of this MO. Nonetheless, a definite similarity of these transitions (and the excited states formed by these transitions) of 2-phenylphenanthroxazole with the α- and p-transitions of phenanthrene and phenanthroxazole is manifested in experiment, as will be noted below in discussing the fluorescence characteristics of these compounds.

As a consequence of the high degree of localization of the spectrally important MO on the phenanthrene fragment, the molecule of I, at least from the standpoint of spectroscopy, cannot be regarded as an analog of 2,5-diphenyloxazole with a 5-phenyl radical that is fixed rigidly by a phenylene bridge, since the role of the latter is by no means limited to spatial fixation. Let us also note that, owing to the complex configurational composition of the $S_0-S_1$ and $S_0-S_2$ transitions of 2-phenylphenanthroxazole,† a distinct spectroscopic classification cannot be given to this type of molecule, as was done previously for structures of the type



where X is a bridge grouping: CH═CH, N═CH, CO–O, or CO–NH [6].

Our analysis of the orbital nature of the electronic transitions enables us to explain the experimentally observed low-frequency shift of the long-wave absorption band when electron-acceptor substituents are introduced into the para position of the 2-phenyl ring of the molecule of I, and also the very weak influence of electron-donor substituents (in particular the methoxy group) on the position of the long-wave band. Within the framework of simple concepts of perturbation theory, this is explained by the high degree of localization of the lowest unoccupied molecular orbital on the carbon atom in position 4 of the 2-phenyl ring and by the considerably smaller degree of localization of the highest occupied MO on this atom.

In Fig. 1 we show the absorption and fluorescence spectra, in octane, of compound I and one of its model structures — the molecule of 2,5-diphenyloxazole. In Table 1 we have listed the spectral and luminescence characteristics of the various compounds in solvents differing in polarity. Values are given for the positions of the bands in the absorption and fluorescence spectra, the quantum yields, the excited-state lifetimes, and the corresponding calculated values of the rate constants of primary photophysical processes — emission of fluorescence $k_f$ and nonradiative degradation $k_d$. As can be seen from the data of Fig. 1, the rigid structure of the molecules of phenanthroxazole derivatives is responsible for the more distinct manifestation of vibrational structure in the absorption and fluorescence spectra in comparison with those of the analogous derivatives of diphenyloxazole. Moreover, fixation of the benzene radical in position 5 of the oxazole ring of PPO by a phenylene bridge leads to a decrease of internal lability of the molecule, and consequently to a decrease of the Stokes shift and a corresponding increase in the overlap of absorption and fluorescence spectra. (For this reason, in many cases in Table 1, in the interest of comparability of data, instead of $\nu_{max}$ we have listed frequencies of the second minimum in the spectrum of the second derivative of the corresponding absorption or fluorescence spectrum.)

The introduction of substituents into the para-position of the 2-phenyl radical generally leads to a bathochromic shift of the long-wave absorption band and a bathofluoric shift of the emission spectrum. The quantum yield of fluorescence increases slightly upon substitution. In polar solvents, for phenanthroxazole derivatives with acceptor substituents (other than the nitro derivative, the fluorescence of which is completely extinguished as a consequence of the negative influence of low-lying $T_{n\pi}$-levels of the nitro group [7]), long-wave solvatofluorochromic shifts of the emission bands are characteristic; along with this, the vibrational structure becomes less distinct.

We were somewhat surprised by the spectral and fluorescence characteristics of the chloro derivative. For example, the quantum yield of its fluorescence was almost 1.5 times that of the analogous yields for the unsubstituted compound I or its fluoro derivative III; also, the solvatofluorochromic shift of the center of gravity of the fluorescence spectrum when the change was made from octane to dimethylformamide (1170 $cm^{-1}$), was almost double the spectral shifts for compound I (590 $cm^{-1}$) or III (620 $cm^{-1}$). For the chloro derivative, we observed that the vibrational structure of the fluorescence spectrum disappears in polar solvents, as is characteristic for strong acceptor substituents.

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†$S_0-S_1$: 49% ($\chi^{1-1'}$) + 20% ($\chi^{1-2'}$); $S_0-S_2$: 42% ($\chi^{1-1'}$) + 28% ($\chi^{1-2'}$).

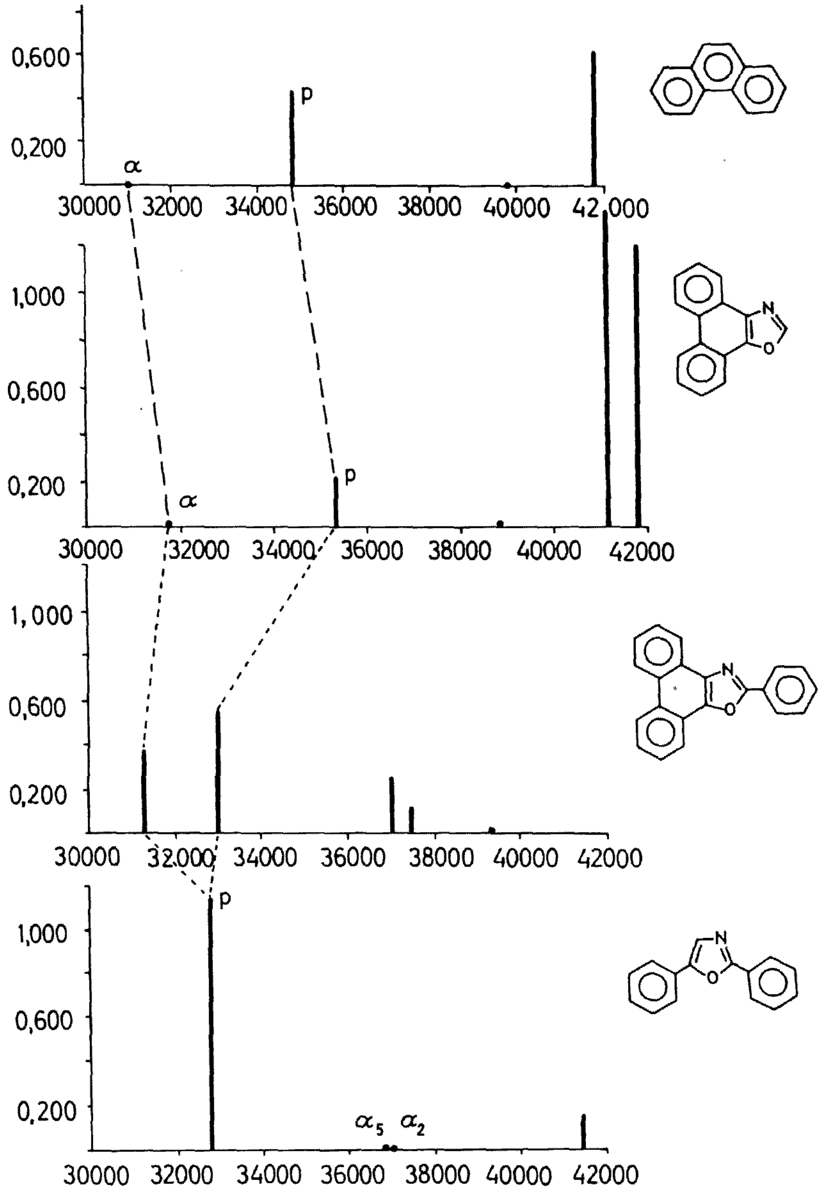

Fig. 2. Absorption spectra of phenanthrene, [9,10]phenanthroxazole, 2-phenyl-[9,10]phenanthroxazole, and 2,5-diphenyloxazole, calculated by SCF PPP CI method.

These facts can be explained by a hypothesis of a change in nature of the fluorescent state. Thus, for compound I and its derivatives with weak donor substituents such as $OCH_3$ or F,† the fluorescent state is similar in nature to the α-type "phenanthrene" state. The introduction of even such a weak acceptor substituent as chlorine results in inversion of the $S_1$ and $S_2$ states of the 2-phenylphenanthroxazole. The $S_0-S_1$ transition, which is similar in nature to p-type states, is allowed, in contrast to states similar in nature to α-type states (this is equally true for the $S_1-S_0$ transition). This situation is manifested experimentally in the series of 2-phenylphenanthroxazole derivatives in the nearly twofold increase of the rate constant of fluorescence emission ($k_f$, Table 1) for compounds with a fluorescence state of the p-type (Cl, CN, $C_6H_5$, etc.) in comparison

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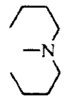
†A fluorine atom introduced directly into the benzene ring manifests acceptor properties, characteristic for the most electronegative element of the periodic system, only within the framework of the induction effect of the substituent; it is a donor within the framework of the conjugation effect, as can be seen for example by comparing its constants $\sigma_m^+$ (+0.352) and $\sigma_p^+$ (−0.247) [8].

TABLE 1. Spectral and Kinetic Characteristics and Rate Constants of Primary Photophysical Processes — Fluorescence Emission and Nonradiative Degradation of Energy of Electronic Excitation — for a Series of Derivatives of 2-Phenyl-[9,10]phenanthroxazole

| Compound | R | Solvent | $\nu_a$, cm$^{-1}$ | $\nu_f$, cm$^{-1}$ | $\Delta\nu_{St}$, cm$^{-1}$ | $\varphi_f$ | $\tau_f$, nsec | $k_f \cdot 10^{-7}$, sec$^{-1}$ | $k_d \cdot 10^{-8}$, sec$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| I | H | Octane | 28480 | 26280 | 2200 | 0,494 | 4,743 | 10,4 | 1,07 |
| | | Toluene | 28700 | 26020 | 2680 | 0,563 | 3,965 | 14,2 | 1,10 |
| | | DMF | 28880 | 26120 | 2760 | 0,632 | 3,917 | 16,1 | 0,939 |
| II | Cl | Octane | 28720 | 26060 | 2660 | 0,700 | 2,700 | 25,9 | 1,11 |
| | | Toluene | 28520 | 28540 | 2880 | 0,675 | 2,110 | 32,0 | 1,54 |
| | | DMF | 28680 | 24960 | 3720 | 0.774 | 2,155 | 35,9 | 1,05 |
| III | F | Octane | 28580 | 26320 | 2260 | 0,418 | 4,937 | 8,46 | 1,18 |
| | | Toluene | 28760 | 26080 | 2680 | 0,525 | 4,411 | 11,9 | 1,08 |
| | | DMF | 28880 | 26140 | 2740 | 0,631 | 4,863 | 13,0 | 0,759 |
| IV | CN | Octane | 27320 | 26220 | 2580 | 0,451 | 1,903 | 23,7 | 2,89 |
| | | Toluene | 27720 | 23700 | 4000 | 0,772 | 2,056 | 37,6 | 1,11 |
| | | DMF | 26700 | 22520 | 4180 | 0,756 | 2,624 | 29,0 | 0.915 |
| V | $COOCH_3$ | Octane | 27580 | 26440 | 2580 | 0,731 | 1,856 | 39,4 | 1,45 |
| | | Toluene | 27660 | 23820 | 3840 | 0,746 | 1,939 | 38,5 | 1,31 |
| | | DMF | 27620 | 22000 | 5620 | 0,732 | 2,570 | 28,5 | 1,04 |
| VI | $NO_2$ | Octane | 27460 | — | — | — | — | — | — |
| | | Toluene | 27180 | — | — | — | — | — | — |
| | | DMF | 26180 | — | — | — | — | — | — |
| VII | $C_6H_5$ | Octane | 28900 | 26500 | 3800 | 0,720 | 1,534 | 46,9 | 1,83 |
| | | Toluene | 28720 | 24500 | 4220 | 0,784 | 1,461 | 53,6 | 1,48 |
| | | DMF | 27320 | 23960 | 3360 | 0,700 | 1,683 | 41,6 | 1,78 |
| VIII | $OCH_3$ | Octane | 28240 | 26040 | 2200 | 0,477 | 4,459 | 10,7 | 1,17 |
| | | Toluene | 28880 | 25800 | 2560 | 0,539 | 4,195 | 12,9 | 1,10 |
| | | DMF | 28580 | 25840 | 2740 | 0,587 | 5,365 | 10,9 | 0,770 |
| IX | $N(CH_3)_2$ | Octane | 26800 | 25000 | 2620 | 0,713 | 1,697 | 42,0 | 1,69 |
| | | Toluene | 26460 | 24380 | 2080 | 0,755 | 1,483 | 50,9 | 1,66 |
| | | DMF | 26220 | 23360 | 2860 | 0,666 | 2,030 | 32,8 | 1,65 |
| X |  | Octane | 26040 | 25680 | 1860 | 0,728 | 1,336 | 54,5 | 2,04 |
| | | Toluene | 25720 | 24780 | 2220 | 0,784 | 1,363 | 57,5 | 1,58 |
| | | DMF | 26640 | 22320 | 4320 | 0,675 | 2,841 | 23,8 | 1,37 |
| XI | *o*-OH | Octane | 28660 | 26120<br>20040 | 2540<br>8620 | 0,069 | — | — | — |
| | | Toluene | 28380 | 25720<br>20100 | 2660<br>8280 | 0,112 | — | — | — |
| | | DMF | 28520 | 25740<br>20360 | 2780<br>8220 | 0,033 | — | — | — |
| XII | 9-anthryl | Octane | 25120 | 19580 | 5540 | 0,618 | 4,269 | 14,5 | 0,896 |
| | | Toluene | 24500 | 19200 | 5300 | 0,610 | 4,450 | 13,7 | 0,877 |
| | | DMF | 24360 | 19080 | 5280 | 0,648 | 5,185 | 12,5 | 0,679 |

with compounds having a fluorescent state of the α-type (H, F, $OCH_3$). With practically unchanged values of rate constants for nonradiative degradation, this leads to a significant increase of the quantum yield and a decrease of fluorescence lifetime.

Compounds with strong donor substituents (alkylamino groups) have a p-type fluorescent state as a consequence of participation in their formation by the high-lying HOMOs that are introduced by the alkylamino groups into the system of orbitals of the base molecule. Also characteristic for these compounds are higher quantum yields of emission and a considerable sensitivity to the polarity of the solvent. The quantum yield for compound X (with a "structurally fixed" dialkylamino group) is naturally greater than the yield for compound IX (with a free amino group), owing to the better conjugation of the substituent with the $\pi$-system of the molecule and the absence of fluorescence quenching upon possible formation of a TICT state [9], which is characteristic for dialkylamino derivatives in polar solvents. We should note, however, that the fluorescence efficiency in dimethylformamide for both compounds IX and X is somewhat lower in comparison with fluorescence in octane or toluene. In our case, apparently, a different quenching method is included, other than the traditional fluorescence quenching method that is usually invoked to explain this sort of behavior of dialkylamino derivatives in polar solvents, including the formation of nonluminescing TICT states [9].

Compounds XI (o-OH) and XII (9-anthryl analog) constitute a special group in the series of phenanthroxazole compounds we have investigated. In planning their synthesis, we set ourselves the task of reducing the overlap of absorption and emission spectra, which is critical from the standpoint of possible use in scintillation technology, by means of an increase of the Stokes shift of fluorescence as a result of reversible photoprocesses taking place in the excited state. Now let us examine the spectral characteristics of these compounds in more detail.

Compound XII fluoresces in the green region of the spectrum, while absorbing light only in a slightly longer-wave region in comparison with the other phenanthroxazole derivatives that have been investigated. The Stokes shift is 2-2.5 times that for compound I, and the quantum yield of emission, regardless of the solvent, remains quite high (0.6-0.65). The absorption spectrum of this compound does not manifest the vibrational structure that is characteristic for phenanthroxazole derivative and also for anthracene derivatives, thus providing evidence in favor of a nonplanar molecular structure of the anthryl derivative in the ground state. Our calculation of the structure of this compound within the framework of the molecular mechanics model [10] has shown that the dihedral angle between the planes of the phenanthroxazole and anthryl fragments, as a consequence of steric hindrance, is about 60°. Thus, there is a considerable disruption of conjugation in this molecule in the ground state. As shown by quantum-chemical calculations, the order of the ordinary bond connecting these fragments in the $S_1^*$ state should increase quite substantially. As a result of transition to the excited state, the molecule of XII should be flattened, leading to a decrease of the structurally relaxed fluorescent state in comparison with the original Franck–Condon state, and to an increase of the Stokes shift of fluorescence.

For the other representative of this group, compound XI, a characteristic feature is the presence of a rather strong intramolecular hydrogen bond between the proton of the o-hydroxyl group and the nitrogen atom of the oxazole ring. Upon excitation of such molecules, there is a high probability of intramolecular proton phototransfer [11]; as a result, the fluorescence spectrum exhibits emission bands of both the initial form ($\sim$26,000 cm$^{-1}$) and the phototautomer ($\sim$20,000 cm$^{-1}$). The fluorescence excitation spectra at 26,000 and 20,000 cm$^{-1}$ are identical and correspond quite well to the absorption spectrum, indicating that this reaction takes place only in the excited state. The kinetics of fluorescence quenching in the short-wave band are monoexponential, in the long-wave band biexponential with a negative preexponential factor for the smaller of the exponentials. This may be evidence in favor of irreversibility of the proton phototransport reaction (phototaumerization) taking place in the excited state [12].

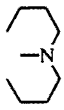
In contrast to compound XII, for which a very nearly adiabatic course of the photoprocess is characteristic, we find that for the o-hydroxy derivative, the proton transfer reaction in the excited state is accompanied by substantial induced quenching of fluorescence (the quantum yield of emission is lower in comparison with the unsubstituted compound or the $OCH_3$ derivative, by a factor of approximately 5-8). when the change is made from octane to toluene, the reaction efficiency increases slightly, as indicated by an increase of the relative intensity of the long-wave band (simultaneously, the total quantum yield of fluorescence increases). At the same time, in dimethylformamide, the relative intensity of emission of the phototautomer is much lower, and this change is also accompanied by a decrease in the total efficiency of fluorescence. One of the probable reason for this behavior is competition between processes of forming an intramolecular hydrogen bond and an intermolecular hydrogen bond with molecules of the high-basicity solvent dimethylformamide.

A more detailed investigation of photoprocesses taking place upon excitation of compounds XI and XII will be reported in our future publications.

## EXPERIMENTAL

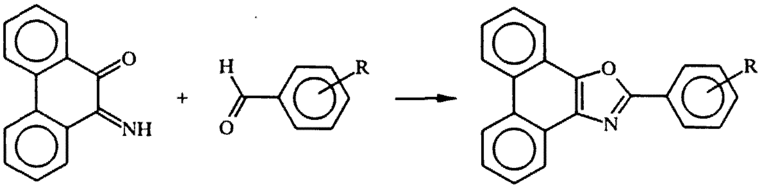
Electronic absorption spectra were measured in a Hitachi U3210 spectrofluorimeter, fluorescence excitation and emission spectra in a Hitachi F4010 spectrofluorimeter. Quantum yields of fluorescence were measured relative to quinine bisulfate in 1 N sulfuric acid ($\varphi$ = 0.546 [13]) with the introduction of a quadratic correction for refractive index. The

TABLE 2. Melting Points and Elemental Analyses of Synthesized Derivatives of 2-Aryl[9,10]phenanthroxazole

| Compound | Empirical formula | R | mp, °C | Calculated N, % | Found N, % |
|---|---|---|---|---|---|
| I | $C_{21}H_{13}NO$ | H | 179...180 | 4,8 | 4,7 |
| II | $C_{21}H_{12}ClNO$ | 4-Cl | 259...260 | 4,3 | 4,3 |
| III | $C_{21}H_{12}FNO$ | 4-F | 228...229 | 4,5 | 4,4 |
| IV | $C_{22}H_{12}N_2O$ | 4-CN | 309...310 | 8,7 | 8,7 |
| V | $C_{23}H_{15}NO_3$ | 4-COOCH$_3$ | 252...253 | 4,0 | 3,9 |
| VI | $C_{21}H_{12}N_2O_3$ | 4-NO2 | 256...257 | 8,2 | 8,0 |
| VII | $C_{27}H_{17}NO$ | 4-C$_6$H$_5$ | 333...334 | 3,8 | 3,7 |
| VIII | $C_{22}H_{15}NO_2$ | 4-OCH$_3$ | 214...215 | 4,3 | 4,3 |
| IX | $C_{23}H_{18}N_2O$ | 4-N(CH$_3$)$_2$ | 236...237 | 8,3 | 8,3 |
| X | $C_{27}H_{20}N_2O$ |  | 261...263 | 7,2 | 7,5 |
| XI | $C_{21}H_{13}NO_2$ | 2-OH | 231...232 | 4,5 | 4,4 |
| XII | $C_{29}H_{17}NO$ | (9-Anthryl) | 311...312 | 3,5 | 3,6 |

fluorescence lifetime was determined by means of a nanosecond pulse fluorimeter operating in the photon count mode (see [14] for description); the kinetic data were processed by the least squares method [15, 16]. Quantum-chemical calculations by the SCF PPP CI method, with an accounting for up to 100 singly excited configurations, were performed with the set of parameters proposed in [17].

The compounds investigated in the present work, I-XII, were obtained by condensation of 9,10-phenanthrenequinonemonoimide with aromatic aldehydes in isopropyl alcohol solution in the presence of piperidine. The melting points and elemental analyses of these compounds are given in Table 2.



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