Chemistry of Heterocyclic Compounds, Vol. 32, No. 8, 1996

SYNTHESIS OF PORPHYRINS WITH REACTIVE GROUPS ON PHENYL RINGS.

8.* AZO DYES ON TETRAPHENYLPORPHYRINS

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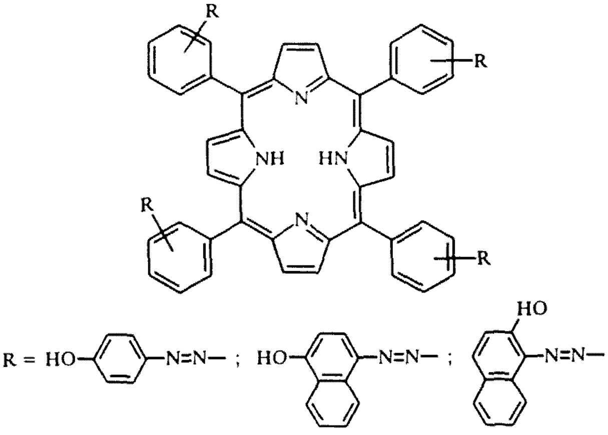
Porphyrins having covalently attached residues of azo dyes on the periphery of the molecule have been synthesized by the diazotization of tetraaminophenylporphyrins and subsequent azo coupling of the diazonium salts with phenol, and with α- and β-naphthols. The possibility of π–π electron interaction of the two chromophoric systems has been studied.

Porphyrins and their metal complexes possess several unique properties which are determined by the functional groups in the porphyrin ring. There is considerable interest in porphyrins having bulky substituents on the periphery of the molecule capable of interacting with the central portion of the porphyrin ligand.

Porphyrins containing covalently attached residues of azo dyes have been synthesized for the purpose of studying the possible interaction of the two chromophoric systems.



The synthesis of porphyrin azo dyes was carried out according to Scheme 1.

The initial tetra(nitrophenyl)porphyrins were obtained by the condensation of pyrrole with nitrogenzaldehydes [2]. Tetra(aminophenyl)porphyrins were synthesized in almost quantitative yield by the reduction of the porphyrin nitro derivatives with stannous chloride in hydrochloric acid [2].

We have established that the tetra(aminophenyl)porphyrins are readily diazotized with sodium nitrite in aqueous mineral acid solution. The diazonium salts obtained are fairly stable, they decomposed significantly at temperatures greater than 25°C. Azo coupling of the porphyrin diazonium salts with phenol, and with α- and β-naphthols leads to porphyrins containing residues of azo dyes in the meso positions.

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*For communication 7, see [1].

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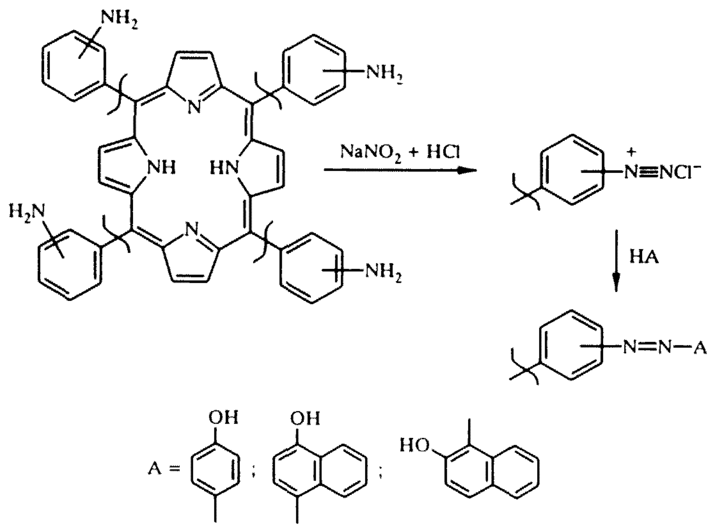
Scheme 1



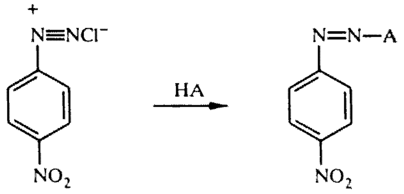
Porphyrin azo dyes containing phenol residues were soluble in aqueous alkaline solution while porphyrin azo dyes containing residues of α-naphthol were only soluble in aqueous alcoholic solutions of alkali. Porphyrin azo dyes containing residues of β-naphthol were insoluble in alkaline solution but possessed some solubility in solvents such as benzene and chloroform. This is probably caused by the formation of stable intramolecular hydrogen bonds between the hydroxyl group and a nitrogen atom of the azo bridge of the azo dye residues.

In order to increase the solubility of the porphyrin azo dyes in nonpolar solvents they were alkylated at the hydroxyl group with butyl bromide in DMF in the presence of potassium carbonate [3].

Porphyrin azo dyes are reduced by the action of stannous chloride in hydrochloride acid with the formation of the initial tetra(aminophenyl)porphyrins.

The yields and some properties of the compounds obtained are given in Table 1.

It is known from literature data that the porphyrin ring is a more electron-accepting substituent than a phenyl ring and corresponds to a nitro group in strength of electron-accepting properties [4]. Consequently model compounds were obtained by azo coupling of p-nitrobenzene diazonium chloride with phenol and with α- and β-naphthols (Table 2).



When analyzing the EAS of the porphyrin azo dyes it was impossible to draw an unambiguous conclusion as to whether the π system of the azo dye interacts with the π system of the porphyrin ring. The Soret band of tetraphenylporphins (λ_{max} ~400 nm; ε ~$5 \cdot 10^5$) is found alongside the broad absorption band of the azo dye residue (λ_{max} ~500 nm; ε ~$3.5 \cdot 10^4$), which does not permit a confident judgement to be made on whether transfer of π electron density from the azo dye residues to the porphyrin ring has taken place. However the sharp reduction in intensity of the Soret band and the growth in intensity of the electronic transition bands and also their bathochromic shift indicate the existence of such interactions.

The position of bands in the EAS is practically independent of the introduction of alkyl substituents. However an increase in the intensity of the Soret band and a reduction in intensity of the remaining bands compared with hydroxy substituted porphyrin azo dyes was observed for all the butoxy substituted compounds. This is probably linked with the high electron-donating properties of the hydroxyl group compared with the butoxy group.

TABLE 1. Yields and Some Properties of the Porphyrin Azo Dyes Obtained

Compound	Substituent in phenyl rings	R_f*	EAS, λ_{max}, nm ($\log \varepsilon$)					IR spectrum, cm^{-1}			Yield, %
			I	II	III	IV	Soret	ν_{OH}	δ_{OH}	ν_{CO}	
I	3-(4-Hydroxyphenylazo)	0,20 (A)	647 (3,91)	590 (4,00)	553 (4,15)	517 (4,48)	428 (5,72)	3260	1344	1265	89
II	4-(4-Hydroxyphenylazo)	0,63 (B)	650 (4,00)	595 (3,96)	559 (4,35)	521 (4,39)	435 (5,54)	3260	1362	1282	98
III	3-(4-Hydroxynaphthylazo)	0,63 (B)	651 (3,87)	602 sh (3,78)	548 sh (4,42)	518 (4,67)	430 (5,31)	3300	1348	1268	90
IV	4-(4-Hydroxynaphthylazo)	0,58 (B)	655 (3,87)	595 sh (4,19)	563 (4,51)	520 sh (4,67)	437 (5,16)	3300	1365	1280	93
V	3-(2-Hydroxynaphthylazo)	0,71 (C)	651 (3,92)	592 (4,00)	552 sh (4,32)	521 (5,00)	425 (5,34)	3260	1340	1270	88
VI	4-(2-Hydroxynaphthylazo)	0,45 (D)	657 (4,22)	610 sh (4,23)	567 (4,65)	497 (4,99)	430 (5,05)	3240	1338	1275	96
VII	3-(4-Butoxyphenylazo)	0,90 (E)	648 (3,79)	593 (3,87)	553 (4,11)	518 (4,48)	429 (5,70)			1246	90
VIII	4-(4-Butoxyphenylazo)	0,93 (E)	653 (3,93)	595 (3,93)	560 (4,33)	522 (4,38)	434 (5,54)			1246	95
IX	3-(4-Butoxynaphthylazo)	0,78 (E)	651 (3,80)	593 (3,83)	553 (4,12)	518 (4,45)	427 (5,53)			1242	87
X	4-(4-Butoxynaphthylazo)	0,74 (E)	652 (4,07)	594 (4,06)	561 (4,46)	521 (4,53)	436 (5,50)			1248	95
XI	3-(2-Butoxynaphthylazo)	0,90 (D)	651 (3,80)	593 (3,83)	553 (4,12)	518 (4,45)	427 (5,53)			1246	70
XII	4-(2-Butoxynaphthylazo)	0,20 (D)	654 (4,11)	597 sh (4,40)	571 (4,69)	516 (4,99)	428 (5,47)			1248	75

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*R_f for system: A) acetone–hexane, 1:1; B) benzene–ethyl acetate, 1:1; C) benzene–ethyl acetate, 3:1; D) chloroform; E) benzene.

TABLE 2. Electronic Absorption Spectra (EAS) of Model Compounds

Compound	EAS, λ_{max}, nm (log ε)	
	I	II
p-Nitrophenylazophenol	566 sh (254)	391 (4,37)
p-Nitrophenylazo-α-naphthol	507 (4,37)	373 (4,17)
p-Nitrophenylazo-β-naphthol	491 (3,38)	330 (3,95)

In the case of all the para substituted compounds the Soret band was shifted bathochromically and its intensity was less than for the meta isomers. This is probably linked with the transmission of the electronic effect of the substituent from the para position of the phenyl ring which is impossible for substituents at another position.

EXPERIMENTAL

The electronic spectra were recorded on a Specord M-400 spectrophotometer, and IR spectra on a Specord M-80 instrument in KBr disks. The individuality and purity of compounds was established by TLC on Silufol.

The elemental analysis data for the compounds obtained were close to calculated values.

Tetra-[3-(4-hydroxyphenylazo)phenyl]porphin (I). A solution of sodium nitrite (0.12 g: 1.74 mmole) in water (1 ml) was added dropwise with stirring and cooling to 5°C to a solution of tetra-(3-aminophenyl)porphin (0.25 g: 0.37 mmole) in 1 N HCl (3 ml). The mixture was stirred at 5°C for 30 min. A solution of sodium acetate (0.14 g: 1.71 mmole) in water (2 ml) and phenol (0.15 g: 1.6 mmole) in 3% aqueous KOH solution (5 ml) was added to the diazonium salt solution and the mixture stirred at room temperature for 1 h. The mixture was diluted to 100 ml with water and filtered. The filtrate was neutralized with HCl to pH 7, the porphyrin filtered off, washed with aqueous 10% ammonia solution, then with water, and dried to constant weight at room temperature. For purification the porphyrin was dissolved in boiling ether (100 ml) and chromatographed on a column (2.5 × 60 cm) of silica gel (L 100/250) eluting with ether. The eluate was evaporated to 5 ml and porphyrin (I) was precipitated with hexane (30 ml). Yield was 0.37 g.

Tetra-[4-(4-hydroxyphenylazo)phenyl]porphin (II) was obtained similarly from tetra-(4-aminophenyl)porphin. Yield was 0.39 g.

Tetra-[3-hydroxynaphthylazo)phenyl]porphin (III). A solution of sodium nitrite (0.12 g: 1.74 mmole) in water (1 ml) was added dropwise with stirring and cooling to 5°C to a solution of tetra-(3-aminophenyl)porphin (0.25 g: 0.37 mmole) in 1 N HCl (3 ml). The mixture was stirred at 5°C for 30 min. Sodium acetate (0.14 g: 1.71 mmole) in water (2 ml) and α-naphthol (0.21 g: 1.46 mmole) in 3% aqueous KOH solution (5 ml) were added with stirring to the solution of diazonium salt obtained and the mixture was stirred for 1 h at room temperature. The mixture was diluted to 100 ml with water, the porphyrin filtered off, and washed with 10% aqueous Na_2CO_3 solution, then with water, and dried to constant weight at room temperature. For purification the porphyrin was dissolved in boiling ethyl acetate (50 ml) and chromatographed on a column (2.5 × 60 cm) of silica gel (L 100/250), eluting with ethyl acetate. The eluate was evaporated to 5 ml and porphyrin (III) precipitated with hexane (30 ml). The solid was filtered off, and dried to constant weight at room temperature. Yield was 0.45 g.

The following were obtained analogously: tetra-[4-(4-hydroxynaphthylazo)phenyl]porphin (IV) from tetra-(4-aminophenyl)porphin and α-naphthol (yield 0.40 g), tetra-[3-(2-hydroxynaphthylazo)phenyl]porphin (V) from tetra-(3-aminophenyl)porphin and β-naphthol (yield 0.45 g), and tetra-[4-(2-hydroxynaphthylazo)phenyl]porphin (VI) from tetra-(4-aminophenyl)porphin and β-naphthol (yield 0.43 g).

Tetra-[3-(4-butoxyphenylazo)phenyl]porphin (VII). A mixture of compound (I) (0.2 g: 0.183 mmole), butyl bromide (0.4 g: 3.09 mmole), anhydrous potassium carbonate (0.4 g: 3.09 mmole), and DMF (30 ml) was stirred magnetically at room temperature for 24 h, then poured into water (150 ml), the mixture heated to boiling, and filtered. The precipitate was dried at room temperature to constant weight then dissolved in chloroform (50 ml). The solution was loaded onto a column (2.5 × 60 cm) of Al_2O_3 of activity grade II, which was eluted with chloroform. The eluate was evaporated to 5 ml and porphyrin (VII) precipitated with methanol (30 ml). Yield was 0.22 g.

The following were obtained analogously: tetra-[4-(4-butoxyphenylazo)phenylporphin (VIII) from (II) (yield 0.23 g), tetra-[3-(4-butoxynaphthylazo)phenyl]porphin (IX) from (III) (yield 0.18 g), tetra-[4-(4-butoxynaphthylazo)phenyl]porphin (X) from (IV) (yield 0.19 g), tetra-[3-(2-butoxynaphthylazo)phenyl]porphin (XI) from (V) (yield 0.10 g), and tetra-[4-(2-butoxynaphthylazo]porphin (XII) from (VI) (yield 0.16 g).

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