U.P.B. Sci. Bull., Series B, Vol. 68, No. 3, 2006

SYNTHESIS AND SPECTROPHOTOMETRIC STUDY OF TETRAPHENYLPORPHYRINE

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Lucrarea de față prezintă sinteza tetrafenilporfirinei (TPP) printr-o variantă originală a metodei clasice constând în reacția dintre pirol şi benzaldehida în prezența acizilor organici. TPP a fost caracterizată spectral prin UV-vis, IR si fluorescenta.

The present paper describes the synthesis of tetraphenylporphyrine (TPP) through an original variation of the classic method, consisting in reaction between pyrrole and benzaldehyde in the presence of organic acids. TPP was sprectrally characterised through UV-vis, IR and fluorescence.

Keywords: tetraphenylporphyrine, synthesis, pyrrole, benzaldehyde, organic acids, fluorescence, UV-vis, IR.

Introduction

Porphyrines show to be extremely important among natural compounds, and are called „the pigments of life". They are important "catalysts" for biochemical processes in living bodies. Porphyrines are being used as additives in foods and cosmetics. In 1912, Kuster [1] has proposed the first representation of a porphyrine nucleus that led to the synthesis of natural porphyrines. The tetraphenylporphyrine was between the first porphyrines obtained by heating a mixture of pyrrole, benzaldehyde and pyridine at 150 ºC [2]. This method also allowed the synthesis of: tetranaphtylporphyrine (TNP), tetrasulphophenylporphyrine (TSPP), tetrasulphonaphtylporphyrine (TSNP) [3,4]. Besides these, the existing literature mentiones the synthesis of porphyrines complexed with metals: Cu^{2+}, Mn^{3+}, Fe^{2+}, Fe^{3+}, Cr^{3+} [5-9].

The goal of our studies was to synthesise tetraphenylporphyrine through a new method, consisting in the reaction between pyrrole and benzaldehyde in the presence of organic acids.

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Experimental

The synthesis of tetraphenylporphyrine was performed in a a round-bottom jar heated by gas flame, featuring a reflux condenser and termometre. A mixture of 0.34 moles pyrrole (P), 0.17 moles benzaldehyde (B) and 9 moles organic acid (AH) was refluxed during a preestablished period (e.g. 30 minutes). The condensation was followed by thin-layer cromatrography on silicagel, having as eluent the mixture of benzene/acetic acid (4/1). The solution was slowly cooled to room temperature and then vacuum filtered. Raw tetraphenylporphyrine (TPP) crystals were washed with 100 mL ethanol/acetone (10/1) mixture, 100 mL distilled hot water (to remove benzoic acid), 30 mL ethanol, and finally essorated.

Purification of the raw TPP was done using a solution of 1.31 g of 2,3-dichloro-3,6-dicyanobenzoquinone (DDQ) solved in 40 ml benzene and 600 ml chloroform [10]. This mixture was refluxed for 3 hours, and then was let to cool down and crystalyse at room temperature. The obtained crystals were vacuum filtered and purified by liquid chromatography on a Al_2O_3 column, the eluent being a mixture of benzene/acetic acid (4/1). The purified TPP came up as powder having a granulation of 1-1.5 nm. Granulometry was determined using an AIR-JET device. Crystals were analysed by UV-vis spectroscopy, fluorescence and IR, respectively, using SPECORD, AMINCO BOWMAN and UNICAM SP 1100 spectrophotometres.

Results and discussion

Syntheses of tetraphenylporphyrine were performed in conditions resumed in Table 1.

Table 1.

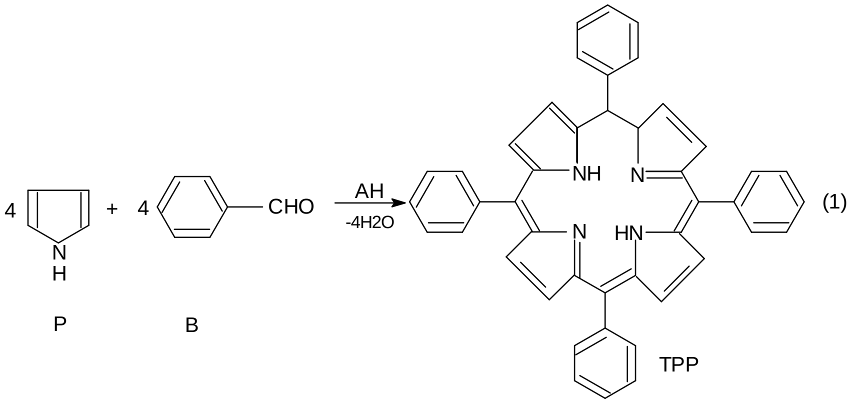
Reaction conditions for TPP syntheses*

Experiment	P (mole)	B (mole)	Molar ratio P/B	Reaction medium (AH)	AH (mol)	Reflux time (min)	t (° C)	Yield (%)
1	0.34	0.17	2:1	PA	9.1	30	120	20
2	0.68	0.36	2:1	PA	18.2	30	120	15.32
3	0.17	0.09	2:1	PA	4.5	30	120	17.15
4	0.34	0.17	2:1	AA	11.8	30	118	14.13
5	0.68	0.36	2:1	AA	23.6	30	118	8.79
6	0.17	0.09	2:1	AA	5.9	30	118	11.12
7	0.34	0.17	2:1	BA	7.4	30	165	0.001
8	0.34	0.17	2:1	PA	4.5	20	120	4.03
9	0.34	0.17	2:1	PA	9.1	30	120	20
10	0.34	0.17	2:1	PA	9.1	45	120	18.95
11	0.34	0.17	2:1	PA	18.2	60	120	16.25

*P = pyrrole; B = benzaldehyde; AH = organic acid; PA = propionic acid; AA = acetic acid; BA = butanoic acid

The available data regarding this reaction show that the condensation process in pyridine follows a mechanism established by Badyer [11] and a zero order kinetics, with oxidation being the rate determining step [12].

As it is shown in Table 1, TPP syntheses by pyrrole condensation in the presence of organic acids occur quite easily, but have low yields. These yields are due after purification steps. The main reaction of the process is (1).



sFrom the first 7 experiments analysis, it can be concluded that the best reaction medium is propionic acid, that led to the best yields in porphyrine, of about 17 %, and the worst is butanoic acid. The medium change is decisive for the reaction yield. In experiments 8-11, performed with specific quantities that led to best yields, the reaction time was varied. The results show that an increase of the reaction time, no longer than 45 minutes, gives better yields. Thus, the domain in which the parametres fit (temperature, medium, reaction time) is quite narrow.

Table 2 shows the UV-vis data for TPP obtained in experiment 9 in comparison with those found in literature [13].

Table 2.

UV-vis characteristics for TPP in benzene

Absorbtion bands for TPP	I	II	III	IV	Soret
λ (nm)	646	590	548	515	418
λ (nm) [13]	647	592	548	515	419
ε ($Lmol^{-1} cm^{-1}$)	3776	5410	7668	18559	457337
ε ($Lmol^{-1} cm^{-1}$) [13]	3400	5300	8100	18700	478000

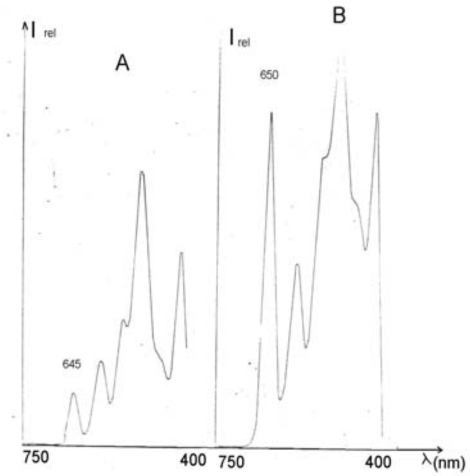


Fig. 1. Fluorescence spectra for TPP purified with DDQ in benzene

A. Excitation spectrum
A. Emission spectrum

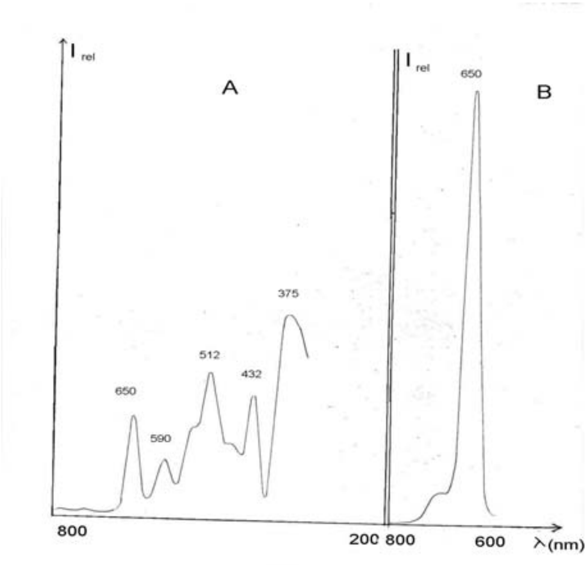


Fig 2. Fluorescence spectra for TPP purified by chromatography

A. Excitation spectrum
B. Emission spectrum

A good agreement between obtained data and literature can be seen, in both positions for absorbtion peaks and values for molar extinction coefficients. This agreement was noticed only for TPP samples that were purified with DDQ. In TPP samples purified only by chromatography, the spectral peaks as well as their extinction coefficients are different than those in literature, that pleads for the existance of some impurities in these samples. Tetraphenylchlorine (TPC) was identified as the main impurity in the raw TPP, as previously shown in other synthesis methods, in literature. TPC absorbtion characteristics are different than that for TPP, as it is shown in Table 3. The Soret band is significantly less intense in TPC as compared to TPP, while the band for the higher wavelength (~650 nm) is significantly larger.

Table 3.

UV-vis characteristics for TPC in benzene

Λ (nm)	654	600	543	518	418
ε ($Lmol^{-1} cm^{-1}$) [13]	41700	5800	10800	15000	18350

The obtained fluorescence spectra for the purified TPP are also in concordance with literature data [14]. The maximum values for fluorescence emissions are located in visible, at wavelengths arround 600 nm.

When coloidally dispersed in aquous solutions or in a solid state, porphyrines do not exibit fluorescence. It is known that porphyrine fluorescence is strongly influenced by impurities [15]. Consequently, by fluorimetry strong fluorescent impurities can be detected in weak fluorescent samples, as well as those impurities that have their fluorescence emission in a different domain as compared to its sample. However, TPC cannot be detected by fluorescence-related methods, because the wavelength for TPC fluorescence emission is in the same domain as that for TPP (~650 nm) and their emission outputs are close.

Figs. 1 and 2 show the fluorescence spectra for 2 samples of TPP, purified by cromatography and DDQ, respectively. In both cases, the emission spectrum has an intense peak at 650 nm. Excitation spectra are in agreement with TPP characterstics for absorbtion spectra, shown in Table 1.

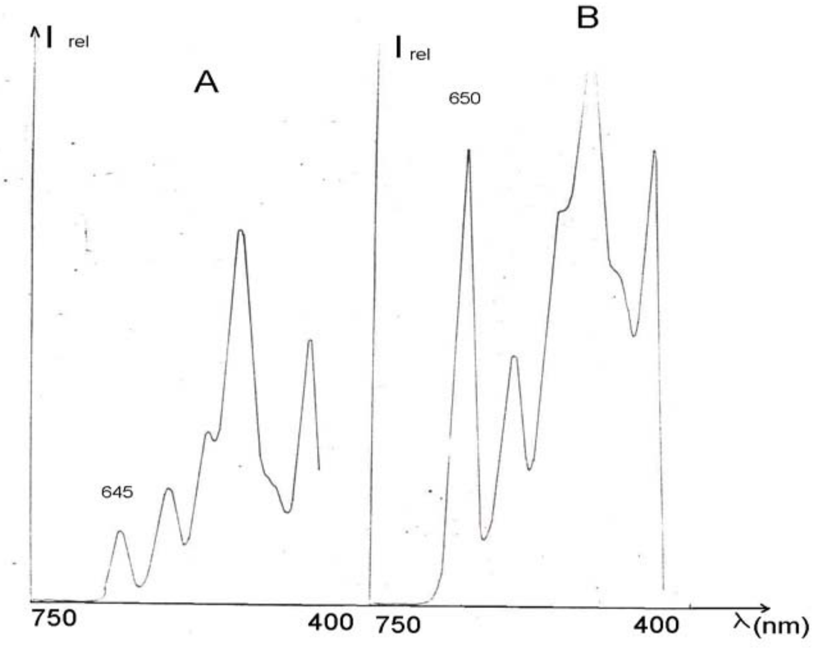


Fig. 3. Fluorescence excitation spectra for synthetic TPP samples containing different amounts of TPC: 0.43 % (A); 2.7 % (B)

When comparing excitation spectra for several TPP samples containing different amounts of TPC (Fig. 3), significant differences can be seen for the particular band located at the higher wavelength. It appears at 645 nm and 650 nm (or more) when small and higher amounts of TPC are present, respectively. This batochromic shift of 5 (or 4) nm, as well as an increase of the band intensity compared to the other bands, is observed for samples containing more TPC. Consequently, a fluorimetric test for TPP samples impurified with TPC was possible due to the fact that TPP has a very high absorbtion peak at 645 nm.

TPP samples synthesised according to Table 1 have also been analysed by IR spectroscopy. Table 4 shows the main absorbtion bands for the TPP obtained in experiment 9, which had the best synthesis yield.

Table 4.

IR absorbtion bands (cm $^{-1}$) in KBr for TPP purified with DDQ (TPP/DDQ) and chromatographically (TPP/chr.) according to exp. no. 9

(s=strong, sh=shoulder, m=medium, w=weak, vw=very weak)

TPP/DDQ	TPP/chr.	Functional groups
3480m		N-H extension in pyrrole
3340m	3345m	N-H extension in porphyrines
	3300vw	N-H extension in porphyrines
3255vw		=C-H extension in phenyl Substituted phenyl rings and pyrrole rings
3160vw	3150vw	
3120vw	3120vw	
3070m	3070m	
2940w		Asymmetric meso C-H extension
2870w		Symmetric meso C-H extension
1600s	1600s	Characteristic of chlorine
1565w	1567m	-C=C-pyrrole extension
	1490sh	Phenyl(-C=C-)
1445s	1445s	Deformation C-H pyrrole
1037m	1037s	i.p. deformation C-H
1007s	1007s	Porhyrinic pyrrole
		C-C extension
985s	985s	Porphyrines pyrrole
970s	970s	Porphyrines pyrrole
910vw	905sh	C-C-C i.p. deformation
880m	880s	C-H o.p. deformation
802s	802s	i.p. C-C-C deformation
787s	787s	pyrrole
		C-C-C i.p. deformation
725sh	725sh	N-H deformation in TPP meso
702s	702s	Deformation of o.p. pyrrole ring
	688sh	N-H deformation in o.p.
642w	642m	Deformation pyrrole i.p.
620w	622.5m	pyrrole
560w	558sm	N-H deformation o.p.

i.p. = in-plane; o.p.=out-of-plane

Conclusions

Syntheses of TPP starting from benzaldehyde and pyrrole in carboxilic acid media have shown that the best reaction medium is propionic acid. Reaction occurs with optimal yield by refluxing the mixture of benzaldehyde, pyrrole and carboxilic acid for 30 minutes. The medium exchange influences decissively the reaction yield. UV-vis and IR spectra for raw and purified mixtures have shown that the purification of the final mixture led to different results, DDQ treatment leading to more pure TPP than column chromatography purification.

REFERENCES

1. *W, Kuster,* Z. Physiol. Chem., 1912, 82, 463.
2. *P. Rothemund,* J. Amer. Chem. Soc., 1935,57,2010.
3. *C.D.Nenitescu* "Chimia Organica" vol.II, Ed. Didactica si Pedagogica, Bucuresti, 1974, 597.
4. *J.E.Falk* Porphyrins and metalloporphyrins BDA Library, Elsevier Publishing Company, 1964,8.
5. *A. R. Battesby*, Acc. Chem. Res. 1990, 19, 147.
6. *C.Jin, R. Wang, P. Ji,* Shipin Gangyo Keji, 1995, 3, 29 cf.Chem. Abstr. 1995, 123, 337816K.
7. *S. Bi, Y. Lai, H. Bi*, Faming Zhuanti Shenqing Gangkai Shuoming Shu CN 1,082,049 (Cl. C 0773/02), 1994 cf. Chem Abstr. 1995, 122, P 248288b.
8. *J. Tsushima, Y. Kuroda, M. Nakatsuka*, Takarabine Kk, Nippon Shokuhin Kau Hatsn. Kenky, Jpn. Kokay Tokkyo Koho J. P. 0700, 112 (Cl. A 23f3/16) 1995 cf. Chem Abstr. 1995, 122, P 186018c.
9. *A. Staviak, J. Wilska, J. Jeszke*, Przem. Spazyw, 1993, 47, 15 cf. Chem. Abstr.1993, 119, 115721d.
10. *L. Floru, I. Sebe, C. Tarabasanu* "Sinteze de intermediari aromatici si coloranti organici" 1981, 161.
11. *G.M. Badyer*, *R. A Jones*, *R.C. Lauslett* Australian J. Chem 1964, 17, 1028.
12. *J.B. Kim*, *J.J. Leonard*, *F.R Lang*: J. Amer. Chem, 1972, 94, 3985.
13. *G.M.Badyer*, *R.A Jones*, *R.C. Lanslett*: Australian J. Chem. 1964, 17, 1020.
14. *A.T. Balaban,M. Banciu,I. Pogany*," Aplicatii ale metodelor fizice in chimia organica" Editura Stiintifica si Enciclopedica, Bucuresti, 1983, 20.
15. *J.E Falk* Porphyrins and metalloporphyrins B.D.A Library, Elsevier Publishing Company, 1964, 73.