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SYNTHESIS OF TETRAPHENYLPORPHINS WITH REACTIVE GROUPS IN THE PHENYL RINGS. 7.* SALTS OF TETRAKIS(N,N,N-TRIMETHYL-AMINOPHENYL)PORPHINS

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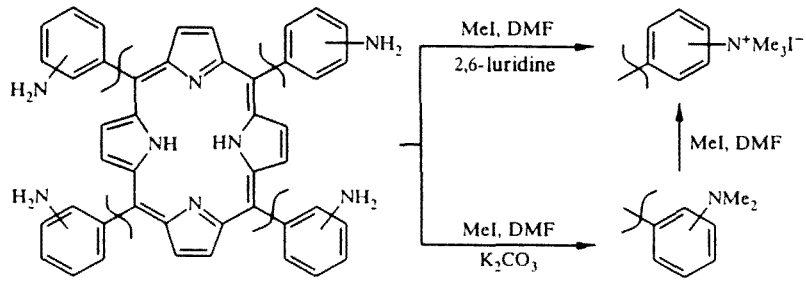
Tetrakis(N,N-dimethylaminophenyl)porphins and water-soluble salts of tetrakis(N,N,N-trimethylamino-phenyl)porphins have been obtained by the alkylation of tetrakis(aminophenyl)porphins with methyl iodide.

There is considerable interest at present in the study of water-soluble porphyrins connected with the possibility of using them as models of biological systems, as drugs, and as homogeneous catalysts in aqueous media. The most promising water-soluble porphyrins are based on the tetraphenylporphins which are readily obtained by the condensation of pyrrole with benzaldehydes and subsequent modification of the substituents in the phenyl rings.

We have obtained water-soluble tetrakis(carboxymethyl-oxyphenyl)porphins previously [2]. The basic drawback of these porphyrins is that they are soluble only in alkaline media. The aim of the present work was to obtain porphyrins soluble in both acid and alkaline solution. Porphyrin derivatives based on trimethylammonium salts are compounds of that type. The only known derivatives are tetrakis(4-N,N,N-trimethylaminophenyl)porphin salts obtained by the methylation of tetrakis(4-N,N-dimethylaminophenyl)porphin with toluene-p-sulfonic acid methyl ester [3]. However the initial tetrakis(4-N,N-dimethyl-aminophenyl)porphin is formed in insignificant yield (~5%) on condensing p-dimethylamino-benzaldehyde with pyrrole in propionic acid [3].

We have developed a new method for synthesizing iodides of the isomeric trimethylaminophenylporphins by quaternizing the available tetrakis(aminophenyl)porphins [4] with methyl iodide in boiling DMF using 2,6-lutidine as base:



We have established that on using potassium carbonate as base the reaction stops at the stage of forming tetrakis(N,N-dimethylaminophenyl)porphins. In addition we also obtained the iodides of tetra(N,N,N-trimethylamino-phenyl)porphins by the alkylation of tetra(N,N-dimethyl-aminophenyl)porphins with methyl iodide in boiling DMF.

The meta and para isomers of tetra(N,N,N-trimethyl-aminophenyl)porphin iodides were soluble in water and insoluble in nonpolar organic solvents. On the other hand, the perchlorates of these porphyrins were practically insoluble in water. All salts of the ortho isomer were also insoluble in water, which is probably linked with steric hindrance of the solvation process.

*For Communication 6, see [1].

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TABLE 1. Yields and Some Properties of the Porphyrins Obtained

Porphyrin	R_f	Electronic spectra, λ_{max}, nm (log ε)						IR spectra, cm^{-1}		Yield, %
		I	II	III	IV	Soret	solvent†	$\nu_{C=N}$	ν_{NH}	
I	0,8, 0,46, 0,2, 0,04 (A–C, 1 : 10)	627 (3,92)	579 (3,69)	–	–	434 (5,38)	S	1296	3384	
		653 (3,49)	595 (3,72)	556 (3,76)	519 (4,21)	422 (5,27)	P			
II	0,18, 0,36 (X)	626 (4,19)	576 (4,18)	–	–	432 (5,41)	S	1320	–	62
		664 (3,75)	606 (3,68)	565 (3,84)	529 (4,14)	432 (5,11)	P			
III	0,77 (C)	665 (3,77)	610 (3,77)	568 (3,77)	526 (3,97)	426 (4,81)	P	1352	–	60 (A) 68 (B)
IV	0,68 (P–C, 4 : 1)	643 (4,42)	592 (3,92)	–	–	434 (5,45)	S	1352	3352	
		649 (3,59)	592 (3,72)	557 (3,85)	518 (4,18)	427 (5,19)	P			
V	0,66 (C)	600 (4,57)	651 sh (3,95)	–	–	440 (5,54)	S	1352	–	79
		652 (3,80)	594 (3,84)	555 (3,88)	520 (4,36)	424 (5,23)	P			
VI		650 (4,61)	597 sh (3,90)	–	–	440 (5,60)	S	1330	–	75 (A)
		642 (3,60)	577 (3,79)	550 (3,70)	514 (4,21)	411 (5,54)	W			79 (B)
VII	0,47 (A–H, 2 : 1)	655 (4,53)	595 (3,98)	–	–	433 (5,54)	S	1352	3344	
		664 (4,05)	–	574 (4,32)	529 (4,10)	437 (5,79)	P			
VIII	0,53 (M)	650 (4,47)	601 (3,89)	–	–	440 (5,42)	S	1352	–	84
		671 (3,91)	–	582 (4,24)	532 (3,91)	445 (5,20)	P			
IX		650 (4,62)	600 (4,02)	–	–	440 (5,59)	S	1352	–	87 (A)
		634 (3,72)	578 (3,89)	550 (3,89)	514 (4,23)	412 (5,59)	W			82 (B)
X	0,21 (C)	648 (3,98)	592 (3,98)	554 (4,18)	517 (4,42)	421 (5,89)	C	1360	3390	
XI	0,23 (M–C, 1 : 4)	650 (3,70)	592 (3,77)	554 (3,97)	517 (4,22)	420 (5,56)	C	1360		62

*Method of synthesis is given in parentheses.

†A) is acetone, H) hexane, M) methanol, P) pyridine, C) chloroform, S) 0.3 N HCl, and W) water.

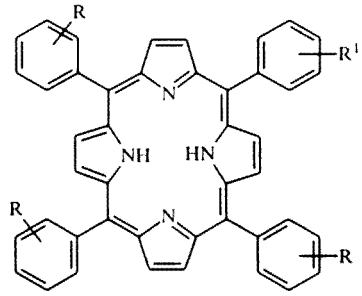
A monotrimethylaminophenyl substituted porphyrin was also obtained by the alkylation of 5-(4-aminophenyl)-10,15,20-triphenylporphin with methyl iodide. The porphyrin obtained was insoluble in aqueous solution but was very soluble in organic solvents.

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

Resolution into atropoisomers took place on chromatography on Silufol of the ortho isomers of aminophenylporphyrins and dimethylaminophenylporphyrins. However, we were unable to resolve tetra(2-N,N,N-trimethylaminophenyl)porphyrin into atropoisomers. This is probably linked to the high polarity of the eluent used.

Analysis of the electronic spectra showed that the bands for the electronic transitions for the ortho substituted porphyrins had a strong hypsochromic shift and a significantly lower intensity compared with the meta and para isomers. This indicates a reduction in the planarity of the porphyrin ring in the ortho isomers compared to the meta and para isomers.

Bands for the skeletal vibrations of the CN bonds (near 1350 cm^{-1}) were traced in the IR spectra of all the porphyrin amino derivatives. The bands for the stretching vibrations of the NH bonds of the amino groups (near 3350 cm^{-1}) vanished on alkylation but were present in the IR spectra of the initial tetrakis(aminophenyl)porphins.



I R = R^1 = 2-NH_2; II R = R^1 = 2-$N(CH_3)_2$; III R = R^1 = 2-$N^+(CH_3)_3I^-$; IV R = R^1 = 3-NH_2;
V R = R^1 = 3-$N(CH_3)_2$; VI R = R^1 = 3-$N^+(CH_3)_3 \cdot I^-$; VII R = R^1 = 4-NH_2; VIII R = R^1 = 4-$N(CH_3)_2$;
IX R = R^1 = 4-$N^+(CH_3)_3 \cdot I^-$; X R = H, R^1 = 4-NH_2; XI R = H, R^1 = 4-$N^+(CH_3)_3 \cdot I^-$

EXPERIMENTAL

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

The data of elemental analysis for C, H, and N of compounds (I)-(XI) corresponded to calculated values.

Tetrakis(2-N,N-dimethylaminophenyl)porphin (II). A mixture of tetrakis(2-aminophenyl)porphin (I) [4] (0.2 g, 0.3 mmole), methyl iodide (0.8 g, 5.63 mmole), anhydrous potassium carbonate (1 g, 7.24 mmole), and DMF (10 ml) was boiled under reflux for 1 h, poured into water (100 ml), the mixture heated to boiling, cooled, and filtered. The solid was washed with water, dried at room temperature to constant weight, dissolved in chloroform (50 ml), and chromatographed on a column (2.5 × 60 cm) of activity grade III aluminum oxide, eluting with chloroform. The first dark red zone of porphyrin (II) was collected. The eluate was evaporated to 5 ml and the porphyrin precipitated with methanol (30 ml). Yield was 0.14 g.

The tetrakis(3-N,N-dimethylaminophenyl)porphin (V) was obtained analogously from tetrakis(3-aminophenyl)porphin (IV) [4] (yield was 0.18 g) as was tetrakis(4-N,N-dimethylaminophenyl)porphin (VIII) from tetrakis(4-aminophenyl)porphin (VII) [4] (yield was 0.19 g).

Tetrakis(2-N,N,N-trimethylaminophenyl)porphin Tetraiodide (III). A. A mixture of porphin (I) (0.2 g, 0.3 mmole), methyl iodide (0.8 g, 5.63 mmole), 2,6-lutidine (0.26 g, 2.43 mmole), and DMF (10 ml) was boiled under reflux for 1 h. The mixture was cooled to room temperature and filtered on a Buchner funnel. The solid was washed with acetone (30 ml) and dried to constant weight at room temperature. Yield was 0.24 g.

Tetrakis(3-N,N,N-trimethylaminophenyl)porphin tetraiodide (VI) was obtained analogously from porphin (IV) (yield was 0.30 g), as was tetrakis(4-N,N,N-trimethylaminophenyl)porphin tetraiodide (IX) from porphin (VII) (yield was 0.35 g).

B. A mixture of porphin (II) (0.2 g, 0.26 mmole), methyl iodide (0.2 g, 1.41 mmole), and DMF (10 ml) was boiled under reflux for 1.5 h. The mixture was cooled to room temperature and filtered on a Buchner filter. The solid was washed with acetone (30 ml) and dried to constant weight at room temperature. Yield was 0.24 g.

Tetrakis(3-N,N,N-trimethylaminophenyl)porphin tetraiodide (VI) was obtained analogously from porphin (V) (yield was 0.28 g), as was tetrakis(4-N,N,N-trimethylaminophenyl)porphin tetraiodide (IX) from porphin (VIII) (yield was 0.29 g).

5-(4'-N,N,N-Trimethylaminophenyl)-10,15,20-triphenyl-porphin (XI). A mixture of 5-(4'-aminophenyl)-10,15,20-triphenylporphin (X) [1] (0.32 mmole), methyl iodide (0.2 g, 1.41 mmole), 2,6-lutidine (0.1 g, 0.94 mmole), and chloroform (10 ml) was boiled for 2 h, cooled to room temperature, and chromatographed on a column (2.5 × 60 cm) of activity grade III aluminum oxide, eluting with chloroform. The eluate was evaporated to 5 ml and porphin (XI) was precipitated with methanol (30 ml). Yield was 0.16 g.

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