heated at 80-90°C for 5 min, after which it was cooled, and the precipitate was removed by filtration and washed with acetone to give 0.1 g (47%) of colorless needles of salt Ia with mp 205-207°C (no melting-point depression was observed for a mixture with a genuine sample of iodide Ia). Evaporation of the acetone left 0.09 g (49%) of colorless needles of pyrazole IIIa with mp 111-112°C; the product was identical to IIIa.

B) Triethylamine in Acetonitrile. A solution of 0.7 g (2 mmole) of iodide VIIa and 0.35 ml (2.5 mmole) of triethylamine in 5 ml of acetonitrile was refluxed for 1 h, after which the mixture was evaporated to dryness, and the residue was washed with water and chloroform to give 0.05 g (14%) of yellow-green crystals that were identical to IIa. Chromatography of the chloroform solution with a column filled with $Al_2O_3$ (elution with chloroform) gave 0.3 g (66%) of pyrazole IIIa.

C) Potassium Carbonate in DMF. A mixture of 0.2 g (0.5 mmole) of ketimine VIIb and 0.1 g (0.7 mmole) of potassium carbonate in 2 ml of DMF was heated at 80-90°C for 5 min, after which it was cooled and diluted with 10 ml of water, and the precipitate was removed by filtration to give 0.11 g (86%) of colorless needles of IIIb with mp 111-112°C (no melting-point depression was observed for a mixture of this product with a genuine sample of pyrazole IIIb).

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# ORGANIC LUMINOPHORES WITH ORANGE-RED AND RED LUMINESCENCE

É. A. Shevchenko V. E. Bondarenko,
and V. V. Proshkina

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New organic luminophores that have orange-red and red luminescence and contain conjugated 1,3,5-triaryl-2-pyrazoline and 7H-imidazo[1,2-b]benz[de]isoquinoline-7-one groupings in the same molecule were synthesized. The introduction of a 2-naphthyl residue in the 1 position of the pyrazoline ring and annelation of 1,2-naphthylene or 4,5-naphthylene systems to the imidazole ring in place of the phenylene system lead to bathochromic and bathofluoric effects. The luminescence maxima of the synthesized compounds are found at 575 to 645 nm, and the quantum yields range from 0.7 to 0.9.

Primarily luminophores with blue luminescence are known in the 1,3,5-triaryl-2-pyrazoline series [1]. By combining 1,3,5-triaryl-2-pyrazoline and 7H-benzimidazo[1,2-b]benz[de]isoquinolin-7-one groupings in the same molecule we have synthesized seldom encountered luminophores with orange-red luminescence, including 3(and 4)-(1,5-diphenyl-2-pyrazolin-3-yl)-7H-benzimidazo[1,2-b]benz[de]isoquinolin-7-one (Ia) with a luminescence maximum in toluene at 595 nm and a quantum yield of 0.9 [2]. Inasmuch as it is a strong electron acceptor, the 7H-benzimidazo[1,2-b]benz[de]isoquinolin-7-one residue interacts with the unshared electrons of the $N_{(1)}$ atom, thereby giving rise to strong bathochromic and bathofluoric effects. Two isomers that differ from one another with respect to their melting points and IR spectra but have virtually identical electronic absorption spectra and luminescence spectra are formed in the synthesis of Ia. It is therefore unnecessary to isolate the individual isomers for various applications [3].

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TABLE 1. 3(and 4)-(1,5-Diaryl-2-pyrazolin-3-yl)-7H-imidazo[1,2-b]benz[de]isoquinolin-7-ones

| Compound | Ar | Ar′ | Ar″* | mp, °C | $\lambda_{max}$(abs), nm ($\varepsilon \cdot 10^{-4}$) | $\lambda_{max}$(lum), nm ($\eta$) | N found, % | Empirical formula† | N calc., % | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|
| Ia | $C_6H_5$ | $C_6H_5$ | $C_6H_4$ | 262—263 | 505 (2,51) | 595 (0,90) | 11,2 | $C_{33}H_{22}N_4O$ | 11,4 | 65 |
| Ib | $C_6H_5$ | H | $C_6H_4$ | 100—101 | 505 (2,08) | 595 (0,85) | 13,6 | $C_{27}H_{18}N_4O$ | 13,5 | 42 |
| Ic | $C_6H_5$ | 4-$CH_3OC_6H_4$ | $C_6H_4$ | 237—238 | 510 (3,16) | 600 (0,90) | 10,6 | $C_{34}H_{24}N_4O_2$ | 10,7 | 63 |
| Id | $C_6H_5$ | 4-$(CH_3)_2NC_6H_4$ | $C_6H_4$ | 258—259 | 515 (2,75) | 610 (0,70) | 13,2 | $C_{35}H_{27}N_5O$ | 13,1 | 61 |
| Ie | 2-$C_{10}H_7$ | $C_6H_5$ | $C_6H_4$ | 271—272 | 520 (2,23) | 630 (0,80) | 10,5 | $C_{37}H_{24}N_4O$ | 10,4 | 60 |
| If | $C_6H_5$ | $C_6H_5$ | 1,2-$C_{10}H_6$ | >350 | 525 (2,67) | 625 (0,82) | 9,8 | $C_{37}H_{24}N_4O$ | 9,8 | 52 |
| Ig | 2-$C_{10}H_7$ | $C_6H_5$ | 1,2-$C_{10}H_6$ | 225—226 | 530 (2,71) | 640 (0,70) | 9,3 | $C_{41}H_{26}N_4O$ | 9,5 | 50 |
| Ih | 2-$C_{10}H_7$ | 4-$CH_3OC_6H_4$ | $C_6H_4$ | 219—220 | 530 (2,2) | 630 (0,72) | 9,8 | $C_{38}H_{26}N_4O_2$ | 9,8 | 46 |
| Ii | 2-$C_{10}H_7$ | 4-$CH_3OC_6H_4$ | 1,2-$C_{10}H_6$ | 203—204 | 530 (2,74) | 640 (0,70) | 9,6 | $C_{42}H_{28}N_4O_2$ | 9,0 | 64 |
| Ij | 2-$C_{10}H_7$ | 4-$CH_3OC_6H_4$ | 4,5-Acenaphthenylene | 160—161 | 530 (2,81) | 640 (0,80) | 8,6 | $C_{44}H_{30}N_4O_2$ | 8,6 | 46 |
| Ik | 2-$C_{10}H_7$ | 4-$(CH_3)_2NC_6H_4$ | $C_6H_4$ | 267—268 | 520 (2,18) | 630 (0,72) | 12,2 | $C_{39}H_{29}N_5O$ | 12,0 | 45 |
| Il | 2-$C_{10}H_7$ | 4-$(CH_3)_2NC_6H_4$ | 1,2-$C_{10}H_6$ | 275—276 | 525 (2,76) | 640 (0,77) | 11,1 | $C_{43}H_{31}N_5O$ | 11,0 | 53 |
| Im | 2-$C_{10}H_7$ | 4-$(CH_3)_2NC_6H_4$ | 4,5-Acenaphthenylene | 185—186 | 525 (2,93) | 640 (0,75) | 10,8 | $C_{45}H_{33}N_5O$ | 10,6 | 43 |

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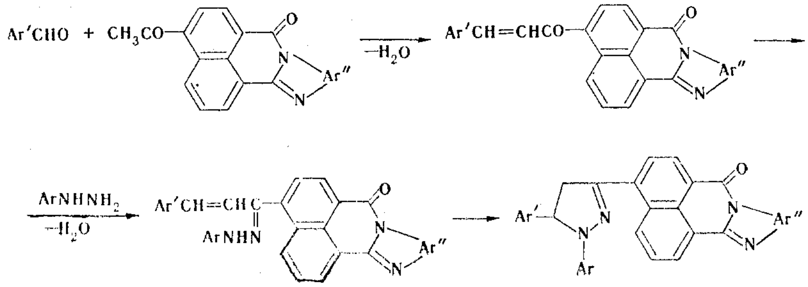
*The 1,2-naphthylene grouping is depicted by 1,2-$C_{10}H_6$.

†The compositions of all of the compounds were also confirmed by determination of the percentages of C and H.

The aim of the present research was to obtain substances that have structures similar to that of Ia but, however, luminesce in the longer-wave region. In view of the fact that the introduction of polycyclic or styryl groupings in the 3 position of the pyrazoline ring makes it possible to shift the luminescence to the blue-green or green region of the spectrum [4], while the introduction of a nitro group shifts the luminescence to the yellow-green region [5], to reach our goal it was necessary to either lengthen the conjugation chain of Ia or intensify the polarization in the direction from the pyrazoline ring to the 7H-imidazo-[1,2-b]benz[de]isoquinolin-7-one residue.

We obtained new organic luminophores with orange-red and red luminescence (Ib-m, Table 1) via the scheme previously used for the synthesis of Ia.



Ia-m

The synthesized compounds are mixtures of isomers. In the simplest cases (for example, in the case of Ic, d, h) two isomers are formed, whereas the formation of four isomers is possible when the phenylene system in the 7H-benzimidazo[1,2-b]benz[de]isoquinolin-7-one grouping is replaced by a polycyclic residue. Data on the spectral-luminescence properties of the products are presented in Table 1.

As in the case of the simplest 1,3,5-triaryl-2-pyrazolines, substituents in the 5-phenyl group of the pyrazoline ring give rise to a slight bathochromic effect (Ic, d).

We were able to shift the luminescence significantly to the long-wave side as compared with Ia by introduction of a 2-naphthyl residue in the 1 position of the pyrazoline ring (Ie, h, k) or by annelation of 1,2-naphthylene or 4,5-acenaphthylene residues to the imidazole ring in place of the phenylene residue (If, g, i, j, l, m). The introduction of each of these groups of atoms leads to bathochromic and bathofluoric effects; the luminescence $\Delta\lambda$ values range from 25 to 35 nm. An increase in the chain of conjugated double bonds in the investigated system due to the simultaneous introduction of a 2-naphthyl group in the pyrazoline part and a 1,2-naphthylene or 4,5-acenaphthylene grouping in the 7H-imidazo[1,2-b]benz[de]isoquinolin-7-one part of the molecule leads to an even greater long-wave shift of the maxima in the absorption and luminescence spectra; the $\Delta\lambda$ values range from 30 to 45 nm (Ig, i, j, l, m). The luminescence quantum yields of the synthesized compounds range from 0.7 to 0.9.

## EXPERIMENTAL

The absorption spectra of toluene solutions (c $10^{-4}$-$10^{-5}$ mole/liter) of the compounds were recorded with an SF spectrophotometer. The luminescence spectra were recorded with an apparatus consisting of a ZMR-3 monochromator, an FÉU-18 optical emission detector, and an M-95 microammeter. The photoluminescence was excited with an SVDSh-500 lamp, from the spectrum of which light with a wavelength of 365 nm was isolated by means of a DMR-4 quartz monochromator. The absolute luminescence quantum yields ($\eta$) of solutions in toluene were determined by the equal-absorption method [6].

3(and 4)-(1,5-Diaryl-2-pyrazolin-3-yl)-7H-benzimidazo[1,2-b]benz[de]isoquinolin-7-ones (Ia-e, h, k), 3(and 4)-(1,5-Diaryl-2-pyrazolin-3-yl)-7H-naphth[1',2'- and 2',1'-4,5]imidazo-[1,2-b]benz[de]isoquinolin-7-ones (If, g, i, l), and 3(and 4)-(1,5-Diaryl-2-pyrazolin-3-yl)-7H-acenaphtheno[4',5'- or 5',4'-4,5]imidazo[1,2-b]benz[de]isoquinolin-7-ones (Ij, m). All of these compounds, except for Ib, were obtained by refluxing 0.01 mole of the corresponding arylhydrazine in 50-100 ml of ethanol in the presence of 0.05-0.1 mole of potassium hydroxide.

3(and 4)-(1-Phenyl-2-pyrazolin-3-yl)-7H-benzimidazo[1,2-b]benz[de]isoquinolin-7-one (Ib). A 0.4-g (5 mmole) sample of 40% formalin, 0.7 g (5 mmole) of 33% dimethylamine, and 1 ml of ethanol were added to a solution of 1.2 g (4 mmole) of 3(and 4)-acetyl-7H-benzimidazo[1,2-b]-benz[de]isoquinolin-7-one in 20 ml of acetic acid, and the mixture was refluxed for 3 h. A solution of 1 ml (10 mmole) of phenylhydrazine in 5 ml of ethanol was added, and the mixture was refluxed for 5 h. It was then poured into water, and the precipitate was removed by filtration, washed with water, and dried.

The substances were purified by chromatography of benzene solutions of them on aluminum oxide.

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# OXIDATION OF SOME HETARYLHYDRAZINES WITH SELENIUM DIOXIDE

Yu. A. Sedov

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The oxidation of 2-benzimidazolyl- and 2-quinoxalinylhydrazines with selenium dioxide in hydrochloric acid in the presence of cuprous chloride leads to the formation of 2-chloro derivatives of the heterocycles. When the reaction is carried out in ethanol, 2-benzimidazolylhydrazines give symmetrical formazans. In both cases oxidation proceeds through a step involving the formation of hetarenediazonium salts.

The oxidation of aqueous acidic solutions of arylhydrazine with selenium dioxide leads to the formation of arylamines, azoamino derivatives, and, when azo components are present, azo dyes. It is assumed [1] that the reaction proceeds through the intermediate formation of arenediazonium derivatives.

It seemed of interest to study this reaction as applied to some heterocyclic hydrazines. With this as our goal, we investigated the oxidation of 2-benzimidazolyl- and 2-quinoxalinylhydrazines (Ia-c) with selenium dioxide. 2-Chloro-substituted derivatives (IIIa-c) were obtained in 37, 58, and 10% yields, respectively, by oxidation of these compounds in hydrochloric acid in the presence of cuprous chloride. The low yield of 2-chloroquinoxaline IIIc is due to its partial hydrolysis under the reaction conditions (or during its isolation) to 2-quinoxalone (IVc), which was isolated from the reaction mixture in 13% yield. The oxidation of phenylhydrazine under the same conditions gives chlorobenzene (IIId). The structures of all of the compounds were confirmed by comparison of their data and IR spectra with the data and spectra for genuine samples [2, 3].

$$\underset{\text{Ia-d}}{R{-}NH{-}NH_2} \xrightarrow[HCl]{SeO_2} \underset{\text{II}}{[R{-}N{\equiv}N]^+Cl^-} \xrightarrow[HCl]{Cu_2Cl_2} \underset{\text{IIIa-d}}{RCl} \xrightarrow{H_2O} \underset{\text{IVc}}{R{-}OH}$$

I, III, IV a R=2-benzimidazolyl, b R=1-methyl-2-benzimidazolyl, c R=2-quinoxalinyl, d $R=C_6H_5$

The formation of chloro derivatives can be explained if it is assumed that the oxidation of hydrazines I proceeds, as in the case of [1], through a step involving the formation of the corresponding diazonium salts II with subsequent replacement of the diazo group by chlorine in the presence of cuprous chloride. This reaction can be regarded as the variant of the Sandmeyer reaction as applied to nitrogen-containing heterocyclic compounds.

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