

# Unequivocal synthesis of *meso*-tetraphenyltetrabenzoporphine

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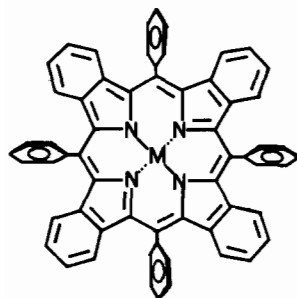
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## Abstract

The reaction of 3-benzylidenephthalimidine (3-BPI) with zinc benzoate as a chelating agent has led to the only tetramerization of 3-BPI to yield *meso*-tetraphenyltetrabenzoporphinato zinc (ZnTPTBP), while the use of zinc acetate has provided a complicated mixture of ZnTBPs with *meso*-phenyl substituent(s), the number of which is from one to four. From the FD-MS data and 3D(dimensional)-HPLC analysis, it is shown that this reaction product is contaminated with the benzyl adducts of ZnTPBP. This benzyl fragmentation probably occurs by the high temperature pyrolysis of 3-BPI.

## Introduction

*meso*-Tetraphenyltetrabenzoporphine (TPTBP) has a structure with



M=Zn or H<sub>2</sub>

an extended  $\pi$ -electron system by benzo-substitution to the  $\beta$ ,  $\beta'$ -pyrrole carbon atoms of tetraphenylporphine (TPP) and is therefore expected to be more sensitive to visible light on account of red-shifting on the visible absorption spectrum, compared to TPP [1]. Our detailed study on the preparation of *meso*-tetraphenyltetrabenzoporphinato zinc (ZnTPTBP) using the procedures previously reported by Russian workers (the reactions of either 3-benzylidene-

phthalimidine or the combination of phthalimide potassium and phenylacetic acid with zinc acetate) [2] and Remy (the reaction of isoindole with benzaldehyde in the presence of zinc acetate) [3] has revealed that their methods lead to a mixture of tetrabenzoporphine zinc complexes with *meso*-phenyl substituent(s), the number of which is from one to four [4]. Therefore, since no report has succeeded in the complete preparation of ZnTPTBP, our attention has been focused on finding a preparative method for an authentic ZnTPTBP.

In this paper, we report the unequivocal synthesis of TPTBP.

## Experimental

### Preparation of *meso*-tetraphenyltetrabenzoporphine

#### *meso*-Tetraphenyltetrabenzoporphinato zinc (ZnTPTBP)

A mixture of 10 mmol of 3-benzylidenephthalimidine (3-BPI) and 75 mmol of zinc benzoate was well ground together and put into a 100 ml round flask, which was fitted with an air condenser and a N<sub>2</sub> inlet, and then heated at 360 °C for 1 h on a salt bath. The reaction product was extracted with hot dioxane and purified by repeated column chro-

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matograph on aluminum oxide (MERCK 1097) using benzene as an eluent. A careful purification carried out by TLC on aluminum oxide (MERCK 5756) using a solvent mixture of benzene/hexane (1/1) as an eluent gave 10 mg of ZnTPTBP.

#### *meso-Tetraphenyltetrabenzoporphine (H<sub>2</sub>TPTBP)*

A total of 190 mg of ZnTPTBP was dissolved in 10 ml of chloroform, then 7 ml of trifluoroacetic acid were added gradually at room temperature. After stirring for 3 h, the reaction mixture was poured into a mixture of ethanol and water, and neutralized with anhydrous sodium carbonate. The green compound floating on the solvent was filtered with suction and dried *in vacuo*. A careful purification by TLC in a similar manner to that above led to 160 mg of H<sub>2</sub>TPTBP.

#### *Physical measurements*

Ultraviolet-visible absorption spectra were taken in dichloromethane solutions on a JASCO Ubest-30 spectrophotometer.

3-Dimensional high-pressure liquid chromatography (3D-HPLC) was carried out in a system consisting of a JASCO model 880-PU HPLC pump equipped with a MERCK LiChrospher RP-18 Hiber column (particle size 5  $\mu$ m; 125 $\times$ 4 mm I.D.) and a Ohtsuka Denshi MCPD-350PC spectro multichannel photo-detector by which the visible absorption spectrum of each eluent was instantly obtainable ranging from 230 to 800 nm with a 1.4 nm resolution.

Field desorption mass spectra (FD-MS) were measured with a Hitachi M-80 mass spectrometer at 20–30 mA.

<sup>1</sup>H NMR spectra were obtained on a NICOLET 360NB nuclear magnetic resonance spectrometer.

## Results and discussion

As previously described, zinc acetate is used as a chelating agent in both reactions of phthalimide potassium (PIK) with phenylacetic acid and isoindole with benzaldehyde for the synthesis of ZnTPTBP. Kopranenkov *et al.* have reported that the reaction of PIK with zinc acetate in the presence of an excess of sodium acetate at 360 °C gives ZnTBP [5]. Our additional study\* has revealed that the formation of ZnTBP can be achieved without sodium acetate in the Kopranenkov method. This suggests that zinc

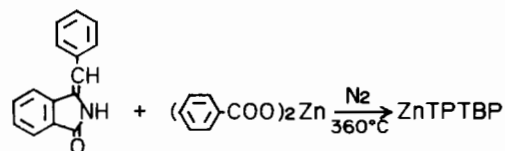
\*The reaction of PIK with zinc acetate at 360 °C gave ZnTBP, which was identified from its UV-Vis absorption spectrum: B (409, 433 nm), Q (583, 628 nm) in pyridine; <sup>1</sup>H NMR spectrum: *meso*-Hs, 11.35; benzene ring-Hs, 8.26 and 9.97 ppm; in DMF-d<sub>2</sub>; FD-MS: *m/z* = 572.

acetate serves as both the methine carbons and the central metal sources to tetramerize PIK. This result allows us to assume that zinc acetate reacts with PIK in such high temperature conditions to produce 3-methylidenephthalimidine (3-MPI) as an intermediate leading to the formation of ZnTBP, as suggested by Kopranenkov [5].

On the other hand, it has been reported that the reaction of 3-BPI with zinc acetate leads to a complicated mixture of ZnTBPs with a different number of *meso*-phenyl substituents [4]. In this reaction, it is presumed that 3-BPI reacts with zinc acetate with the pyrolysis of itself at such a high temperature to give an intermediate like 3-MPI and then both 3-MPI and 3-BPI participate in the formation of the ZnTBP resulting in the production of a complicated mixture of ZnPTBPs.

We have employed zinc benzoate as an inert chelating agent because it does not have any active unit like the methyl group of zinc acetate. Hence, the use of zinc benzoate is expected to lead only to the tetramerization of 3-BPI to ZnTPTBP, as shown in Scheme 1.

Figure 1 shows the visible absorption spectrum of this reaction product, in which the formation of metallo-tetrabenzoporphine is indicated by the characteristic absorption Soret (455 nm) and Q (650 nm) bands in dichloromethane (Table 1). Both bands are significantly red-shifted in comparison with those of ZnTPP (Soret: 423, Q: 552 and 597 nm in dichloromethane) because of the extended  $\pi$ -electron system by the annellated benzene rings to the  $\beta$ ,  $\beta'$ -



Scheme 1.

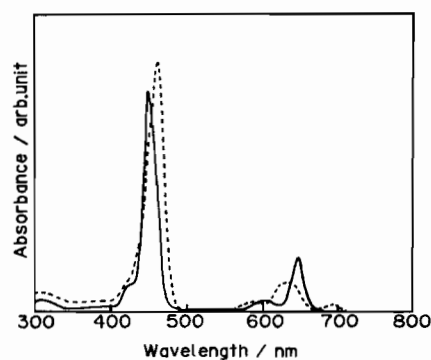


Fig. 1. Ultraviolet and visible absorption spectra of ZnTPTBP and H<sub>2</sub>TPTBP in dichloromethane.

TABLE 1. Absorption data of ZnTPTBP and H<sub>2</sub>TPTBP in dichloromethane

	Soret band		Q band	
	(1,0)	(0,0)	(1,0)	(0,0)
ZnTPTBP	427(4.44)	455(5.30)	603(3.98)	650(4.70)
H <sub>2</sub> TPTBP		462(5.30)	589(3.93)	635(4.40) 696(3.77)

log  $\epsilon$  values are given in parentheses.

pyrrole carbon atoms of TPP. The hyper absorptions in pyridine (Soret: 474, Q: 657 nm) are also observed, compared with those of ZnTBP (Soret: 433, Q: 628 nm in pyridine). Moreover, these absorption maxima are red-shifted in comparison with those (Soret: 433, Q: 630 nm in dichloromethane) of the product obtained by the reaction of 3-BPI in the presence of zinc acetate. This means that the product obtained by our method is different from that obtained by the previously reported procedure for ZnTPTBP.

The detection of the  $m/z = 876$  ion peak in FD-MS confirms that this reaction product is ZnTPTBP having a molecular weight of 876, as shown in Fig. 2(a). This structural elucidation is further supported by the <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>,  $\delta$  (ppm): *meso*-phenyl Hs: 8.56 (*o*-H, 8H), 8.21 (*p*-H, 4H), 8.12 (*m*-H, 8H); benzene ring-Hs: 7.40, 7.50 (16H). This result is consistent with that previously reported [4]. While the benzene ring Hs of TBP are located at low magnetic field in <sup>1</sup>H NMR owing to the deshielding effect of the porphyrin ring current [6], the low field shift is suppressed in the case of ZnTPTBP. This is due to the shielding effect of the *meso*-phenyl residues on the chemical shift of the peripheral protons, since the plane of the *meso*-phenyl groups is forced to be perpendicular to that

of TBP because of the significant steric hindrance by the planes of the neighboring isoindole units.

Although these spectral data of the reaction product of 3-BPI in the presence of zinc benzoate are in line with the structure of ZnTPTBP, the reaction product is contaminated with minor components with 966 and 1056 mass ion peaks. These impurities are assignable to the benzyl adducts of ZnTPTBP on the basis of the 90 mass number difference(s) corresponding to benzyl fragment(s). This phenomenon has been similarly observed in the case of the reaction of 3-BPI with zinc acetate [4].

This method using zinc benzoate as an inert chelating agent has allowed the reaction of PIK as the isoindoles source with phenylmalonic acid as the *meso*-phenyls source to be examined. Although this reaction has surely led to form ZnTPTBP from its spectral data, visible absorption data in CH<sub>2</sub>Cl<sub>2</sub>: Soret (427, 455 nm) and Q (603, 650 nm); <sup>1</sup>H NMR in CD<sub>3</sub>Cl,  $\delta$  (ppm): *meso*-phenyl Hs: 8.56 (*o*-H, 8H), 8.21 (*p*-H, 4H), 8.12 (*m*-H, 8H); benzene ring-Hs: 7.50, 7.40 (16); and FD-MS ( $m/z = 876$ ), the benzyl fragmentation resulting from the probable pyrolysis of phenylmalonic acid at such a high temperature also takes place in this case, confirmed by the FD-MS data ( $m/z = 966, 1056$  and 1146).

3D-HPLC analysis of the reaction product of 3-BPI with zinc benzoate is carried out to certify the existence of two minor components with the benzyl fragment(s). Figure 3 shows the HPLC contour plots of the product and reveals that the usage of a solvent mixture of MeOH/acetone (8/2 vol. ratio) as an eluent results in the successful separation into three components at 5.1, 5.9 and 7.0 min, respectively. As shown in Fig. 3, there is little difference in their absorption peaks. This suggests that these eluents have the same framework in their structures and the benzyl fragment(s) does not affect the  $\lambda_{\max}$  of the parent molecule, ZnTPTBP.

The treatment of ZnTPTBP with trifluoroacetic acid in chloroform [7] has led to the removal of the central metal ion. The visible absorption spectrum of the demetallated macrocyclic compound is shown in Fig. 1. The Q band splits into two bands, Q<sub>x</sub>(0,0) and Q<sub>y</sub>(0,0) as a consequence of the weakened

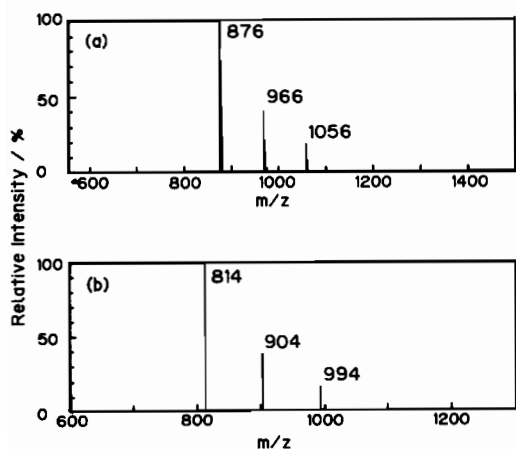


Fig. 2. Field desorption mass spectra of: (a) the reaction product of 3-BPI with zinc benzoate at 360 °C; (b) its demetallated compound by using trifluoroacetic acid.

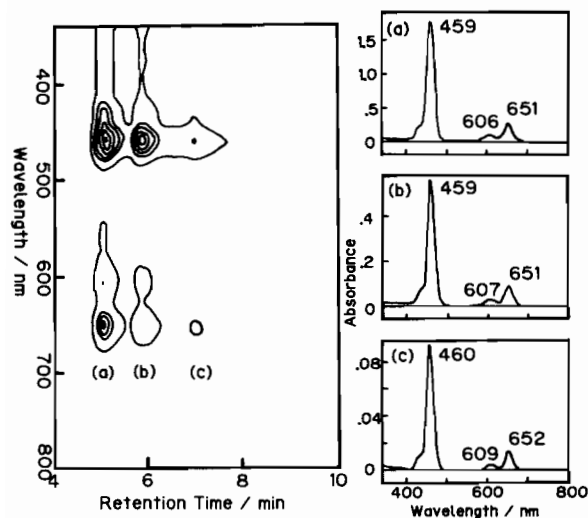


Fig. 3. 3D-HPLC contour plots for the reaction product of 3-BPI with zinc benzoate, and ultraviolet and visible absorption spectra of each elution at (a) 5.1, (b) 5.9, (c) 7.0 min. A mixture of MeOH/acetone = 8/2 (vol. ratio) was used as an eluent; flow rate 1 ml/min.

symmetry of the  $\pi$ -cloud from  $D_{4h}$  to  $D_{2h}$  [8]. The mass ion peak of  $m/z = 814$  is in agreement with the molecular weight of  $H_2TPTBP$ . The NH proton signal appears at a high magnetic field of  $-1.12$  ppm because of the shielding effect by the porphyrin ring current on  $^1H$  NMR in acetone- $d_6$ . In addition to the parent ion peak of  $m/z = 814$  of  $H_2TPTBP$ , ion peaks of  $m/z = 904$  and  $994$  with 90 mass number

difference(s) are still detected on the FD-MS, as shown in Fig. 2(b). This implies that these two ion peaks are the compounds with the benzyl fragment(s) bonded covalently to parent TPTBP.

In conclusion, the displacement of the chelating agent from zinc acetate to zinc benzoate for the tetramerization of 3-BPI affords the unequivocal production of  $ZnTPTBP$ .

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