BRIEF COMMUNICATIONS

ORGANIC ORANGE-RED LUMINOPHORES CONTAINING A PYRAZOLINE NUCLEUS AND A 1,8-NAPHTHOYLENE-1',2'-BENZIMIDAZOLE GROUPING

B. M. Krasovitskii and E. A. Shevchenko

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Isomeric orange-red luminescing substances containing a pyrazoline ring and a 1,8-naphthoylene-1',2'-benzimidazole grouping have been synthesized. An investigation of the UV absorption spectra, luminescence spectra, and IR spectra of the individual isomers has shown the desirability of separating the mixture of them formed in the synthetic process.

1, 8-Naphthoylene-1', 2'-benzimidazole (I) and many of its derivatives substituted in the benzene or the naphthalene nucleus are effective luminophores with yellow or yellow-green luminescence [1, 2].



Fig. 1. Absorption and luminescence spectra in toluene of III (1) and IIIa (2).

By combining in one molecule the 1,8-naphthoylene-1',2'-benzimidazole and 1,3,5-triarylpyrazoline groupings we have obtained luminophores with an orange-red and red luminescence (II) which luminesce both in the form of crystals and in solution [3].



 R_1 is an unsubstituted or substituted aromatic or heterocyclic radical, R_2 is an unsubstituted aromatic radical, and R_3 is an alkyl, aryl, or alkoxy group or halogen.

The scheme of the synthesis of the luminophores (II) and some of their properties can be considered with the isomeric compounds V and Va ($R_1 = p-CH_3OC_6H_4$; $R_2 = C_6H_5$; $R_3 = H$) as examples. The reaction of 4-acetylnaphthalic anhydride with o-phenylenediamine forms two isomeric acetylnaphthoylenebenzimidazoles (III) and (IIIa).



The condensation of each of them with anisic aldehyde leads to the unsaturated ketones IV and IVa.



When IV and IVa are heated with phenylhydrazine, the phenylhydrazones are formed which cyclize to Vand Va.



The position of the acetyl group in III and IIIa was established by the conversion of these compounds into the known 4- and 5-benzoylnaphthoylenebenzimiadzoles VII and VIIa [4] (see Experimental). For this, making use of the different solubilities of III and IIIa in ethanolic alkali, we separated them from one another and, by oxidation with sodium hypochlorite, converted them into the corresponding carboxylic acids (VI, VIa), from the chlorides of which and benzene by the Friedels-Crafts reaction we obtained VII and VIIa.

The absorption spectra of III and IIIa differ comparatively little from one another; there are greater differences in their luminescence spectra (Fig. 1): III luminesces in the region of shorter wavelengths than IIIa. A similar pattern is observed for the unsaturated ketones obtained from them.

In a comparison of the optical properties of the final products of synthesis, we did not observe any substantial differences either in the absorption spectra or in the luminescence spectra of the isomeric compounds V and Va (Fig. 2). The differences caused by the structural features of each of these substances are

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more pronounced in the IR spectra of their solutions in CCl₄: for both isomers there is a band in the 1370 cm^{-1} region and in one of them this is adjoined by a band in the region of higher frequencies and in the other by a band in the region of lower frequencies.

The luminophore Va is more readily soluble in organic solvents than V. This provides the possibility of separating a mixture of them if the separation of the isomers is not carried out at intermediate stages of the synthesis.

The use of the luminophores V and Va or a mixture of them as dyes for polymeric materials—in amounts of 0.001-0.01% of the weight of the polymer—makes it possible to obtain intense and light-fast fluorescing colorations by the dyeing of polystyrene and other plastics [5].

EXPERIMENTAL

Condensation of 4-acetylnaphthalic anhydride with o-phenylenediamine. A mixture of 34.2 g of 4-acetylnaphthalic anhydride, 23.1 g of o-phenylenediamine, and 350 ml of 1% sulfuric acid was boiled under reflux for 8 hr. After the mixture had been cooled, the precipitate was filtered off, washed on the filter with water, and dried. The yield of the mixture of III and IIIa was 40 g (90%). Mp 198°-210° C. Found, %: N. 8.96, 9.11. Calculated for C₂₀H₁₂N₂O₂, %: N.8.97.

Separation of a mixture of III and IIIa. Forty grams of the mixture of isomers obtained from 4-acetylnaphthalic anhydride and ophenylenediamine, 400 ml of ethanol, and 80 ml of 15% KOH was stirred with heating in the water bath for 6 hr. Then it was cooled to room temperature and the insoluble III was filtered off, washed on the filter with 150 ml of ethanol and 300 ml of water, and dried. It was then recrystallized from glacial acetic acid, chlorobenzene, and xylene. Yield 13 g, mp 248°-249° C. Found, %: N 8.89, 9.02, Calculated for C₂₀H₁₂N₂O₂, %: N8.97.

The filtrate was diluted with a fourfold amount of water and the precipitate of IIIa that deposited was filtered off, washed on the filter with water (150-200 ml) and dried. The benzene solution was chromatographed on Al₂O₃. Yield 9.5 g, mp 205^o-207^o C. Found, %: N 8.84, 8.72. Calculated for $C_{20}H_{12}N_2O_2$, %: N 8.97.

Condensation of III and IIIa with anisaldehyde. a) A mixture of 2 g of III, 20 ml of ethanol, and 1.5 ml of anisaldehyde was boiled for 10 min. After the reaction mixture had been cooled to room temperature, 20 ml of 10% NaOH was added and it was stirred for 3 hr, after which the precipitate was filtered off and washed on the filter with 30 ml of ethanol and 50 ml of water and was dried. It was recrystallized from glacial acetic acid. The yield of IV was 1.4 g (51%), mp 233°-234° C. Found, %: N 6.75, 6.70. Calculated for $C_{28}H_{18}N_2O_3$, %: N 6.51.

b) The condensation of IIIa with anisaldehyde was carried out similarly. The yield of IVa from 2 g of IIIa was 1.6 g (59%), mp 207°-208° C. Found, %: N 6.68, 6.52. Calculated for $C_{28}H_{18}N_2O_3$, %: N 6.51.

5-(p-Methoxyphenyl)-3-(1, 8-Naphthoylene-1', 2'-benzimidazol-4-yl)-1-phenyl- Δ^2 -pyrazoline (V). A mixture of 1 g of IV, 20 ml of ethanol, 10 ml of 10% NaOH, and 1 ml of phenylhydrazine was boiled under reflux for 3 hr. After cooling, the precipitate was filtered off, washed on the filter with ethanol (50 ml), and dried. A benzene solution was chromatographed on Al₂O₃. Yield 0.9 g (75%), mp 263°-264° C. Found, %: N 10.92, 10.87. Calculated for C₃₄H₂₄N₄O₂₁%: N 10.77.

5-(p-Methoxyphenyl)-3-(1, 8-naphthoylene-1', 2'-benzimidazol-5-yl)-1-phenyl-△²-pyrazoline (VA). This was synthesized analogously. The yield from 1 g of IVa was 0.85 g (70%), mp 241-242° C. Found, %: N 10.53, 10.65. Calculated for $C_{34}H_{24}N_4O_2$, %: N 10.77.



Fig. 2. Absorption and luminescence spectra in toluene of V (1) and Va (2).

Oxidation of III and IIIa, a) A mixture of 7 g of III, 280 ml of a saturated solution of calcium hypochlorite, and 35 ml of 10% NaOH was boiled under reflux for 8 hr and cooled, and the precipitate was filtered off and boiled with 100 ml of 10% HCl, again filtered off, and heated at the boil with 500 ml of 5% sodium carbonate solution. The filtered solution was neutralized with hydrochloric acid. The precipitate that deposited was filtered off, washed with water, dried, and recrystallized from nitrobenzene. Yield 5.3 g (75%), mp > 300° C. Found, %: N 8.97, 9.11. Calculated for C₁₉H₁₀N₂O₃, %: N 8.91.

b) Compound IIIa was oxidized similarly. The yield of VIa from 3 g of IIIa was 2.5 g (83%), mp > 300° C. Found, %: N 8.74, 8.62. Calculated for $C_{19}H_{10}N_2O_3$, %: N 8.91.

4-Benzoyl-1, 8-naphthoylene-1', 2'-benzimidazole (VIII) was obtained by a published method [4] from VI and was purified by the chromatography of a benzene solution on Al_2O_3 . Mp $198^{\circ}-199^{\circ}$ C ($198^{\circ}-199^{\circ}$ C [4]).

5-Benzoyl-1,8-naphthoylene-1',2'-benzimidazole (VIIa). Obtained similarly. Mp $235^{\circ}-237^{\circ}$ C ($235^{\circ}-236^{\circ}$ C (4)).

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All-Union Scientific-Research Institute for Monocrystals, Scintillation Materials, and Particularly Pure Chemical Substances, Khar'kov