CONJUGATED BIFLUOROPHORS CONTAINING 1,3,5-TRIPHENYL-2-PYRAZOLINE

AND 2,5-DIPHENYL-1,3,4-OXADIAZOLE GROUPS

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1,3,5-Triaryl-2-pyrazoline and 2,5-diaryl-substituted forms of 1,3,4-oxadiazole are examples of efficient organic luminophors and are used in laser [1] and scintillation [2] technology, as luminescent dyes and optical decolorizers of polymer materials [3, 4], and for many other purposes, where the photostability of luminophors is important.

We synthesized conjugated biofluorophors (I, II), which included the structural groups 1,3,5-triphenyl-2-pyrazoline and 2,5-diphenyl-1,3,4-oxadiazole with a common aromatic ring. In so doing, we were mindful of the fact that introducing an electron-acceptor oxadiazole group into the N-phenyl radical of triarylpyrazoline can increase the photostability of the pyrazoline fragment of the molecule.

The compounds I were synthesized by the method usually employed for preparing diaryloxadiazoles. The method consisted of condensing 3,5-diphenyl-1-(4-carboxyphenyl)-2-pyrazoline acid chloride with substituted forms of benzhydrazide followed by cyclization of N,Ndiaroylhydrazines by heating them in phosphorous oxychloride:



The compounds II, containing different substituents in the 3-phenyl radical of the pyrazoline fragment, were obtained by condensation of substituted α - β -unsaturated ketones with 2-phenyl-5-(4-hydrazenophenyl)-1,3,4-oxadiazone according to the scheme

$$R' - (D - CH = CH - Ph + H_2N - NH - (II)$$

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$$R' - (D - CH + CH - Ph + H_2N - (II)$$

$$R' - (D - CH + CH - Ph + H_2N - (II)$$

$$R' - (D - CH + CH + (H_2N - (II))$$

$$R' - (D - CH + (II))$$

$$R' - (D - CH + (II))$$

$$R' - (II)$$

R' = H, OCH₃, N(CH₃)₂, SO₂F, NO₂, CH = CH--C₆H₅.

The compound Ia (R = H) was obtained by both methods and thus its structure was confirmed by countersyntheses.

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	R	Absorption		Luminescence	
Com- pound		λ_{max} , nm	ε·10 ⁻³	^λ max, nm	η
Ia	Н	385	51,0	430	0,42
Ιb	C ₆ H₅	385	68,0	425	0,48
Ic	OCH3	385	42,8	$445 \\ 425 \\ 445$	0,50
Ιđ	$N(CH_3)_2$	388	58,6	430	0,50
Ie	COOCH ₃	390	51,3	455 435 450	0,52
lf Ila	NO ₂ OCH ₃	405 385	$\substack{32,9\\45,5}$	575 420	$\substack{0,33\\0,40}$
Пp	N(CH ₃) ₂	395	59,6	437	0,51
IJc	SO ₂ F	420	38,8	510	0,60
Πq	NO ₂	415*		Weak orang	e lumines-
IIê 2,5-D oxadi	CH=CH-C ₆ H ₅ ipheny1-1,3,4-	410 282	59,4 $26,0$	cence 457 350	0,50 0,43
1, 3, 5-Tripheny1-2- pyrazoline		360	20,0	440	0,45

TABLE 1. Spectral-Luminescence Characteristics of Bifluorophors I and II (in toluene)

*Qualitatively, poor solubility.

The compounds I, II can be regarded, on the one hand, as substituted 1,3,5-triphenyl-2-pyrazolines, containing in the para position of the N-phenyl radical as electron-acceptor substituent — a phenyloxadiazone group. On the other hand, they can also be regarded as substituted 2,5-diphenyl-1,3,4-oxadiazoles, containing in one of the phenyl rings a substituted pyrazoline ring, having electron-donor properties. When interpreting the spectral-luminescence properties of the synthesized substances (Table 1) we regard these compounds as substituted forms of triphenylpyrazoline.

It has been shown previously that for compounds with this structure, where as arylethylene group was additionally introduced between the N-phenyl radical of the fragment A and the oxadiazone ring of the fragment B, the electronic transition responsible for the fluorescence is localized in the fragment B, though the arylazomethine group of fragment A affects it as a result of some displacement in this direction of a lone electron pair [6]. Analogous regularities are also observed in the spectral-luminescence properties of the compounds I, II.

The absorption maximum of the simplest of the compounds (Ia) exhibits a bathochromatic shift compared with the spectra of triphenylpyrazoline and diphenyloxadiazole, which are its structural fragments, by 25 and 103 nm, respectively; the extinction coefficient more than doubles.

The substituents R in the para position of the phenyl radical of oxadiazole fragment with the exception of the nitro group, do not affect significantly (or at all) the position of the absorption maxima. The interaction of the nitro group with the lone pair electrons of nitrogen atom, common to both fragments, of the pyrazoline ring gives rise to a bathochromatic shift of the absorption band by 20 nm. In the excited state this interaction is intensified and in the fluorescence spectrum the long-wavelength shift is equal to 130 nm.

Most compounds I fluoresce in the blue region with a quantum yield of 0.42-0.52. The nitro group shifts the fluorescence into the orange-red region, but the intensity of the luminescence of the nitro substituted compound is lower than for other compounds of this series ($\eta = 0.33$).

For the bifluorophor II the methoxy group in the para position of the 3-phenyl radical of the pyrazoline fragment does not affect the position of the absorption and fluorescence maxima, and a strong electron-donor substitutent — the dimethylamine group — gives rise to bathochromatic and bathofluoric shifts, equal to 10 and 15 nm, respectively.

Com- pound	Found, % N	Empirical formula	Computed, % N	™ _{melt} , °C
Ia Ib Ic Id Ie If IIa IIb IIc IId IIe	$12,91 \\ 11,00 \\ 12,00 \\ 14,62 \\ 11,35 \\ 14,53 \\ 12,06 \\ 14,61 \\ 10,75 \\ 14,42 \\ 10,41 \\ 10,41 \\ 10$	$\begin{array}{c} C_{29}H_{22}N_4O\\ C_{35}H_{22}N_4O\\ C_{35}H_{24}N_4O_2\\ C_{31}H_{27}N_5O\\ C_{31}H_{42}N_4O_3\\ C_{29}H_{21}N_5O_3\\ C_{30}H_{43}N_4O_2\\ C_{31}H_{27}N_5O\\ C_{30}H_{24}N_4O_2\\ C_{31}H_{27}N_5O\\ C_{29}H_{21}N_5O_3\\ C_{29}H_{21}N_5O_3\\ C_{29}H_{21}N_5O_3\\ C_{29}H_{21}N_5O_3\\ C_{37}H_{28}N_4O \end{array}$	12,68 10,81 11,86 14,43 11,20 14,37 11,86 14,43 10,69 14,37 10,29	$\begin{array}{c} 226 - 228\\ 251 - 253\\ 235 - 237\\ 241 - 243\\ 243 - 245\\ 261 - 263\\ 247 - 249\\ 245 - 247\\ 205 - 206\\ 289 - 291\\ 235 - 237\end{array}$

TABLE 2. Results of Elemental Analysis and Melting Points of Bifluorophors I and II

*Analysis for S, found 6.90%; computed 6.71%.

Stronger effects are observed when electron-acceptor sulfofluoride and nitro groups are introduced (compounds IIc, IId). The quantum yield for the sulfofluoride-substituted is higher than and the quantum yield for the nitro-substituted compound is significantly lower than for Ia.

The introduction of the phenyloxadiazole radical in the para position of the N-phenyl ring in triphenylpyrazoline has a photostabilizing effect. Thus when a toluene solution of the compound Ia is irradiated with unfiltered light from a mercury-quartz lamp at a distance of 12 cm from the light source the luminescence intensity at maximum irradiation drops by 25% 9 h, while the intensity of luminescence of triphenylpyrazoline decreases by 50% under the same conditions.

The absorption spectra were obtained with an SF-4 spectrophotometer; the luminescence spectra were obtained on an apparatus consisting of a ZMR-3 mirror monochromator, an FÉU-18 optical radiation detector, and an M-95 microammeter. Photoluminescence was excited with a SVDSh-500 lamp, from whose spectrum light with wavelength 365 nm was separated with a DMR-4 monochromator. The absolute quantum yields of luminescence of toluene solutions (η) were determined by the equal-absorption method [7].

The compounds I and II were obtained by the procedures usually employed by synthesizing 1,3,5-triaryl-substituted forms of 2-pyrazoline [8] and 2,5-diaryl-substituted forms of 1,3,4-oxadiazole [9]. The melting points and the elemental analyses of the synthesized substances are presented in Table 2.

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