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Synthesis and Properties of 2,3-Bis-(2'-pyridyl)-6,7-benzoquinoxaline

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Many substituted quinoxalines and pyrazines are potential chelating ligands toward transition metal ions. The metal complexes of a series of substituted pyrazines, 2,3-bis-(α -pyridyl)-5,6-dihydropyrazine (I), 2,3-bis-(α -pyridyl)pyrazine (II), and 2,3-bis-(α -pyridyl)quinoxaline (III), were investigated in 1959 by Goodwin and Lions (1). This study showed that substituents in the 5,6-positions of the pyrazine ring influenced the nature of the resulting metal chelates.

More recently, 2,3-di-(2-pyridyl)-5,6-benzoquinoxaline (IV) was prepared for the purpose of studying its carcinogenic properties (2).

In this laboratory, the isomeric compound, 2,3-bis-(2'-pyridyl)-6,7-benzoquinoxaline, was prepared in a similar manner by refluxing the corresponding aromatic diamine with α -pyridyl.

This compound is under investigation (together with a series of similar reagents) as a chelating agent for selected transition metal ions.

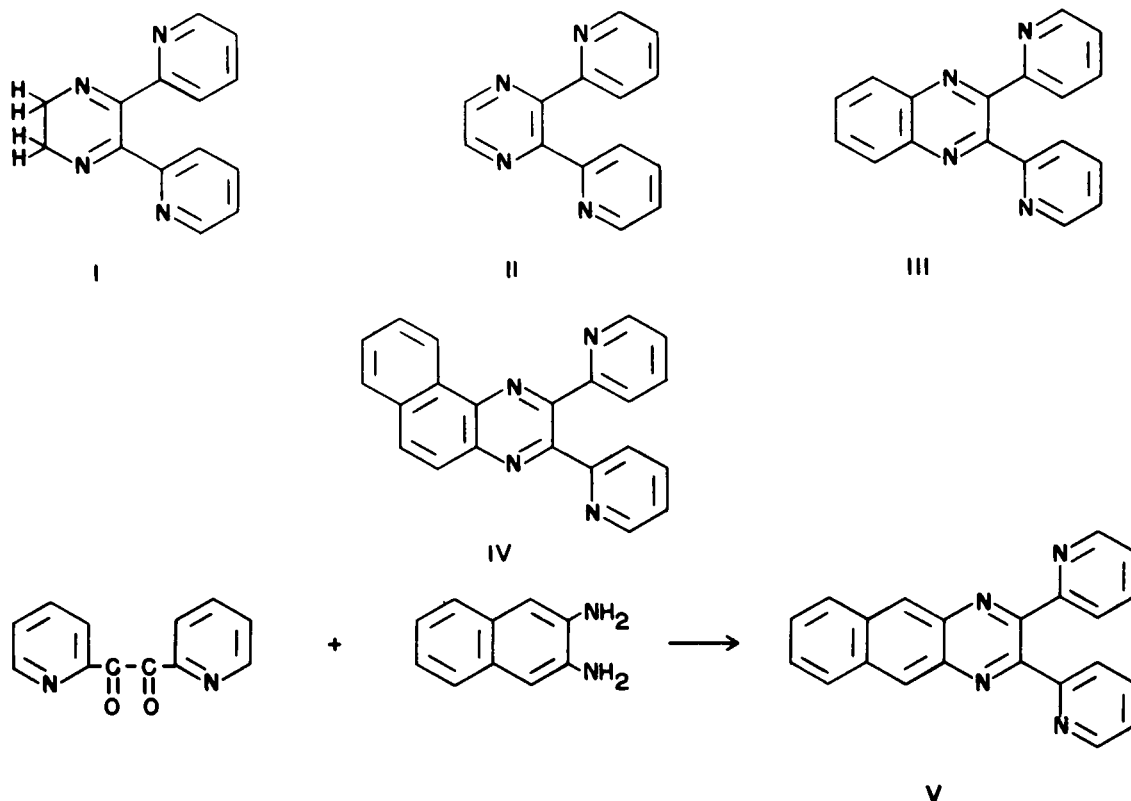
The compound under consideration (V) was found to be soluble in benzene, chloroform, dimethylformamide, and dioxane. It is slightly soluble in dilute acid, carbon tetrachloride, ethanol, ethyl acetate, and methanol, and insoluble in water.

The absorption spectrum of 2,3-bis-(2'-pyridyl)-

6,7-benzoquinoxaline in an acidified aqueous solution (pH 2.70) shows absorption maxima at 387, 304, and 227 m μ with corresponding molar absorptivities of 7,400, 43,300 and 36,600 (3). The fluorescence spectrum of this same solution shows a wave-length of excitation at 465 m μ with a fluorescence peak at 580 m μ . A solution of (V) in absolute ethyl alcohol displays an excitation wave length of 417 m μ (with minor excitation at 339 m μ) and fluorescence at 520 m μ (4). There is little detectable change in the absorption spectrum when using ethyl alcohol or dilute acid as a solvent.

The n. m. r. spectrum of 2,3-bis-(2'-pyridyl)-6,7-benzoquinoxaline in deuterated chloroform exhibits an isolated peak at 8.84 p.p.m., integrating to two protons, and a series of overlapping multiplets from 7.10 to 8.44 p.p.m., integrating to twelve protons (5). All measurements were made using tetramethylsilane as an internal reference.

The infrared spectrum of (V) in KBr shows the following discernable maxima: 725, 747, 767, 779, 793, 820, 855, 873, 892, 920, 960, 990, 1005, 1045, 1073, 1095, 1149, 1182, 1246, 1283, 1365, 1445, 1453, 1483, 1580 and 1601 cm⁻¹. All peaks are sharp.



EXPERIMENTAL

A solution of 3.2 g. (0.202 mole) of 2,3-diaminonaphthalene (L. Light and Co., Ltd., Colenbrook, England) and 4.3 g. (0.202 mole) of α -pyridyl (K and K Laboratories, New York, N. Y.) in 75 ml. of absolute ethyl alcohol was refluxed for 1/2 hour. Upon cooling, the desired product crystallized and was filtered. The product (4.9 g.), recrystallized as yellow needles from absolute ethyl alcohol, had a melting point of 171-172°C. A yield of 72% of theoretical was realized by this method.

Anal. Calcd. for $C_{22}H_{14}N_4$: C, 79.01; H, 4.23; N, 16.76. Found: C, 78.78; H, 4.44; N, 16.78.

REFERENCES

- (1) H. A. Goodwin and F. Lions, *J. Am. Chem. Soc.*, **81**, 6415 (1959).
- (2) N. P. Buu-Hoi and G. Saint-Ruf, *J. Chem. Soc.*, 2258 (1961).
- (3) All ultraviolet and visible absorption studies were performed on the Cary Model 14 Recording Spectrophotometer.
- (4) All fluorescence data were collected on the Aminco-Bowman Spectrophotofluorometer.
- (5) The spectrum was obtained on a solution containing 100 mg./0.7 ml. on the Varian A-60 Nuclear Magnetic Resonance Spectrometer.

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