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FIRST SYNTHESIS OF ETHYLENEBISPORPHYRINS

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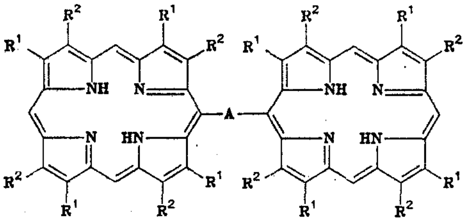
The study of bisporphyrins is one of the main modern directions of the chemical and physicochemical investigations in the area of prophyrins. These compounds have proven to be convenient models for the clarification of processes of energy transfer in photosynthesis and for the study of various catalytic systems (see review in [1]).

While studying the chemical properties of ethanebisporphyrins, the synthesis of which will be described in a separate communication, we discovered that compounds (Ia-c) are converted in acetic acid at 70°C after 20 min in a yield close to quantitative into new substances having significantly higher chromatographic mobilities on silica gel in comparison with the initial porphyrins.

Analysis of PMR and mass spectral data of the isolated compounds made it possible unambiguously to ascribe to them the structure of the previously unknown ethylenebisporphyrins (IIa-c).



Ia- c II a-c

I A = CH_2–CH_2; II A = CH═CH; I, II a R^1 = Me, R^2 = Et; b R^1 = R^2 = Et; c R^1 = R^2 = Pr

There were intense peaks for the molecular ions in the electron impact mass spectra of compounds (IIa-c) reaching 100% for the metal complexes which indicated their high stability in comparison with ethanebisporphyrins [m/z (relative intensity, %): IIa 980 (M^+, 100), 492 (65), 490 (83), 488 (95), 478 (92); IIb 1092 (M^+, 41), 560 (31), 558 (33), 548 (51), 546 (51), 534 (100); IIc 1316-1319 (100), 672 (13), 658 (50), 646 (17)].

A singlet signal was observed in the PMR spectra of the ethylenebisporphyrins in the region of 8.5 ppm for the bridge protons which on protonation of the porphyrins is shifted to the region of meso-proton signals. For example, the PMR spectrum of compound (IIb) ($CDCl_3$) was δ 10.12 and 9.93 (4H and 2H, two s, meso-H), 8.56 (2H, s, CH═CH), 4.13, 4.11, 4.08, and 3.89 [(latter not resolved) all to α-CH_2], 1.98, 1.96, 1.93, and 1.0 (all t, β-CH_3), –2.72 ppm (s, NH); ($CDCl_3$ + 1% CF_3COOH), δ: 10.26 (2H, s, CH═CH), 10.19 and 9.92 (4H and 2H, two s, meso-H), –0.43 and –2.03 ppm (two s, NH).

The presence of an immensely broadened Soret band in the electronic spectra was a characteristic of the ethylenebisporphyrins (IIa-c). The band partially masked the four band spectra in the visible spectrum, which is traditional for porphyrins, but a splitting of the

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Soret band into two components was observed in the spectra of the metal complexes, 406 and 419 nm for copper, 410 and 426 nm for zinc, and 405 and 415 nm for nickel complexes. On protonation of porphyrin free bases the spectrum acquired a pattern of the fluorene type. The spectrum of compound (IIb) in chloroform was λ_{max}, nm ($\varepsilon \cdot 10^{-3}$): 421 (240), 480 sh (32.8), 510 (30.6), 546 (12.4), 581 (12.7), 634 (4.8); on adding 1% CF_3COOH, λ_{max}, nm ($\varepsilon \cdot 10^{-3}$): 402 (18.8), 508 (52.3), 770 (10.3).

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SYNTHESIS OF N-HETEROCYCLIC ANALOGUES OF 2,5-DIARYLOXAZOLES

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2-Hetaryl-5-aryloxazoles are efficient luminophores. The method described for the synthesis of 5-phenyl-2-(2-phenyl-4-quinolyl)oxazole (I) is a multistage, laborious technological process which is accompanied by side reactions which lead to the formation of resinous impurities [1]. The need to isolate the intermediate products and free them from these impurities substantially reduces the yield of the luminophore, and adversely affects its luminescence.

We have synthesized (I) and other 2-(4-quinolyl)-5-aryloxazoles by the Robinson–Gabriel reaction [3] in one step, by heating equimolar amounts of cinchoninic or 2-phenylcinchoninic acid with ω-aminoaryl methyl ketones in phosphoryl chloride under nitrogen at 125°C. Since the phosphoryl chloride functions simultaneously as a solvent and a cyclohydrating agent, there is no need to isolate the acid chloride or the amide. The use of an inert gas prevents the formation of resinous products, and increases the yields and quality of the luminophore.

The method is also applicable to the synthesis of other carboxy-substituted nitrogen heterocycles. For example, reaction of isonicotinic acid with ω-aminoacetophenone under these conditions affords 2-(4-pyridyl)-5-phenyloxazole, and reaction of 2,2'-diquinolyl-4-carboxylic acid with ω-aminoacetophenone gives 2-(4-diquinolyl-2,2')-5-phenyloxazole.

5-Phenyl-2-(4-quinolyl)oxazole: yield 59%, mp 134-135°C (from heptane with alumina); λ_{max} (ε) absorption (in ethanol): 235 (30,300), 350 nm (15,900); λ_{max} fluorescence (in ethanol) 430 nm (η 0.52).

5-Phenyl-2-(2-phenyl-4-quinolyl)oxazole: yield 55%, mp 157-158°C (from heptane), as reported in [1].

2-(2-2'-Diquinol-4-yl)-5-phenyloxazole: yield 60%, mp 218-219°C (from benzene–heptane, 1:2); λ_{max} (ε) absorption (in ethanol): 260 (50,000), 330 nm (24,500; λ_{max} fluorescence (in ethanol): 455 nm (η 0.46).

2-(4-Pyridyl)-5-phenyloxazole: yield 65%, mp 97-97.5°C [4].

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