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STRUCTURE OF 1,2-TETRANAPHTHOPORPHINE

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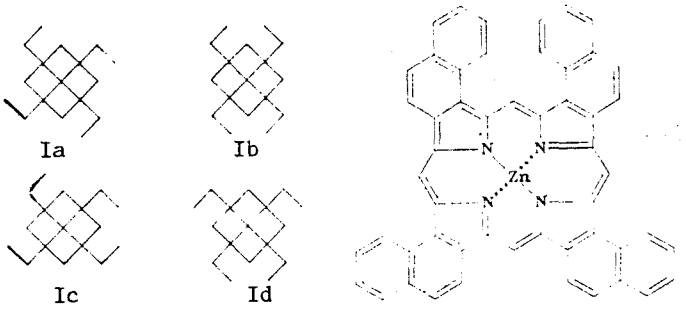
The common method of synthesizing tetrapyrrole macroheterocycles by template tetramerization of asymmetrically substituted porphinogens around a coordinated metal atom frequently produces a mixture of isomers, the number of which approaches or equals the number of fragment combinations possible. For example, isomers were formed during synthesis of metal complexes of 1,2-naphthalocyanine from 1,2-dicyanonaphthalene [1] and of tetra (tert-butyl)porphyrazine from tert-butylmaleonitrile [2]. In the latter case, preparative high-pressure liquid chromatography (HPLC) was used to separate the three isomers.

Earlier we prepared tetra-1,2-naphthoporphine (I) and its Zn complex [3], in which it is theoretically possible to propose the presence of four isomers Ia-d.



A preliminary conclusion about formation of primarily one low-symmetry isomer was made on the basis of polarized fluorescence spectra [4]. However, its structure was not determined. Due to steric hindrances between the aromatic fragments, formation of isomer Ib (cf. [2]) is not likely. Only one isomer with a retention time 10.07 min was found by HPLC for the Zn complex of I (Kratos instrument, 25-cm column, 4.6-mm inner diameter, silica gel sorbent, 637 nm spectrophotometric detection, isopropyl alcohol mobile phase, 1 ml/min flow rate). The structure of this isomer was elucidated by ^{13}C NMR spectroscopy. Three signals at 102.90, 99.07, and 95.84 ppm in the ratio 1:2:1 are seen for the meso-carbon atoms in the spectrum of the Zn complex in DMF at 25°C. This enabled the isomer to be assigned to type Id, since an isomer of type Ic should have four signals from meso-carbon atoms according to symmetry. Thus, template tetramerization yielding the Zn complex of the tetranaphthoporphine produces only one isomer of type Id. This can be explained using a synthesis scheme for tetraarenoporphines [5] that passes through an intermediate bisisoindole.

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SIMPLE METHOD FOR N-ALKYLATION OF 5-R-TETRAZOLES USING tert-BUTANOL

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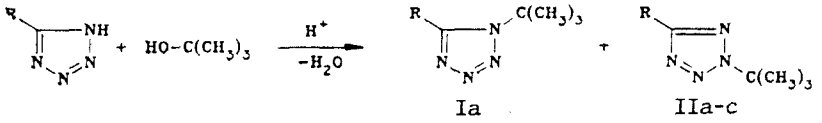
Direct tert-butylation of the pyrrole nitrogen atom in heterocycles occurs rarely [1] and is generally performed by an indirect method. Hence 1-tert-butyltetrazoles are obtained by decomposition of the gem-diazine t-Bu-C$(N_3)_2$Ph [2], reaction of methyl tert-butyl ketone with trimethylsilylazide [3], and by treating N-tert-butylacetonitrilium salts with sodium azide [4]. 5-Substituted tetrazoles can be tert-butylated by reaction with tert-butanol and dicyclohexylcarbodiimide [5]. However, this has been little applied because of its length and the need for careful adherence to numerous conditions.

We now show how direct tert-butylation of 5-R-tetrazoles can be achieved with tert-butanol and azeotropic distillation to eliminate water.



Ia IIa-c

I, II a R=CH_3, b R=C_6H_5, c R=CF_3

The PMR and ^{13}C NMR spectroscopy show that reaction of tert-butanol with 5-methyltetrazole gives a mixture of the 1- and 2-tert-butyl isomers Ia:IIa in the ratio 1:5. In contrast, reaction with 5-phenyl- and 5-trifluoromethyltetrazoles only yields the 2-isomers IIb and IIc. This agrees with the proposed effect of a 5-substituent on tetrazole ring alkylation [1].

A solution of tert-butanol (3.7 g, 50 mmoles) in chloroform (15 ml) was treated with concentrated H_2SO_4 (5-6 drops) and the 5-R-tetrazole (25 mmoles) and refluxed using a Dean and Stark apparatus until water (0.45 ml) had been removed. The product was diluted with chloroform (85 ml) and washed with Na_2CO_3 solution until the wash liquid was alkaline, and then with water until neutral. The chloroform solution was dried over $MgSO_4$ and then distilled to give the N-tert-butyltetrazoles Ia, IIa-c.

1-tert-Butyl-5-methyltetrazole (Ia). According to [3, 4], mp = 76-77°C. PMR spectrum: 2.70 (3H, s, Me), 1.69 ppm (9H, s, t-Bu). Yield 14%.

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