SYNTHESIS AND SPECTRAL-LUMINESCENCE PROPERTIES OF 1-(4'-FORMYLPHENYL)-3,5-DIARYL-2-PYRAZOLINES

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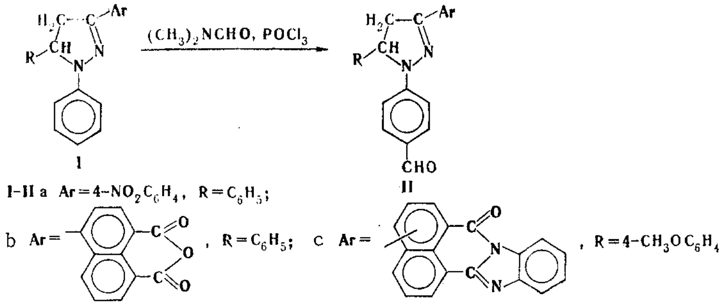
It was demonstrated by means of the IR and PMR spectra that 1-phenyl-3,5-diaryl-2-pyrazolines that contain a grouping with a strong electron-acceptor effect, viz. a 4-nitrophenyl or 4-naphthalanhydride group or a 1,8-naphthoylene-1',2'-benzimidazole fragment, in the 3 position undergo Vilsmeier formylation, like unsubstituted 1,3,5-triphenyl-2-pyrazoline, in the para position of the 1-phenyl ring. An investigation of the spectral-luminescence properties of the synthesized 1-(4'-formylphenyl)-3,5-diaryl-2-pyrazolines showed that the introduction in the 1-phenyl ring of an electron-acceptor aldehyde group, which is inferior with respect to its acceptor effect to the groupings in the 3 position of the heteroring, does not change the nature of the long-wave absorption band. Substantial hypsochromic and hypsofluoric effects as compared with the corresponding 1-phenyl-unsubstituted compounds are noted in the electronic spectra of these compounds.

1,5-Diphenyl-3-aryl-2-pyrazolines that contain an electron-donor substituent in the 3-aryl group readily undergo Vilsmeier formylation in the para position of the 1-phenyl ring [1-3]. The activation of the N-phenyl group of these compounds is explained [1, 2] by its strong interaction with the electron pair of the N_1 atom.

In the present research we studied the possibility of formylation of 1-phenyl-3,5-diaryl-2-pyrazolines (I) that contain groupings with a strong electron-acceptor effect in the position:



An intense absorption band at 1680 and 1689 cm^{-1}, respectively, which can be assigned to the stretching vibrations of the C = O bond of an aldehyde group, is observed in the IR spectra of the products isolated in the reaction of Ia, b with dimethylformamide (DMF) in the presence of phosphorus oxychloride. In addition to this band, absorption corresponding to the stretching vibrations of a C = N bond at 1600 cm^{-1} and a number of other bands that are characteristic for 1,3-diaryl-2-pyrazolines [4] appear in the spectra.

The PMR spectrum of the product of formylation of pyrazoline Ia contains quartets of nonequivalent protons of the 4 position (3.21 and 3.90 ppm, $J_{gem} = 17.4$, $J_{45} = 6.1$ and 12.4 Hz [5-8]), a 5-H quartet (5.47 ppm), a singlet of a formyl proton at 9.68 ppm, and a multiplet of phenyl protons (6.7-7.7 ppm). This constitutes evidence that under the conditions of the Vilsmeier reaction an aldehyde group is not introduced in the 4 position of the pyrazoline ring as assumed in [9] but rather in the para position of the 1-phenyl ring, as in the case of other 1,5-diphenyl-3-aryl-2-pyrazolines [1-3]. Compounds Ib, c behave in the same way, although in the IR spectra of the product of formylation of Ic in both the solid state and in chloroform we were unable to clearly observe an absorption band of an aldehyde C = O bond, which is evidently overlapped by the C = O band of the

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TABLE 1. Characteristics of I and II

Compound	mp, °C	N found, %	Empirical formula	N calc., %	Yield, %	Absorption in toluene		Fluorescence in toluene	
						λ_{max}, nm	$\varepsilon \cdot 10^{-4}$, liters · mole^{-1} · cm^{-1}	λ_{max}, nm	quantum yield
Ia	—	—	—	—	—	445	2,16	568	—
Ib	—	—	—	—	—	495, 345 [19]	1,20; 1,58 [19]	585 [19]	0,30
Ic[a]	—	—	—	—	—	510, 340 [13]	3,02; 1,90 [13]	600 [13]	0,90 [18]
IIa, form A	181—182	9,6	$C_{22}H_{17}N_3O_3$	10,1	60	435, 336, 422; 317, 327[b]	3,20; 2,30 —	540 —	— —
IIa, form B	185—186	9,9	$C_{22}H_{17}N_3O_3$	10,1	60	435, 336, 422; 317, 327[b]	3,20; 2,33 —	540 —	— —
IIb	201—202	6,4	$C_{28}H_{18}N_2O_4$	6,3	50	482, 342	2,68; 2,42	555	0,80
IIc	283—284	9,9	$C_{35}H_{24}N_4O_3$	10,2	83	497, 350	2,74; 2,10	570	0,76

[a] The industrially produced luminophore with red luminescence, which is a mixture of the 4- and 5-substituted isomers, the spectral-luminescence characteristics of which are virtually the same [20]. The product (IIc) of formylation of this luminophore is also the same mixture of 4- and 5-substituted isomers. [b] Data in isooctane.

1,8-naphthoylene-1',2'-benzimidazole grouping (at 1705 and 1694 cm^{-1} in KBr and in chloroform, respectively). However, the analogy in the change in the electronic absorption and fluorescence spectra of II as compared with starting I for all cases (see Table 1) makes it possible to assume that they have a similar structure.

In various experiments under virtually unchanged conditions of synthesis we isolated IIa in two forms: A bright-red finely crystalline powder with mp 181-182°C (form A) and bright-orange acicular crystals with mp 185-186°C (form B). The IR spectra of these forms in the solid phase give coincident principal bands that are characteristic for 1,3-diaryl-substituted 2-pyrazolines but differ somewhat with respect to the relative intensities of the peaks at 700-900 cm^{-1}. Forms A and B are identical in solutions and give identical absorption and fluorescence spectra, as well as identical PMR spectra. It may be assumed that forms A and B are polymorphic modifications. Polymorphic forms are also characteristic for 1,3-diphenyl-5-(p-chlorophenyl)-2-pyrazoline [10].

Thus we have established that the introduction of groupings with a strong electron-acceptor effect in the 3 position of the pyrazoline ring does not change the specificity of the formylation of 1-phenyl-3,5-diaryl-2-pyrazolines. Consequently, in the ground state of these molecules interaction of the electron pair of the N_1 atom with the π-electron system of the N-phenyl group is more substantial than interaction with the electron-acceptor grouping in the 3 position.

A comparison of the spectral-luminescence characteritics of IIa-c with the data for the analogous I (see Table 1) shows that introduction of an aldehyde group in the para position of the 1-phenyl ring in Ia-c gives rise to hypsochromic and hypsofluoric effects. This principle is in agreement with the concept [11-13] that the long-wave absorption band of 1,3,5-triphenyl-2-pyrazoline and Ia-c is due to intramolecular transfer of charge from the $C_6H_5{-}N <$ grouping to the $-N{=}C{-}Ar$ group. The aldehyde group substantially reduces the electron-donor properties of the aniline fragment of the investigated molecules, which somewhat hinders the indicated intramolecular charge transfer on passing to the excited state and is reflected in the increase in the energy of the $S_0 \rightarrow S^*_1$ transition. Thus the introduction of a second weaker electron-acceptor substituent in the 1-phenyl ring in 2-pyrazoline derivatives Ia-c, which contain groupings with a strong electron-acceptor effect in the 3 position is not accompanied by a change in the character of the $S_0 \rightarrow S^*_1$ transition and the corresponding long-wave absorption band. This principle differs qualitatively from that observed [14] when an aldehyde or other electron-acceptor group is introduced in the 1-phenyl ring of 1,3,5-triphenyl-2-pyrazoline or substituted 1,3,5-triphenyl-2-pyrazolines that contain substituents with a relatively weakly expressed electronic effect in the 3-phenyl ring. In these cases the nature of the $S_0 \rightarrow S^*_1$ transition changes, and this is responsible for the specific peculiarities in the spectral-luminescence properties of compounds of this type.

The effect of electron-acceptor aryl groupings in the 3 position of the pyrazoline ring on absorption and fluorescence λ_{max} bands of IIa-c does not differ qualitatively from the effect in the Ia-c series. It should be noted that the conclusions regarding the character of the intramolecular electron interactions in triaryl-2-pyrazolines that we drew in this paper and in previous communications [1, 2, 15] make it possible to precisely

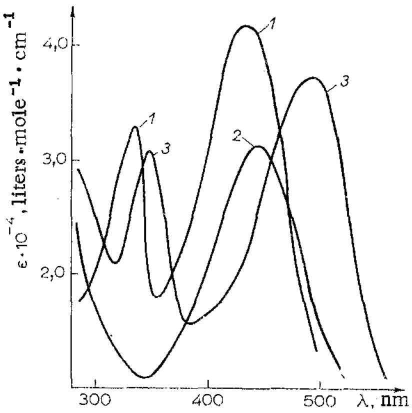

Fig. 1. Absorption spectra in toluene: 1) IIa; 2) Ia; 3) IIc.

determine the reasons for the significant bathochromic and bathofluoric effects due to electron-acceptor substituents introduced in the 3-phenyl ring. We cannot agree with the assumption [11] that this principle is due to the cooperation of the electron-acceptor substituents in the 3-phenyl ring and polarization of the chromophore system of the molecule in the ground state. It follows from [1, 2, 14, 15] that the predominant electronic shifts in the 1,3,5-triphenyl-2-pyrazoline molecule in the ground (to the 1-phenyl ring) and excited (to the 3-phenyl ring) states proceed in opposite directions; according to the results obtained in the present research, electron-acceptor substituents in the 3-phenyl ring do not substantially change the character of the electronic interactions in the ground state. The above-indicated strong effect of such substituents on λ_{max} of the long-wave absorption band and the fluorescence band should therefore be ascribed to the fact that they promote the electronic shifts that are characteristic for the excited S^*_1 state (intramolecular transfer of charge from the aniline fragment to the arylazomethine group) by lowering the energy of this state.

The weak interaction of the cross-conjugated aniline and hydrazone fragments of the IIa-c molecules due to the counterpolarizing effects of the electron-acceptor groupings in both fragments in the ground state may be manifested in an increase in the probability of the electron transitions corresponding to local excitation. Thus, in contrast to Ia, a second band of comparable intensity appears in the spectrum of IIa, in addition to the long-wave absorption band (see Fig. 1). With respect to its characteristics (position, intensity, and the development of a vibrational structure in isooctane) it is similar to the long-wave π,π^* band of p-dimethylaminobenzaldehyde (λ_{max} 320 nm in isooctane [14]). Consequently, the transition corresponding to this band is localized primarily in the formyl-substituted aniline fragment and is characterized by a shift of the electron density from the heteroring N_1 atom to the aldehyde group. A similar band, which, however, is shifted bathochromically somewhat as compared with the band of IIa, is also observed in the absorption spectra of aldehydes IIb, c (Fig. 1), although in these cases absorption in the spectra of the starting 2-pyrazolines Ib, c (see Table 1), which is evidently associated with local excitation of the aryl grouping in the 3 position, is also present in the same region.

Compounds IIb, c, which fluoresce in the yellow and orange regions of the spectrum, respectively, with high quantum yields, may find application as organic luminophores for coloring polymeric materials, in compositions for luminescence defectoscopy, etc. [16]. Aldehyde IIa is characterized by relatively weak luminescence; this is in agreement with the concept [17] of the quenching effect of a nitro group in aromatic compounds.

Compound IIb, which contains an anhydride grouping, dissolves in alkalis to give the corresponding salts of 4-[1-(p-formylphenyl)-5-phenyl-2-pyrazolin-3-yl] naphthalene-1,8-dicarboxylic acid. These salts are soluble in water and fluoresce intensely in a shorter-wave region of the spectrum as compared with anhydride IIb (for example, the fluorescence λ_{max} of the sodium salt in water is 510 nm). The short-wave shift of the fluorescence spectrum of the salt as compared with the spectrum of IIb is evidently a consequence of the weaker electron-acceptor properties of the naphthalene-1,8-dicarboxylic acid dianion grouping as compared with the napththalanhydride group. These salts can be used as water-soluble organic luminophores with yellow-green luminescence.

EXPERIMENTAL

The IR spectra of the synthesized compounds at 700-3800 cm^{-1} (NaCl and LiF prisms) were recorded with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in $CDCl_3$ were recorded with a Tesla BS-487 spectrometer (80 MHz) with tetramethylsilane as the internal standard. The absorption and fluorescence spectra were recorded by the method in [2]. The fluorescence quantum yields were determined by the equal-absorption method relative to 4-(1,5-diphenyl-2-pyrazolin-3-yl)-N-phenylnaphthalimide (quantum yield 0.7) [18].

1-(p-Formylphenyl)-3-(p-nitrophenyl)-5-phenyl-2-pyrazoline (IIa). This compound was obtained by formylation of Ia [8] with dimethylformamide (DMF) in the presence of phosphorus oxychloride by the method in [9]. The yield was 60%. The reaction product was purified by chromatography of a benzene solution on aluminum oxide with subsequent recrystallization from isopropyl alcohol. In various experiments we obtained form A as a bright-red finely crystalline powder with mp 181-182°C and form B as bright-orange acicular crystals with mp 185-186°C.

4-[1-(p-Formylphenyl)-5-phenyl-2-pyrazolin-3-yl]naphthalic Anhydride (IIb) and 4(5)-[1-(p-Formylphenyl)-5-anisyl-2-pyrazolin-3-yl]-1,8-naphthoylene-1',2'-benzimidazole (IIc). These compounds were obtained in the same way as IIa by formylation of, respectively, Ib [19] and Ic (the industrially produced luminophore with red luminescence). The reaction product after hydrolysis of the intermediate complex was removed by filtration, washed with water until the wash waters were neutral, and dried. The products were purified by chromatography of the benzene solutions on aluminum oxide with subsequent recrystallization from ethanol–chlorobenzene (10 : 1). The characteristics of the products are presented in Table 1.

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