EXPERIMENTAL

The initial I had bp 142° C (710 mm), d_4^{20} 0.9505, n_D^{20} 1.50232. The construction of the apparatus for the oxidation of I and that of the system for collecting the reaction products have been described previously [15].

The determination of the nicotinic acid was carried out by a polarographic method [16]. Gas-liquid chromatography with a DIP-1 flame ionization detector was used for the analysis of the other reaction products. The stationary phase was Tween-20 deposited on a INZ-600 support previously treated with a 5% solution of potassium hydroxide (grain dimensions 0.25–0.5 mm). The amount of the liquid phase was 25% of the weight of the support. The stainless steel column, 2 m long and 4 mm in internal diameter, was thermostated at 140° C. The carrier gas was nitrogen-containing ammonia (0.1–0.2%), passed at the rate of 0.05 l/min. Under these conditions the retention times of compounds IV, I, II, and V, were 4, 5, 24, and 27 minutes, respectively.

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INVESTIGATIONS ON BENZODIAZINES

X. The Luminescence Properties of Some Quinazoline Derivatives*

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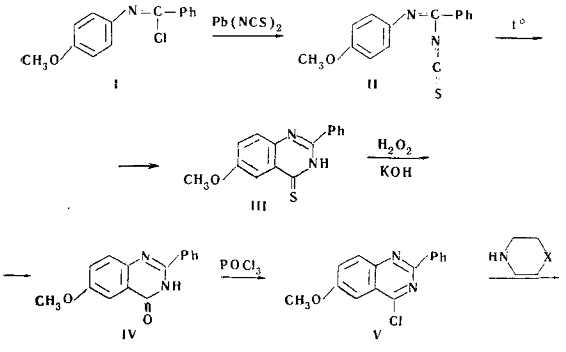
The luminescence properties of 6-methoxy-2-phenyl-4-piperidinoquinazoline and 6-methoxy-4-morpholino-2-phenylquinazoline, synthesized for the first time, have been studied.

In the course of investigations that we have carried out on quinazoline derivatives, we have synthesized the previously unknown 6-methoxy-2-phenyl-4-piperidinoquinazoline (**VIa**) and 6-methoxy-4-morpholino-2-phenylquinazoline (**VIb**) by the following route:



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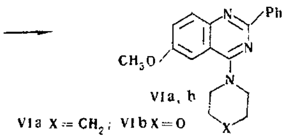
*For part IX, see [1].



VIa, b
VIa X = CH_2; VIb X = O

A feature of compounds **VIa** and **VIb** is the violet fluorescence arising under UV irradiation from crystals and solutions in hydrocarbon solvents. Solutions of both compounds in hexane and ethanol absorb over a wide spectral range; the two compounds are similar in respect of the intensity of the absorption (Figs. 1 and 2). The luminescence spectra of **VIa** and **VIb** in hexane and benzene have comparatively narrow bands in the 350–450 nm region with well-defined maxima almost coinciding for the two compounds. The long-wave absorption band, which, judging from its intensity (log ε 4.0 at λ_{max} 355 nm) is a $\pi-\pi$ band, shows mirror symmetry with the luminescence band (Fig. 3).

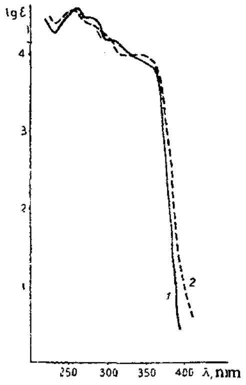


Fig. 1. Absorption spectra of VIa in hexane (1) and in ethanol (2).

The absolute quantum yields of solutions of the compounds studied in hexane and in benzene are comparatively low, but in the second of these solvents the quantum yield is considerably higher than in the first. Thus, for **VIa** it is 0.06 in hexane and 0.16 in benzene. In hydroxyl-containing solvents (ethanol, acetic acid), compounds VIa and **VIb** do not luminesce. In a mixture of benzene and ethanol (1 : 1), the quantum yield of **VIa** falls by a factor of 2 in comparison with the solution in benzene. The luminescence bands of crystals of both compounds are somewhat wider than those of the solutions, and their maxima are shifted in the long-wave direction as compared with solutions in hexane by ~40 nm. When **VIa** and **VIb** are dissolved in concentrated sulfuric acid, a faint yellow luminescence which disappears on dilution of the solution with water is observed.

EXPERIMENTAL

N-(p-Anisyl)benzimidoyl isothiocyanate (II). A solution of 0.1 mole of N-(p-anisyl)benzimidoyl chloride (I) [2] in 100 ml of absolute benzene was treated with 32 g of lead thiocyanate, and the mixture was boiled on the water bath for 2 hr. Then, it was filtered, and the benzene was distilled off from the filtrate. This gave a red oil, which was used without further purification to obtain the quinazolinethione. Yield 80–85%.

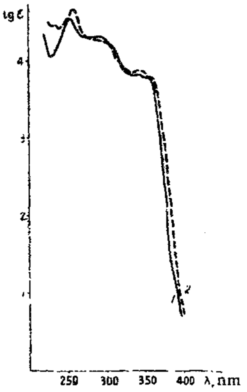


Fig. 2. Absorption spectra of VIb in hexane (1) and in ethanol (2).

6-Methoxy-2-phenylquinazoline-4-thione (III). A solution of 0.1 mole of II in 60 ml of m-xylene was boiled for 2 hr. On cooling, a precipitate deposited. Yellow needles (from benzene), mp 222–223° C, yield 40%. Found, %: C 67.42; H 4.54; N 10.36; S 12.08. Calculated for $C_{15}H_{12}N_2OS$, %: C 67.14; H 4.51; N 10.44; S 11.95.

6-Methoxy-2-phenylquinazoline-4-one (IV). A solution of 0.02 mole of III in 10% KOH (2- to 3-fold excess) was heated to 80° C, and a 30% solution of hydrogen peroxide was slowly added. The reaction mixture first acquired an intense yellow coloration, and then became colorless. It was filtered, and the product was precipitated from the filtrate with acetic acid. Colorless needles (from isopropanol), mp 247–248° C, yield 90%. Found, %: C 71.37; H 4.96; N 11.02. Calculated for $C_{15}H_{12}N_2O_2$, %: C 71.42; H 4.79; N 11.11.

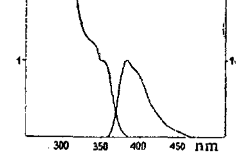


Fig. 3. Normalized absorption and luminescence spectra of **VIa** (upper graph) and VIb (lower graph) in hexane.

4-Chloro-6-methoxy-2-phenylquinazoline (V). This was obtained by a published method [3] as colorless or faintly yellowish needles, mp 126–128° C. Found, %: Cl 13.70. Calculated for $C_{15}H_{11}ClN_2O$, %: Cl 13.10.

6-Methoxy-2-phenyl-4-piperidinoquinazolines (VIa) and 6-methoxy 4-morpholino-2-phenylquinazoline (VIb). To a solution of 0.01

mole of the chloroquinazoline **V** in dry benzene was added 0.02 mole of piperidine or morpholine. The mixture was left at room temperature for 1 hr. The precipitate that had deposited was filtered off, and the benzene was distilled off from the filtrate to give the reaction product in the form of colorless crystals readily soluble in hot ethanol. **VIa:** mp 121–123° C (from ethanol). Found, %: C 74.96; H 6.56; N 13.59. Calculated for $C_{20}H_{21}N_3O$, %: C 75.21; H 6.63; N 13.16. **VIb:** mp 94–96° C (from ethanol). Found, %: C 71.41; H 5.88. Calculated for $C_{19}H_{19}N_3O_2$, %: C 71.01; H 5.96.

The absorption spectra of compounds **VIa** and **VIb** were studied on an SF-4 spectrophotometer, and the luminescence spectra on an apparatus consisting of a SVDSh-500 quartz-mercury lamp from the spectrum of which the excitation line at 365 nm was isolated, a ZMR-3 mirror monochromator, and a FEU-18 [photoelectric multiplier]. The absolute quantum yields were determined by the method of equal absorption [4].

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