ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 6, pp. 1255–1259. © Pleiades Publishing, Ltd., 2008.
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meso-Tetraalkyltetrabenzoporphyrins and Their Zinc Complexes. Synthesis and Properties

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Received July 6, 2007

Abstract—A number of meso-tetraalkyltetrabenzoporphyrin zinc complexes having alkyl substituents with different lengths were synthesized by reaction of excess phthalimide with zinc salts of aliphatic carboxylic acids. The corresponding free bases were obtained by treatment of the complexes with sulfuric acid. The spectral properties of the complexes and ligands and thermal stability of the former were studied.

DOI: 10.1134/S1070363208060273

The possibility for diverse modification of tetrabenzoporphyrin which is the most important synthetic analog of porphyrin determines wide prospects of studies in this field. Variation of substituents in the meso positions of tetrabenzoporphyrin molecule provides a tool for controlling physicochemical properties of substituted tetrabenzoporphyrins. A quite interesting group of tetrabenzoporphyrin derivatives consists of *meso*-tetraalkyltetrabenzoporphyrins. Unlike parent tetrabenzoporphyrin, *meso*-tetraalkyltetrabenzoporphyrins are characterized by improved solubility in many organic solvents; therefore, such compounds can be purified by chromatographic methods and subjected to detailed studies of applied character.

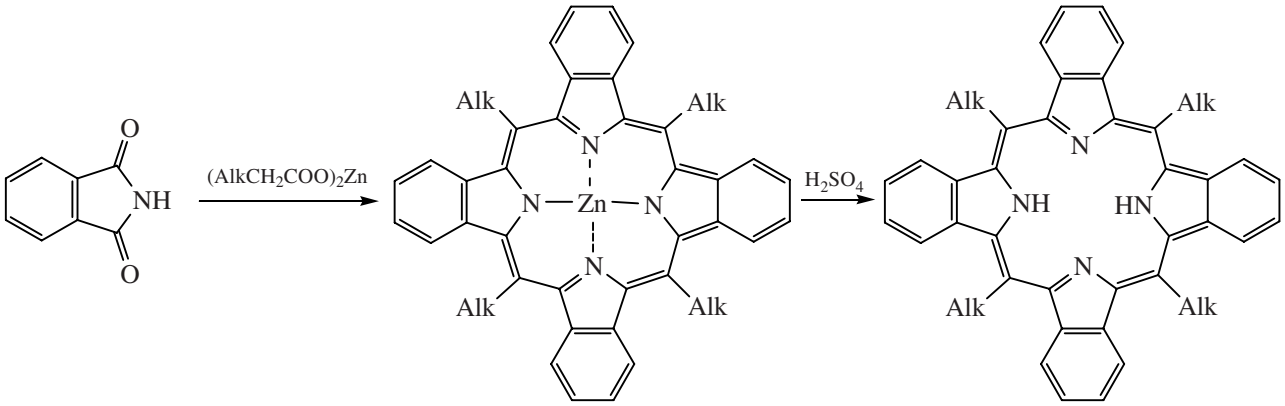
Zinc complexes of *meso*-tetraalkyltetrabenzoporphyrins were synthesized for the first time in 1984 [1] following a three-step procedure utilizing monoalkylmalonic acids as starting compounds. However, the large number of steps and low accessibility of the initial reagents stimulated search for more practical methods for the synthesis of *meso*-tetraalkyltetrabenzoporphyrins.

It is known that metal complexes of *meso*-tetraaryltetrabenzoporphyrins can be obtained by template condensation of phthalimide (**I**) with excess arylacetic acid in the presence of zinc(II) hydroxide [2]. Our attempts to synthesize zinc complexes of *meso*-tetraalkyltetrabenzoporphyrins in such a way, i.e., by reaction of phthalimide (**I**) with excess aliphatic carboxylic acid zinc salt, were successful only in the case of lower carboxylic acids, propionic and butyric, while the reactions with zinc(II) octanoate, decanoate, and octadecanoate failed. Presumably, the reason is that it was impossible to attain sufficiently high temperature (320–330°C) which was necessary to complete the process because of the low boiling point of the reaction mixture (250–270°C). No positive results were obtained when sodium hydroxide was added to the reaction mixture, though the required temperature was reached: in this case, charring occurred.

We succeeded in performing the reaction at high temperature without addition of alkaline reagents by changing the reactant ratio, namely using 50% excess of phthalimide. As a result, we isolated zinc complexes **II–VI** of *meso*-tetraalkyltetrabenzoporphyrins which were then subjected to demetalation by treatment with sulfuric acid to obtain the corresponding free ligands **VII–XI**. The formation of zinc complexes **II–VI** and porphyrins **VII–XI** may be illustrated by Scheme 1.

Compounds **II–XI** are green substances that are characterized by different solubilities in organic solvents. They were isolated and purified by chromatography on aluminum oxide of activity grade II according to Brockmann using specially selected eluent in each case. The structure of tetraalkyltetrabenzoporphyrins **VII–XI** and their zinc complexes **II–VI** was confirmed by elemental analysis and electronic and ^{1}H NMR spectroscopy (Table 1).

Scheme 1.



I **II–VI** **VII–XI**

II, **VII**, Alk = CH_3; **III**, **VIII**, Alk = C_2H_5; **IV**, **IX**, Alk = C_6H_{13}; **V**, **X**, Alk = C_8H_{17}; **VI**, **XI**, Alk = $C_{16}H_{33}$.

The electronic absorption spectra of compounds **II–XI** (Fig. 1, Table 1) strongly resemble the spectra of tetrabenzoporphyrin and its zinc complex [3]. Presumably, even long alkyl substituents in the *meso* positions weakly affect the electronic and steric structure of the tetrabenzoporphyrin macroring.

The ^{1}H NMR spectrum of complex **V** contains a downfield multiplet in the region δ 7.71–7.28 ppm, which belongs to 16 protons in the isoindole fragments. Eight protons in the α-methylene groups resonate as a triplet at δ 2.73 ppm, 48 protons in the other methylene groups give rise to a singlet at δ

Table 1. Yields, elemental analyses, and electronic absorption and ^{1}H NMR spectra of compounds **II–XI**

Comp. no.	Yield, %	Eluent	Found, %/calculated, %			Electronic spectrum ($CHCl_3$), λ_{max}, nm (log ε)	^{1}H NMR spectrum (CCl_4), δ, ppm
			C	H	N		
II	22	Toluene–pyridine, 50:1	75.28	4.55	8.24	623 (4.58), 575 (4.28), 421 (5.01)	
			76.25	4.48	8.89		
III	20	Chloroform–acetone, 1:1	77.12	5.67	7.89	624 (4.57), 575 (4.28), 423 (5.02)	
			77.02	5.29	8.17.		
IV	15	Chloroform	80.01	7.62	5.88	624 (4.55), 574 (4.26), 426 (5.03)	7.73–7.37 m (16H), 2.75 t (8H),
			79.14	7.53	6.15		1.36 s (32H), 0.88 t (12H)
V	14	Chloroform	80.12	9.14	6.00	623 (4.58), 576 (4.25), 423 (5.01)	7.71–7.28 m (16H), 2.73 t (8H),
			79.85	8.28	6.39		1.36 s (48H), 0.89 t (12H)
VI	17	Chloroform	81.15	11.77	3.62	625 (4.53), 575 (4.23), 427 (5.00)	7.75–7.33 m (16H), 2.76 t (8H),
			81.61	10.14	3.81		1.33 s (112H), 0.89 t (12H)
VII	77	Toluene–pyridine, 50:1	85.06	5.61	9.13	665 (4.08), 605 (4.12), 435	
			84.78	5.34	9.89	(4.97), 420 (4.79)	
VIII	80	Chloroform-acetone, 1:1	84.14	6.43	8.22	666 (4.08), 606 (4.11), 435	
			84.85	6.15	9.00	(4.96), 422 (4.78)	
IX	68	Chloroform	85.88	9.12	5.92	664 (4.07), 610 (4.12), 434	7.72–7.34 m (16H), 2.74 t (8H),
			85.06	8.33	6.61	(4.99), 421 (4.79)	1.32 s (32H), 0.88 t (12H),
							–2.15 s (2H)
X	72	Chloroform	86.11	9.72	4.13	665 (4.03), 609 (4.10), 434	7.73–7.23 m (16H), 2.75 t (8H),
			85.13	9.03	5.84	(4.96), 423 (4.75)	1.33 s (48H), 0.89 t (12H),
							–2.11 s (2H)
XI	79	Chloroform	85.88	11.23	3.55	667 (4.10), 609 (4.13), 432	7.75–7.31 m (16H), 2.77 t (8H),
			85.29	10.74	3.98	(4.92), 425 (4.77)	1.35 s (112H), 0.85 t (12H),
							–1.98 s (2H)

1.36 ppm, and 12 protons in the terminal methyl groups appear as a triplet at δ 0.89 ppm. The ^{1}H NMR spectra of complexes **VI** and **VI** differe from the spectrum of **V** only in the relative signal intensity (Table 1). Unlike zinc complexes **II–VI**, ligands **IX–XI** displayed in the ^{1}H NMR spectra upfield signals from the NH protons in the region δ –2.15 to –1.98 ppm; the corresponding signal of unsubstituted tetrabenzoporphyrin is located in a slightly stronger field, at δ –2.53 ppm [4]. These data confirm our assumption that alkyl groups in the meso positions insignificantly affect the geometric structure of the macroring. In fact, quantum-chemical calculations (AM1) of compound **VIII** with full geometry optimization showed that the macroring in its molecule is characterized by a light saddle-like distortion and that the isoindole fragments deviate from the macroring plane by a dihedral angle of 11–14°. Thus the results of quantum-chemical calculations agree well with the spectral parameters of the synthesized compounds.

meso-Substituted tetrabenzoporphyrins are promising from the viewpoint of their use as catalysts in various processes [5] which often occur at elevated temperature. Therefore, such catalysts should meet some important conditions, specifically high thermal stability. In the present work we examined the stability of zinc complexes **II–VI** to thermooxidative decomposition. The results are collected in Table 2. It is seen that all the examined compounds are highly stable on heating on exposure to air. The thermal decomposition of **II–VI** is a multistep process, as follows from the presence of several peaks on the DTG and DTA curves. The decomposition patterns of compexes **II–VI** are fairly similar (Fig. 2). In all cases, the first step (<95–180°C; Table 2) involves removal of occluded solvent molecules, which is likely to be accompanied by essential reorganization of the crystal lattice (a small exothermic effect is observed on the DTA curve).

The thermal decomposition of *meso*-tetraalkyltetrabenzoporphyrin zinc complexes is accompanied by evolution of gaseous products (Fig. 2, DTG curve). According to [6], in such cases the use of the temperature of decomposition as a measure of thermal stability is inappropriate. For example, the temperature of decomposition of $[Ni(NH_3)_6]Cl_2$ changes from 90 to 185°C [6], depending on the sample weight, shape of the crucible, and composition of self-generating atmosphere. Therefore, in keeping with generally accepted view, it is better to estimate the thermal stability of a compound using the energy of activation

Table 2. Parameters of thermooxidative decomposition of zinc complexes **II–VI**

Comp. no.	Alk	Temperature, K	T_{dec}, K	E_a,[a] kJ mol^{-1}	ln A[b]
II	CH_3	295–398	443	50	11.0
		443–653			
		699–762			
		781–905			
III	C_2H_5	293–426	493	86	19.7
		493–653			
		668–741			
		741–890			
IV	C_6H_{13}	293–699	518	107	22.3
		518–618			
		618–753			
		763–873			
V	C_8H_{17}	289–367	463	58	14.0
		367–415			
		463–660			
		660–728			
		764–882			
VI	$C_{16}H_{33}$	295–451	523	109	22.0
		523–660			
		660–738			
		757-865			
ZnTBP			630	205	33.0

[a] ±(3–4)%. [b] ±(0.2–0.8)%.

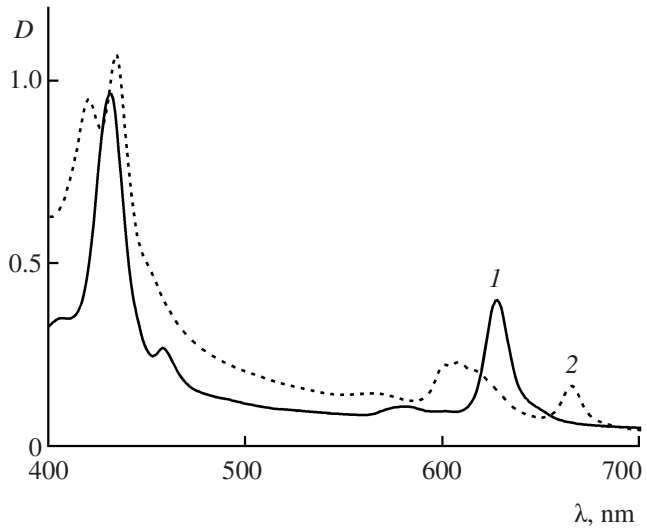


Fig. 1. Electronic absorption spectra of compounds (*1*) **VI** and (*2*) **XI** in chloroforme.

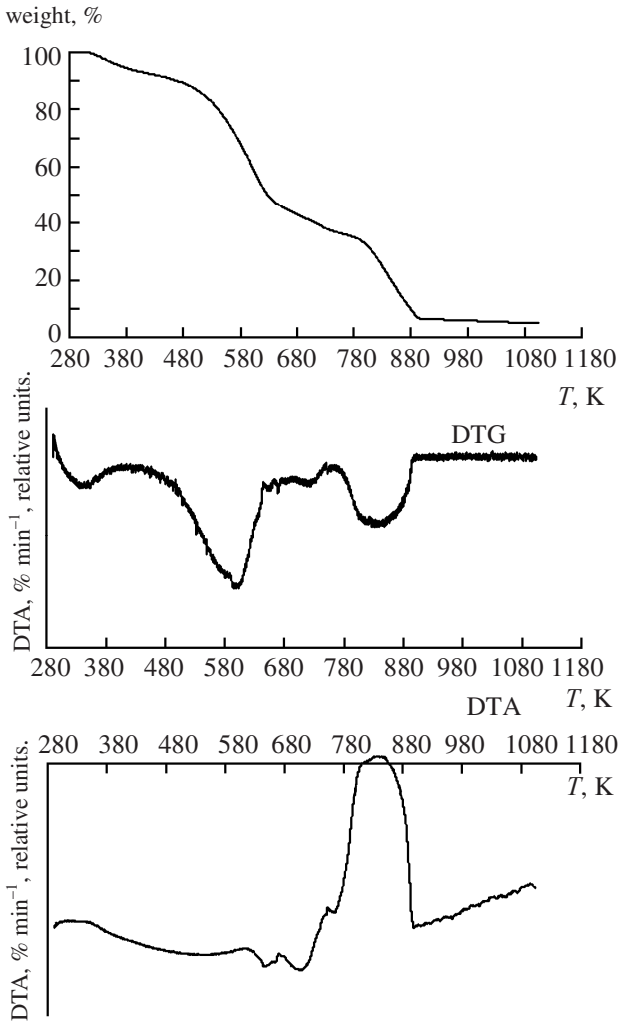


Fig. 2. Thermogram of complex **II**.

of the thermal oxidation process. The kinetic parameters were determined according to Coats–Redfern and Sestak–Berggrein [7] (Table 2). The obtained data indicated the following thermooxidative stability series of *meso*-tetraalkyltetrabenzoporphyrin zinc complexes: **II** < **V** < **III** < **IV** < **VI**. The general trend is that the stability of complexes **II–VI** rises with extension of the meso-alkyl substituent. An exception is complex **V**. Compound **V** displayed a sharp peak on the DTG curve in the temperature range from 367 to 415 K and the corresponding large weight loss, 13% calculated on $C_{68}H_{84}N_4Zn$. This step was accompanied by endothermic peak on the DTA curve. These findings led us to presume that removal of gaseous decomposition products initiated melting of the sample.

It is interesting that *meso*-tetraalkyltetrabenzoporphyrin zinc complexes **II–VI** are less thermally stable than unsubstituted tetrabenzoporphyrinatozinc(II) (ZnTBP) [7]. Analogous relations were observed previously while studting zinc complexes of tetraphenylporphyrin, phthalocyanine, and their alkyl-substituted derivatives. The reason is that the thermal decomposition of alkyl-substituted porphyrins begins with elimination of alkyl groups. Comparison of the weight loss in the second step with the contribution of alkyl groups to the molecular weight of *meso*-tetraalkyltetrabenzoporphyrin complexes showed that oxidation of peripheral substituents in complexes **II–VI** is not a separate step.

All complexes **II–VI** fit the isokinetic relationship $\ln A = 0.1818E_a + 2.872$ ($r^2 = 0.970$), which suggests a common mechanism of their thermooxidative decomposition and confirms the validity of estimation of the thermal stability of these complexes by E_a values.

EXPERIMENTAL

The electronic absorption spectra were measured on a Hitachi UV-2001 spectrophotometer. The ^1H NMR spectra were recorded from solutions in $CDCl_3$ on a Bruker AMD-200 spectrometer (200 MHz) using tetramethylsilane as internal reference. The IR spectra (400–4000 cm^{-1}) were obtained on an Avatar 360 FT-IR instrument from thin films. The elemental compositions were determined on a FlashEA 1112 CHNS–O Analyzer. Thermal decomposition of complexes **II–VI** was studied on a thermoanalytical setup described in [8]. The detailed procedures for the calculation and statistical processing of kinetic parameters of thermal decomposition were reported in [7].

5,10,15,20-Tetraalkyltetrabenzoporphyrin zinc complexes II–VI *(general procedure)***.** A mixture of 0.03 mol of phthalimide **I** and 0.02 mol of the corresponding carboxylic acid zinc salt was heated to 320°C and kept for 1.5 h at that temperature. The mixture was cooled, dissolved in an appropriate solvent, and subjected to column chromatography on aluminum oxide of activity grade II according to Brockmann. The major green fraction was collected.

5,10,15,20-Tetraalkyltetrabenzoporphyrins VII–XI *(general procedure)***.** Complex **II–VI**, 0.5 g, was dissolved in 10 ml of concentrated sulfuric acid, and the solution was kept for 2 h at 20°C and poured into 50 ml of water. The precipitate was filtered off, washed with 20 of water and 20 ml of 10% aqueous ammonia, and dried. It was then dissolved in an appropriate

solvent and subjected to column chromatography on aluminum oxide of activity grade II according to Brockmann. The major green fraction was collected.

ACKNOWLEDGMENTS

This study was performed under financial support by the Presidium of the Russian Academy of Sciences (program on organization of work of young scientists in the priority fields of basic research, project no. 01.02.007-00982) and by the Russian Foundation for Basic Research (project no. 07-03-00427a).

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