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Oxidation Kinetics of Zn-5,15 Bis(*ortho*-methoxyphenyl)-2,3,7,8,12,13,17,18-octamethylporphyrin with Organic Peroxides in *o*-Xylene

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Abstract—With the purpose of further investigation of the effect of the steric strain of the porphyrin macroring in metal porphyrins on their redox properties, kinetics of oxidation of Zn-5,15 bis(*ortho*-methoxyphenyl)-2,3,7,8,12,13.17,18-octamethylporphyrin with organic peroxides in *o*-xylene at 295°C were studied spectrophotometrically to show that this process leads to complete destruction of the complex. Kinetic characteristics (k_{ef}, k_v) of the process were evaluated. The structure of the zinc porphyrin and its oxidation intermediates were obtained by quantum- chemical calculations. Steris strains in the metal prophyrin macroring were revealed and shown to enhance in the course of the reaction. An effect of the degree of deformational strain on the oxidation rate was noted.

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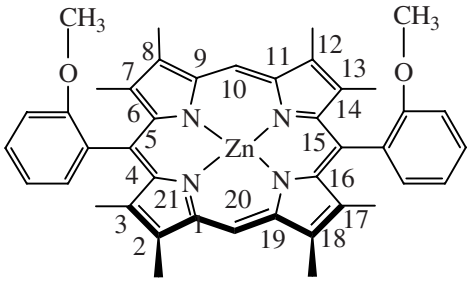
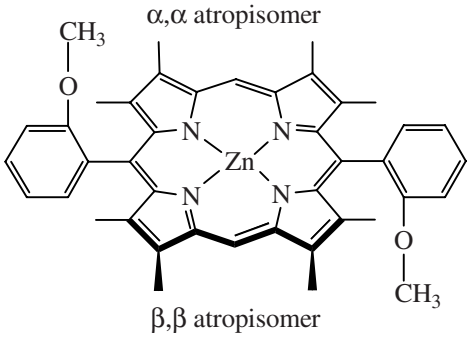
As known, metal porphyrins model various natural processes [1–4]. The unique properties of metal porphyrins are associated with the electronic effects of substituents, ability of the central atom to coordinate with molecules of different nature, and conformational changes in the macroring [5–8]. It has become evident over the past years that variation of deformational strains in the porphyrin macroring is one of the most effective tools for controlling properties of porphyrins. With the purpose of further investigation of the effect of deformational strains in metal porphyrins on the redox properties of the latter, we studied the kinetics of oxidation of Zn-5,15-bis(*ortho*-methoxyphenyl)-2,3,7,8, 12,13,17,18-octamethylporphyrin (ZnP) with organic peroxides in *o*-xylene.

Zinc-5,15-bis(*ortho*-methoxyphenyl)-2,3,7,8,12,13, 17,18-octamethylporphyrin exists as a mixture of two atropisomers.

Because of the close chromatographic mobility, these isomers are hardly separable. Therefore, In our oxidation study were dealt with their mixture.

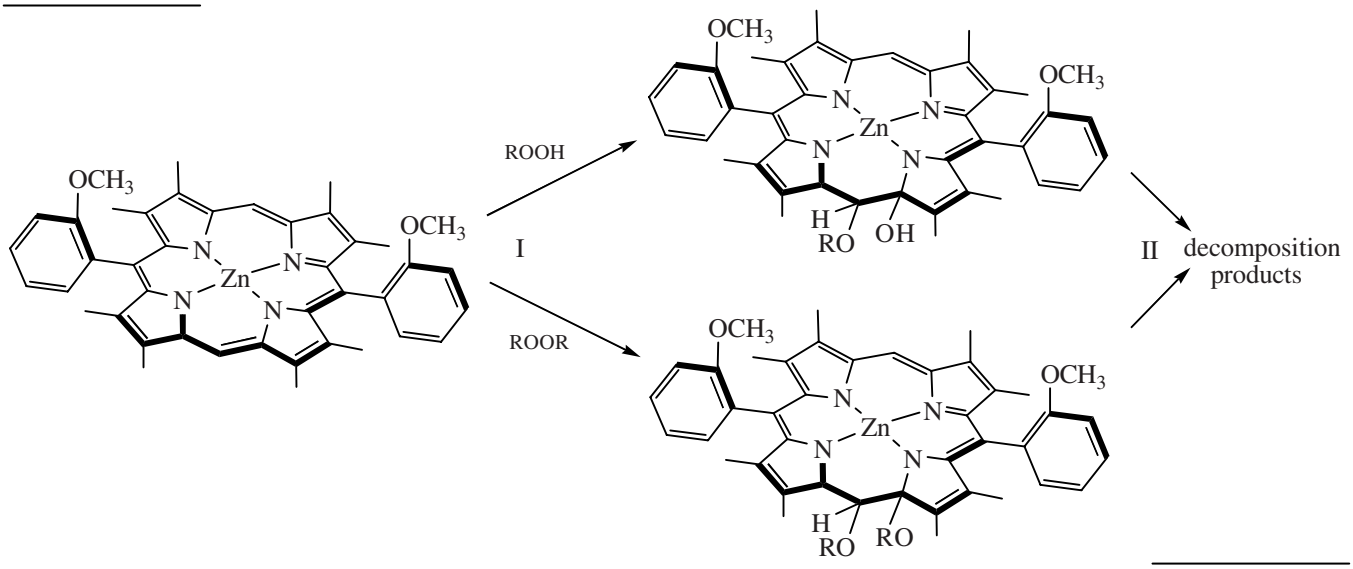
As known, reagent grade xylenes contain a sufficient amount of peroxides capable of participating in redox transformations of metal porphyrins.





Oxidation can involve either the central atom or the periphery of the macroring [9–15]. In our case, only the second pathway is possible [16]. The reaction progress and features depend on the structure of and steric strains in the molecular ligand.

There are two possible oxidation mechanisms of the zinc porphyrin [16]. The first involves hydroxylation [14]. Note that *o*-xylene contains peroxides like $CH_3C_6H_4CH_2OOH$ and $CH_3C_6H_4CH_2OOCH_2C_6H_4CH_3$. Therefore, this reaction proceeds according to the following scheme:



The formation of C–OR and C–OH bonds disturbs conjugation in the macroring because of redistribution of the electronic density in it. Structural changes enhance deformation of the macrocyclic compound. As a result, an unstable sterically strained complex with an open conjugation system is formed and decomposes to give colorless products (Fig. 1.) The limiting stage in this case is stage I.

The second probable mechanism of the reaction under study is a free-radical one. The activation of the peroxide yields $RO^{\cdot}$ and $HO^{\cdot}$ radicals which attack the *meso* or α position of the sterically strained zinc porphyrin to form such radicals as $ZnP^{\cdot}(RO)$, $ZnP^{\cdot}(HO)$, and $ZnP^{\cdot}$ [17]. The radical forms exist in the excited state, and they are deformed and very unstable. This all leads to destruction of the chromophore to form colorless reaction products (Fig. 1). The rate-limiting stage of this mechanism is the formation of macrocyclic radicals, and all the other steps proceed faster.

The oxidation kinetics of ZnP (c_{ZnP} 1.43×10^{-5}–4.2×10^{-5} M) with organic peroxides (C_p 1.1×10^{-6} M) were studied spectrophotometrically. The reaction had a pseudo-first order in peroxide ($n = 1$), what followed from a linear time dependence of ln (c_0/c_τ) and fairly constant k_{app} values (Fig. 2, Table 1).

$$dc_{perox}/dt = k_v[\text{peroxide}]. \quad (1)$$

The apparent oxidation rate constants increase lineary with increasing concentration of zinc porphyrin (log k_{app} = 0.742log c_{ZnP} – 1.812) (Fig. 3). Least-squares treatment of dependence (2) gave a true rate constant (k_v = 0.0115 s^{-1} mol^{-1} l) and reaction order in metal (0.74, i.e. *m* is about 1).

$$\log k_{ef} = \log k_v + m\log [\text{ZnP}]. \quad (2)$$

The rate equation for the oxidation reaction is the following:

$$-dc_{ZnP}/dt = k_v [\text{ZnP}][\text{peroxide}]. \quad (3)$$

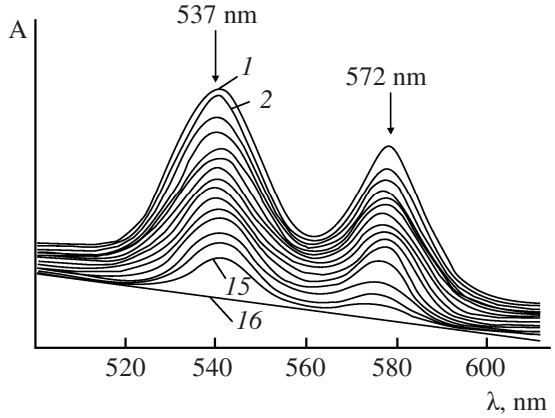


Fig. 1. Evolution of the electronic absorption spectrum while oxidation of ZnP (c_{ZnP} 1.43×10^{-5} M) in *o*-xylene (C_p 1.1×10^{-6} M) at 295 K; time, s: (*1*) 0; (*16*) 5012, (*2–15*) intermediate moments.

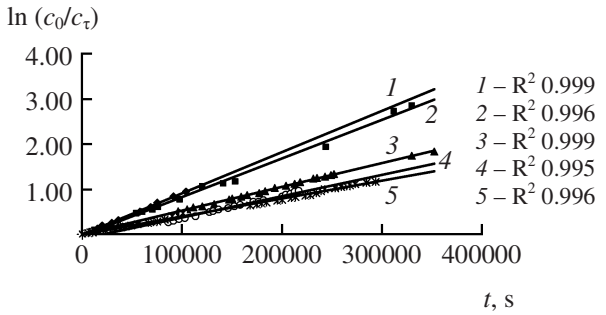


Fig. 2. Dependence of ln (c_0/c_τ) on τ for oxidation of ZnP with peroxides at 295 K; c_{ZnP}, M: (*1*) 4.2×10^{-5}, (*2*) 3.9×10^{-5}, (*3*) 2.13×10^{-5}, (*4*) 1.77×10^{-5}, (*5*) 1.43×10^{-5} (c_{perox} 1.1×10^{-6} M).

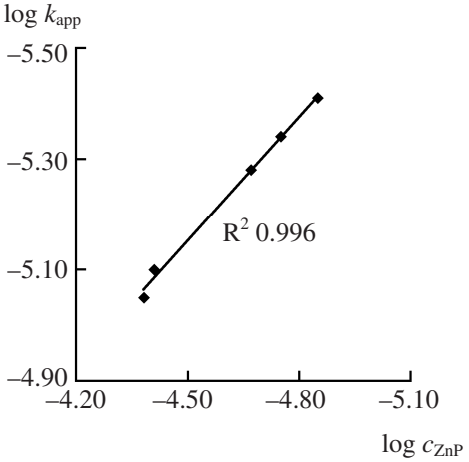


Fig. 3. Dependense of apparent oxidation rate constant on ZnP concentration.

Note that RO˙ and HO˙ radicals generated in the free-radical reaction are deactivated by the decomposition products of the complex.

Basing on our present data and data reported previously for a "capped" zinc porphyrin [16] we established that the oxidation rate of zinc porphyrins with peroxides is controlled by the nature of the porphyrin ligand and the degree of steric tension of its macroring. Hence, a "capped" zinc porphyrin with a highly distorted macroring is oxidized 20 times faster (k_v 0.218 s^{-1} mol^{-1}) than the compound under study. At the same time, zinc-5,15-bis(*n*-butoxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyrin and zinc-5,15-(*p*-butyloxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrin is not oxidized with peroxides [16].

Table 1. Kinetic parameters of oxidation of ZnP with *o*-xylene peroxides at 295 K

$c_{ZnP} \times 10^5$, M	$k_{app} \times 10^6$, s^{-1}
c_{perox} 1.1×10^{-6} M	
4.20	8.91
3.90	7.94
2.13	5.25
1.77	4.57
1.43	3.89
k_v 0.0115 s^{-1} mol^{-1} l	

Deformation of the macroring in the zinc porphyrin under study was confirmed by quantum-chemical calculations (Table 2, Fig. 4).

Comparison with the averaged metal porphyrin structure with the weakest internal strain [18] with the optimized ZnP molecule shows that the latter structure is nonplanar, slightly saddle-like deformed, and sterically strained (Table 2, Figs. 4, 5). The planes containing phenyl substituents form with the N_4 plane

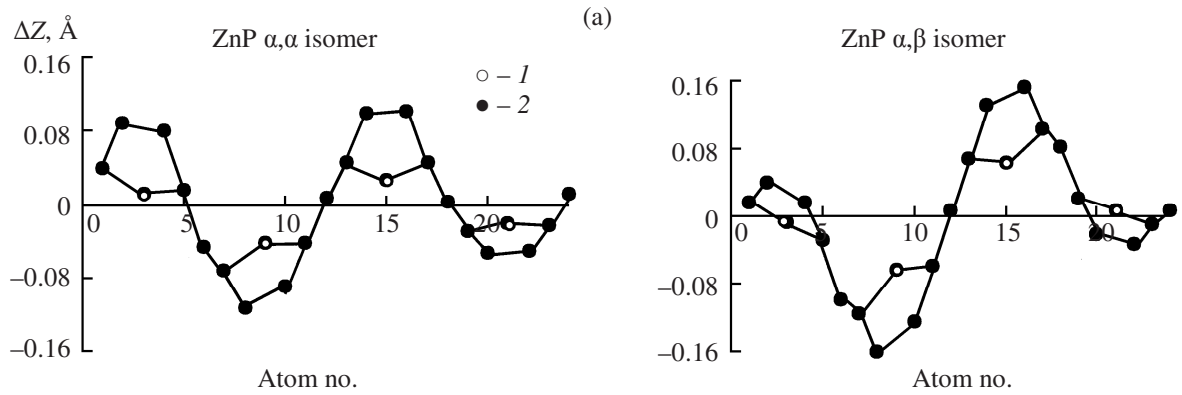


Fig. 4. Deviations of skeletal atoms of the (a) porphyrin macroring (Δ*Z*) α,β-ZnP and (b) oxidation intermediates from the molecular mean plane. (*1*) Nitrogen atoms, and (*2*) carbon atoms.

Fig. 4. (Contd.)

(b)

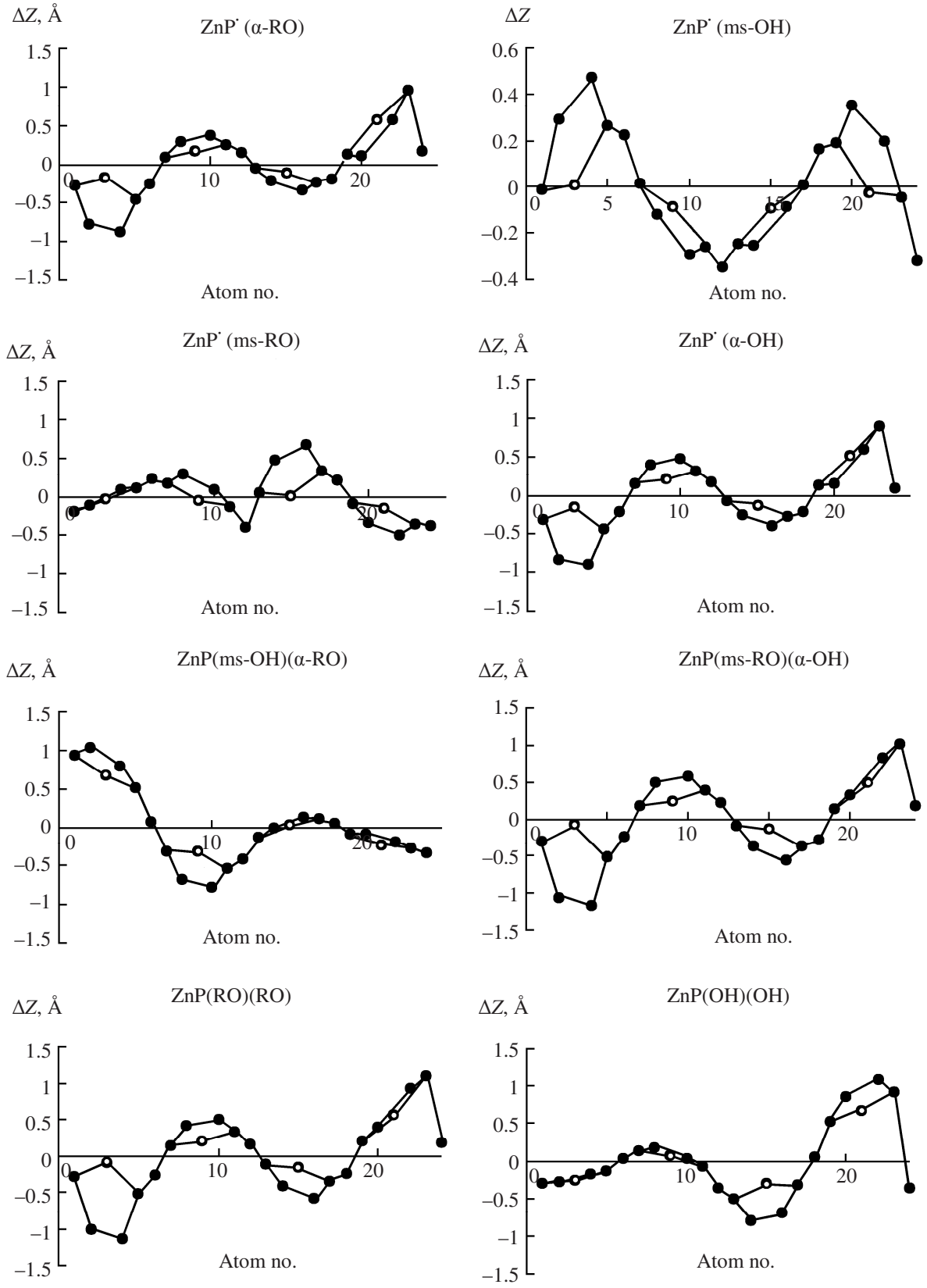

ΔZ, Å
ZnP• (α-RO)
Atom no.
ΔZ
ZnP• (ms-OH)
Atom no.
ZnP• (ms-RO)
ΔZ, Å
Atom no.
ZnP• (α-OH)
ΔZ, Å
Atom no.
ZnP(ms-OH)(α-RO)
ΔZ, Å
Atom no.
ZnP(ms-RO)(α-OH)
ΔZ, Å
Atom no.
ZnP(RO)(RO)
ΔZ, Å
Atom no.
ZnP(OH)(OH)
ΔZ, Å
Atom no.

Table 2. Selected geometric characteristics of the sterically strained zinc porphyrin

Complex	N_{22}–N_{24} N_{23}–N_{21} Å	Zn–N_{22} Zn–N_{24} Å	Zn–N_{23} Zn–N_{21} Å	Ct–Zn Å	C_{20}–O Å	C_{19}–O Å	C_5–C_{15} C_{10}–C_{20} Å	$P_{N\,4}$ Å	$N_{22}ZnN_{23}$ $N_{21}ZnN_{24}$ deg	$N_{22}ZnN_{21}$ $N_{23}ZnN_{24}$ deg	$C_4C_5C_6$ $C_{14}C_{15}C_{16}$ deg	$C_9C_{10}C_{11}$ $C_1C_{20}C_{19}$ deg	$C_{20}C_{19}C_{18}$ deg	$C_{20}C_{19}N_{24}$ $C_{18}C_{19}N_{24}$ deg
α,α isomer														
ZnP	4.0692	2.0347	2.0842	0.0230			7.1277	11.6472	93.30	86.72	123.98	126.15	122.45	128.25
	4.1682	2.0348	2.0844				6.8315		93.29	86.73	123.99	126.14		109.29
ZnP(RO)·	4.0956	2.0199	1.9767	0.2518	1.4326	1.4033	6.8828	11.5690	94.37	90.14	124.18	125.34	109.67	113.86
(OH)[a]	3.9748	2.1066	2.0241				6.9725		90.08	88.50	124.32	118.09		102.13
ZnP(RO)·	3.9671	1.9774	2.0248	0.2595	1.4002	1.4159	6.9858	11.7096	95.69	90.01	124.44	125.91	113.17	106.06
(OH)[b]	4.1148	2.0235	2.1609				6.6879		92.34	87.28	124.88	110.63		107.70
ZnP(RO)·	4.1029	2.0101	1.9743	0.2987	1.4211	1.4197	6.8675	11.5845	94.75	89.58	124.40	125.37	108.75	111.65
(RO)	3.9600	2.1361	2.0108				6.9653		91.11	88.05	124.44	118.29		102.09
ZnP(HO)·	4.0758	2.0263	1.9793	0.2834	1.3999	1.4043	6.9841	11.6715	95.34	89.38	124.76	125.81	113.96	106.02
(OH)	3.9669	2.1180	2.0279				6.6731		93.09	88.02	124.29	109.65		102.57
$ZnP^{\bullet}$·	4.1482	2.0641	2.0390	0.0889	1.4396		6.9167	11.6636	93.46	87.84	124.87	125.92	122.02	127.95
$(RO)_{meso}$	4.0959	2.0879	2.0587				7.0422		91.56	87.27	124.75	115.46		110.02
$ZnP^{\bullet}$·	4.0907	2.0365	2.0715	0.0226	1.4263		7.0706	11.6846	93.51	87.07	124.45	126.02	121.19	128.79
$(OH)_{meso}$	4.1732	2.0544	2.1019				6.9384		91.73	87.68	124.51	116.51		109.96
$ZnP^{\bullet}$·	4.1325	2.0155	1.9854	0.2763		1.4277	6.9305	11.6166	95.50	89.44	124.09	125.94	109.11	113.54
$(RO)_{\alpha}$	3.9550	2.1538	1.9983				6.8429		91.35	87.24	124.06	126.91		102.69
$ZnP^{\bullet}$·	4.1130	2.0241	1.9859	0.2741		1.4158	6.9458	11.5918	95.18	89.02	124.03	125.91	110.58	113.66
$(OH)_{\alpha}$	3.9592	2.1253	2.0010				6.8313		91.84	87.45	124.01	125.94		102.69
α,β isomer														
ZnP	4.0873	2.0665	2.0636	0.0248				11.6033	93.43	86.60	124.27	126.67	122.85	128.09
	4.1193	2.0211	2.0561						93.25	86.75	123.57	125.51		109.05
ZnP(RO)·	4.0541	2.0156	1.9772	0.2099	1.4329	1.4033	6.8868	11.5331	93.71	89.74	124.71	124.89	110.00	114.01
(OH)[a]	3.9976	2.0602	2.0519				6.9559		90.57	88.88	123.84	117.72		102.05
ZnP(RO)·	4.0011	1.9789	2.0305	0.2679	1.4006	1.4195	6.9779	11.6581	95.13	88.17	123.93	125.77	113.41	106.84
(OH)[b]	4.0597	2.0579	2.0879				6.6728		92.81	88.98	125.38	110.47		102.75
ZnP(RO)·	4.0534	2.0135	1.9783	0.2591	1.4216	1.4214	6.8782	11.5524	94.09	88.80	123.96	125.16	109.03	111.96
(RO)	3.9946	2.0729	2.0454				6.9451		90.24	90.27	124.94	117.83		102.13
ZnP(HO)·	4.0422	2.0267	1.9800	0.2776	1.4002	1.4063	6.9837	11.6285	94.61	88.68	125.25	125.45	114.23	106.53
(OH)	3.9947	2.0723	2.0531				6.6551		93.62	88.31	123.79	109.64		102.58
$ZnP^{\bullet}$·	4.1447	2.0591	2.0447	0.0375	1.4405		6.9237	11.6702	93.48	87.17	124.25	125.94	121.72	128.23
$(RO)_{meso}$	4.1056	2.0862	2.0625				7.0495		91.83	87.61	124.69	116.22		110.04
$ZnP^{\bullet}$·	4.0881	2.0357	2.0715	0.0204	1.4264		7.0664	11.6821	93.48	87.05	124.41	126.01	121.23	128.77
$(OH)m_{eso}$	4.1740	2.0526	2.1027				6.9339		91.76	87.70	124.50	116.54		109.95
$ZnP^{\bullet}$·	3.9449	1.9810	2.0272	0.2667		1.4306	6.9464	11.6284	95.31	87.24	124.15	125.99	109.60	114.16
$(RO)_{\alpha}$	4.1508	19965	2.1578				6.8409		91.53	89.33	124.13	126.78		102.95
$ZnP^{\bullet}$·	3.9456	1.9800	2.0290	0.2649		1.4157	6.9461	11.6017	95.21	87.19	124.05	125.96	110.99	113.32
$(OH)_{\alpha}$	4.1349	1.9945	2.1397				6.8304		91.89	89.16	124.07	126.30		102.74

[a] Compound with the OR group in the 20 position and the OH group in the 19 position of the macroring. [b] Compound with the OR group in the 19 position and the OH group in the 20 position of the macroring.

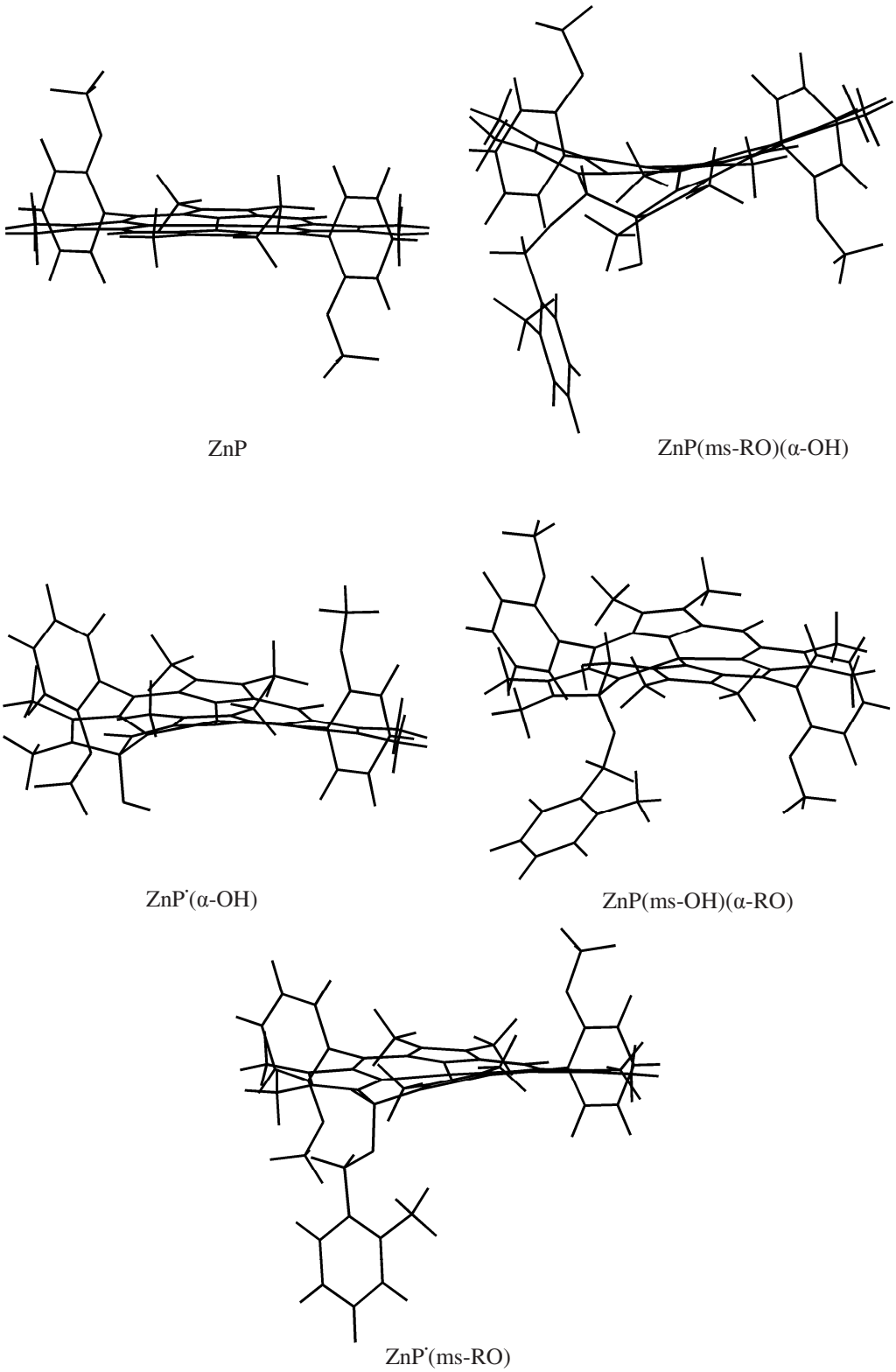


Fig. 5. Structure of the α,β isomer of ZnP and intermediates of the oxidation reaction, as given by PM3 calculations.

angles of about 86°–88° and 84°–86° for the α,α and α,β isomers, respectively. The methoxy groups are located in the phenyl ring planes. The bond angle between the phenyl carbon atom and the methoxy group (C_p–O–C) in the two isomers varies in the range 117.54°–117.65°. The N_4 plane is paral-lelogram-shaped with the perimeters (P_{N4}) 11.6472 E and 11.6033 E for the α,α and α,β isomers, respec-tively.

The reaction of peroxides with the metal porphyrin affects the type of deformation of the latter. Hence, the saddle-like deformation in ZnP(*meso*-RO)(α-OH), ZnP(OR)(OR), ZnP$^-$(α-OH), and ZnP$^-$(α-RO) is strongly enhanced to waviness. In the case of ZnP(α-RO)(*meso*-OH), ZnP(HO)(OH), ZnP$^-$(*meso*-OH), and ZnP$^-$(*meso*-RO), the enhancement of the saddle-like deformation is not so significant, while the degree of waviness increases, and a considerable deviation of one of the pyrrole fragments and the neighboring *meso*-C atom from the molecular mean plane takes place. The latter atom is the orientation center for the OH or RO group (Fig. 5). Deviations of the OCH_3 substituents from the phenyl ring planes by angles of about 24°–28° are observed. The C_f–O–C angle decreases by 2°. Increased deviation of Zn from the N_4 (Ct–Zn) plane and changes in bond angles and coordination cavity dimensions take place (Table 2). Hence, the formation of C–OR and C–OH bonds enhances the sterical strain of the macroring (Table 2, Fig. 4) and leads finally to disturbance of conjugation and destruction of zinc porphyrin. It follows from the aforesaid that the oxidation pathway and progress are influenced by the presence and degree of deformation of the macrocyclic compound.

EXPERIMENTAL

Zn-5,15-bis(*ortho*-methoxyphenyl)-2,3,7,8,12,13,17,18-octamethylporphyrin was prepared according to the standard procedure [19–21]. Electronic absorption spectrum in benzene [λ_{max}(log ε): 413.9(5.18), 540 (4.22), 574.4(4.04)].

The electronic absorption spectra were registered on a SPECORD M-400 instrument.

Oxidation kinetics were studied by the procedure described in detail in [22]. The apparent oxidation rate constants (k_{app}) were evaluated from the optical densities of the solution, measured at definite time intervals, using formally first-order Eq. (4) under the condition of metal porphyrine excess (λ 537 nm).

$$k_{app} = (1/\tau)\ln (c_0/c_\tau). \quad (4)$$

Here c_0 and c_τ are the initial and current peroxide concentrations, respectively.

The k_{app} values were optimized and rms deviations were determined by least-squares treatment using the Microsoft Excel and ggh.exe(QB-45) programs by the Guggenheim method. The results obtained by the two programs were coincident with each other. The relative error in k_{app} was 3–5%.

ACKNOWLEDGMENTS

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