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Reinvestigation of synthetic methods for zinc *meso*-tetraphenyltetrabenzoporphyrin

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Abstract

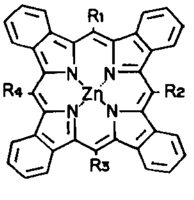
The reaction of 3-benzylidenephthalimidine (3-BPI) with zinc acetate for the preparation of the *meso*-tetraphenyltetrabenzoporphyrin zinc complex (Zn–P_4TBP) is reinvestigated. From the structural analyses of the reaction product with ultraviolet–visible absorption spectra, field desorption mass spectra (FD-MS) and ^{1}H NMR spectra, it is shown that this reaction procedure gives a complicated mixture of Zn–TBP derivatives with *meso*-phenyl substituent(s) the number of which is from one to four. The product obtained by the reaction of isoindole with benzaldehyde in the presence of zinc acetate is also discussed.

Introduction

Tetrabenzoporphyrins (TBP) have been attracting interest particularly in optical [1] and electrical functions [2]. However, studies on the properties and applications of these macrocyclic compounds have often been faced with difficulties because of the low solubility in common organic solvents [3] and the poor compatibility with polymeric materials. These solubility problems may be overcome by introducing *meso*-substituents as in the case of porphyrin, the solubility of which is improved by tetraphenyl-substitution at the *meso*-positions.

Among some preparative methods for the zinc complex of *meso*-tetraphenyltetrabenzoporphyrin (Zn–P_4TBP) [4–6], the reaction of 3-benzylidenephthalimidine (BPI) with zinc acetate [4] has attracted our keen interest because of the simple procedure using readily available starting compounds.

In the present work, we report the structural analysis of the reaction product to reveal that the reaction gives a complicated mixture of zinc TBP derivatives with *meso*-phenyl substituent(s) the number of which is from one to four.



R1~R4 = H or Phenyl

Structure of *meso*-phenyl substituted tetrabenzoporphyrin

Experimental

Preparation and purification of meso-phenyl substituted Zn–TBP

A mixture of BPI (15.47 g, 70 mmol) and zinc acetate (11.52 g, 52 mmol) was heated at 360 °C for 1 h uner N_2 atmosphere. The crude product was washed with hot water and extracted with THF. The evaporation of the solvent gave a deep purple residue (9.2 g) which was chromatographed first on a 4×30 cm column of aluminum oxide (Merck 1097) with dioxane and subsequently further purified by TLC on aluminum oxide (Merck 5756), using a solvent mixture of benzene/hexane/THF (10:10:1) as an eluent, to give five major green fractions. The reaction

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of *p*-tolylidenephthalimidine or *p*-anisylidenephthalimidine with zinc acetate was carried out in the same manner.

Physical measurements

Field desorption mass spectra (FD-MS) were carried out with a Hitachi M-80 mass spectrometer. Ultraviolet and visible absorption spectra were obtained on a JASCO Ubest-30 spectrophotometer. ^{1}H NMR spectra were measured with a NICOLET NT-360NB nuclear magnetic resonance spectrometer.

Results and discussion

FD-MS of the reaction product of BPI with zinc acetate indicated that it consists of tetrabenzoporphyrin zinc complexes substituted with various numbers of phenyl residue including Zn–P$_4$TBP of $m/z=876$, as shown in Fig. 1. TLC of the crude product led to the separation into five major compounds. The electronic absorption spectra of the compounds shown in Fig. 2 are all characteristic of metallo–TBP [7], and the absorption maxima of both Soret and Q bands are gradually red-shifted in the order of fraction (fr.) 5, fr. 4 (=fr. 3), fr. 2 and fr. 1.

The results of the FD-MS measurement summarized in Table 1 exhibited that a major ion peak (m/z) of 876 corresponding to the molecular weight of Zn–P$_4$TBP was detected only in fr. 1. A regular difference of 76 mass number which is presumed to be the phenyl group was found in the series of the parent ion peaks of five fractions. These facts suggest that the reaction of 3-BPI with zinc acetate gives a mixture of Zn–TBP derivatives with *meso*-phenyl substituent(s), the number of which is from one to four.

The ^{1}H NMR spectrum confirmed the assignment of fr. 1 showing $m/z=876$ to Zn–P$_4$TBP which possessed both of the *meso*-phenyl proton signals (20H) and the benzene ring proton signals (16H) on the isoindole units (Fig. 3). Fr. 2 of $m/z=800$ and fr. 3 of $m/z=724$ have the methine proton signals at $\delta=10.60$ ppm in CD$_2$Cl$_2$ and $\delta=11.07$ ppm in acetone-d$_6$, respectively. This reflects the lack of phenyl group(s) at the *meso*-position(s). Further analysis of these fractions by means of two dimensional *J*-correlated NMR I^{1}H–^{1}H COSY) spectra revealed

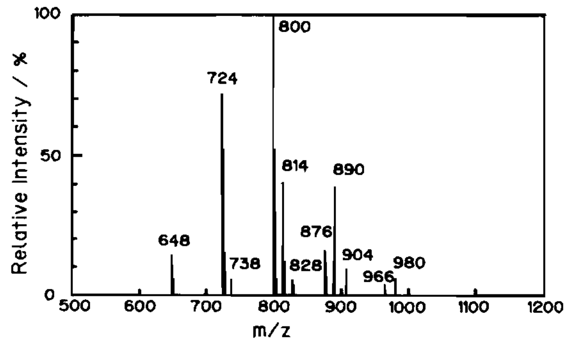

Fig. 1. Field desorption mass spectrum of the reaction product of 3-BPI with zinc acetate at 360 °C.

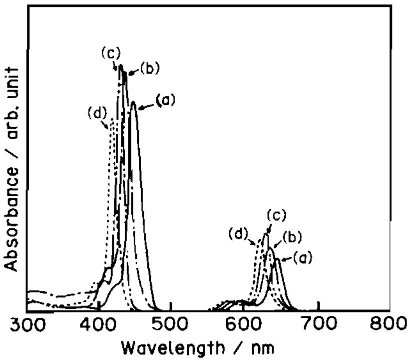

Fig. 2. Ultraviolet and visible absorption spectra of *meso*-phenyl substituted tetrabenzoporphyrin zinc complexes in dichloromethane after purification by TLC. (a): Zn–P$_4$TBP (fr. 1), (b): Zn–P$_3$TBP (fr. 2), (c): Zn–P$_2$TBP (fr. 3 and 4), (d): Zn–P$_1$TBP (fr. 5).

TABLE 1. The assignment of the FD-MS data of the reaction product of 3-BPI with zinc acetate, after isolation by means of TLC

Fraction no.	Compound	m/z	Yield (%)^a
1	Zn–P$_4$TBP	876, 966, 1056, 1146	0.4
2	Zn–P$_3$TBP	800, 890, 980	4.9
3	Zn–P$_2$TBP^b	724, 814, 904	5.4
4	Zn–P$_2$TBP	724, 814, 904	N.D.^{c}
5	Zn–P$_1$TBP	648, 738, 828	N.D.^{c}

^{a}Contain the Zn–TBPs with $m/z=90$ fragment(s). ^{b}An isomer substituted with two neighboring phenyl groups at *meso*-position. ^{c}Not determined.

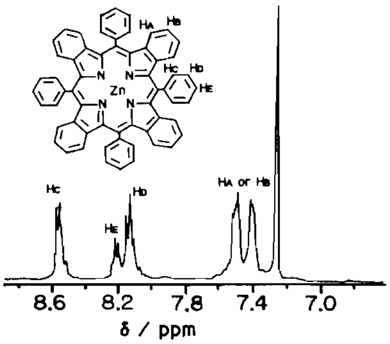

Fig. 3. 360 MHz ^{1}H NMR spectrum of Zn–P$_4$TBP in CDCl$_3$.

TABLE 2. Visible absorption spectra data of *meso*-phenyl substituted tetrabenzoporphyrin zinc complexes in pyridine

Complex	λ_{max} (nm) (absorption ratio)				
	Soret band		Q band		
Zn–P$_4$TBP[a]	447 (0.124)	474 (1.0)	616 (0.056)	657 (0.137)	
Zn–P$_3$TBP[a]	430 (0.135)	456 (1.0)	598 (0.053)	643 (0.235)	
Zn–P$_2$TBP[a]	421 (0.152)	447 (1.0)	590 (0.055)	636 (0.323)	
Zn–P$_4$TBP[b]	446 (5.26)	472 (5.34)	595 (4.40)	635 (4.80)	660 (4.56)[c]

[a]This work. [b]For these data Remy's paper was referred to [6]. [c]log ϵ.

that fr. 2 is assignable to the triphenyl-TBP zinc complex (Zn–P$_3$TBP) and that fr. 3 is Zn–TBP substituted with two phenyl groups at the neighboring *meso*-positions (Zn–P$_2$TBP), respectively. Fr. 4 showing the same mass number of major ion peaks as that of fr. 3 is thus assumed to be the isomer of Zn–P$_2$TBP substituted with two phenyl groups at the opposite *meso*-positions.

As shown in Table 1, each fraction has additional minor ion peaks, each mass number of which is the sum of m/z of the major peaks and 90 or 90×2 mass number. This implies that each fraction is contaminated with TBP zinc complexes substituted with one or two additional benzyl group(s). In order to confirm this assignment of the minor products, the reactions with zinc acetate were carried out using *p*-tolylidenephthalimidine (TPI) and *p*-anisylidenephthalimidine (API) in stead of BPI, and the FD-MS analysis was made on the reaction products. The MS spectral patterns of both products were quite similar to that from BPI and supported the formation of Zn–TBPs substituted with various numbers of *p*-tolyl or *p*-anisyl groups. Along with these major ion peaks, there existed minor ion peaks which correspond to the sum of m/z of each major ion peaks due to the arylated Zn–TBPs plus mass number of 104 or 104×2 for TPI and 120 or 120×2 for API, respectively. These suggest that both reaction products are mixed with arylated Zn–TBPs having additional *p*-methylbenzyl fragment(s) of $m/z=104$ and *p*-methoxybenzyl fragment(s) of $m/z=120$, respectively.

Although the reaction mechanism is unclear, the formation of such a complicated mixture is obviously due to the high temperature reaction conditions. In this respect, an alternative synthetic method for Zn–P$_4$TBP reported by Remy [6] was reexamined because the reaction of isoindole with benzaldehyde in the presence of zinc acetate also requires a high temperature. Judged from the electronic absorption spectrum of the product given in Table 2, Remy's procedure gives a mixture of at least Zn–P$_2$TBP and Zn–P$_4$TBP.

Conclusions

Careful structural elucidation of the reaction product of BPI with zinc acetate revealed that this procedure proposed so far to prepare Zn–P$_4$TBP results in the formation of a complicated mixture of Zn–TBPs substituted with tetra-, tri, di-, and monophenyl group(s), respectively, and optionally substituted with benzyl fragment(s). Another synthetic method for Zn–P$_4$TBP by the reaction of isoindole with benzaldehyde in the presence of zinc acetate was found to yield a mixture of at least tetra- and diphenyl Zn–TBP and not suitable for obtaining pure Zn–P$_4$TBP.

References

1 (a) O. N. Korotaev, E. I. Donskoi and V. I. Glyadkovskii, *Opt. Spectrosc., 59* (1985) 492; (b) W. E. Moerner, T. P. Carter and C. Braeuchle, *Appl. Phys. Lett., 50* (1987) 430; (c) T. P. Carter, C. Braeuchle, V. Y. Lee, M. Manavi and W. E. Moerner, *Opt. Lett., 12* (1987) 370; (d) T. P. Carter, C. Braeuchle, V. Y. Lee, M. Manavi and W. E. Moerner, *J. Phys. Chem., 91* (1987) 3998.

2 (a) T. E. Phillips, R. P. Scaring, B. M. Hoffman and J. A. Ibers, *J. Am. Chem. Soc., 102* (1980) 430; (b) M. Hanack and T. Zipplies, *J. Am. Chem. Soc., 107* (1985) 6127; (c) F. W. Kutzler and D. E. Ellis, *J. Chem. Phys., 84* (1986) 1033; (d) K. Yamashita, *Chem. Lett.,* (1982) 1085; (e) K. Yamashita, Y. Harima, H. Kubota and H. Suzuki, *Bull. Chem. Soc. Jpn., 60* (1987) 803.

3 (a) L. Edwards, M. S. Gouterman and C. B. Rose, *J. Am. Chem. Soc., 98* (1976) 7638; (b) V. A. Vogler and H. Kunkely, *Angew. Chem., 90* (1978) 808.

4 V. N. Kopranenkov, S. N. Dashkevich and E. Ya, Lykyanets, *Zh. Obshch. Khim., 51* (1985) 2513.

5 V. N. Kopranenkov, E. A. Makarova and S. N. Dashkevich, *Khim. Geterotsikl. Soedin.,* (1985) 1372.

6 D. E. Remy, *Tetrahedron Lett., 24* (1983) 1452.

7 M. Gouterman, in D. Dolphin (ed.), *The Porphyrins,* Vol. 3, Part A, Academic Press, New York, 1978, p. 21.