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LUMINESCENCE PROPERTIES OF 5-OXAZOLONE DERIVATIVES CONTAINING A PYRAZOLINE RING

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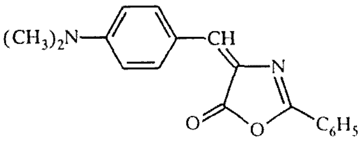
New difluorophors have been synthesized containing both 2-phenyl-4-benzyliden-5-oxazolone and 1,3,5-triaryl-2-pyrazoline fragments. A study was carried out on the effect of the structure of these compounds on their spectroluminescence properties in solvents of different polarity. Positive solvatofluorochromy was detected. The use of these compounds as luminescent dyes for polymers was proposed taking account of their solvatofluorochromic effects.

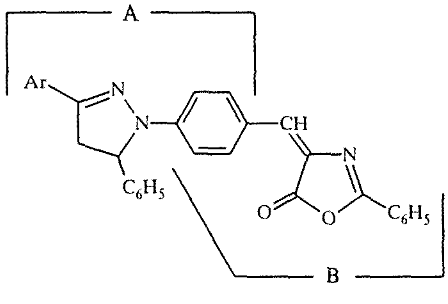
There have been only a few orange-red and red organic luminophors reported. Among 5-oxazolone derivatives, 2-phenyl-4-(4-dimethylamino)benzyliden-5-oxazolone (I) has been reported as an orange-red luminophor [1].



I

This compound has a bright color but relatively low emission intensity in the solid state and only weak emission in organic solvents. Furthermore, this luminophor is sensitive to the action of mineral acid reagents.

In a search for orange-red and red oxazolone luminophors lacking the abovementioned disadvantages, we synthesized difluorophor derivatives II.



II a-d

IIa—d a Ar = C_6H_5, b Ar = 4-C_6H_5—C_6H_4, c Ar = 4-C_6H_5—CH=CH, d Ar = 4-$NO_2C_6H_4$

In this search, we took account that the pyrazoline ring, which has electron-donor properties, is the basis for luminophor molecules with strong fluorescence in various spectral regions both in the solid state and in organic solvents [2-4].

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TABLE 1. Spectroluminescence Data for I-IV

Compound	UV spectrum, λ_{max}, nm (lgε)	Flourescence, λ_{max}, nm			
		Toluene	Acetone	Dimethylformamide	in the solid state
I	470 (4,74)	510	510	515	630
IIa	495 (4,87)	530	570	595	630
IIb	505 (4,93)	560	595	620	655
IIc	505 (4,78)	545	590	615	640
IId	495 (4,85)	580	625	640	660
III	360 (4,59)	420	420	420	No fluor.
IV	360 (4,28)	440	445	450	455

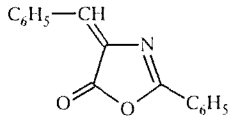
TABLE 2. Indices for IIa-IId

Compound	Брутто-формула	Mp, °C	IR spectrum, $\nu_{C=O}$, см$^{-1}$	Yield, %
IIa	$C_{31}H_{23}N_3O_2$	251...252	1780	50
IIb	$C_{37}H_{27}N_3O_2$	216...217	1786	42
IIc	$C_{33}H_{25}N_3O_2$	265...266	1785	35

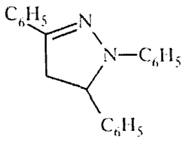
Products II were obtained by the condensation of 1-(4-formylphenyl)-3-(4-aryl-5)phenyl-2-pyrazolines with hippuric acid in acetic anhydride in the presence of sodium acetate. The synthesis of formyl-substituted 1,3,5-triaryl-2-pyrazolines was carried out as described by Kutulya et al. [5] using the Vilsmeier–Haake reaction.

According to the classification of difluorophors proposed in our previous work [6], these products are asymmetric conjugated difluorophors. Features of the structure of both fluorophor groups are much less evident in their spectroluminescence properties than for the corresponding pure compounds and, on the other hand, new properties arise due to the structure of the conjugated π-electron system formed.

Table 1 gives the spectroluminescence properties of II. Since the difluorophors synthesized contain structural fragments of model compounds III and IV, the spectral characteristics of the latter are also given in this table.



III



IV

The absorption spectra of II clearly show a strong band bathochromically-shifted relative to the corresponding bands in the spectra of III and IV.

In order to interpret the nature of the long-wavelength absorption band of the difluorophors studied, we must bear in mind that their chromophore system involves two interacting fragments, A and B. Some localization of electronic excitation in the separate fragments may be expected for such molecular systems.

The electron-donor nitrogen atom of the pyrazoline ring, which is common for both structural fragments of the difluorophor, interacts with the electron-withdrawing aryl groups in fragment A and also with the electron-withdrawing oxazolone ring in fragment B.

Kutulya et al. [7] have shown that there is delocalization of the $2p_z$ electron pair of the amine nitrogen atom in both directions upon excitation to the S_1 state in IV: to the N-phenyl group and to the azomethine group, $-N=C-Ar$. The relative contribution of the electron displacements in the former fragment increases steadily upon the introduction of increasingly strong electron-withdrawing substituents into the phenyl group. Similar behavior is found with increasing length of the π-electron system at position 1 of the pyrazoline ring in the case of IIa-IId. Comparison of the spectral data of I and IIa shows that they differ only slightly in transition energy ($\Delta\nu = 1000$ cm^{-1}). Thus, we may assume that the corresponding transition is localized in fragment B although the $-N=C-Ar$ group has a significant perturbation effect.

Extension of the conjugation chain of the aryl group at position 3 in IIb and IIc also causes some bathochromic shift of the absorption maximum due to enhancement of the perturbing effect of the π-electron system of the arylazomethine group.

The long-wavelength absorption band of difluorophors IIa-IId is much stronger than for I. Such an increase in the probability of the electronic transition is a consequence of the perturbing effect of fragment A and the greater total length of the molecular π-electron system, which increases the probability of its interaction with the light wave field.

All these products fluoresce not only in the solid state but also in solution at room temperature although the emission intensity of the solutions is relatively low.

The changes in the position of the fluorescence maxima of solutions of IIa-IId relative to structural features, similar to the behavior of the absorption spectra, are in accord with the interpretation given for the $S_0 \rightarrow S_1^*$ transition. Differences in the structure of fragment A are more evident in the fluorescence spectra than in the absorption spectra. The positions of the fluorescence maxima of II in toluene vary in the range from 530 to 580 nm. In the solid state, the maxima lie in the range from 630 to 660 nm and the emission intensity is 5-10 times greater than for I. Even nitro derivative IId has strong emission. Here, we encounter the phenomenon that the quenching effect of the nitro group is most evident when the fluorescence maximum lies at wavelengths shorter than 500 nm [8].

Further studies showed that the color of the emission of solutions of II depends significantly on the solvent polarity (see Table 1). The color of the emission of the solutions may be varied in a broad range from yellow-green to red by varying the polarity of the solvent. This suggests the use of II for luminescence dyes of polymer materials taking account of the polymer polarity. Thus, IIa imparts an orange-red color to polystyrene and polymethyl methacrylate with strong yellow-orange fluorescence for polystyrene and orange-red fluorescence for polymethyl methacrylate. Emission at even longer wavelengths is found for these polymers using luminophors IIb-IId, which have red fluorescence in polar media.

EXPERIMENTAL

The IR spectra were taken on a Specord IR-75 spectrometer in KBr pellets. The electronic absorption spectra were taken on a Specord M-40 spectrophotometer in $2\cdot10^{-5}-4\cdot10^{-5}$ mole/liter toluene solutions. The fluorescence spectra were taken on an apparatus consisting of a ZMR-3 mirror monochromator, FÉU-22 photoamplifier, and M-95 microamperometer. The photoluminescence was excited with a DRSh-500 lamp. Light with wavelength 365 nm was separated from the spectrum using a DMR-4 monochromator.

Purity of compounds was checked by thin layer chromatography on Silufol UV-254 plates using 9:1 benzene–ethanol as eluent. Chromatograms were developed with UV light. The indices of the compounds synthesized are given in Table 2.

Elemental analysis showed that nitrogen content in the compounds synthesized corresponded to the calculated values.

(2-Phenyl)-4-[(3-aryl-5-phenyl-2-pyrazolin-1-yl)benzyliden]-5-oxazolones (IIa-IId). A mixture consisting of 3.6 g (20 mmoles) hippuric acid, 30 mmoles corresponding formyl-substituted 1,5-diphenyl-3-aryl-2-pyrazoline, and 0.8 g (10 mmoles) anhydrous sodium acetate was maintained in 20 ml acetic anhydride at 100°C for 15 min. The precipitate obtained upon cooling was filtered off, washed with ethanol, and purified by recrystallization from benzene in the presence of alumina.

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