TETRA-2,3-(5-TERT-BUTYLPYRAZINO)PORPHYRAZINES

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Aza analogs of phthalocyanine – vanadyl (II) and copper (III) complexes of tetra-2,3-(5-tert-butylpyrazino)porphyrazine – which have increased solubility in organic solvents, were obtained for the first time from 5-tert-butylpyrazine-2,3-dicarboxylic acid (I). Acid I [imide with mp 207° (from alcohol)] was synthesized in 52% yield by oxidation of 2-tert-butylquinoxaline [1] with potassium permanganate in 70% aqueous pyridine. The 2-tert-butylquinoxaline was obtained by condensation of tert-butylglyoxal [2] with o-phenylenediamine. In addition to metal complexes II and III, tetra-2,3-(5-tert-butylpyrazine)porphyrazine is also formed and was separated by chromatography on aluminum oxide and identified from the presence of a characteristic doublet of bands in the visible region in the electronic spectrum. In the case of synthesized complexes II and III, it has proved possible for the first time to investigate the absorption spectrum of aza analogs of phthalocyanine over a broad range (250-800 nm). The position of the intense band at 340 nm is independent of the aza substitution in the benzene ring, in contrast to the long-wave band, which undergoes a strong hypsochromic shift.

EXPERIMENTAL

Vanadyl Complex of Tetra-2,3-(5-tert-butylpyrazino)porphyrazine (II). A mixture of 0.45 g of acid I, 2.4 g of urea, 0.53 g of VCl_3, and a catalytic amount of NH_4VO_3 was heated slowly to 235° and held at this temperature for 15 min. The mixture was cooled and washed with boiling water, and the complex was extracted with boiling chloroform. The chloroform solution of the complex was chromatographed on aluminum oxide with elution of a blue fraction by chloroform. The eluate was evaporated to dryness to give 0.26 g (40%) of II. λ_{max}, nm (log ε): 645 (5.14), 586 (4.42), 343 (4.90), and 292 (4.71) (in benzene). Found: C 58.5, 58.2; H 5.2, 5.3%. $C_{40}H_{40}N_{16}OV \cdot H_2O$. Calculated: C 57.9; H 5.1%. The copper complex (III) was similarly obtained in 37% yield from I, urea, CuCl, and a catalytic amount of $(NH_4)_2MoO_4$. λ_{max}, nm (log ε): 631 (5.22), 572 (4.51), 340 (5.01), 294 (4.70) (in chloroform). Found: C 55.9, 55.9; H 5.1, 5.1%. $C_{40}H_{40}CuN_{16} \cdot 3H_2O$. Calculated: C 55.7; H 5.4%.

LITERATURE CITED

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2. R. C. Fuson, H. Gray, and J. J. Gouza, J. Am. Chem. Soc., 61, 1937 (1939).

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