SYNTHESIS, STRUCTURE, AND SPECTRAL FLUORESCENCE PROPERTIES OF 1,4-DI(5-PHENYL-2-OXAZOLYL)BENZENE HETEROANALOGS

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Novel organic luminophors belonging to the oxazole and oxadiazole classes of compounds have been synthesized, namely, thiophene and furan analogs of 1,4-di(5-phenyl-2-oxazolyl)benzene. The optical properties of these compunds have been studied both theoretically and experimentally. Their IR spectra have been measured and their UV absorption, fluorescence, and excitation spectra have been analyzed. Details of their electronic structure and their principal spectral fluorescence parameters have been calculated using the PPP method. Possible methods or pathways for improving the spectral fluorescence parameters of organic luminophors in these classes of compounds in the visible region of the spectrum have also been analyzed.

1,4-Di(5-phenyl-2-oxazolyl)benzene (POPOP) is among the most well-known organic luminophors belonging to the oxazole class of compounds with highly quantitative spectral fluoresence properties; this compound is used as an active element in optical lasers and in scintillators [1-4]. The unique photophysical properties of POPOP can be interpreted on the basis of its electronic and three-dimensional structure characteristics.

Our goal in the present paper was to explore the synthesis and examine the spectral fluoresence properties of, POPOP heteroanalogs, differing in structure from POPOP by the presence of benzene, furan, and thiophene rings in a variety of bonding sequences relative to the oxazole and oxadiazole rings.

Heterosubstituted analogs of POPOP can be synthesized by reaction of α-aminomethyl aryl ketones or aromatic (heteroaromatic) acid hydrazides with acyl chlorides, followed by cyclodehydration of the condensation products. For example, treatment of 5-(5-phenyl-2-oxazolyl)-thiophene-2-carboxylic acid chloride with α-aminoacetophenone gave 2,4-di(5-phenyl-2-oxazolyl)-thiophene (I).
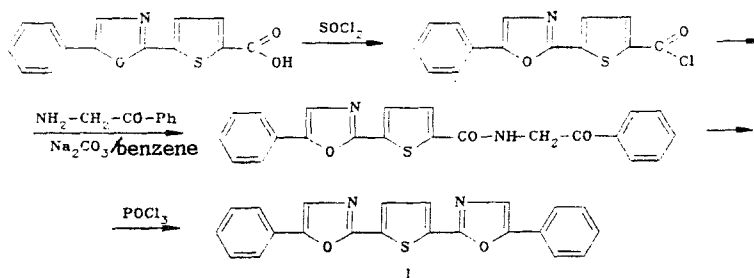
This compound can also be synthesized from thiophene-2,5-dicarboxylic acid dichloride and α-aminoacetophenone. However, it is difficult to purify the product from this reaction, and the yield is substantially lower.

The method of sequential azole ring construction opens up the possibility of preparing compounds of unsymmetrical structure and is thus of significant interest, despite the difficulties associated with the multistage synthesis of the 5-(5-phenyl-2-oxazolyl)thiophene-2-carboxylic acid starting materials. Thus, the derivatives 2-(5-phenyl-2-oxazolyl)-5-(5-phenyl-1,3,4-oxadiazol-2-yl)thiophene (II) and 2-(5-phenyl-2-oxazolyl)-5-[(2-thienyl)-1,3,4-oxadiazol-

TABLE 1. Characteristics of the Newly Synthesized Compounds

Compound	Molecular formula	mp, °C	Yield, %	Compound	Molecular formula	mp, °C	Yield, %
I	$C_{22}H_{14}N_2O_2S$	176...178	75	V	$C_{21}H_{13}N_3O_3$	224...226	95
II	$C_{21}H_{13}N_3O_2S$	198,5...200,5	80	VI	$C_{18}H_{10}N_4O_2S_2$	288...290	90
III	$C_{19}H_{11}N_3O_2S_2$	198...200	91	VII	$C_{18}H_{10}N_4O_4$	268...270	85
IV	$C_{21}H_{13}N_3O_2S$	253,5...255,5	90				

2-yl]thiophene (III) were prepared by replacement of α-aminoacetophenone (in the above reaction sequence) by benzoic and thiophene-2-carboxylic acid hydrazides, respectively.
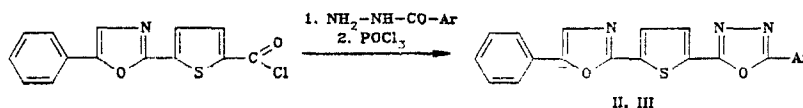
II Ar= phenyl; III-Ar = 2-thienyl

In an analogous manner, 1-(5-phenyl-2-oxazolyl)-4-[5-(2-thienyl)-1,3,4-oxadiazol-2-yl]-benzene (IV) and 1-(5-phenyl-2-oxazolyl)-4-[5-(2-furyl)-1,3,4-oxadiazol-2-yl]benzene (V) were synthesized from thiophene-2-carboxylic acid chloride or pyromucic (furan-2-carboxylic acid) chloride with 4-(5-phenyl-2-oxazolyl)benzoic acid hydrazide; use of terephthalic acid dihydrazide under the same conditions gave 1,4-di[5-(2-thienyl)-1,3,4-oxadiazol-2-yl]benzene (VI) and 1,4-di[5-(2-furyl)-1,3,4-oxadiazol-2-yl]benzene (VII) (Table 1).

IV, VI X=S; V, VII X=O
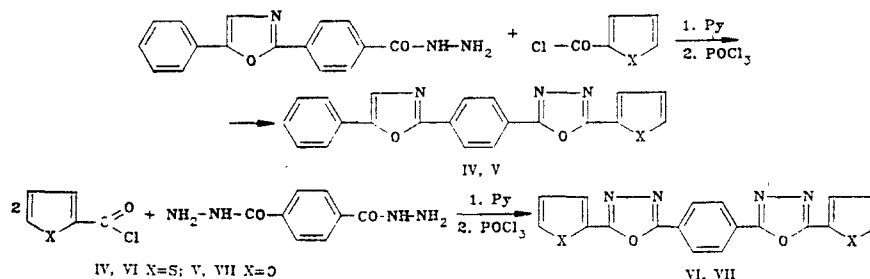
It is thus possible to prepare heterosubstituted POPOP analogs of a variety of structures by combining different α-aminomethyl aryl ketones or acid hydrazides with aromatic or hetero-aromatic acid chlorides.

The IR spectra of compounds I-VII are missing absorption bands due to the carbonyl and amino groups in the 1600-1700 and 3100-3500 cm^{-1} regions, respectively. The greatest number of bands is observed in the frequency range 600-1600 cm^{-1}, and are due to bond vibrations of the thiophene, furan (700-730, 1030-1085, 1400-1420, 1500-1550 cm^{-1}), benzene (600-650, 800-840, 1000-1030, 1600-1620 cm^{-1}), oxazole (770-780, 1530-1600 cm^{-1}), and oxadiazole (700-710, 1530-1600 cm^{-1}) rings. It is difficult to make reliable and specific band assignments to different vibrations; further work is required for this purpose.

In order to study the optical properties of compounds I-VII we measured their UV absorption, excitation, and fluorescence spectra in different solvents, and also measured their fluorescence quantum yields. in toluene solution (Table 2 and Fig. 1a). In ethanol, in contrast to toluene solution, it is possible to observe the entire UV absorption spectrum, up to the short-wavelength boundary (50·10^3 cm^{-1}). The spectral parameters of POPOP (VIII) were determined simultaneously with those of compounds I-VII, and were found to be in complete agreement with the existing literature data [6].

According to the data in Table 2, compounds VI and VII have the lowest short-wavelength absorption; these contain two oxadizaole rings. Compounds I-III, containing oxazole rings, have the longest wavelength absorption. Comparing these to POPOP we conclude that replacement of the central benzene ring by a thiophene ring results in a bathochromic shift of approximately 30 nm of the intense long-wavelength absorption band. A hypsochromic shift of the long-wavelength band (~20 nm) is observed upon replacement of oxazole rings by oxadiazole

TABLE 2. Principal Spectral Fluorescence Parameters of Compounds I-VII in Toluene

Compound	λ_{max}^{abs}, nm	ν_{max}^{abs}, cm^{-1}	λ_{max}^{fluor}, nm	ν_{max}^{fluor}, cm^{-1}	λ^{O-O}, nm	ν^{O-O}, cm^{-1}	$\varepsilon \cdot 10^3$ liter/mole·cm	η	Stokes $\Delta\nu$, cm^{-1}
I	390	25641	460	21739	425	23530	48,16	0,36	3902
II	373	26810	452	22124	413	24213	42,98	0,39	4686
III	378	26455	460	21739	419	23866	49,57	0,38	4716
IV	353	28329	433	23095	394	25381	44,20	0,86	5234
V	352	28409	432	23148	392	25510	51,00	0,91	5261
VI	339	29499	410	24390	374	26738	44,43	0,61	5109
VII	335	29851	422	23697	394	25189	47,62	0,66	5144
VIII*	360	27778	418	23924	389	26051	54,83	0,97	4254

*The quantum yield of commercial POPOP (VIII) was measured in ethanol solution.

rings. In the case of substitution of only a single oxazole ring by oxadiazole the hypsochromic shift is smaller (~10 nm). Replacement of the terminal benzene rings by furan or thiophene rings has a significantly smaller effect on the frequency of the long-wavelength band.

In the UV absorption spectra of these compounds intense, broad long-wavelength bands with ε values $(44-51) \cdot 10^3$ liter/mole·cm can be distinguished from less intense medium short wavelength bands with ε values $(5-15) \cdot 10^3$ liter/mole·cm; these bands are separated by a deep absorption minimum with an ε value of $5 \cdot 10^3$ liter/mole·cm (Fig. 1). Based on earlier reported data [1-4] we assume that the long-wavelength absorption bands can be attributed to $\pi\pi^*$-type electronic transitions. $n\pi^*$-Type absorption bands are not observed.

It is clear that several $S_0 \to S_n^*$ transitions (n = 1, 2, 3), differing in both intensity and polarization, are represented in the long-wavelength absorption region. The most intense transition is the $S_0 \to S_1^*$, which is the longest wavelength and most intense ($f_e \geq 1.9$). The $S_0 \to S_1^*$ transition is polarized along the length of the molecular axis, while the $S_0 \to S_n^*$ transitions in higher energy states are polarized at various angles to this axis. Examination of the configuration interaction matrix reveals that the $S_0 \to S_1^*$ transition has a single configuration, with the largest contribution from the singly excited state $\psi^2_{HOMO \to LUMO} \approx 0.9$ (with HOMO on LUMO). All of the other $S_0 \to S_n^*$ transitions are multi-configuration, have two- to three-orders of magnitude lower probability, and have not been considered in detail. Analysis of the electron density matrix indicates that the highest density values are localized on the nitrogen atoms in the oxazole and oxadiazole rings. Meanwhile, the densities are significantly lower (weak acceptor properties) on the other heteroatoms, namely, oxygen and sulfur. Upon excitation to the lowest singlet state S_1^* both the atomic and fragment densities are redistributed to a large extent. The electron density is diminished significantly on the carbon atoms in free positions on the oxazole and oxadiazole rings, and also in the para-positions on the terminal benzene, thiophene, and furan rings. As a result, the $S_0 \to S_1^*$ transition involves intramolecular charge transfer, the magnitude and direction of which depends on the nature, benzene, furan, or thiophene, of the ring in the composition of the compound. The long-wavelength absorption bands are thus apparently formed from one-electron $S_0 \to S_1^*$ transitions of a general molecular type. In the lowest S_1^*-state the oxazole and oxadiazole rings possess electron acceptor (withdrawing) charcteristics, the benzene, furan, and thiophene rings electron donating properties. Calculation of the excitation localization numbers reveals that the greatest percent localization (35%) is centered or concentrated on the central rings (benzene or thiophene), 20-25% on the oxazole or oxadiazol rings, and about 10% on any of the terminal rings (benzene, furan, or thiophene).

All of the compounds studied have relatively high quantum yields ($\eta = 0.36-0.93$), the values of which depend on the sequence or bonding arrangement of benzene, oxazole, oxadiazole, furan, and thiophene rings relative to one another. The highest η values are observed for compounds IV-VII; the characteristic feature of these compuonds is the presence of a benzene ring as the central ring, located between either oxazole or oxadiazole rings. The lowest η values are observed in the case of compounds I-III, in whch the central ring is a thiophene ring. When the central ring is a thiophene ring, this leads not only to a reduction in η values, but also to a bathochromic shift of the absorption and fluorescence bands (30-50 nm), an increase in the energy of the pure O—O electronic transition, and an increase in the
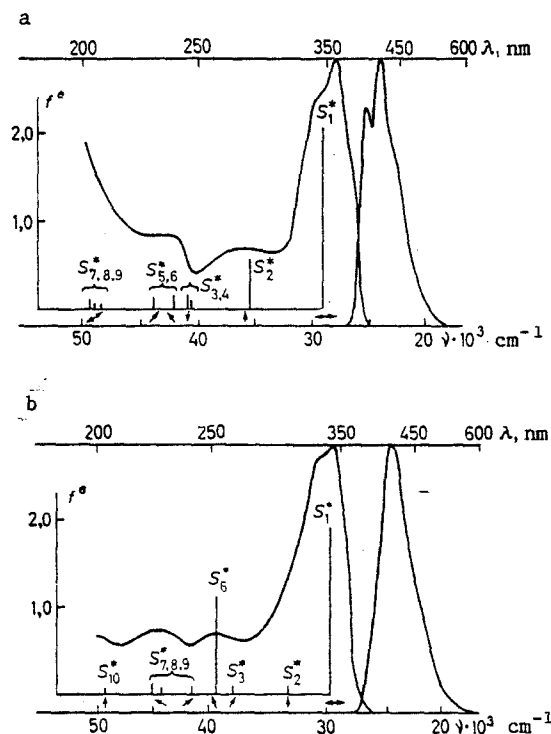
Fig. 1. Absorption and fluorescence spectra of POPOP (a) and compound VII (b) in ethanol. Under the experimentally determined UV spectra curves of compounds VII and VIII (POPOP) we have shown graphically the frequencies, oscillator strengths, and polarizations of the singlet-singlet $S_0 \rightarrow S_n^*$ electron transitions ($\pi\pi$-type).

Stokes loss. Replacement of an oxazole ring by oxadiazole results in a hypsochromic shift of the fluorescence band and a decrease in the Stokes shift(compounds I and II, V and VI).

Previous estimates [7] have shown that these organic luminophors have low radiation lifetimes (τ_0 < 10 nsec), high radiation decay constants ($K_f = 10^{-9}$ sec^{-1}), and large induced emission cross sections ($\sigma_{31}^{max} > 10^{-16}$ cm^2); these compounds therefore may be assigned, based on the classification scheme proposed by D. N. Shigorin [8], to the fifth spectral luminescence type, $\sigma\pi$ln-class. The favorable coupling of principal spectral fluorescence characteristics makes these compounds promising materials for lasers. The results of our studies of the photophysical properties of these compounds will be reported separately.

EXPERIMENTAL

UV absorption spectra were measured on a Specord M-40 spectrophotometer, IR spectra on a Specord 75-IR spectrophotometer using KBr pellets, and excitation and fluorescence spectra on an SLM-4800S (USA) spectrofluorometer. Spectra were recorded using a two-channel photomultiplier scheme. Fluorescence spectra were corrected using a Hewlett Packard computer and were graphed to scale on a plotter; UV spectra were graphed in the form of functions of logarithm of the molar extinction coefficient versus frequency $\varepsilon = f(\nu)$ [cm^{-1}]. Quantum yields were determined according to the procedure described in [2, 9] for dilute solutions c ~ 10^{-5}-10^{-7} mole/liter. Anthracene, with a η value of 0.22, was used as the reference standard. The error in the measurements was less than 10%.

Quantum mechanical calculations were carried out within the PPP approximation [10, 11] using the Hinze-Jaffe parameters [12]. The Matag-Nishimoto equation [13] was used to estimate the two-center Coulomb integrals $\gamma_{\mu\nu}$.

Sample purity was assessed by TLC using Silufol UV-254 plates (with benzene or trichloroethylene eluent).

The results of sulfur and nitrogen elemental analysis agreed with calculations for all of the newly synthesized compounds.

5-(5-Phenyl-2-oxazolyl)thiophene-2-carboxylic Acid Chloride. A mixture of 5.2 g (0.02 moles) 5-(5-phenyl-2-oxazolyl)thiophene-2-carboxylic acid [14] and 50 ml thionyl chloride was refluxed in a glycerol bath until the precipitate had completely dissolved, and then an additional 2 h. Excess thionyl chloride was removed by steam distillation under vacuum, and the residue, consisting of an almost quantitative yield of 5-(5-phenyl-2-oxazolyl)-thiophene-2-carboxylic acid chloride, was used in subsequent syntheses without further purification.

General Method for the Synthesis of Compounds I-III. To a suspension of 0.02 moles α-aminoacetophenone (benzhydrazide or thiophene-2-carboxylic acid hydrazide) in 50 ml water was added a solution of 5.5 g (0.02 moles) 5-(5-phenyl-2-oxazolyl)thiophene-2-carboxylic acid chloride in 50 ml benzene. A saturated solution of sodium carbonate was added in small portions with vigorous stirring, such that the reaction mixture remained alkaline throughout the reaction. The mixture was stirred for 4 h, and the resulting precipitate was washed several times with 50-80 ml portions of water until the wash water was neutral, filtered and dried.

The condensation product, which was obtained in practically quantitative yield, was refluxed in 80 ml phosphorus oxychloride until the insoluble material had either completely dissolved or reprecipitated, and then an additional 2 h. The mixture was cooled to 18-22°C and poured with stirring onto 400-500 g crushed ice. The resulting precipitate was washed with water (0.5-1.0 liter) until the wash water remained neutral, filtered, dried, and purified by column chromatography on Al_2O_3 (h = 40 cm, d = 2 cm) with trichloroethylene eluent. The product was recrystallized from trichloroethylene or dichloroethane.

General Method for the Synthesis of Compounds IV-VII. To a suspension of 0.02 moles 4-(5-phenyl-2-oxazolyl)benzoyl hydrazide or terephthalic acid dihydrazide in 50 ml pyridine at 18-22°C was added dropwise a stoichiometric amount of thiophene-2-carboxylic acid chloride or pyromucic acid chloride. The mixture was stirred for 4 h at 60°C, cooled to 18-22°C, and poured onto 400 ml water. The resulting precipitate was washed with water (0.5-1.0 liter) until the wash water remained neutral, filtered, and dried. The condensation product, obtained in almost quantitative yield, was cyclized by refluxing in excess phosphorus oxychloride and purified in the same manner as compounds I-III above.

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