ORGANIC LUMINOPHORES OF THE PYRAZOLINE SERIES WITH TWO UNCONJUGATED FLUOROPHORES

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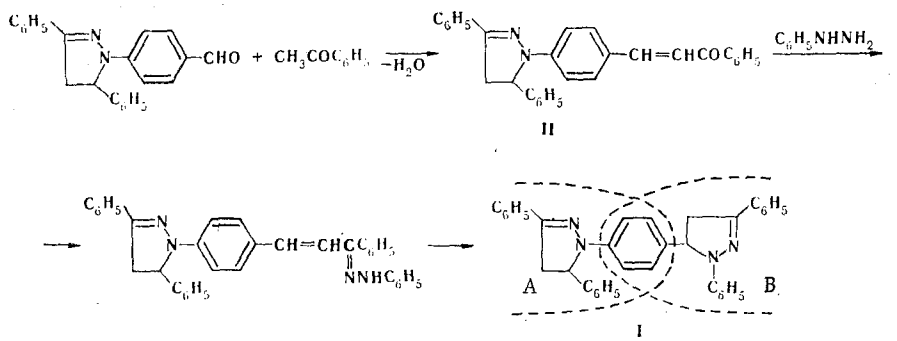
Condensation of 1-(p-formylphenyl)-3,5-diphenyl-2-pyrazoline with 4-acetyl-N-phenylnaphthalamide and a mixture of 3- and 4-acetyl-7H-benzimidazo[1,2-b]benz[de]isoquinolin-7-ones and subsequent heating of the products with phenylhydrazine were used to synthesize luminophores with orange and orange-red luminescence that have high quantum yields in aromatic solvents. Intramolecular transfer of the electronic excitation energy is observed for these compounds in toluene.

Aromatic substituted 2-pyrazolines are effective organic luminophores and are used in scintillation technology [1], in coloring polymeric materials [2], in the dosimetry of radioactive emissions [3], and for other purposes. We have obtained and investigated luminophores of the pyrazoline series with two disengaged fluorophores, each of which contains a pyrazoline ring. One of the fluorophores (A) in these compounds is a residue of the 1,3,5-triphenyl-2-pyrazoline (TPP) molecule that is bonded in the para position of the N-phenyl grouping with a saturated hydrocarbon link of a second pyrazoline ring, which interrupts the conjugation chain between the fluorophores. It is interesting to follow the change in the luminescence properties of the synthesized substances from the shift to the long-wave region of the absorption maximum of fluorophore B.

Compound I, which was mentioned in [4], was obtained by condensation of 1-(p-formylphenyl)-3,5-diphenyl-2-pyrazoline [5] with acetophenone in an alcoholic alkaline medium and subsequent reaction of the resulting 1-[4-(benzoylvinyl)phenyl)]-3,5-diphenyl-2-pyrazoline (II) with phenylhydrazine.



Luminophores III and IV were synthesized via a similar scheme, but 4-acetylnaphthalic acid phenylimide and a mixture of 3- and 4-acetyl-7H-benzimidazo[1,2-b]benz[de]isoquinolin-7-ones [6,7], respectively, were introduced in place of acetophenone into the condensation with 1-(p-formylphenyl)-3,5-diphenyl-2-pyrazoline.

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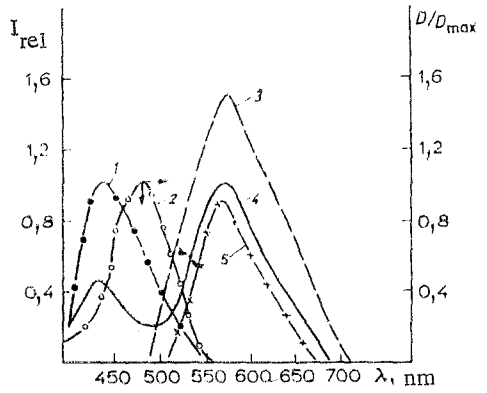
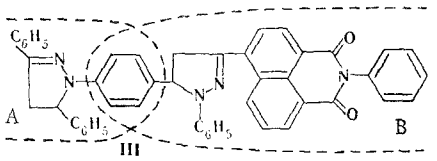
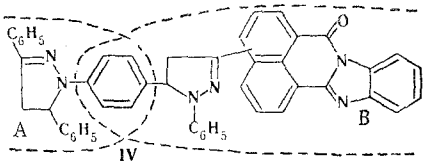


Fig. 1. Luminescence (1, 3-5) and absorption (2) spectra in toluene: 1) 1,3,5-triphenyl-2-pyrazoline; 2) and 5) bright-orange 575-PT luminophore; 3) 1-(3,5-diphenyl-2-pyrazolin-1-yl)-4-[1-phenyl-3-(1,3-dioxo-2-phenyl-2,3-dihydro-1H-benz[de]-isoquinolin-6-yl)-2-pyrazolin-4-yl]-benzene (III); 4) mixture of III and bright-orange 575-PT luminophore.


III


IV

Luminophore IV is a mixture of isomers that differ from one another with respect to the position of the pyrazoline ring in the naphthalene ring. The difference in the structures of the isomers should not have a substantial effect on the spectral-luminescence properties of these substances [7].

Compound I contains two TPP residues in which the pyrazoline rings are not included in the overall conjugation chain, despite the fact that the A and B fragments have a common aromatic ring. Complete additivity with respect to the spectrum of TPP is observed in its absorption spectrum (λ_{max} 360 nm): The maxima coincide, and the intensity of the absorption of I (ε = 40,500) is twice the intensity observed for TPP (ε = 20,000). The luminescence spectra are also close, the positions of their maxima (440 nm) coincide, and the absolute quantum yields for the two compounds are identical (η = 0.45).

Compounds III and IV differ to a considerably greater degree with respect to the spectral-luminescence properties of the fluorophores that form them. The first compound is a luminophore with orange luminescence, while the second compound is a luminophore with orange-red luminescence. Bands for which both fluorophores are responsible are clearly seen in their absorption spectra. However, the luminescence spectra contain only bands that correspond to luminescence of the fragment with longer-wave emission (Fig. 1). It was natural to assume that the absence of a short-wave band in the luminescence spectra is associated with intramolecular nonradiating energy transfer, in which the A fragment is the energy donor, and the B fragment is the energy acceptor. To verify this assumption we studied the spectral luminescence properties of equimolar mixtures of model compounds with structures similar to the A and B fragments and compared them with the properties of luminophores III and IV.

The absorption and luminescence spectra of each of the components of the mixture of compounds that model the fragments of luminophore III are shown in Fig. 1. It may be noted that the luminescence band of TPP, which corresponds to the A fragment, overlaps quite well with the absorption band of the bright-orange 575-PT luminophore, which is similar to the B fragment. This creates conditions for intermolecular energy transfer from the molecules of the first substance to the molecules of the second substance. In fact, a comparison of the luminescence spectra of toluene solutions of TPP and the bright-orange 575-PT luminophore with the luminescence spectra of their equimolar mixture in the same solvent at a concentration of $1 \cdot 10^{-4}$ mole/liter shows that a small amount of transfer of the electronic excitation energy from the luminophore donor to the luminophore acceptor occurs in the mixture. The intensity of the luminescence of the mixture in the same region of the spectrum in which the luminescence maximum of the long-wave luminophore lies is somewhat higher than in the case of the individual luminophore acceptor. At the same time, the intensity of the lumi-

nescence of the luminophore donor decreases as compared with TPP. Figure 1 also shows that intramolecular energy transfer between the fluorophores of III is considerably greater than intermolecular transfer in the mixture. A short-wave band is completely absent in the luminescence spectrum of III, whereas the maximum of the long-wave band is found in the same place as the long-wave maximum in the luminescence spectrum of the mixture. The intensity of the luminescence of III is greater by a factor of 1.5 than the luminescence intensity of the mixture. A similar phenomenon is observed when one compares the spectra of IV and the mixture of luminophores that model the individual fragments of its molecules.

Thus the intramolecular transfer of the electronic excitation energy between the fluorophores of luminophores III and IV is more effective than intermolecular transfer in solutions of mixtures of the luminophores, the structure of which correspond to the individual fluorophores of these substances.

EXPERIMENTAL

The absorption spectra of toluene solutions were measured with an SF-4A spectrophotometer, while the luminescence spectra were measured with an apparatus consisting of a ZMR-3 mirror monochromator and an FEU-18 optical emission detector, as compared with an FEU-49B optical emission detector and an M-95 microammeter for the luminophore with orange luminescence; the photoluminescence was excited with a DRSh-500 lamp, from the spectrum of which light with a wavelength of 365 nm was separated by means of a DMR-4 quartz monochromator. The absolute quantum yields were determined by the equal-absorption method [8]. Ultrapure toluene was used as the solvent for the spectral measurements.

1-(3,5-Diphenyl-2-pyrazolin-1-yl)-4-(1,3-diphenyl-2-pyrazolin-5-yl)benzene (I). A 6.6-g (0.02 mole) sample of 1-(p-formylphenyl)-3,5-diphenyl-2-pyrazoline was dissolved in 100 ml of ethanol at room temperature, 3.6 g (0.03 mole) of acetophenone and 20 ml of a 10% solution of sodium hydroxide were added, and the mixture was stirred for 4 h. The precipitated 1-[4-(benzoylvinyl)phenyl]-3,5-diphenyl-2-pyrazoline (II) [9] was removed by filtration, washed to remove the alkali, and crystallized from ethanol to give 6.2 g (73%) of product. A 4.3-g (0.01 mole) sample of ketone II was dissolved in 50 ml of acetic acid, and the solution was refluxed with 5 ml (0.05 mole) of phenylhydrazine for 4 h. The precipitate was removed by filtration and purified by chromatography of a solution in benzene with a continuous-operation column filled with aluminum oxide to give 3.5 g (68%) of a product with mp 217-218°C. Found: C 83.2; H 5.8; N 10.6%. $C_{36}H_{30}N_4$. Calculated: C 83.4; H 5.8; N 10.8%.

A similar reaction of 9.6 g (0.03 mole) of 1-(p-formylphenyl)-3,5-diphenyl-2-pyrazoline, 9.5 g (0.03 mole) of 4-acetylnaphthalic acid N-phenylimide [6], and 5 ml (0.05 mole) of phenylhydrazine gave 8 g (37%) of 1-(3,5-diphenyl-2-pyrazolin-1-yl)-4-[1-phenyl-3-(1,3-dioxo-2-phenyl-2,3-dihydro-1H-benz[de]isoquinolin-6-yl)pyrazolin-2-yl]benzene (III) with mp 214-215 °C. Found: C 80.7; H 5.0; N 9.6%. $C_{48}H_{35}N_5O_2$. Calculated: C 80.9; H 4.9; N 9.8%. A similar reaction of 3.3 g (0.01 mole) of 1-(p-formylphenyl)-3,5-diphenyl-2-pyrazoline, 3.9 g (0.01 mole) of a mixture of 3- and 4-acetyl-7H-benzimidazo[1,2-b]-benz[de]isoquinolin-7-one [7], and 5 ml (0.05 mole) of phenylhydrazine gave 5 g (70%) of 1-(3,5-diphenyl-2-pyrazolin-1-yl)-4-[1-phenyl-3-(7-oxo-7H-benzimidazo[1,2-b]benz[de]isoquinolin-3(and 4)-2-pyrazolin-5-yl]benzene (IV) with mp 268-270°C. Found: C 79.3; H 4.5; N 11.6%. $C_{48}H_{36}N_6O$. Calculated: C 79.4; H 4.7; N 11.8%.

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BROMO DERIVATIVES OF 1-(4-HYDROXYPHENYL)DIHYDROURACIL AND 1-(4-HYDROXYPHENYL)-5- OR -6-METHYLDIHYDROURACILS

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Bromination of 1-(4-hydroxyphenyl)dihydrouracil and its 6-methyl derivative with bromine in refluxing acetic acid gave 1-(3,5-dibromo-4-hydroxyphenyl)-5-bromo-, 1-(3,5-dibromo-4-hydroxyphenyl)-5-bromo-, and 1-(3,5-dibromo-4-hydroxyphenyl)-5-bromo-6-methyldihydrouracils and 1-(3,5-dibromo-4-hydroxyphenyl)-5-methyluracil. 5-Bromo- and 5,5-dibromodihydrouracils were dehydrobrominated, and the same compounds undergo decomposition to 3,5-dibromo-4-hydroxyphenylurea upon alkaline hydrolysis.

A number of studies has been devoted to the bromination of 1-aryldihydrouracils. It has been pointed out [1] that 1-(1-naphthyl)-5-bromodihydrouracil is formed in the bromination of 1-(1-naphthyl)dihydrouracil, but later in [2] it was demonstrated that under these conditions replacement by bromine takes place in the aromatic ring rather than in the heterocyclic ring to give 1-(4-bromonaphthyl)dihydrouracil.

In the present research we accomplished the bromination of 1-(4-hydroxyphenyl)dihydrouracil (Ia) and its derivatives (Ib,c) with bromine in refluxing acetic acid. Depending on the amount of bromine used for the bromination of dihydrouracil Ia, 1-(3,5-dibromo-4-hydroxyphenyl)-5-bromodihydrouracil (IIa) or 1-(3,5-dibromo-4-hydroxyphenyl)-5,5-dibromohydrouracil (IIIa) is formed in good yield. Bromination of the heteroring of 1-hydroxyphenyldihydrouracils takes place when 2 moles of bromine are added per mole of dihydrouracil Ia, i.e., the amount that is necessary for replacement of the hydrogen in the aromatic ring. A small amount of 5-bromodihydrouracil IIa is also formed, this is easily followed by means of NMR spectroscopy. In the synthesis of IIa 5-10% of 5,5-dibromodihydrouracil IIIa is also formed.

1-Substituted thymines were obtained by the action of bromine in refluxing glacial acetic acid on 1-substituted 5-methyldihydrouracils [3]. Consequently, replacement of the hydrogen atom in the 5 position of the heteroring by bromine is accompanied by dehydrobromination. Under the same conditions 1-(3,5-dibromo-4-hydroxyphenyl)-5-methyluracil (IVb) was obtained from Ib.

However, the bromination of 1-(4-hydroxyphenyl)-6-methyldihydrouracil (Ia) leads to the formation of 1-(3,5-dibromo-4-hydroxyphenyl)-5-bromo-6-methyl-dihydrouracil (IIc), and we were unable to detect the corresponding 5,5-dibromo derivative.

1-Substituted 5-bromodihydrouracils are converted to the corresponding uracils by the action of nucleophilic reagents [1,4] and also by heating at the melting points [5]. Dehydrobromination occurs when bromodihydrouracils IIa,c are refluxed in dimethylformamide (DMF) in the presence of lithium chloride or in solutions of alkalis. Dibromo derivative

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